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A New System for Forming High-Contrast Direct-Positive Images

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A very-high-contrast direct-positive image was obtained when a prefogged AgBr photographic emulsion containing certain bipyridinium salts, such as 1-*n*-butyl-4-(4'-pyridyl)pyridinium bromide hydrochloride (Compound 1), was processed with a developer that contains Metol and ascorbic acid as developing agents. Results of photographic and electrochemical studies suggested that Compound 1 has two functions, as an electron acceptor and as a precursor of a nucleator. A theory was developed that, during exposure, Compound 1 acts as an electron acceptor, which produces a direct-positive image, and that Compound 1 is neutralized during development to form 1-*n*-butyl-4-(4'-pyridyl)pyridinium bromide (Compound 2), which acts as a nucleator during development and produces very-high-contrast images.

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Introduction

In a previous paper,[1] we reported a new function for pyridinium salts in silver halide photographic systems. We found that contrast and apparent photographic speed increase substantially when a photographic film is processed with a developer containing an aminophenol-type developing agent and ascorbic acid in the presence of a pyridinium salt derivative. Very high contrast (greater than 15 between densities 0.5 and 3.0 above base + fog) was obtained for a negative-working film. Based on the results of a mechanistic study, we proposed that the resulting high contrast and the apparent increase in photographic speed result from a nucleation reaction of a pyridinium salt derivative during development.

Further investigation on the use of pyridinium salts in photographic systems led us to an interesting phenomenon. We found that a very-high-contrast direct-positive image could be obtained by using a certain type of bipyridinum salt. A very high contrast (greater than 15 between densities 0.5 and 3.0 above D_{min}) direct-positive image was obtained when a prefogged AgBr photographic emulsion containing 1-*n*-butyl-4-(4'-pyridyl)pyridinium bromide hydrochloride (Compound 1) was processed with a Metol/ascorbic acid developer. When 1,1'-di-*n*-butyl-4,4'-bipyridinium dibromide (*n*-butyl viologen, Compound 3), a well-known electron acceptor, was used instead of Compound 1, a direct-positive image resulted but very high contrast could not be obtained. Our understanding of which properties of Compound 1 were responsible for the production of very-high-contrast direct-positive images is interesting to relate. In this article, we report on the results of photographic and electrochemical studies of Compound 1 and related compounds. A possible mechanism for the production of very-high-contrast direct-positive images is discussed.

Experimental

Preparation of Bipyridinium Salts. ***1-n-Butyl-4-(4'-pyridyl)pyridinium Bromide (Compound 2)***. A mixture of 3.12 g (20 mmol) of 4,4'-bipyridine, 3.0 g (22 mmol) of 1-bromobutane, and 30 mL of dioxane was stirred magnetically at 80°C for 6 h. Precipitated crystals were filtered and recrystallized with 30 mL of isopropanol. Filtered crystals were dried to provide 2.9 g (yield 49%) of 1-*n*-butyl-4-(4'-pyridyl)pyridinium bromide. The structure was confirmed by IR, NMR, and MS.

1-n-Butyl-4-(4'-pyridyl)pyridinium Bromide Hydrochloride (Compound 1). One gram of 1-*n*-butyl-4-(4'-pyridyl)pyridinium bromide was dissolved in 20 mL of ethanol and reacted with HCl gas at room temperature for 1 h. Evaporation of the ethanol provided 1.1 g (yield 98%) of 1-*n*-butyl-4-(4'-pyridyl)pyridinium bromide hydrochloride. The structure was confirmed by IR, NMR, MS, and elemental analysis.

1,1'-di-n-Butyl-4,4'-bipyridinium Dibromide (n-Butyl Viologen, Compound 3). A mixture of 1.56 g (10 mmol) of 4,4'-bipyridine and 13.7 g (100 mmol) of 1-bromobutane was mixed by means of magnetic stirring at 90°C for 1 h. Precipitated crystals were filtered and recrystallized with 30 mL of isopropanol. Filtered crystals were dried to provide 2.4 g (yield 56%) of 1,1'-di-*n*-butyl-4,4'-bipyridinium dibromide (*n*-butyl viologen, Compound 3). The structure was confirmed by IR, NMR, and MS.

The structures of the bipyridinium salts discussed are shown in Fig. 1.

Film and Developer

Monodisperse AgBr cubic crystals having an average edge length of 0.19 µm were prepared by a controlled double-jet method. A fogged direct-positive emulsion was prepared by treating the AgBr emulsion with hydrogen tetrachloroaurate (III) tetrahydrate and formamidine sulfinic acid. The emulsion was fogged by adding hydrogen tetrachloroaurate (III) tetrahydrate at a level of 1.95 µmol/mol Ag and formamidine sulfinic acid at a level of 2.44 µmol/mol Ag and heating for 90 min at 70°C. After the emulsion was fogged, either Compound 1 or 3 was added to the fogged emulsion at a level of 5 mmol/mol Ag. The emulsion was coated on a PET base at a coverage of 38 mg Ag/dm^2.

