A New Method of Predicting the Oxidative Discoloration of Silver Images

Chika Honda

Development Center Section No. 2, Photographic Materials Development Division, Photographic Products Manufacturing Headquarters, Konica Corporation, No. 1 Sakura-mahi, Hino-shi, Tokyo, Japan 191

An accelerated test for the oxidative discoloration of developed silver images has been studied. While hydrogen peroxide testing has been used to predict the oxidative discoloration of developed silver images in monochrome photographic materials, this method is sometimes impractical when applied to materials stored under a "normal atmosphere" in which the contents of aggressive oxidizing chemicals are small or nonexistant. The article presents a new testing method that uses incubation in an atmosphere of compressed oxygen to accelerate oxidative discoloration. Such incubation for one or two months was found to reproduce the oxidative discoloration occurring in radiographic films stored under a normal atmosphere for four or five years under the climatic conditions of the Tokyo area. And an induction period in which discoloration is imperceptible was observed in the blue density increase of this accelerated testing. From these results, the mechanism of the oxidative discoloration is discussed and the rate-determining process of this discoloration reaction is presumed to be ion migration in the gelatin layer.

Journal of Imaging Science and Technology 42: 148–152 (1998)

Introduction

The image stability of monochrome photographic materials such as microfilms, black-and-white prints, holograms, and radiographic films has long received wide study,[1] and two main occurrences of silver image discoloration have been cited.[2] The first occurs when improper fixing and/or washing allows excessive amounts of hypo or complexes of silver ions and fixing agents to remain in photographic materials. This results in discoloration during storage when the metallic silver images are converted through chemical reactions with sulfide compounds into silver sulfide.[3] The second discoloration, and the focus of our concern here, occurs even when fixing and washing of the silver halide materials are conducted properly. Discoloration here is caused by ambient oxygen molecules and/or other oxidizing chemicals that oxidize developed silver grains, producing colloidal silver particles in the layers of photographic materials through complex reaction steps during the storage of the materials.[4]

In the case of improper fixing and/or washing, the method to measure residual hypo in processed silver-gelatin photographic materials has been established for evaluation of the image stability.[5] The discoloration is easily reproduced by oven tests with high temperature and humidity. For discoloration caused by oxidizing chemicals, a hydrogen peroxide method, for example, has been proposed for evaluation of image stability.[6] This method is applied to the image permanence testing of sulfide-toned silver images that prevent the oxidative discoloration.[7] However, it is sometimes hard for the method to estimate practically the image stability stored under a "normal atmosphere" or "normal storage conditions" in which contents of aggressive oxidizing chemicals, such as nitrogen oxide gas, sulfide oxide gas, and ozone in ambient air are small or nonexistant, because the hydrogen peroxide method is too oxidative to reproduce the discoloration quantitatively. In other words, until now, no method of predictively reproducing the oxidative discoloration that occurs under normal storage conditions has been reported.

This study presents an accelerated method of quantitatively estimating the image stability of developed silver in radiographic films subjected to oxidative discoloration under normal storage conditions. This new method accelerates discoloration by incubating photographic materials in an atmosphere of compressed oxygen gas without using any aggressive oxidizing chemicals, such as hydrogen peroxide, NOx, or SOx.

In this article, the results from three independent experiments of this new testing method are reported: (1) our new testing for 54 days reproduced the discoloration observed in radiographic films stored for 49 months (four years and one month) on our laboratory shelf; (2) the relationship between our subjective evaluation and an objective evaluation of blue density measurement in discoloration is shown; and (3) by increasing blue density by discoloration along the incubation term, an induction period was observed in the initial stage of the discoloration process. From these results, the reaction mechanism of oxidative discoloration is discussed.

Experimental

In our experiments, discoloration of silver images in properly processed radiographic silver-gelatin materials was produced by long-term storage in our radiographic film boxes on the shelf in our facilities or by our accelerated testing. Evaluation of discoloration was conducted subjectively and/or objectively. The colloidal silver particles in discolored film after accelerated testing were observed by electron microscopy.

Original manuscript received March 26, 1997.

