EVALUATION OF HAIR DYES USING PHOTOELECTRIC COLORIMETRY

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In the manufacture of hair coloring products, the importance of control cannot be over-emphasized. To produce hair dye colors which will not vary from one production batch to another and which will consistently duplicate the desired shade on a subject's hair presents complex problems.

The method of standardization employed at present by most manufacturers is a visual evaluation by an experienced colorist.

Generally, in the laboratories of hair dye manufacturers, the accepted method of hair color evaluation is the dyeing of human hair swatches and color assessment by an expert technician.

The trained colorist is not only able to determine color difference in terms of strength, but he is also capable of estimating the quantitative magnitudes of these differences. This skill is learned by experience and careful tutelage forming the traditional basis for color assessment in all the industries concerned with colors. It is understandable that even an experienced colorist cannot reproduce his judgments perfectly. Color technicians, since they are individuals with characteristic visual differences, are often not in agreement on their observations. They are handicapped because they occasionally must work with increments of color that are just within their powers of discrimination, and the latter are not always capable of faithfully reproducing their decisions. This difficulty, coupled with the fact that all hair is different in texture and in its affinity for color pick-up, made it obvious that a better method of evaluation should be employed.

This paper concerns a new application of an old system to solve this problem. Color standardization utilizing instrumental methods has been accepted in the paint, plastics, ceramics and textile industries. In the dye industry the use of colorimetry, or transmission spectrophotometry, has been applied in the control of the dye bath and the manufacture of the

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production batch (1). The basic philosophy of the instrumental approach is to establish techniques, associated with physical instruments, that will enable the color perception of the normal individual to be expressed quantitatively and to provide a universally acceptable reference system for use in scientific and commercial application of color.

As a result of our experimental investigation, we have established that it is desirable to employ the simplest practical application of instrumental reflectance colorimetry. This is meant in the sense that a minimum background of work is needed before the colorimeter is put into routine service. It is first necessary to establish that the chosen instrument has sufficient reproducibility of measurement on the colored system of interest and then to set tolerance limits in terms of instrumental readings by correlation with the visual assessment method previously employed. This can normally be done in the course of production by routinely operating both the instrumental and visual methods side by side for a period of time long enough to determine the suitability of the instrument for this purpose. We have used the scheme of color classification of the *Commission Internationale de l'Eclairage* (C.I.E.), a trichromatic system of colorimetry which is described in detail in a number of publications (2–4). This system enables a color to be specified by three individual wavelengths of the visual spectrum matched by normal observers, using adjustable amounts of three physically defined light sources or primaries, red, green and blue.

This description of the color perception of the normal eye in terms of three defined standards was adopted by the C.I.E. from the data provided by Wright and Guild of the International Commission on Illumination (I.C.I.) in 1931 (5). The National Bureau of Standards unit of color differences has been derived in the manner of the C.I.E. system, and its use in individual applications is widespread in the United States (6).

The instrument which we have used is the Color-Eye, Model D, manufactured by the Instrument Development Laboratories, Incorporated, Attleboro, Mass. This is a photoelectric tristimulus colorimetric instrument. It transcribes the tristimulus specifications of a surface color, according to the I.C.I. Standard, to arbitrary values which may be recorded and graphed for the purpose of matching.

A short discourse on reflectance colorimetry is in order (7). A light beam, C.I.E. Illuminant A, is reflected from a sample to a phototube. The Color Eye utilizes the flicker photometer principle. In the flicker system, the flicker motor drives an optical mirror so that light from the sample and standard are alternately focused on a photomultiplier tube. If light from the sample and standard are identical, the photocell output will be unchanged by the flicker. If the two differ, an alternating current will be generated in the photocell circuit.

Regardless of the brightness level of the sample or standard, or the light transmission, or the intensity of illumination, a given per cent difference in color will give a finite a.c. voltage to the meter. In effect, the sensitivity of the photocell is varied inversely with brightness of light reaching it, just as the iris of the human eye and accommodation of the brain act to decrease the eye sensitivity when a brighter object is viewed. The range of automatic accommodation of the instrument is comparable to that of the eye, but it is faster and has no fatigue factor with time.

To obtain the tristimulus values, all one has to do is to insert into the light beam, prior to its reaching the photocell, the desired primary filters. The electronic system automatically transmits the a.c. output through a component necessary to express the difference between sample and standard in terms of reflected light.

The per cent values, or readings, of the instrument are designated by the letters X, Y and Z, which are known as the tristimulus values, each letter representing the amount of one of the primary stimuli.

The results obtained from the instrument indicate that, when two samples have the same values of X, Y, Z, the quality of the reflected light from the samples for the specified illuminant is approximately the same. Therefore, dye classification by the equivalence of the tristimulus values appears to give sufficiently good approximations for matching.