A negative emulsion was prepared by sensitizing the AgBr emulsion described earlier with sodium thiosulfate pentahydrate instead of fogging with hydrogen tetrachloroaurate (III) tetrahydrate and formamidine sulfinic acid.

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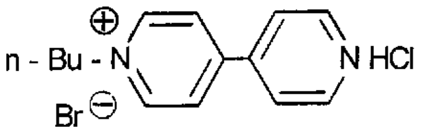
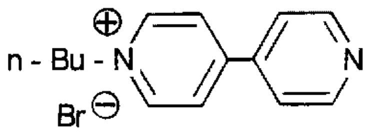


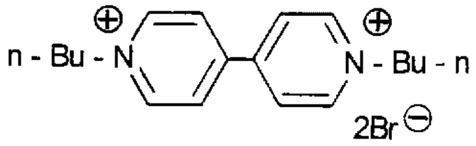
1-n-Butyl-4,4'-bipyridinium bromide hydrochloride

compound 1



1-n-Butyl-4,4'-bipyridinium bromide

compound 2



1,1'-di-n-Butyl-4,4'-bipyridinium dibromide (n-Butyl viologen)

compound 3

Figure 1. Structures of bipyridinium salts used in the study.

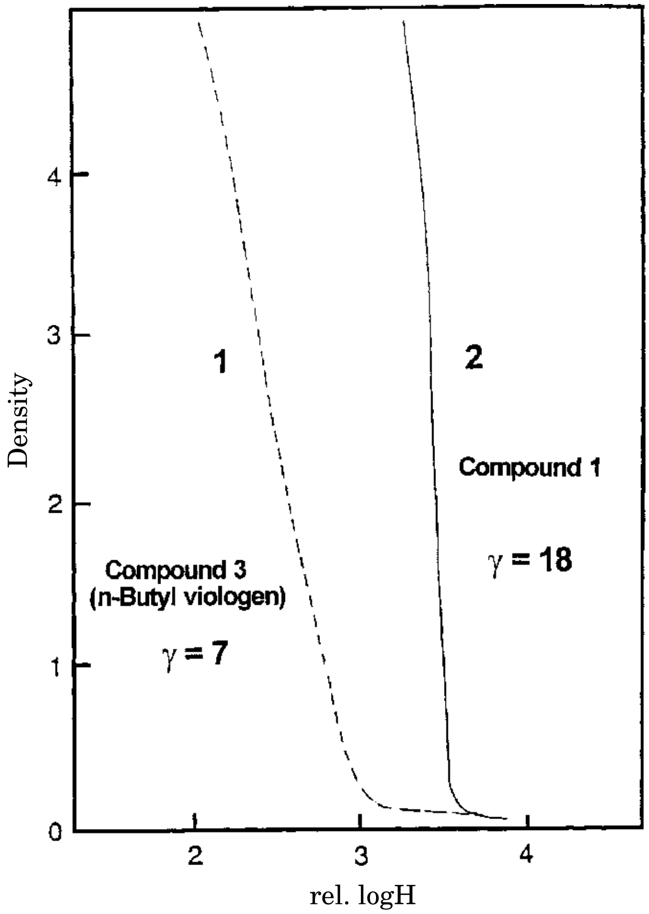


Figure 2. Effect of bipyridinium salts on a prefogged AgBr direct-positive emulsion. Either Compound 1 (Curve 2) or Compound 3 (Curve 1) was added to the emulsion at a level of 5 mmol/mol Ag. Films were developed for 3 min at 30°C by a Metol/ascorbic developer.

The AgBr emulsion was sensitized by adding sodium thiosulfate pentahydrate at a level of 2.44 µmol/mol Ag and heating for 70 min at 60°C. The emulsion was coated on a PET base at a coverage of 38 mg Ag/dm^2.

Both direct-positive and negative films were exposed by a tungsten lamp through a step tablet. Exposed films were developed by a Metol/ascorbic acid developer with the following basic formulation.

Metol	2.5 g
Sodium L-ascorbate	10 g
$NaBO_2 \cdot 4H_2O$	70 g
KBr	1 g
Water to	1 L

The developer pH was adjusted to 10.8. Development temperature was 30°C. Depending on the purpose of the experiment, bipyridinium salts were added to the developer and a modification of the development procedure was made. Details of the development conditions are described in each section.

