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Opacification: Solving the Fundamental Problems

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ABSTRACT

This report describes some of the fundamental problems associated with the opacification program in the Polaroid SX-70 photographic integral system. Phthalein dyes which at a pH of 14 absorbed over the visible spectrum, were stable in alkali for over a year, had pK_a *values above 13 and were immobile in the photographic system were synthesized to solve these problems.*

INTRODUCTION

Dr Edwin Land conceived of the integral instant color film which was to become Polaroid SX-70 film.[1] Unlike the earlier Polacolor film in which the negative and positive sheets were superposed with a layer of viscous reagent spread between them after exposure to light, the new film would have the two sheets superposed prior to exposure. Polacolor film required the positive to be peeled away to view the transferred image; the new film would keep the two sheets together after the transfer image was formed. The positive sheet would be transparent, to permit exposure to light of the negative positioned under it, and the transfer image would be viewed through the transparent base of the positive sheet against a white layer formed by titania dispersed in the reagent. A mirror in the camera exposure system would correct the geometry of the positive image.

Since the film would develop in ambient light outside the camera, it was necessary to protect the negative from further exposure during development.

The back of the negative could be protected by an opaque layer, but the front sheet was to be transparent to allow the negative to be exposed in the picture-taking mode (Fig. 1). A titania-pigmented reagent layer inserted between negative and positive would opacify the negative during development and allow the dye image that had transferred to the positive sheet to be viewed against the white background. However, the titania layer was not sufficiently opaque to protect the negative against further exposure if the ambient light level was high.

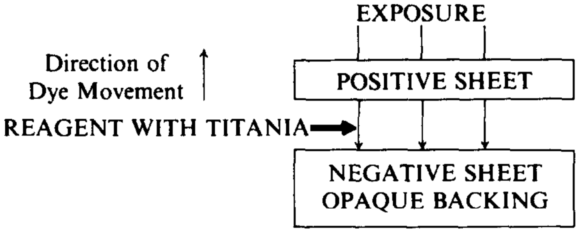


Fig. 1

In the summer of 1967 this problem and Dr Edwin Land's 'chemical darkroom' solution were discussed with us. Land proposed to add a pH-sensitive dye to the reagent to provide opacity at high pH.[2] He realized that the pH of the system dropped from about 14 down to 5 in the course of development and neutralization, and noted that phthaleins were colored on the basic side and colorless when acidified. He felt that this was a practical approach to the problem, based on his tests with thymolphthalein and other available phthaleins.

The solution was incomplete, however, because there were several fundamental chemical problems left unsolved. The phthalein dyes were to be in the strongly alkaline reagent from the time the pods which contain the photographic reagent were manufactured until the time when the picture was taken. Phenolphthalein is only colored in a narrow range of alkalinities; as the pH is raised the dye disappears.[3,4] An equilibrium is set up between the dye in the quinone methide form and the colorless carbinol formed by attack of hydroxide on the *meso* carbon atom. Furthermore, cleavage of the triarylmethane system under long-term alkaline conditions might render the decolorization irreversible.[4,5,6]

Another problem to be solved was due to the fact that the pH during neutralization of the photographic system tended to drop to around 10 and stay there for a time before dropping to the final pH (H. G. Rogers, 1968, pers. comm.). This meant that some of the color of the phthalein dye would remain for an undesirable length of time after the image had been formed, unless the phthalein dye had a pK_a above 13. The known phthalein dyes had pK_a values no greater than 10·5–11.

Phenolphthalein has a sharp absorption peak at 555 nm. We wanted to find a mixture of phthalein dyes which would give the needed opacity across the entire sensitivity spectrum of the emulsion layers while using the smallest possible concentration of dyes.

The phthaleins in the alkaline reagent were likely to move with the water front down into the negative during the development period. This could mean that the topmost blue-sensitive emulsion would be unprotected, would be light-struck, and would hold back image dyes that should transfer, giving images of reduced density and altering the color balance of the resulting picture (H. G. Rogers, 1968, pers. comm.). The solution to this problem seemed to be to attach immobilizing tails to the phthalein dyes.

ALKALINE STABILITY

Phenolphthaleins undergo the series of reactions shown in Fig. 2,[3,4] and under severe alkaline conditions have been reported to break down to 4,4′-dihydroxybenzophenone and benzoic acid.[5,6]

We found four routes to increase alkaline stability (see Appendix).

