Influence of Drying Temperature Profile on a Multi-Layer Photographic System

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Abstract

During a coating process, the drying temperature profile can be one of the significant factors which influences the image uniformity of a multilayer dye diffusion photographic system. One of the common issues involving multilayer films containing latex has been related to the premature film formation of latex during drying, causing the trapping of moisture underneath. The pressure due to this trapped moisture increases with increase in temperature and creates random fracture patterns in this layer. Experimental evidence from cross-sectional photomicrographs confirms the presence of such fractures. This non-homogeneity of the structure results in poor image quality due to the disruption of dye diffusion path from the negative to the positive image receiving sheet. The problem was eliminated by shorter falling rate period in the drying zone to remove any excess moisture, and lower temperature and shorter residence time in the conditioning zone.

Introduction

Structure of Film

The film studied is the negative unit of a color photographic film system. The basic structure of the system has been described by Walworth and Mervis[1], in Chapter 6, titled 'Instant Photography and Related Reprography Processes' of "Imaging Process and Materials" and is illustrated in Figure 1. The photographic system consists of three sandwiches, each containing light sensitive silver halide emulsion as well as appropriate image forming dye layers. The sandwiches are separated by barrier interlayers, containing film forming latex, to prevent interactions between the image forming layers. Moreover, these interlayers also provide delays to the rates of permeation for the dyes, generated from reaction with alkali from processing reagents. The rates of dye migration are very critical for optimum color separation and image quality. For sharp images the dye diffusion path should be vertical. Lateral diffusion of dyes decreases sharpness and resolution of color images.

The image receiving sheet consists of a mordant layer and a clearing layer coated on a clear polyester base. The film is exposed through the clear upper sheet. The processing reagent in the pod contains alkali and other chemicals and is spread between the negative and image receiving sheet. The final color image is viewed by light reflected from the white pigment component of the reagent layer.

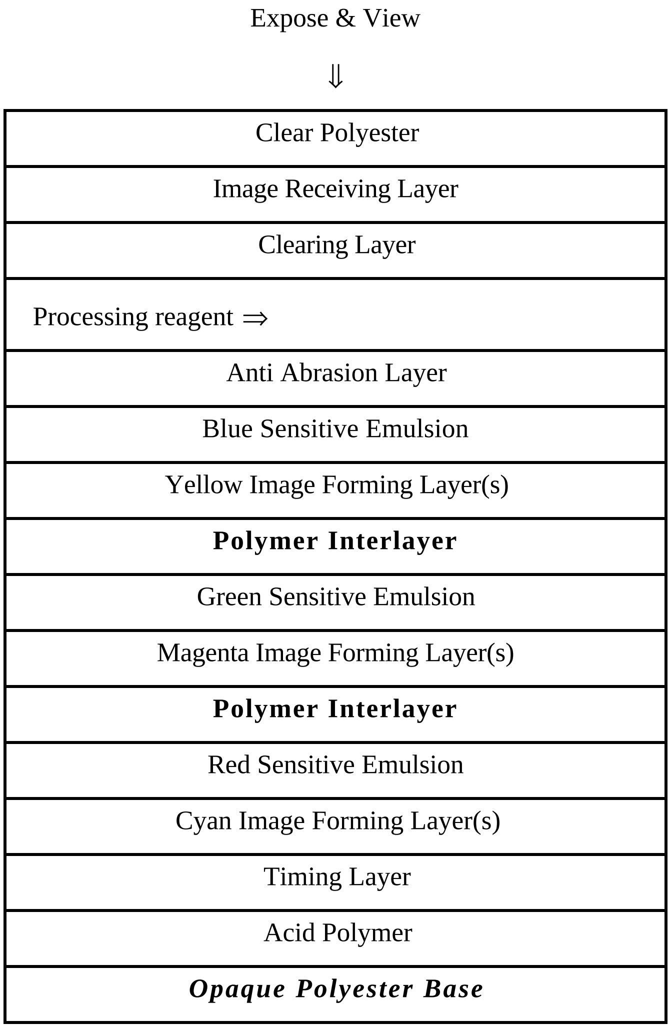

Figure 1. Film structure

Dryer System

The coated photographic films are dried in multiple zone dryer systems. The drying curves for such systems are shown in Figure 2. The critical steps for drying are discussed below.[2]

