



TECHNICAL PAPERS



REGIONAL
TECHNICAL CONFERENCE

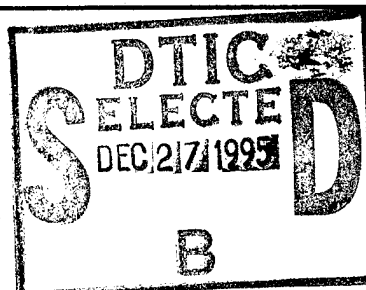
CONTROL
OF
COLOR AND APPEARANCE



October 16 & 17, 1979

SHERATON POSTE - INN
Routes 70 & 295
Cherry Hill, New Jersey 08034

19951218 042

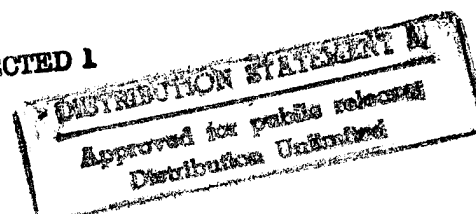


SOCIETY OF PLASTICS ENGINEERS, INC.

PHILADELPHIA SECTION

DEPARTMENT OF DEFENSE
PLASTICS TECHNICAL EVALUATION CENTER
ARRADCOM, DOVER, N. J. 07801

DTIC QUALITY INSPECTED 1



PLASTEC 34449

*MSG DIA DROLS PROCESSING - LAST INPUT IGNORED

*MSG DIA DROLS PROCESSING-LAST INPUT IGNORED

-- 1 OF 1

DTIC DOES NOT HAVE THIS ITEM

-- 1 - AD NUMBER: D429134
-- 5 - CORPORATE AUTHOR: SOCIETY OF PLASTICS ENGINEERS GREENWICH CONN*
-- 6 - UNCLASSIFIED TITLE: CONTROL OF COLOR AND APPEARANCE.
--11 - REPORT DATE: OCT 16, 1979
--12 - PAGINATION: 54P
--20 - REPORT CLASSIFICATION: UNCLASSIFIED
--21 - SUPPLEMENTARY NOTE: PROCEEDINGS: REGIONAL TECHNICAL CONFERENCE,
-- 'CONTROL OF COLOR AND APPEARANCE,' 16-17 OCT 79, CHERRY HILL, N. J.
-- SPONSORED BY SOCIETY OF PLASTICS ENGINEERS, PHILADELPHIA SECTION.
--22 - LIMITATIONS (ALPHA): APPROVED FOR PUBLIC RELEASE; DISTRIBUTION
-- UNLIMITED. ~~AVAILABILITY: SOCIETY OF PLASTICS ENGINEERS, INC., 14~~
-- ~~TATUMFIELD DRIVE, BROOKFIELD CENTER, CT. 06007.~~
--33 - LIMITATION CODES: 1

-- END

Y FOR NEXT ACCESSION

END

Alt-Z FOR HELP3 ANSI

3 HDX 3

3 LOG CLOSED 3 PRINT OFF 3 PARITY

CONTROL OF COLOR AND APPEARANCE

Regional Technical Conference of the Society of Plastic Engineers

Sponsored by the Philadelphia Section
and the Color and Appearance Division

Sheraton Poste-Inn

Cherry Hill, NJ

October 16-17, 1979

Conference Committee

Conference Chairman	Stephen H. Bauer	Molding Methods, Inc.
CAD Program Committee	Dr. James Davidson	MacBeth Div., Kollmorgen Corp.
	Charles Leete	MCCA Inc.
	Frank L. Fasano	American Hoechst Corp.
Registration Chairman	Bruce Kozak	Cincinnati Milacron Co.
Printing Chairman	Stephen H. Bauer	Molding Methods, Inc.
SPE Advisor	Hugh Andrews	Scovill Inc.

Officers of the Phila. Section

President	Norman Yeager	Kelling Plastics Inc.
President Elect	Bruce Kozak	Cincinnati Milacron Co.
First Vice President	Edward Evers	Reed Prentice Co.
Secretary	Donald Hellenbeck	Clifton Plastics Inc.
Treasurer	Douglas Stevenson	Stauffer Chemical Co.
Councilman	William Filbert	E. I. DuPont & Co.
	(alt) Salvadore DeMarco	DeMarco Design Inc.

TABLE OF CONTENTS

	<u>Section</u>
"Color Vision and Visual Evaluation" Bonnie Swenholt Eastman Kodak Company Rochester, New York	1
"How to Choose and Maintain a Standard" Joseph J. Smith & Boris Gutbezahl Rohm and Haas Delaware Valley, Inc. Bristol, Pennsylvania	2
"How to Measure the Color of Fluorescent Plastics" Fred W. Billmeyer, Jr. Rensselaer Polytechnic Institute Troy, New York	3
"Gloss, Haze and Yellowness Measurements of Plastic Sheet and Film" John S. Christie, Jr. Hunter Associates Laboratory, Inc. Fairfax, Virginia	4
"Color Systems Payback Analysis" Richard Abrams Columbus Coated Fabrics Borden Inc. Columbus, Ohio	5
"Application of Polymer Characterization in Computerized Dark Color Matching" David L. Alston Applied Color Systems Inc. Princeton, New Jersey	6
"Evaluation and Implementation of an In-House Color Program" William A. Jarrett Crane Plastics, Inc. Columbus, Ohio	7

Accession For	
NTIS GRA&I	☒
DTIC TAB	☐
Unannounced	☐
Justification	
<i>DTIC memo</i>	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

THE APPLICATION OF VISUAL COLOR APPRAISAL

B.K.Swenholt

The visual evaluation of color is so much an automatic process in our daily lives that it seems almost ridiculous to have it as the subject of a talk. After all, "What you see is what you get!" Or is it?

The last half century has produced tremendous progress in the measurement and specification of color stimuli. The science of colorimetry provides sound technology and modern instrumentation provides rapid and repeatable determination of color stimulus specification. By the application of this science and its tools we can state without equivocation when two colors will match. Since this is true, why then do we bother with visual appraisal at all?

The answer to that question lies in the nature of the visual process itself and our limited understanding of how color vision works. In the time allowed, we can consider but a few of the factors that must be better understood before instruments can replace visual appraisal.

First, two stimuli can be considered to have identity of color if they have identical spectrophotometric characteristics. Let us examine this assertion by observation.

Slide #1

This is the spectrophotometric curve of the filter used to produce the spot of light I shall show you in the next three slides. In each of those slides, the light coming to your eyes from the screen in the center of the illuminated area will be identical.

In this slide, you see only a small medium brightness spot of

Slide #2

light which I expect most of you would call white. Although it is not dazzling, it is the brightest area in view and so becomes the reference white.

If now, I surround an identical area with the unmodified light from the projector, two changes are seen almost immediately.

Slide #3

The central spot now appears somewhat darker than before and requires a hue name for discription. Exactly what hue name is used doesn't matter very much right now since we are all looking at the same patch. I shall call it "pink". No, I am not suffering from morning-after illness---nor is my color vision anomolous. I am merely anticipating the next slide.

Slide #4

Remember, the energy reaching your eyes from the central spot is exactly the same now as it was in the previous two slides. Only the surround has changed. By now my use of the color name, pink, to describe it should be more acceptable to most of you.

We have just seen that three identical stimuli have produced three different color perceptions--different because the area around the stimulus was changed. In order to predict what physical characteristics would be required for a stimulus seen in this surround to match the central stimulus of this slide

Slide #5

we need to know a lot more about color perception than we currently do. Fortunately, much work is being done to acquire that knowledge. In the not too distant future such predictions may be possible. For the present, however, we must struggle along with things the way they are. It matters not what measurements tell us about the character of color stimuli--What you see is what you see!

This brief demonstration establishes the fact that stimulus specification is not sufficient for predicting the perception it will produce. The surround and stimulus interact and affect the adaptation state of the viewer. Colors are perceived relative to this adaptation. This is not a new fact. That adaptation plays a large role in perception is a primary motivation for establishing standard viewing conditions for the visual evaluation of color. The fact that the three patches I first showed you were isomeric did not alter the fact that each was a different color because of the different adaptation produced by the change of surround.

A related and also familiar phenomenon is one of temporal relations. The right side of the screen is a nearly uniform area with a black dot in the middle. If you will now focus your attention on the black dot on the left of the screen while you count slowly to twenty--then shift your attention back to the black dot on the right, you will see a figure on the right similar in outline to that of the figure on the left. The perception can be enhanced by looking back to the left for a few seconds then back to the right again.

This "afterimage" is also the result of changed adaptation. The retinal area stimulated by the figure on the left ^{has} ~~have~~ changed sensitivity. Since there is but little red or blue light in that figure, the red and blue sensitivity has increased in much the same way that overall

sensitivity increases when one enters a darkened room. Since the area on the right has roughly equal amounts of red, green and blue light available, the afterimage is seen as a sort of purple figure.

If we repeat this experiment but have a field on the right of the screen that has very little blue light

Slide #7

a different hue is seen in the afterimage.

Having seen how easily the perception of color is changed, of what value is color measurement? Indeed, how can we rely on visual appraisal? Each method of evaluation has its place and value provided the limitations of each are recognized.

For analytical purposes--determining what colorants and in what concentrations --determining what is physically present--physical measurement is the most reliable. Even here a data base must be established to provide the correlation between color measurement and chemical analysis before the measurements will be interpretable. This is particularly true if abridged spectrophotometry such as colorimetry or densitometry is used. Once that correlation has been established, physical measurement provides a reliable means of quality control monitoring.

But what of tolerance limits? How can these be determined? Since the motivation for the use of color is its visual impact, the only realistic means of establishing limits of acceptability, at this time, is by visual appraisal. Having been reminded of how easily the response of color perception is altered, we are reminded of the great care with which our viewing conditions must be specified.

Much of what we know about human color vision has been learned from experiments designed to isolate the variables. The observations providing the data on which colorimetry is based were made of essentially isolated colors. Putting these isolated variables back together, so to speak, in order to predict color perception from stimulus measurement has proved to be an impossible task. The interactions are not, so far, predictable from knowledge of the elements. Many current studies are considering these interactions and experimenters are using complex fields of view. Unless, or more optimistically until, we are successful in predicting perceptual changes for a given stimulus with changing adaptation conditions, visual evaluation will remain a necessary procedure for establishing aims and tolerances.

Metamerism, the fact that two colors which match when seen under one

illuminant may not match when seen under another, is of as much importance when establishing tolerances as it is when establishing aims. The size of the color mismatch that can be tolerated under one illuminant may be unacceptable in another illuminant. It is necessary to provide viewing conditions for visual evaluation that approximate the range of conditions for which the color application is being evaluated. Certainly, for some applications, there will be only one illuminant type of importance. Paint for an automobile is an example. While it is desirable that any "touch-up" should match no matter when or where the automobile is seen, it must match in daylight quality at rather high levels of illumination--it is not good enough that it match only at twilight. It would be the height of folly to establish color tolerances for such a product when viewed under a 100 watt incandescent lamp. Color coatings for a refrigerator, on the other hand, may be critically examined under daylight conditions, fluorescent lamps, incandescent lamps and mixtures of any two or all three. Fortunately, the level of the illumination does not need to be so high for the refrigerator as for the automobile.

While metamerism is a primary reason for examination under a variety of illuminants--the color shifts to be expected can be predicted from measurement. The importance of those shifts is difficult to predict without visual evaluation.

The changes of color perception that occur as a result of adaptation modification by the surround are not yet predictable with any accuracy. For that reason when it is known that a given color will be seen with a particular surround--appraisal of that color should be made with its intended surround.

With all the uncertainties of color vision, it is still possible to obtain reliable visual assessments if the spectral quality, the brightness and the appropriateness of the illuminant are controlled. If the color of the surround for the stimulus in question is either unknown or likely to be variable, a neutral surround similar in lightness to the stimulus will usually provide reasonable viewing conditions.

To answer the question with which we started, Yes, what you see is what you get--but it may not be what the manufacturer thought you were getting unless visual appraisal under the proper conditions was a part of the quality assurance program.

Since color is not a physical thing but a perception, only a visual appraisal can determine your preference for this

Slide #

1-4

or this

Slide #

HOW TO CHOOSE AND MAINTAIN A STANDARD

Boris Gutbezahl
Joseph J. Smith
Rohm and Haas Delaware Valley Inc.
P. O. Box 219
Bristol, PA

INTRODUCTION

Our company is a multi-plant manufacturer of various plastic products ranging in optical properties from the clear, water-white acrylics sold as Plexiglas^R sheet ^{AND} molding pellets to the opaque acrylic/PVC alloy sold as Kydex^R sheet.

Initial color development and the ultimate quality control practices employed are under the control of a centralized laboratory located in Bristol, PA. As a manufacturer of the colored plastic products, separate from Bristol, our procedures and practices are changed and modified to meet the real world situation while satisfying our customer's needs. We have suffered many growing pains and learned from our mistakes. Ultimately we have developed a system that should be universally applicable. Since the general trend is toward multi-plant manufacture of the same nominal color, we thought it worthwhile to discuss our system with you.