Electrochemical Study

Cyclic voltammetry of bipyridinium salts was performed on an EG&G Princeton Applied Research Model 273 potentiostat-galvanostat in acetonitrile containing 0.1 M tetra-*n*-butylammonium perchlorate as a supporting electrolyte. A three-electrode cell configuration was employed. The working electrode was a platinum wire, and the reference electrode was a saturated calomel electrode (SCE). The counter electrode was a coiled platinum wire. Solutions were degassed with nitrogen gas prior to the measurement.

Results and Discussion

Production of High-Contrast Direct-Positive Image

Figure 2 shows the photographic effects of Compound 1 and Compound 3 (*n*-butyl viologen) on a prefogged direct-positive emulsion. The emulsion contained either Compound 1 or Compound 3 at a level of 5 mmol/mol Ag, as described earlier. Although it is not shown in the figure, the emulsion that did not contain a pyridinium salt was totally fogged and did not give any images. However, as shown in Fig. 2, direct-positive images were obtained by the presence of either Compound 1 or Compound 3 (*n*-butyl viologen) in the emulsion. Significant differences in the contrast and the apparent photographic speed were observed with the two bipyridinium salts. Straight-line gamma was 18 for Compound 1 and 7 for Compound 3. Straight-line gamma was measured between densities 0.5 and 3.0 above D_{min}. Compound 1 gave much higher gamma than Compound 3 (*n*-butyl viologen) and it thus gave very high contrast. Compound 1 resulted in a 1.0 log H slower speed than Compound 3 at $D = 3.0$ (speed at the toe may be more important in practical use but speed at $D = 3.0$ was used merely to discuss the photographic characteristics).

Because Compound 1 gave a direct-positive image, it is clear that Compound 1 acts as an electron acceptor in a

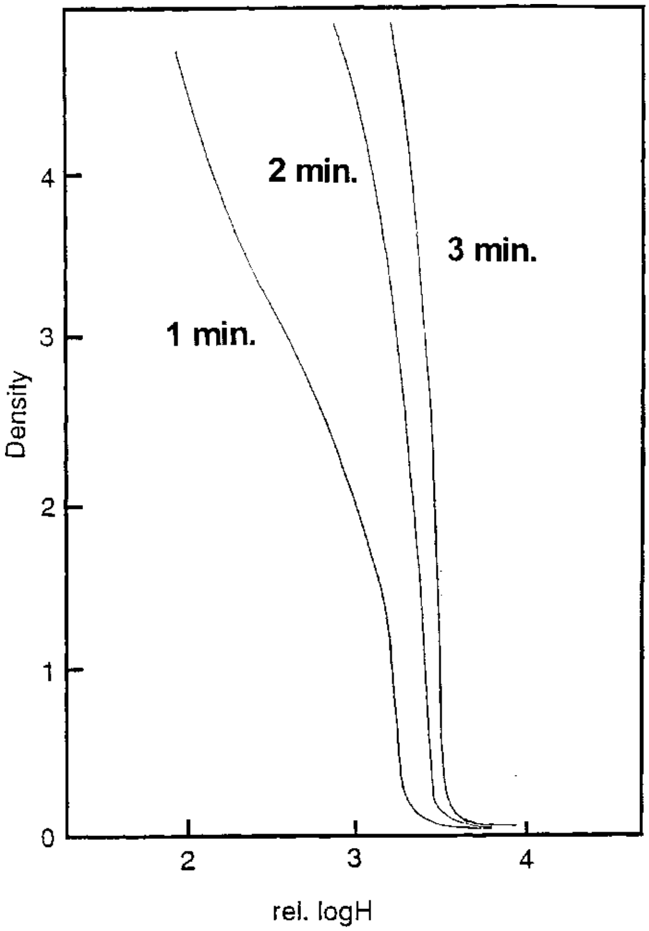


Figure 3. Development time series for the film containing Compound 1 in the experiment of Figure 2.