* IS&T Member

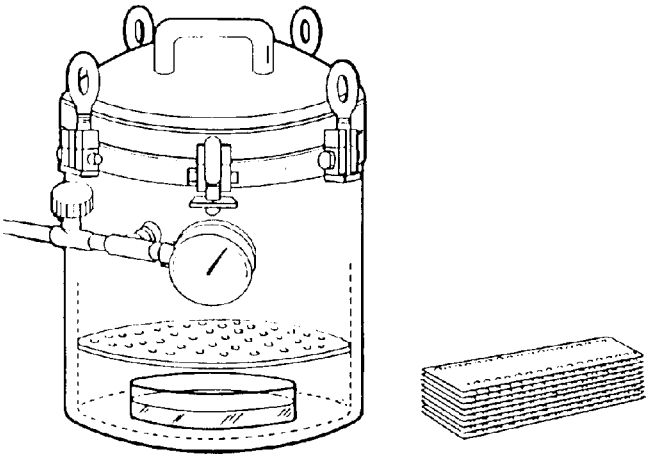

Figure 1. Illustration of testing vessel and embossed TAC sheets.

Preparation of Processed Samples for Comparison of Discoloration During Shelf Storage and During Accelerated Testing. To correlate the discoloration of stored and accelerated test samples, we used 30 × 25 cm radiographic sheet films manufactured before 1990 by Fuji, Kodak, and Konica. These films had a silver iodobromide emulsion and were green- or blue-sensitive. The films were exposed with a step wedge such that optical density ranged from nonexposed fog to the maximum density after processing. They were developed with Kodak PR-Omatt processing chemicals at the developing temperature of 32°C with 210-s cycle time in a Kodak M6 automatic processor. The developed films were cut to form two sample groups: one was kept on the shelf in our laboratory for 49 months and the other was further cut into 3 × 13 cm samples for this accelerated test for 54 days. The storage conditions of the processed samples on the shelf in our facility were not controlled.

Preparation of Samples for Comparison of Subjective and Objective Evaluations of Discoloration. Samples of exposed and processed radiographic films were prepared here in the same manner as above, except that the full size, uncut sheets were stored on the shelf of our laboratory for 54 months. Although the storage term here was longer than the samples stated above, this was only for our convenience for scheduling.

Preparation of Samples for Comparison of Discoloration at Various Incubation Terms During Accelerated Testing. The exposed and processed samples of three kinds of radiographic films were prepared to estimate the discoloration depending on the term of incubation in this accelerated test. Film sheets of 30 × 12.5 cm were exposed with a step wedge as described above, but were processed by Kodak X-Omatt chemicals in a Kodak 480RA automatic processor at a developing temperature of 35°C with a 90-s-cycle time. The developed films were cut into 3 × 13 cm samples for this accelerated testing.

Accelerated Test Procedure. Figure 1 shows the testing vessel used in our accelerated testing. This stainless steel vessel was equipped with a pressure gauge and the lid fitted with an O-ring to maintain high oxygen pressure. In the bottom of the vessel, a petri dish contained a saturate solution of cobalt chloride ($CoCl_2$:$6H_20$, 60 g, dissolved in 14-cc pure water) that maintained humidity at 51% RH at 55°C.

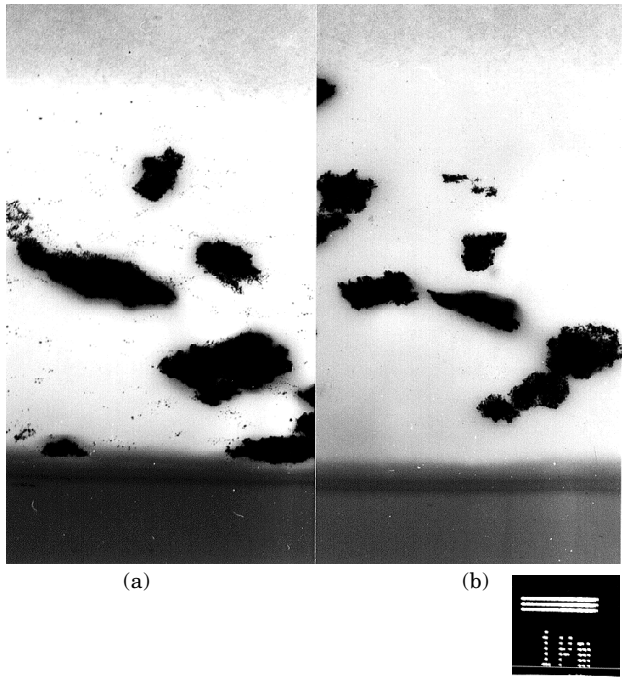

Figure 2. Cross sections of (a) moderately discolored sample by the accelerated testing and (b) sample with no discoloration. Magnification of 10,000×.

