Image Stability of Printing-Out Images

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It is very important to duplicate or restore classical photographic prints considering their present status of deterioration. Our experiments show the stabilities of printing-out images under several storage conditions. Printing-out prints on salted paper, albumen paper, and printing-out-paper (POP) were prepared and incubated under the conditions of high temperatures and humidities. As a result, the degrees of discoloration and fading of the prints were remarkable on the albumen paper print, and smallest on the POP print under the conditions of 20°C and 86% RH. To investigate the effect of gold-protection, both albumen paper prints, toned by Kodak GP-1 solution, and untoned ones were incubated under the conditions of 70°C and 50% RH. This test confirmed that the period for decreasing the density range on the toned albumen paper prints were tested under the humidity conditions of 86%, 70% and 50% RH at 85°C, and the periods required for the density range to decrease by 10% and 22%, respectively, were compared. When such deterioration of a print is going on, it is necessary to duplicate it before the highlight details vanish. The processes and formulae shown in this article may be utilized to duplicate the printing-out images.

Journal of Imaging Science and Technology 43: 567–572 (1999)

Introduction

The developing-out paper currently used to make a photographic print monochrome or in colors appeared after the invention of the dry-plate by Maddox. At the time of the wet-collodion process, printing-out materials such as albumen paper, salted paper and printing-out-paper (POP) were used for printing. Recently classical photographs utilizing those printing materials have been collected and stored in various parts of the world. About 160 years after invention of photography, many prints made in early times have deteriorated badly. Because it is an important problem that a valuable cultural heritage vanishes, the stability, conservation and restoration of photographic images are now great concerns in the photographic world. Fading and deterioration of color photographic prints became a big issue several years ago, and the International Symposium for Image Stability and Conservation was held in 1982. Since then, many studies for color and monochrome photographic prints of developing type have been reported. But with regard to a printing-out images referred to in this article, only Reilly et al.[1] reported on the structure and deterioration in albumen prints.

Photographers and historians have thought it necessary to duplicate or restore classical prints valuable as cultural heritage, while their gradation exists. The purpose of this study is to establish a process of printing-out classical prints and to investigate their image stabilities under some storage conditions. To investigate the stability of printing-out images, we referred to the standard ISO 10214,[2] and incubated them under the conditions of high temperatures and relative humidities to examine dark-fading and deterioration. The results of the incubation tests are discussed in this article. It is obvious that the current black-and-white photographic prints as well as the older printing-out images have deteriorated with age. It is valuable to find the limit of deterioration where the same gradation as the original one is still reproducible and to predict the image stability under some storage environments in order to establish a suitable storage condition for printing-out images.

Experimental

Preparation of the Test Pieces

To prepare test pieces of the printing-out images, we first investigated the literature[3,4] and examined reported processes and formulae. Afterwards, we made each sensitive material by the following processes, exposed them in contact with a step tablet of 21 steps, and then gave treatments of fixation, washing, and gold protection, etc. As a printing-out image consists of fine silver grains, the images are easily oxidized in a short time. To imporve the image stability and the tone of their prints, gold protection is applied to most existing prints. In this study, we reproduced gold protected prints and untoned ones on albumen paper and POP, and untoned ones on salted paper to examine their image stability.

For a Salted Paper Print

First, salted paper is made by immersing fine quality paper in a salt solution. Once dried, the salted paper is sensitized by floating it in a silver nitrate solution. After drying, a salted paper print is made by contact printing with a negative film. The process for a salted paper

Original manuscript received December 4, 1998

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print is as follows. The formulae of the processing solution are shown in Table I.

Process for a Salted Paper Print

1. Salting: Immerse paper in a salting solution for 3 min, and dry it by hanging.
2. Sensitizing: Float the salted paper on a silver-nitrate solution for 3 min, and then dry it in a dark-room.
3. Exposure: Use a metal halide lamp (2kw) .
4. Fixation: After rinsing in running water for 1 min, immerse the print in a plain-hypo solution for 10 min
5. Washing: Over 30 min in running water.
6. Drying: Dry in a ventilation box.

