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The Additive Effect of Polyoxyethylene Compounds on the Photographic Characters of Photographic Emulsion

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The polyoxyethylene compounds were added into the photographic emulsion during the physical ripening of photo sensitive silver halide crystal in this emulsion. The polyoxyethylene compounds improved the photographic properties of the film to a great extent increasing the photo sensitivity and decreasing the fog density.

key words: photographic emulsion, polyoxyethylene, ripening, photo-sensitivity, anti-fog effect

INTRODUCTION

The photographic emulsion is well dispersed fine crystals of silver halide in gelatin. The fine crystals of silver halide is prepared by the reaction of KBr and KI with ammoniacal $AgNO_3$ in aqueous solution of gelatin. The single jet injection, the reversal injection and the double jet injection are the well known methods for preparing the photographic emulsion [1, 2, 3].

These emulsions must go through chemical ripening such as sulfur sensitization [4,5] and/or reducing sensitization and/or metal sensitization [6,7] in order to increase the photo-sensitivity of the emulsions. But unfortunately, there are serious problems that the chemical ripening not only increases the sensitivity but also increases the fog density. Much of the emulsion research carried out in recent years by the photographic industry has, therefore, laid particular emphasis on the search for anti-foggants that approach more closely to the ideal of photographic inertness.

In this research we examined the anti-fog effect of polyoxyethylene compounds.

MATERIALS AND METHODS

The used polyoxyethylene compounds in this experiment are shown in Table 1.

The photographic emulsions were prepared by single jet method and chemical ripening such as sulfur sensitization and gold sensitization.

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Table 1. Polyoxyethylenes used in this experiments.

Chemical structures	Concentration(*mmol*)
n-$C_{16}H_{33}(OCH_2CH_2)_2OH$	9.1
n-$C_{16}H_{33}(OCH_2CH_2)_{10}OH$	4.4
n-$C_{16}H_{33}(OCH_2CH_2)_{20}OH$	1.8
n-$C_{18}H_{37}(OCH_2CH_2)_{20}OH$	1.7
n-$C_{18}H_{37}(OCH_2CH_2)_2OH$	5.6
n-$C_{18}H_{37}(OCH_2CH_2)_{10}OH$	1.4
(9E)-$C_{18}H_{35}(OCH_2CH_2)_2OH$	2.8
(9E)-$C_{18}H_{35}(OCH_2CH)_{10}OH$	1.4

The physically ripen emulsion was prepared using halide aqueous solution and ammoniacal silver nitrate aqueous solution.

The halide aqueous solution was prepared by solving 10 g of phenylcarbamyl gelatin, 1.5 mol of KBr, 4.8 *mmol* of KI and 0 ~9.1 *mmol* of single and/or mixed polyoxyethylene in 800 *ml* of distilled water at 45°C.

The ammoniacal silver nitrate aqueous solution was prepared by mixing 1.35 *mol* of $AgNO_3$ and equivalent amount of NH_4OH aqueous solution in 860 *ml* of distilled water at 30°C.

To halide aqueous solution under agitation at 48°C, ammoniacal silver nitrate aqueous solution was added over a period of 90 seconds and the mixture was ripen for 40 minutes. The ammonia concentration was controlled and the pH was maintained at 11.0. The ripening was arrested by adding ammonium sulfate(10 wt%) at 35°C to give a pH 5.2. The mixture was desalted and washed with water at 15°C by a conventional method. To this emulsion, 2600 *ml* of distilled water and 229 g of inert gelatin were added. The pAg(7.7) and pH(6.4) were controlled by addition of Na_2CO_3(10 wt%) and KBr(1 wt%) solutions at this time and this mixture was agitated for 30 minutes at 48°C.

The chemically ripen emulsion was prepared by sensitization of the physically ripen emulsion as shown below. 0.158 *mmol* of $Na_2S_2O_3$, 0.16 *mmol* of $HAuCl_4$ + NH_4SCN complex and 1.67 *mmol* of 7-hydroxy-5-methyl-1,3,7-tri-azaindolizine were added into the physically ripen emulsion during agitation at 50 ℃ and was ripen for propriety times.

These emulsions were settled with stabilizer, hardener and other additives in accordance with standard method and it was coated with protect layer on both sides of the blue colored photographic polyester film and dried.