The test samples were banded with embossed TAC sheets inserted between the test samples, and the banded samples were stood on end in the vessel with the lid tightly closed. Oxygen gas was injected into to the vessel from an oxygen tank and compressed to 1.2 kg/cm^2 as indicated by the pressure gauge, and the vessel bled to ambient pressure. This procedure was repeated twice, and the compressed oxygen on the third time was kept at the pressure of 1.2 kg/cm^2. The vessel itself was put in a temperature chamber controlled to 55°C. The pressure gauge then read 1.4 kg/cm^2. The vessel was kept in the temperature chamber for a fixed number of days for each testing purpose.

Evaluation of Discoloration. The discoloration of films was evaluated subjectively and/or objectively. For subjective evaluation, samples were hung on a viewing light box typical of those used by radiologists and rated for discoloration as follows: (1) imperceptible, (2) barely perceptible, (3) slight, (4) moderate, and (5) heavy. Some samples stored on the shelf were discolored unevenly on the sheets, and therefore, the evaluation was from an estimation of the yellow and discolored areas. For objective evaluation, a Sakura optical densitometer PDA65 manufactured by Konica was used to measure the optical density of blue light in those areas where the optical density of visible light was 1.0.

TEM Cross-Section Photographs. To obtain TEM (transmission electron microscope) photographs of film sample cross sections, film samples were covered with epoxy resin, then cut into 0.5-μm slices. A driving voltage of 200 kV was used with a TEM manufactured by JEOL Ltd.

Results

TEM images of two film sample cross sections are shown in Fig. 2. Sample (a), obtained from our accelerated testing for 30 days, was moderately discolored, with a blue—light optical density of 1.00. Sample (b), obtained from film

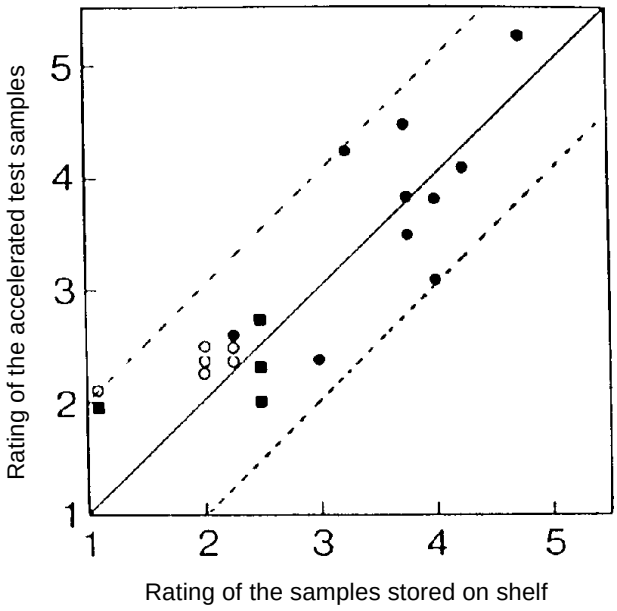

Figure 3. Relationship of discoloration between the samples that underwent the accelerated test for 54 days and those stored on the shelf for 46 months: solid circle, Green-sensitive double-coated film; open circle, Blue-sensitive double-coated film; solid square, Green-sensitive single-coated film.

stored on the shelf for 24 months, was not discolored, with a blue-light optical density of 0.90. The upper part of the grainy zone in each film is the protective film layer and the lower part is film substrate. In sample (a), the colloidal silver particles are observed in the gelatin layer. In sample (b), colloidal silver particles are hardly observed.

Shown in Fig. 3 is the relationship between the subjective discoloration ratings for the samples of our 54-day accelerated testing and the samples stored for 49 months on the shelf in our facilities. The sample groups of ratings at 4 and 5 (moderate and heavy) and of ratings at 1 through 3 (imperceptible, barely perceptible, and slight) are clearly discriminated in accelerated testing as observed in the samples stored on the shelf. All the evaluated results fall within the inside between the dotted lines that show accuracy of ±1 for the ratings.

Figure 4 shows an example of the relationship between the subjective discoloration ratings and the blue density measured with a densitometer. The rating at 2, barely perceptible, corresponds to the blue density of 0.93, and the rating at 1, imperceptible, to the blue density of 0.88. Consequently, increasing blue density of the nondiscolored film by 0.05 makes the discoloration barely perceptible.

In Fig. 5, blue density in discoloration by the accelerating test is shown. In the initial stage of the testing until 30 days for the lower two samples, blue density increases gradually. The blue density was measured at the part where visible density was 1.0, and the visible density did not change after this testing substantially, although the blue densities increased in accordance with discoloration of silver image as shown here.