(1) Substitution of alkyl groups on the phenolic rings, or fusing rings on the phenol, shifted the hydroxylation equilibrium in favor of the colored quinone methide form. Thus, thymolphthalein (A) and 1-naphtholphthalein (B) are preponderantly in their colored forms at

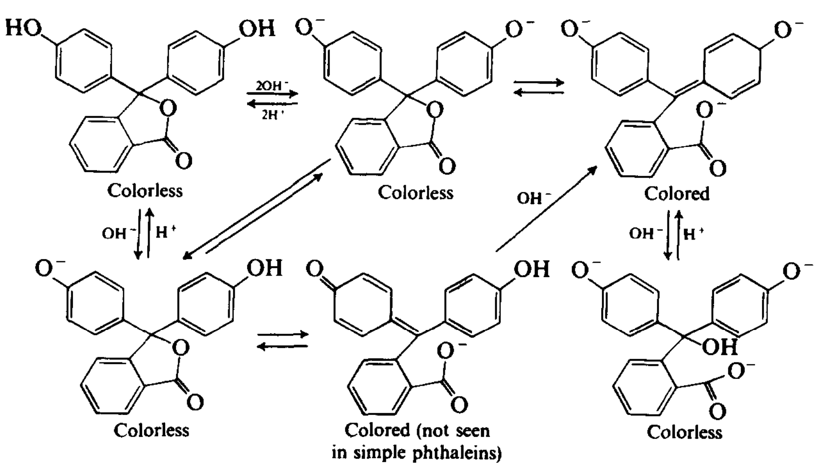
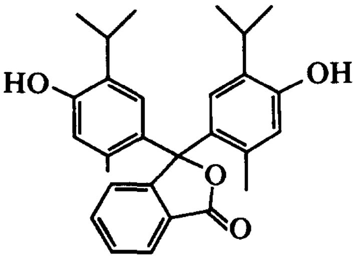
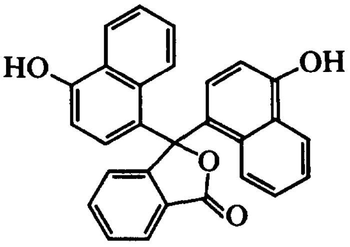


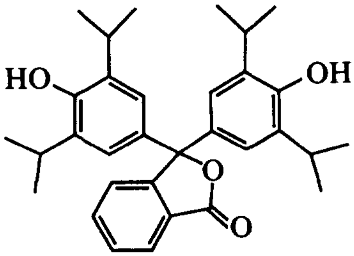
Fig. 2.



(A)



(B)



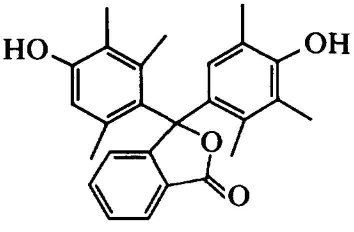
(C)

pH 14. 2,6-Di-isopropylphenolphthalein (C) and 2,3,5-trimethylphenolphthalein (D) are more than 99·5% in the colored form at pH 14.

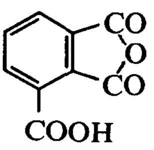
(2) The introduction of an additional negative charge in a position adjacent to the meso carbon increases alkaline stability. Dyes prepared from hemimellitic anhydride (E) are stable, but moving the additional negative charge further away loses the effect, since phthaleins made from 1,2,4-benzenetricarboxylic acid (F) do not show enhanced stability.[7]

(3) Location of the carboxylate group closer to the *meso* carbon prevents hydroxylation. Phenolnaphthalein (G) made from 1,8-naphthalic anhydride is 99% in the colored form at pH 14. The position of the *peri* carboxylate anion is closer to the *meso* carbon than is the *ortho* carboxylate in phenolphthalein.[8,9]

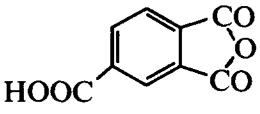
(4) Certain heterocyclic phthaleins show high stability. Indolephthalein (I) is 98% in the colored form at pH 14.



