Methode 2. Bis(N-2-pyrrolylmethylen-*p*-chloranilin)-Kupfer(ii)—Chelat : Eine Mischung von 0.2 g Imin (Ⅶ) in 6 ccm EtOH und 0.1 g $(AcO)_2Cu \cdot H_2O$ in 10 ccm H_2O wurden im Scheide-trichter durchgeschüttelt. Die organische Schicht wurde von der wässerigen abgetrennt und bei Zimmertemperatur stehengelassen. Die dunkelvioletten Kristalle kristallisierte man aus AcOEt um.

Die Eigenschaften sowie die analytischen Daten sind in Tabelle Ⅲ zusammengefaßt.

Es sei besonders Herrn Prof. Toyozo Uno für seine Unterstützung dieser Arbeit gedankt. Die Autoren danken auch dem Mikroanalytischen Laboratorium der Universität Kyoto für die Mikroanalysen und Herrn K. Machida und Frl. I. Uchida für die Messungen der Infrarot Spektren.

Zusammenfassung

Es wurden N-2-Pyrrolylmethylen-anilin, -*p*-toluidin, -1-naphthylamin, -2-naphthylamin, -*p*-anisidin, -*p*-phenetidin, -*p*-chloranilin und -*p*-bromanilin dargestellt. Schwach basische Amine, z.B. *p*-Nitroanilin und *m*-Aminobenzolsulfonsäure, reagierten nicht mit 2-Pyrrolcarboxaldehyd. Die erhaltenen N-2-Pyrrolylmethylenamine erzeugten mit Eisen (iii), Kobalt(ii), Kupfer(ii), Palladium(ii), Silber, Platin(iv), Gold(iii) und einigen anderen Metallen gefärbte Niederschläge, die in Essigsäure Äthylester löslich waren. N-(1-Methyl-2-pyrrolylmethylen)-*p*-toluidin verhielt sich anders als das unsubstituierte Imin (Ⅱ). Die Kupferchelate sind tiefblaue bzw. schwarze Kristalle, die in Essigsäure Äthylester die Absorptionsmaxima bei 350∼380 mμ haben, und enthalten Kupfer und Liganden im Verhältnis von 1:2. Bei der Komplexbildung verschob sich nach wenigen Frequenzen bei 10 bis 20 cm^{-1} die C=N Bande in der Nähe 1620 cm^{-1}.

(Eingegangen am 17. Oktober, 1960)

UDC 77.012 : 547.785.5 : 546.57

96. **Kiyoshi Futaki** : Influences of Benzazoles and Related Compounds on the Color of Developed Silver from Liquid Photographic Emulsion.

(*Photographic Division, Mitsubishi Paper Mills Co., Ltd.*[*1])

It is well known that certain compounds show marked effect on the color of developed silver images if they are added to photographic emulsions or developers. Previous papers[1,2] of this series dealt with the influences of some active heterocyclic compounds on the color of developed silver with relation to the chain length of their alkyl substituents, and demonstrated the usefulness of the "liquid emulsion technique" for testing the effect of additions to emulsions.

The present paper deals with further application of the same technique for studying the influences of some benzazoles and related compounds on the color of developed silver. Names and structural formulae of the compounds tested (25 in all) are listed in Table I. Effect of heterocyclic rings, fused benzene ring, and some functional groups in the compounds on the color of developed silver is also discussed on the basis of properties of the compound such as dissociation constant or adsorbability on the surface of silver chloride.

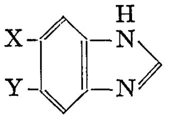
[*1] Nagaoka-cho, Otokuni-gun, Kyoto (二木 清).

1) K. Futaki, Y. Ohyama, T. Iwasaki : Phot. Sci. & Eng., **4**, 97 (1960).

2) K. Futaki : Nippon Shashin Gakkai Kaishi, **24**, 8(1961).

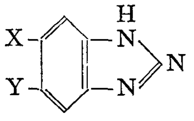
Table I.

