Article: Experiments on the Image Stability of Resin-Coated Black & White Photographic Papers
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Introduction

The image stability of photographic materials is a major concern of Archives, Museums, and Galleries around the world. Image stability is also a concern of professional photographers and more recently, it has been brought to the attention of the consumer. Since resin-coated papers are a relatively new material, and they have changed in composition since their inception, the effects of time on these products is not known.

Resin-coated materials were introduced for colour emulsions in 1968 and black-and-white emulsions approximately four years later. With processing times of up to one hour for colour papers(most of that for washing chemicals from the paper base), and a growing demand for faster customer service, some changes were necessary. Obviously, if the paper was made impermeable to chemical solutions, processing times would be substantially reduced, not to mention shorter drying times.

In a fibre-based paper a fine quality paperstock(100% rag or purified woodpulp) is coated with a gelatin/barium sulphate solution. On top of this is laid a layer of gelatin containing the light sensitive silver halide. Resin-coated papers consist of the same quality paper, extrusion coated with polyethylene containing titanium dioxide on the image side, then coated with the gelatin/silver halide layer.(fig.1) The polyethylene prevented water and chemicals from soaking into the paper.

In theory, the polymerization of ethylene(to produce polyethylene), results in a straight carbon chain. In reality, reactive side chains are produced and these carbon-carbon bonds are weaker than the carbon-hydrogen bonds(fig.2)[1]. If these bonds are broken the result is a loss of flexibility causing cracks in the material.

Though original colour materials were unstable due to poor dye stability, resin-coated papers introduced new problems. After several years these prints would yellow, crack, and turn brown around the edges. However, since early colour photographs faded within a shorter period of time, the RC base outlasted the image. When applied to black and white materials, the situation is reversed. Well processed b&w fibre based papers have a lifespan upwards of 100 years. Early RC based b&w papers had lifespans of less than 10 years. Problems included cracking of the base, oxidation of the image silver (which will be describe later), discolouration of the base, and formation of colloidal silver. From the day of their inception RC papers have been continually improved and today the b&w materials have a useful lifespan of several generations. For most people this would be adequate, but for the individuals and institutions mentioned above, this is a short time-frame.

This investigation was undertaken to determine the long-term stability of resin-coated b&w materials. The most recently available RC papers were compared to their fibre-based counterparts in terms of their image stability. Image stability can be monitored several ways. The print may be viewed under an electron microscope to view the silver grains directly before and after a test. This however is a destructive procedure. Another method employs the use of a microdensitometer or a densitometer. These instruments measure the optical density of a photograph in various areas of a print before and after testing. This is a non-destructive test, reliable, and already employed to monitor photographic exhibits before and after display.

For the most part, when b&w photographs deteriorate there is a loss of image density or a change in image tone, and the image "fades". Just what is an acceptable level of fading? Currently, for colour photographs, a density loss of 10% from an area having an original density of 1.00 is acceptable. For b&w photographs there is no equivalent standard. In this investigation, comparisons were made between different paper samples put through similar tests.

Factors Affecting Image Stability

So far, I have discussed why RC papers were introduced, the difference between the two paper types, and how to monitor changes in the print. What causes a photograph to deteriorate? Why does a silver tea set have to be polished? These two questions can be answered in one statement: silver oxidizes. On the tea set it is referred to as "tarnish". In a photograph it can be silver oxide, silver sulfide, silver sulphate, or colloidal silver. Fortunately the silver is embedded in gelatin which slows down the oxidation reaction. There are several factors that can cause a change in the image silver structure. They can be divided up into two groups: **variables in processing** and **post-processing conditions**(fig. 3.)

Changes in developer and fixer types, as well as fixing and washing times affect image stability. Harmful post-processing conditions are high heat and humidity, various gases and pollutants, residual processing chemicals, light that is high in UV intensity, or any combination of the above. Several tests were employed to simulate these conditions.

Testing Procedures

To simulate high heat and high humidity conditions over a long period of time, paper samples were placed in a dessicator with a salt solution(to maintain a high relative humidity of 70%) and placed in an oven set at 60 C for 30 days. This is the American National Standards Institute(ANSI)[2] test for image stability of b&w materials. High humidity provides a good environment for reactions to ocurr between image silver and residual processing chemicals. Combined with an increase in temperature, reactions progress at a greater rate.

Light aging simulates long term exposure of the photograph to light. Light high in energy can, in the presence of gases and residual processing chemicals, increase the rate of oxidation of the image silver. Areas of high density in the photograph absorb light in the form of heat which can help to degrade the image. For this test samples were placed six inches from a lightsource consisting of eight UV flourescent tubes.

