A NEW FILM MAKING SYSTEM ATTAINING HIGH QUALITIES, FAST ACCESS AND SOLUTION STABILITY

Kimitaka Kameoka*, Eiichi Okutsu*,
Yoshitaka Akimura** and Shigenori Moriuchi*

Abstract: This paper reports a new white light film making system having high image qualities, high speed processing and highly stable solution. In reprodction processes, lith-developments have been used for their high image qualities. In general, high image qualities are due to high contrast on the characteristic curve . To get high contrast, acceleration in the development in the high exposure areas and retardation in the low are necessary. Acceleration depends on the quantity of produced semiquinone radicals and is measured by "the width of image expansion". Concentration of sulfite ions is kept at a minimum in lith developer for producing semiquinone radicals, consequently resulting in lack of solution stability. Fuji's new development system realizes high image qualities and high solution stability, with high pH and high concentration of sulfite ions in the developer . By utilizing a retarder which makes high contrast developing possible at a high temperature, the system attains high speed processing.

Introduction

Lith-developers contain only hydroquinone as developing agent. These developers are used widely in reproduction processes because of their high image qualities. In general, high image qualities are due to high contrast of the characteristic curve (G is more than 10). High contrast in lith-development can be explained mainly by the high activity of semiquinone radicals as suggested by Yule(1945). He stated that semiquinone radicals are produced autocatalystically by disproportionation reaction between hydroquinone and quinone, and give rise to infectious

* Research Laboratories, Ashigara, Fuji Photo Film Co. Ltd.
** Ashigara Factory, ibid..

development. This idea is supported by many researchers: Wood(1964), Umberger(1966), Zwicky(1966)and Eggers(1971).

On the other hand, Lu Valle(1958) suggested quinone derivatives as the reason for high contrast, and James(1968) suggested the activity of the compounds produced by condensation reaction between quinone and amino-group of gelatin. Suga(1975) proposed that quinones accelerate development in high exposure areas by producing semiquinone radicals and at the same time, retard development in low exposure areas by oxidizing small latent images. And Okutsu (1973) pointed out the effect of pH lowering near the areas being developed. Recently Zwicky(1977) suggested the acceleration of development by silver ion complexes. In last year's TAGA, Kerr(1982) considerated lith-effects emphasizing the importance of induction period.

Under the condition in which sulfite ions are in high concentration, high contrast is not possible by lith-development. By semiquinone theory, sulfite ion reacts with quinone and produces hydroquinone monosulfonate which is low activity, and consequently autocatalystic chain reaction for production of semiquinone radicals cannot occur. We at Fuji support the idea of the semiquinone. In the present paper our experimental results and a new film making system based on this theory, are described.

Lith-developments have high contrast and have been used to get high image qualities. From the practical standpoint, their high contrast owes to the balance between acceleration of development by semiquinone radicals and retardation of development by retarder —— in most cases retarders are polyethylene oxide compounds. To get acceleration effect, it is necessary to keep sulfite ions at a minimum. Consequently, lith-developers are easily oxidized and unstable. On the other hand,lith-developments have long induction period because of the existance of retarders. So, access time of lith-development is slow and when processed at high temperatures for the purpose of fast access, lith-developments no longer attain high contrast. We believe that is why polyethylene oxide compounds have little effect on retardation at high temperatures. Consequently, lith-developments cannot be processed in fast access time.

Another development systems which have been used in film making are the so-called "rapid access systems". The fact that these systems utilize phenidone-hydroquinone development, is well-known. They are superior in access time and solution stability but inferior in image qualities.

Rapid access systems are mainly used when a large number of reproductions are needed at fast access time at the cost of qualities.

No system can accomplish high image qualities, high speed processing and highly stable solution. Our research began with the hope to reach high quality in all three points.