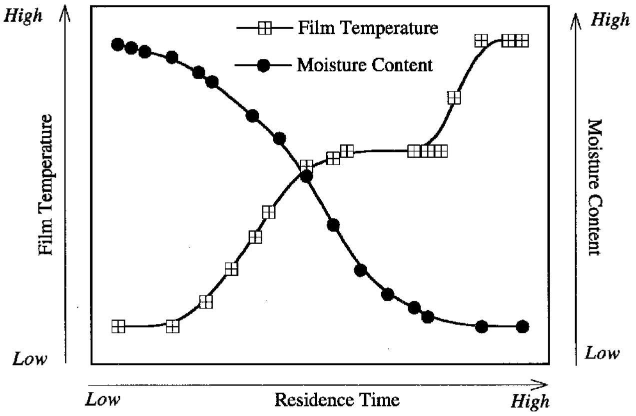

Figure 2. Drying curve.

At the early stage the moisture removal occurs at a constant rate due to a continuous supply of liquid from the coated structure to the top surface. The temperature remains fairly constant by cooling due to the latent heat loss. The drying defects occurring at this stage are due to the coated film on the substrate being very mobile, which causes dryer bands, blow around, framing, etc. During the next stage, the falling rate period, mass transfer within the coating becomes a limiting factor. With constant heat input moisture removal occurs at a gradually decreasing rate associated with increase in temperature. Solidification and microstructure continue to form at this stage. The rate of moisture removal at this stage and the temperature profile in this zone are very critical. Several types of defects may occur due to the lack of proper process conditions. For example, a very rapid removal of moisture can cause skinning which is fast solidification of the top surface.

Subsequent to drying the coated films are subjected to equilibrating conditions by applying additional heat to make them ready for finishing. It is necessary to remove the appropriate amount of moisture from the film before it enters the conditioning zone. However, if the temperature settings and residence times for drying and conditioning are not optimized, these goals are not achieved. Over drying or under drying can damage the structure as well as the functionality of the layers of the imaging system.

Background

Observations

It was observed that negatives after treatment in the conditioning zone showed spots on their surfaces after drying. The area of the negative surface covered by spots increased with time, as described in Figure 3, reached a maximum and gradually disappeared in 2-3 weeks. The negatives not subjected to such conditioning showed very rapid, almost instantaneous appearance of spots soon after the film exited the dryer. For these unconditioned negatives, the level of spots reached a maximum and disappeared completely within a few hours. The data are plotted in Figure 4. When samples of both types of negatives were processed the conditioned films showed non-uniformity in dye density, measured by increase in granularity, which unlike the spots, did not disappear with time, even in 10 weeks, indicating its presence to be due to a permanent defect in the film structure. The data are shown in Figure 5. The films not conditioned did not show such high level of non-uniformity at any time. The slow appearance and disappearance of spots correlates with the presence of a permanent change/damage in the film.

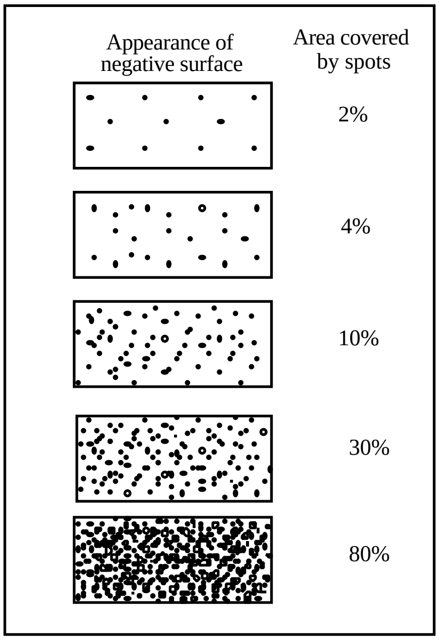

Figure 3. The change of film surface due to appearance of 'spots.'

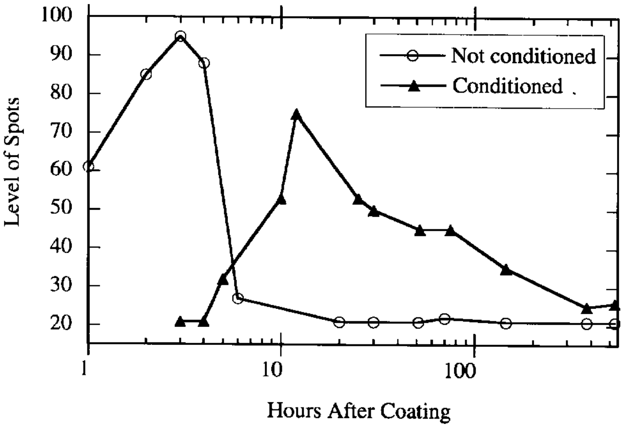

Figure 4. Effects of conditioning of film on the appearance of spots.