Discussion

Minagawa[4] has presented the following reaction steps for oxidative discoloration:

1. The silver atoms of developed silver grains are oxidized into silver ions mobile in the gelatin layer.
2. The mobile silver ions migrate within the gelatin layer.

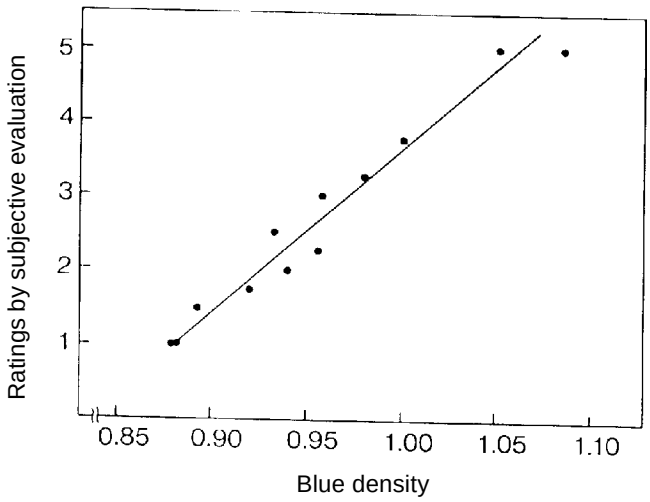

Figure 4. Relationship between rating by subjective evaluation and the objective evaluation of blue density measurement.

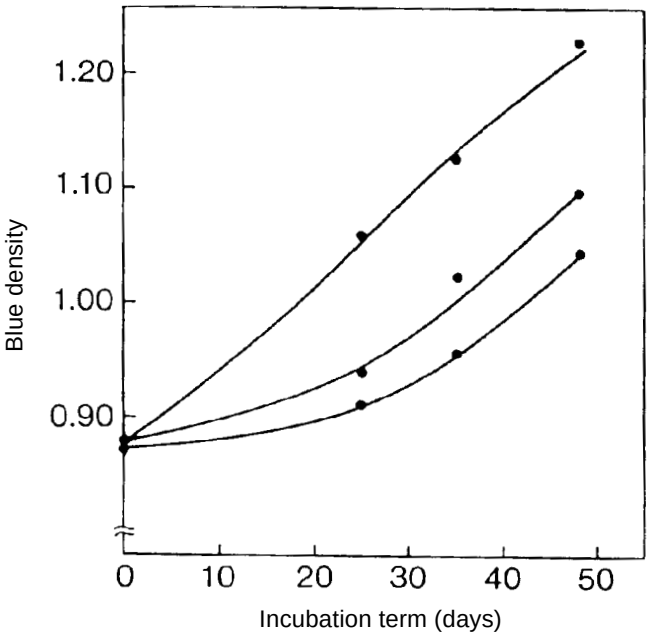

Figure 5. Blue density increase of samples discolored by the accelerated testing.

3. The silver ions are reduced into silver atoms at some site of the gelatin layer.
4. The three steps above repeat to produce colloidal silver particles that scatter light of a wavelength determined by the diameters of the particles and blue light is scattered to change the silver image from black to yellow.

In the test samples after incubation of compressed oxygen for 54 days, colloidal silver particles were observed as shown in Fig. 2. In another incubation test of the same radiographic film at 65°C and humidity at 80% RH without compressed oxygen gas for about 1 month, we observed no colloidal silver particles by an electron microscope, although the silver image changed to brown. The compressed oxygen gas plays an important role in this method and accelerates the oxidation in the first step of the discoloration mechanism presented by Minagawa. In Fig. 3, two films with a 1 rating for the samples stored on the shelf

fall in the rating of 2 for accelerated testing samples. The compressed oxygen atmosphere might affect samples in accelerated testing excessively for the films that sustain against oxidative discoloration in normal atmosphere at room temperature for 49 months.

The substitution of air in the vessel by oxygen and its compression at 1.2 kg/cm^2 increase the amount of oxygen gas present to more than 10 times that usually found in the atmosphere. The incubation at 55°C may accelerate the oxidation in the first step as well as migration of silver ions in the second step and reduction in the third step. Now, let us represent the whole discoloration reactions as below.

$$A \xrightarrow{k} B$$

where A is the non-discolored state, B, the discolored state, and k, the discoloration reaction rate.