Investigation of Acceleration of Development under High Sulfite Ion Concentration

At first, investigation for a system which produces a lot of semiquinone radicals under the high concentration of sulfite ions, was attempted. We expected that a high quantity of semiquinone would produce high image qualities and high concentration of sulfute ions would keep the solution stable. As reported by Hefter(1975), even under the high concentration of sulfite ions, if the pH value of the solution is high, enough semiquinone radicals are produced. The quantities of semiquinone radicals are measured by the use of Electron Spin Resonance Spectrometer Model JES ME-3X made by Japan Electron Optics Laboratory Co. Ltd.. Fig. 1

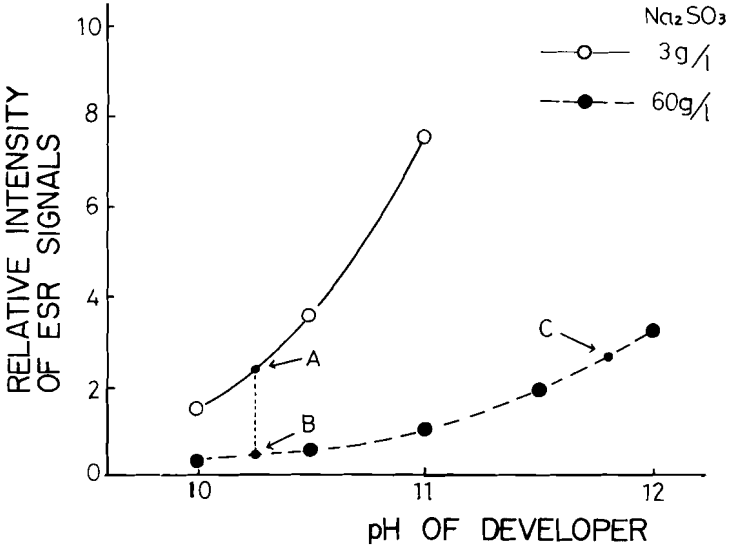

Fig. 1. Dependence of the relative intensity of ESR signals of semiquinone radicals on pH of developer.

shows the dependence of relative intensity of ESR signals of semiquinone radicals on pH and concentration of sulfite ions. In this figure lith-developer corresponds to point A (concentration of sodium sulfite is 3 grams per liter and pH equals 10.25). When concentration of sodium sulfite is raised to 60 grams per liter without pH change(point B), intensity of ESR signals lowers to a fourth of A. But at this sodium sulfite concentration,if pH is raised to 11.8 (point C), intensity of ESR signals could be seen near A, as in the case of lith-development. Characteristic curves of these three cases are shown in Fig. 2. This figure shows

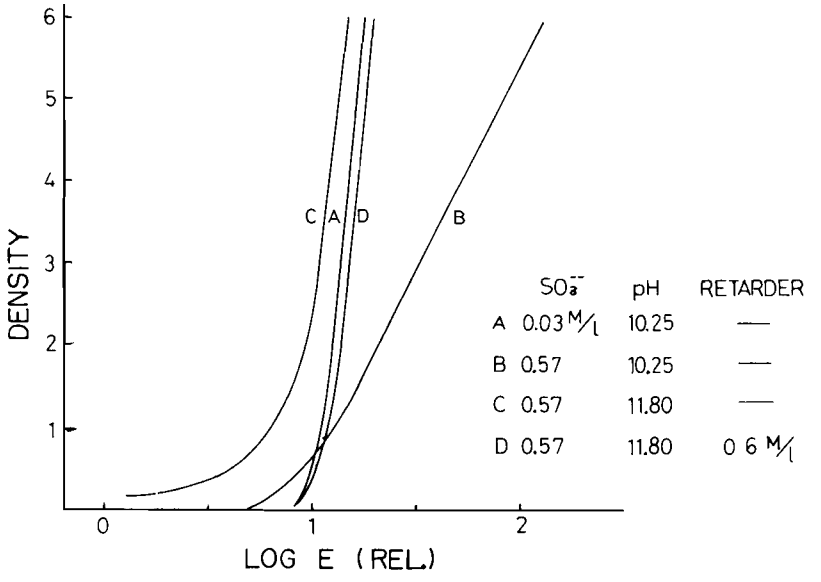

Fig. 2. Effects of sulfite ions, pH and retarder.

that even under high concentration of sulfite ions, if developer is high in pH near to 12, acceleration of development in high exposure areas, considerably occurs, compared with the case of lith-development. On the other hand, there is not enough retardation of development in low exposure areas. Therefore, retardation effect was investigated.