For an Albumen Paper Print

An albumen paper print is also made of fine quality paper. As shown below, first an albumen solution composing of 300 mL of hen's egg white and 7 g of ammonium or sodium chloride is prepared. After floating the paper on the solution, we dry it by hanging. Then it is sensitized by floating on the silver nitrate solution shown in Table II, and after exposure it is treated by washing, gold-protection, fixation, and final washing.

Process of an Albumen Paper Print

1. Preparation of albumenized paper: Float the paper on the albumen solution for 3 min, then hang it to dry. After drying, the albumenized paper is presssed with heating for for 90 s at the temperature of 80°C to be made flat.
2. Sensitizing: The albumen paper is floated on a silver nitrate solution for 90 s, and then dried by hanging in a dark room.
3. Exposure: 10 min at the distance of 0.7 m when a metal-halide lamp (2kw) is used.
4. Washing: It is washed in a water bath until turbidity disappears.
5. Gold-protection: Immerse in Kodak GP-1 solution for 10 min.
6. Washing: For 10 min in running water.
7. Fixation: Fix for 10 min in a plain hypo solution.
8. Final washing: Over 30 min.
9. Drying: Dry in a ventilation box.

For a POP Print

On a POP, silver-halide usually comprises an excess mol ratio of silver. This POP is made by coating the silver-excess emulsion shown in Table III onto baryta paper. The emulsion is made as follows: First, solution A is swollen for 30 min, and it is then dissolved at 55°C. Solution B maintained at 55°C is added to it, and finally, solution C is added with stirring.[5] The emulsion coating is done at the temperature of 40°C by use of a spiral bar.

Process of a POP Print

1. Emulsion coating: The silver-excess emulsion is coated on the paper by use of a sprial bar (#60), then dried in a dark room.
2. Exposure: For 10 min at a distance of 1 m using a metal-halide lamp (2kw).
3. Washing: Wash for 5 min in running water.
4. Gold-protection: Immerse the print in Kodak GP-1 solution for 10 min.
5. Washing: Wash for 10 min.
6. Fixation: Immerse in a plain-hypo solution for 10 min.
7. Final washing: Over 30 min.
8. Drying: Dry in a ventilation box.

TABLE I. Processing solutions for making salted paper.

Salting solution:	
	NaCl 18g, NH_4Cl 12g,
	Water to make 1,000 mL
Sensitizing solution:	
	$AgNO_3$ 70g, Citric acid 20g,
	3N-HNO_3 5mL, Water to make 500 mL

TABLE II. Formulae of silverizing and gold-protection (Kodak GP-1) solutions.

Silver izing sol.:		
	Water 500mL, AgNO 60g,	
	Citric acid 40g.	
Kodak GP-1:		
	Sol. A:	Water 750mL,
		Chloroauric acid 1% sol. 10mL
	Sol. B:	Water 125mL, sodium rhodante 10g.

* Before use both solutions are mixed and made up to 1,000mL by pouring water.

TABLE III. Formulae of emulsion for POP (after Valenta[5]).

Sol. A:	Water 140mL, Gelatin 19.2g,
	Ammonium chloride 0.56g.
Sol. B:	Water 28mL, Tartaric acid 1.56g,
	Sodium bicarbonate 0.28g,
	Aluminum potassium sulfate 0.36g.
Sol. C:	Water 32mL, citric acid 1.6g,
	Silver nitrate 6.4g

Incubation Tests

Although the incubation tests differ in the condition and period for each print, all tests examined the image stability with respect to dark fading by use of a thermo-hygrostat, Tabai Expec PR-1G. We tested samples at high-humidity of 86% RH, which is the test condition used in photographic enclosure tests.[6] Relative humidity of 86% is the state of saturation. From the viewpoint of the environment for preservation of photographs, it is reasonable to incubate under conditions of 70% RH.[7] Most photographs in museums are usually exhibited and preserved under the condition of 50% RH or thereabout. Therefore, the incubation test for photographs was done under these conditions of 86% RH, 70% RH or 50% RH. The test condition is described in connection with each print.