(I) Benzimidazoles



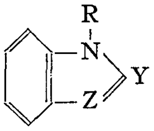
	X	Y	
a)	H	H	Benzimidazole
b)	CH_3	CH_3	5,6-Dimethylbenzimidazole
c)	Cl	H	6-Chlorobenzimidazole
d)	NC	H	6-Cyanobenzimidazole
e)	O_2N	H	6-Nitrobenzimidazole

(II) Benzotriazoles



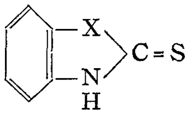
	X	Y	
a)	HO_3S	H	Benzotriazole-5-sulfonic acid
b)	NC	H	5-Cyanobenzotriazole
c)	H	H	Benzotriazole
d)	Cl	H	5-Chlorobenzotriazole
e)	CH_3O	H	5-Methoxybenzotriazole
f)	CH_3	CH_3	5,6-Dimethylbenzotriazole

(III) Benzazoles



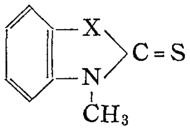
	R	Y	Z	
a)	CH_3	N	N	1-Methylbenzotriazole
b)	H	N	CH	1*H*-Indazole

(IV) Benzazoline-2-thiones



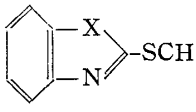
a)	X=NH	2-Benzimidazolinethione
b)	X=O	2-Benzoxazolinethione
c)	X=S	2-Benzothiazolinethione

(V) 3-Methylbenzazoline-2-thiones



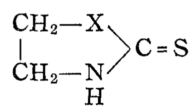
a)	$X=N(CH_3)$	1,3-Dimethyl-2-benzimidazolinethione
b)	X=O	3-Methyl-2-benzoxazolinethione
c)	X=S	3-Methyl-2-benzothiazolinethione

(VI) 2-Methylthiobenzazoles



a)	$X=N(CH_3)$	1-Methyl-2-methylthiobenzimidazole
b)	X=O	2-Methylthiobenzoxazole
c)	X=S	2-Methylthiobenzothiazole

(VII) Azolidine-2-thiones



a)	X=NH	2-Imidazolidinethione
b)	X=O	2-Oxazolidinethione
c)	X=S	2-Thiazolidinethione

Experimental

Development——The experimental procedure used in the present work is identical with that reported in the previous paper,[1] i.e., a photographic silver chloride stock emulsion was diluted with 1% gelatin solution and was developed in liquid state for 10 min. at 25° by a dilute Phenidone-hydroquinone developer after adding a small amount of one of various organic compounds. The development was stopped and the emulsion was fixed by adding a small portion of a stop solution and a fixer in succession. Finally, spectrophotometric density of silver dispersion was measured. The compositions of the photographic emulsion and the processing solutions used in the present experiments were also identical with those used in the previous work.

Apparent Acidic Dissociation Constants——Approximately 0.01*N* solution of compounds in 50% MeOH was titrated potentiometrically with 0.1*N* NaOH at 25°. The pH at the half neutralization point was taken as the pKa′.

Amount of Compounds Adsorbed on Silver Chloride——The quantity of compound adsorbed from neutral solution was determined as follow : The same silver chloride emulsion (stock emulsion) as described above was diluted 50 times with H_2O in this case instead of 1% gelatin solution, 10 cc. of this diluted emulsion was mixed with 0.5 cc. of a solution of one of various agents in MeOH, and kept at 25° for 30 min. in a weighing bottle. The liquid emulsion was then centrifuged and the amount of unadsorbed compound in the supernatant solution was measured photometrically using a Beckman-type spectrophotometer.

The blank solution was prepared in the following manner : 10 cc. of the diluted emulsion described above was mixed with 0.5 cc. of MeOH and centrifuged to remove AgCl (pH of the emulsion prepared by diluting the AgCl stock emulsion with 1% gelatin solution was 6.30 and that of the emulsion prepared by diluting it with H_2O was 6.40).