Investigation of Retardation of Development in the Low Exposure Areas

Under the condition of high pH and concentrated sulfite, ions, enough retardation effect is not possible with polyethylene oxide compounds. And processing at high

temperatures using these compounds, there are still retardation weaknesses in the low exposure areas.

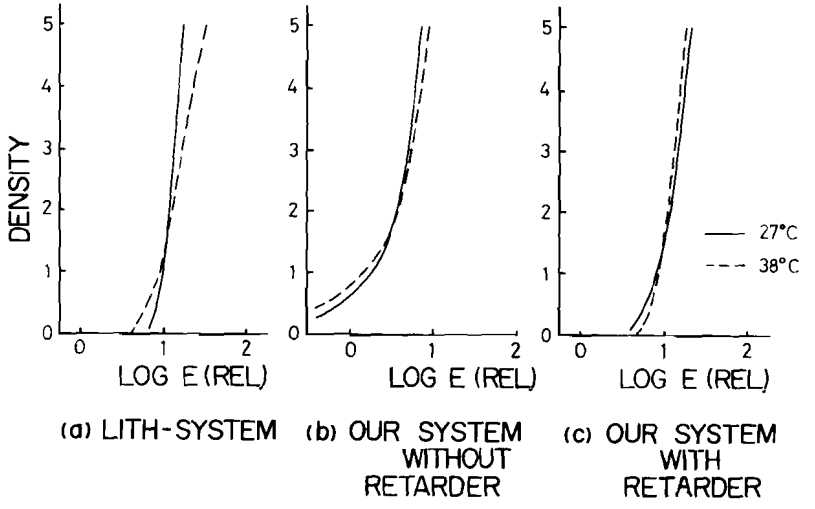

Fig. 3. Effect of developing temperature.

Lith-developments at high temperature do not have high contrast as is shown in Fig. 3(a). This is perhaps also why polyethylene oxide compounds have weak effect on the retardation of the low exposure areas relative to acceleration in the high exposure areas by semiquinone radicals.

After an intense search for retarder, indazole derivatives were found to be ideal as retarder. By the addition of these compounds, high contrast can be attained(Fig. 2), and to make matters even better, this high contrast can be kept in high temperature processing. Fig. 3(c) shows the dependence of the characteristic curve on processing temperature. When processing with retarder, contrast at 38°c is a little higher than that at 27°c.

In Fig. 4, density against developing time curves are shown in the different exposure levels. The case without retarder is (a), with benztriazole compound is (b) and with indazole compound is (c). Indazole compound intensively restrains the development of the low exposure level.

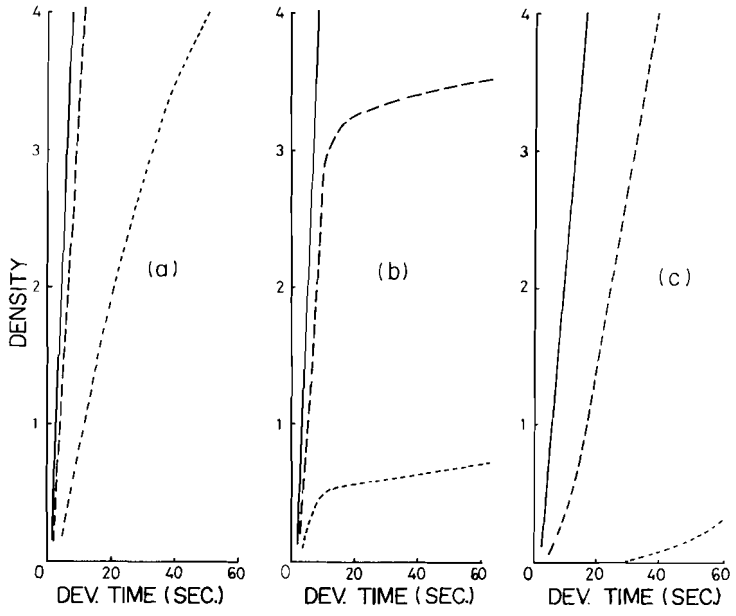

Fig. 4. Effect of retarders of development for different exposure levels. Density against developing time at low exposure level (————), at middle exposure level (– – — — —) and at high exposure level (- - - - - - -) are shown. Developing Temperature : 38°c
(a) : without retarder
(b) : with benztriazole compound
(c) : with indazole compound