The range of color that can be achieved in most plastics is very large. Unfortunately, so are the tastes of most of our customers. Once taste has been satisfied by an initial offering, a standard for the color must be set and maintained. Batch-to-batch variations must be minimized in case multi-unit installations or replacement parts are needed. Many corporations select a color as a corporate symbol. Some of you may not have heard of Rohm and Haas brown, but Coca-Cola red and Chrysler blue form a definite image in your mind and eye. If there is a significantly off-shade installation, you know the consequences will be rattling to the whole corporate contract.

METHOD OF STANDARD DEVELOPMENT

When a new color is to be developed, there is usually a physical sample to be matched. This is forwarded to the Color Laboratory with the conditions under which it is to be used, i.e., indoors or outdoors, by transmitted or reflected light, illumination used, etc. These conditions must be translated by the laboratory into standard terms that are meaningful to the color scientists. These terms can then be inputted into computerized color matching programs.

There are problems of appearance as well as color that arise in the selection of the new color. We have received swatches of textured cloth, ladies' shoes--always individual ones, never a pair--and mottled pieces of stone as samples. There is no way we can duplicate all these surface textures in the laboratory. In fact, our file of existing samples, for the most part, consists of glossy surfaces. This is where the color matcher's judgement is called upon to try and discount appearance factors. The salesman must be included too, to help decide whether an "appearance match" or a "color match" is really needed.

When you have been in the color development business for thirty years or so, there's seldom a case where there is nothing in the existing file that isn't at least similar to the customer's submission. This provides a good starting point for visual color matching.

Today, when instrumentation is such a vital part of the color field, it may be all that is really needed. The customer's sample can be measured on a recording spectrophotometer. Very often the shape of

the spectrophotometric curve is enough to tell the color matcher what colorants the customer's sample contains. The very least the curve does is provide guidance as to which colorants should be used in attempting a match. In any case, starting with the spectrophotometric curve, a series of physical trials are made until a satisfactory match is obtained. The spectrophotometric curve is obtained from this match. First, it records the information for posterity; and, secondly, it makes sure the offering is minimally metametric.

SELECTING STANDARDS BY INSTRUMENTAL METHODS

A. TENTATIVE STANDARD

When the customer gives his approval to a sample sent him, a tentative standard is used as a control for the first and succeeding production runs until at least ten have been completed. Tentative color tolerances are also established during this period.

B. PERMANENT STANDARD

We make at least ten runs before selecting a permanent standard to monitor the variability inherent in the process for the colorant combinations used, and to evaluate the effect of changing lots of colorant. The transfer of a formulation from the laboratory to the plant is not without difficulty. Thus, it is important that the permanent standard be selected from a plant run which is within one unit of total color difference (ΔE Hunter System) of the laboratory tentative standard approved by the customer. When a production mix has been judged, both visually and instrumentally, close enough to the tentative standard to be considered "the standard," part of that batch is set aside.

STANDARD SELECTION WITHOUT INSTRUMENTATION

Basically, the method of selection of this standard is the same as with instrumentation, but the actual piece is, of course, selected visually. The added step in this process is the selection of limit pieces.

A. SELECTION OF LIMITS

Those samples not chosen as "the standard" are re-examined and an attempt is made to select appropriate pieces as limits. This is usually done on the basis of lightness-darkness differences from the established standard. If none of these samples is suitable, limiting pieces are prepared. This is done by taking the standard formulation and varying the colorants by $\pm 10\%$, 15% , or 20% , depending upon the range you wish to allow for the particular color.

CARE AND DISTRIBUTION OF STANDARDS

Only one sample prepared from the "standard batch" is designated and stamped as the "standard" for that color. Preparation of this piece may involve injection molding, if the plastic is a molding pellet, or just a cutting of a sheet material.

Other physical pieces made from the "standard batch" will be serially designated as "working standards". These "working standards" are measured against the "standard" piece and distributed with any factors possibly needed to correct the measurements for standard color. The corrections may arise for a number of reasons, including possible differences in thickness. The color "standard" itself is used only for these initial measurements and is kept in dark storage. The spectrophotometric data for it are

maintained separately and permanently in a "standards" book in case the color "standard" should ever become lost or otherwise unusable.

The "working standards" are the physical pieces used by the quality control departments in each manufacturing location to compare against current production. Thus, all production in any plant is indirectly measured against the single "color standard" which is kept in dark storage.

The "working standards" may become defaced and unusable after periods of prolonged use or because of carelessness. The local quality control departments are constantly looking for any evidence suggesting this possibility. They know they need only request another new "working standard" from the Color Laboratory to resolve any issues. One of our plants prefers to keep two "working standards" for each color they produce.

Many of our products are used in outdoor applications; therefore, the remainder of the samples are used for outdoor exposure testing. One sample is retained as a control, and a specified number of samples are placed on outdoor racks with no backing. The samples face South at a 45° angle. The samples are washed every three months and are brought into the laboratory after one year, two years, etc., for visual evaluation and/or instrumental measurement. In this way, weatherability of the combined colorants is checked. We have learned that, unlike single component colorant systems, combined component colorant systems do not weather well. A well known example is the poor weathering of a red dye used in automotive tail-light lenses in combination with a white pigment such as TiO_2 .

REVISION OF STANDARDS (KEEPING THE SYSTEM UP-TO-DATE)

There are situations which require the revision of "the standard." It is unrealistic to think a standard, once developed, will never be subject to revision. Raw materials, colorants, and methods of manufacture change. These changes are reflected in the production of the final colored product. Obviously, such changes come about very gradually, because every attempt is made to stay within the allowable tolerances of "the standard." Yet, there comes a time when cumulative changes require a reformulation of the color and establishment of a new standard. If, for example, certain colorants are no longer available, every attempt is made to reformulate the affected colors. This requires a long drawn-out process of elimination, details of which have been covered in a paper given by Messrs. A. J. Pentz and R. R. Streeper entitled, "How to Select Colorants for Acrylics" at the last Cherry Hill Color RETEC.

After a suitable colorant replacement has been obtained, the process of rematching the "standard" for the particular color must be undertaken. In some cases an exact rematch is submitted to marketing for their approval. They may, in turn, go back to the customer(s). If the approval is forthcoming, the standard selection process previously described is started again.

STANDARDS AND SPECIFICATIONS

Before an item becomes firmly established in production, tolerances are developed around the tentative standard. We prefer to set tolerances around ΔL , Δa , Δb , and ΔE , rather than ΔE alone. It is wise to look closely at all of the production during the interim period to be sure

the final specifications reflect measurements, process capability, visual examination, and customer satisfaction. A strict instrumental determination may cause problems because totally acceptable data may on occasion have an unacceptable visual appearance.

In order to set a permanent specification, agreement must be reached between representatives of the color laboratory, sales, manufacturing, and quality control. At this point all representatives may be able to view samples of production representing color variations in the specification range. Data is also available to manufacturing. They determine the percentage of their production that has met the color tolerance and the reasons for rejection of those batches that have not (color, distortion, dirt, etc.). Once in agreement, the specification is officially set and recorded. When the specification is published, it cannot be changed unless all parties agree to the change.

REPLENISHING THE SUPPLY OF WORKING STANDARDS

When the supply of available working standards is depleted to a predetermined amount for a specific color, the Color Laboratory checks with Sales to see at which plant that color is next scheduled for manufacture. When the place of manufacture is determined, this location is requested by memo to set aside material for working standards from their first good production run--when one lab measurement is within one or less ΔE units of the standard.

The Color Laboratory will then measure a sample of the batch and, if its color measurement and evaluation agree with those of the manufacturing plant, the batch is used to prepare additional working standards.

All standards, working standards and replica standards, should be in

dark storage and not exposed to light or excessive heat.

Whether it be for a premium plastic or any other colored product line, a comprehensive, well maintained standards program is an absolute must. The viability of the product stands or falls on good color reproducibility. A haphazard approach to coloring and maintenance of standards will lead to poor product quality, loss of confidence by the customer and eventual disappearance of the business.

It is, of course, our aim to produce colors to close and reproducible tolerances, and this can be accomplished by adherence to realistic standards. Occasionally, there may be a slight shift away from the standard, but this must be corrected swiftly. More often than not, the customer will tolerate an occasional shift, but what he will not stand for is a random variation. Generally, it is true that product uniformity is more important than absolute adherence to close tolerances. In either case, the standards are the guidepost to keep the operation on target.

HOW TO MEASURE THE COLOR OF FLUORESCENT PLASTICS

Fred W. Billmeyer, Jr.

Department of Chemistry

Rensselaer Polytechnic Institute

Troy, New York 12181

ABSTRACT

The color of fluorescent plastics could be measured to obtain correlation with visual appearance, to meet signal specifications, or as an aid in formulation. Each objective requires a different measurement and calculation method, none of which is easy. To do any of the jobs right, spectrophotometers with $45^\circ/0^\circ$ geometry are required; colorimeters or integrating-sphere instruments will give only approximate results varying widely among instruments. Obtaining correlation with visual results requires identically the same light source for both instrument and visual judgments; this is usually impractical. Specifications are usually written for CIE Ill. D_{65} , for which there is no corresponding light source. Calculation methods must be used to compute what the samples would have looked like under D_{65} . Accurate formulation of fluorescent plastics cannot yet be done, but by measurements and calculations the true reflectance curve of the sample can be obtained as an aid toward computer formulation.

INTRODUCTION

One of the very convenient features of color measurement for ordinary, that is nonfluorescent, samples is that the results do not depend upon what kind of light source is used in the instrument. Of course the color coordinates of the sample do depend on the light source under which it is viewed, and on who is viewing it as well. This information is put in separately from the measurement step, however: In the case of a spectrophotometer, the instrument provides the spectral reflectance curve, and for this any convenient instrument source can be used. Then the color coordinates are obtained by calculation, usually using CIE data for some standard illuminant and a standard observer. The same reflectance data can be used to obtain correct color coordinates for many different illuminants and observers. In the case of a colorimeter, the only difference is that the computation is done by the use of optical analog filters; a convenient instrument source is still used that does not need to bear any relation to the illuminant for which the color coordinates are obtained.

Now let us consider fluorescent samples, by which we mean those that absorb radiant power (that is, light) in one wavelength region and emit radiant power in a region of longer wavelength. The emitted power is called fluoresced power, and the process is called fluorescence. Two kinds of fluorescent samples of interest to the plastics industry, that differ only in the wavelength regions involved, are fluorescent whitening agents (FWA's), which absorb power in the ultraviolet and fluoresce in the short-wavelength (blue) region of the visible, and colored fluorescent samples, often called the "dayglo" type, which absorb power

in the short-wavelength visible region and fluoresce in the longer wavelength visible region.

The considerations of instrument measurement described above do not apply to fluorescent samples. Instead, the exact nature of the light source in the instrument, and of the arrangement of the optical components of the instrument, play a major role in determining the answers one gets. As a result, one or both of two things happen that lead to unsatisfactory results. First, the results obtained vary considerably from instrument to instrument; and second, they fail to correlate adequately with the visible appearances of the samples.

This paper first describes what the instruments actually measure for fluorescent samples and shows how this depends on the light source and other instrument variables. It then describes what needs to be done in order to measure fluorescent samples satisfactorily for three important cases: to obtain good correlation with their visible appearance; to meet specifications on their color; and to aid in formulating color matches.

WHAT IS MEASURED?

Consider a fluorescent sample -- for convenience let us say an orange "dayglo" type -- observed in daylight. In common with nonfluorescent orange samples, it absorbs power in the short-wavelength visible region, where it has low reflectance, and reflects most of the incident power in the long-wavelength visible region. In addition, some of the absorbed power is emitted in the long-wavelength region as fluorescence. What is seen is the sum of both the reflected and the emitted power. Curve R in Fig. 1 shows the spectral reflectance of such a sample¹, curve F shows its fluorescence, and curve T shows the sum of the two. Curve E shows, on a relative scale, the efficiency of radiation incident on the sample for exciting fluorescence.

In standard terminology, such as that of the CIE^{2,3} power radiated in a specified direction (as to the eye of an observer) from a specified sample area is called radiance. In an instrument, the radiance from a sample would normally be compared to that from a (nonfluorescent) white reflectance standard, and the relative radiance that results is called a radiance factor. What the eye sees from a fluorescent sample is the total radiance, the sum of the fluoresced and reflected radiance, and this is what we require the instrument to measure. Using the spectrophotometer as our example throughout since it provides more fundamental information, we wish to measure the spectral total radiance factor, $\beta_T(\lambda)$:

$$\beta_T(\lambda) = \beta_R(\lambda) + \beta_F(\lambda)$$

The spectral total radiance factor is the sum of the reflected and fluoresced radiance factors, each taken as a function of the wavelength.

To measure $\beta_T(\lambda)$, the instrument must be operated to correspond to the visual situation we first described. The sample must be irradiated with polychromatic light, as shown in Fig. 2, which is based on the common integrating-sphere illuminating-viewing geometry. If a simulation of daylight is desired, there may be a filter between the light source and the integrating sphere. The radiance from the sample is analyzed by passing it through the monochromator in the viewing beam to the detector. By comparing the radiance from the sample to that from the white standard, the detector provides a measure of the spectral total radiance factor.