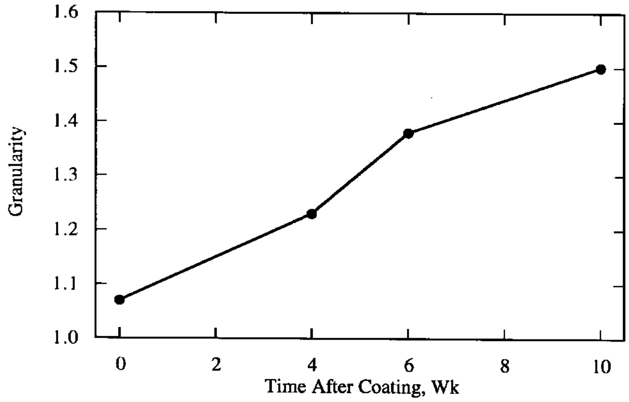

Figure 5. Increase of non-uniformity with time for conditioned negative.

Hypothesis

During the drying process of a multilayer film, gradual loss of moisture occurs by the diffusion of moisture through the layers. If one or more of the layers contain a film forming material, such as the films coated in the current product, which coalesce during drying, they can form an impermeable layer. The temperatures and residence times in the drying and conditioning zones, as well as the composition of the layer are expected to have significant effects on the phenomenon.

Results and Discussion

As described in the earlier section, the thin film drying process can be divided into three regions: first is the constant rate period in which a constant supply of liquid water to the top of the film where water evaporates into the dryer. Next is the falling rate period in which water moves to the top surface by liquid flow in porous medium and vapor diffusion through the empty pore space. The last step is the post falling rate or equilibrium period where the primarily mechanism of transport of water to the top layer is due to vapor diffusion. It is evident that the falling rate position would influence the properties of a dried film to a significant extent.

A study of the effect of falling rate period in the drying zone (Figure 2), which influences the length of time when the temperature is higher due to the absence of latent heat loss, shows that a shorter falling rate period results in lower moisture content in films before they enter the conditioning zone. The results are listed in Table I.

During the falling rate period, part of the void space of the solid matrix is filled with liquid, with the remaining void space is occupied by vapor from the evaporation of the liquid phase.[3] Between liquid and vapor phases, a localized liquid/vapor equilibrium is established within the interstices of the porous medium. As the moisture is being removed from the top surface, vapor diffuses through the pores due to a concentration gradient across the porous network. At this stage, the drying process relies primarily on the diffusion mechanism of vapor molecules. Also, as evaporation takes place, the saturation of the liquid phase gradually decreases within the pore space. Liquid flows in a partially saturated porous medium by capillary pressure driven flow and Haines jump, depending upon the surface tension, viscosity, wettability, and geometry of the system. Although these parameters may vary during drying, the process tends to empty the larger pores and breaks up the liquid into discontinuous clusters bounded by small pores. One more complication is added to the drying process by the changes of the pore structure of the porous medium. This is due to the fact that coating materials including dispersions, binders, thickeners, and surfactants go through a series of structure transformations, such as, phase separation, particle agglomeration, and binder migration and immobilization, during the drying process. During the post falling rate period, the process of rearranging and packing of the solid matrix continues which results in further shrinkage of the total volume and the closing down of the pore spaces. Therefore, the rate of diffusion of the vapor phase slows down and the pressure builds up as a result of less pore volume and higher temperature. As indicated, latex has been used in photographic system as an interlayer separating the primary color sandwiches. The critical characteristics of the latex are different from gelatin polymer in its film formation properties. Film formation is a result of coalescence of latex particles by way of interpenetration of the polymer chains on the surface and viscous flow under capillary pressure exerted by the menisci of liquid. Thus, the major factors controlling the latex film formation in the dryer are the temperature and residence time.

