Jesper Stub Johnsen
The National Museum of Denmark
Department of Conservation
P.O Box 260
Brede
2800 Lyngby, Denmark

ABSTRACT

Six different chemical treatment processes for restoring discolored and faded silver gelatin negatives on glass plates and film bases is described. It is shown that an iodine-alcohol process, the Kodak Cupric Chloride Special Bleach Bath and the Kodak Stain Remover S-6 can be used with only a very small change in the original density. Accelerated aging of treated negatives does not affect the stability when compared to undiscolored black-and-white negatives. Discolored and faded negatives continues to deteriorate during accelerated aging.

KEYWORDS

Black-&-White Negatives, Image Quality, Surface Cleaning, Bleach and Redevelopment Processes, Restoration, Accelerated Aging, Stability.

INTRODUCTION

In this paper six chemical treatment processes for restoring faded and discolored silver-gelatin negatives is described.

The deterioration and fading of black-and-white negatives are caused by factores such as poor processing and bad storage. The image silver is oxidized and silver ions and other silver compounds are formed[1]. This means that the printing quality and information in the original negative is more or less changed.

The main purpose of the project was to estimate if chemical treatment processes can be used to restore discolored and faded silver gelatin negatives without unacceptable change in the original image density now and in the future.

Chemical aftertreatment of negatives had been used since the beginning of photography. The processes involved are toning, harmonizing, intensification, reduction or removing of discolorations and redevelopment of bleached images. Procedures and recepies can be seen in almost every manual of photography[2].

The restoration of photographic materials by use of chemicals is a controversial subject. In most cases it is recommended that a duplicate negative is made before treatment[3]. Some authors say that the results are both unpredictable and irreversible[4]. However it is possible to restore faded and discolored images (see fig. 1) and it is also the only way to restore the images.

