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UNDERGRADUATE RESEARCH THESIS

"The Quantitative Identification of E-6 Chemical Processing Errors"

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ABSTRACT

This thesis contains descriptions of current methods of identifying chemical processing errors, followed by a description of a proposed method for quantitatively identifying chemical processing errors. The goal of this research is to determine the relationships between chemical deviations in the first developer of Kodak Color Reversal Process E-6 and the resulting changes in the sensitometric parameters of Kodak film type Ektachrome 64 Professional (Daylight). These relationships are presented in graphical form in a section of this thesis entitled "Results and Conclusions".
INTRODUCTION

This thesis describes an approach to the detection of chemical processing errors in Kodak Color Reversal Process E-6 when used with Kodak Film Type Ektachrome 64 Professional (Daylight). Although this work deals with a specific process, the approach is general and should be applicable to any conventional black and white or color process.

A brief summary of current methods of chemical processing error detection is given first, followed by the outline of a proposed improved method.

To date, the detection of chemical processing errors is approached in three basic ways and combinations of the three.

1) Visual (subjective) judgement of processed film.
   A problem is identified when a processed strip of film differs visually from standard, correctly processed film. Judgement is based on visual color, density and contrast differences. Although this is a fast and easy method, it is limited in that it yields no quantitative data to help in determining the cause of a chemical processing error, and in that a single visual fault such as a color imbalance will have many equally probable causes.

2) Use of control strips and control charts.
   This method is based on density measurements
of several specific density patches. The measured value is plotted on a graph which indicates expected variability for each patch. When a value falls outside the expected limits of variability, the process is considered "out of control". Density deviations from the normal are sometimes plotted as a function of levels of chemistry in a specific solution, but in practice this is a cumbersome, unreliable method due to the large number of factors which can affect an isolated neutral or color density patch. The results indicate that a problem exists, but give little or no information about a specific chemical problem.

3) Chemical analysis of processing solutions.

If a problem is indicated by one of the other methods, chemical analysis is the only reliable method to locate the cause of the problem. Analytic chemical techniques have been developed for virtually all chemistry found in processing solutions. Most of these techniques are both accurate and precise for error detection work. The price paid for knowledge of the exact cause of the problem is either system down-time or continuous analysis. Both are expensive in time and money.

None of the above methods are entirely satisfactory for fast retrieval and processing of photographic information as required for example, in space and defense reconnaissance, and large scale commercial processing. The drawback in chemical error detection is a combination of lack of knowledge of the cause of a problem, and time and money spent in locating the
cause.

The method this work is based on makes use of the quantitative relationships between chemical deviations in process chemistry and the corresponding changes in several sensitometric parameters.

Justification for this work is derived from the lack of data about these relationships in color reversal processes. Without this data, no judgement can be made on the value of this method as an aid to error detection by chemical analysis.

The goal of this research is to determine the relationships between chemical deviations in the first developer of Kodak Color Reversal Process E-6 and the resulting changes in the sensitometric parameters obtained from Kodak Film Type Ektachrome 64 Professional (Daylight).

In this work, only the first developer chemistry has been modified. Time restrictions did not allow the research of modifications to other processing solutions. The first developer was isolated because speed and contrast are largely determined in this solution.
EXPERIMENTAL

This section describes the background research necessary for the experimental work as well as a description of procedures and apparatus used in the collection of data.

The bulk of the experimental work consisted of exposing, processing, and taking density measurements of color reversal filmstrips. Some time was also used in preparing the first developer solution modifications, and in maintaining control of processing solution temperature and pH.

As this work was used to detect small differences in speed, contrast, minimum density and maximum density caused by modifications to the first developer, minimum processing variability was sought and an accurate estimate of the variability had to be made. Since the experimental work lasted for four months, variability as a function of time had to be accounted for and minimized. Presented below is a description of the method by which gross variability was controlled from beginning to end of the process.