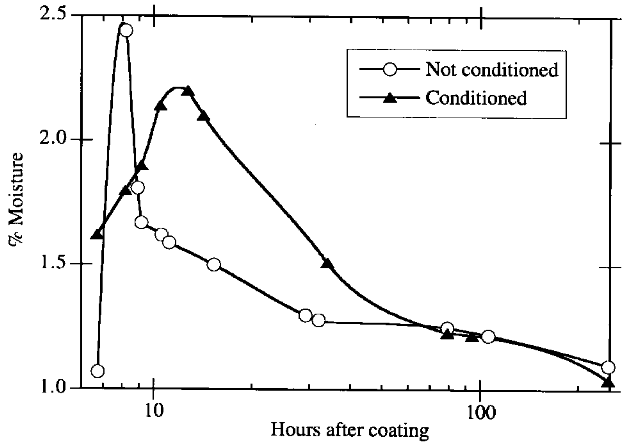

Figure 6. Moisture levels of films as a function of time after coating effects of conditoning.

With a later critical point of longer falling rate period, the rate of removal of moisture is lower and the amount of residual moisture is higher when the film enters the conditioning zone. On the other hand, an earlier critical point causes more moisture loss before it enters the conditioning zone, shown in Table I, and also reduces the extent of latex film formation. Further evidence is obtained from the results of Karl-Fischer titration experiments for the variation of the moisture content of the coated films with time, when stored under ambient conditions, showed increase in moisture level, followed by decrease with time, for conditioned and unconditioned film. The results are plotted in Figure 6. The profiles are similar to the appearance and disappearance of spots on the surface of negatives, indicating the spots to be due to condensed moisture.

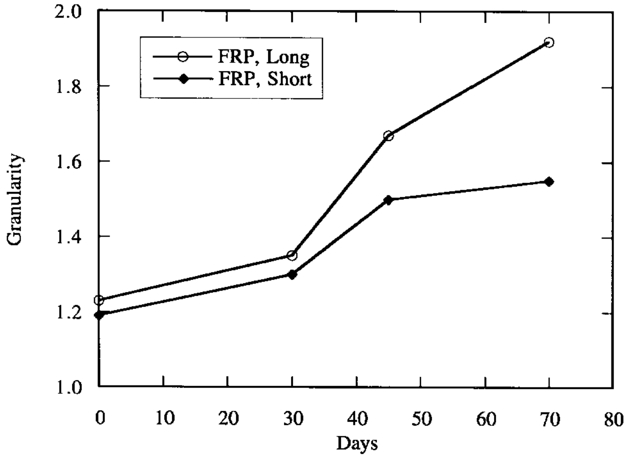

Figure7a. Effects of falling rate period on granularity.

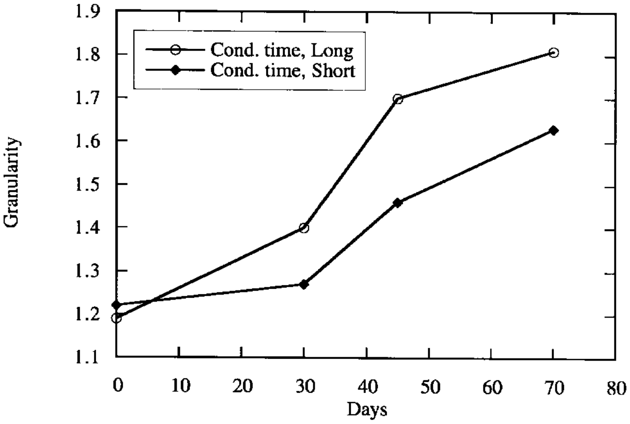

Figure 7b. Effects of conditioning time on granularity.

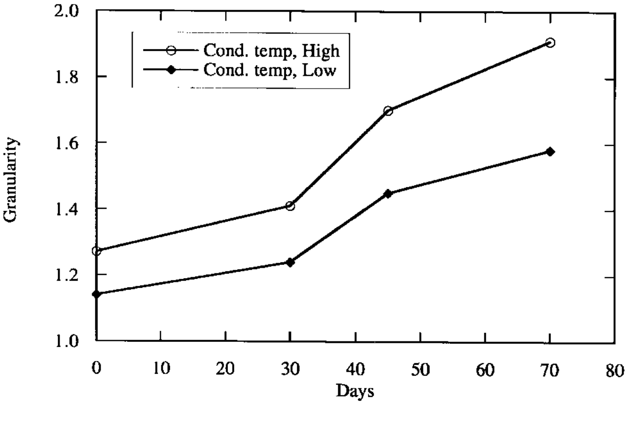

Figure 7c. Effects of conditioning temperature on granularity.