The quantity of compound adsorbed from alkaline medium resembling a developing system was determined as follow : The AgCl stock emulsion was diluted 50 times with H_2O and 4 cc. of this diluted emulsion was mixed with 0.2 cc. of a MeOH solution of one of various agents. 4 cc. of an aqueous solution prepared from Na_2CO_3 and KBr in the same concentration as the developer was then added. This liquid emulsion mixture was kept at 25° for 30 min. and centrifuged. The amount of unadsorbed addition agent was measured photometrically (pH of the liquid prepared by mixing an aqueous solution of Na_2CO_3 and KBr with that diluted with 1% gelatin solution was 10.60, and that of the liquid prepared by mixing an aqueous solution of Na_2CO_3 and KBr with the emulsion diluted with H_2O was 10.92).

The samples and each wave length used in colorimetric determination are shown in Table II.

Table II. Wave-length used in Colorimetry

Compound	neutral (pH 6.40) (mμ)	alkaline (pH 10.92) (mμ)
Benzimidazole (Ia)	271	271
6-Chlorobenzimidazole (Ic)	279	279
6-Cyanobenzimidazole (Id)	262	282
6-Nitrobenzimidazole (Ie)	310	346
Benzotriazole-5-sulfonic acid (IIa)	261	—
Benzotriazole (IIc)	258	—
1-Methylbenzotriazole (IIIa)	264	—
1,3-Dimethyl-2-benzimidazolinethione (Va)	303	—
3-Methyl-2-benzoxazolinethione (Vb)	295	—
3-Methyl-2-benzothiazolinethione (Vc)	321	—
2-Methylthiobenzothiazole (VIc)	281	—

Results and Discussion

1. Benzimidazoles and Benzotriazoles

Benzimidazoles (I) : As a typical example of this group of compounds, the spectrophotometric densities of the developed silver dispersions containing 5-nitrobenzimidazole are shown in Table III and Fig. 1. The curve for the control (broken line) shows strong

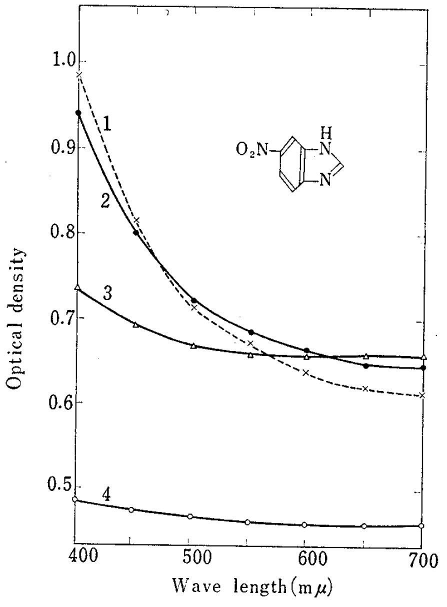


Fig. 1.

Spectrophotometric Curves for Silver developed with Various Amounts of 5-Nitrobenzimidazole

Concentration in mole/mole AgCl
1 : control
2 : 1×10^{-2}
3 : 2.5×10^{-2}
4 : 5×10^{-2}

Table III. Spectrophotometric Density and Color Ratio for Silver Developed with Various Amounts of 5-Nitrobenzimidazole

Wave length (mμ) / Amt. added (mole/mole AgCl)	Density (D)							Color ratio D(400 mμ)/D(700 mμ)
	400	450	500	550	600	650	700	
None	0.980	0.815	0.715	0.678	0.638	0.620	0.615	1.59
1×10^{-2}	0.940	0.805	0.720	0.680	0.658	0.647	0.650	1.45
2.5×10^{-2}	0.735	0.693	0.668	0.650	0.639	0.637	0.638	1.15
5×10^{-2}	0.487	0.474	0.469	0.462	0.459	0.460	0.460	1.06

absorption at a shorter wave length. With increasing concentration of this compound the photometric density at longer wave length increases with the color shifting to blue-black.

According to the proposal of James and Vanselow,[3] the ratio of the density measured at 400 mμ to that at 700 mμ was taken as the indication of "color" of the silver dispersion. The color ratio, however, varies slightly from one experiment to another, because of the inevitable variation of conditions. To eliminate this slight variation and to smooth out the data obtained, adjusted color ratios were used for comparison of the results. This is accomplished by adjusting the ratio of the control to 1.70.

