An Evaluation of the Silver Image Stability of Radiographic Films against Oxidation through Incubation with Compressed Oxygen

Chika Honda, Haruhiko Sakuma, and Masaaki Taguchi
Konica Corporation, Photographic Products Manufacturing Headquarters
Hino-shi, Tokyo, Japan

Abstract

We have employed incubation with compressed oxygen to evaluate the silver image stability of radiographic films against oxidation. With this accelerated testing method, the oxidative discoloration of silver images observed in processed radiographic films after several years of shelf storage was reproduced by incubating test samples for thirty to forty days at 55°C, 51%RH in oxygen compressed to 1.4kg/cm^2. We found that processing factors such as types of automatic processor and processing chemistries influence the oxidative discoloration of silver images in radiographic films. This could be explained with the amounts of residual hypo in our observation that oxidative discoloration has a negative correlation to the amounts of residual hypo in film after processing. This suggests that adequate amounts of residual hypo prevent oxidative discoloration, although larger amounts of residual hypo naturally cause silver sulfide discoloration. We also observed that the organic restrainer PMT(1-phenyl-5-mercaptotetrazole) prevents oxidative discoloration when present in the developing chemistry.

Introduction

In many fields, including medical imaging, the imaging permanence of monochromatic silver photographic images is exceptionally important because the images are used as records. The discoloration of such silver photographic images is usually found after several years of shelf storage, so accelerated test methods have been designed to predict such discoloration [1].

In monochromatic silver halide photographic materials, it is well known that there are two major mechanisms of silver image discoloration , and these two are classified by their causes [2]. The first is silver sulfide discoloration, which is caused by a reaction between a silver image and an exceptional volume of residual hypo resulting from the improper processing of film. This discoloration can be quickly duplicated by the incubation of silver images under conditions of high humidity, and methods of such accelerated testing have long been established [1-b,c,d]. The second mechanism of silver image discoloration is oxidative discoloration, which is caused by the oxidation of silver images and the reactions that follow, resulting in the generation of colloidal silver particles. Elsewhere, we have presented a new method of accelerated testing employing incubation with compressed oxygen to evaluate the stability of silver images against oxidation [1-a]. Here, we apply this testing method to the oxidative discoloration of radiographic films, and, because medical radiographic films are now developed mainly with automatic processors, we place our focus on there.

Experimental Procedures

Fig.1 shows the testing vessel used in our accelerated testing [1-a]. 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 saturated solution of cobalt chloride ($CoCl_2{:}6H_2O$, 60g, dissolved in 14cc pure water) which maintains humidity at 51% RH at 55°C.

The radiographic films used here to illustrate this method include both green-sensitive films (Films A and B) and blue-sensitive films (Films C and D). These films were cut into testing strips, exposed with a wedge, and then developed in automatic processors designed for medical use. Three types of automatic processors were used (Types 1, 2, and 3), along with four processing chemistries (Chemistries 1, 2, 3, and 4), consisting of fixed combinations of developing and fixing solutions.

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

The discoloration in test strips after the incubation was evaluated subjectively by direct observation and/or objectively by measurement of blue density in area where visual density equaled 1.0. The discoloration was subjectively ranked as 1 imperceptible (no discoloration), 2 slight, 3 moderate, 4 strong and 5 sever. The amounts of residual hypo in processed films were obtained from a calibration curve correlating blue density and the chemically analyzed amounts of hypo. For this, droplets of nitric silver solution with acetic acid (7.5g of nitric silver and 12.5cc of 28% acetic acid in 1000cc of water) were applied to the film, and blue density was measured in the area where silver sulfide thereby formed.

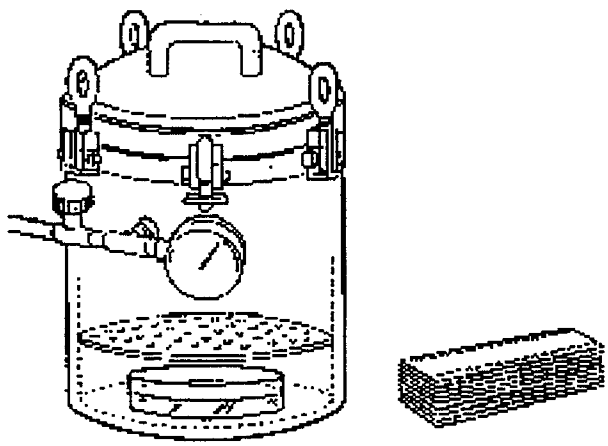

Figure 1. Test vessel and embossed TAC sheets

Results

The various automatic processors and developing chemistries studied resulted in varying degrees of discoloration. Fig.2 gives subjective rankings of the discoloration of Films A and C after thirty-three days of accelerated testing. Using the same processing chemistry (Chemistry 1), both films showed greater discoloration when processed in the Type-1 automatic processor than when processed in the Type-2 automatic processor. Similarly, Fig.3, presenting the increases in blue density, indicates the discoloration of Films B and D after thirty days of accelerated testing. Using the same automatic processor (Type-3), the two films showed parallel variations in discoloration according to the four processing chemistries used.

