

Alkynylaminobenzoxazoles as Photographic Addenda

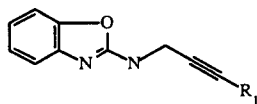
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Abstract

N-2-propynyl-2-benzoxazolamine (PBA) and N-2-butynyl-2-benzoxazolamine (BBA) are useful addenda for increasing the photographic speed of blue spectrally sensitized emulsions, as well as for improving latent image stability. The speed of a thin, tabular, run iodide emulsion can be increased two stops and its latent image effectively stabilized by the addition of BBA during chemical sensitization. Although the exact mechanism of these materials is not known, they appear to be reduction sensitizers imparting selective and controlled reduction characteristics to the surface of silver halide grains. Harnessing the potency of the alkynylaminobenzoxazoles requires application of surface and/or redox active co-addenda. Although nearly identical in structure, PBA and BBA do not always have the same photographic effect, but, rather, constitute a useful pair with one or the other being the addenda of choice depending on the emulsion type and/or sensitization procedure.

Introduction

N-2-propynyl-2-benzoxazolamine (PBA, Figure 1) was first described as a photographic addenda by Lok, Freeman, and Baum^{1a} in 1983. A year later they described the use of N-2-butynyl-2-benzoxazolamine^{1b} (BBA, Figure 1).



PBA: $R_1 = H$ BBA: $R_1 = CH_3$

Figure 1. Alkynylaminobenzoxazoles.

Both compounds were observed to increase fresh speed and to improve latent image keeping with a sulfur and gold sensitized, silver bromide, octahedral emulsion. The nonspectrally sensitized emulsion was treated with the alkynylaminobenzoxazole following chemical ripening.

Since the publication of these patents there have been additional patents dealing with the ability of alkynylaminobenzoxazoles to increase speed and stabilize latent image keeping.²

This paper describes the treatment of blue spectrally sensitized, thin, tabular, iodobromide emulsions with alkynylaminobenzoxazoles. Optimum use of these compounds produced substantial speed increases and improved latent image keeping as expected, but required the careful application of surface and/or redox active co-addenda.

Although the exact mechanism by which these materials act is unknown, it seems reasonable to assume they are reduction sensitizers in light of the following: (a) their photographic effect resembles that of known reduction sensitizers such as dimethylamineborane (DMAB), stannous chloride, and pH treatment;³ (b) Lok, Leone, and Williams described a ring closure reaction catalyzed by either Ag(I) or Au(I), whereby PBA or BBA led to a dihydropyrimidine which was observed to reduce Au(I) to Au(0).⁴ It seems likely that this same reaction sequence could also reduce Ag(I) to Ag(0).

Experimental

The emulsions utilized in this study are described in Table 1 and consisted of iodobromide tabular emulsions prepared by double-jet addition of silver and halide. The 'iodide in the run' refers to the amount of iodide added simultaneously with bromide. The 'iodide in the dump' is the amount of iodide dumped in the kettle during a pause in the precipitation. The thin, tabular emulsions studied here, such as E1 in Table 1, varied in size but were prepared and sensitized in a similar manner that has been previously described.^{2c}

TABLE 1. Emulsion Characteristics

Emulsion	Size ECD/Thkn (μm)	Iodide in Run (%)	Iodide in Dump (%)	Bromide Shell (%)	Total Iodide (%)
E1	2.80/0.065	3.16	0	5	3.0
E2	0.77/0.14	0	1.5	30	1.5
E3	1.42/0.12	1.5	3.0	30	4.05

Note: Size dimensions are equivalent circular diameter (ECD) and thickness. % Iodide is calculated on a molar basis based on the total make. Bromide shell is % of total silver precipitated.