It is not our desire to go into the physical or optical principles necessary to describe reflectance or color absorbancy instruments. Nor do we intend to delve into the mathematical procedures required for the definition of tri-color stimuli used in the colorimeter. This may be found, for those who may be interested, in the many excellent publications on the subject (2–4, 6).

The dyed human hair swatches, which are customarily used to evaluate color pick-up visually, proved to give poorly reproducible results when they were read on the colorimeter. This was probably due to the non-uniform affinity of the hair for the dye materials. It was decided that a suitable substitute be made for human hair. By experimentation, it was found that the monochromatic absorption of a dye on certain textile fabrics, as on the hair, is proportional to the concentration of the dye present. Textile fibers which were found to be unsuitable included synthetics, such as cellulose acetates and nylon, silk, cotton and linen (8, 9). Wool, because of its keratin protein composition, was found to be satisfactory (10). Many of the woolen materials that were tried also had undesirable qualities. Cashmere, flannel and some worsteds gave a surface with too great a nap. A tightly woven wool worsted, obtained from Test Fabrics, Incorporated, New York City, was found to give excellent and reproducible results.

Samples of the cloth were dyed, employing the same controlled conditions that are used in the dyeing of a test subject's hair. Great care was taken to maintain the following conditions constant: dyeing time, dye bath concentration, temperature, washing solutions and drying procedures.

The colorimeter is calibrated by a standard which is provided with the instrument. Then the dyed wool patch is instrumentally compared with an undyed, identical patch of wool. The tristimulus values are recorded and graphed on a specialized graph paper provided for the purpose. The standard wool patches used for a particular color are produced from a retained color sample which has been previously accepted by a color expert in our Dye Color Center. This standardized color has satisfactorily been applied to the hair of many subjects.

When, for example, we dye our wool patches with a warm brown dye, we may find that our readings will be plotted above that of our standard. This indicates that the color take-up is too slight and produces a brighter hue or weaker color. This has been confirmed on the dyeing of natural hair. The indication, that more of the dye material must be added to our production batch, is obvious. If we over-correct with too great an addition of dye material, our readings are plotted below our standard. This also has been confirmed on a subject's head. By exercising great care and from the experience of many observations and adjustments, a good colorist may usually make a proper correction in a single addition or dilution.

The method of control outlined has been primarily presented for the control of finished products. This, however, is not the only use which may be made of this system. Specifications for raw materials may be formulated by the use of this form of colorimetry. The approximate purity of individual dyes may be estimated. The effectiveness of bleaching prior to applying dyes can readily be revealed.

It would appear that we have diminished, to a great extent, the problem of color control on hair dyes. Actually this is only partly true. An old axiom, that all control chemists know well, states, "The control is only as good as the standard used." Our standard, the dyed textile patch, has a distressing fault. We may perform a test of a sample against a standard and obtain a near perfect match. However, after an extended period of time, they will not match because of fading of either the sample or the standard, or both. The fading of a standard patch will necessitate a complete restandardization cycle and presents an entirely new problem. We have decided that this can be corrected by the preparation of colored ceramic tiles which will give the identical values as those of our wool patches. We are attempting, at the present time, to correlate our work with this idea.

The use of the tristimulus colorimeter to conduct the routine control of hair coloring products is in no way to be considered a means to replace the expert colorist. The expert is still needed to establish the standards by which the instrument may be calibrated. The colorimeter will, however, relieve him of the time-consuming and tedious drudgery involved in the continuous control of solutions. The operation of the instrument may be relegated to a technician. The expert colorist is now able to apply his skills to more important matters. This system, thus, is more efficient and economical without sacrificing quality of product.

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REFERENCES

(1) Davidson, H. R., and Godlove, I. H., *Am. Dyestuff Reptr.*, **39,** 628 (1950).
(2) Alderson, J. V., Atherton, E., and Derbyshire, A. N., *J. Soc. Dyers Colourists*, **77,** 657 (1961).
(3) Trotter, I. F., *Ibid.*, **78,** 76 (1962).
(4) Glasser, L. G., and Troy, D. J., *J. Opt. Soc. Am.*, **42,** 652 (1952).
(5) Wright, W. D., *Trans. Opt. Soc. (London)*, **30,** 141 (1928–29).
(6) Hunter, Richard S., *Circulars of the National Bureau of Standards*, **429,** 1 (1942).
(7) "Instructional Manual No. 1000G for Model D Color Eye," Instrumental Development Laboratories, Inc., Attleboro, Mass. Copyright 1956.
(8) Wilmsmann, H., *Am. Perfumer Aromt.*, **75,** 41 (1960).
(9) Moore, W. R., *J. Soc. Dyers Colourists*, **69,** 149 (1954).
(10) Brommelsick, William F., and Von Bergen, Werner, *Am. Dyestuff Reptr.*, **44,** 73 (1955).