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The Use of Instrumentation in Cosmetic Color Control

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Synopsis—For many years color measurements have been used in laboratories for the evaluation of color differences. Up until the last few years, however, they were usually employed only for qualitative evaluation in production. During recent years new measuring instruments, techniques, and computers have been developed in order to permit routine use in color production problems. These new techniques are described. Some of the basic theory is reviewed, but the emphasis is on the practical application. The use of a colorant mixture computer is described in detail.

Introduction

Within the plastics, textiles, and paints fields the use of instrumentation for color control has become much greater during the past few years. Over 150 installations in these fields have proved to be successful in reducing costs, improving quality, and increasing production. The interest in instrumentation is now spreading into the cosmetic industry. The problems which will be encountered here are similar to those in other fields, and there is every reason to suppose that instrumentation for cosmetic color control will prove as beneficial as it has in other industries.

Among the first of these instrumental systems, and by now the most widely used, is that employing the Davidson and Hemmendinger Colorant Mixture Computer (COMIC). It is the purpose of this paper to describe briefly the theory behind this system and to discuss some applications in cosmetics.

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Color Theory

The primary specification of the color of a given sample is based on the spectrophotometric curve. The solid line in Fig. 1 is the spectrophotometric curve of a beige powder in the form of pressed cake. Plotted horizontally on the graph is the wavelength of light. The vertical dimension of the graph represents the relative amount of light reflected by the sample. Figure 1, for example, shows that less than 30% of the blue light is reflected and about 60% of the red light is reflected. The exact reflectance of the sample for any wavelength of light may be read directly from the curve.

The spectrophotometric curve of a colored product has several useful properties. If two samples have identical spectrophotometric curves, one will be a color match for the other, assuming no differences between them in texture or gloss. Furthermore, these two samples will appear to be a match regardless of what light is used for illumination and regardless of whether the observer has normal color vision. Unfortunately, however, the converse is not true. One cannot assume that if two samples are a color match under one particular illumination they have identical spectrophotometric curves and will match in all illuminants. The samples may be metameric; that is, they may match under one illuminant but not under another. In this case the spectrophotometric curves will not be identical. This problem of metamerism is responsible for many of the color matching problems in industry.

Another important property of the spectrophotometric curve of a mixture of pigments is that it exhibits the spectral characteristics of the individual pigments used in the mix. The color represented by Fig. 1, for example, was made with an iron oxide red, Mapico®* yellow, ultramarine blue, and white (titanium dioxide). The spectrophotometric curves of these pigments are shown in Figs. 2 and 3. It should be noted that the characteristic valleys which appear in the curves of the mixtures of the colored pigments with white also show up in Fig. 1, i.e., when all three pigments are used in the mixture. The Mapico yellow shows a characteristic dip in the 400 to 450 nm range in both Figs. 1 and 3. The red shows the same slope in the 550 and 580 nm range in both Figs. 1 and 2. The characteristic slope of the ultramarine blue in the region 650 to 700 nm shown in Fig. 3 is repeated in Fig. 1, although somewhat obscured by the red and yellow. Because these pigment characteristics are retained in mixtures, appropriate pigments may be

* Mapico is a trade name of Columbian Carbon Co., Trenton, N. J.

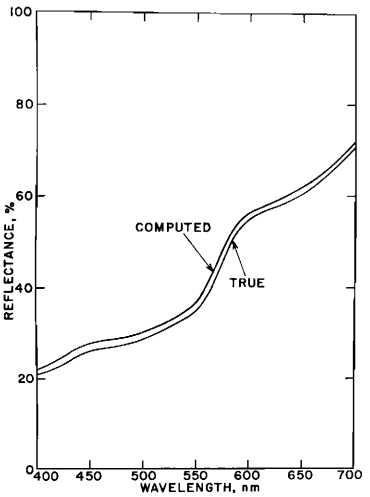

Figure 1. Spectrophotometric curves of a pressed cake sample ("True") containing red iron oxide, Mapico yellow, ultramarine blue, and titanium dioxide and the predicted curve ("computed") based on the known pigment quantities