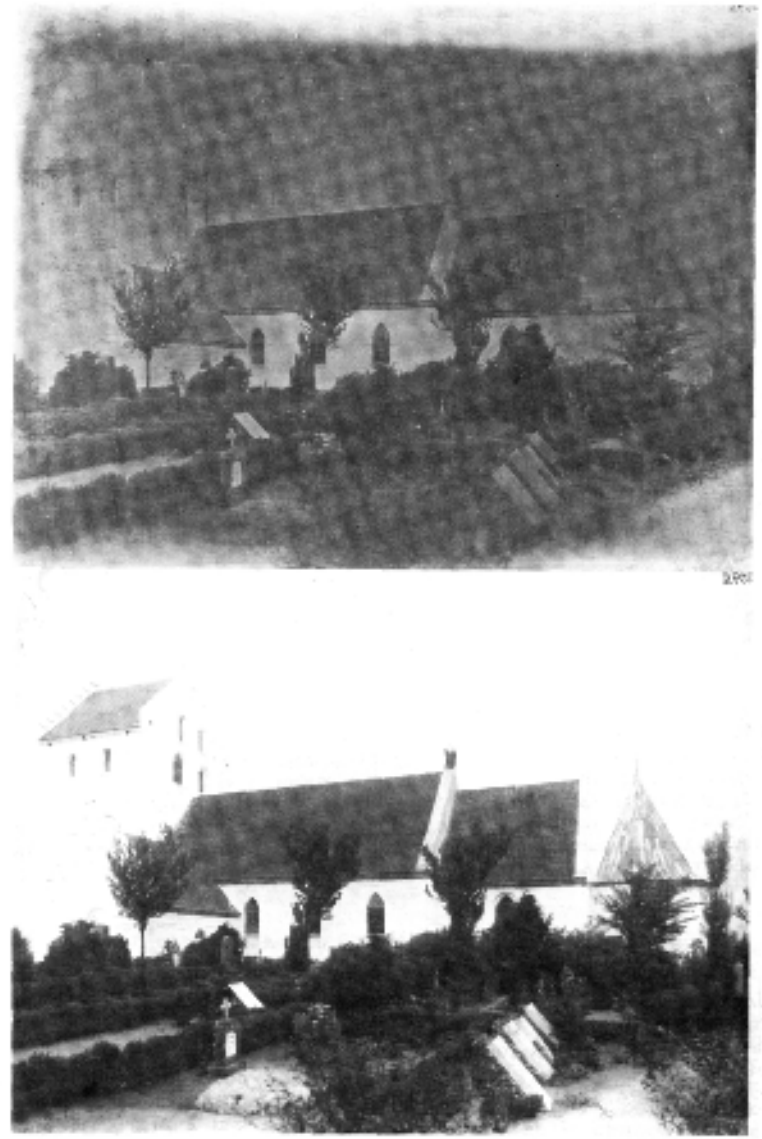


Figure 1: Top: Print from a discolored and bleached negative. Bottom: Print from the same negative after restoration.

TREATMENT PROCESSES

The following chemical treatment processes were used in the project.

Iodine in alcohol:
The iodine in alcohol process was introduced by Weyde[5] in 1972 and can be used to remove silver tarnish from the surface of silver gelatin emulsions. For a short treatment time in the solution, the alcohol does not swell the emulsion, and the iodine can only react with the surface silver. Silver iodide formed by the reaction is removed by a ordinary fixing solution and the negative is finally washed.

Thiourea and citric acic:
Many solutions containing thiourea have been used to remove discolorations from glass plate negatives[6]. In this paper a solution af thiourea and citric acid in water described by Mattsson[7] has been used. The negative is treated until all discolorations disappear.

Kodak Cupric Chloride Special Bleach Bath:
As the first bleach and redevelopment process for removing stains and discolorations the Kodak Cupric Chloride Special Bleach Bath[8] was chosen. The discolored negative is bleached in a solution of cupric chloride and citric acid in water. The bleach bath converts silver to silver halide including the discoloration or stain if it is either silver or silver sulfide. The silver halide is then redeveloped to form the image silver.

Kodak Stain Remover S-6:
Reducing negatives with permanganate was introduced by Namias[9] in 1899. When using a sulfite-free pyro developer a image is formed by a combination of metallic silver with yellow staining of the gelatin. In 1919 Wilsey[10] described how to lower the contrast of pyro developed negatives by using Namiasn permanganate solution with sodium chloride added. The Image silver is oxidiced to chloride. At the same time the yellow oxidation products from the pyro developer are dissolved. The silver chloride image is then redeveloped. Known as The Kodak Stain Remover S-6[11] it is also recommended for removing other discolorations.

Potassium Dichromate No. 1:
Solutions of potassium dichromate and hydrochloric acid have been used to intensify and reduce negatives. They have also been used to remove discolorations from negatives without changeing the image density[12]. A solution of equal parts of potassium dichromate and hytdrochloric acid is used as bleaching bath converting the image silver to silver chloride. The negative is then redeveloped in e.g. a amidol developer[13].

Potassium Dichromate No. 2:
Karnstädt and Pollakowski[14] have described this variation of the Potassium Dichromate No. 1 process. The image is bleached to silver chloride by a solution of potassium dichromate and hydrochloric acid. The negative is then treated with stannous chloride to reduce staining. Finally the negative is redeveloped.

MATERIALS

New film:
To evaluate the change in the original density of an image when treated in the chemical processes, a test image were made on Kodak T-max 100 films. The films were exposed to a test image made up of a Kodak Gray Scale Q14, Kodak Gray Chart R27, USAF 1951 3-Bar Resolving Power Test Chart and a black-and-white print. All films were processed to archival standard including test for residual thiosulfate[15]. The test films were not treated in a sulfur or a selenium toning bath.

Glass plate negatives:
A number of discarded silver gelatin glass plate negatives with typical discolorations and stains were chosen for the test.

EXPERIMENTAL

First a number of new films and glass plate negatives were treated in one of each treatment procedures.

Second the treated negatives were stored under accelerated aging conditions to estimate the stability of the restored negatives. Three sample sets were kept at 60% RH ± 2% RH and 70°C respectively 80°C and 90°C.

Third a sample set of treated film negatives and glass plate negatives were tested in oxidizing atmospheres containing 500 ppm respectively 1000 ppm and 2000 ppm of hydrogen peroxide at 20°C for 18 hours. The test is described by Image Permanence Institute[16].