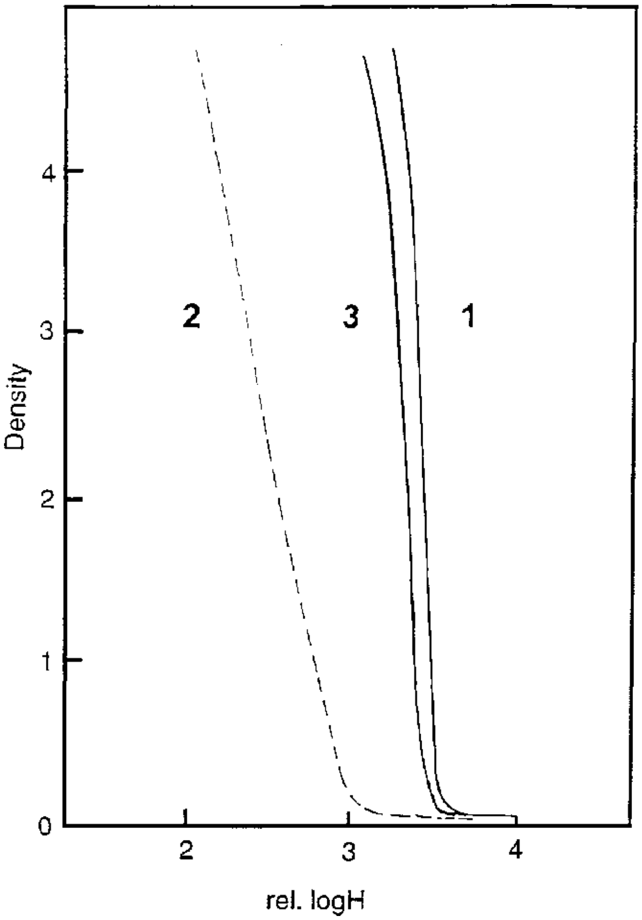


Figure 4. Effect of wash treatment of the exposed film before development. Films containing Compound 1 at a level of 5 mmol/mol Ag were used. *Curve 1* (control), the exposed film was developed without wash treatment. *Curve 2*, the exposed film was washed and then developed. *Curve 3*, the exposed film was washed and processed by the developer to which Compound 1 was added at a level of 70 μmol/L. Development time was 3 min at 30°C.

prefogged emulsion, as does Compound 3 (*n*-butyl viologen), which is a well-known electron acceptor.[2,3] The results of cyclic voltammetry , which are shown in a later section, showed that the cathodic peak potential of Compound 1 was – 0.46 V versus SCE. This value supports the theory that Compound 1 will act as an electron acceptor in a photographic emulsion.

Figure 3 shows the effect of development time on characteristic curves for Compound 1. It shows that contrast increased as development time lengthened, suggesting that Compound 1 acts as a contrast enhancement agent during development.

Effect of Wash Treatment before Development

The results of Figs. 1, 2, and 3 indicate that Compound 1 has two roles in a prefogged emulsion, as an electron acceptor during exposure and as a contrast enhancement agent during development. However, it is uncertain whether the low speed that is seen with Compound 1 can be attributed to the inefficient electron-accepting ability of Compound 1 or to the increased development capability of the developer in the presence of Compound 1. To separate and clarify the two roles, the following experiment was performed. A direct-positive emulsion that contained Compound 1 at a level of 5 mmol/mol Ag was used. Two film samples were exposed and then washed with a 2.5×10^{-3} M KBr aqueous solution for 30 min at room temperature to remove Compound 1 from the emulsion layer of the film sample. One film sample was developed with the basic formula for a Metol/ascorbic acid developer. The other film sample was developed with a Metol/ascorbic acid developer to which 70 μmol/L of Compound 1 had been added to see the effect of Compound 1 in the development. A control sample was processed by the same procedure except that no wash treatment was applied. The results are shown in Fig. 4.

As shown in Fig. 4, the photographic speed (at $D = 3.0$) apparently increased significantly as a result of the wash treatment. The apparent photographic speed increase was 1.04 log H at $D = 3.0$. At the same time contrast decreased significantly. Straight-line gamma decreased from 18 (control) to 7 as a result of the wash treatment. As shown in Fig. 2, Compound 3 (*n*-butyl viologen) also gave a gamma of 7. The characteristic curve of the washed film was almost identical to that of Compound 3 (*n*-butyl viologen, Curve 1 in Fig. 2). However, as shown in Fig. 4, a characteristic curve similar to that of the control was obtained when the washed sample was processed with a developer that contained 70 μmol/L of Compound 1. The gamma increased from 7 (in the absence of Compound 1) to 18 (in the presence of Compound 1 at a level of 70 μmol/L in the developer), which is the same as that of the control (Curve 1 in Fig. 4). Thus very high contrast was obtained by the addition of Compound 1 to the developer. A significant decrease of apparent photographic speed (at $D = 3.0$) was also observed. The apparent photographic speed decrease was 0.91 log H at $D = 3.0$.

The results of Fig. 4 confirmed that the presence of Compound 1, either in the emulsion or in the developer during development, was necessary to produce very high contrast. We are now certain that Compound 1 has two roles: as an electron acceptor during exposure and as a contrast enhancement agent during development. It was also confirmed that the low speed produced by Compound 1 can be attributed to the increased development capability in the presence of Compound 1. The results of Figs. 2 and 4 show that the production of high contrast is not a result of restraining the development, but a result of the increase in development capability, such as acceleration of development, infectious development, nucleation, or a combination of those reactions. It is likely that a reaction is involved by which AgX grains undevelopable under normal development conditions are made developable.