Now suppose the instrument's monochromator is set to the region in which fluorescence is emitted, say 600 nm for the orange sample. And suppose the power in the instrument light source is suddenly changed in the short-wavelength region, say 450 nm, for example by changing the nature of the filter between the source and the integrating sphere. Then there will be a different amount of power incident on the sample at 450 nm, a different amount of power absorbed at 450 nm, and correspondingly a different amount of fluorescence emitted at 600 nm. Thus $\beta_F(600)$ has changed even though $\beta_R(600)$ has not, so that $\beta_T(600)$ has changed. Thus what the instrument measures for a fluorescent sample depends on the nature of its light source (including the filter and, as we shall see later, the effects of the integrating sphere).

Now consider another type of instrument, as in Fig. 3, which has the monochromator in the illuminating beam. A classic example is the Hardy-type spectrophotometer made by General Electric and later Diano (Diano-Hardy I). Here, if the monochromator is set to 600 nm, there is no fluorescence generated since no light in the short-wavelength excitation region reaches the sample. Only $\beta_R(600)$ is measured. If the monochromator is set to 450 nm, however, power is absorbed and fluorescence takes place. The detector is not sensitive to the kind of radiance being emitted and merely records its presence. Thus the instrument indicates falsely that there is radiance produced at 450 nm when in fact it is at longer wavelengths. An entirely different quantity, called the conventional reflectance⁵ because "conventional" instruments of the period measured it, is produced in this case. Its spectral curve is shown in Fig. 4.

In summary, what is measured for fluorescent samples depends upon both the arrangement of components in the instrument and the nature of its light source and associated filters.

CORRELATION WITH VISUAL APPEARANCE

Since most fluorescent samples are produced with their appearance in daylight in mind, we find in recent years that most color measuring spectrophotometers are designed to utilize monochromators in the viewing beam and light sources that simulate daylight. In a sense this is a waste, because both features (for reasons that are outside the scope of this paper) are costly and detract from instrument performance, yet are not required unless fluorescent samples must be measured.

Aside from these considerations, how well do these instruments, designed to produce measurements of fluorescent samples as seen in daylight, do their job? One might at least expect them all to give the same answer. In various studies in our laboratory, we have investigated this, measuring the same or identical samples on a variety of current and recent instruments. The results for one such sample, a yellow-orange, are shown in Fig. 5. All the instruments had the integrating-sphere geometry and daylight simulator sources, and all were operated in exactly the same way. The result is that each instrument measures its own "private brand" of spectral total radiance factor, different from all the others, in many cases by really huge amounts.

Obviously, not all of these results can be correct in the sense of providing good correlation with what the observer sees on visual examination of the sample, and we are left without any clear way of judging which instrument's daylight simulator does the best job. We can, however, set up a criterion: If the spectral power distribution falling on the sample for the visual judgment is the same as that falling on the sample in the instrument, then we should expect the two results to have a chance of correlating satisfactorily.

How easy is it to get these two spectral power distributions the same? We can at once give up all thoughts of using natural daylight as the visual source, unless very sophisticated special instruments -- spectroradiometers -- are available for the instrumental measurement. We can also discard all commercial viewing booths, since none of these is exactly duplicated as an instrument source. As a last resort, can we remove the source from the instrument and use it for the visual judgments?

We have done this for some special studies, but even this does not solve all the problems. First of all, it cannot even be done, conveniently or not, with most instruments. Instrument sources are just not designed to be used for visual observations, and vice versa.

If the instrument source, with its modifying filters, could be removed and set up for visual observations, would the problem be solved? The answer is no, because the integrating sphere itself influences the sample.⁶ This results from the long-known influence of the sample itself and the walls and ports of the integrating sphere on sphere efficiency.^{7,8} The effect cancels out for non-fluorescent samples measured in double-beam instruments, but it means that the radiant power on a fluorescent sample in an integrating-sphere instrument depends upon the nature of the sample, and is significantly different for every different sample used. About the only way I know of to avoid this problem is to utilize spectrophotometers that have $45^\circ/0^\circ$ geometry, and there are very few of these, otherwise suitable for fluorescence measurement, on the market.

Even with the use of $45^\circ/0^\circ$ geometry and identical sources for the visual and instrumental measurements, there is another factor to be taken into account. This is the illuminant data used in obtaining color coordinates from the spectral radiance factors. These cannot be for any standard source, but must be based on the exact source irradiating the sample. Very few laboratories, in my experience, are equipped to measure the spectral power distribution of a real source, and not all instruments can accept data for such a source into their microprocessor. For this reason alone, the use of colorimeters, which are usually "locked into" a single standard source, by virtue of their optical-analog filters, is ruled out for the serious measurement of fluorescent samples.

Another approach is worth considering. It is to provide sets of standard fluorescent samples which could be used to allow the adjustment of instruments in some way that would assure the desired good correlations. The adjustment might be a physical one, modifying lamps or filters, or a prescribed calculation routine similar to those discussed in the next section. But the details of this approach have not even begun to be studied at this writing.

In summary, the user who wishes to insure that he can measure fluorescent samples in a way that correlates with his visual observations is doomed to failure until he can obtain -- or some instrument manufacturer will provide -- identical sources for visual observing and the instrument, a spectrophotometer utilizing $45^\circ/0^\circ$ geometry with the monochromator in the viewing beam, and the exact spectral power distribution of the source in the integration program.

MEETING SPECIFICATIONS

Fluorescent plastics are used in a number of safety and signal applications which are subject to color specifications. A number of the applicable specification documents are, unfortunately, out of date and essentially meaningless today.

They specify use of instruments no longer available, or fail to specify the illuminant or measurement conditions correctly.

Specifications are now being written, however, which meet the requirements of good color science. This does not mean, we shall see, that they are easy to meet. Most of them specify the use of $45^\circ/0^\circ$ geometry, avoiding the problem of integrating-sphere effects but severely limiting the choice of instruments that can be used. It is to be hoped, however, that a really well conceived specification would allow the use of integrating-sphere geometry provided it could be demonstrated that results could be achieved that were equivalent to those obtained with $45^\circ/0^\circ$ geometry. How this can be done will be described in a moment.

More importantly, those of the newer specifications concerned with daylight appearance require that the sample be irradiated with a source equivalent to CIE Illuminant D_{65} . Now this cannot be done, strictly speaking. The CIE has not recommended such a source, and has not even agreed to date on how to evaluate possible candidates.^{9,10} Each instrument manufacturer provides a source which he feels is an adequate simulator of D_{65} , but the disparity of results obtained with these various simulators, shown in Fig. 5, provides convincing evidence that we do not now know how to provide a fully satisfactory D_{65} simulator for any instrument. How then can one hope to meet a specification calling for results equivalent to those obtained if the sample had been irradiated with D_{65} ?

We have studied this problem, and provided an answer recently reported to the CIE.^{11,12} It is possible to predict by calculation the spectral total radiance factors that fluorescent samples would have when irradiated with a standard illuminant such as D_{65} from measurements of the samples made using sources that simulate the standard illuminant. Our report evaluates several different calculation methods¹³⁻¹⁶ using integrating-sphere instruments, and shows that the choice of calculation method is less important than starting from a reasonable simulator of the standard illuminant and accounting properly for the effect of the integrating sphere. Our "best case" result is illustrated in Fig. 6, where it is seen that the spectral total radiance factor of the same orange sample calculated for a specified source, from results obtained with a different source, can scarcely be distinguished from the curve directly measured with that specified source. In this case, the CIELAB color difference corresponding to the two curves is less than 0.4 unit. For six different colored samples (including one FWA) measured on two different integrating-sphere instruments, the mean CIELAB color difference was still less than one unit.

How do the calculation methods work? Briefly, they require the following steps:

1. The spectral total radiance factor $\beta_T(\lambda)$ must be separated into its fluoresced and reflected components. There are several methods for doing this,¹⁷ the best of which^{18,19} requires use of a special instrument with two monochromators, in the illuminating and viewing beams, respectively. Lacking this, the usual spectrophotometer can be used¹³ to provide several measurements in which the irradiation from the instrument source is modified by introducing sharp cut-off filters; the reflectance curve can be obtained from these data, and the fluorescent curve by subtraction. The filters required differ from one color of sample to another; a minimum of three or four must be properly selected for each fluorescent color tested. Even for FWA's the single "UV cut-off filter" with which some colorimeters are equipped has virtually no value except for crude qualitative testing.

2. The spectral power distribution that actually irradiates the sample, including all effects of the integrating sphere, must be measured. This requires the use of a spectroradiometer, though some instruments can themselves be used as spectroradiometers. A standard source is required to calibrate the spectroradiometer.

3. Depending upon the calculation method used, a further quantity called the external efficiency may have to be determined. This is the ratio of the radiation emitted by fluorescence to the radiation incident on the sample in the excitation region. This quantity can be determined with the special two-monochromator instrument mentioned earlier, or from measurement of the conventional reflectance.¹⁴ In this case, a standard detector is required to calibrate the instrument.

4. The calculation methods utilize the experimental values just described to compute, from the experimental spectral fluorescent radiance factor $\beta_F(\lambda)$ and the two spectral power distributions (that actually irradiating the sample and that of D_{65}), what β_F would be under D_{65} irradiation.

5. Finally, the new value of $\beta_F(\lambda)$ is added to $\beta_R(\lambda)$ to provide the desired value of $\beta_T(\lambda)$ for D_{65} irradiation. This can then be integrated with D_{65} as the illuminant to give correct color coordinates for the sample as it would appear when irradiated by D_{65} . This is what the better specifications call for.

In summary, it is possible with many measurements and great care, but with good accuracy, to compute the quantities necessary to assure conformance to workable signal or safety color specifications for fluorescent materials. From what I have seen, however, I doubt that more than half a dozen laboratories in the country can currently make all the required measurements and calculations.

FORMULATION

Finally, a few words about computer formulation of fluorescent samples. This too is a problem for which there are no easy solutions. Here are some of the considerations that should be taken into account.²⁰ The quantity $\beta_F(\lambda)$ which we have been discussing is an apparent fluorescent radiance factor, representing what emerges from the sample after the true fluorescence generated within it finds its way out. In the process, some of the fluorescence originally generated can be lost by chemical processes called quenching. Because the excitation and emission curves usually overlap (see curves E and F in Fig. 1), more of the fluorescence may be reabsorbed and re-emitted in a process called cascading. In principle, all these can be calculated, but the situation is so complicated that I know of no published evidence of attempts to apply the principles.

What is usually done²¹ is to separate the fluorescence and reflectance, as previously described, and treat them separately. The reflectance curve is matched by the usual Kubelka-Munk technique for nonfluorescent samples. The fraction of the total power absorbed (in the excitation region) by the fluorescent colorant is calculated for the resulting formulation. By reference to results obtained with calibration samples, the true $\beta_F(\lambda)$ corresponding to this amount of absorption is determined. To the extent possible, quenching and cascading are accounted for to provide the apparent $\beta_F(\lambda)$ emerging from the surface of the sample. This is then added to $\beta_R(\lambda)$ calculated for the formulation to give a computed $\beta_T(\lambda)$ which can then be used to obtain color coordinates. All this must be repeated until the iterative process of calculating a match converges. Again there are no refer-

ences to this scheme being used. The author concludes²¹ "since the number of fluorescent dyes and pigments is very limited, and since fluorescent samples are relatively easy to match by the colorist, an elaborate computational method of formulation is not urgently wanted".

CONCLUSION

The title of this paper carries an implied question: how does one measure the color of fluorescent plastics? The answer seems to be: with great difficulty. For most of the purposes behind these measurements, we know how one ought to proceed; more importantly, we now know exactly what pitfalls to avoid. This is perhaps the most important lesson to be learned. It seems to me to be far better to know enough to say "No, I cannot make that measurement correctly and here is why," rather than to make an incorrect measurement that can only be misleading. And, if the stakes are high enough, the correct methods of making the measurements, though complicated, are always there to be tried.

ACKNOWLEDGEMENT

The Ph.D. thesis research of David H. Alman and Tak-Fu Chong provided much of the background information for this paper. The support of their work by the Allied Chemical Company, the Ford Motor Company, the 3M Company, PPG Industries, and the Sherwin-Williams Company is greatly appreciated. This is Contribution No. 94 from The Rensselaer Color Measurement Laboratory.

REFERENCES

1. The samples were made with Blaze Orange and Arc Yellow Acrylic Lacquer Safety Paints manufactured by the Day-Glo Color Corp., Cleveland. With the exception of those in Fig. 5, all measurements discussed in this paper were made with a Zeiss DMC 25 reflectance spectrophotometer.
2. International Lighting Vocabulary, Publication CIE No. 17, Bureau Central de la CIE, Paris, 1970.
3. Radiometric and Photometric Characteristics of Materials and their Measurement, Publication CIE No. 38, Bureau Central de la CIE, Paris, 1977.
4. David H. Alman, A Method for Determining Excitation Spectra of Opaque Fluorescent Diffusers, Ph.D. Thesis, Rensselaer Polytechnic Institute, 1975.
5. Fred W. Billmeyer, Jr., Analysis of the conventional reflectance of fluorescent samples, Applied Optics **13**, 1007-1008 (1974).
6. David H. Alman and Fred W. Billmeyer, Jr., Integrating-sphere errors in the colorimetry of fluorescent materials, Color Res. Appl. **1**, 141-145 (1976).
7. Arthur C. Hardy and O. W. Pineo, The errors due to finite size of holes and samples in integrating spheres, J. Opt. Soc. Am. **21**, 502-506 (1931).
8. David G. Goebel, Generalized integrating-sphere theory, Applied Optics **6**, 125-128 (1967).
9. Gunter Wyszecki, Development of new CIE standard sources for colorimetry, Die Farbe **19**, 43-76 (1970).