The sensitization procedure for E1 and other run iodide, thin, tabular emulsions involved the sequential addition to the emulsion of sodium thiocyanate, a finish modifier (3-(2-methylsulfamoyl)ethyl)-benzothiazolium tetrafluoroborate), yellow sensitizing dyes (D1 and D2 in Figure 2) in equimolar amounts,⁵ optionally a dihydroxybenzene and an alkynylaminobenzoxazole,^{2f} followed by sulfur and gold sensitization with 1,3-dicarboxymethyl-1,3-dimethyl-2-thiourea and aurous bis(1,4,5-trimethyl-1,2,4-triazolium-3-thiolate). The emulsion was then incubated at 55 °C for 15 minutes, cooled to 40 °C, and 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene (TAI) or 5-bromo-4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene was added followed by 1-(3-acetamidophenyl)-5-mercaptotetrazole (APMT).

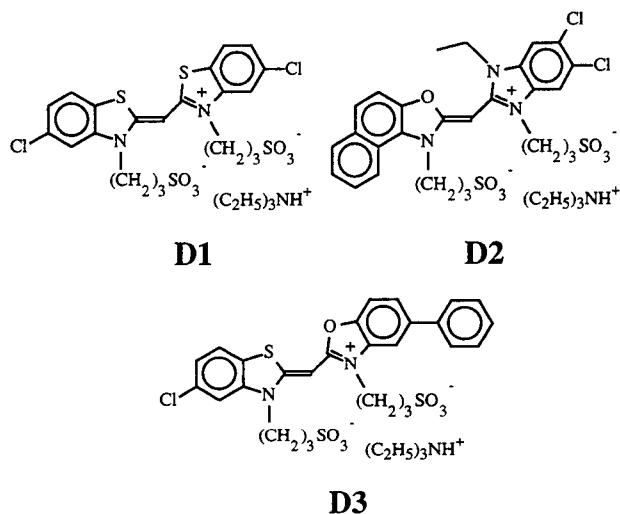


Figure 2. Yellow sensitizing dyes.

Emulsions E2 and E3 were prepared according to the method described by Johnson and Wightman.⁶ The sensitization procedure resembled that for E1 except dyes D1 and D3 were used in equimolar amounts,⁵ the APMT was added after the dye, the sulfur and gold sensitizers were sodium thiosulfate and sodium aurous thiosulfate, and the chemical ripening was at 65 °C for 5 minutes.

The emulsions were coated on cellulose acetate support in a simple single-layer format over a pad of gelatin with a gelatin overcoat to protect the coating from abrasion. The emulsion layer contained both a yellow image forming coupler and a yellow development inhibitor releasing

coupler as described previously.^{2e} Exposures were performed at 1/50 s, 5500 °C with a Kodak Wratten 2B filter. Processing was done in a standard C-41 color process for 3.25 min at 37.8 °C. D-min, or fog, is defined as the optical density observed through both the support and coated layer in the absence of exposure. Speed is measured as $\log E$ where E is the exposure in lux-sec necessary to produce a density 0.15 above D-min.

Raw stock keeping (RSK) changes are measured by first incubating a coating for 1 week at 48.9 °C/50% relative humidity (RH) and then exposing and immediately processing. Latent image keeping (LIK) changes are measured by first exposing the coating and then incubating as in the RSK experiment before processing. In both keeping experiments the control is a coating kept at 0 °C, exposed, and immediately processed with the incubated samples.

Results and Discussion

Although PBA and BBA are structural analogs differing in only a methyl group, the two compounds do not always produce the same effect. For instance, the addition of PBA or BBA to a uniform run iodide emulsion (E1) following chemical ripening produced very similar responses (Table 2) as suggested by Lok, Freeman, and Baum.^{1b} When the alkynylaminobenzoxazoles were added to emulsion E1 in a smaller amount before the chemical ripening step, BBA continued to perform well whereas PBA caused an increase in fog and a speed loss as described by Eikenberry, Lok, and Chen (Table 2).^{2e}

TABLE 2. Effect of Alkynylaminobenzoxazoles on Fresh Response

Emulsion	Additive	Level $\mu\text{mol}/\text{mol}$	Addition Point	D- min Gain	Speed Change
E1	PBA	100	After	0.01	0.09
E1	BBA	100	After	0.01	0.09
E1	PBA	10	Before	0.05	-0.22
E1	BBA	10	Before	0.02	0.12
E2	PBA	17	Before	0.06	0.40
E2	BBA	16	Before	0.09	0.34
E3	PBA	12	Before	0.05	-0.11
E3	BBA	11	Before	0.05	0.06

When the substrate was changed to a dump iodide emulsion (E2) and the addition preceded chemical ripening, both compounds gave a substantial speed increase with PBA slightly better than BBA. With a run/dump iodide emulsion (E3), PBA again caused a loss in speed while BBA yielded a modest increase.