Gas tests are similar to dark aging in design. Low levels of certain gases over a period of time affects the photographic image. For this test samples were exposed to higher levels of hydrogen peroxide[3] and in a another test, hydrogen sulfide gas. Both are strong oxidizers of silver.

Silver Oxidation

The mechanism for silver degradation as described by Feldman(1981, fig.4)[4] is as follows: oxidation of the silver enables it to migrate. In its oxidized state, denoted by the Ag^+, it can be reduced or oxidized by light or certain gases. This migration can be easily seen on older photographs. Viewed at an oblique angle, areas of high density have a shiny mirror like appearance sometimes referred to as "silvering out".

Processing Changes

As mentioned previously, changes in processing have an effect on image stability. It is well known that improper fixing or washing of a photograph affects its stability, therefore changes in the developer were made. Samples of all paper types were developed in Kodak D-72 or Selectol developer.

For the resin-coated papers the washing time was varied. One, two, and four minute wash times were employed as recommendations for these materials varies from source to source.

To monitor how the various aging and processing conditions affected each paper types' stability, density readings were taken before and after each test. Incorporated into each sample were twelve 21-step density strips. Each strip is divided into 21 areas successively increasing in density from white to black(fig.5). Density readings give an indication as to wether or not the silver image structure has changed due to test conditions.

Two manufacturer's RC papers were tested against their fibre-based counterparts. They were Kodak Polyfiber, Polycontrast RC II, and Polyprint RC; Ilford Ilfobrom and Ilfospeed papers. All papers had glossy surfaces and were of normal contrast (grade 2). The fibre-based papers had a double weight support.The normal processing for both paper types is shown in figure 6.

Sensitometry

Sensitometry, once mastered, is a quick, quantitative method of determining the response of photographic materials to light. Basically, it is optical density plotted against exposure, resulting in a characteristic curve(fig.7). After the testing of a photograph some change in density usually ocurrs, thereby changing the shape and slope of the characteristic curve. It is this change in the characteristic curve that is used to determine the stability of a given material.

Not only are density changes important,**where** they ocurr affects the slope of the curve. Below are two curves (fig.8a, 8b). Under the same test conditions one photograph lost density from all areas, shown by the first curve. The second curve exhibits a greater loss of density in the "toe" or low density areas. This distortion of tones can be seen in the corresponding photograph. From this example it shows that the slope, regardless of density loss, must be maintained. With this criteria in mind, the characteristic curves(after testing)of the RC and fibre-based papers were compared.

Test Results: Accelerated Aging

After comparison of the characteristic curves from each test group of twelve samples, the following results were obtained:

After dark aging both manufacturer's fibre-based papers had greater image stability.

After light aging samples for 170 hours, no difference between paper types was detected.

All samples exposed to hydrogen sulfide gas showed a definite change in image tone, but for both Kodak and Ilford products the fibre-based materials showed much smaller changes in density.

Papers exposed to hydrogen peroxide gas produced some very interesting results. The resin-coated papers of both manufacturers exhibited smaller changes in density than the fibre-based papers. However,in the RC sample, the silver migrated toward the surface, and the surface quality had changed.

Test Results: Processing Changes

The change of developer affected each paper differently depending on the test conditions. After dark aging papers processed with D-72 had greater stability than those papers processed in the Selectol developer. After both gas tests, the fibre-based papers processed with Selectol were more resistant to change, but all RC papers were less resistant to change. This sounds confusing but there are other factors involved besides the structure of the support base. These include the emulsion layer thickness, the silver morphology, and the hardness of the gelatin. With these different factors, it is impossible to expect these materials to react consistently for each test. A more controlled experiment(changing only one factor) would have to be conducted.

Under all aging conditions the RC papers that were washed for 4 minutes exhibited greater stability than RC papers washed for one to two minutes. This is in agreement with Kodak publication G-1 and others.

Conclusions

In conclusion, based on the above tests, the RC papers still exhibit problems such as changes in surface quality and reduction of support flexibility after aging. Changes in density are greater in RC papers than in fibre-based papers after aging, and after exposure to hydrogen sulfide gas.

The change of developer in processing affects image stability but further tests are necessary.

Recommendations and Discussion

At present, the only accepted conservation technique for photographs is to make a duplicate negative and a well processed copy print. Since the RC papers exhibited greater density losses and changes in surface texture after aging, copying will enhance, or at the least, duplicate these faults. Therefore, for long term storage, a properly processed fibre-based material is preferred. Accelerated aging tests plus naturally aged photographs of the fibre-based variety, spanning several decades, gives a complete picture of the stability of these materials. With RC papers only accelerated aging data is available at this time. Though better than its predecessors, there is still room for improvement of image stability in resin-coated papers.