A Macbeth TR 524 densitometer was used to measure image density. The visual as well as the blue filter were used. The density curve, the density range and the average gradient vere calculated for each film negative. The minimum, medium, and maximum density on each glass plate negative were also measured. The relative densities (see figures 10-11) were calculated by dividing the density before aging (d_0) in the density at the measured time t (d_t). A relative density value of 1.0 shows that no change had occured during accelerating aging.

FIGURE 2.
Density Curves on Film Negatives

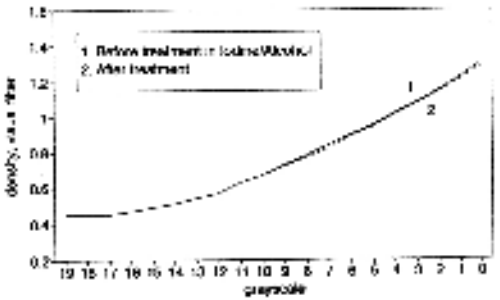


FIGURE 3.
Density Curves on Film Negatives

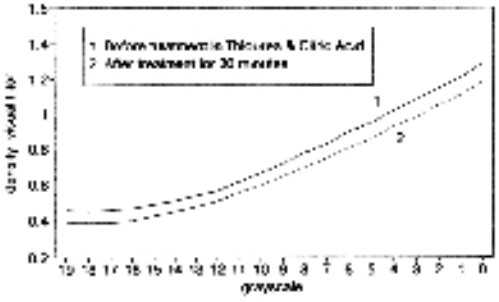


FIGURE 4.
Density Curves on Film Negatives

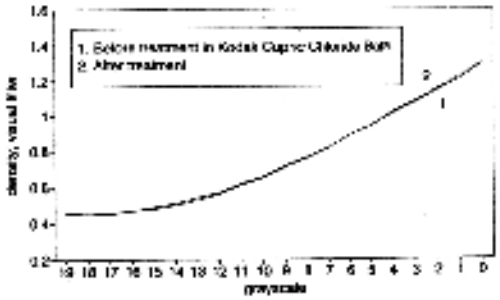


FIGURE 5.
Density Curves on Film Negatives

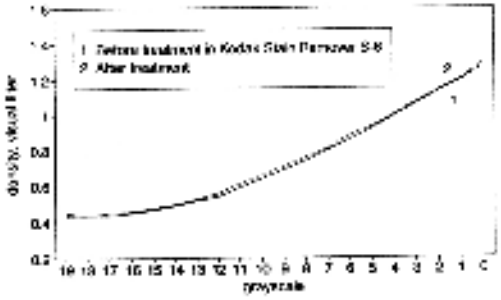


FIGURE 6.
Density Curves on Film Negatives

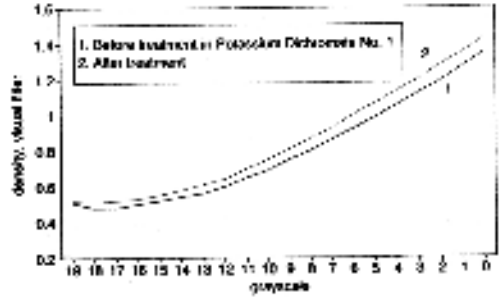
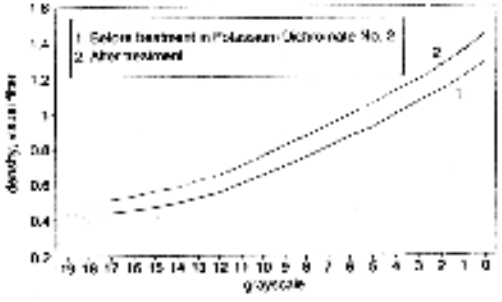
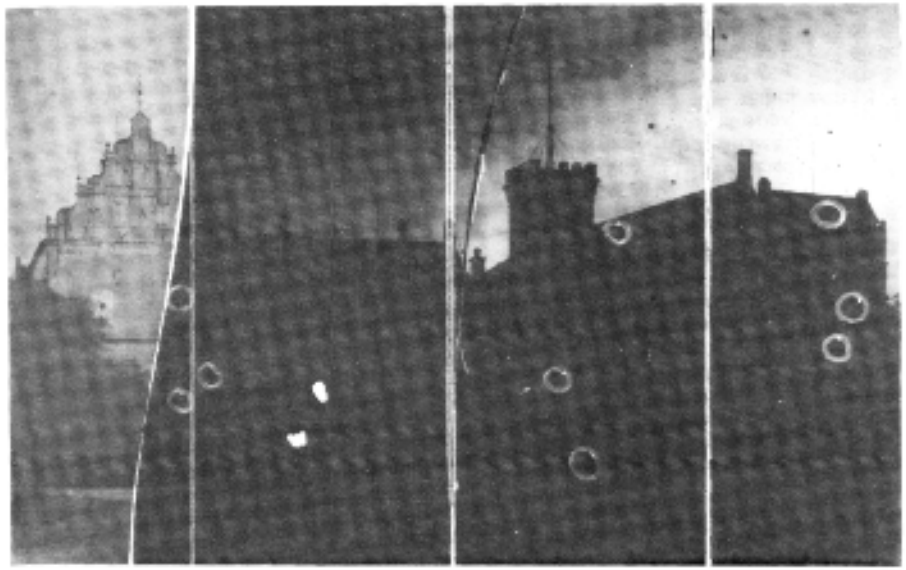