The effect of some benzimidazoles on the color ratio is shown in Fig. 2. As indicated in this figure, the nitro compound (Ie) shows the strongest blue-black toning effect among the substituents of this group of compounds and the effect tends to decrease with decreasing electron-attraction effet of a substituent in the order of nitro, cyano, chloro, and hydrogen.

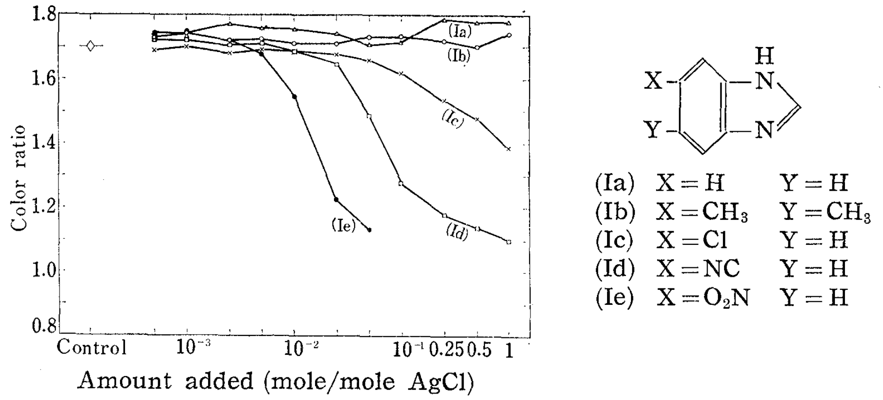


Fig. 2. Relationship between Color Ratio and Amount of Various Derivatives of Benzimidazole added

The hydrogen atom bonded to nitrogen atom in the imidazole ring tends to dissociate more easily to a proton with increasing electron-attraction effect of a substituent at 5- or 6-position of the compound. The apparent acidic dissociation constant of these compounds is shown in Table IV. The dissociation constants of the compounds, (Ib), (Ia), and (Ic), as acid were however too small and could not be determined by potentiometric titration.

Table IV. Apparent Acidic Dissociation Constants of Benzimidazoles

Compound	pKa′ as acid (in 50% MeOH)	pKa′[4] as base (in 50% EtOH)
5,6-Dimethylbenzimidazole (Ib)	>11.5	5.48
Benzimidazole (Ia)	>11.5	4.98
5-Chlorobenzimidazole (Ic)	>11.5	3.92
5-Cyanobenzimidazole (Id)	11.05	—
5-Nitrobenzimidazole (Ie)	10.68	2.68

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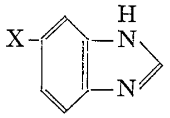
3) T. H. James, W. Vanselow: Phot. Sci. & Eng., **1**, 104 (1958).

As is known, these compounds are amphoteric and their pKa′ as base[4] are shown in the Table for reference. It is expected that, in this class of compounds, pKa′ as acid increases with increasing pKa′ as a base and therefore acidic dissociation constant as acid can be expected to decrease in the order of (Ie), (Id), (Ic), (Ia), (Ib). Comparison of this Table and Fig. 2 indicates that blue-black toning effect increases with increasing value of the acidic dissociation constant (i.e., decreasing pKa′) of the compounds as acid.

In neutral photographic emulsion, all of these compounds were hardly adsorbed on the surface of silver chloride, but in emulsion at sodium carbonate-alkalinity of developing condition, as shown in Table V, the amount of compounds adsorbed increases with increasing dissociation constant as acid. Each value listed in the Table is the amount absorbed during 30 minutes in the alkaline emulsion. However, quantity of compound adsorbed during development is perhaps smaller than the values listed in the Table, because most of silver chloride grains in the emulsion are reduced to silver in only 5 minutes by the development. These experimental observations indicate that blue-black toning effect of benzimidazoles is strictly related to their dissociation constant as acid and, though these compounds are not adsorbed on silver chloride before development, they are adsorbed at alkaline pH of developer and show blue-black toning effect. The fairly good correlation between adsorbability of the compounds and acidic dissociation constant leads to the assumption that these compounds are possibly adsorbed as an anion on silver chloride.