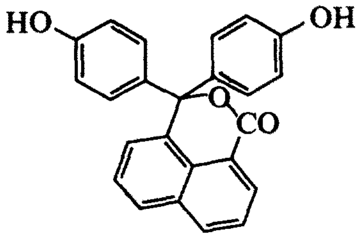
(D)



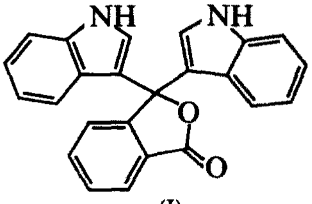
(E)



(F)



(G)



(I)

These techniques allowed us to design phthalein dyes which were almost entirely in the colored form at pH 14, and long-term testing (see Appendix) showed that such structures were stable to the attack of alkali and other nucleophiles for prolonged periods of time.

HIGH-p*K* PHTHALEINS

The choice of p*K* range for our dyes was based on two limitations. On the one hand, the reagent was buffered at around 14·5 by hydroxyethylcellulose which was present as a thickener. Therefore a dye with a p*K* of 13·5 would be 90% in the colored form. A dye with higher p*K* would be less efficient. The 13·5 value seemed to be as high as we could go. On the other hand, the opacification system should be colorless by the time that the pH had dropped to 10, since at that point the pH drop slowed down, while the transfer of the image dyes was complete. This put a lower limit of about 12·5 on the p*K* range.

The first step in the generation of color of phenolphthalein dyes is the ionization of the parent phenols. When we compared the p*K* of a phenol with that of its phthalein we found that the phthalein had a significantly lower p*K*. For example, while 1-naphthol has a p*K* of 9·3 in aqueous solution, its phthalein has p*K*s of 7·0 and 8·1. Trimethylphenols have p*K*s at 10·8–10·9, while 2,3,5-trimethylphenolphthalein shows two p*K*s, at 8·9 and 10·4.

While the values for the phenols were measured in aqueous solution and those of the phthaleins in 20% alcohol–80% water solutions (to approximate the organic–aqueous ratio in the photographic reagent), which introduced a measure of uncertainty in these comparisons, it became clear that we could not expect to obtain phthaleins of p*K* above 13 without breaking new ground.†

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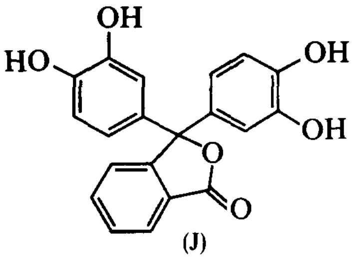
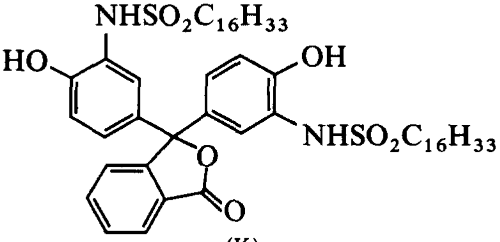
† pK_a values were determined from spectra of the dyes in KOH solutions and several phosphate buffers; 20% ethanol solutions were used to approximate the environment of the dyes in the photographic reagent.

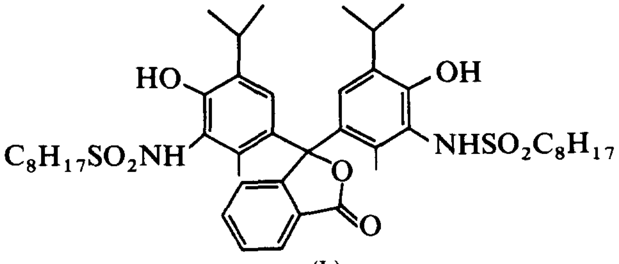
Several clues came from our earliest experimentation aimed at shifting the absorption spectrum to longer wavelength. For example, catecholphthalein (J) was made to shift absorption into the red region, but in addition we found that the p*K*s were at 11·2 and 12·7. 2-Hexadecylsulfonamidophenolphthalein (K) had p*K*s at 11·8 and 12·8 (but only 1% was in the colored form in 1N sodium hydroxide). The closely related 6-octylsulfonamidothymolphthalein (L) was found to have a p*K* of 13·4.