Incubation for a Salted Paper Print

The salted paper print was tested by incubation under the conditions at four different temperatures between 90°C and 50°C and RH of 86%. The periods and conditions of the tests were as follows;

a) 50°C, 86% RH: 1,700 h
b) 70°C, 86% RH: 1,344 h
c) 80°C, 86% RH: 1,200 h
d) 90°C, 86% RH: 700 h
e) 85°C, 50% RH: 1,200 h

Incubation for an Albumen Paper Print

With the albumen paper print, the test was done under conditions of five different temperatures between 85°C and 50°C at 86% RH. In another test, the print was incubated under two conditions of 50% RH and 70% RH at 85°C.

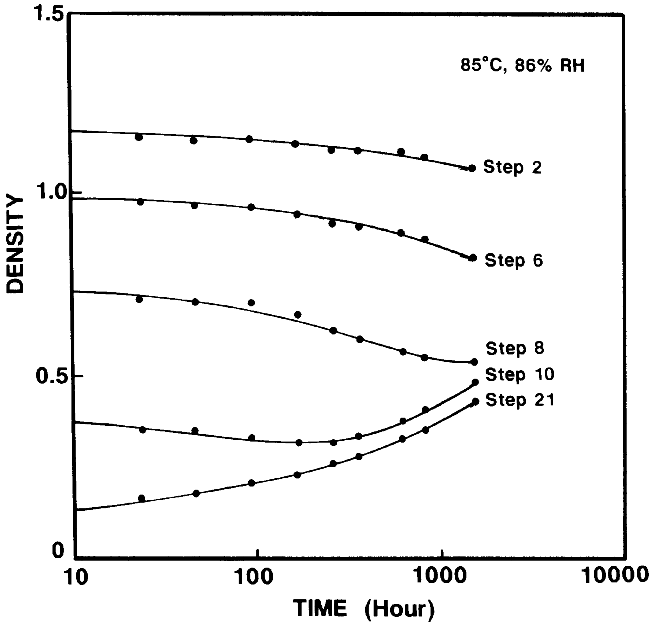

Figure 1. Changes in the density for untoned salted paper print on incubation at 85°C, 86% RH.

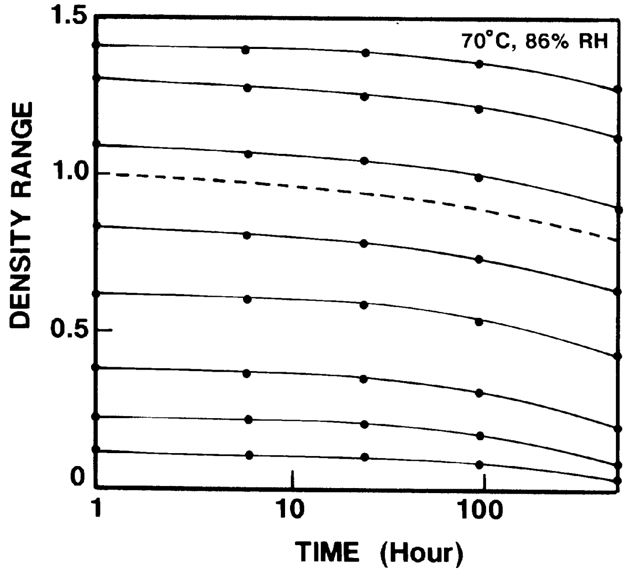

Figure 2. Changes in the density range of albumen paper print toned by GP-1 solution on incubation at 70°C, 86% RH.

a) 50°C, 86% RH: 1,700 h
b) 60°C, 86% RH: 1,100 h
c) 70°C, 86% RH: 550 h
d) 80°C, 86% RH: 1,562 h
e) 85°C, 86% RH: 192 h
f) 85°C, 70% RH: 363 h
g) 85°C, 50% RH: 1,200 h

Discoloration of the albumen paper print appeared in a short time. So the incubation tests were done for the toned sample under the conditions of 86% and 70% RH. At the condition of 85°C and 50% RH, both the sample toned by GP-1 solution and the untoned one were tested together, so as to compare the density decrease by deterioration.