The color reversal film used in this work was supplied by Daniel Neuberger of Eastman Kodak Research Laboratories, in Rochester, New York. The film was packaged in a light and moisture tight container which had been stored at approximately 42 degrees F. since its manufacture several months before. This film was then stored at approximately 40 degrees F. until its first use. After its first use it was stored in the original container
at approximately 65 degrees F. All filmstrips used in this research were taken from this several hundred foot roll, end to end deviations being ignored. For the purpose of the experiment, only this one roll from a single lot was used so that no lot-to-lot variability was introduced.

Six-inch strips were cut from the roll and exposed in a daylight balanced Kodak Process Control Sensitometer, through a 21-level stepped wedge. Since the latitude of the film was greater than the range of exposure levels available in a single exposure, a second exposure was added, with a 2.1 Neutral Density filter in the optical path. All exposures were made three to five minutes prior to processing, which negated any effects due to storage conditions of exposed film and latent image fading.

The film was processed in a Paterson System 4 single reel tank, with the filmstrips on the outer guides. Prior to, and during processing, the tank was kept two-thirds immersed in a running water bath which was used to maintain temperature. The plastic Paterson tank was chosen over a metal tank for its better insulating properties, faster load and dump times, and provision for temperature measurements of the in-tank solutions.

The water bath for temperature control was contained in a 14"x17" deep tray and supplied by an Oscar-Fisher temperature controlled line. After a 15-20 minute warm-up, the in-line temperature could be maintained to ± 1 degree F. with minor adjustments, and the bath and solution temperatures to within ± ½ degree F. Temperature measurements were made with a Kimbal
thermometer, with .2 degree F. increments and certified accuracy of 1.5 degree F. All processing solutions, contained in 10 ounce glass bottles, were also immersed in this bath to maintain temperature.

All processing solutions were available in concentrated liquid form and were mixed to working strength as needed. These solutions were used to two-thirds the recommended shelf-life. The first developer solution was used much less than this, being discarded after each variation. A Corning Research pH meter was used to check and adjust the pH of processing solutions to ± .1 pH units for each run. Normal pH for each solution was measured from the first batch of solutions mixed. As the actual values of solution pH were not known, the assumption was made that freshly mixed chemistry from a freshly opened E-6 chemistry kit would be at the proper pH. As experimentation progressed, this assumption seemed reasonable, as verified by the measured pH values of other batches of fresh solution.

After air-drying the filmstrips, density measurements were made on a MacBeth TR-102 Densitometer, which was 95% accurate to ± .03 over the period used. Readings were made through a filter corresponding to visual measurements as well as through red, green, and blue filters. These density values were plotted as a function of log exposure. From these graphs, measurements of speed, contrast, minimum and maximum density were made and plotted as a function of variations made in the first developer.

As stated before, the working-strength processing solutions
were mixed from liquid concentrates with distilled water. The chemical composition of the first developer was not available and complete chemical analysis was not feasible due to time limitations. Several analyses of probable chemical constituents were made, which yielded concentration levels of bromide, sulfite, and thiocyanate. Tests were run with increased concentrations of these three components. Analyses for hydroquinone and phenidone were also made. The analyses performed in this research and analyses for hydroquinone and phenidone performed independently by Charles Augello, using standard chemical analysis techniques failed to show a correlation, and tests were not performed with hydroquinone and phenidone due to this uncertainty. Other factors tested were dilution of the first developer, processing time, processing temperature, and the pH of the first developer. No interactions of these factors were considered, due to time limitations.

In order to get an estimate of the variability inherent in normal processing, fifteen exposure series were made and processed. The data obtained from these strips was used to find the sample mean and standard deviation for the normal process. This information was utilised to help determine the extent of replication needed, and was later used to judge if first developer deviations resulted in a change in the mean values of the parameters measured and also if variability was changed.

Most of the samples were replicated three times, and three to five levels of each deviation were investigated. The sample
mean and standard deviation for each change was computed and compared with the normal processing values to determine if the sample size was adequate.
RESULTS AND CONCLUSIONS

The following pages are a graphical presentation of the results of this work. Comments on each graph would be useless as the relationships encountered were not simple. Some general discussion is in order, however, concerning trends and results of special interest.

