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Color Photographic Development Accelerators. Part V: Selective Development Acceleration of Hydrazine Compounds 1,3,4-Thiadiazole Heterocyclic System

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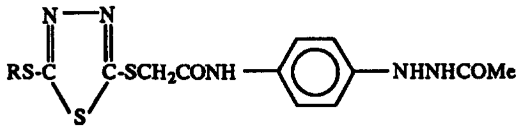
ABSTRACT

Photographic speed can be increased by incorporating selective development accelerators (hydrazine derivatives with adsorbed groups) into several types of silver halide emulsion because of the stronger accelerating action on image development than on fog formation. The development acceleration of the selective development accelerators depends on the pH of the developer. The higher the pH of the developer, the stronger the development acceleration of these compounds. When the pH of the developer rises to 12·50, the 'hydrazine effect' (super high contrast and short toe) is obtained. The accelerating action of the selective development accelerators appears over a wider pH range of developer, whereas that of the hydrazine compounds without adsorbed groups occurs only at higher pH of the developer (pH > 11·50) under the same experimental conditions.

1 INTRODUCTION

We have previously synthesized new selective development accelerators based on hydrazine compounds containing the 1,3,4-thiadiazole system.[1] The hydrazine moiety in the compound is anticipated to operate as a development accelerator to increase the rate of image development and hence increase the photographic speed, while the 1,3,4-thiadiazole moiety acts as a development inhibitor, decreasing the reactivity of silver halide by forming an adsorption layer on the surface of unexposed grains and hence inhibiting fog formation. A high efficiency of development accelera-



Compound	R
1	Me
2	Et
3	n-Bu
4	n-hexyl

Fig. 1. The structure of selective development accelerators.

tion was observed when the functionalized hydrazine compounds were incorporated into a color negative material,[1] and the development acceleration may be independent of the color coupler system in the emulsion, but dependent upon the direct interaction between these compounds and silver halide, due to their adsorptivity on silver halide grains.[2] In order to confirm this, the effect of these compounds on the photographic properties of silver halide emulsions in the absence of a color coupler system needed to be investigated.

The present paper provides data on the development acceleration of the functionalized hydrazine compounds in several monodisperse silver halide emulsions. The results obtained may be helpful in clarifying the nature of their development acceleration mechanism.

2 EXPERIMENTAL

The structure of the selective development accelerators investigated is shown in Fig. 1. The photographic behavior of compounds 1–4 was examined using the three types of monodisperse emulsion listed in Table 1. Emulsions A, B, and C were prepared by a conventional double-run method. All the emulsions were composed of inert gelatin and the ratio of gelatin to silver for each emulsion is also given in Table 1. Emulsions

TABLE 1
Silver Halide Emulsions Used

Emulsion	*Crystal habit*	*Average grain size (μm)*[a]	*Ratio of gelatin to silver (w/w)*	*Halide composition*
A	Cubic	0·16	1·2	$AgBr_{98.5}I_{1.5}$
B	Cubic	0·31	1·0	AgBr
C	Octahedral	0·84	1·2	AgBr

[a] Average diameters of circles whose areas are identical to the projected areas of the emulsion grains.

TABLE 2
Developer Composition[a]

Hydroquinone	40 g
Anhydrous sodium sulfite	60 g
Sodium carbonate	60 g
Potassium bromide	10 g
Water (to make)	1 liter

[a] pH was adjusted to 10·00–12·50 by controlling the amount of solid sodium hydroxide in the developer.

A and C were S + Au sensitized, while emulsion B was chemically unsensitized.

Ethanolic solutions of compounds 1–4 were added to the emulsions, which were then coated on a cellulose triacetate film base. The strips were exposed by using a Xiang-Feng Sensitometer and were developed at 20°C in a developer having the composition shown in Table 2, and then subjected to stop, fixation, wash and dry.

The development densities were read on a photoelectric cell densitometer. Emulsion speed is expressed as $S_n = 8/E_n$, where E_n is the exposure corresponding to a developed density of n above fog.

In order to ascertain whether introduction of an adsorbed group into the hydrazine compound is the important condition for the development acceleration caused by compounds 1–4, the photographic behaviour of *N*′-formyl-*N*-phenylhydrazine (reference compound 5) and *N*′-benzoyl-*N*-phenylhydrazine (reference compound 6) were also examined under the same experimental conditions, so that a comparison could be made.