Although the alkynylaminobenzoxazoles are useful with a variety of emulsions, BBA is especially effective with thin, tabular emulsions having a large surface area. This type of emulsion was used in the examples that follow. A speed increase of 2 stops was obtained when an emulsion 1.82 x 0.054 μm , with a surface area of 930 m^2/mol was treated with 30 $\mu\text{mol}/\text{Ag mol}$ of BBA (Figure 3).

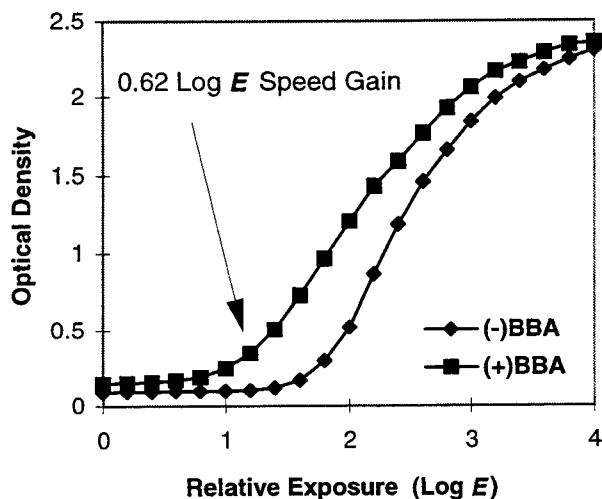


Figure 3. Effect of adding 30 $\mu\text{mol/Ag mol}$ BBA to a 3% run iodide emulsion, $1.82 \times 0.054 \mu\text{m}$, sensitized with 1.0 mmol/Ag mol D1 + 1.0 mmol D2.

Optimum use of alkynylaminobenzoxazoles requires the employment of two and sometimes three additional addenda. These addenda are from the family of tetraazaindenes, mercaptotetrazoles, and hydroxybenzenes. A tetraazaindene, such as TAI, is essential for controlling fresh fog. As can be seen in the time-of-development curves in Figure 4, the presence of TAI reduces fog at all development times (Curve B vs. Curve C).

The data in Figure 4 illustrate another aspect of emulsions treated with an alkynylaminobenzoxazole. The position of Curve B relative to the Curve A (+/- BBA) indicates an improvement in emulsion efficiency rather than increased development, since Curve B is clearly not an extension of Curve A.

APMT is useful for preventing an excessive increase in incubation fog. As can be seen in Figure 5, substantial reductions in fog were observed for two different emulsions treated with BBA and APMT and incubated for 1 week at 48.9 °C/50% RH. A slight increase in the speed gain after incubation was observed for emulsion E4 while a substantial reduction in speed gain was obtained for emulsion E5.

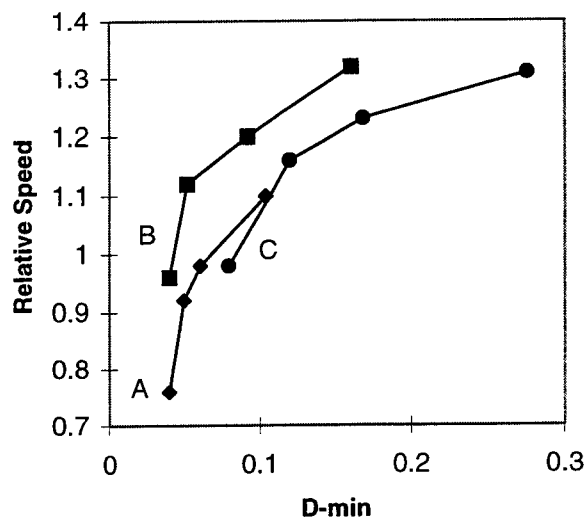


Figure 4. Speed vs. D-min for development times of 2.0, 3.25, 4.5, and 5.75 min using a 3% run iodide emulsion, $2.29 \times 0.050 \mu\text{m}$.

