Studies on P-Q Photographic Monobaths (X)

Film-Clearing Time and Minimum Time for Complete Processing in Monobaths

(Received July 7, 1974)

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Abstract

Relations between the film-clearing time and the minimum time required to complete the processing in monobaths containing thiosulfate and thiocyanate as fixing agents have been investigated. It has been found that, in monobath processing, developing is always finished within the film-clearing time and fixing is complete at the time or above. Therefore, the minimum time for the complete monobath processing may be determined at the minimum time required to complete the fixation. The minimum time to complete the fixation can't be estimated by the measurement of the film-clearing time when thiocyanate is used alone or at higher ratio (over 50 mole %), but it can be estimated when thiosulfate is employed alone or at higher ratio (50 mole % or above). In most of the monobaths commonly used, since thiosulfate is employed alone or at higher ratio as fixing agents, the minimum time for the complete monobath processing may be probably estimated by measuring the film-clearing time.

§ 1. Introduction

In recent years, there has been a need for methods of easy processing of silver halide materials in several fields. Monobath processing is one of the methods to meet this need. Because it can be carried out in a single solution, instead of two or more, and does not require skilled technicians or complicated apparatus. Standardization of time, temperature and agitation are relatively less important in monobath processing than in conventional processing.

In the case of monobath processing, it is practically useful to determine the minimum time required to complete the processing. In practice, the minimum time for the complete monobath processing of a photographic film has been usually estimated in a monobath without developing agents by measuring the film-clearing time which is the time required for the disappearance of the last visible traces of emulsion. Recently, we performed the measurements of the film-clearing time in monobaths containing developing agents by means of near infrared ray, and investigated the effect of developing agents on the time. We found that developing agents don’t affect the film-clearing time in the higher pH range but most of them prolong it in the relatively lower pH range (below 11).

The relation between the film-clearing time and the minimum time required to complete the fixation in typical sodium thiosulfate fixers have been reported by earlier workers. Warwick and others found approximately 5% of the original silver halide still in the emulsion layer at the point of film-clearing. On the other hand, Lumiére and Seyewetz found that thorough washing removes all of the silver from the emulsion if fixation is stopped at the film-clearing time. This result has been confirmed by several others. Recently, Kulanek and Hähnel found that the film-clearing rate is significantly faster than the fixing rate when sodium thiosulfate is employed as the fixing agent.
agent in a fixer but not when ammonium thiosulfate is used. They also looked at the kinetics of fixing using ammonium thiocyanate and found that the fixing rate is significantly slower than the film-clearing rate.

To determine the minimum time required for the complete monobath processing, however, it may be important to pay attention to the minimum time not only to complete the fixation but also to finish the development of silver dissolved from silver halide grains by fixation upon already developed grains. In the case of the processing in monobaths containing thiosulfate and thiocyanate as fixing agents, physical development plays important role in the development, as it was pointed out in our previous reports. The minimum time to finish the development may be determined by the measurement of the time at which both density growth and developed-silver growth almost stopped.

The present work was carried out to investigate the relations among the film-clearing time, the minimum time to finish the development and the minimum time to complete the fixation in thiosulfate-thiocyanate monobaths, and to discuss the determination of the minimum time required to complete the monobath processing.

§2. Experimental Procedure and Results

Two types of commercial photographic films were used in the work; Sakura Konipan SS Negative Film (135 roll) which coated at 0.380 mg Ag/cm², and Fuji Fine Grain Positive Film, Type 71336 (35 mm) which coated at 0.326 mg Ag/cm². Two kinds of experimental thiosulfate-thiocyanate monobaths (Table 1) and several published thiosulfate monobaths (Table 2) were used. To the experimental monobaths, sodium thiosulfate and potassium thiocyanate as fixing agents were added in various mixing ratios (100:0, 50:50, 30:70 and 0:100 in mole %) and total molecular con-

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Table 1 Experimental thiosulfate-thiocyanate monobaths

Table 2 Published thiosulfate monobaths
concentrations (0.1–1.5 mole/l). Freshly prepared solutions were used for all the experiments. The film-clearing time was measured with the automatic film-clearing recorder which had been assembled in our earlier work with a near infrared source, a water-jacket cell, an Ag-O-Cs phototube, an amplifier and a recorder.6) Processings were all carried out at 20°C without agitation holding the emulsion layer downward in enough volume of the monobath. The mass of developed silver or residual silver salts per unit area of processed films was determined by means of X-ray fluorescence spectrometry under the same conditions of our previous studies.7)