The discoloration reaction rate at the average temperature in storage on the shelf $k1$ and the reaction rate at the applied temperature in the accelerated testing $k2$ are correlated with the following Eq. 1, one of thermodynamic formula, and we may predict the activation energy of oxidative discoloration from the result obtained in Fig. 3.

$$\text{where } \log k1/k2 = (\mathrm{E}/2.303\mathrm{R}) \times (1/T1 - 1/T2), \quad (1)$$

$k1$ = reaction rate at $T1$.
$k2$ = reaction rate at $T2$
$T1$ = average temperature of storage on the shelf
$T2$ = temperature of accelerated testing
E = activation energy.

The average temperature and relative humidity in 1994 observed in the Tokyo area by the Meteorological Agency were 16.9°C and 62% RH, respectively. In this test method, the discoloration occurs 27.6 times faster than that in storage on the shelf, because 49 months (1491 days)/54 days = 27.6. When we take into account the effect of the compressed oxygen in the vessel, the effect of the elevated temperature in the accelerated reaction might be extracted to be $k1/k2$ = 27.6/10 = 2.76. Applying Eq. 1 gives an activation energy in the discoloration under normal atmosphere of 5.0 kcal/mol. The value of 5.0 kcal/mol drawn here corresponds to the activation energy of ion migration, suggesting that the rate-determining process in the oxidative discoloration will be the silver ion migration in the second step. This suggestion implies that silver ion scavengers such as mercaptan and other organic sulfide compounds, and iodide ions remained in processed films would protect effectively the oxidative discoloration from their preventing of silver ion migration.[4,11]

From the discussion above, it might appear that the period of oxidative discoloration could be estimated by constructing Arrhenius plots based on this test method. However, the reduction process in the third step has not been clarified. We should also consider that too high of temperature might produce unknown subside reactions in addition to the discoloration that may disturb the result of Arrhenius plotting. Consequently, we need more research, especially on the reduction process in step 3 in this discoloration for accurate estimation by this test method using Arrhenius plotting.

In Fig. 3, a correspondence of discoloration between the practical storage of films for 49 months and the accelerated testing for a term of 54 days is obtained. In practice, however, storage conditions such as temperature and relative humidity vary significantly among hospitals and medical facilities and the composition of film envelopes have an affect on discoloration. The results in Fig. 3 generally suggest that the discoloration produced by acceleration of one or two months would correspond with the discoloration of films stored for about four years under storage conditions similar to those found in Tokyo.

In Fig. 4, the subjective evaluation perception of discoloration by eye is correlated with the objective evaluation of measurement of blue optical density in our experiments. In rendering these subjective evaluations, the observers viewed the test samples just as consumers would observe actual radiographic images, making this evaluation a realistic estimation of discoloration. However, the subjective evaluation is limited in universal validity, because it could be affected by subtle human emotional waver and might be different depending on each individual susceptibility. The objective evaluation would be generalized easily, however it might not always represent precisely the practical recognition of discoloration through human eyes, because the discoloration is not always observed evenly on the film sheets in practice.

Note that an induction period of discoloration occurs, which is clear for the two samples discolored less comparatively in Fig. 5. The initial stage where blue density is up to 0.97 will be the induction period that corresponds with the processes from the first step of silver ion formation until the growth of colloidal particles that can reflect blue light.

In this work, the new evaluation method of discoloration is applied to radiographic films with silver halide grains so coarse that the oxidative discoloration is not easily anticipated, because the oxidative discoloration has been reported in past only for microfilms, black-and-white prints, and holograms with developed silver grains smaller than those of radiographic films.[1] Today, radiographic films are usually processed in automatically at a developing temperature higher than 30°C in accordance with a processing cycle time from 30 to 210 s. In such developing processes, chemical development is dominant for a silver iodobromide emulsion of radiographic films rather than physical development, i.e., the developed silver grains of the radiographic films will consist of metallic silver filaments. Although developed silver grains it radiographic film look coarse, however the specific surface area of developed silver grains consisted with filament will be comparatively wide enough to be attacked by oxygen molecules and/or oxidants of a small content in ambient air.[8]

In Fig. 3, note that green-sensitive double-coated films discolor more readily than blue-sensitive double- and single-coated films. Generally the silver halide grains in blue-sensitive films are larger than those in green-sensitive films, and the amount of silver halide per unit area of film in blue-sensitive films is greater than that in green-sensitive films.[9] The residual hypo of blue-sensitive double-coated films after processing tends to remain more than that in green-sensitive double-coated films. The residual hypo may inhibit oxidative discoloration.[10] The large amount of silver halide on one side and the thick emulsion layer in single-coated films also may contain a large enough amount of residual hypo to protect the oxidative reaction, compared with the double-coated green-sensitive films. Other factors in films that make variation of discoloration tendency are chemical additives that remain in films after their processing. From this discussion, it is easy to predict that the additives of developer, fixing agent, and washing conditions in processing as well as processing cycle time will affect the image stability of radiographic films.[7,10,11]