Experiments on Image Expansion

Okutsu(1973) measured image qualities by the width of image expansion and reported that image expansion depends on the quantity of semiquinone radicals. Fig. 5 shows the comparison among lith-development, rapid access development and Fuji's development system. The width values are measured by the same method as described in Okutsu's . In our new developing system, about half of the image expansion produced by lith-development, is possible.

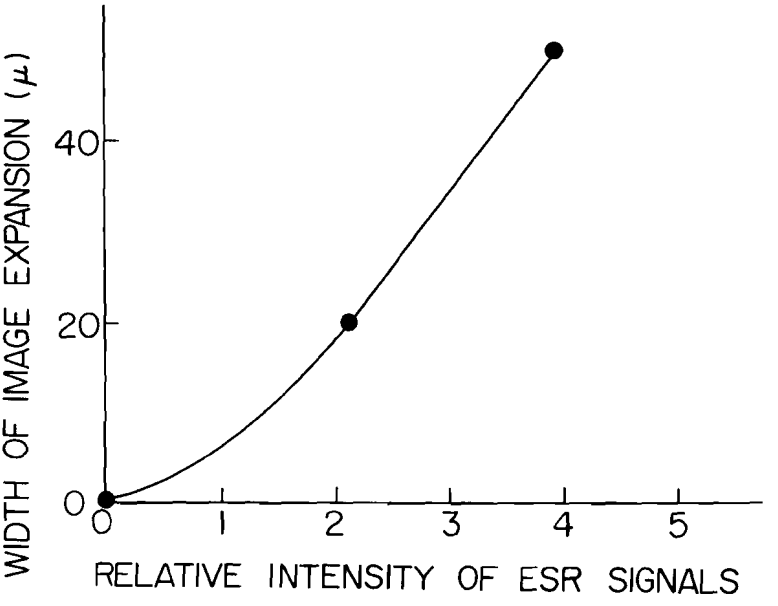

Fig. 5. Dependence of the width of image expansion on the relative intensity of ESR signals of semiquinone radicals

Attained Image Qualities

In Fig. 6, image qualities of processed film are shown. This is a comparison in the superimposition work. Fuji's new system reproduces fine lines as well as lith-development. By use of this system in the contact work, various kinds of work which can be achieved only by lith-development, for example: larger spread and choke work, can be done in fast access time.

Attained Solution Stability

In Fig. 7, detorioration of hydroquinone against time lapse exhausion is shown. Fuji's new developer which is high in pH and high in sulfite ion concentration, is as stable as conventional rapid access developer.

Summary

Contradiction between image qualities and stability in hydroquinone developers is resolved by using a developer with high pH and high concentration of sulfite ions.

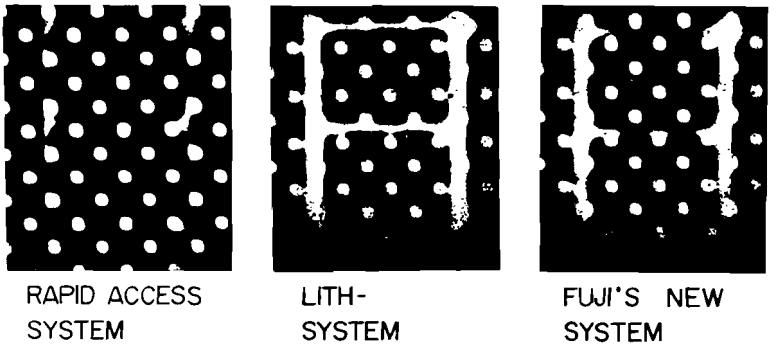

Fig. 6. Comparison of image quality in the superimposition work among development systems.