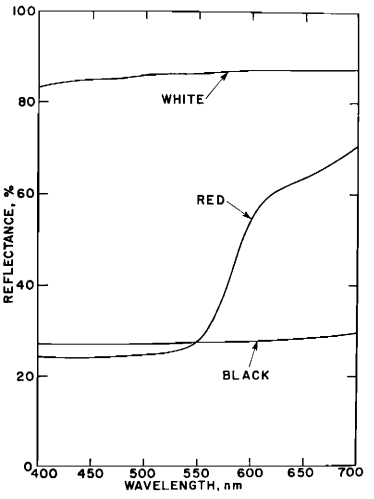

Figure 2. Spectrophotometric curves of pressed cake samples containing white only, a mixture of 1% red iron oxide and 99% white, and a mixture of 1% black and 99% white

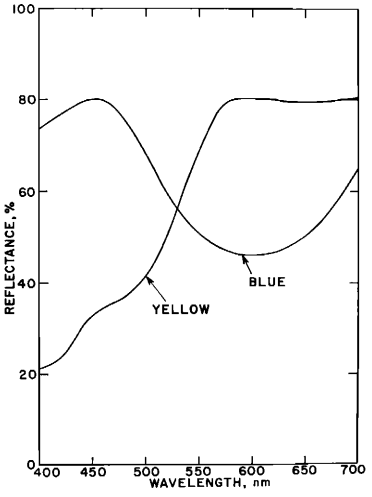

Figure 3. Spectrophotometric curves of pressed cake samples containing 1% ultramarine blue and 99% white, and 1% Mapico yellow and 99% white

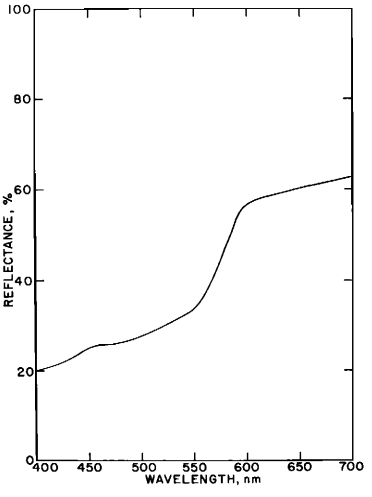

Figure 4. Spectrophotometric curve of a pressed cake sample containing Mapico yellow, red iron oxide, black and titanium dioxide

chosen on the basis of the spectrophotometric curve. For example, if an attempt were made to match the color shown in Fig. 1 with a powder containing black in place of ultramarine blue, a curve similar to that shown in Fig. 4 would have been obtained. Notice that the flat curve of the black as shown in Fig. 2 produces a flatter curve than does the blue in region 600 to 700 nm. Thus if black rather than blue had been used, only a metameric match to the powder the curve of which is shown in Fig. 1 would have been obtained. It might be a satisfactory match under one light but not under another. On the basis of the spectrophotometric curve, then one should attempt to match the sample with blue rather than black as the dulling component. Although the choice of pigments required to match the color of Fig. 1 is fairly obvious from the curve shapes, the choice is frequently not this apparent and becomes clear only after quantitative calculations have been made.

Determination of the amount of pigment required is usually based on the Kubelka-Munk (1) theory. The basic relationship may be expressed in the following equation, where K/S is the ratio of the coefficient of absorption to the coefficient of scatter and R is the reflectance.

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

This equation is true for an opaque material at any given wavelength of light. It may be assumed that the value K/S is proportional to the per cent concentration of colored pigment relative to white pigment in the material and that the K/S value in a mixture of pigments is a simple additive function of the K/S values for the individual pigments. These assumptions are described mathematically in equation 2 and are valid except for colors in which the white pigment content is very low.

$$K/S_M = C_A K/S_A + C_B K/S_B + C_C K/S_C + K/S_W \qquad 2$$

The values K/S_A, K/S_B, and K/S_C are values for unit concentration of pigments A, B, and C in white and C_A, C_B, and C_C are the concentrations of the pigments in the mixture. K/S_W is the value for the white alone; K/S_M is the value for the mixture. All of the K/S values, of course, are for the same wavelength. By the use of this equation, the K/S value for a specified mixture of pigments can be predicted, providing the K/S values for the individual pigments at unit concentration are known. Equation 1 may then be used to compute the predicted reflectance at the