Processing equipment and processing chemistries in general are clearly both factors. Varying combinations of automatic processors and developing chemistries can be expected to give a variety of discolorations. Although the discoloration will be influenced by many factors in automatic developing process, we would like to focus on washing in the processing because of the importance of residual hypo in films.

Fig.4 indicates a distinct increase in discoloration in Film A when washing temperature is raised to 40°C, which is consistent with the fact that water at high temperatures more effectively washes out residue such as hypo from films. Fig.5 indicates that films with less residual hypo tend discolor more.

In addition, because the organic restrainer PMT was found in the developer of Chemistry 3, but not in the developer of Chemistry 1 (see Fig.3). We added PMT to the developer of Chemistry 1 in order to examine PMT's effect on the discoloration. Addition of PMT to the developing solution of Chemistry 1 made the ranks of discoloration for Film A and C recovered to around the ranks obtained from processing in Type 2 automatic processor shown in Fig.2. The results, in Fig.6, suggest that PMT restrains discoloration.

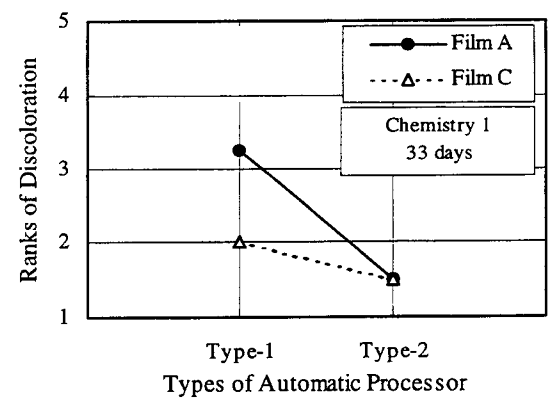

Figure 2. Effect of automatic processor type on discoloration

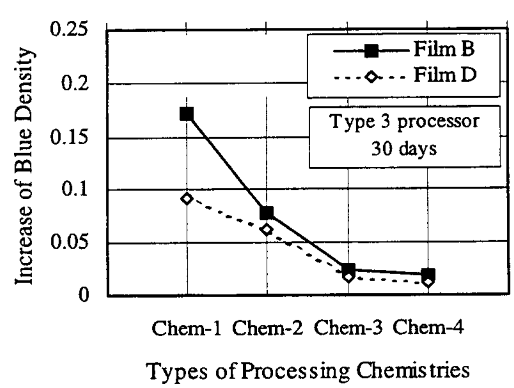

Figure 3. Effect of processing chemistry on discoloration

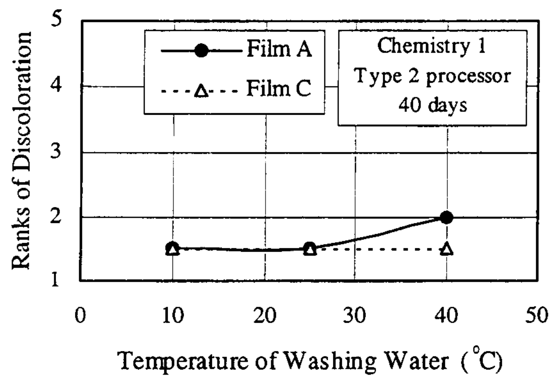

Figure 4. Effect of washing temperature on discoloration

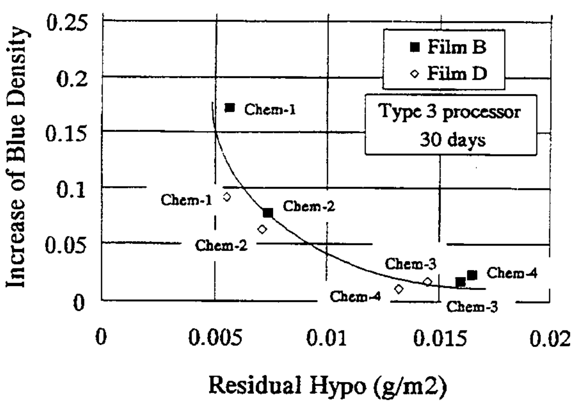

Figure 5. Effect of residual hypo on discoloration as related to processing chemistry