Incubation for a POP Print

The POP print was incubated under conditions of four temperatures between 85°C and 60°C at 86% RH, and the condition of 85°C and 50% RH. By these tests, the image stability under the conditions of normal temperature at 86% RH and that at 86% RH and 50% RH at 85°C may be compared. Density decreases for the toned and untoned prints may also be compared. The incubation period on each condition is as follows:

a) 60°C, 86% RH: 326 h
b) 70°C, 86% RH: 1,219 h
c) 80°C, 86% RH: 428 h
d) 85°C, 86% RH: 157 h
e) 85°C, 50% RH: 1,120 h

Density Measurements

When a photographic print is stored for a long period, yellowing of the base and density decrease in the image area appear by deterioration. The yellow stain and density decrease are easily detected using a blue filter, as the colors of printing-out images are brown or yellowish sepia. So all densities before and after incubation for each print are measured with a blue filter (Wratten #47) by use of a densitometer (Macbeth RD-514). This apparatus is using a light source of status A.

Results and Discussion

The density decreases in prints by deterioration are shown in Fig. 1. The figure shows the density decreases after incubation of an untoned salted paper under the condition of 85°C at 86% RH. From Fig. 1, it is found that the density of the yellow stain on the portion of step 21, corresponding to the maximum density of the step tablet increases with the time of incubation, while the density on the image area where printing-out silver exists, decreases by deterioration. The area of the print corresponding to a density of about 0.5 in a high light portion decreases in density; afterwards it increases owing to yellow stain (see steps 10 and 8).

A similar variation by deterioration is seen on the other prints. Figure 2 illustrates the density decreases when an albumen paper print toned by GP-1 solution is incubated under the condition of 70°C and 86% RH. The figure shows the values after subtraction of the base density from the measured value of each step. It is evident in this figure that the density range of each step decreases uniformly on deterioration. We suggest that the high density portion decreases its density on deterioration, and that the low density one increases in density owing to yellow stain. In this case the yellow stain was measured with a blue fitler; the density increases by 0.3 over a period of 20 days.

In Fig. 3, gold-protected albumen paper prints and untoned ones are compared. It is confirmed by the data in the figure that the gold-protected print is slower than the untoned one with respect to the rate of density decrease. On the untoned print the portion corresponding to approximately density 0.3, slightly decreased in density at an early stage of incubation test: density started increasing on the tenth day due to the increment of yellow stain. When the print was gold-protected, the decrease in the density of step tablet print out was lower, and the yellow stain on the base was reduced.

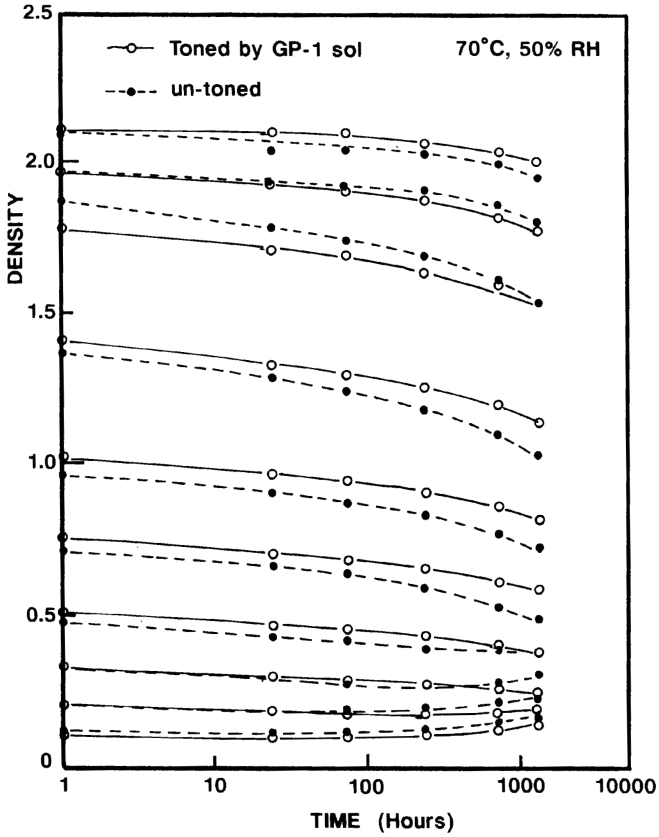

Figure 3. Changes in the density of the gold-protected albumen paper print and the untoned one incubated at 70°C, 50% RH.