Relation between the time at which density growth stopped and the film-clearing time. In this experiment, the resulting series of monobaths, based on the experimental thiosulfate-thiocyanate formula I in Table 1, were used to determine both the times. Various published thiosulfate monobaths shown in Table 2 were also used. Sensitometric strips were exposed with the JIS type III Sensitometer and developed in the monobath for varying times up to 10 min. (Positive) or 20 min. (Konipan SS) at 20°C without agitation. After the required interval of development, the strips were removed from the monobath and dipped in Kodak SB-1 stop bath for 30 sec. The strips were then fixed in Kodak F-5 fixer for 5 min. (Positive) or 10 min. (Konipan SS) at 20°C, and washed in running water for 1 hr. and air dried. The diffuse densities of the processed strips were measured with the Narumi type NLM-DV Densitometer. The time at which density growth almost stopped was indicated as ‘the developing time’ in figures. Since this time was nearly the same at every exposure level as illustrated in the upper half of Fig. 1 or in Figs. 5 to 7, the measurements of the time were carried out at a higher exposure level (Log E=0.70).

In the experimental thiosulfate-thiocyanate monobaths, when the total molecular concentration of fixing agents was raised at the same mixing ratio to decrease the film-clearing time, ‘the developing time’ was also decreased and it was always shorter than the film-clearing time, as shown in Figs. 2 and 3. With the higher ratio of thiocyanate (70 or 100 mole %), the film-clearing time couldn’t be measured with the film-clearing

![Fig. 1](image1.png)  

Relation between ‘the developing time’ and the film-clearing time at various thiosulfate concentrations in the thiosulfate monobaths.

![Fig. 2](image2.png)
Fig. 3 Relation between the developing time and the film-clearing time at various total concentrations of thiosulfate-thiocyanate (mixing ratio; 50 mole % portions).

Relation between the time at which silver growth stopped and the film-clearing time Three kinds of monobaths containing 0.2 mole of thiosulfate, 0.3 mole of thiosulfate-thiocyanate (50 mole % portions) or 0.5 mole of thiocyanate per liter of solution, which based on the experimental thiosulfate-thiocyanate formula I in Table 1, were used in the experiment to determine both the times. Only in the case of the 0.5 mole/l thiocyanate monobath, 0.1 g of 2-mercaptopbenzothiazole per liter was added to prevent the stain, and the film-clearing time was measured in the solution without developing agents. Consequently, the true time of film-clearing in the 0.5 mole/l thiocyanate monobath are probably greater than the data in Fig. 7, as developing agents prolong the film-clearing time in this pH level. The exposing and the processing of sensitometric strips were carried out in the same way of the preceding experiment by use of Konipan SS film.

The lower half of Fig. 1 illustrates the growth of developed-silver with the processing time at various exposure levels, and Figs. 5 to 7 show the results of this experiment. The time at which developed-silver growth almost stopped was indicated the silver-growing time in figures. The time varied by the change of exposure level, although the developing time varied little at any exposure level. When the exposure level was lowered, the silver-growing time increased, and such phenomenon was most remarkable in the 0.3 mole/l thiosulfate-thiocyanate monobath.

The results obtained indicate that...
silver-growing time’ is usually longer than ‘the developing time’ but both times are always shorter than the film-clearing time. It is consequently said that the extent of physical development is negligible after the film-clearing time. The minimum time to finish the development is certainly shorter than the film-clearing time in the thiosulfate-thiocyanate monobaths.

Relation between the film-clearing time and the minimum time to complete the fixation The resulting series of monobaths, based on the experimental thiosulfate-thiocyanate formula II in Table 1, were used in this experiment to determine both the times. Each monobath tested was adjusted to pH 7.0 or 12.0 by the addition of sulfuric acid or sodium hydroxide. The pieces of unexposed films were introduced into the monobath and fixed for varying times up to 15 min. (Positive) or 30 min. (Konipan SS) at 20°C without agitation. After the required interval of fixation, the pieces were removed from the monobath and washed in running water for
Fig. 8 Relation between processing time and the amount of residual silver salts in the strips which were thoroughly washed.