TABLE V. Amount of Benzimidazoles adsorbed in Na_2CO_3 Alkaline Solution



Amount of Compd. added (mole/mole AgCl)	Amount adsorbed (%)			
	H	Cl	CN	NO_2^-
1×10^{-1}	3.0	3.2	12.5	18
5×10^{-2}	4.5	5.2	14	21
2.5×10^{-2}	6.0	8.0	18	26
1×10^{-2}	10	11.5	24	34

Benzotriazoles (II) and Related Compounds: Spectrophotometric densities of the developed silver with increasing amount of benzotriazole (IIc) are shown in Fig. 3. Effect

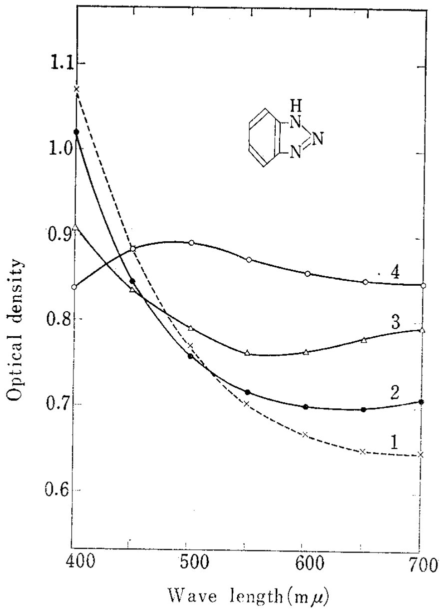


Fig. 3.

Spectrophotometric Curves for Silver developed with Various Amounts of Benzotriazole

Concentration in mole/mole AgCl
1 : control
2 : 5×10^{-3}
3 : 2.5×10^{-2}
4 : 1×10^{-1}

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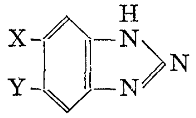
[4] M.T. Davies, P. Mamalis, V. Petrow, B. Sturgeon: J. Pharm. Pharmcol., 3, 420 (1951).



(IIa) X=HO_3S Y=H
(IIb) X=NC Y=H
(IIc) X=H Y=H
(IId) X=Cl Y=H
(IIe) X=CH_3O Y=H
(IIf) X=CH_3 Y=CH_3

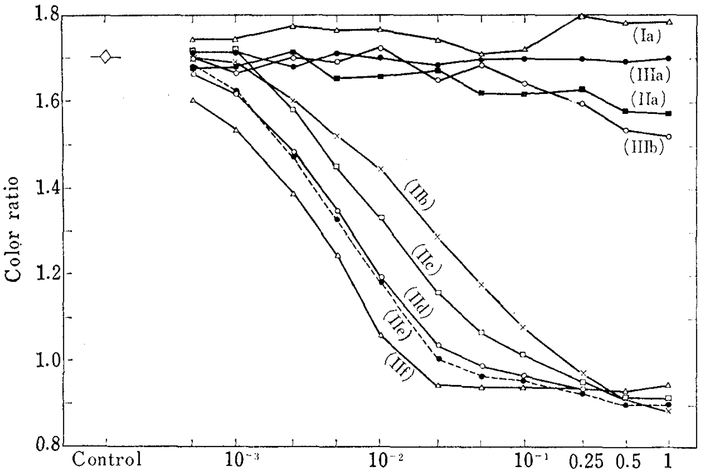
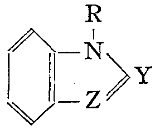


Fig. 4. Relation between Color Ratio and Amount of Some Benzotriazoles and Related Compounds added



(Ia) R=H Y=CH
Z=N
(IIIa) R=CH_3 Y=N
Z=N
(IIIb) R=H Y=N
Z=CH

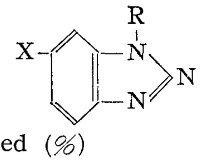
of the amount of some benzotriazoles (IIa∼IIf) and of related compounds (IIIa and IIIb) on the color ratio of the developed silver is shown in Fig. 4. As indicated in this Figure, benzotriazole (IIc) shifts markedly the color of developed silver towards blue-black with increasing amount of the agent added. Benzotriazole (IIc) has a hydrogen atom bonded to nitrogen atom in the molecule. This hydrogen atom is dissociable as a proton in alkaline solution. Such type of hydrogen generally plays an important rôle. For example, 1-methylbenzotriazole (IIIa), in which this type of dissociable hydrogen atom is substituted by a methyl group, does not show any toning effect. Moreover, it is quite interesting that benzimidazole (Ia) and indazole (IIIb) are almost inactive in spite of the close resemblance of their chemical structure to that of benzotriazole (IIc). As shown in Table IV,