3 RESULTS AND DISCUSSION

3.1 Relationship between the structure of the selective development accelerators and their photographic properties

The photographic characteristic data of emulsion A with and without incorporation of compounds 1–4 are given in Table 3. The coatings were made at 6·5 g/m^2 of silver and developed at a developer pH of 10·50 for 10 min.

The results in Table 3 indicate that incorporation of compounds 1–4 into emulsion A leads to a photographic speed increase of 100–172% and a contrast increase of 2·20–2·86, whereas no increase in fog is observed. Additionally, Table 3 showed that increasing the length of the alkyl

TABLE 3
Photographic Characteristic Data of Emulsion A

Compound	*Laydown* $\times 10^3$ *(mol/mol Ag)*	*Relative sensitivity*[a]	*Contrast* (γ)	*Fog* (D_0)
—	0	100	6·20	0·04
1	2·4	272	8·86	0·02
2	2·4	230	8·53	0·04
3	2·4	209	8·80	0·02
4	2·4	200	8·40	0·04

[a] The relative sensitivity of emulsion A in the absence of the compounds examined is assumed to be 100 at a density of 0·02 above fog.

chain in the molecule of the compounds examined causes a decrease in the accelerating action on image development. This substitution effect was also observed when these compounds were incorporated into a color negative material,[1] and may result from the decrease of adsorbed molecular number per unit area on the surface of silver halide grains with the increase of the length of the alkyl chain in the molecule.[2]

3.2 Effect of developer pH on the development acceleration of the selective development accelerators

It is known that the 'hydrazine effect' (super high contrast and short toe) caused by *N*'-acyl-*N*-phenylhydrazine is affected by the alkalinity of the developer.[3–7] In a highly alkaline developer, the magnitude of the 'hydrazine effect' is increased. In practice, however, a developer with a high pH-level is undesirable because of its instability towards air oxidation. In order to show whether our compounds could cause strong development accelerating action in a developer with quite weak alkalinity, we studied their photographic behavior in the developer at different pH levels and made a comparison with that of compound 5 in which no adsorbed group exists.

The photographic characteristic data of emulsion B with compound 3 or compound 5, and without the examined compounds developed in a developer at five pH levels, for 5 min are given in Table 4. The coatings were made at 2·85 g/m^2 of silver.

It is apparent from Table 4 that the efficiency of the increases in sensitivity, contrast and maximum density (D_{max}) is high for emulsion B with compound 3 developed using a developer pH of 10·00–11·50. The higher the developer pH, the stronger the development acceleration of compound 3, whereas almost no development acceleration is observed when compound 5 was incorporated into emulsion B in the developer pH range 10·00–11·50. However, a highly alkaline developer (developer pH ≥12·50) is still needed to cause the 'hydrazine effect' for compound 3. In this case, there are no large differences in the efficiency between compounds 3 and 5, as indicated in Table 4. The results in Table 4 indicate that the advantage of the hydrazine compounds with adsorbed groups over those without the adsorbed groups is that the former can effectively accelerate the image development even at lower developer pH and may be more suitable for practical work.

3.3 Development selectivity

In practice, it is not difficult to increase the rate of image development, but it is difficult to increase the rate of image development without an accompanying increase in the rate of fog formation. As Hillson[8] stated, it is possible to develop more grains merely by extending the development

TABLE 4
Photographic Characteristic Data of Emulsion B in a Developer at Varying pH

Developer pH	D_0	γ	$S_{1\cdot0}\times100$	D_{max}
Emulsion B without the compounds examined				
10·00	0·01	3·00	0·42	1·50
10·50	0·02	3·23	0·58	1·88
11·00	0·03	4·00	0·67	2·21
11·50	0·04	4·20	0·71	2·55
12·50	0·04	4·40	0·73	>4·00
Emulsion B with compound 3 of 5·40 mmole/mole AgBr				
10·00	0·02	7·30	1·37	>4·00
10·50	0·03	6·67	1·65	>4·00
11·00	0·03	7·66	1·76	>4·00
11·50	0·03	7·30	1·97	>4·00
12·50	0·03	10·0	6·89	>4·00
Emulsion B with compound 5 of 10·0 mmole/mole AgBr				
10·00	0·01	3·33	0·42	1·50
10·50	0·02	4·30	0·58	1·88
11·00	0·03	4·50	0·67	2·21
11·50	0·03	4·50	0·74	2·55
12·50	0·03	9·30	4·57	>4·00

time. The question is whether the extra developed grains contribute more to the image or to the fog.