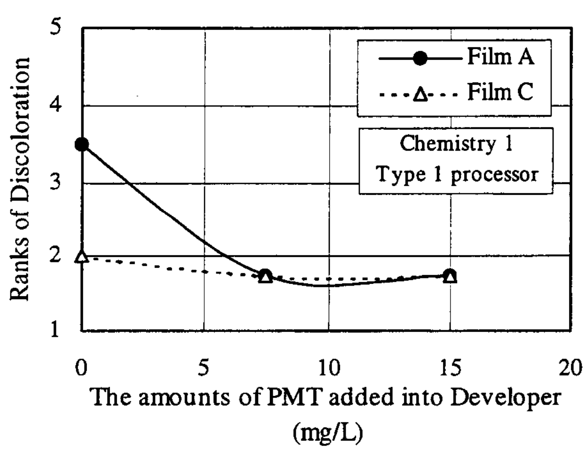

Figure 6. Effect of PMT on discoloration

Discussion

We report elsewhere that discoloration observed in incubation testing with compressed oxygen for approximately one month corresponds to yellowing after three or four years of storage at ambient temperature and humidity in Tokyo area [1-a)]. Subsequently the results of the accelerated testing reported here can likewise be expected to reproduce such yellowing.

The numerous factors affecting oxidative discoloration can be categorized as pertaining to either film, processing, or storage. The green-sensitive films (Films A and B) tended to discolor more than the blue-sensitive films (Films C and D) in all our accelerated tests. This observation has been discussed elsewhere [1-a)]. Film can incorporate Ag-guards to protect against oxidative discoloration [3)]. Although high humidity is inductive to oxidative discoloration [4)], we fixed the humidity at 51% RH in our testing. We did not deal with peroxide compounds such as NOx and SOx which have strong oxidative power [1-e)]. In order to prevent from the attack by such oxidative agents during storage of film, it has been recommended that silver images are treated chemically to be coated with sulfur or auric ions [5)]. Our study here, however, focuses solely on processing factors.

Fig.2 shows the effect that differing the type of automatic processor has on discoloration. Mechanically, many factors comes into play, including arrangement of the film-transporting rollers in the processing baths, the number of the rollers, roller pressure, the materials of which rollers are composed, and in particular, the rollers in squeezing process following washing. Processing conditions such as the duration of the developing, fixing, washing, squeezing stages also greatly affect discoloration, as do the temperatures of the various baths and washing water. We will not, however, discuss such factors individually, but will, instead, treat such factors as belonging to an independent, closed system. In discussing the results found in Fig.2, we will presume that even the effects on discoloration of individual machines of the same type will differ. It might be important to note that in real world situations, operators not only use a variety of developing chemistries, but they also develop films with processing cycles ranging anywhere from 30 seconds to 210 seconds, so oxidative discoloration can be expected to vary substantially from machine to machine.

A residual hypo of below 0.10 g/m^2 has been recommended for medium-term (minimum of ten years) storage of silver images[1-d)], and, with image permanence in mind, automatic processors, processing chemistries, and radiographic films have all been designed to minimize residual hypo. However, it has been found that, because residual hypo guards against oxidative attack by oxygen or peroxides in ambient air, adequate small amounts of residual hypo effectively prevent oxidative discoloration[6)]. The result in Fig.5 are consistent with this finding.

Regarding PMT, we suspected from the result in Fig.6 that the difference between Chemistries 1 and 3 in Fig.3 was due mainly to PMT's presence in chemistry 3. In Fig.5, films processed with Chemistry 3 contains more residual hypo than those processed with Chemistry 1, suggesting that PMT may prevent oxidative discoloration by helping to retain adequate small amount of hypo in the processed films.

Summary

1. Incubation tests with compressed oxygen can duplicate the oxidative discoloration produced in differing degrees among various types of automatic processors, developing chemistries, and washing temperatures.

2. Such testing indicates that films without a minimum of residual hypo tend to suffer oxidative discoloration.

3. Such testing also indicates that the addition of PMT into a developing solution can prevent oxidative discoloration.

References

1. a) C. Honda, *J. Imaging Sci. Tech.*, to be published.
b) R. Henn and N. H. King, *Photogr. Sci. Eng.*, **5**, 46 (1961).
c) D. F. Koppert, G. W. Lerson, B. A. Hutchins and C. C. Bard, *J. Applied Photogr. Eng.*, **8** (5), 83 (1982).
d) ISO 10602, 1993 (E).
e) H. Iwano, S. Kishimoto, T. Koshimizu and K. Ohmura, *J. Imaging Sci. Tech.*, **38**, 140 (1990).
2. K. B. Hendriks, Imagimg Process and Materials, Van Nostrand Reinhold, 1989, p.637
3. M. Torigoshi, K. Ohmura, S. Yagami and H. Iwano, *Sci. Publ. Fuji Photo Film*, No.29, 31 (1984).
4. L. H. Feldman, *J. Applied Photogr. Eng.*, **7** (1), 1 (1981).
5. J. M. Reilly, P. Z. Adelstein, D. W. Nishimura and K. M. Cupriks, *J. Imaging Sci. Tech.*, **38** (4), 328 (1994).
6. A. Sasai, *J. Soc. Photogr. Sci. Tech. Jpn.*, **52**, 582 (1989).