Curve A: 1 g/Ag mol TAI.

Curve B: 1g TAI + 50 $\mu\text{mol/Ag mol}$ BBA.

Curve C: 50 $\mu\text{mol/Ag mol}$ BBA.

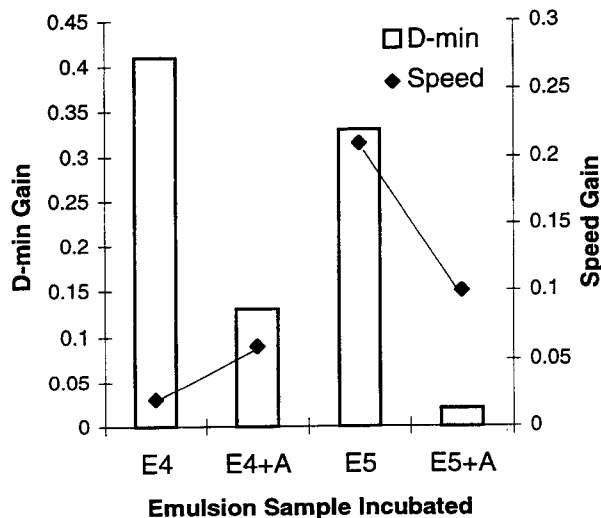


Figure 5. Effect of APMT (A) on D-min and speed gain following incubation at 48.9 °C/50% RH for 1 week. Two different 3% run iodide emulsions were studied. E4 is $2.97 \times 0.058 \mu\text{m}$ and was treated with 20 $\mu\text{mol/Ag mol}$ of BBA + 100 mg of APMT. E5 is $1.82 \times 0.054 \mu\text{m}$ and was treated with 10 $\mu\text{mol/Ag mol}$ BBA + 200 mg of APMT.

A third additive can be used when excessive fog occurs inexplicably with certain emulsions treated with BBA.^{2f} Disulfocatechol, disulfohydroquinone, and monosulfohydroquinone (DSC, DSH, and MSH respectively, in Figure 6) all proved useful for this purpose with the hydroquinones effective at a much lower concentration (Figure 7). The speed gain induced by BBA was increased 0.02 to 0.07 by these addenda.

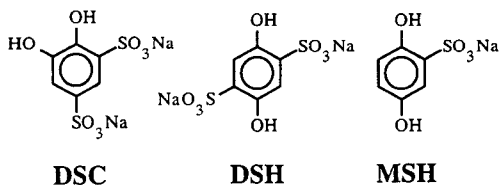


Figure 6. Dihydroxybenzenes Useful for Controlling Fog.

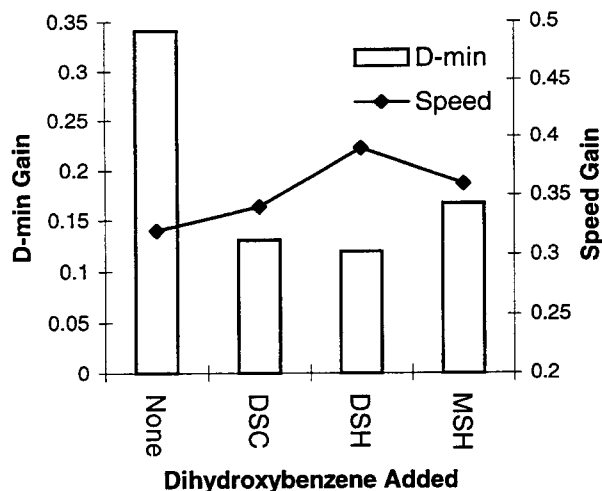


Figure 7. Effect of different dihydroxybenzenes on D-min and speed gains observed when a 3.2% run iodide emulsion, $3.20 \times 0.055 \mu\text{m}$, was treated with $26.9 \mu\text{mol/Ag mol}$ BBA. DSC added at 100 mg/Ag mol , DSH and MSH at 10 mg . D-min and speed gains are relative to a sample sensitized identically but without BBA or