FIGURE 7
Density Curves on Film Negatives





Part no. 1 Part no. 2 Part no. 3 Part no. 4

Figure 6: Discolored glass plate negative. Part no. 1: Discolored, but unaged. Part no. 2: Aged in 70°C/112 days. Part no. 3: Aged in 80°C/56 days. Part no. 4: Aged in 90°C/28 days. All at 60% RH.

RESULTS

Figure 1 shows a print from a discolored and faded glass plate negative before and after treatment in the Kodak Cupric Chloride Special Bleach Bath. As it is shown, it is possible to reconstruct a discolored black and white negative which then can print a normal black and white image.

Figure 2 – 7 shows density curves before and after treatment in the six chemical treatment processes. In figure 2 (iodine in alcohol) and in figure 3 (thiourea and citric acid) the reduction in density depends on the treatment time. For the iodine in alcohol process (figure 2) and the two Kodak bleach and redevelopment processes (Kodak Cupric Chloride Special Bleach Bath (figure 4) and Kodak Stain Remover S-6 (figure 5)) the density curves does not change. For the other processes (figure 3, 6 & 7) there is an unacceptable change in density after treatment.

Figure 9: Glass plate negative.

Part no. 1: Damaged and discolored plate.

Part no. 2: Restored in Kodak S-6 and aged for 112 days/70°C.

Part no. 3: Restored in Kodak S-6 and aged for 56 days/80°C.

Part no. 4: Restored in Kodak S-6 and aged for 28 days/90°C.

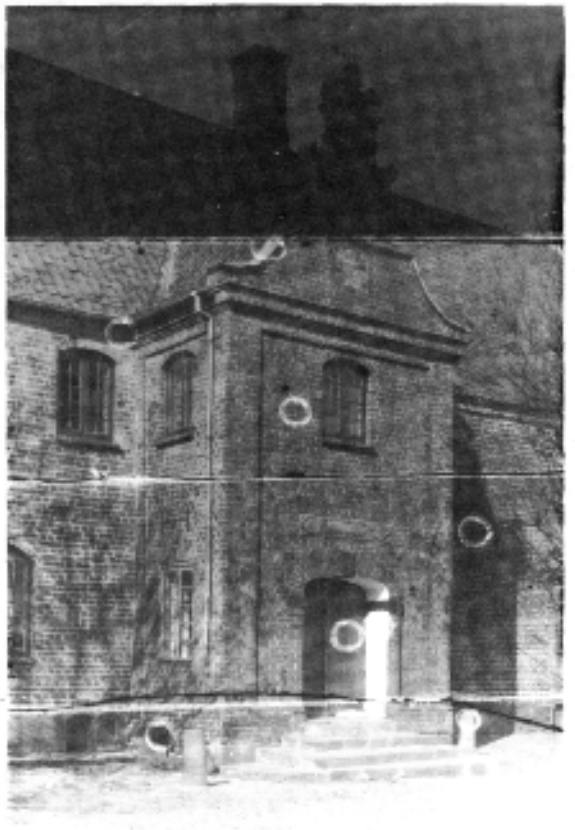


Figure 8 shows a print of a discolored and untreated glass plate negative after accelerated aging. It is obvious that the image continue to bleach until the image disappear (parts no. 2-4 in figure 8).