Since the wash treatment of the film containing Compound 1 gave about the same speed and contrast as the film that contained Compound 3 (*n*-butyl viologen), Compound 1 and Compound 3 are expected to have about the same electron-accepting property. There is significant difference between those compounds, however, in the effect on development.

Electrochemical Measurements

Figure 5 shows cyclic voltammograms of Compounds 1 and 2 in acetonitrile. Cyclic voltammograms of Compound 1 were also measured in the presence of 48% KOH solution. An excess of 48% KOH solution to neutralize Compound 1 was added to the sample solution containing Compound 1. In the absence of KOH solution, Compound 1 showed two cathodic peaks whose peak potentials were at – 0.46 and – 1.02 V. The first reduction peak potential (– 0.46 V) is almost the same as that of *n*-butyl viologen (Compound 3) measured in acetonitrile (– 0.45 V versus SCE).[1] Those redox potentials led us to believe that Compound 1 acts as an electron acceptor in the photographic emulsion system.[4,5] When 48% KOH solution was added to the solution containing Compound 1, the first cathodic peak at – 0.46 V disappeared, as shown in Fig. 5. The second cathodic peak at – 1.02 V remained almost unchanged and was the same as the cathodic peak potential (– 1.03 V) of Compound 2. Those behaviors suggest that Compound 1 was neutralized by a base to form Compound 2 and then lost its electron-accepting property.

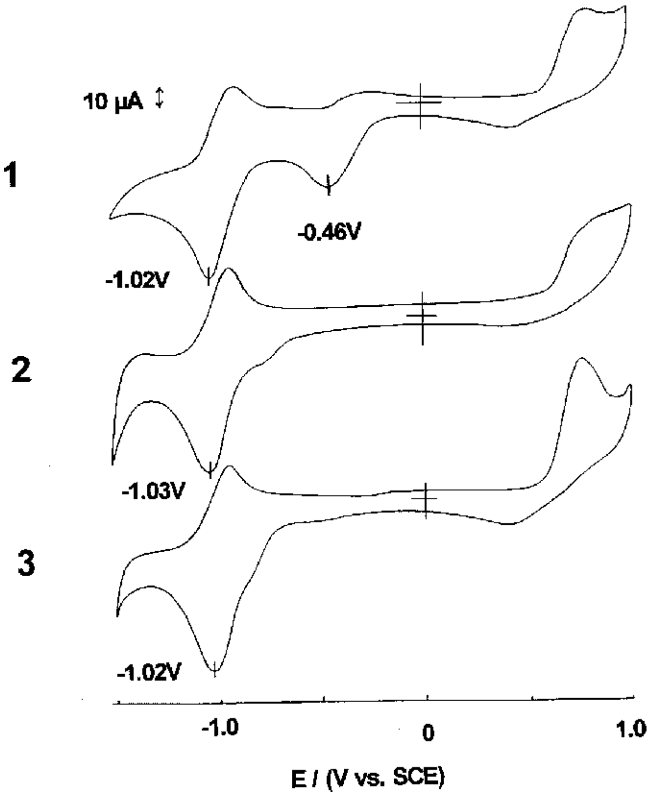


Figure 5. Cyclic voltammograms of bipyridinium salts. Compound 1 in the absence (*Curve 1*) and presence (*Curve 2*) of 48% KOH solution. *Curve 3*, Compound 2.

Effects of Compounds 1 and 2 on a Negative Emulsion

As described earlier, we reported the production of a high-contrast image using a pyridinium salt in a negative emulsion system.[1] A very-high-contrast image was obtained when a negative film was developed with a Metol/ascorbic acid developer in the presence of a pyridinium salt. It was also reported in the previous article that neither methyl viologen nor *n*-butyl viologen gave very high contrast in the negative system. Therefore, we expect a very-high-contrast image to be obtained by Compound 1 or 2 in a negative emulsion system if the mechanism of the production of very high contrast in the direct-positive emulsion system is essentially the same as in the negative emulsion system. To confirm this assumption, the effects of Compounds 1 and 2 on a negative emulsion were examined. A negative film (sulfur- sensitized AgBr emulsion described in the experimental section) was developed by a Metol/ascorbic acid developer to which Compound 1 or 2 had been added at a level of 70 μmol/L. Compound 2 was also tested, because it was likely that Compound 1 would be neutralized by a base in the developer to form Compound 2 during the development.