Figure 2 gives photographic speed *versus* development time plots for emulsion A with and without the incorporation of compound 2, developed at developer pH 10·50. The coatings were made at 6·5 g/m^2 of silver. Figure 3 gives the photographic speed and fog *versus* development time plots for emulsion C with and without the incorporation of compound 3 or reference compound 6, developed at developer pH 12·00. The coatings were made of 3·75 g/m^2 of silver. The photographic speed in Figs 2 and 3 is expressed as log E_n, where E_n is the exposure needed to give densities of n above fog. Here, the development selectivity may be expressed as the ratio of the rate of photographic speed increase to that of fog increase.

It is evident from Fig. 2 that excellent improvement in development selectivity is observed in the presence of compound 2 for emulsion A in the low, middle and high exposed areas, while the fog is negligible and independent of the development time at the experimental conditions used. Figure 3 shows that the photographic speed increase is faster and

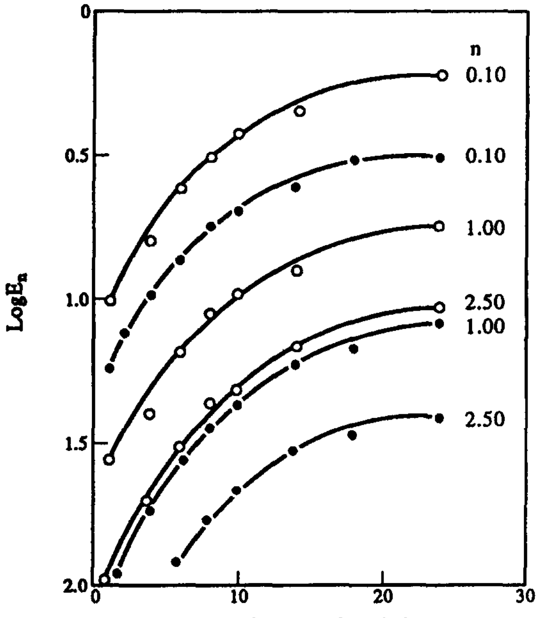


Fig. 2. Photographic speed, calculated as the logarithm of the relative exposure E_n needed to give densities of n = 0·10, 1·00 and 2·50 above fog, for emulsion A with compound 2 of 0 (●) and 2·4 (○) mmole/mole AgX, plotted against development time at developer pH of 10·50. Fog densities were negligible and independent of the development time at the experimental conditions.

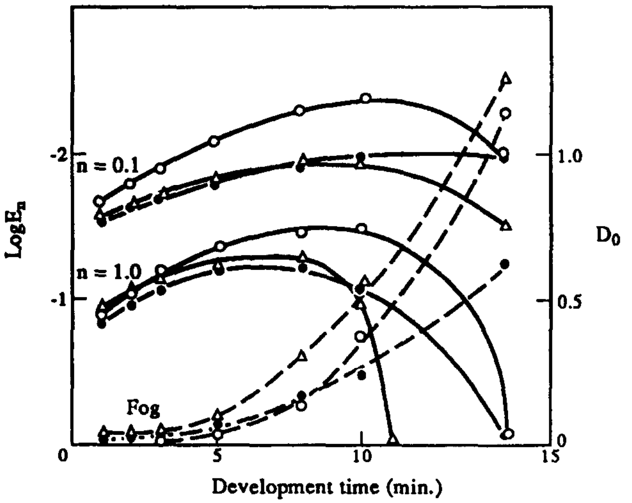


Fig. 3. Photographic speed (full lines) and fog (dashed lines) of emulsion C with compound 3 of 0 (●) and 0·70 (○), and comparative compound 6 of 1·0 (Δ) mmole/mole AgBr at development pH of 12·00, against development time plots.

the fog increase is lower for emulsion C with compound 3 than that without compound 3 so that an improvement of development selectivity can be observed in the initial minutes of the development, whereas further extension of the development causes a rapid increase in fog and decrease in photographic speed for the emulsion with compound 3. When the reference compound 6 was incorporated in emulsion C, almost no improvement in development selectivity could be observed over the whole range of development time, as shown in Fig. 3. The results in Figs 2 and 3 indicate that the functionalized hydrazine compounds may be most suitable selective development accelerators when they are used in low-fogged emulsions.

4 CONCLUSIONS

Selective development acceleration is observed over a wide pH range of developer when selective development accelerators based on hydrazine derivatives containing a 1,3,4-thiadiazole heterocyclic system are incorporated into a number of monodisperse silver halide emulsions.

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