Figure 9 shows a print of a glass plate negative after accelerated aging. The glass plate negative was originally discolored but the three parts (parts no. 2-4) were treated in Kodak Stain Remover S 6 before aging. There is no change in the measured image density after aging.

Figure 10

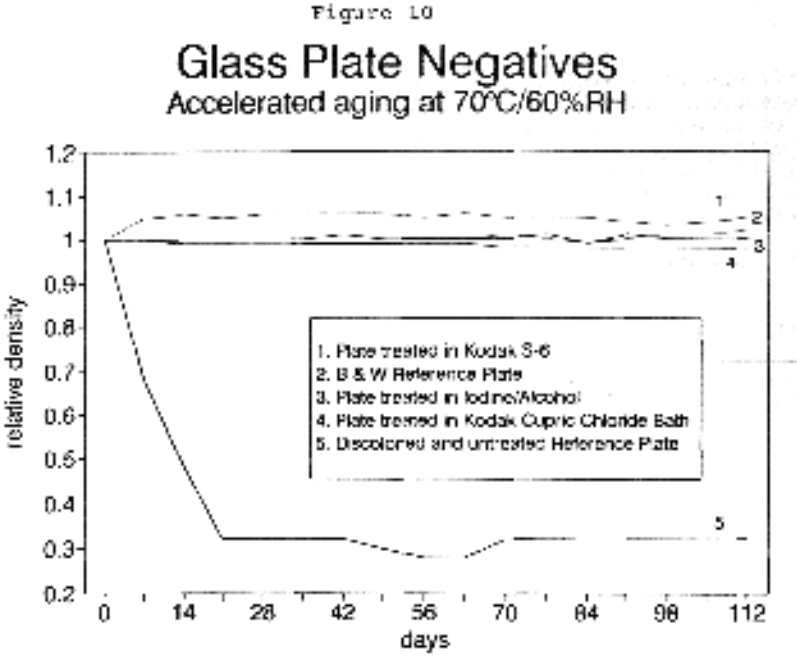


Figure 10 shows the density change during aging for glass plate negatives treated in the alcohol solution with iodine (curve no. 3), the Kodak Cupric Chloride Special Bleach Bath (curve no. 4) and the Kodak Stain Remover S 6 (curve no. 1). These data are compared to the data for discolored negatives (curve no. 5) and for normal black-and-white glass plate negatives (curve no. 2). While the untreated negative is fading during aging, the treated negatives and the control without discolorations does not change.

When treated controls as well as untreated controls were exposed to the oxidizing hydrogen peroxide atmosphere none of the negatives resisted staining except the negatives treated in thiourea and citric acid. Further examination showed that negatives treated in 8 minutes in the thiourea solution gave full protection.

In figure 11.1 Another notable observation is illustrated. When a normal and therefore untreated - black-and-white glass plate was exposed in the hydrogen peroxide atmosphere, a dramatic build-up of yellow occured (column no. 1). The stain formation on treated negatives were not so dramatic. This indicate that treated negatives is more stable than untreated negatives. This is confirmed in figure 11.2 where the relative

density change after peroxide testing is shown for new film negatives. None of the new films (including the reference in column no. 1) showed essential difference in stain formation. They have all been processed just before the peroxide test.

DISCUSSION

Discolored and faded images can be restored in the iodine and alcohol solution, the Kodak Cupric Chloride Special Bleach Bath and Kodak Stain Remover S-6. However it is not a precise reconstruction of the original silver image. Hendriks[17] has described the formation and migration of silver ions in an oxidizing atmosphere. The migration of silver ions is belived to be irreversible and therefore is it not possible to get the original image silver with chemical treatment processes.