Results are shown in Fig. 6. Both Compounds 1 and 2 gave similar characteristic curves and showed very high contrast with a gamma of over 20. An apparent increase in photographic speed was also observed. Both Compounds 1 and 2 gave peculiar characteristic curves, which had local maxima in the density. After reaching the maximum, the density decreased as the exposure was increased. This part of the characteristic curve is a reversal response. Only a slight increase in density occurred in the relative log H exposure region of 2 or greater. This phenomenon may be interpreted as a self-quenching reaction, which has been reported in hydrazide nucleation systems.[6] The characteristic curves with a local maximum density shown in Fig. 6 suggest that the production of very high contrast by Compound 1 or 2 is due to a nucleation reaction by which silver halide grains undevelopable under normal conditions become developable.[6] The behavior of Compounds 1 and 2 is very similar to the results previously reported in which characteristic curves with a local maximum density were obtained by the addition of 1-benzyl-3-carbamoyl pyridinium salt or 1-benzyl-1, 4-dihydronicotinamide (reduced compound of 1-benzyl- 3-carbamoyl pyridinium salt) to the developer.[1]

Because very high contrast was obtained by Compounds 1 and 2 in the negative film system, we expect the mechanism that produces very high contrast in a direct-positive system in the presence of Compound 1 to be the same as that of the negative system.[1] We also expect, for the same reason, that a nucleation reaction is involved in the production of very-high-contrast direct-positive images as well as in the negative system.

Mechanism of Production of High-Contrast Direct-Positive Image

Although the mechanism of the production of very high contrast is not fully understood, we expect that the high

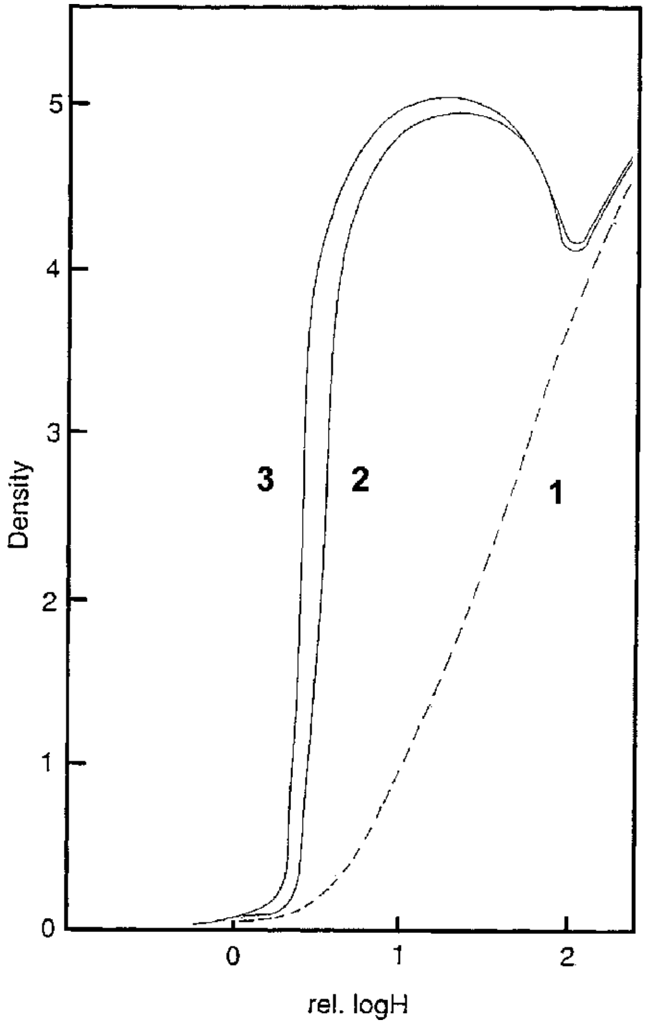


Figure 6. Effects of Compounds 1 and 2 on a negative emulsion. A negative film was developed by a Metol/ascorbic acid developer in the presence of Compound 1 or 2. *Curve 1* (control), no bipyridinium salts were added to the developer. *Curve 2*, Compound 1 was added to the developer at a level of 70 μmol/L. *Curve 3*, Compound 2 was added to the developer at a level of 70 μmol/L. Development time was 3 min at 30°C.