10. David H. Alman and Franc Grum, A comparison of several proposed methods for evaluating daylight simulators in the ultraviolet range, Color Res. Appl. 4, 00-00 (1979).

11. Evaluation of Methods for Predicting the Spectral Radiance Factors of Fluorescent Samples Under Standard Illuminants from Measurements of the Samples made using Sources Simulating those Illuminants, Publication CIE No. 00, Bureau Central de la CIE, Paris, in preparation.

12. Fred W. Billmeyer, Jr., and Tak-Fu Chong, "Evaluation of Methods for Predicting the Colors under Standard Illuminants of Fluorescent Samples Measured under an Arbitrary Source," in publication CIE No. 00, Proceedings 19th Session CIE (Kyoto, 1979), Bureau Central de la CIE, Paris, in preparation.

13. D. Eitle and E. Ganz, A method for determining tristimulus values of fluorescent specimens (original in German), Textilveredlung 3, 389-392 (1968).

14. David H. Alman and Fred W. Billmeyer, Jr., New method for the colorimetric measurement of opaque fluorescent samples, Color Res. Appl. 2, 19-25 (1977).

15. Eugene Allen and C. L. Sanders, private communication, 1977.

16. Franc Grum and Lorenzo Costa, private communication, 1977.

17. David H. Alman, Fred W. Billmeyer, Jr., and Daniel G. Phillips, "A Comparison of One-Monochromator Methods for Determining the Reflectance of Opaque Fluorescent Samples," in Publication CIE No. 36, Proceedings 18th Session CIE (London, 1975), Bureau Central de la CIE, Paris, 1976, pp. 237-244.

18. Franc Grum, "Use of True Reflectance and Fluorescence for Color Evaluation of Achromatic and Chromatic Fluorescent Materials," in Publication CIE No. 21B, Proceedings 17th Session CIE (Barcelona, 1971), Bureau Central de la CIE, Paris, 1972, paper 71.22.

19. L. Costa, F. Grum and D. J. Paine, Absolute luminescence spectra via digital technique and time-resolved spectroscopy, Applied Optics 8, 1149-1155 (1969).

20. Eugene Allen, Fluorescent Colorants: true reflectance, quantum efficiency and match prediction, J. Color Appearance 1(5), 28-32 (1972).

21. Ernst Ganz, Problems of fluorescence in colorant formulation, Color Res. Appl. 2, 81-84 (1977).

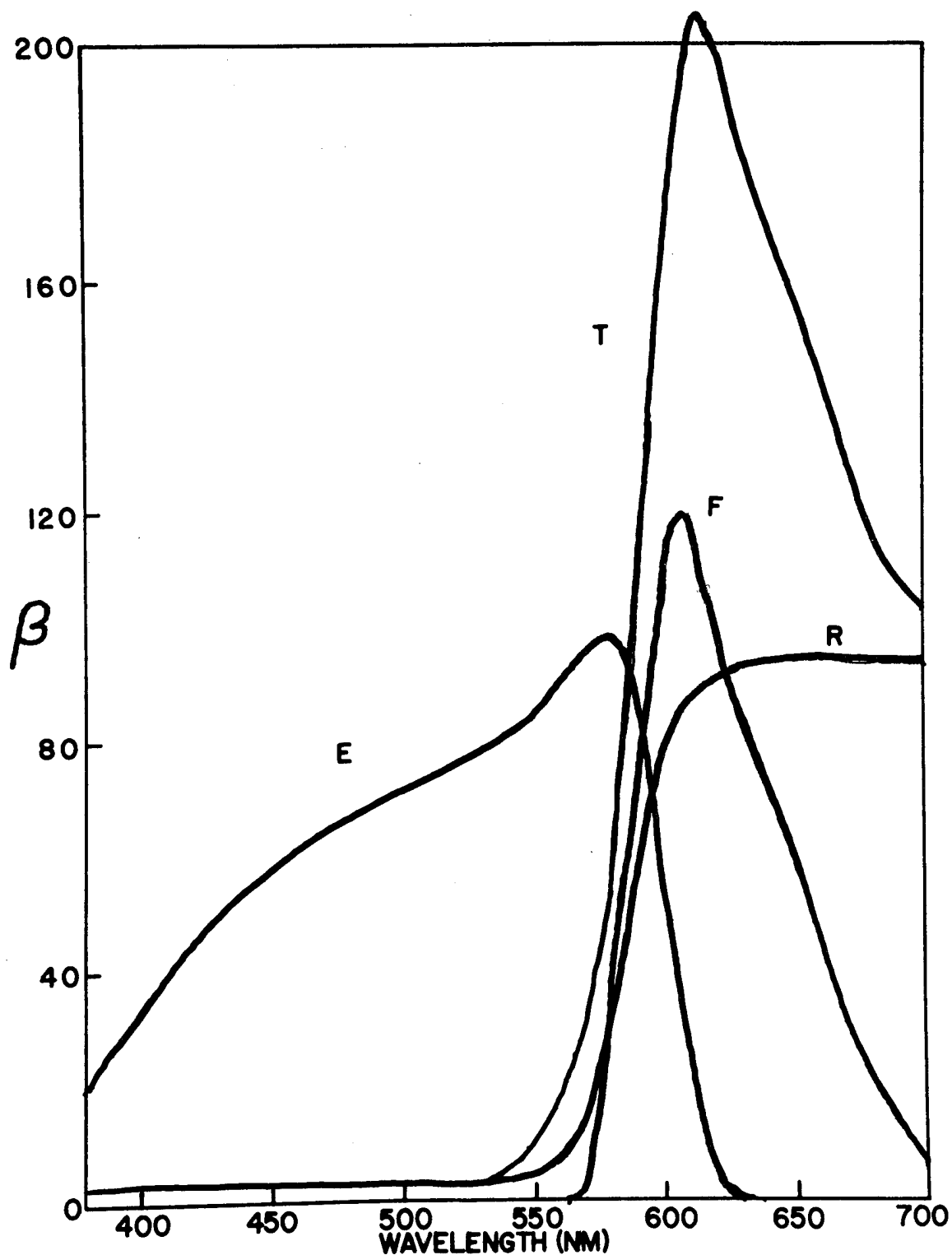


Figure 1. Spectral total radiance factor (curve T), fluoresced radiance factor (F), reflected radiance factor (R), and relative excitation (E) for an orange fluorescent sample, measured with a source simulating daylight. Note that curve T, the sum of the reflected and fluoresced radiance factors, and even the fluoresced radiance factor alone (curve F) for a strongly fluorescent plastic can exceed 100%, whereas this is the upper limit for the reflected radiance factor.

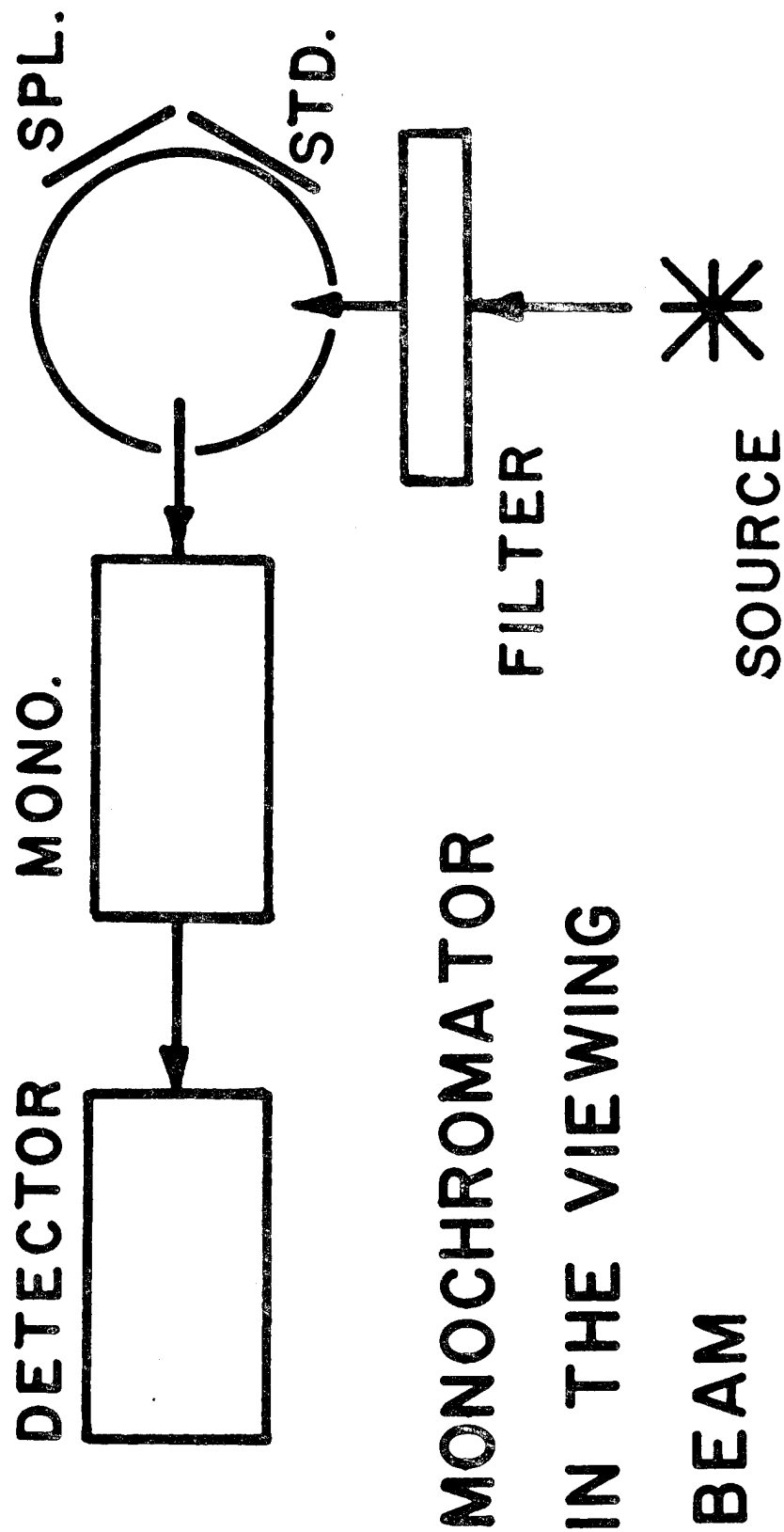


Figure 2. Schematic showing arrangement of components in a spectrophotometer suitable for measuring the spectral total radiance factor.⁴