Table VI. Apparent Acidic Dissociation Constants of Benzotriazoles

Compound	pKa′ as acid in 50% MeOH	Compound	pKa′ as acid in 50% MeOH
5,6-Dimethylbenzotriazole (IIf)	9.30	5-Chlorobenzotriazole (IId)	7.70
5-Methoxybenzotriazole (IIe)	8.82	5-Cyanobenzotriazole (IIb)	6.58
Benzotriazole (IIc)	8.76		

pKa′ of benzotriazole (IIc) is 8.76 and that of benzimidazole (Ia) is larger than 11.5. In spite of structural resemblance, dissociation constants of the latter compound as acid is much smaller than that of the former. The dissociation constant is probably related to the adsorbability of the compound on silver chloride. As shown in Table VII, benzotriazole can be adsorbed on silver chloride, but 1-methylbenzotriazole (IIIa) which has no dissociable hydrogen atom is hardly adsorbed. Therefore, dissociable hydrogen atom in the molecule of benzotriazole also plays an important rôle in this case.

Table VII. Amount of Benzotriazoles adsorbed



Amount of Compd. added (mole/mole AgCl)	Amount adsorbed (%)		
	(IIc) R=H, X=H	(IIa) R=H, X=HO_3S	(IIIa) R=CH_3, X=H
1×10^{-1}	4.6	0	0.7
5×10^{-2}	8.0	0	0
2.5×10^{-2}	15	0	0
1×10^{-2}	28	0	0

In order to investigate in more detail the relationship between activity of the agents and their acidic dissociation constants, several derivatives (IIa~IIf) of benzotriazole substituted in the benzene ring were synthesized and tested. As shown in Fig. 4 and Table VI, expected correlation was not found between the activity of the agent and acidic dissociation constant. However, dissociation constant of each compound (II) is far larger than that of benzimidazoles (I), and each of the compounds (II) except (IIa) shows strong blue-black toning effect. It seems that the dissociation constant is also important in this case, but other unknown factors also affect the activity of a compound and the results obtained are confusing. The reason why benzotriazole-5-sulfonic acid (IIa) does not affect the color of developed silver is perhaps due to its very slight adsorbability as shown in Table VII. Sulfonic group prevents adsorption of the compound, as a result of very high solubility or electrostatic repulsion from colloidal silver chloride.

2. Heterocyclic Thiones and Related Compounds

Benzazoline-2-thiones (IV) and Azolidine-2-thiones (VII) : Fig. 5 is a typical example in the group of these compounds (VII). The tendency of the absorption by the developed silver to increase in the longer wave length with increasing concentration of 2-imidazolidinethione (VIIa) is very marked. The relationship between the color ratio and the amount of (IV) and (VII) added is shown in Fig. 6.