TABLE I

Pigment Calibrations

	White		1% Red Oxide			1% Mapico Yellow			1% Ultramarine Blue		
	R	K/S	R	K/S_M	K/S_R	R	K/S_M	K/S_Y	R	K/S_M	K/S_B
400	83.0	0.017	24.1	1.195	1.178	20.5	1.542	1.525	73.5	0.048	0.031
450	84.8	0.014	24.1	1.195	1.181	33.1	0.676	0.662	79.9	0.025	0.011
500	85.7	0.012	24.8	1.140	1.128	42.0	0.401	0.389	68.3	0.074	0.062
550	86.2	0.011	27.8	0.938	0.927	71.0	0.059	0.048	50.6	0.241	0.230
600	86.9	0.010	54.5	0.190	0.180	80.1	0.025	0.015	46.0	0.317	0.307
650	87.0	0.010	63.5	0.105	0.095	79.5	0.026	0.016	50.4	0.244	0.234
700	87.4	0.009	70.5	0.062	0.053	81.5	0.021	0.012	65.5	0.091	0.082

same wavelength,* and this prediction may be made for a large number of wavelengths. It will be apparent, therefore, that by means of equations 1 and 2 the spectrophotometric curve of any mixture of pigments may be predicted, providing the values for the individual pigments are known. An example will help to clarify the method.

Table I lists the reflectances of 1% concentrations of red oxide, Mapico yellow, and ultramarine blue in titanium dioxide. These values were taken directly from the spectrophotometric curves of the pigments shown in Figs. 2 and 3 and are given for the wavelengths shown. In the next column to the right of that giving the reflectance, the corresponding K/S values are given. These values are for the mixture of 1% colored pigment and 99% white and are equivalent to the K/S_M value given by equation 2 for one colored pigment plus white. In order to get the K/S values for the pigment alone, the K/S values for white, which are also given in the table, are subtracted. This has been done to obtain the "corrected" K/S values in the next column to the right. It is these corrected values labeled K/S_Y, K/S_R, and K/S_B which must be used in equation 2.

Now let us try to predict the reflectance at 500 nm of a mixture of:

Red oxide	0.5%
Mapico yellow	0.5%
Ultramarine blue	0.2%
White	98.8%

Using equation 2 and the values in Table I one finds:

$$K/S_M = 0.5 \times 1.128 + 0.5 \times 0.389 + 0.2 \times 0.62 + 0.012 = 0.782$$

The tables of K/S *vs.* R indicate that a K/S value of 0.782 corresponds to a reflectance of 30.7%. Thus one would predict the reflectance of this mixture to be 30.7% at 500 nm. The actual reflectance of the mixture, labeled "True" in Fig. 1, is 28.6%. Similar calculations can be made at each of the wavelengths for which data are tabulated. This has been done, and the results are plotted in Fig. 1 (labeled "Computed") so that the predicted curve may be compared with the actual curve. It will be noted that the predicted curve is 1½ to 2% higher than the true curve. The two different colors represented by these two curves would not be a sufficiently good match for most cosmetic applica-

* In practice, however, tables of K/S *vs.* R are used rather than calculations in accordance with equation 1. Such a table appears in Ref. 1.

tions, but they would be close enough so that an adjustment, as will be described below, would produce a color which would be an acceptable match to the standard. The error in prediction may be due to a number of causes such as variations in pigment strength, grind, or errors in sample preparation.

The manner in which this spectrophotometric theory is utilized will be described below. For a full understanding of the computer, however, some colorimetric theory will also be required.

The color of a sample may be described in terms of its tristimulus values, X, Y, and Z. If two samples have the same tristimulus values, they will match under the illuminant for which these values were computed even if the spectrophotometric curves are not identical. The tristimulus values may be computed from the spectrophotometric curve by means of equation 3.

$$\begin{aligned} X &= \int E\bar{x}Rd\lambda \\ Y &= \int E\bar{y}Rd\lambda \\ Z &= \int E\bar{z}Rd\lambda \end{aligned} \qquad 3$$

E is the relative distribution of energy in the light source used for viewing the sample, $\bar{x}$, $\bar{y}$, and $\bar{z}$ are values dependent on the characteristics of the human eye, R is the reflectance of the color, λ is the wavelength of light, and the integration is carried out over the entire visible spectrum. All of these values vary with wavelength, and the values for $\bar{x}$, $\bar{y}$, $\bar{z}$, and E have been standardized by the International Commission on Illumination. The computation is usually made either by an automatic computer attached to a recording spectrophotometer or by a combination of filters and photocells in a colorimeter. Similarly, the difference in color between two samples having differences of ΔR in their spectrophotometric curves is given by equation 4.