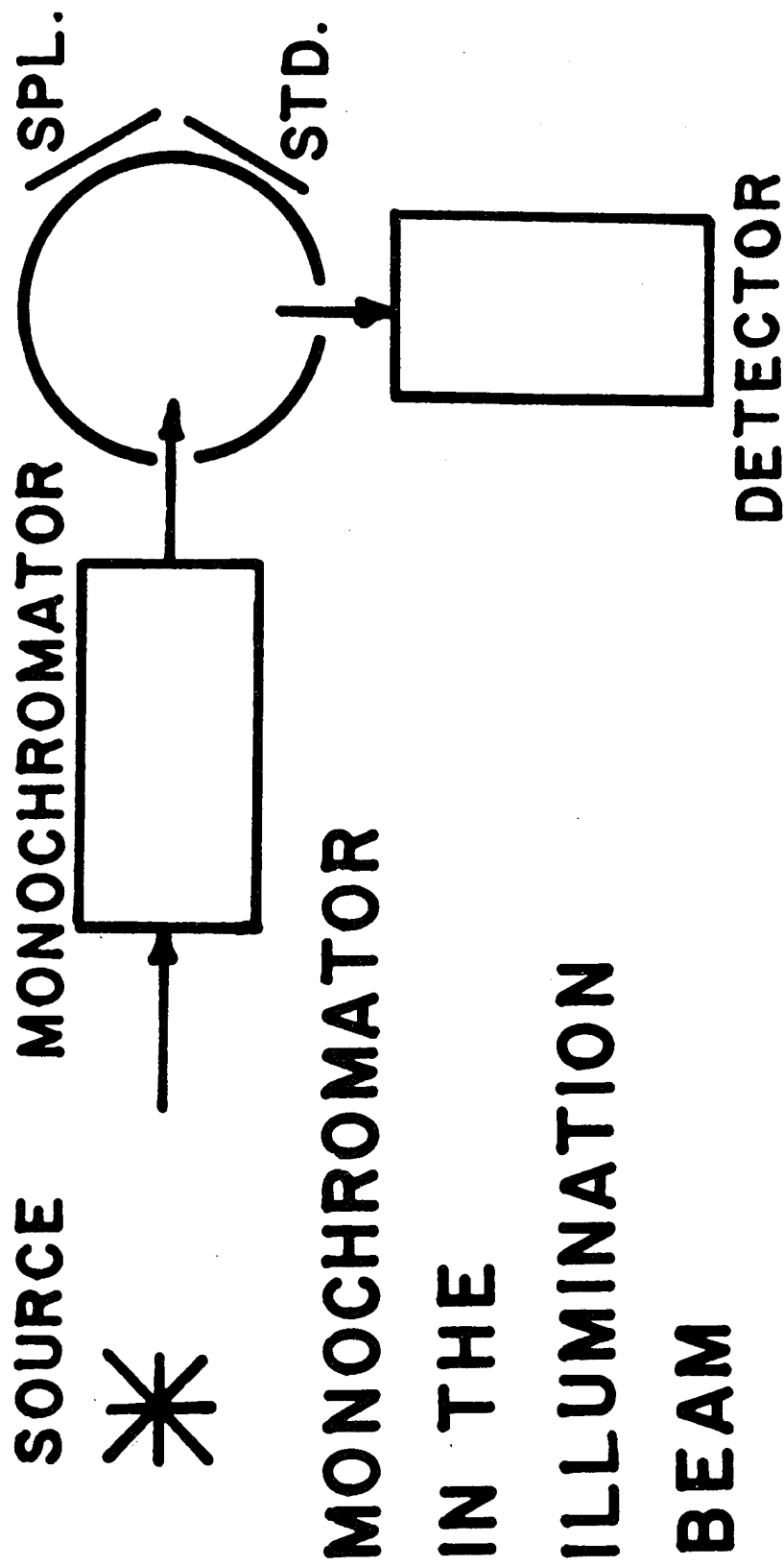


Figure 3. Schematic showing arrangement of components in a spectrophotometer that measures the conventional reflectance.⁴

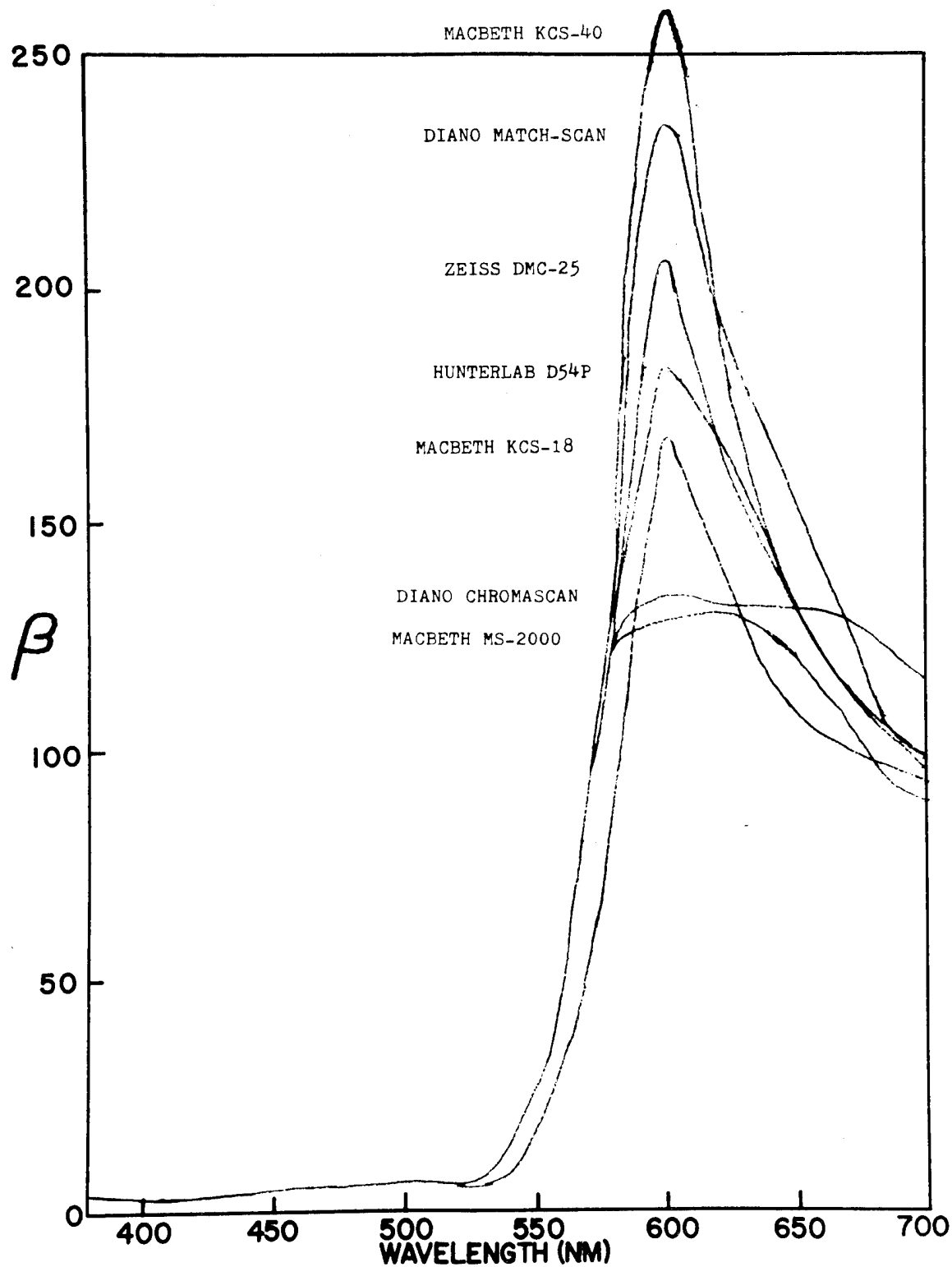


Figure 5. Spectral total radiance factor of a yellow fluorescent sample, measured using the daylight simulators of the commercial spectrophotometers identified on the figure.

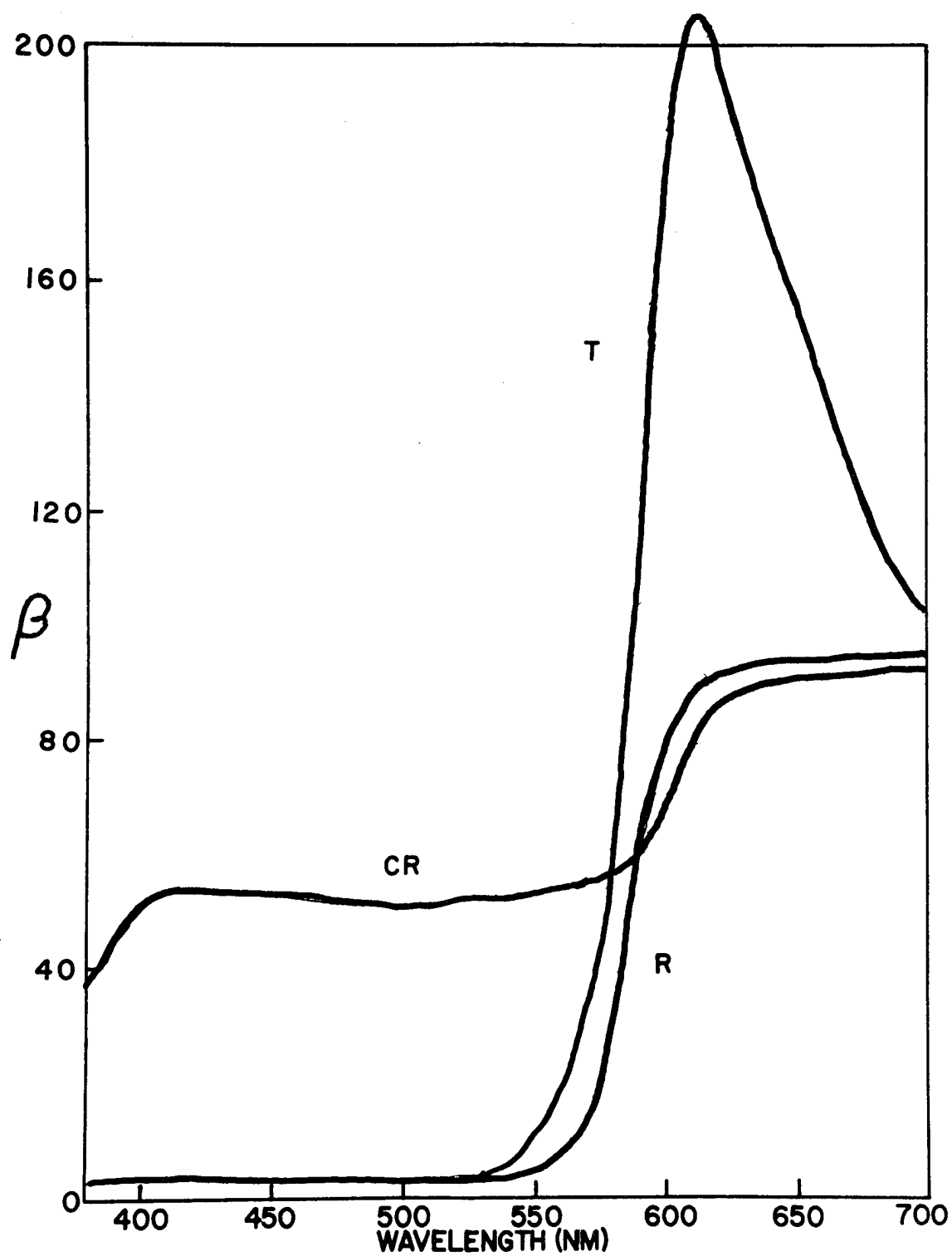


Figure 4. Spectral total radiance factor (curve T), reflected radiance factor (R), and conventional reflectance (CR) for the orange fluorescent sample of Fig. 1.

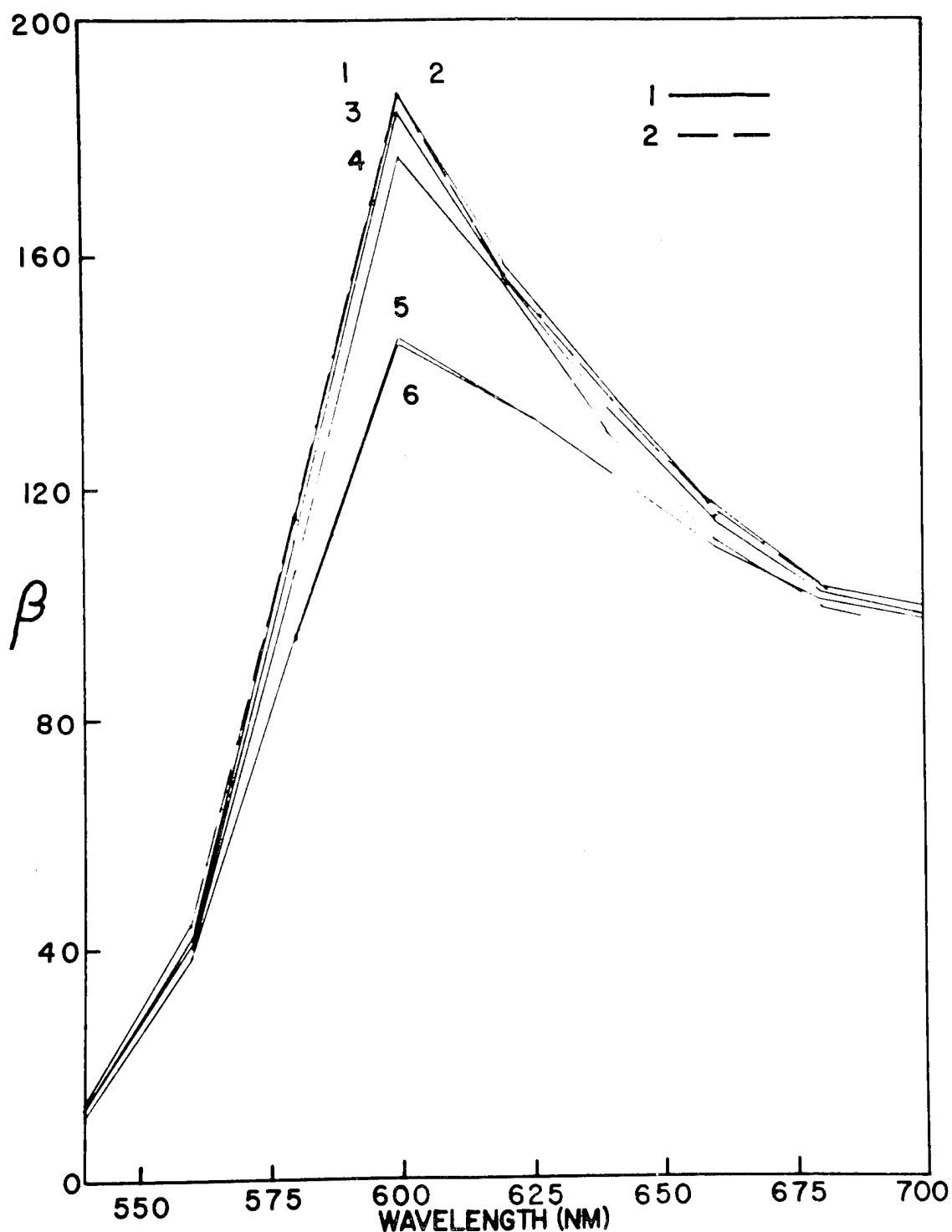


Figure 6. Spectral total radiance factor curves (in the fluorescence emission region only) of the orange fluorescent sample of Fig. 1. Curve 1 is experimental data obtained with a specified daylight simulator. Curve 2 (dashed line barely distinguishable from curve 1) is "best case" calculated data based on measurements using a different simulator; the difference between the simulators was about as great as the difference between either of them and CIE D₆₅. Curves 3-6 represent less accurate but experimentally simpler approaches discussed in ref. 12.