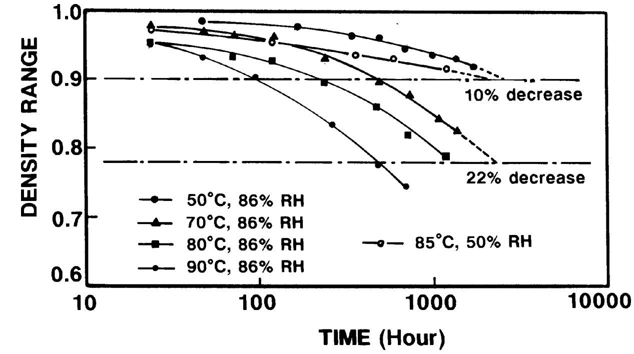

Figure 4. Decreases of the density range for untoned salted paper print on incubation.

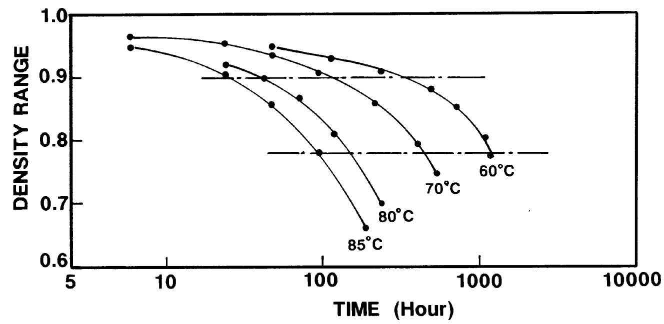

Figure 5. Decreases of the density range for the gold-protected albumen paper print on incubation at the RH of 86%.

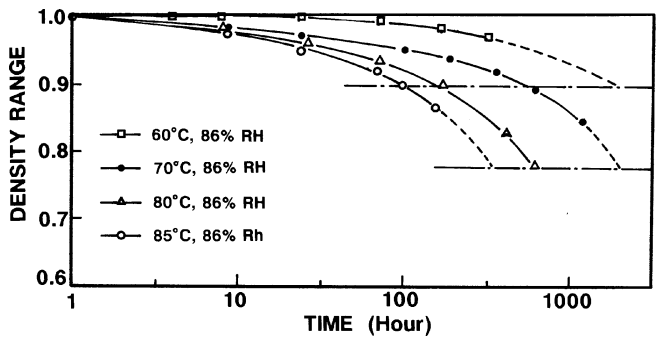

Figure 6. Decreases in the density range for POP print toned by GP-1 solution on incubation at the RH of 86%.

Image Stability at the Storage Condition of 86% RH

The density of a photographic print is decreased by incubation as shown in Figs. 1 to 3. The density is measured at each step of incubation, and the change of the density range is examined, with the density range before the test normalized to 1.0. Figures 4 to 6 indicate the change of the density range when salted paper, albumen paper and POP prints are incubated at several temperatures and at 86% RH, respectively. From these figures, the times when the density range decreases by 10% and 22% are obtained. By graphing reciprocal absolute temperatures on the abscissa, and plotting the times when the density range decreases by 10% and 22% on the ordinate, Figs. 7 to 9 are obtained. For the case of the 10% density decrease, the density of a dense area is decreased and that of the base area is increased, but a delicate highlight tone still exists, while for the case of the 22% decrease, the major highlight tone vanishes with the increase of yellow stain.[9] So it is necessary to duplicate an ancient photograph during the period of the 10% decrease of the density range, in order to reproduce the same gradation as in the original.

These data correspond to the Arhenius' equation, and the image stability at normal temperature is inferred[8] by extrapolating the plots in the direction of lower temperatures. Figure 7 shows the image stability of a salted paper print without gold-protection. It is presumed from the figure that the times required for the density range to decrease by 10% and 22% at 86% RH at 20°C are 6.5 ± 1.3 years and 29 ± 6 years, respectively.

In Fig. 8, the image stability of the gold-protected albumen paper print is presented. From the figure, the time when the density range decreases by 10% and 22% at 86% RH and 20°C are presumed to be 6 ± 1.2 years and 21 ± 4 years, respectively. In Fig. 9, for the gold-protected POP, we infer 71 ± 14 years and 250 ± 50 years, respectively.

