A Study of Latent Image Fading in SO-343

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A STUDY OF LATENT IMAGE FADING IN SO-343

by

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A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in the School of Photographic Arts and Sciences in the College of Graphic Arts and Photography of the Rochester Institute of Technology

March, 1974

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ABSTRACT

Experimental evidence indicates that a high intensity, short duration exposure produces surface image exclusively in this emulsion. The ensuing fading was shown not to be caused by internal migration of the latent image. The high intensity exposure produced a massive amount of sub image nuclei which could subsequently be rendered developable by a low intensity post exposure. This latensification failed to achieve an improvement in image stability, in that the amount of fading was shown to be solely a function of the density of the fresh exposure. It was hypothesized that although this treatment did raise some grains from an unstable state of developability to stable one, a proportionate amount of grains were brought from undevelopability to one of developable instability. Washing the film in either distilled water or a solution of $5 \times 10^{-4}$ N KBr was effective in stabilizing the image against fading.
INTRODUCTION

Field use of Kodak's SO-343 High Resolution film has shown that when it is given a short duration-high intensity exposure, a significant degree of latent image fading will occur. This problem becomes acute when it is necessary to make multiple exposures on the same piece of film over a period of a few hours. By the time the last exposure is made, unacceptable changes have occurred in the first image. Initially it appeared possible that this situation could be corrected, or at least the problem reduced, by the application of a uniform low intensity post exposure to the image area. Justification for this reasoning is as follows:

Previous work\(^1,^2\) has shown that latent image formation can be divided into two stages; the first being the initial formation of the stable, but non-developable sub-latent image center, and the second the subsequent growth to a developable size. These studies have also shown that the failure of the reciprocity law for high and low intensities is dependent upon which stage of image formation is inefficient. Image formation at low intensity was shown to be subject to inefficiency in the initial stage of image formation, but more fully efficient in forming developable images in the second. The efficiency of high intensity exposure was just opposite, i.e., more fully efficient in the first stage and less in the second. Although the emulsions used in these experiments differed greatly from SO-343, it is felt that the basic mechanism of a two stage formation of latent image still holds. Differences probably
occur in the relative sizes of "stable" and "developable" latent image centers in the different emulsions.

High intensity exposure, such as is given to S0-343 in making images for microcircuits, has been shown to cause smaller, more disperse L.I. centers\(^2\). These centers are very close to the threshold of developability, i.e., a difference of one or two atoms of silver could make the grain developable or undevelopable. If only slight thermal degradation (loss of one or two atoms) of an initially developable center occurs after exposure, it could render it undevelopable. It was hypothesized that, if after the first high intensity exposure, a uniform low intensity post exposure is given to the film, these small but developable centers will be increased in size to a point where the loss of one or two or possibly more silver atoms will not render it undevelopable. Also it is possible that the larger image is less likely to lose silver in the first place. As will be shown in subsequent sections, the latensification was exceptionally large, but the improvement in stability was not obtained; apparently many sub image specks were increased to the size necessary for developability, but the proportion of those large enough to be stable was not materially changed.

**EXPERIMENTAL**

The initial high intensity (H.I.) exposures were produced with pulsed Xenon lamps at exposure times of \(10^{-3}\) seconds and \(4 \times 10^{-6}\) seconds. For the former exposures an EG & G Mark IV Sensitometer was used, while for the latter a telecentric pro-
jection system using an EG & G FX-108 lamp was employed (Diagram 1). A thirty second waiting time between H.I. exposures was used. Variability measurements over a sample of twenty exposures using a #580 EG & G Radiometer showed a $\pm 2\sigma$ variation of 0.007 Log H. The low intensity exposures of one second were produced using the shutter mechanism of a Nikomat 35mm SLR camera and a #1630 GE lamp with a constant voltage transformer. The low intensity exposure was found to have a Log H variation of 0.028.

While the Mark IV sensitometer had a 21-step tablet and produced a range of densities between base plus fog to > 4.0, the microsecond apparatus was limited to only four exposure levels. One 0.10 and one 0.20 N.D. filters were crossed at the field stop to produce four pie-wedged exposures in the circular image area (~1cm diameter). When it became necessary to change the overall exposure level, additional N.D. filters were added at the aperture stop.

All determinations of the amount of fading or latensification were made by comparison of the control and experimental images on the same piece of film. This was done to compensate for variations in processing conditions from run to run. Because the amount of fading in the first few hours was smaller and less reproducible, the hold time between exposure and processing for fading tests was held constant at twenty four hours. The only difference between control and experimental exposures was that the former was given immediately before processing (within three minutes).
For latensification studies, the time between exposing and processing for both exposures was within three minutes. Here, "control" means the exposure did not receive any latensification.