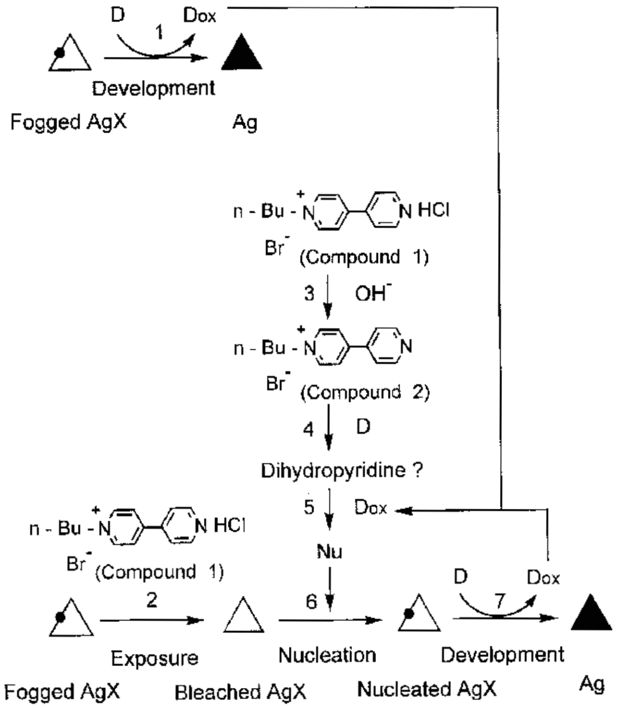
contrast is produced by a reaction mechanism similar to that seen in the production of very-high-contrast images on negative emulsion by a pyridinium salt. The major difference in the overall reaction from the negative system is that Compound 1 has two roles in the production of high-contrast direct-positive images. One is as an electron acceptor during exposure. The other is as a precursor of a nucleator during development. During exposure, Compound 1 acts as an electron acceptor, which gives a direct-positive image in a prefogged direct-positive emulsion. Because the wash treatment of the exposed film sample that contained Compound 1 gave about the same characteristic curve as the film sample that contained *n*-butyl viologen (Compound 3), the effect of Compound 1 as an electron acceptor on a prefogged direct-positive emulsion is probably about the same as that of *n*-butyl viologen (Compound 3). During development, Compound 1 is neutralized to become Compound 2, which acts as a neuleator. Because very-high-contrast images were obtained by processing a negative emulsion with a developer to which Compound 1 or 2 was added, it is expected that Compound 1 will be neutralized to become Compound 2 and that the mechanism of the production of very high contrast in the direct-positive system is essentially the same as that of the negative system.

A possible reaction mechanism for the production of very-high-contrast direct-positive images is illustrated in Fig. 7. Reaction 1 shows development of fogged silver halide grains by Metol and ascorbic acid. Reaction 2 shows photobleach of fogged silver halide grains by exposure in the presence of Compound 1 as an electron acceptor. During exposure, Compound 1 is expected to exist as a hydrochloride, which is a strong electron acceptor. Reaction 3 shows neutralization of Compound 1 by a base in the developer to produce Compound 2 during development. Note that Compound 2 is no longer a strong electron acceptor. Reaction 4 shows the production of dihydropyridines by reduction of Compound 2 by developing agents. Assuming that Compound 2 follows the same reaction mechanism as that of 1-benzyl-3-carbamogylpyridinium salt used as a model compound in the negative emulsion system,[1] Compound 2 will be reduced to dihydropyridine derivatives such as 1-*n*-butyl-1,4-dihydro-4-(4'-pyridyl)pyridine or 1-*n*-butyl-1,2-dihydro-4-(4'-pyridyl)pyridine in the developer. An attempt to isolate those intermediates has not yet succeeded and is under way. Reaction 5 shows imagewise generation of active species of nucleation. It is assumed that reaction of dihydropyridines with the oxidation product of a developing agent will generate an active species for nucleation. Because the production of the oxidation product of a developing agent is an imagewise reaction, generation of the active species is also expected to be an imagewise reaction. Reaction 6 shows imagewise nucleation of silver halide grains by the active species derived from dihydropyridines. The active species will reduce photobleached silver halide grains in the vicinity of developed silver halide grains so that those photobleached silver halide grains become developable. Thus, it is expected that the onset of development of fogged silver halide grains that were not photobleached by the exposure leads to the nucleation and development of adjacent photobleached silver halide grains. Nucleation and development will continue until most grains in the vicinity of fogged silver halide grains are developed. Therefore overall development will become infectious development.

In a direct-positive emulsion, the oxidation product of a developing agent will be produced by the development of unexposed or underexposed fogged silver halide grains, instead of exposed silver halide grains in the case of a negative emulsion. Also, the silver halide grains to be nucleated in a direct-positive emulsion system will be silver halide grains photobleached by exposure instead of unexposed or underexposed silver halide grains in the case of a negative emulsion. This explains the results that, contrary to the case of a negative emulsion system, nucleation and infectious development of a direct-positive emulsion system lead to a decrease of the apparent photographic speed unless the fogging conditions are adjusted.