The sample films were exposed for 1/50 seconds in sensitometer(JIS III, Nalumi Co., USA), developed for 90 seconds at 35 ℃ in developer replenisher(Korea Photo-Chemicals Co.), fixed in fixer replenisher(Korea Photo-Chemicals Co.) and were throughly washed with water. Accurate measurement of sensitivity and fog density of these sample films were carried out by using of densitometer(model X-Rite 316T, X-Rite Co., USA).

RESULTS AND DISCUSSION

The values of the sensitivity, contrast and fog density are very important to estimate the photographic characters of the photographic films. In order to examine the effect of polyoxyethylene compounds on the photographic characters, the values of the sensitivities, contrasts and fog densities of the established standard film were compared with thouse of the sample films that were treated with polyoxyethylene compounds.

Table 2. The polyoxyethylene effect on the photographic properties of the photographic emulsion.

Additives	Quantites (*mmol*)	Relative Sensitivies	Contrasts	Fog Densities
None	-	80	3.0	0.12
n-$C_{16}H_{33}(OCH_2CH_2)_2OH$	9.1	90	3.15	0.05
n-$C_{16}H_{33}(OCH_2CH_2)_{10}OH$	4.4	100	3.15	0.04
n-$C_{16}H_{33}(OCH_2CH_2)_{20}OH$	1.8	100	3.15	0.03
n-$C_{18}H_{37}(OCH_2CH2)_{20}OH$	1.7	100	3.2	0.03
n-$C_{18}H_{37}$(OCH2CH2)2OH	5.6	100	3.2	0.02
n-$C_{18}H_{37}(OCH_2CH_2)_{10}OH$	1.4	100	3.2	0.02
(9E)-$C_{18}H_{35}(OCH_2CH_2)_2OH$	2.8	100	3.2	0.02
(9E)-$C_{18}H_{35}(OCH_2CH_2)_{10}OH$	1.4	100	3.2	0.02

Relative sensitivities, contrasts and fog densities of polyoxyethylene treated films in comparison with those of the standard film are shown in Table 2. The relative sensitivities were increased to 12.5 % and 25 % as the results of polyoxyethylene treatment. The contrasts were increased from 5 to 6.6 %. On the other hand, Table 2 displays the remarkable diminution of fog densities. These results are very encouraging because all of the established anti-foggants not only reduced fog densities but also sensitivities and contrasts. The addition of polyoxyethylene compounds, therefore, can considerably improve photographic industry.

Table 3 displays very clearly spectacular effects of mixed polyoxyethylene compounds(7 + 8, 5 + 7) improving the photographic characters to a great extent. In both cases, the fog densities vanished completely giving great improvement in the photographic chemistry.

Table 3. The effect of mixed polyoxyethylenes on the photographic properties in the photographic emulsion.

Compounds	Quantites (*mmol*)	Relative Sensitivies	Contrasts	Fog Densities
Standard	-	80	3.0	0.12
(9E)-$C_{18}H_{35}(OCH_2CH_2)_2OH$ (9E)-$C_{18}H_{35}(OCH_2CH_2)_{10}OH$	1.4 1.0	100	3.2	0.0
n-$C_{18}H_{37}(OCH_2CH_2)$10OH (9E)-$C_{18}H_{35}(OCH_2CH_2)_2OH$	0.8 1.4	100	3.2	0.0

CONCLUSION

Polyoxyethylene compounds increase sensitivities and contrast to a remarkable extent and decrease the fog densities of the photographic films completely giving spectacular improvement in the photographic chemistry.

The effective additives among the polyoxyethylene compounds tested were *n*-$C_{16}H_{33}(OCH_2CH_2)_2OH$, *n*-$C_{16}H_{33}(OCH_2CH_2)_{10}OH$, *n*-$C_{16}H_{33}(OCH_2CH_2)_2$0OH, *n*-$C_{18}H_{37}(OCH_2CH_2)_2OH$, *n*-$C_{18}H_{37}(OCH_2CH_2)_{10}OH$, *n*-$C_{18}H_{37}(OCH_2CH_2)_{20}OH$, *(9E)*-$C_{18}H_{35}(OCH_2CH_2)_2OH$ and *(9E)*-$C_{18}H_{35}(OCH_2CH_2)_{10}OH$.

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