Times between the high and low intensity exposures were kept at a minimum. For the millisecond exposure there was a lapse of about ten seconds; for the microsecond exposure, it was approximately five.

Processing of all tests was done in a nitrogen burst processor. A variability study indicated that all eight rack positions could be considered as producing the same result, i.e., no position showed a noticeable difference in level or variability from the others. For all experiments, a minimum of three replications were run.

RESULTS & DISCUSSION

Disposition of the Latent Image

Although D-19 was used in the majority of the experiments, it was necessary to resort to a developer with negligible solvent action in order to determine if the latent image was of the surface or internal variety. Following the procedure outlined by Berg, Marriage and Stevens\(^3\) a Metol-ascorbic acid developer\(^4\) was used for the surface image. A 1.0 g/l potassium ferricyanide bleach containing .0125 g/l phenosafranine\(^5\) was followed by the Metol-ascorbic acid solution with the addition of 1.0 g/l potassium iodide to reveal internal image.

The surface developer produced densities from 0.0-4.0 for
the millisecond exposure and greater than 3.0 for the maximum Log H of the microsecond exposure.

After a one minute bleach, all surface image had been destroyed. With standard exposure there was no developed density after bleaching using the internal developer. Next, each exposure was increased by an order of magnitude (ten repetitions). After the one minute bleach, there was again no image using either of the two developers.

In order to see if the latent image fading was a result of internal migration of the image⁶, both the 1X and 10X levels of the millisecond and microsecond exposures were held for twenty four hours before processing. Development of unbleached 24 hour old images resulted in a very noticeable loss in density. However, after bleaching, processing in either the surface or internal developer yielded no image. (This was to be expected, in that there was no evidence of internal traps to which the image could transfer).

It appears that 1) this material produces surface image exclusively and 2) latent image fading is produced by something other than internal image migration. We know definitely that the bleaching destroyed all of the surface latent image but can only speculate as to whether any internal image which might have been present was affected by the bleaching process. Unlike previous experiments where the grain sizes were on the order of a micron or so, the idea of a separate and distinct interior of a grain approximately 55 nanometers in diameter is questionable. Further, a "negligible" solvent action of a
grain one micron across might become substantial with reference to one of this size.

Effects of Development

It is known that at most of the photographically useful exposure levels with active developers such as D-19 the majority of the time between initial contact of an individual grain with developer and full development is consumed waiting for the development to begin. That is, once a grain begins to develop it goes to completion quite rapidly compared to the time between its first contact with the developer and the initiation of development. This is especially true in the toe region of the curve, and we would expect the development time to be shorter for very fine grains. That being the case, we can expect that the increases in density seen when going from five to fifteen minutes development (Figure 1) can be attributed primarily to an increased number of grains having developed.

In fine grain emulsions whose grains tend to form very few filaments, increases in size of the developed grains can result from thickening of the filaments by solution physical development. This is undoubtedly another factor contributing to the observed increases in density with increased development time in as much as the amount of solution physical development tends to increase with time. Which of these two processes is more responsible for the observed changes and which is more prevalent in the toe as opposed to the straight line, cannot be determined from these data.
Latensification--Alteration of the D Log H curve

Figure 2 illustrates the effect of a 1 second post exposure on the shape and position of the D Log H curve for 15 minute development in D-19. Density levels produced by the 1 second L.I. exposure alone were never more than .08 above base plus fog (0.04).

The latensification produced a decrease in gamma from 6.6 to 4.2. The exposure corresponding to the toe of the H.I. curve had become part of the straight line portion and a pronounced toe was formed in the Log H range where the microsecond exposure produced no developable centers. These facts demonstrate that there must have been a massive amount of subimage produced by the initial exposure. The subsequent increase in density then, must have been caused by an increase in the number of grains being developed. It appears that the hypothesis of a low intensity exposure being very efficient in the second half of latent image formation is quite valid for the material.

The elongation of the range of differentiable exposures indicates that the sensitivity distribution of the grains was widened. If one pictures a histogram of grain sensitivities with most of the initially developable grains located in the right hand tail, the effect of latensification would be to shift the developability cutoff point down toward the left so as to encompass more grains.
Effects of Development on Latensification

Curves 1 and 2 in Figure 3 are replotted latensified $D \log H$ curves for 5 and 15 minute development respectively. Note that the scale of the abscissa has been expanded. Curves 3 and 4 show, for a given level of exposure, the amount of that density which was produced by latensification only.

As can be seen by this graph, or by curves 1 and 2 in Figure 4, increasing development increased the degree of latensification obtained. This result is contrary to that obtained by James and Vanselow\textsuperscript{10} which indicated that increasing development decreases the latensifying effect of a low intensity post exposure. In that curves 1 and 2 (Figure 3) received identical exposures, it appears that 15 minute development picked up grains which were latensified by an amount too small to initiate development in five minutes. That is, the latensification increased the number of grains with initiation periods between five and fifteen minutes relative to the number with periods with five minutes or less. This longer time was able to develop grains which were on the "developability" borderline of size and stability.