Image Stability at Different Humidities and on the Prints with and without Gold-Protection

For an albumen-paper print, the incubation tests are done under the conditions of 50% and 70% RH at 85°C after the tests at 86% RH. And for a salted paper print and a POP print, the tests are done under the conditions of 50% RH and 85°C. The decrease of the density range when an albumen paper print is incubated at different humidities at the same temperatures, is shown in Fig. 10. It is found that the times when the density range decreases by 10% and 22% at the temperature of

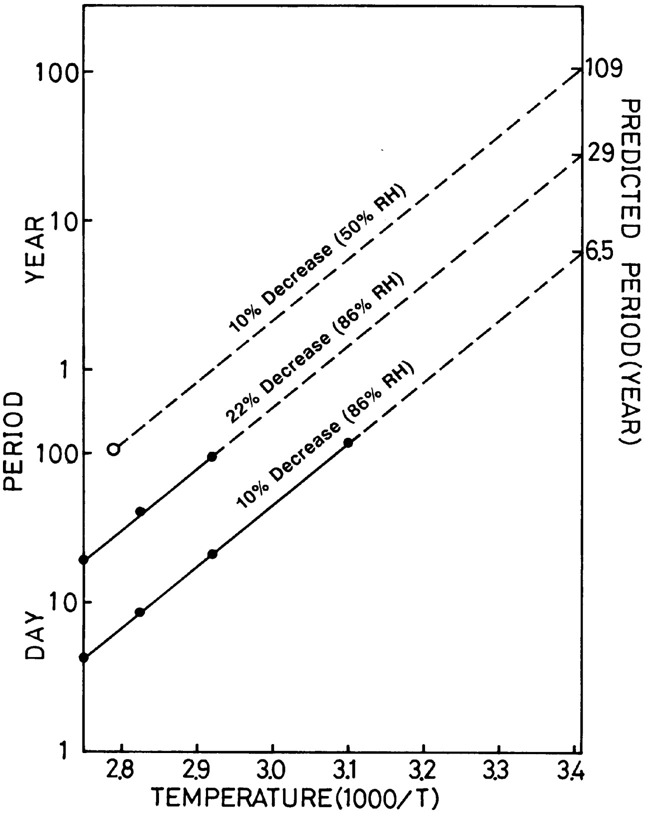

Figure 7. Prediction of the dark-fading period for an untoned salted paper print.

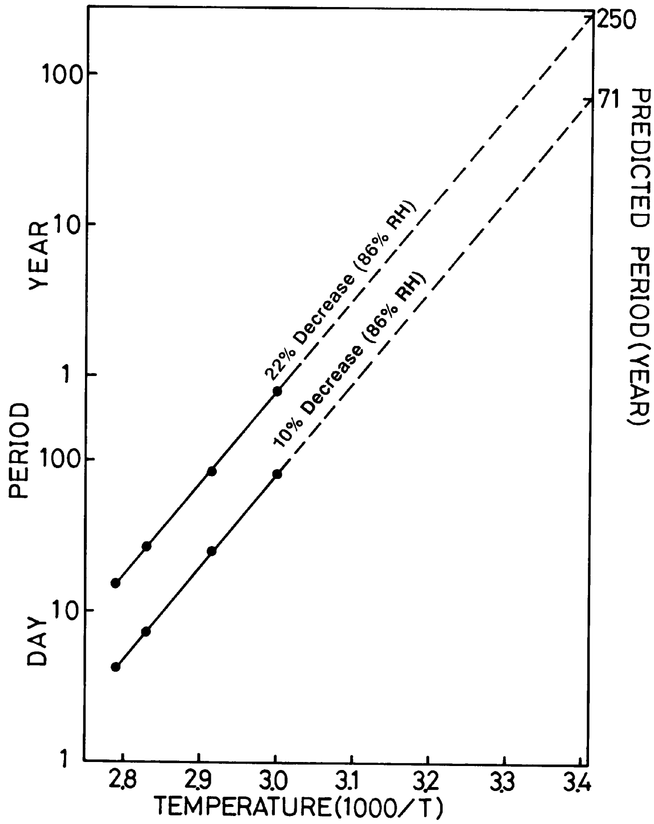

Figure 9. Prediction of the dark-fading period for a gold-protected POP print.