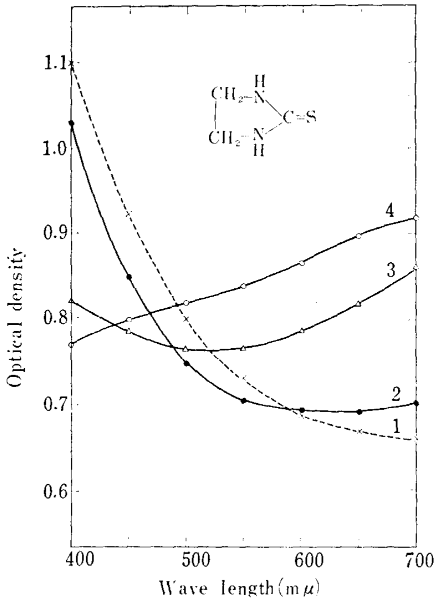
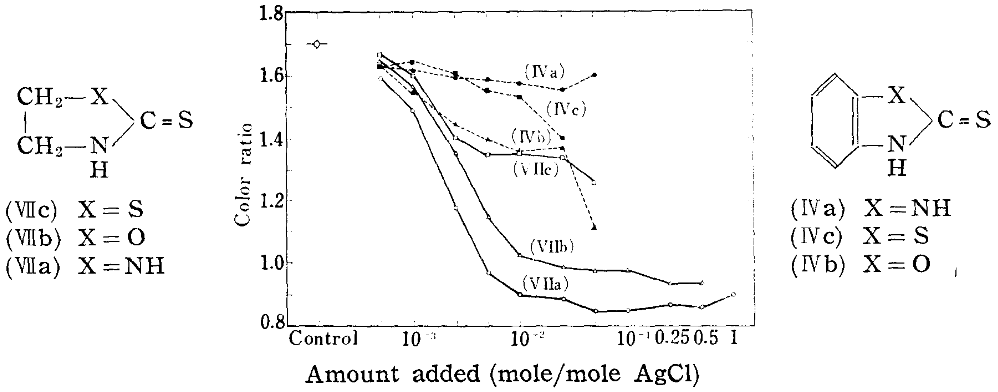


Fig. 5.

Spectrophotometric Curves for Silver developed with Various Amounts of Imidazolidine-2-thione

Concentration in mole/mole AgCl
1 : control
2 : 1×10^{-3}
3 : 5×10^{-3}
4 : 5×10^{-2}



Amount added (mole/mole AgCl)

Fig. 6. Relationship between Color Ratio and Amount of Benzazoline-2-thiones and Azolidine-2-thiones added

The effect of benzene ring of the molecule of such heterocyclic thiones as (IV) is very distinct and azolidines (VII) show stronger blue-black toning action than corresponding benzazoline-2-thiones (IV); for example, 2-imidazolidinethione (VIIa) surpasses 2-benzimidazolinethione (IVa) in the blue-black toning activity, as does 2-oxazolidinethione (VIIb) over 2-benzoxazolinethione (IVb) and 2-thiazolidinethione (VIIc) over 2-benzothiazolinethione (IVc). These observations are comparable with the effect of alkyl group substituted at the 2-position of 1,3,4-oxadiazoline-5-thiones in which the color of the developed silver became more blue-black with decreasing number of carbon atoms in the alkyl chain.[1]

3-Methylbenzazoline-2-thiones (V) and 2-Methylthiobenzazoles (VI): As a typical example of this group of compounds, the spectrophotometric density of the developed silver dispersions containing 3-methyl-2-benzothiazolinethione (Vc) is shown in Fig. 7. The effect of (V) and (VI) on the color ratio of developed silver is shown in Fig. 8. 2-Alkylthiobenzazoles (VI) are almost inactive, while 3-methyl-2-benzazolinethiones (V), isomer of (VI), show blue-black toning action, and the effect of 1-methyl-2-benzothiazolinethione (Vc) is especially marked. 3-Methyl-2-benzoxazolinethione (Vb) does not show any noticeable effect. As previously reported,[2] however, the color of the developed silver shifts towards blue-black with increasing number of carbon atoms in the alkyl chain substituted at the 3-position of this molecule. These results indicate that the effect of heterocyclic thione group on blue-black toning action is far stronger than that of thio-ether group.

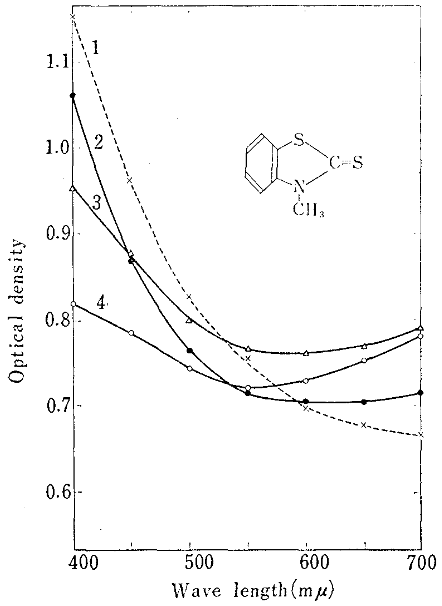


Fig. 7.