$$\begin{aligned} \Delta X &= \int E\bar{x}\Delta Rd\lambda \\ \Delta Y &= \int E\bar{y}\Delta Rd\lambda \\ \Delta Z &= \int E\bar{z}\Delta Rd\lambda \end{aligned} \qquad 4$$

If one can predict the spectrophotometric curve of a sample having a given pigment formula by means of equations 1 and 2, then one can also predict the color by use of equation 3 and the predicted reflectance values. It will be apparent that one can also predict the color difference between two samples having known pigment composition by use of equations 1, 2, and 4. Although this technique predicts color from known pigment formulas, the method gives, at least in theory, a means

of predicting a pigment formula to match a given color. If one tries to match the color specified in Fig. 1, for example, one can guess at a formula, compute the curve, and compare it with Fig. 1. On the basis of the differences between the predicted and desired curves, one can estimate a new formula and try again. By successive trials, one can eventually arrive at a pigment formula for which the predicted curve would be identical with the desired curve; and this formula would then be the predicted formula for matching the sample. The difficulty of course, lies in the amount of time required to make these calculations. It is at this point that computers can solve the problem.

Practical Use of the Colorant Mixture Computer

The Davidson and Hemmendinger Colorant Mixture Computer, COMIC, is a high-speed computer designed specifically for solving equations equivalent to equations 2 and 4. The control panel is shown in Fig. 5. Values of K/S for the individual pigments to be used in match-

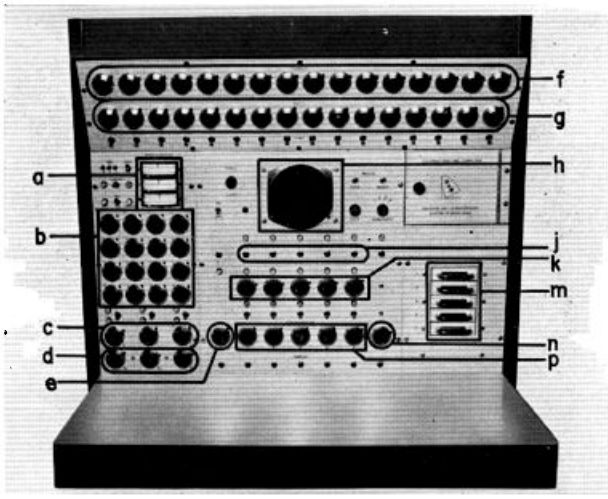

Figure 5. Control panel of the Colorant Mixture Computer

ing are adjusted in individual plug-in boxes, five of which can be placed into the computer at one time. These plug-in boxes are labeled "*m*" in the figure and are often referred to as "primaries." Usually a box is available to represent each of the pigments which might be considered for a match, and these boxes are set up before the computer is used for any matching problems. These K/S values are derived from the spectrophotometric curves of mixtures of the colored pigment and white similar to those shown in Figs. 2, 3, and 4. Since the computer can

handle the values for 16 wavelengths, the values chosen are usually at 20 nm intervals from 400–700 nm.

The standard to be matched is measured at the 16 wavelengths, and the K/S values are set on the dials labeled "*f*" in Fig. 5. On the oscilloscope tube "*h*" 16 dots appear. These dots represent the spectrophotometric curve of the standard to be matched. The operator first chooses the pigments he wishes to try and inserts the plug-in boxes representing them. If by adjusting the concentration dials "*p*" he can bring all of the dots down to the zero line, he has chosen correct pigments for a nonmetameric match, and the required amounts will appear on the concentration dials. The position of the dots is actually a display of the difference between the solution of 16 equations similar to equation 2 and the K/S values for the standard. When the dots are all on the zero line, the differences between the predicted K/S values and the desired K/S values are zero, indicating that the spectrophotometric curve predicted for the mixture of pigments is the same as that of the standard to be matched.