If we start at the left side of curves 3 and 4 (Figure 3) and move to the right, we see that increasing the exposure causes a comparative increase in the degree of latensification. However, for both development conditions a level of exposure is reached whereafter further increases in the level of initial exposure cause a decrease in the amount of latensification obtainable. This is probably due to a decrease in the number
of near developable marginal grains available to be nudged over the developability barrier by latensification.

If we consider a one-dimensional scale of all possible grain developabilities partitioned into three sections: "undevelopable", "marginal" (some will develop, some won't) and "developable", we can picture what happened. When we set a development time, we for the most part, determine where the two separation points between the three sections will fall. Secondly, a given level of exposure will produce a particular distribution of grain developabilities in the emulsion. This distribution can then be superimposed on the scale. If, for a given set of processing conditions, the majority of the developabilities produced fall in the "marginal" category, the only density that is produced will be from the few grains which happened to fall into the "developable" range and the few marginal grains which, due to random chance, also develop. The remaining "marginal" grains, of which there are many, are available for latensification. If we increase the exposure level we accordingly shift the distribution of produced developabilities down toward the 'developable' end. Now there are more developable grains and proportionately fewer marginal ones available for latensification. The shift in the peak latensification exposure level can be understood in that increasing the development time moves the demarcations on the sensitivity line down toward the left. That is, some grains which were considered "undevelopable" before are now "marginal" and some previously "marginal" are now "developable".
The intensity of the first exposure also appears to have a visible effect on the degree of latensification obtained (Figure 4). Over the range of initial densities from 0.04 to approximately 0.80, the microsecond exposure appears to have produced a substantially greater amount of sub image than did the millisecond exposure. This seems to agree with the work done by Burton and Berg\textsuperscript{2} indicating that higher intensities tend to produce more sub image centers. However beyond 0.8, the millisecond exposure produced substantially more sub image than did the microsecond. Had the graph been large enough, the latensified density at an initial density of 1.90, would be at 4.40.

If we were to produce a graph similar to Figure 3 for the millisecond exposure, the latensification curve would not have attained a peak in the range of exposures used, i.e., the amount of latensification increases all the way up. This can be seen in Figure 4 by inspecting the difference between curve 3 and the no latensification line at successive exposure levels.

This may be explained in terms of the sensitivity line in that the lower intensity exposure, associated with the longer exposure time, produces a narrower, more peaked distribution of sensitivities.

**Effect of Washing on Latensification**

Washing the film in distilled water for six minutes and drying before exposure further increased the amount of latensification produced (Figure 4, curve 4). Because of the severe dust problem encountered in washing, accurate numerical differ-
ences are not obtainable. However, the trend indicated is quite valid.

The density produced by the low intensity exposure alone was twice (0.20) that of the unsoaked film (0.10). However, the levels of density for the unlatensified exposures remained the same; that is, there was no detectable change in high-intensity sensitivity.

Factors in Fading

A plot of density loss in twenty four hours versus initial density level is shown in Figure 5. As can be seen from the graph, images produced by a high intensity exposure (10^{-6} second, curve 1) or by a high plus a low intensity exposure (10^{-6} +1 second, curve 2), both faded as practically the same function of freshly exposed density level. That is, the degree to which an image faded depended essentially upon its original density level and not on the manner in which the exposure was made. This result was obtained in several independent runs. Increasing the low intensity exposure time to one minute did not alter the amount of fading observed.

Contrary to expectation, the L.I. exposure does not seem to be increasing the stability of the already developable image centers so that they will not degrade to a point of undevelopability; or, it may be that although some latent image nuclei are enlarged enough to be stable as many more are enlarged enough to become developable but still unstable. In the range of immediately developed densities from 0.0 to 1.60 the loss in
density is a constant fraction of the number of the initially developable grains.

This function of initial density level holds for both five and fifteen minute development times, although the exposure for a given density is greater by $0.60 \log H$ for five minute development. The curve for five minute development would fall right in the middle of the curves in Figure 5.

The amount of fading produced for a millisecond H.I. exposure was observed to be greater than that for a microsecond exposure. This result, which can be observed in Figure 5, was verified in four separate experiments. It is unexpected considering the evidence (Figure 4) that the millisecond exposure formed a smaller proportion of sub image.

Because of the results of Haase et.al.\textsuperscript{11} in using non-actinic light to stabilize the latent image in AgCl single crystal sheets, red light post exposures were given to microsecond H.I. images, in hopes of doing the same.