GLOSS HAZE AND YELLOWNESS MEASUREMENTS OF PLASTIC SHEET AND FILM

The thrust of the other papers presented at this meeting emphasize the fact that color is the most important visual appearance attribute to be controlled during the production of plastic materials and components. However, other factors such as gloss, image clarity, haze, translucency whiteness (or lack of yellowness) as well as texture become critically important, particularly when the end product is supposed to be uncolored or clear. Many packaging materials, bottles, windows, and light enclosures are examples of this type product. Even in applications where colors ranging from off-white through highly chromatic are predominant, these other attributes can have an important affect on appearance. Examples are structural and trim parts for automobiles, appliances and now even furniture and buildings. Synthetic textile fibers also exhibit variation in most of these attributes, but because of their unique characteristics, they are outside the scope of this paper.

The paper will concentrate on the above mentioned spatial (geometric) attributes of appearance. I will attempt to define the terms, identify the optical characteristics which cause these effects, and describe some of the important characteristics of instrument measuring systems. Some measurement problems and possible solutions will be cited.

John S. Christie, Jr.
Hunter Associates Laboratory, Inc.

7/3/79

4-1

FORMULATION AND CONTROL FOR ECONOMICAL USE OF COLORANTS

DR. RICHARD L. ABRAMS

DIRECTOR QUALITY ASSURANCE
COLUMBUS COATED FABRICS
DIVISION OF BORDEN CHEMICAL
BORDEN, INC.

FORMULATION AND CONTROL FOR ECONOMICAL USE OF COLORANTS

Dr. Richard L. Abrams, Columbus Coated Fabrics, Division Borden Chemical
Borden, Inc.

Abstract

The cost of pigment or pigment concentrates is a significant concern in many plastic formulations; and pigments are becoming increasingly expensive. Intelligent formulation and control of the coloring process are essential to avoid wasting valuable pigment.

Precise formulation may be aided by the color systems now available, which consist of a color measuring instrument interfaced to a digital computer. Judgment is, however, still necessary in proper application of these systems. Savings using this approach are often great enough that a mini-computer based color system can be justified on raw material savings alone.

Process control and raw material quality control are also important elements of economical coloring. Poor control can lead to an excess of process adjustments, or even to downgraded material.

In essence, one should generate as precise a formula as possible and adhere strictly to it in production.

INTRODUCTION

In this time of rising prices and uncertain economic outlook, with memories of raw material shortages behind us and the possibility of more shortages in the future, wise and economical use of all raw materials is extremely important.

Pigments have been used in some segments of the plastics industry in greater amounts than is necessary. New technology has produced compact and relatively inexpensive digital computer interfaced with spectrophotometers. These, when combined with judgment and good process control, can substantially reduce excessive use of pigment.

FORMULATION

One of the basic rules of good formulation is best expressed in the words of Henry David Thoreau - "Simplify, simplify, simplify!" Use of too many pigments can amplify control problems, and even lead to situations where two colors made with the same pigments are metameric to one another. For instance, if a brown contains yellow, orange, red, black and white, either red or orange can make up for a lack of redness under daylight when orange would be the proper correction, a metameric situation will result, with the color appearing redder under incandescent light than the standard.

Another situation in which simplification of pigment formulation is useful is in the type of printing often done in the coated fabrics industry. This is a type of printing where inks are matched for each station in the printing process. That is, each color in the pattern is individually matched, rather than process printing - matching the overall pattern by overlaying primary color inks, usually cyan, magenta, yellow and sometimes black.

In coated fabrics printing pastel colors are often printed on white bases. A common practice is to add white to the ink to achieve pastel colors. A more economical method is to take advantage of the white base by using transparent or translucent inks whenever possible, allowing the white to "come through" and provide the pastel effect. This requires lower pigment concentration.

An added advantage of eliminating white where possible, is that any ink left over from one run can be re-used in a greater variety of other colors than that containing white; less pigment can be added in making deeper colors.

Choosing the most economical pigments is not simply a matter of selecting the lowest price per pound. Selections will be limited by end use. Such properties as light fastness, heat resistance, toxicity, bleed, heat stability, and other factors dictated by specific application may severely restrict the possible pigment choices. For most processors, it is also wise to limit, as much as possible, the variety of pigments carried in inventory, since storing pigments which are seldom used presents an unnecessary financial burden and ties up capital. If a non-metameric

match is required, this may restrict the choice of pigments to those used in the item which you are matching. A computer color system is valuable in determining what pigments will produce a non-metameric match or one with an acceptable degree of metamerism. The system may give a variety of acceptable matches using suitable pigments, and this will give the option of choosing the least expensive formulation.

If the correct pigments have been chosen, it is a reasonably straightforward procedure to produce a good color match, either visually or by instrument and computer.

Once a color is matched, the precise amount of pigment needed to color a given amount of material should be determined. This is a very important step; and care in this aspect of formulation can make a difference of up to a factor of ten in the cost of pigmentation.

Color matching has too often been merely the process of determining the proper proportions of pigments to one another, and the total amount of pigment needed has been guessed at or set at arbitrary levels convenient to formulators. Since the pigment is often the most expensive component in a compound, colorant concentration should be a primary factor in economical formulation.

Optimum pigment concentration depends on end use. One criterion is the opacity desired. In general, the most economical formulation for a color is that which gives precisely the opacity needed for the end use and no more. Other considerations may enter in determining the minimum pigmentation in a material. Pigments may be used to protect other components of a material from degradation on exposure to light, or to help cover color changes from thermal degradation or stress whitening.

Opacity can be defined either as transmission opacity or reflection opacity. In transmission, the light source and the observer are on opposite sides of the film or object. The opacity is complete only when no light is visible through the material. Light travels directly through the film once, and a high pigment concentration is needed to block the light completely. In reflection, the light source and observer are on the same side of the object or film. If material on a surface is not fully opaque, light travels through it, strikes the surface, and returns through the material to the observer. Because of the longer path length of the light, less pigment is needed for full opacity. Thus, materials which are used to cover a surface, such as wallcovering, or upholstery can have less pigment than a similar material used to block light, such as an opaque window shade.

Reflection opacity is usually measured by placing the material over a surface with a pattern of black and white. Visual determination of reflection opacity is made by judging whether the pattern is visible. Instrumental determination is made by measuring reflectances over white and black, and comparing them by some method. A very common measurement made is

"contrast ratio", the ratio of the reflectance under tristimulus "Y" of the material over a black surface divided by that over a white surface. In strict terms, this is not fully indicative of the visual opacity, especially in some saturated colors, but it is a useful guide. A somewhat more accurate measure is the determination of the color difference of the material over black from the same material over white. Either of the instrumental methods mentioned or the visual method can be used as a working definition for opacity.

Optimization of pigment loading for opacity can be done in a number of ways. If facilities are limited, and a great deal is to be run of a given color, a "cut and try" method can be used, reducing pigment experimentally until the optimum level is reached. Most computer-based color systems have programs for pigment optimization. The minimum pigmentation for a given batch size at any thickness can be computed. The user specifies the opacity desired. A difficulty arises, however, if there is a filler, flame retardant or other substance in the formula which scatters light. Some programs do not compensate for this, and at reduced pigment levels, such substances contribute significantly to the color. A simple way to compensate for this is to compute the white value of each such substance used. An amount of white pigment, equivalent to the white contribution of the substance can be deducted. The white equivalent of a filler may be determined by preparing a sample with a known amount of white and a known amount of black or other colorant and matching the color of this sample as closely as possible, using the same amount of colorant and adding filler. If an existing color formula is reduced by 80%, an amount of white equivalent to 80% of the scattering value present in the rest of the formula should be removed.

If a formula has, for instance, calcium carbonate filler equivalent to one pound of white pigment and has ten pounds of white pigment, there is the equivalent of eleven pounds of white pigment. If the color is reduced 80%, there are two pounds of white in the formula, and the equivalent of one additional pound of white, or, effectively, three pounds of white where 2.2 pounds of white are needed, so 0.8 pounds of white should be deducted to keep the color in balance. If there is not enough white in the formula, the proportions can be adjusted to a point where the filler provides all of the white value needed. Most fillers do not have the same color characteristics as white, but in practice, it is generally in very dark colors - where the "undertone" of the white pigment is not as important - that this adjustment is the greatest. Significant pigment reduction in colors which contain no white are limited to cases where there is little or no white contribution from the rest of the formula. In such cases, it may be desirable to take steps to reduce the amount of white - contributing materials in the formula, or to substitute other substances which do not scatter as much light, such as "low - opacity" versions of flame retardants.

In the author's experience, optimization of pigment loading alone has generated sufficient cost savings to justify the expenditure for computer-based color systems, and savings in color matching time and by good pigment choice have generated further significant savings.

PRODUCTION CONTROL

After a good formula is established, checked and rechecked on a laboratory scale, it is released to the plant. At this point, manufacturing control becomes the most important factor in keeping costs to a minimum. Every effort should be made to conform closely to the formula by raw material control, process control, and the use of sensible color tolerances.

Colorant raw materials should be checked for strength, shade, and consistency. Pigments can be used in a raw form, dispersed in a liquid, or dispersed in a solid material. Raw pigments are the least expensive, but may be difficult to handle, since dusting and resulting cross-contamination is possible. Color control may be complicated by the fact that raw pigments develop color in processing, often at different rates. There is also a possibility that undispersed particles can cause lumps or streaks in the product.

Liquid dispersions may be quite convenient to use in some systems. Care should be taken, however, to see that the colorants do not change on storage. Strength can change through such processes as flocculation and settling of the pigment, and evaporation of the liquid may be a problem in some media.

Solid dispersions are usually the most expensive, but are more stable on storage than many liquid systems and do not have the handling and mixing problems of raw pigments. Particle size and particle size distribution of solid pigment dispersions are important considerations if there is a dry-blending operation in the process, or if shear and heat are insufficient in the process to break down large particles of dispersions.

The principles of testing any form of pigmentation are generally the same. Shade should be checked in masstone and tint both; strength is most readily checked in tint. Sample preparation conditions should be kept as constant as possible and similar to conditions encountered in use. This is particularly important in raw pigments, since strength and shade can vary with the process. A large enough supply of reference pigment from one chosen lot should be set aside for tint tests anticipated over a reasonable length of time. The reference pigment is usually white for colors used for their absorption characteristics, and black or a colored pigment for testing lots of white and other scattering pigment. Care should be taken to see that the reference pigment is not in a form which will change strength or shade on storage. Tint levels should be chosen for convenience in detecting strength differences; very light tints are the most sensitive for this. Evaluation can be done visually or instrumentally, but methods should be agreed on between customer and supplier if the tests are to be used for acceptance or rejection of lots.

The costs of poor pigment control are twofold:

- (1) If pigment strength is low, the buyer of pigment is effectively paying the same price for less coloring value.

- (2) If control is poor, process adjustment must be made, which consumes plant time and requires added pigmentation.

The next concern is good general industrial practice. Weighing of colorants is a critical step, and great care should be taken to maintain precision and accuracy. Scales must be kept clean and in good calibration, and good weighing technique is important. In weighing small quantities of pigment it is often helpful to establish "letdowns", dilutions of pigments 10%, or some other convenient percentage of the standard colorants. Poor weighing of a good formula leads to more corrections, wasting time and material. In tinted white, this is particularly true, since small excess amounts of tinting pigments may require massive amounts of white for correction.

When a batch of blended material is sampled for color correction or approval, care must be taken to see that the sample taken is representative of the batch as a whole. Color corrections based on poor samples can be too large or small, or even in the wrong direction, requiring further corrections. In large batches, it is often desirable to sample from two or more different locations, and combine the samples for evaluation.

A final consideration, too seldom thought of in terms of cost, is the color tolerance. Too tight a color tolerance for a given application can be expensive because of additional color correction, requiring expenditures of time and colorants. It may also result in reprocessing or internal downgrades. Too loose a tolerance can lead to customer rejections and returns. Decisions made on color approval are best made by using a combination of visual and instrumental techniques.