Acknowledgements

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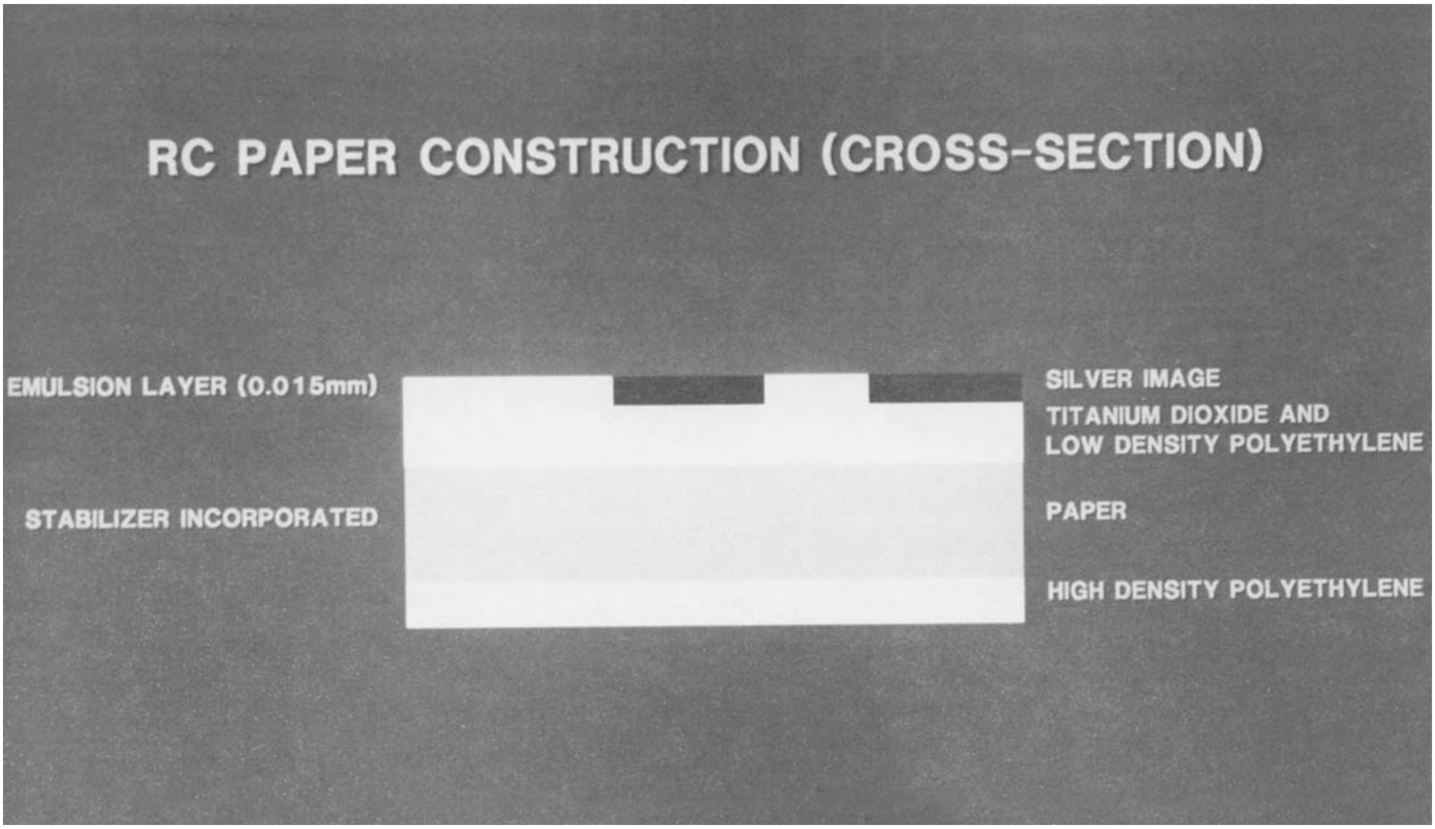