Figure 6 presents an example of use of the computer for matching a color similar to that shown in Fig. 1. The pattern of dots on the oscilloscope tube are shown for each step in the match. Figure 6a shows the position of the dots representing the spectrophotometric curve of the standard to be matched. Since this is an absorption curve, it is inverted with respect to the normal spectrophotometric curve shown in Fig. 1. On the basis of this curve the operator decides which pigments to try. He chooses a red oxide, Mapico yellow, and ultramarine blue; he plugs the boxes representing these pigments into the computer and adjusts the concentration dials to bring the dots onto the straight line. Several steps in this process are illustrated in Figs. 6b, c, and d. Addition of the blue by means of the appropriate concentration dial adjusts the dots in the long wavelength region of the spectrum; addition of the red brings the dots in the middle of the spectrum down to the line; and, finally, addition of yellow straightens out the line in the short wavelength region at the left. In this case, the operator chose the proper pigments, and therefore all of the dots can be brought to the zero line. This indicates that a nonmetameric match to the standard may be made with the pigments chosen, and the required amounts of each pigment are shown on the concentration dials. However, if the operator had chosen to dull the color with a black instead of the blue, he would have found it impossible to bring all of the dots down to the zero line. In other words, no values of concentration could have been found which would permit

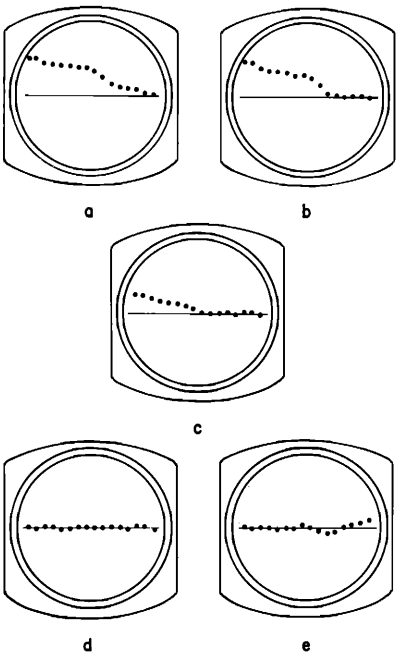

Figure 6. Appearance of the COMIC oscilloscope tube during various stages of solving a matching problem

a solution of 16 equations of the form of equation 2 so that all 16 predicted K/S_M values were equal to the K/S values of the standard to be matched. The appearance of the line of dots would have been similar to that shown in Fig. 6e. If this situation arose, the operator would select a different set of pigments and repeat the operation until an appropriate combination had been selected.

The first trial formula will not, of course, produce a perfect match to the standard. The size of the color difference will depend upon many factors, including the accuracy of the calibration of the primaries, the degree of control over the dispersion of the pigments, and the degree to which the equation truly represents the process. Color differences of from three to eight MacAdam (2, 3) units can be expected on the first trial. Although in most cases a mismatch of this magnitude would be larger than could be tolerated, it is sufficiently small so that computed adjustments will produce an acceptable match after one or two corrections.

Adjustments to the first trial may be made either spectrophotometrically or colorimetrically. If a spectrophotometric correction is to be

made, the reflectance values of the trial sample are converted to K/S values and placed on the dials labeled "*g*" in Fig. 5. The values for the standard are, as before, placed on the dials labeled "*f*." The dots on the cathode ray tube take up positions representing the differences in K/S values between the standard and the trial. Appropriate pigments are then added to, or subtracted from, the formula by means of the concentration dials and polarity switches, labeled "*j*" in Fig. 5, until the dots are all on the zero line. The formula adjustments are then read from the concentration dials, and the signs of the adjustments are given by the polarity switch positions.

Color adjustments may be made more rapidly and in most cases more accurately on the basis of tristimulus values if the color adjustment is small. The differences in tristimulus values (ΔX, ΔY, and ΔZ) between the standard and sample are obtained from a colorimeter or by computation from the spectrophotometric curves using equations 3 or 4. These values are placed on the computer dials labeled "*c*" in Fig. 5. Sixteen values for the standard are then placed on the dials labeled "*b*." These are known as $dR/d(K/S)$ values (4) and are used to convert the voltage differences in the computer which represent K/S differences into reflectance differences, ΔR, for use in equation 4 with which the predicted values of ΔX, ΔY, and ΔZ are computed for any pigment alteration. Three meters, labeled "*a*," are then nulled by means of the concentration dials and switches to obtain the formula correction. If more than three colored pigments are used, the formula is not unique; that is, many different combinations of pigment ratios will produce a colorimetric match. Only one of these combinations will produce a nonmetameric (or spectrophotomeric) match. In this case, the colorist must reduce the problem to control of three pigments, either by using only three pigments to make his adjustment or by specifying one or more of the pigment ratios.