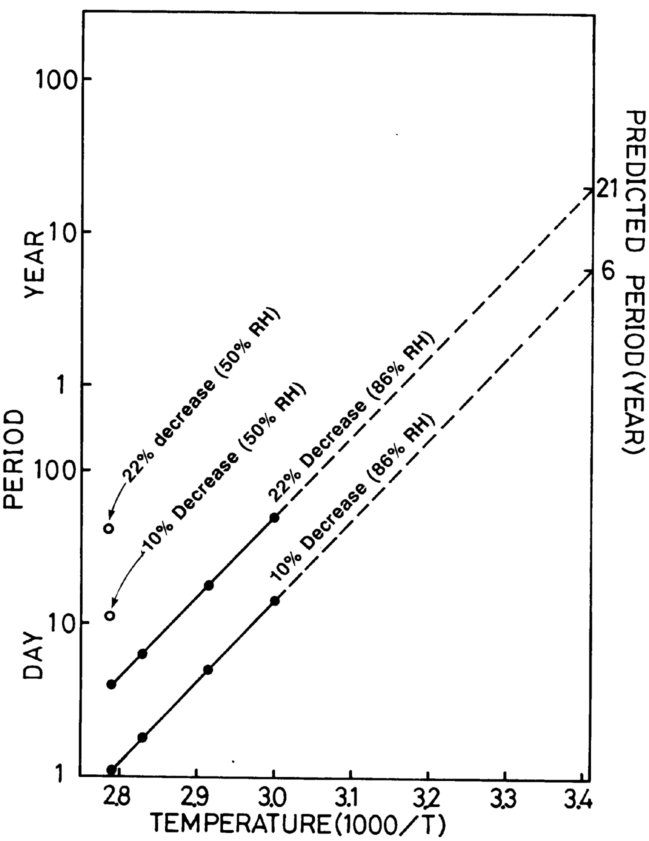

Figure 8. Prediction of the dark-fading period for a gold-protected albumen paper print.

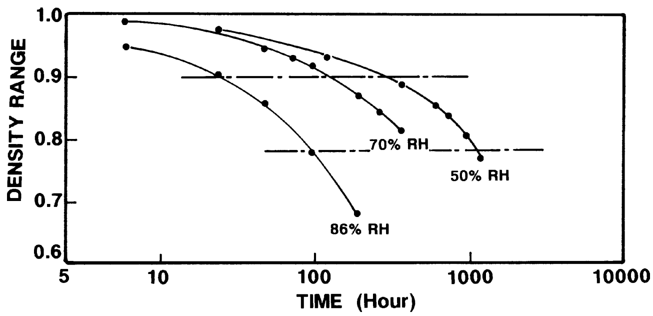

Figure 10. Comparison of the decreases of density range when gold-protected albumen paper prints are incubated under the conditions of 86% RH, 70% RH and 50% RH at the temperature 85°C.

85°C are 26 h and 96 h, respectively, when the humidity is 86% RH, 126 h and 500 h at 70% RH, and 288 h and 1,400 h at 50% RH, respectively.

The decreases in the density range when untoned salted paper and POP prints, and gold-protected albumen paper and POP prints are incubated under the same conditions of 50% RH and 85°C are shown in Fig 11. The decrease in the density range is scarcely seen for the toned POP print, and it is the greatest for the albumen paper print. From Fig. 11, the time of 10% decrease at 50% RH and 85°C can be presumed to be after 288 h, 520 h, and 2,000 h of incubation for the toned albumen paper print, and the untoned POP and salted paper prints, respectively.

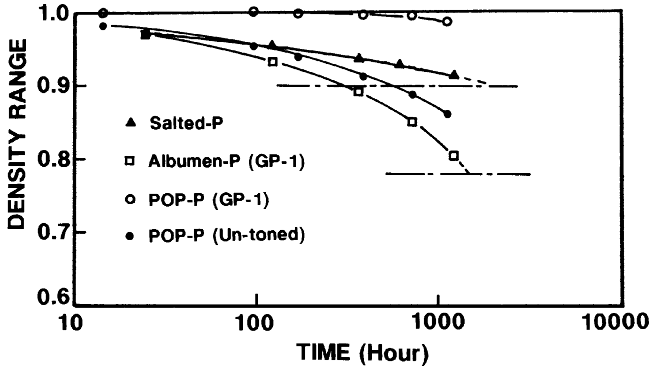

Figure 11. Comparison of the decreases of density range when the salted paper, albumen paper, and POP prints are incubated under the conditions of 85°C and 50% RH.