Measurements of speed throughout the research showed the blue sensitive layer to be the fastest and the red sensitive layer to be the slowest. The contrast in the blue sensitive layer was typically higher than in the red sensitive layer. In both cases, the green sensitive layer was roughly between the blue and the red sensitive layers. These differences were generally small, and not apparent visually.

One of the more interesting deviations was an increase in the first developer processing time from six to ten minutes. This brought about a $1\frac{1}{2}$ stop increase in speed, improved color balance, and a slight increase in contrast. Minimum and maximum density levels were virtually unchanged.

Increasing the first developer temperature 10 degrees (to 110 degrees F.) gave a favorable two-thirds stop increase in speed, while leaving contrast and minimum density levels unchanged. A drop of .1 in maximum density was noted at this temperature.

Predictable speed losses were noted with increased bromide
levels and with a decrease in pH. Changes in sulfite and thiocyanate levels showed no significant speed changes at the concentrations tested. Contrast, minimum density and maximum density were also unchanged with an increase in sulfite and thiocyanate.

It is interesting to note the similarity of affect of time, temperature and pH on speed, and to some extent, contrast. This could indicate a relationship between these three factors, as is common in photographic developers. This relationship is illustrated graphically, following the graphs of factor vs. parameters.

No attempt at placing control limits on these graphs was made. Apparent discontinuities were always retested with fresh chemistry to determine their validity.

In the following graphs, color coding has been implemented to designate the response of the specific layers in the film. Black designates the visual curve, while blue designates the blue-sensitive layer, green designates the green-sensitive layer, and red designates the red-sensitive layer.
FILM SPEED
CORRELATION OF TEMPERATURE AND pH

1ST DEVELOPER TEMP. (°F)
90 95 100 105 110

1ST DEVELOPER pH
8.6 9.1 9.6 10.1 10.6
It is apparent that the task of compiling a complete set of data concerning all conceivable factors is one of such magnitude that it would be feasible only for a large, sophisticated, well-staffed analytical laboratory to undertake. Also, there remain unanswered questions concerning the actual practical advantage of using sensitometric parameters instead of control strips.

1) Are control strips unsuitable for their particular applications? Do they consistently identify errors correctly?

2) Control strips consist of "patches", which when processed represent speed, contrast and color balance information. Are these accurate? Does a change in density of the speed patch, for example, always indicate a change in speed?

3) It has been noted that many different changes in factors provide the same changes in sensitometric parameters. Thus, it is unlikely that this error detection method would be useful in accurately pinpointing the error. It may be useful in eliminating enough possibilities that an acceptable minimum of actual chemical analysis is needed.

These questions, though not within the scope or intentions of this thesis, are important, and should be taken into consideration by those seeking to improve upon the efforts set forth in this thesis. As the scope of this thesis is severely limited by it's nature, the specific information concerning the E-6 Ektachrome process is of little practical value in industry. The value of the research represented by this document is that
it introduces one to the problems involved in processing error detection, and that it provides an outline by which others with the proper resources can pursue more thoroughly the solutions to processing error detection and identification.
APPENDIX

1) pH of normal solutions
   First developer   9.6
   Reversal          5.9
   Color developer   12.0
   Conditioner      6.35
   Bleach           5.5
   Fixer            6.65

2) Speed measurement
   PH2.21-1961. Method of Determining the Speed of a Color Reversal Film

3) Contrast measurement
   Taken as the slope of a line connecting points on the characteristic curve having a log exposure .3 greater and 1.2 less than the speed point. The speed point is defined as the log exposure at a density of 1.00.

4) Concentrations of chemistry analysed
   Sodium sulfite   37.81 grams/liter
   Potassium bromide 3.80 grams/liter
   Sodium thiocyanate .81 grams/liter
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