Figure 1

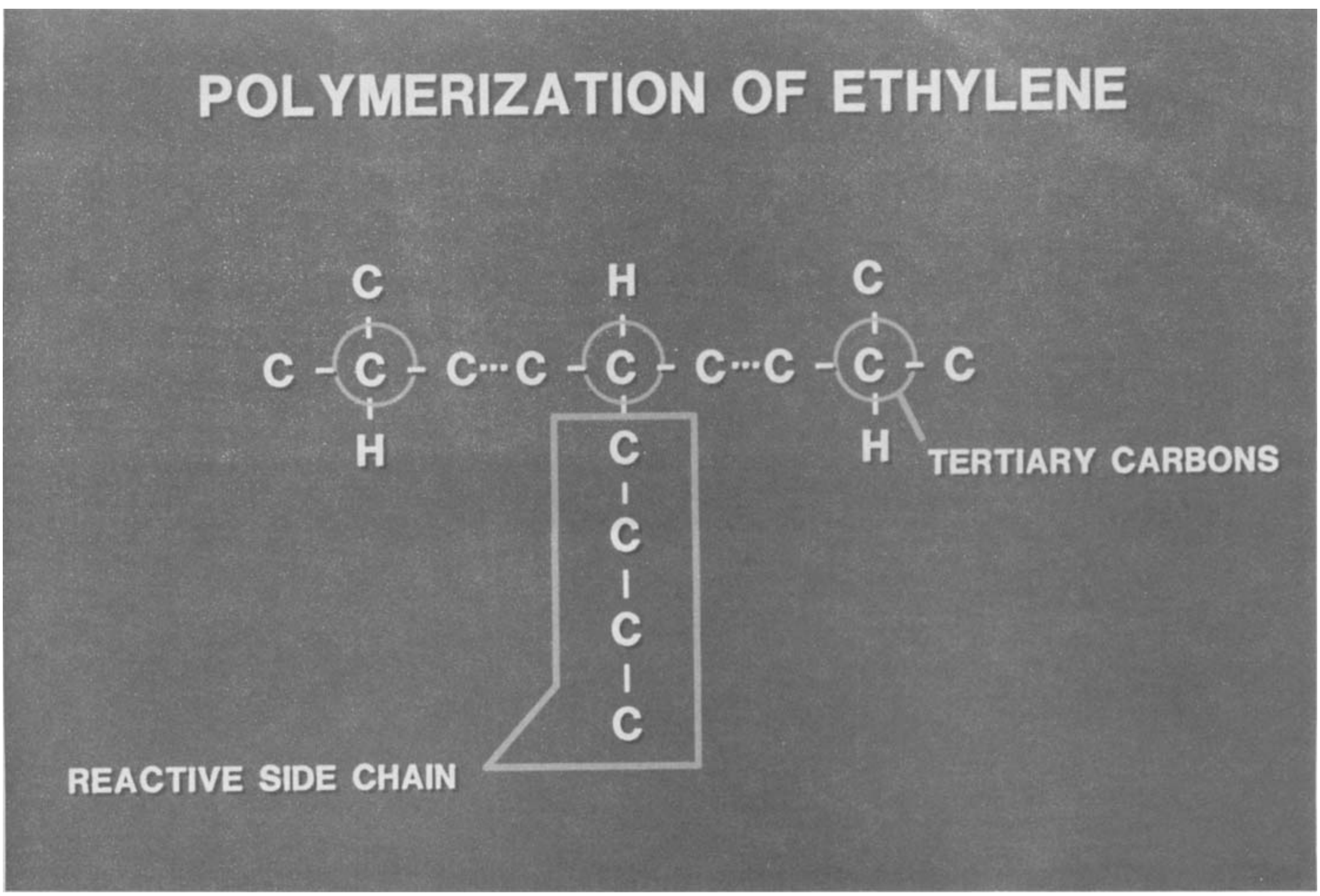


Figure 2

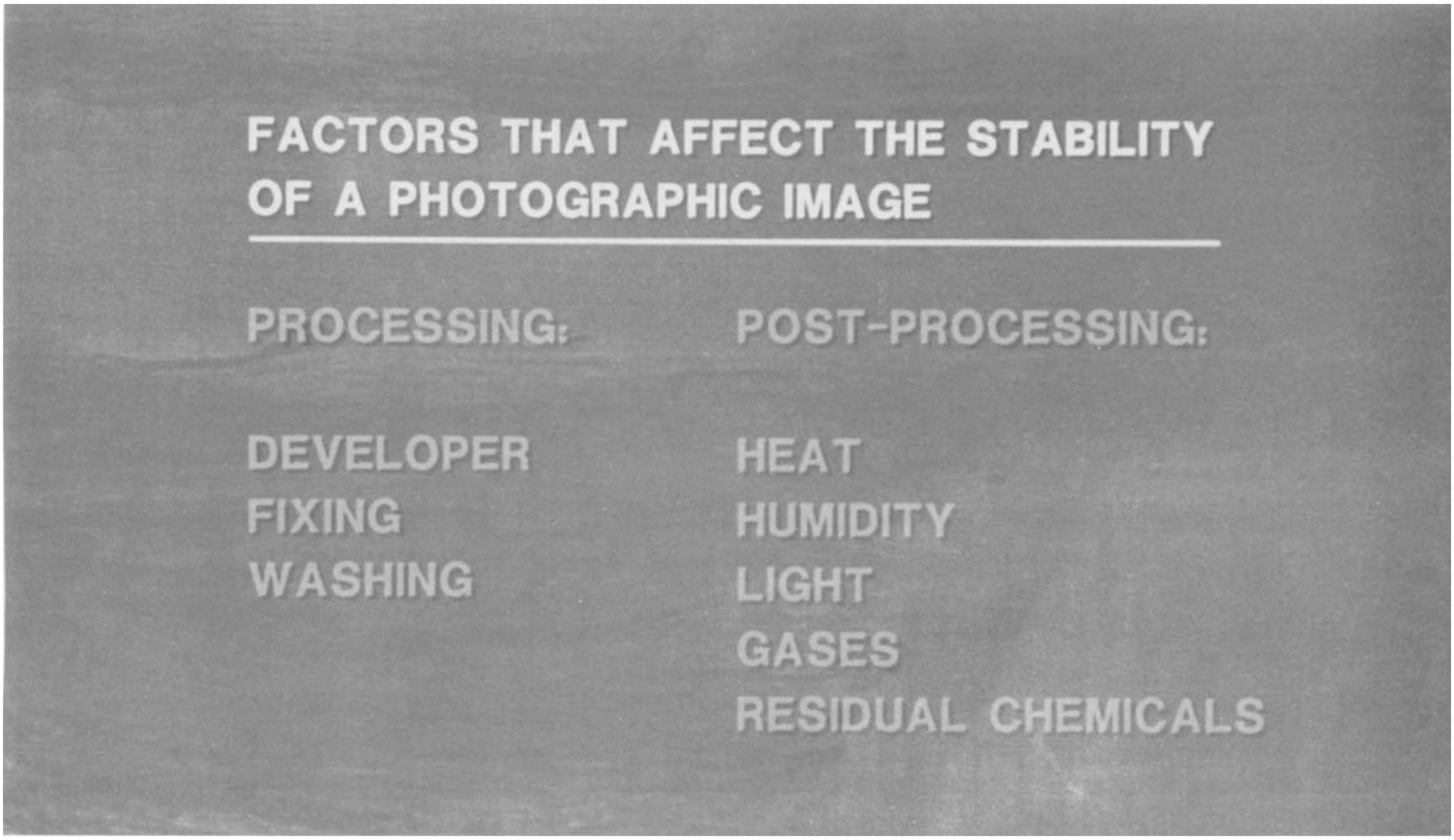


Figure 3