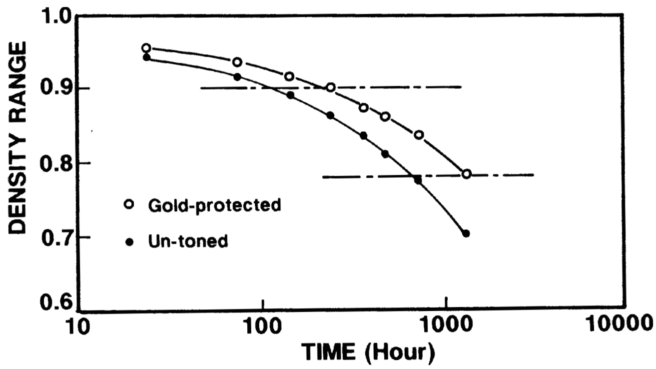

Figure 12. Comparison of the deterioration rates for the gold-protected albumen paper print and the untoned one, when they are incubated under the conditions of 70°C and 50% RH.

With POP prints, as shown in Fig. 11, the image stability is markedly increased by gold-protection. The comparison of density decreases between the tone and untoned albumen paper prints, incubated under the conditions of 50% RH and 70°C, is shown in Fig. 12. In the case of an albumen paper print, the times of 10% and 22% decrease are 115 h and 660 h for the untoned print, and 240 h and 1,320 h for the toned one. By gold-protection of the albumen paper print, the time required for decrease to the same degree is doubled.

Finally, the image stabilities of the albumen paper print incubated in the conditions of several humidities at the temperature of 85°C are compared based on the stability measured at 70% RH. As shown in Table V, it is found that the image stability is one-fifth when the RH is 86% and twice to three times when it is 50% as compared with the stability at 70% RH.

Conclusions

With advancing deterioration of a printing-out-print the density of the dense image area is decreased, while that of the base area increares owing to the rise of yellow stain. Consequently, the high-light density of about 0.5 decreases at first, and then increases when the deterioration is advanced.

For the case of 10% density decrease, the density of a dense area is decreased and that of the base area is increased, but a delicate highlight tone still exists, while

TABLE IV. Comparison of image stability for prints made by the printing-out process under the storage conditions of 20°C and 86% RH.

	10% decrease	22% decrease
Albumen-P (GP-1)	6 ± 1.2 years	21 ± 4 years
Salted-P (Un-T)	6.5 ± 1.3 years	29 ± 6 years
POP-P (Un-T)	56 ± 11 years	204 ± 41 years
POP-P (GP-1)	71 ± 14 years	250 ± 50 years

TABLE V. Comparison of the image stability when the albumen paper prints are tested under different RH at the temperatures of 85°C.

	10% decrease of density range	22% decrease of density range
50% RH	288 h	1,400 h
70% RH	126 h	500 h
86% RH	26 h	96 h

for the case of the 22% decrease, the major highlight tone vanishes with the increase of yellow stain.[9] So it is necessary to duplicate an ancient photograph in the period of the 10% decrease of the density range, in order to reproduce the same gradation as in the original.

The image stabilities of three kinds of printing-out prints have been compared. First the prints are incubated at 86% RH at different temperatures and the time required for the density range to decrease by 10% and 22% is obtained. Secondly their image stabilities on the condition of 86% RH and 20°C are estimated from Arrhenius plots. Of the three kinds of prints, the rate of decrease of density range by deterioration is the fastest on the albumen paper print, and is the slowest on the POP print.

From the results, it is understood that a good storage condition for printing-out images is below 50% RH. We can predict image stabilities in several storage environments. While the deterioration of a print is in progress, it is essential to duplicate it before highlight details vanish, and the processes and formulae shown in this paper may be utilized therefor.

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