(J)



(K)



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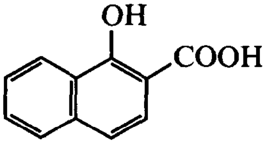
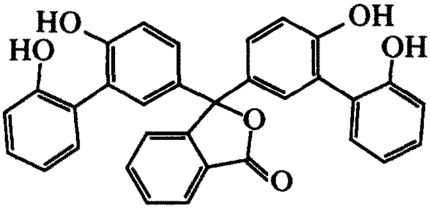


(O)

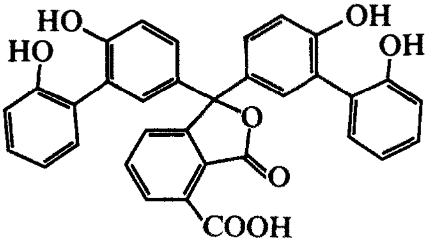
Of great significance for our understanding of these results and for targeting molecules for synthesis for this program was the paper by Musso & Matthies[10] which reported that 2,2′-biphenols and 2-hydroxyphenylnaphthols display higher acidity in their first dissociation than do simple phenols, but lose their second proton at very much lower acidity.

The authors explained that this was due to the formation of a hydrogen bond whose energy of formation supplies part of the energy for dissociating the first proton, and whose cleavage requires additional energy to dissociate the second proton. The p*K* of the second ionization was reported to be above 13. In the event, 2,2′-biphenolphthalein (M) was made and gave a p*K* of 13·7 in *t*-butoxide–*t*-butanol! The phthalein (N) from 2,2′-biphenol and hemimellitic anhydride had a p*K* of 13·4 in 20% methanol–water. A number of phenols and naphthols with acidic groups positioned *ortho* or *peri* to the OH were converted into phthaleins, and 1-naphthol-2-carboxylic acid (O) proved to have a combination of useful properties.

As stated earlier, we found that naphthaleins from 1,8-naphthalic

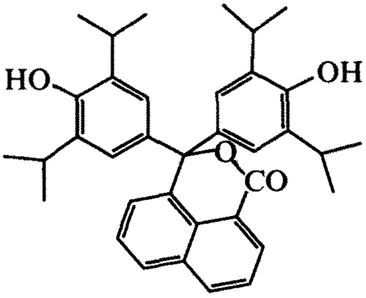


(M)

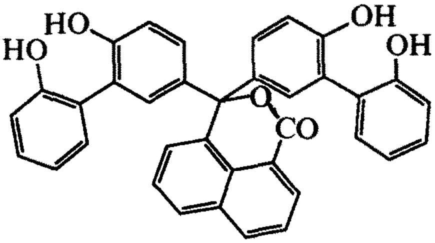


(N)

anhydride are not hydroxylated readily, and are more stable to alkali than are the corresponding phthaleins. As we synthesized molecules to take advantage of these properties we were pleasantly surprised to find that the p*K*s of the naphthaleins were considerably higher than those of the corresponding phthaleins. 2,6-Di-isopropylphenolphthalein (C) had a p*K* of 9·4 in 20% ethanol–water. The p*K* of the naphthalein (P) was found to be 12·1. 2,2′-Biphenolnaphthalein (Q) gave values above 15, as well as could be determined, compared with the 13·7 value for the phthalein.



(P)

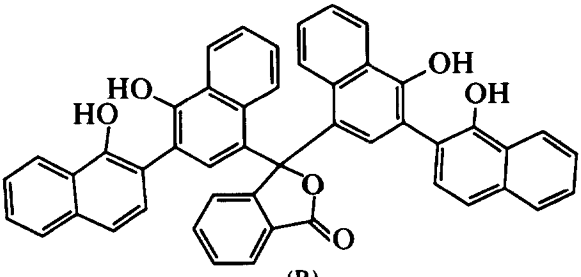


(Q)

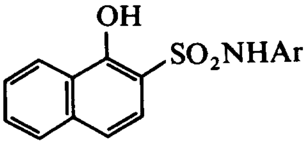
The strain energy in the five-membered phthalide ring apparently contributes to the ease of ring-opening in the case of the phthaleins, while the less-strained six-membered ring in the naphthalein series does not make this contribution. The p*K* of the naphthalein closely approximates that of the parent phenol.