All four combinations of a #29 or a #70 Wratten filter with either a microsecond or one second post exposure were tried. These treatments produced similar results in slightly decreasing the degree of fading which occurred but nowhere near the point where one could say the problem was eliminated. The values of initial density of the individual points given red light latensification demonstrated that there was a moderate occurrence of Herschel effect.

Figure 6, illustrates the degree of fading as a function of initial density for a Metol ascorbic acid developer (3 min.).
There is an increase in fading seen in the surface developer over D-19. Because of the great amount of solution physical development occurring in D-19, much more of the ionic silver present in the emulsion is actually converted to silver metal in that solution than is in the surface developer. Those grains rendered undevelopable by the 24 hour hold are unable to contribute to developed density in the surface developer. However in D-19 those grains which do not develop by themselves are free to contribute their silver ions to the total mass of silver produced during processing.

Apparently a large number of grains lost the ability to develop on their own in 24 hours. D-19 however, gives the appearance that this effect occurs to less of a degree because of the increased density produced by solution physical development.

In order to determine if the fading of the latent image was due to re-halogenation of the silver, several strips were soaked in acetone semicarbazone for six minutes, and then dried, before exposure. In one liter of $5 \times 10^{-4}$ N KBr (so as not to alter emulsion pAg) 10.0 grams of the halogen acceptor were dissolved. A few additional strips were soaked in the bromide solution without acceptor, just as a control.

The results of these tests can be seen in Figure 7. The acetone semicarbazone solution substantially decreased the amount of latent image fading that occurred. However, the bromide solution alone reduced fading more than bromide plus acceptor. On seeing these results, another bromide wash was
performed along with one in distilled water only. This time, a twenty four hour hold caused a marked growth in the image. Because the water wash produced roughly the same effect as the bromide solution, the increase in image stability in the former cannot be attributed to a lowering of pAg. Although there is a substantial amount of variability between these two (bromide only) replicate runs, largely due to dust spots in reading, they both indicate a drastic change from previously obtained results. It appears that some emulsion component(s) which is detrimental to image stability has been removed by washing.

CONCLUSIONS

With grains of this size, we can be assured that alterations in density are brought about by change in the number of developed grains. Hence, any fading that was observed was due to a recession of the latent image in selected grains to below the point of developability.

The high intensity exposure was shown to produce a massive amount of sub image. Subsequent low intensity exposure demonstrated that this sub image had a wide range of developabilities.

No significant improvement in stability was obtained with latensification. Since an increase in density was observed, the secondary exposure did cause some grains to reach a stable, developable state. However, it appears that proportionately many more had been enlarged enough to become developable but still unstable.
There must be some water-soluble component in the emulsion which was removed in washing that has an adverse affect on image stability.
Diagram 1

PROJECTION SYSTEM FOR MICROSECOND EXPOSURE

Achromats
F.L. = 9.0 cm
dia. = 3.0 cm

Aperture Stop
dia. = 1.15 cm

Field Stop
dia. = 2.35 cm

crossed N.D. filters

F.L. = 13.2 cm
dia. = 3.8 cm

source

Film Plane

cm

2.1

5.8

4.2

13.0

1.4

3.0

11.5
Figure 1
Figure 3

1) ○ 10^{-6} sec. exposure + latens.; 15 min. D=19
2) ○ " " " " ; 5 min. D=19
3) ● amount of density in ○ due to latensification
4) ● " " " " ○ " " " "
Figure 4

1) $10^{-6}$ sec. exposure; 5 min. D-19
2) " 15 min. "
3) $10^{-3}$ sec. exposure; "
4) $10^{-6}$ sec. exposure; "

[KBr washed]

INITIAL DENSITY [UNLATENSIFIED]

LATENSIFIED DENSITY
APPENDIX

Processing Conditions (all solutions at 72°F)

Developer
    D-19, 5 or 15 minutes
    Metol-ascorbic acid developer, 3 minutes

SB-1 Stop Bath 30 seconds
Rapid Fixer 45 seconds
Rinse 30 seconds
Hypo Clear 1 minute
Wash 5 minutes
Photo Flo 30 seconds
Dry

Formulations

Surface Developer (1.0 liter)

    Metol 2.50 g.
    Ascorbic Acid 10.00 g.
    Sodium Carbonate 55.60 g.
    pH 10.3 @ 20°C

Bleach (1.0 liter)

    Potassium Ferricyanide 1.000 g.
    Phenosafranine 0.0125 g.
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    Part II: 88B, 84(1948)


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ACKNOWLEDGEMENT

I would like to thank Dr. B.H. Carroll for his keen direction and thorough guidance during the preparation of this study. I would also like to thank the Central Intelligence Agency for their generous funding of this project.