As described earlier, *n*-butyl viologen (Compound 3) did not give very high contrast in a direct-positive system, although it acted as an electron acceptor. The present results are consistent with the results previously reported, in which viologens such as *n*-butyl viologen (Compound 3) and methyl viologen did not give very high contrast in a negative emulsion system.[1]

Although reduction potentials of viologens depend on many factors, such as substituted alkyl groups, counter ions, and the solvent used to measure the redox potentials, the first reduction potentials of viologens are approximately in the range from – 0.45 to – 0.70 V versus



D:	Developing agent
Dox:	Oxidation product of developing agent
Nu:	Active species of nucleator

1 Development of fogged silver halide grains
2 Bleach of fog centers of silver halide grains by exposure in the presence of Compound 1
3 Production of Compound 2 by neutralization of Compound 1 in developer
4 Reduction of Compound 2 by a dihydropyridine by a developing agent
5 Imagewise generation of an active species of nucleation by the oxidation of a dihydropyridine with the oxidation product of a developing agent
6 Imagewise nucleation of bleached silver halide grains by the active species of nucleation
7 Development of nucleated silver halide grains

Figure 7. Possible mechanism for the production of very-high-contrast direct-positive images in the presence of Compound 1.

SCE[7,8] (redox potentials were converted to an SCE reference by subtracting 0.045 V from the value reported versus Ag/AgCl and 0.2412 V from the value reported versus NHE). For example, the half-wave potential for the first reduction step of n-butyl viologen is -0.45 V versus Ag/AgCl (or – 0.50 V versus SCE in acetonitrile.[8] Because redox potentials of viologens are more negative than that of Metol, it is expected that reduced viologens are more potent as developer than Metol. Since the first reduction step of viologen is reversible,[8,9] reduced viologen is considered to serve as a fast developer and release electrons to adjacent developable silver halide grains. If this reaction occurs, development will be accelerated. Although redox potentials of viologens are more negative than that of Metol, they are less negative than the threshold of redox potentials for dyes that work as spectral sensitizing dyes.[4,5] Therefore, it is assumed that reduced viologen does not have enough reducing power to reduce (nucleate) photobleached silver halide grains (or unexposed grains in the case of negative emulsion) and make the grains developable.

It may also be important that most of the viologen exists in an oxidized form, which acts as a strong electron acceptor, although a fraction of the viologen may be reduced by a developing agent. Even if an active species is produced during the development, the active species may be destroyed by viologen. Compound 1, which produced very high contrast in a direct-positive emulsion, is an electron acceptor during exposure but loses the electron-accepting ability by becoming Compound 2 during development, whereas Compound 3 (n-butyl viologen) remains an electron acceptor during development.

On the other hand, reduction peak potentials of pyridinium salts that showed very high contrast either in the negative or in the direct-positive system, including Compound 2, are in the range of – 0.90 to – 1.3 V versus SCE. Those values are much more negative than those of the viologens and are considered to be comparable to the threshold value of the redox potentials for spectral sensitizing dyes. For example, the reduction peak potential of Compound 2 is – 1.02 V versus SCE. Therefore, it is expected that the one-electron reduction product of a pyridinium salt is energetically able to become an active species for the nucleation if such a product is produced in the course of development. As reported in the previous article,[1] a pyridinium salt is reduced to a dihydropyridine, which has high electrochemical overpotential for oxidation and is relatively stable in the developer. Dihydropyridine acts as a source of two electrons and one proton and is able to produce a one-electron reduction product from pyridinium salts by one-electron oxidation followed by deprotonation.[10,11] A previous article demonstrated that 1-benzyl-1,4-dihydronicotinamide (a model dihydropyridine compound) produced very high contrast in the negative system.[1] The assumption was made that production of very high contrast was due to an imagewise nucleation of dihydropyridine and that the oxidation product of Metol was responsible for the imagewise nucleation. We assume that Compound 1 is neutralized and reduced to a dihydropyridine that serves as a nucleator in the same way it does for the case of 1-benzyl-1,4-dihydronicotinamide in the negative emulsion system.

Conclusions

A very-high-contrast direct-positive image was obtained by developing a prefogged direct-positive emulsion containing 1-n-butyl-4-(4'-pyridyl)pyridinium bromide hydrochloride (Compound 1) with a Metol/ascorbic acid developer. Electrochemical and photographic studies show that Compound 1 has two functions in a prefogged direct-positive emulsion: It acts as an electron acceptor in the emulsion during exposure and as a precursor of a nucleator, which increases contrast during development. It was suggested that the production of very high contrast is due to a nucleation reaction of 1-n-butyl-4-(4'-pyridyl) pyridinium bromide (Compound 2), which is produced by neutralization of Compound 1 during development. Comparison of the present results with the production of very high contrast by a pyridinium salt in the negative emulsion system indicates that a dihydropyridine is involved in the nucleation as an intermediate.

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