The use of hydrogen-bonding acidic groups *ortho* or *peri* to the phenolic hydroxyl raises an interesting problem. Loss of the first proton is at significantly lower pH. This first ionization must not open the lactone ring if we are to have color only at high pH. The loss of energy from breaking the hydrogen bond and the loss of resonance energy of the phenol ring must be greater than the gain of energy obtained by opening the lactone ring and relieving ring strain by sp^2 hybridization of the *meso* carbon.

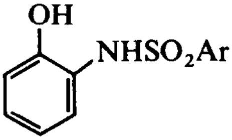
2,2′-Biphenolphthalein (M) shows color only at high pH, with a pK_2 of 13·6. Here, clearly, the strength of the hydrogen bond and resonance energy



(R)



(S)



(T)

of the benzene rings is sufficient to keep the lactone closed after the first ionizations. On the contrary, 2,2′-bis-1-naphtholphthalein (R) shows colored forms at every stage of ionization. The loss of aromaticity of the naphthalene system does not cost the system enough to prevent the opening of the lactone.

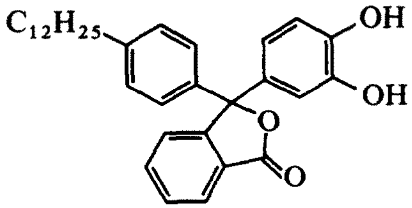
We solved this problem by using hydrogen-bonding substituents of greater acidity than the phenolic hydroxyl group. In particular, carboxyl groups and sulfonamido groups proved to be particularly valuable.[8,9,11]

COVERING THE VISIBLE SPECTRUM

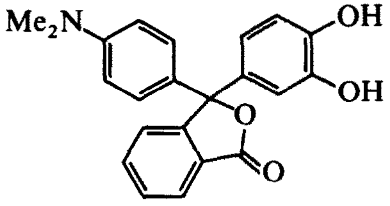
In order to feel confident that we would be able to protect the negative we did a calculation to pinpoint the level of absorption necessary at the sensitivity peaks of our silver emulsions. Peaks were at 400, 480, 570 and 650 nm, but it was quite clear from the overlapping curves that we had to block the entire spectrum from 390 to 680 nm.

Blue-absorbing dyes are not found among symmetrical phenolphthaleins. Unsymmetrical phthaleins, with one phenol and one aromatic ring, are colorless in neutral solvents, but absorb in the blue–green region in base. The efficiency of absorption is low, however. For example, 4-dodecylphenyl-catecholphthalein (U) gives a broad curve in base which peaks at 477 nm, but the extinction coefficient is below 8000. More efficient absorbers have a non-ionizing electron-donating group on the aromatic ring.[12]

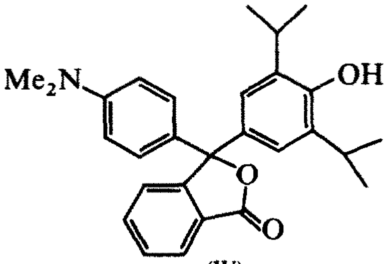
4-Dimethylaminophenyl-catecholphthalein (V) absorbs at 450 and 525 nm with extinction coefficients of 11 000 and 16 000 respectively.



(U)



(V)



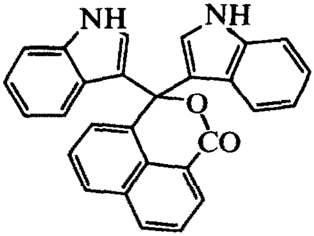
(W)

Similarly, 4-dimethylaminophenyl-2,6-di-isopropylphenolphthalein (W) absorbs at 492 nm with an extinction coefficient of 25 000.

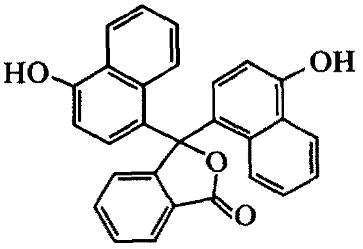
We found that heterocyclic phthaleins, and, in particular, indolephthaleins, are mid-range, i.e. green, absorbers when fully ionized, but that a yellow form, the pK_1 dye, shows up as the pH drops.[13] Indolephthalein (I) peaks at 514 nm and the low-pK form does not show up in the alcoholic alkali system, but in indolenaphthalein (X) pK_1 is high enough, 11·1, so that both peaks are visible at pH 14.