SUMMARY

Economic use of colorants is not a simple matter; it requires a great deal of judgment and some common sense. A delicate balance must be maintained between wasting expensive colorants, affecting product cost, and being concerned with cost saving alone, sacrificing quality. Excellent tools are now available in computer color systems, but human judgment is still the most important element. Well-controlled raw materials, good formulations, close adherence to the formulations, and sensible color tolerances are the elements necessary for cost-effective coloration of products.

FIGURE 1

TRANSMISSION OPACITY

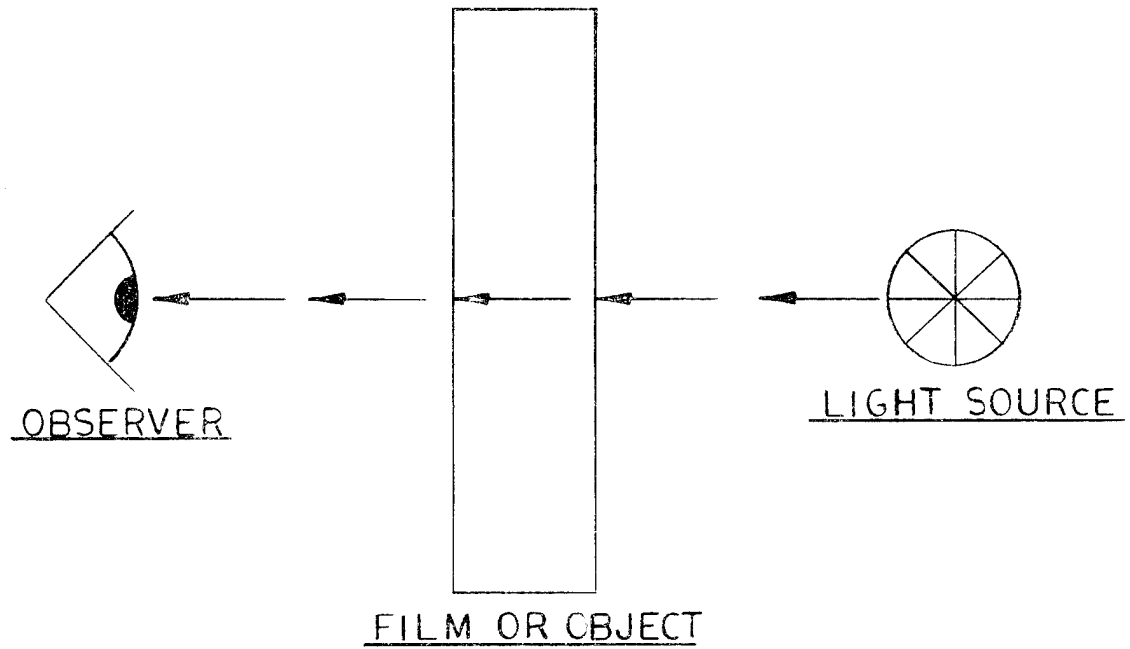


FIGURE 2

REFLECTION OPACITY

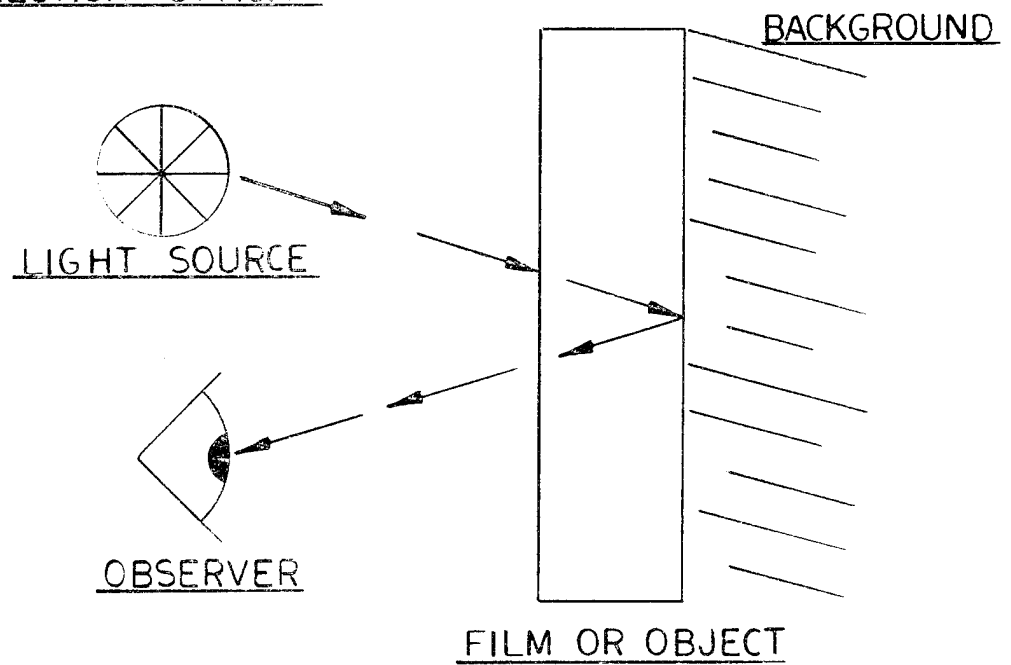
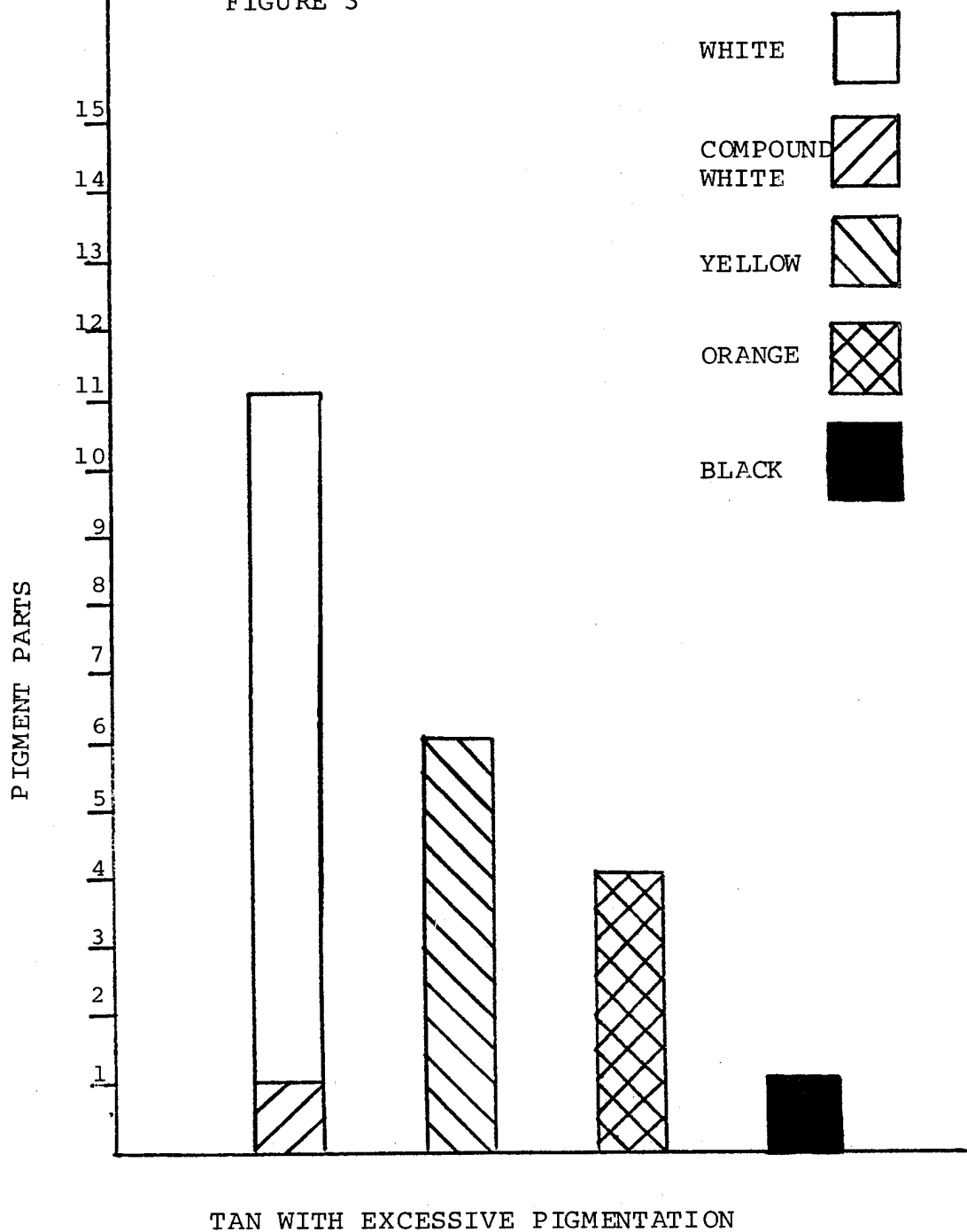
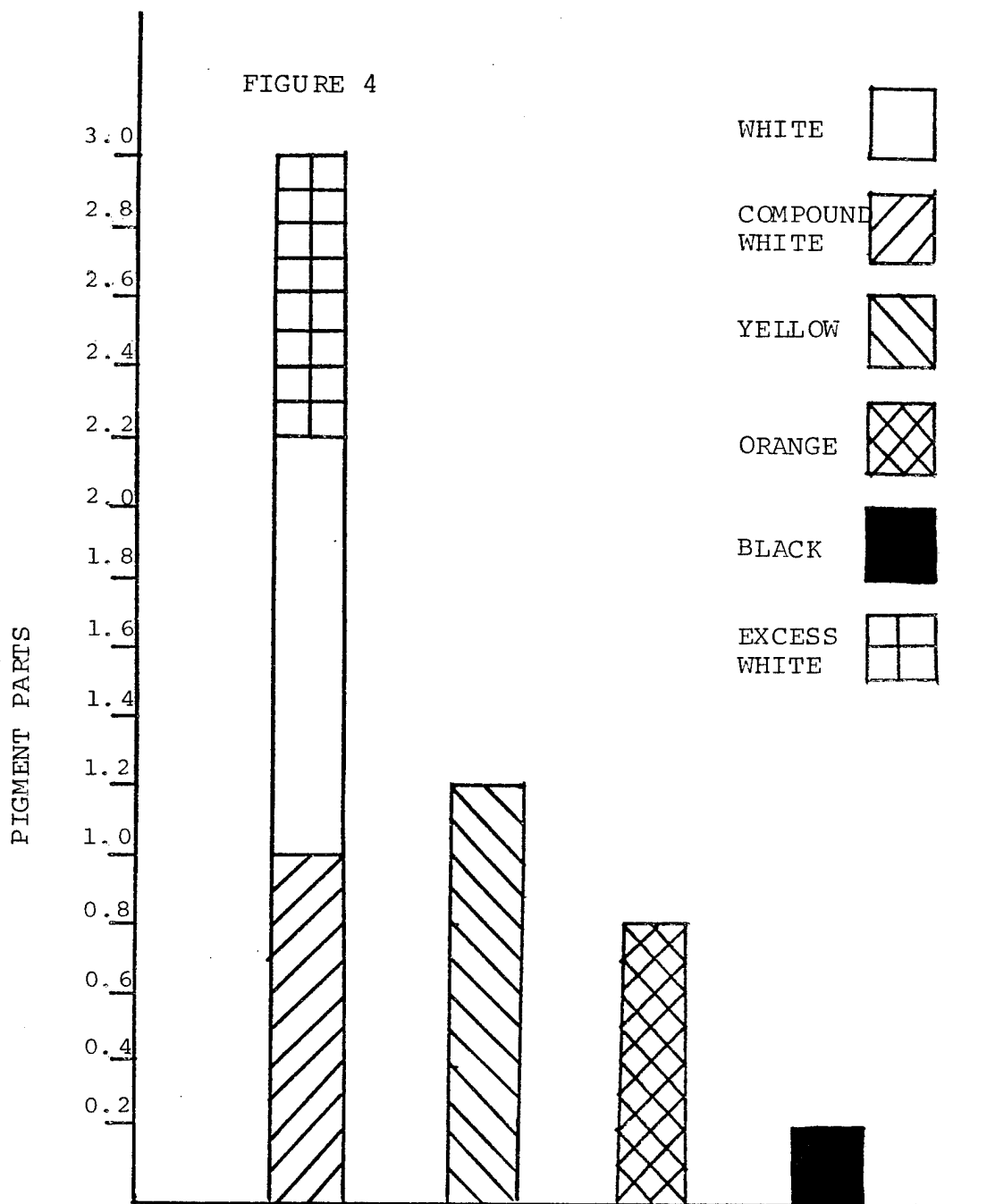


FIGURE 3





SAME COLOR AS FIGURE 3, PIGMENTATION
REDUCED BY 80%, SCALE EXPANDED 5X

APPLICATION OF POLYMER CHARACTERIZATION
IN
COMPUTERIZED DARK COLOR MATCHING

DAVID ALSTON

MANAGER, APPLICATIONS
APPLIED COLOR SYSTEMS INC.
P. O. BOX 5800
PRINCETON SERVICE CENTER
U.S. HIGHWAY ONE
PRINCETON, NEW JERSEY 08540

APPLICATION OF POLYMER CHARACTERIZATION IN COMPUTERIZED DARK COLOR MATCHING

Computerized Color Systems have become a recognized method for solving color problems. The major use of these systems has been in the following areas:

1. Computing the proper ratio of pigments to each other, to satisfy certain color specifications (Color Matching).
2. Determination of total pigment load to satisfy certain opacity parameters at a specified thickness. In many instances the pigment load is determined by the user, based on experience.
3. Adjustments of initial colorant formula to compensate for color variance due to variables in raw materials and production process and techniques (Batch Corrections).