Conclusion

1. This new accelerated testing method can reproduce the oxidative discoloration observed in radiographic films stored for several years under normal storage conditions.
2. The oxidative discoloration produced in one to two months of this accelerated testing generally corresponds to that produced in approximately four years of normal shelf storage in a climate resembling that of Tokyo.
3. Oxidative discoloration in this accelerated testing is accelerated by the use of compressed oxygen gas. The rate-determining process of this oxidative discoloration appears to be the migration of silver ions within the gelatin layer.

Acknowledgments. The author appreciates the efforts for experiments and analyses of the results by Mr. Haruhiko Sakuma and Mr. Masayuki Taguchi who are colleagues in his laboratory. He also thanks Mr. Hisashi Yamaguchi, Director of the Development Center No. 2 in Konica, for his permission to publish this work.

References

1. R. W. Henn and D. G. Wiest, Microscopic spots in processed microfilm: Their nature and prevention, *Photogr. Sci. Eng.* **7**, 253 (1963); L. H. Feldman, Discoloration of black-and-white photographic prints, *J. Appl. Photogr. Eng.* **7**, 1 (1981); J. M. Reilly, N. Kennedy, D. Black and T. Van Dam, Image structure and deterioration in albumen prints, *Photogr. Sci. Eng.* **4**, 166 (1984); K. C. Brown and R. E. Jacobson, Archival permanence of holograms?, *J. Photogr. Sci.* **33,** 177 (1985); S. I. Anderson and R. L. Ellison, Image stability of black-and-white photographic products, *J. Imaging Technol.* **16**, 27 (1990).
2. K. B. Hendriks, *Imaging Process and Material*, Van Nostrand Reinhold, 1989, p. 637.
3. R. W. Henn and N. H. King, A comparison of the effect of residual sodium and ammonium thiosulfates on image permanence, *Photogr. Sci. Eng.* **5**, 46 (1961); D. F. Koppert, G. W. Larson, B. A. Hutchins, and C. C. Bard, A method to predict the effect of residual thiosulfate content on the long-term image stability characteristics of radiographic films, *J. Appl. Photogr. Eng.* **8**, 83 (1982).
4. Y. Minagawa, Stability of photographic silver image, *Hyoumen*, **23,** 252 (1985), (in Japanese)
5. ISO 417: Photography-determination of residual thiosulfate and other related chemicals in process2ed photographic materials—Methods using iodide-amylose, methylene blue and silver sulfide.
6. ANSI/NAPM IT9.15 (1993): American national standard for imaging media (photography)—the effectiveness of chemical conversion of silver images against oxidation—Methods for Measuring; H. Iwano, S. Kishimoto, T. Koshimizu, and K. Ohmura, Method for measuring the stability of silver images to aerial oxidation and the image stabilization by a thiol, *J. Imaging Sci. Technol.* **38**, 140 (1990); J. M. Reilly, P. Z. Adelstein, D. W. Nishimura, and K. M. Cupriks, Protection of microfilm images against oxidation, *J. Imaging Sci. Technol.* **38,** 326 (1994).
7. P. Z. Adelstein, J. M. Reilly, D. W. Nishimura, and K. M. Cupriks, Hydrogen peroxide test to evaluate redox blemish formation on processed microfilm, *J. Imaging Technol.* **I7,** 91 (1991).
8. T. H. James, The stability of silver filaments, *Photogr. Sci. Eng.* **9,** 121 (1965).
9. Y. Satoh, The progress of silver halide photography in medical and graphic arts imaging, *J. Imaging Sci. Technol.* **38,** 36 (1994).
10. A. Sasai, 150 years of photography: mainly its processing technology, *J. Soc. Photogr. Sci. Technol. Jpn.* **52,** 582 (1989), (in Japanese).
11. C. Honda, H. Sakuma and M. Taguchi, An evaluation of the silver image stability of radiographic films against oxidation through incubation with compressed oxygen, *Proceedings of 1997 International Symposium on Silver Halide Imaging: Recent Advances and Future Opportunities in Silver Halide Imaging*, 268 (1997).