The red-absorber was obtained by extending the absorption of phenolphthalein by the introduction of electron-donating groups in the phenol ring *ortho* to the phenolic OH. Catecholphthalein absorbs at 655 nm in aqueous alkali (but is unstable to oxidation). The already-known naphtholphthalein (Y) was made and filled the red end of the spectrum nicely, peaking at 650 nm.

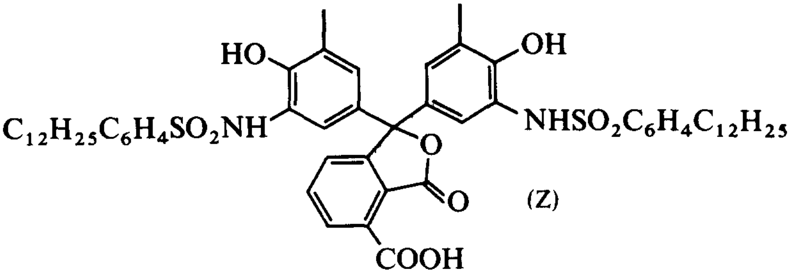
Another fruitful series was obtained by aminating phenolphthaleins in



(X)



(Y)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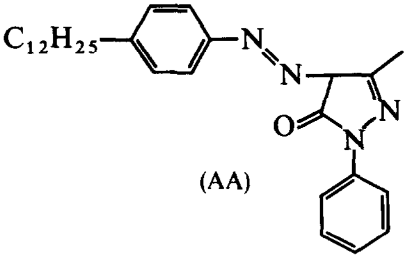
(AA)

the *ortho* position and making the corresponding sulfonamides.[8,9] As one example, 2-methyl-6-(4′-dodecylbenzenesulfonamido)phenol-3″-carboxyphthalein (Z) absorbed a 623 nm with an extinction coefficient of 35 500.

IMMOBILIZING THE DYES

The need for immobilization of the opacification dyes was planned at the beginning of this program because it was recognized that mobile dyes would migrate below the blue-sensitive emulsion, and not protect that silver. Another very important reason for keeping the opacifying dyes in the reagent appeared when photographic testing showed that positioning the dyes within the titania reflecting layer made them over three times more efficient than their solution spectra had indicated (N. Mattucci, 1969, pers. comm.). The increased path length of light traveling through this layer of reflecting particles explains the finding.

As a model experiment a yellow azopyrazolone dye (AA), with an *n*-dodecyl chain to immobilize it, was dissolved in the reagent, and photographic tests were conducted to determine whether the C_{12}-chain was adequate to immobilize an opacifying dye. Microscopic cross-sections showed that the dye had remained almost entirely within the titania layer.

Hexadecylsulfonamido and dodecylbenzene groups were used on early phthaleins. Later the 18-carbon chain was also used to anchor the dyes in the titania layer.

CONCLUSIONS

The studies reported here solved four problems which had the potential to prevent the use of chemical opacification in the Polaroid SX-70 integral photographic film program.[13] These findings resulted in the synthesis of the two opacifying dyes which were used in the film, an indolenaphthalein derivative[14,15] for the blue–green region of the spectrum made by colleagues A. Borror and L. Cincotta, and a carboxynaphthol naphthalein[11] for the red end of the spectrum made by R. Greenwald.

ACKNOWLEDGEMENTS

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APPENDIX

Short-term stability was determined by dissolving the dye in ethanol and diluting with four parts by volume of 1 N KOH, introducing the solution into a Cary 17 spectrophotometer and taking spectral curves to follow the loss of density. Long-term stability was determined in a 1·6N KOH solution of hydroxyethylcellulose pigmented with titania, with or without *N*-phenethyl α-picolinium bromide. The dye was dissolved in this viscous reagent by syringe-to-syringe mixing and the mixture was stored in lead-lined packets. The packets were heated at 60° for 1–6 days then the packets were squeezed between calibrated rollers to spread the contents between two polyester sheets. Reflection spectra of unheated dye reagent and reagent that had been heated for various periods allowed determination of dye stability under conditions closely approximating those to which the dyes would be subjected in the film packs.