The mechanism of the antifoggant activity is not clear since these dihydroxybenzenes have neither an affinity for silver ions nor the ability to oxidize metallic silver. Because these compounds do have reductive potential through the formation of quinones, possibly they are interrupting a redox reaction that leads to fogging silver clusters.

The employment of spectral sensitizing dyes influence the speed/fog position resulting from the addition of BBA. For instance, larger speed gains were observed when BBA was used in conjunction with dyes D1 and/or D2 (Figure 8). The biggest gain in speed occurred at a D1/D2 ratio of 1/2, while the smallest D-min gain was found at a 2/1 ratio. Attempts at treating magenta or cyan dyed emulsions with

PBA or BBA prior to chemical ripening have led to excessive fog.

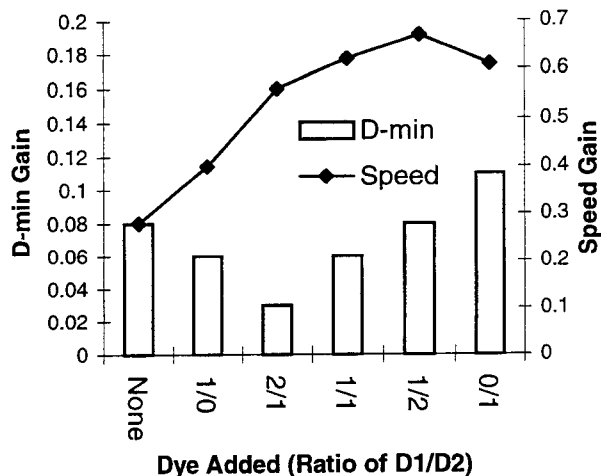


Figure 8. Effect of different sensitizing dyes on D-min and speed gain when a 3.0% run iodide emulsion, $1.82 \times 0.054 \mu\text{m}$, was treated with $30 \mu\text{mol}$ of BBA/Ag mol. Total dye added was 2.0 mmol/Ag mol .

Generally, the speed increase obtained by treating these emulsions with BBA is limited by two factors: (a) the increase in D-min; (b) the ability to sustain the speed in the coated format as the film ages. As can be seen in Figure 9, speed continues to increase with increasing amounts of BBA, but beyond a certain point (ca. $32 \mu\text{mol}$ BBA) the increase in speed diminishes and is not worth the increase in fog.

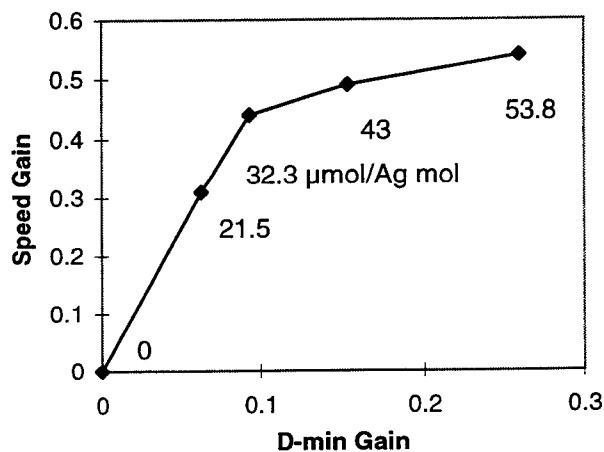


Figure 9. Speed gain vs. D-min gain resulting from the addition of BBA in increasing amounts to a 3% run iodide emulsion, $2.80 \times 0.053 \mu\text{m}$.