Spectrophotometric Curves for Silver developed with Various Amounts of 3-Methyl-2-benzothiazolinethione

Concentration in mole/mole AgCl

1 : control
2 : 5×10^{-3}
3 : 2.5×10^{-2}
4 : 1×10^{-1}

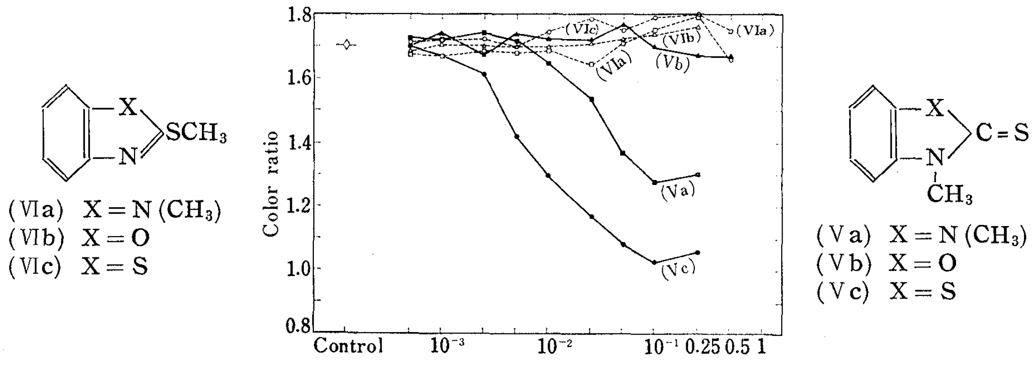


Fig. 8. Relationship between Color Ratio and Amount of 3-Methylbenzazoline-2-thiones and 2-Methylthiobenzazoles added

Table VIII. Amounts of 3-Methyl-2-benzothiazolinethione (Vc) and 2-Methylthiobenzothiazole (VIc) adsorbed

Amount of Compd. added mole/mole AgCl	Amount adsorbed (%)		Amount of Compd. added mole/mole AgCl	Amount adsorbed (%)	
	(Vc)	(VIc)		(Vc)	(VIc)
1×10^{-1}	31	5.2	2.5×10^{-2}	23	10
5×10^{-2}	33	7.2	1×10^{-2}	41	13.5

Results of adsorption experiment indicate that that adsorbability of thione compounds is larger than that of corresponding thio-ether compound, as shown in Table VIII.

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Summary

The effect of benzazoles and related compounds (I to VII; 25 in all) on the color of the developed silver image was examined with a liquid silver chloride emulsion developed by a dilute Phenidone-hydroquinone developer. Blue-black toning effect was found to be related strictly to adsorbability of the compound. Relative importance of acidic dissociation constant of benzimidazoles (I) was recognized.

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97. **Tyunosin Ukita***[1] **and Ryuzo Takeshita***[2] : Organic Phosphates. XV.*[3] Synthesis and Alcoholysis Reaction of 4,4'-Dinitrohydrobenzoin Cyclic Phosphate.*[4]

(*Faculty of Pharmaceutical Sciences, University of Tokyo**[1])

As has been reported in the previous paper[1] of this series, the alcoholysis of hydrobenzoin cyclic phosphate and subsequent hydrogenolysis or acid hydrolysis of the reaction products gave the monophosphate of the alcoholic compounds used. Thus, this cyclic phosphate was found to be available as a novel phosphorylation agent for hydroxylic compound. However, this type of reaction was found most appropriate for primary alcohols which have relatively simple structure, while some polyfunctional hydroxylic compounds, i.e. erythritol and carbohydrates such as hexose, did not alcoholyse this cyclic phosphate under the condition used.

In the present work, as a further study on this type of reaction, 4,4'-dinitrohydro-

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*[1] Hongo, Tokyo (浮田忠之進).

*[2] Present Address : Institute of Public Health, Shirokane-Daimachi, Minato-ku, Tokyo (竹下隆三).

*[3] Part XIV : This Bulletin, **9**, 544 (1961).

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