So far it has been assumed that the operator could find a combination of pigments which would produce a nonmetameric match to the standard. This is not always possible. Perhaps the pigments which will produce a nonmetameric match are not certified or are too expensive. Some other combination must be used, and a metameric match may be required. In this case, the operator will be unable to bring all of the dots down to the zero line. In order to determine the correct formula, he must now place the $dR/d(K/S)$ values for the standard on the dials labeled "*b*" and must set the ΔX, ΔY, ΔZ dials, labeled "*c*," at zero. The K/S values for the standard are as before placed on the dials labeled "*f*." Now the operator lines up the dots on the zero line as nearly

as possible, then makes small changes in the concentration dials, "*p*," until the three meters labeled "*a*" indicate zero.

The production control problem is equivalent to adjustment of a trial formula. A sample of the batch being processed is measured, and adjustments to the batch formula are obtained from the computer. In most production problems a colorimetric adjustment is satisfactory if appropriate procedures have been established. When the system is properly set up, adjustments can be obtained in less than ten minutes, including measuring time, and one correction is usually sufficient.

System Operation

Several steps are required to set up and operate the color control system which has been described. Before any matching or control work can be undertaken, the pigments must be calibrated. A mixture of each pigment with white at a known ratio is made and the reflectance measured; these measurements are converted to K/S values and set into the pigment plug-in boxes.

When a standard is to be matched, it is first measured on a spectrophotometer, and the appropriate K/S values are set into COMIC. A tentative choice of pigments is then made, and the corresponding pigment plug-in boxes are inserted into the computer. If the operator is unable to obtain a straight line on the computer oscilloscope by adjusting the concentration dials, he makes a different pigment selection and tries again. When a straight line or the best line possible with available pigments is obtained, the operator reads the pigment formula from the concentration dials. The proposed formula is then made up and compared either visually or instrumentally with the standard. If it is not a sufficiently close color match, the reflectance values of the sample are converted to K/S values and are placed in the COMIC along with the K/S values of the standard to be matched. Alternatively, the difference in tristimulus values along with the appropriate $dR/d(K/S)$ values may be used. A correction of the formula is then obtained. A new formula is made up, and the entire process is repeated until a satisfactory match has been obtained.

Adjustments in a production batch are handled much as are adjustments to a trial formula. Usually tristimulus values of the batch sample are measured and placed in the computer along with the values for the standard. After nulling the three meters, the operator reads from COMIC the adjustment required to bring the batch to the standard.

Application to Cosmetic Problems

The example cited to show the operation of the color control computer is a real one chosen from some of the work which has been done on compressed cakes. There appear to be no difficulties in applying these methods to the color control of powder in this form. The same holds true for liquid make-up, although the best method of preparing a sample must be established. Multilayer draw-downs* have been found to be very effective; on the few problems studied the results were excellent, even with measurements made on the liquid make-up in a glass cell. In the case of lipsticks and nail polishes, there are problems of computation on shades containing very little white, just as in paints or plastics. There is also the problem of establishing a satisfactory method of sample preparation for lipsticks. These problems may make it impractical to apply these methods to the very brilliant shades, but the more pastel shades should not prove difficult. The success of these methods in the control of hair dye has already been established by one manufacturer who has been using them for this purpose for about two years.

Conclusions

On the basis of work done on cosmetic problems, it can be predicted that the use of instruments for color control will be as successful in cosmetics as it has been in paints, plastics, and textiles. Certainly not all color problems will be solved by instrumentation, although a sufficiently large portion will be solved to more than justify the use of these methods. In the future further improvements in both techniques and instruments can be expected, but the general methods described here have been so successful that we may be sure they are here to stay.

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* A Bird Applicator normally used for paint draw-downs was used, but we found it necessary to allow the first coating to dry, then place a second on top of it.