The effect of increasing levels of BBA on the raw stock keeping (RSK) and latent image keeping (LIK) is shown in Figure 10. In this example, a single yellow emulsion was coated as before, except that the gelatin pad was replaced

with a magenta dye forming layer on top of a cyan dye forming layer to simulate a multilayer film capable of complete color reproduction.

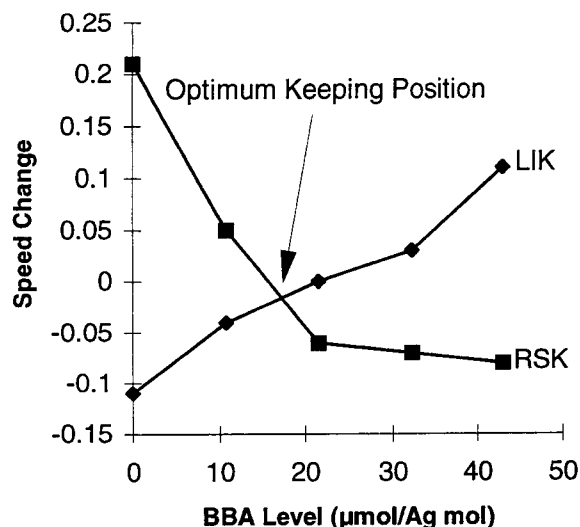


Figure 10. Speed changes vs. BBA level after 1 week keeping at 48.9 ° C and 50% RH with a 3% run iodide emulsion, 3.08 x 0.055 µm. RSK and LIK defined in Experimental Section.

Note that the RSK speed gain observed with the untreated emulsion becomes a speed loss above about 15 µmol BBA/Ag mol. Likewise, the LIK speed loss seen in the absence of BBA becomes a speed gain at about the same point making this level of BBA optimum for keeping. In effect, BBA acts as a titrant capable of taking the emulsion to a stable keeping position.

It is worth noting that this LIK behavior resembles that described by Christianson who studied a blue spectrally sensitized, iodobromide emulsion treated with DMAB.^{3a} Christianson's explanation for the LIK behavior observed seems reasonable here if we assume BBA is a reduction sensitizer. His explanation is based on reduction sensitization producing small silver centers or clusters capable of bleaching dye-trapped holes, which would otherwise attack latent image over time. These silver clusters not only protect the latent image, but can intensify latent subimage through electron release that occurs in the bleaching process, thereby leading to LIK speed gains.

Guo and Hailstone's discussion of reduction sensitization^{3b} furnishes a possible explanation for the RSK behavior. They review proposals that reduction sensitization can lead to silver clusters capable of acting as either electron traps ('P' centers) or as hole traps ('R' centers). Guo and Hailstone interpreted work by Tani and Murofushi⁷ as demonstrating formation of 'R' centers (speed gains) at low reduction sensitizer levels and then formation of 'P' centers (speed losses) at high reduction sensitizer levels.^{3b}

If we assume that the RSK speed gain, observed in Figure 10, in the absence of BBA originates in the formation of 'R' centers caused by reducing impurities in the coated gelatin matrix, then the approach of the RSK speed change

to 0 with increasing BBA could be explained by the formation of these same 'R' centers by BBA during sensitization. In effect, the incubation speed gain is replaced by a fresh speed gain because the 'R' centers that would have formed on incubation are already present in the fresh coating.

The RSK speed losses at higher BBA levels might originate either in the conversion over time of 'R' centers to 'P' centers, or the formation of incipient 'P' centers that become active in trapping electrons only after incubation in the coated matrix. The formation of 'P' centers should have less effect on LIK, since they occur after latent image formation.

Conclusions

1. Alkynylaminobenzoxazoles provide a means of increasing and stabilizing the speed of blue sensitized, thin, tabular emulsions.
2. These compounds appear to act as reduction sensitizers with their effect dependent on the emulsion type and the sensitizing dye employed.
3. Small changes in the structure of the alkynylaminobenzoxazole can have a profound effect on photographic response.
4. A tetraazaindene, a mercaptotetrazole, and a dihydroxybenzene are useful as co-addenda with the alkynylaminobenzoxazole for controlling fog.

Acknowledgment

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