The permanence of silver gelatin images treated in chemical solutions is importent. The negatives in this test has not been treated with toner or other stabilizing treatment processes. While the treated negatives and the untreated controls shows good stability characteristics, the untreated and discolored plates are very unstable. In figure 10 a initial density change can be seen for the treated negatives. I belive that the change has nothing to do with the accelerated aging. James[18] has described the change in density after a few hours exposure of image silver to high temperatures. This might explain the initial density change of the treated plates.

The results in figure 11.1 and 11.2 suggests that a "wet" treatment might improve the stability of the silver image in a oxidizing atmosphere. A totally clean metal surface is very stable. The "wet" treatment of the silver images leaves an almost clean surface. This is not so sensitive in the oxidizing hydrogen peroxide atmosphere than the old glass plate negative which has not been treated in a "wet" solution for many years. However a "wet" cleaning of old glass negative should not be considered in this moment.

CONCLUSION

Discolored and faded black-and-white silver gelatin negatives can be restored in chemical solutions.

A solution of alcohol with iodine can be used for removing silver tarnish on the surface of a silver gelatin emulsion. A short treatment time will not change the characteristic curve of the image.

Discolored negatives can be restored with bleach and redevelopment processes. In this test The Kodak Cupric Chloride Special Bleach Bath and The Kodak Stain Remover S-6 gave apparantly satisfactory results. Only a very small change in the characteristic curves could be measured.

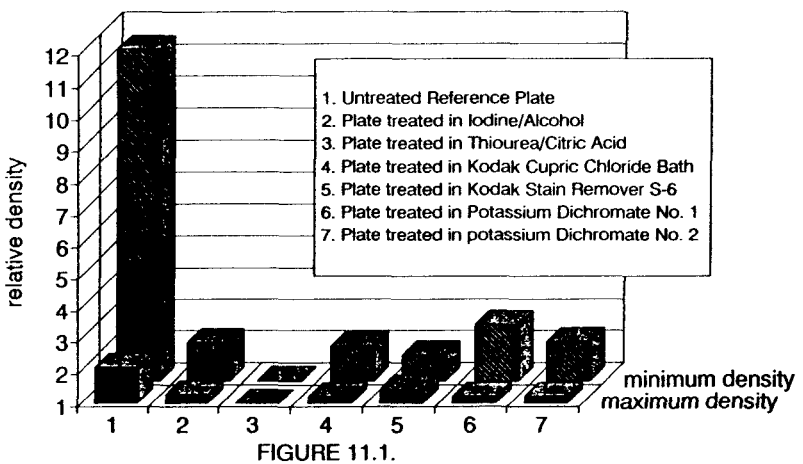


FIGURE 11.1.

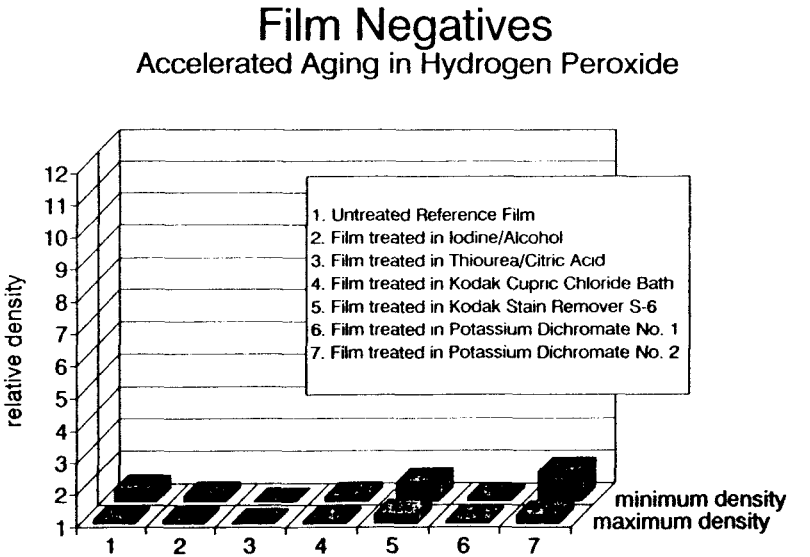


FIGURE 11.2.