Present techniques in today's Color Systems handle the above problems quite well. However improvements can be made when matching in high scatter (filled) and high color (ABS) compounds. Also closer predictions for dark colors can be obtained thru improved colorant and base characterization techniques.

EXISTING METHODS

Most systems today incorporate the Kulbelka-Munk theory of additive color mixing. This theory deals with optical constants of absorption (K) and scatter (S). The relationship of the ratio K/S to that of reflectance is given in the following equation:

$$K/S = \frac{(1 - R)^2}{2R}$$

Where R is the reflectance of the sample

K/S is directly proportional to concentration while reflectance is not. The procedure for prediction a colorant formula incorporates the following equation at each wavelength of consideration (usually 16):

$$K/S_{mix} = \frac{C_w * K_w}{C_w * S_w} + \frac{C_{p_1} * K_{p_1}}{C_{p_1} * S_{p_1}} \dots \frac{C_{p_n} * K_{p_n}}{C_{p_n} * S_{p_n}}$$

Where C = concentration

W = White

P1 thru Pn = Pigments

These equations predict the correct ratios of pigments to white and pigment to pigment to satisfy the given color requirements. In most cases the data file is a relative one based upon the scatter of white being set to some number (usually 1.0). As long as the scatter portion is satisfied by white or pigments having high scatter, the above formulas work well.

But when transparent organic pigments and low white are used, the definition of S for the equation becomes weak. This is due to the fact that most scatter in that situation comes from the base compound. A more correct equation would be as follows:

$$K/S_{\text{mix}} = \frac{C_{\text{BASE}} * K_{\text{BASE}}}{C_{\text{BASE}} * S_{\text{BASE}}} + \frac{C_w * K_w}{C_w * S_w} + \frac{C_{p_1} * K_{p_1}}{C_{p_1} * S_{p_1}} \dots \frac{C_{p_n} * K_{p_n}}{C_{p_n} * S_{p_n}}$$

Where: Base = Polymer Compound

W = White

P = 1st Pigment

P_n = Final Pigment in Mix

C = Concentration

S = Scatter Coefficient

K = Absorption Coefficient

The concentration of polymer (CBASE) in most cases will be well over 90% of the total. Therefore when the total scatter of white is low (CS*SW) the effect of base scatter is very important (CBASE*SBASE).

NEW PROCEDURES

The new procedures call for characterizing the base compound in terms of K and S. This is accomplished by mixing the base compound with white pigment and with black pigment (same approach is used for pigments). Present characterizing programs can compute the necessary K and S for each wavelength of consideration. This base compound scatter and absorption will be relative to the scatter of the white. Since the pigments are also relative to the scatter of white, the base compound becomes relative to the pigments. This allows for accurate scatter definition when no white is used.

In the past all load calculations were made as a function of hide. (Contrast Ratio of Specific Thickness) whether it covered the base compound

enough to permit matching color or not. Consider the following:

1. In high scatter compounds it is possible to have complete hide (98 contrast Ratio or higher) with very little pigment load (maybe less than .1%). It is obvious that high chroma colors cannot be matched at this load.
2. In very clear compounds it is possible to match colors at opacity thickness but be over loaded in pigment at some thinner thickness (Transluents).

Since the base compound is an independent variable of the match, we are always working with a color load situation. If the load for color exceeds that necessary for hide, then the load for color should be used. In this way the loading will be high enough to compensate for compound color (K) and scatter (S).

Also in a no white situation the correct amount of compound scatter is calculated accurately from the compound K and S data. First shot matches and better pigment loads for no white matches will result.

CONCLUSION

Programs to utilize the above concepts will be available by early 1980. Present programs can be utilized to gain above benefits with some limitations.

EVALUATION AND IMPLEMENTATION
OF AN IN-HOUSE COLOR PROGRAM

William A. Jarrett

Crane Plastics, Inc.
Post Office Box 1047
Columbus, Ohio 43216

Introduction

Historically, functional performance - not color - has been the primary criterion in the design and use of profile extrusions. In recent years, however, color and appearance have assumed greater importance. In this paper I will discuss a profile extruder's evaluation and implementation of an in-house color program.

Background

Extrusion grade materials are supplied in pre-colored pellet or cube form. Color availability is typically limited to white, gray and black. Although some resin suppliers offer a variety of colors in extrusion grade compounds, they do not always meet customer color requirements. As a result, a custom color match was necessary. Custom color matches, approval and then delivery were often very slow. For the resin supplier, low volume in colored extrusion grade compounds often meant low profitability. Ultimately higher prices and minimum quantity compound requirements were imposed. Custom profile extruders were forced to order large quantities of pre-colored material and hold un-used inventory hoping for a repeat order. This proved to be even more costly since customer color requirements frequently changed. In addition, in making these minimum runs, the resin compounder often did not meet color match and/or control requirements. Thus, for many custom profile extrusion applications, colored material costs became excessive.

With increasing customer demand for quality color in custom profile extrusion, the profile extruder had to look for a new solution.

An alternative for the profile extruder is to implement a complete in-house color program.

In-House Color Program Guidelines

The primary objective of an in-house color program is to serve customers with faster delivery and accurate colors. It must be recognized that establishing an in-house coloring operation is not easy. To assume the burden of in-house coloring requires a number of operational changes; but, the key to success is extensive staff training, implementation of new processing methods and purchase of new equipment and materials.

Some of the guidelines for establishing an in-house coloring program are:

1. Pick a person who can head up the program and can communicate with both management and production personnel.
 - a. This person should have abilities to cope with color technology and -
 - b. Recognize the practical aspects of implementing new ideas and procedures into an existing business.
2. Determine which customer color requirements really warrant in-house coloring. The Sales Department and Production can usually provide data such as volume, machine requirements and areas of difficulty with respect to specific customers' color requirements.
3. Identify and select the base polymers and/or compounds to be colored. Requirements are:
 - a. Uniform base color.
 - b. Uniform flow performance.
 - c. Good physical properties.
 - d. Material should be forgiving enough to be extruded on various machine sizes with a variety of screws and dies at required rates.
4. Establish base pigment and color concentrate sources. It requires:
 - a. Identifying pigments and color concentrates suitable for use in various polymers or compounds.
 - b. Picking and working with vendors.
 - c. Establishing reasonable color specifications for incoming materials.
5. Establish a means of identifying each color quantitatively.
 - a. This requires acquisition of instrumentation that will provide quantitative color data.

- b. Define acceptable color variation for each material and customer requirement.
- 6. Determine the best method of adding color pigments and concentrates to the base compound. Some equipment to evaluate includes ribbon blenders, drum tumblers, intensive mixers (powder compounds) and hopper feeds at the extruder.
- 7. Establishment of training procedures. Programs should be developed for:
 - a. Color laboratory.
 - b. Quality assurance.
 - c. Production personnel.
 - d. Sales staff.
- 8. Determination of time frames. Set up a time oriented program that includes research and pre-trial, and program launch. Procedures from initial customer color match request, to scheduling of extrusion, quality control and shipment should all be time oriented. Success in developing an in-house color program requires everyone keep an open mind. If people are sure that such a program will not work, it is defeated from the beginning. One must be realistic and dedicated to making the program work. The degree of sophistication of an in-house coloring program must meet the individual company's needs and priorities.

Personnel Training and Equipment Acquisition

Once the decision has been made to implement an in-house color program, the first step is the selection and training of lab personnel in basic color techniques and operation of the equipment necessary to achieve and control a commercial color match in various polymers.

Depending on the degree of sophistication, you can hire a trained color matcher or promote and train from within. Good information sources for training might include lectures and seminars by optical instrument manufacturers, visits to pigment and color concentrate manufacturers and attendance at courses such as those conducted by our Color and Appearance Division of SPE. During the training period, generally one finds there is some basic laboratory equipment that is necessary to evaluate pigments and color concentrates in various polymers and for controlling

quality and color in the finished extrusion. Again, economics and degree of sophistication will dictate the equipment a given company will purchase. Some typical equipment are:

1. Accurate analytical balance.
2. Two roll mill.
3. Heated press.
4. Light booth.
5. Colorimeter.
6. Gloss meter.
7. Intensive Lab Mixer.
8. Brabender Plasticorder with strip extruder and fusion bowl.
9. Abridged or continuous spectrophotometer.
10. Computerized Color Formulation.

Lab personnel must be responsible for pigment and color concentrate selection and proper material formulation. Powder compounds must be color formulated to allow a degree of freedom for batch control. Generally, a minimum of four pigments should be used to permit adjustment to lightness/darkness, redness/greenness, and yellow/blueness. This "adjustment ability" minimizes the effects of color deviations. It's best to check all deviations against a master color standard using the colorimeter. From this analysis color acceptability can be determined and pigment level adjustments defined.

Color concentrate selection should be based on extrusion end-use requirements. Vendors can tailor these to meet specific requirements such as UV stability, or FDA or USDA requirements. Best results are achieved by supplying the vendor with complete information on the base compounds, processing method, operating temperature, physical requirements, color and opacity requirements, color match tolerances, let down ratio, and price range.

In-house blending should only be done with pre-approved ingredients. And, records should be kept on recipes to assure that proper formulas are always being used. Inaccurate weighing is the most frequent cause of color variations. Weighing scales should be regularly maintained and frequently checked for accuracy.

In the powder blending area, the intensive mixer, cooler, screens and work area must be cleaned regularly. Good housekeeping can help prevent color contamination and cut dollar loss.

All pigments should be laboratory tested in the base compound. Then each pigment drum can be tagged with prescribed "add" levels to the base compound. Knowing that the pigment works simplifies the chore of finding the reason for an off-color extrusion by steering the search to a check of the variables in the extrusion process - heat, screw speed, etc.

One of the keys to achieving good color dispersion in extrusion is to take a close look at these process parameters - screw L/d ratio, back pressure, temperatures, speed, die design, and machine size. Experience shows that the best color will be achieved using "low wear" extruders and special mixing screws to achieve maximum color dispersion. Other aids to color dispersion include regulation of temperature and extrusion rates, and addition of screen packs to increase back pressure. Also, proper die design to yield optimum flow characteristics will provide a latitude in melt temperature requirements. Regular quality assurance checks are important for design-function, appearance, and color. QA personnel should be trained in use of the colorimeter and part sample preparation and presentation.

Experience shows that it will take about a year and a half to train personnel, obtain needed equipment, and bring the system on-stream. And, based on experience, there are a number of continuing pitfalls that must be closely watched.

Obsolete Color Concentrates

Even with in-house coloring, it is still possible to end up with obsolete color concentrates due to customer changes. Concentrates are high in cost per pound and, hence, hard to discard. There is no easy way to resell, sell back, or use obsolete color concentrates that have been prepared for a specific base compound.

Elusive Color Opacity

Product thickness, natural compound, and the colorant system all have a role in achieving good color opacity. Often it is difficult to achieve the degree of color opacity required without making a highly loaded color concentrate, or using a different base compound. If opacity is important, run a trial first.

Working with a Common Base Compound

For in-house color, it is best to base all color formulations on the use of just one base compound. This base compound, however, may not have the impact, physical, and weathering properties required by the customer. The key here is to make sure that the end use is established before the color system is finalized.

Skilled Operators Required

Color adds another variable for the operator to watch. A change in barrel heats or flow rates can affect the color, color dispersion and color appearance (gloss). Hence, in addition to perfecting the profile shape, the operator must now have the skill needed to optimize operating conditions to achieve both shape and a quality color match.

Special Die Requirements

Many extrusion dies that work well with conventional or pre-colored compound may not work well with an in-house color system. Often die redesign is required to achieve needed color dispersion and development.

Colored Scrap

In addition to having a higher percentage of scrap (in an effort to "bring the color in" as well as the profile), there is the problem of segregating the colored scrap for regrind use. A profile can be scrapped for physical properties, shape, tolerances, or color reasons. If the reason for "scrapping" was inadequate color, care must be taken not to regrind and rerun this material again or the original color problem will be compounded.

Colorant Add Levels

The problem here is to establish consistent communications between all shifts running the same profile to make sure that colorant add levels are the same - that all formulas for color are closely followed.

Human Error

In-house color is not fool-proof, and even with specialized training there will be errors. Constant checks must be made to ensure proper use of formulas, add levels, etc.

In-house coloring is not easy, but it does offer potential savings and the ability to meet customer needs for quality color. For large volume orders, pre-colored compound is still appealing, because it eliminates extra in-plant handling and capital expenditures. Where short custom color runs are required, however, pre-colored compound is usually not available. If it is available, there is usually a cost premium. Against the exclusive use of pre-colored material, in-house coloring cost savings can quickly pay off the initial capital investment.