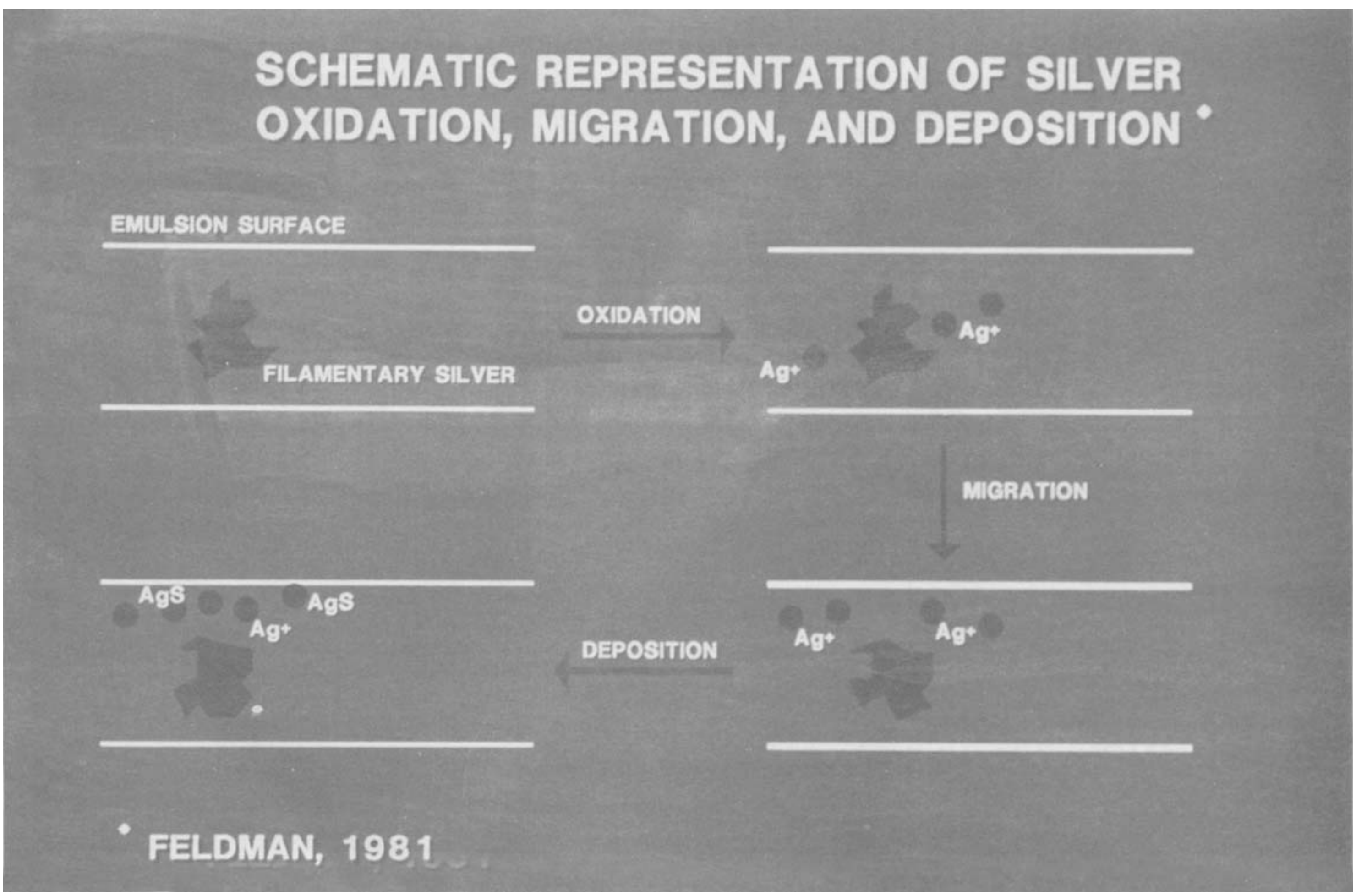


Figure 4

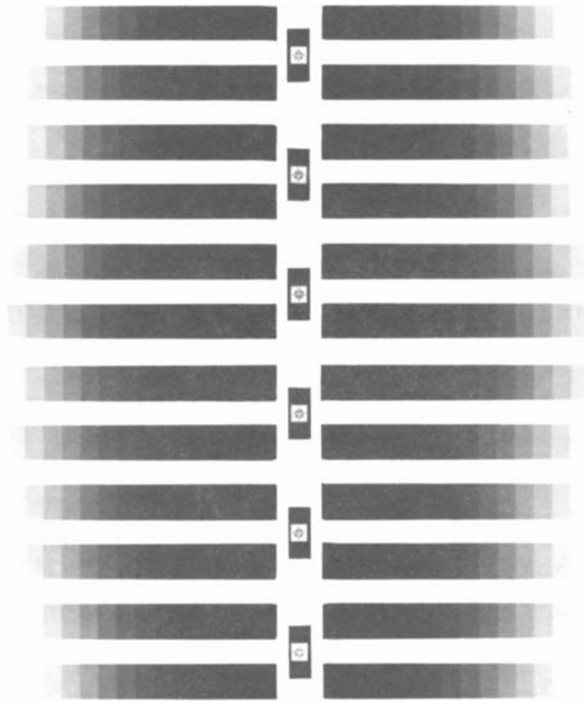


Figure 5: 21-step density strip