Accelerated aging with heat and humidity showed that discolored and stained negatives were very unstable. Negatives treated in the above mentioned processes were as stable as the untreated negatives without stains.

Only the thiourea with citic acid treatment protected against accelerated aging with hydrogen peroxide. Untreated old glass plate negatives showed a dramatic stain formation compared to old as well as new negatives there had been through a "wet" treatment.

At the moment I can not recomment the chemical treatment of discolored and faded black-and-white silver gelatine negatives as a ready for use conservation procedure. Further studies of the stability of the gelatine layer and the deterioration of image silver must be considred.

ACKNOWLEDGMENTS

I wish to thank Mogens S. Koch and René Larsen both with The Royal Danish Academy of Fine Arts, School of Conservation and Tim Padfield, Conservation Department of the Naitonal Museum of Denmark, for contributions to this work.

REFERENCES

1. Hendriks, Klaus B. & Lincoln Ross: The Restoration of Discolored Black-and-White Photographic Images in Chemical Solutions. AIC Preprints, New Orleans, Louisiana, June 1.-5. 1988, pp. 103-107.

2. e.g.: Wall, E.J. (rev. by Franklin I. Jordan): Photographic Facts and Formulas. American Photographic Publishing Co. Boston 1940.

3. Ostroff, Eugene: Conserving and Restoring Photographic Collections. Museums News, May, September, November & December 1974, updated 1976. American Association of Museums 1976, p.13.

4. Swan, Alice: Conservation of Photographic Print Collections. Library Trends, Fall 1981, pp. 268-269.

   Moor, Ian & Angela Moor: Photographs: Images or Artefacts?. The Journal of Photographic Science, Vol. 36, 1988, p. 121.

5. Weyde, Edith: A Simple Test to Identify Gases Which Destroy Silver Images. Photographic Science and Engineering, Vol. 16, No. 4, July-August 1972, p. 286.

6. Enyerat, L.J.: Cleaning Glass Plate Negatives. Exposure 12, 1974, pp. 6-7.

Crabtree, J.I.: Stains on Negatives and Prints: Their Cause, Prevention and Removal. American Annual of Photography, Vol. 35, 1921, p. 236.

Wall, E.J.: Intensification and Reduction: A Chritical Résumè of All Known Methods. American Photographic Publishing, Boston 1927, p. 10.

7. Mattsson, Irene: Bilden Râddas. Nordiska Museet, Stockholm 1985, p. 102.

8. Kodak F-40: Conservation of Photographs. Eastman Kodak Company 1985, pp. 128-130 + 147.

9. Haist, Grant: Modern Photographic Processing, Vol. 2, John Wiley and Sons Inc. 1979, p. 60.

10. Wilsey, R.B.: Intensification and Reduction with Pyro Developers. The British Journal of Photography, Dec. 12, 1919, pp. 721-723.

11. Kodak F-40: Conservation of Photographs. Eastmann Kodak Company 1985, p. 147.

12. Wall, E.J.: Intensification and Reduction; A Chritical Résumé of All Known Methods. American Photographic Publishing, Boston 1927, p. 10.

13. Ibid 12.

14. Karnstädt, Hans & Goetz Pollakowski: Die Mashinelle Restaurierung von vergilbten Schwarzweiss Filmmaterialen. Bild und Ton, heft 3, 1974, p. 80.

15. ANSI/ASC PH 4.8-1985. Residual thiosulfate and other chemicals in films, plates, and papers - determination and measurement.

16. Reilly, James M.; Douglas W. Nishimura; Kaspars M. Cuprics & Peter Adelstein: Stability of Black-and-White Photographic Images with Special Reference to Microfilm. The Abbey Newsletter, Vol. 12, No. 5, July 1988, p. 85.

17. Hendriks, Klaus B. The Stability and Preservation of Recorded Images, in: Imaging Processes and Materials, Neblette's eighth Edition, Van Nostrand Reinhold, New York 1989, p. 647-650.

18. James, T.H.: The Stability of Silver Filaments, Photographic Science and Engineering, Vol. 9, No. 2, March-April 1965, p. 121-132.