Designed experiments were conducted in which the falling rate period in drying zone, the temperature and the residence time in the conditioning zone were varied. The granularity of the processed films as a function of time was determined for each of the conditions. Figure 7A, B and C show the effects of each of these factors on the granularity at varying time intervals after coating. It is apparent that the extent of granularity increase with time is different for each of the factors. Figure 7A shows that the freshly coated films do not show any large difference in granularity with varying falling rate period. However, the difference is more pronounced when the film ages, as shown by the high level of granularity when the falling rate period is longer. Similar difference is apparent between films when the conditioning time is varied, shorter conditioning time resulting in films with higher uniformity than the films conditioned for longer time, as shown in Figure 7B. The results of variation of conditioning temperature, Figure 7C show that higher temperature causes increase in granularity even in freshly coated films, and the effect is more pronounced after the films are aged. The data clearly indicate that low granularity is obtained when the time after the critical point is longer in the drying zone, and the temperature is lower and residence time is shorter in the conditioning zone.

During the conditioning of the films, further ‘sealing’ of the latex layer occurs, which is enhanced at higher temperature and longer conditioning time. As the temperature increases in this final zone, more water vapor accumulates under the barrier layer. Nucleation occurs in the pore spaces when the vapor pressure exceeds the saturation pressure. This causes the formation of micro-droplets of water in the pores. The neighboring water micro-droplets may further coalesce to form larger droplets. As temperature increases, such localized concentration increase of water vapor results in the increase of pressure under the layer, which causes an eruption and creates random fractures of the barrier layer. This phenomenon creates a passage for the trapped moisture to escape. The moisture from underneath the barrier layer continues to move within the porous matrix and funnels out through the narrow passages due to the fractures in the barrier layer to form localized concentrated moisture. Once the film exits from the dryer, and the conditioning zone, water vapor nucleates in a non-uniform pattern and spots appear in a random fashion on the upper surface of the film. Although the spots disappear with time, as the film dries out under ambient conditions, the fractures in the barrier layer are permanent, which causes nonuniformity of dye diffusion during photographic development and increase granularity of the final images. Due to the permanent nature of these fractures, the granularity of the films do not disappear with time. Figure 8, showing a photomicrograph of a cross-sectional view of a film which exhibits high levels of spots and grain, confirms the disturbance in that layer causing fracture in the layer above. When higher level of moisture is trapped in the interstices of the porous coated medium, as in the case of longer falling rate period, the effect is enhanced, shown in Figure 7A. Exposure of the film after the drying zone to higher temperature and extended residence time enhances this phenomenon, as indicated by the data shown in Figures 7B and C. After the film is dry the residual stress inside the film causes further compression of the latex interlayer. This creates more random fractures in the layer, which results in more lateral and nonuniform diffusion of dye, reflected by high levels of granularity.

Composition of barrier interlayer also influences the extent of coalescence of the latex. Materials which enhance film formation at elevated temperature, such as waxy materials cause increase in spots as well as granularity. Replacing polymer by non film forming gelatin eliminates the immediate spots as well as the permanent granularity. Thinner interlayer increases defect, due to faster dry out.

Based on the experimental results, it is apparent that the best product performance, with highest uniformity of migrated dyes and lowest level of grain are obtained when the falling rate position is decreased in the drying zone, and the temperature and residence time are reduced in the conditioning zone.

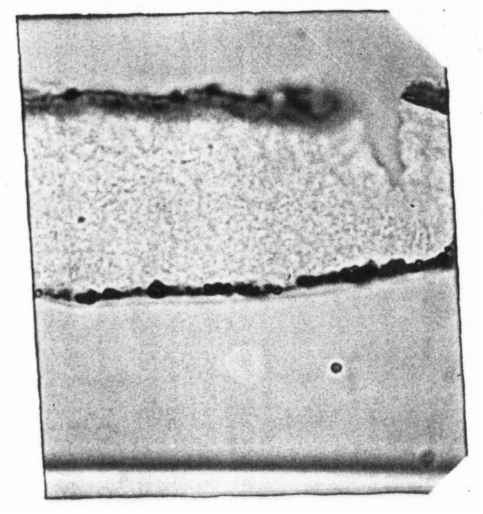

Figure 8. Cross-sectional view of a film showing the disturbance within latex interlayer and fracture in the layer above

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Table I. Effects of Critical Point on Final Moisture Content

Critical Point	Moisture Content, mg/m^2
Standard, X ft	556
Early, 0.36X ft	455

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