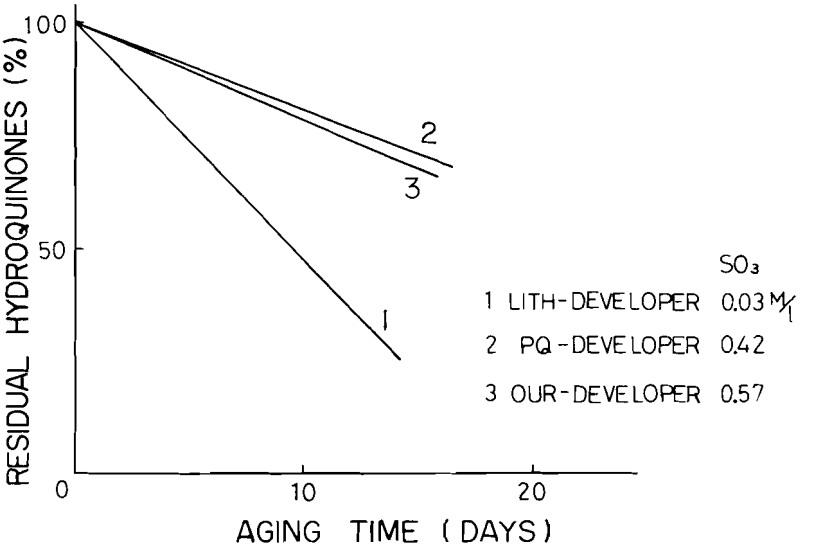

Fig. 7. Comparison of solution stability among development systems

The problem of low contrast in high temperature processing, is overcome by using indazole compounds as retarder.

By combining these ideas given above, we attained high image qualities, high speed processing and highly stable solution.

Acknowledgement

The present authors would like to thank Messrs. H. Ueda, Y. Hayakawa and Y. Oh-ishi for their interest and permission to publish this paper. Thanks are also due to Mr. Y. Sano for the measurement of the ESR spectroscopy, and many other members in these Laboratories for their co-laborations.

Literature Cited

Eggers, J.
1971 "Some Observations on the Behavior of p-Benzoquinone in Developer Solutions," Photogr. Sci. Eng., vol. 15, no. 2, pp. 128-133.

Hefter, H. J.
1975 "ESR Study on Mechanism and Kinetics of Photographic Development in Hydroquinone Developers," Photogr. Sci. Eng., vol. 19, no. 3, pp. 179-183.

James, T. H.
1968 "The Developer Activity of p-Benzoquinone Solutions," Photogr. Sci. Eng., vol. 12, no. 2, pp. 67-79.

Kerr, D. L.
1982 "Lith Development Kinetics and Halftone Dot Formation," TAGA Proceedings, pp. 325-343.

Lu Valle, J. E., and Goldberg, G. M.
1958 "The Photographic Implications of the Chemistry of Quinone," J. Photogr. Sci., vol. 6, pp. 176-184.

Okutsu, E. and Iwano, H.
1973 "Studies on Lith-Development Effects," SPSE Tokyo Symposium, pp. A-3-1—A-3-5.

Suga, T.
1975 "Eine Ableteung aus der Hypothese über den Litheffekt," Bull. Chem. Soc. Japan, vol. 48, no. 9, pp. 2513-2515.

Umberger, J. Q.
1966 "Photographic Development from the Viewpoint of Frank-Condon Electron Transfer," Photogr. Sci. Eng., vol. 10, no. 1, pp. 8-14.

Wood, H. W.
1964 "On the Effect of Polyethylene Oxide on Hydroquinone Development," J. Photogr. Sci., vol. 12, no. 1, pp. 5-14.

Yule, J. A. C.
1945 "Formaldehyde-Hydroquinone Developers and Infectious Development," J. Franklin Inst., vol. 239, no. 3, pp. 221-230.

Zwicky, H.
1966 "Über einige Versuche zur Lithentwicklung," photogr. Korresp., vol. 102, no. 1, pp. 11-16.

1977 "Neuer Anschauungen zum Mechanismus der Lithentwicklung," J. Singnal AM, vol. 5, no. 2, pp. 81-92.