Fig. 9 Relation between the film-clearing time and ‘the fixing time’ at various thiosulfate concentrations (lower half), and the amount of residual silver salts in the strips which were stopped the fixation at the point of film-clearing and thoroughly washed (upper half).

Fig. 10 Relation between the film-clearing time and ‘the fixing time’ at various total concentrations of fixing agents (lower half), and the amount of residual silver salts in the strips which were stopped the fixation at the point of film-clearing and thoroughly washed (upper half).
2 hrs. and air dried. The minimum time to complete the fixation was determined by the processing time which residual silver salts in the pieces was reached to be little detectable after the thorough washing, and it was indicated 'the fixing time' as shown in Fig. 8.

Figs. 9 to 12 illustrate the results of this experiment. 'The fixing time' was approximately equal to the film-clearing time when thiosulfate was employed alone or at higher ratio (50 mole % or above), as shown in Figs. 9 and 10. However, when thiocyanate was used alone or at higher ratio (over 50 mole %), 'the fixing time' was longer than the film-clearing time as shown in Figs. 11 and 12. An increase in the ratio of thiocyanate led to a larger difference between 'the fixing time' and the film-clearing time, and in the case of employing thiocyanate alone, 'the fixing time' was nearly twice the film-clearing time. Such phenomena mentioned above were almost independent of pH of the monobaths. In the upper half of Figs. 9 to 12 are shown the amount of residual silver salts in the pieces of strips which were stopped the fixation at the point of film-clearing and thoroughly washed. It is shown clearly, of course, that almost all of the silver salts was removed from the emulsion when thiosulfate was used alone or at higher ratio, but the large amounts of insoluble silver salts was remained when thiocyanate was employed alone or at higher ratio. In the case of the latter, an increase in the concentration of fixing agents or the ratio of thiocyanate led
to a larger amount of residual silver at the film-clearing time.

From these results, in the thiosulfate-thiocyanate monobaths, we conclude that the fixing time is approximately equal to the film-clearing time at higher ratio of thiosulfate or thiosulfate alone, in a similar results of Lumiere and Seyewetz which investigated in a thiosulfate fixer, but it is significantly longer at lower ratio or in the absence of thiosulfate, in a similar results of Kulanek and Hahn which investigated in a ammonium thiocyanate fixer.

§ 3. Conclusion

In view of the above facts, the most reasonable conclusion is that, in monobath processing, developing is always finished within the film-clearing time and fixing is complete at the time or above. Therefore, the minimum time for the complete monobath processing may be determined at the minimum time required to complete the fixation. In monobaths containing thiosulfate and thiocyanate as fixing agents, the minimum time to complete the fixation can't be estimated by the measurement of the film-clearing time when thiocyanate is employed alone or at higher ratio (over 50 mole %), but it can be estimated when thiosulfate is used alone or at higher ratio (50 mole % or above). It cannot be found a definable relationship among the film-clearing time, the minimum time to complete the fixation and the minimum time to finished the development in monobaths, because they are changed irregularly by differing the factors such as the composition of fixing agents, the kind of monobath formula, the pH of the monobath, the type of the film, etc. The reason that developing is always finished within the time for the complete fixation in monobath processing can be presumed as follows. The fixing is carried out alone in the unexposed area of the film strip, but both developing and fixing are carried out simultaneously in the exposed area. Consequently, since the silver halides in the strip may decrease faster in the exposed area, the developing in the exposed area stops earlier than the fixing in the unexposed area.

In the practical thiosulfate-thiocyanate monobath for commercial negative films which had been published in our previous report, or in most of the monobaths commonly used, the minimum time for the complete monobath processing may be probably estimated by measuring the film-clearing time, since thiosulfate is employed alone or at higher ratio as fixing agents. Only in the case of the monobaths of higher pH range (over 11) which belong to that described above, as developing agents affect little the film-clearing time in the higher pH range, the minimum time required to complete the monobath processing can quite easily be estimated by measuring the film-clearing time in the monobaths without developing agents.

Acknowledgement

The authors would like to acknowledge the continuing guidance and encouragement of Dr. Giichi Muto and Dr. Yoshihiro Wada, University of Tokyo.

References