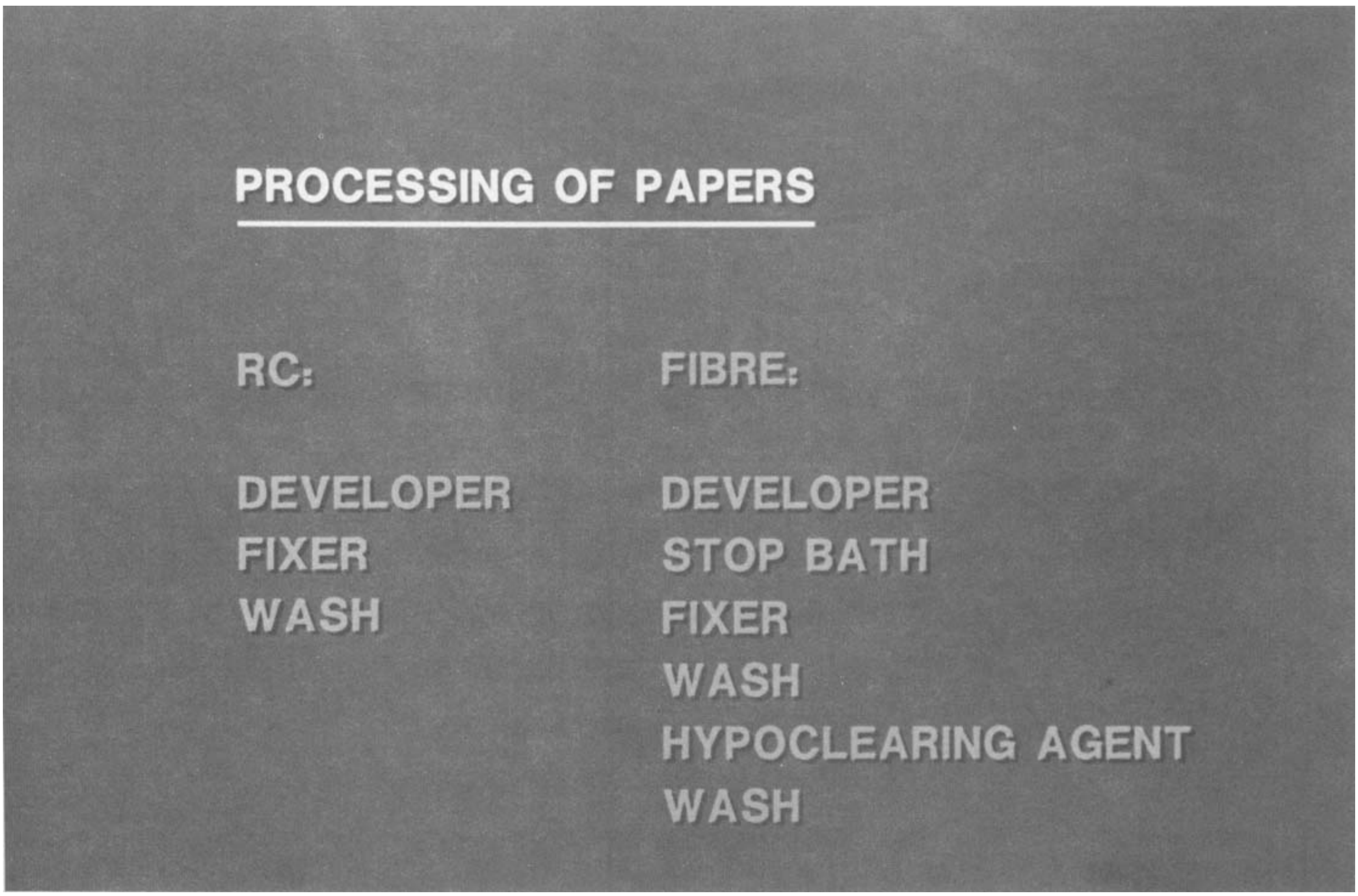


Figure 6

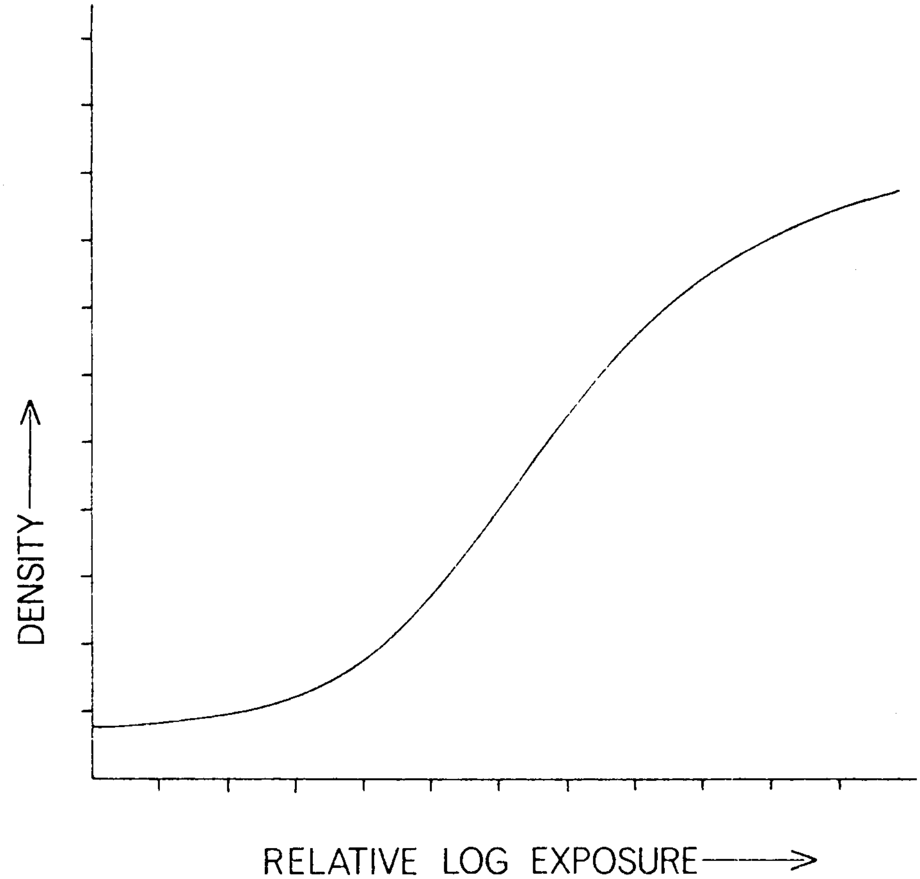
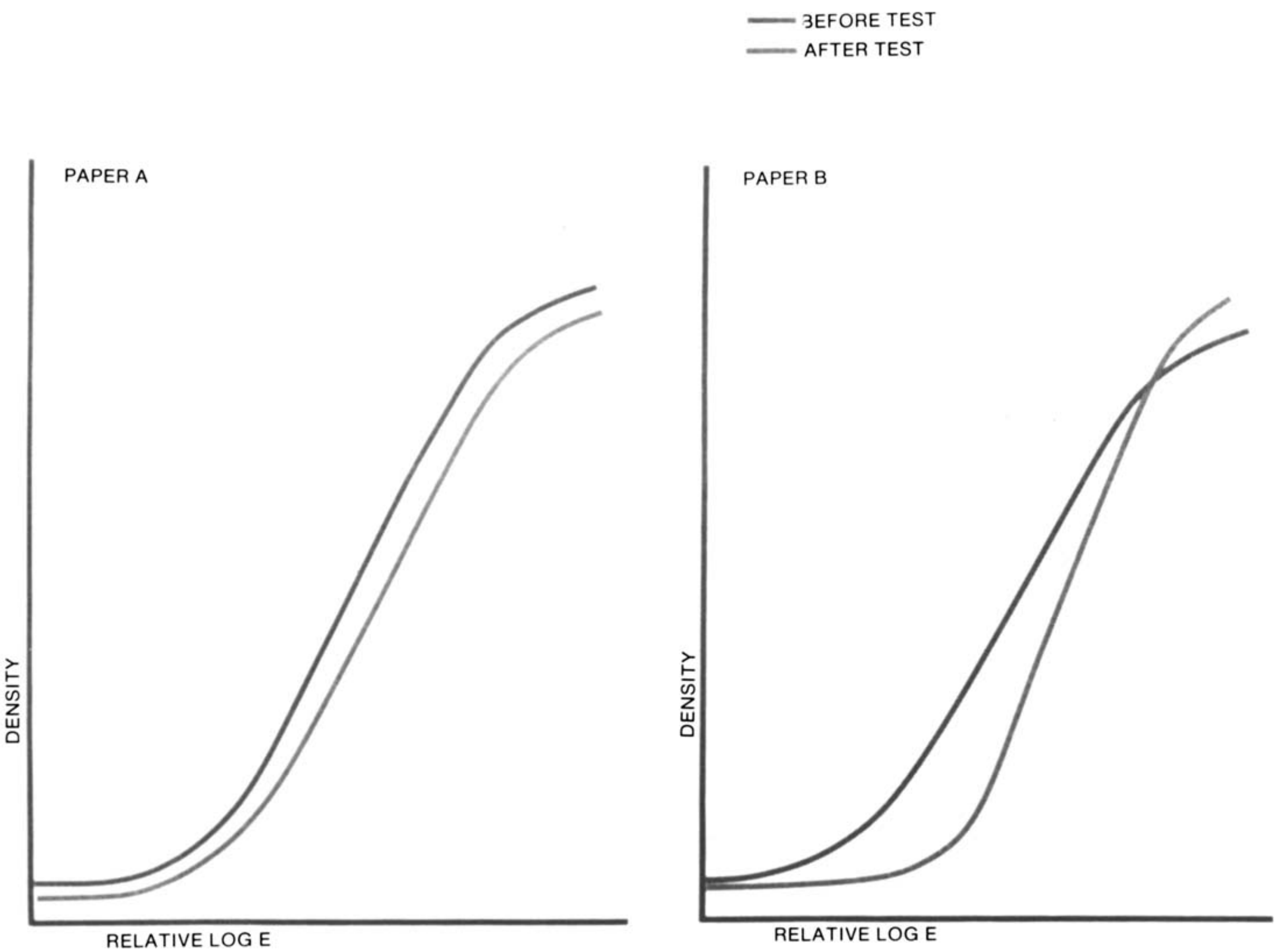


Figure 7



Figures 8a, 8b

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4] Feldman, Larry H., **Discoloration of Black and White Photographic Prints.** Journal of Applied Photographic Engineering, 7:1-9;(1981).