Conversion of silver images on silver halide photographic materials into silverless ones consisting of iron(III) chelates with 8-sulfanylquinoline and some of its derivatives

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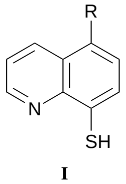
The formation processes of silverless photographic images consisting of iron(III) chelates with 8-sulfanylquinoline, 5-thiomethyl-8-sulfanylquinoline and 5-bromo-8-sulfanylquinoline from an initial silver image on silver halide photographic layers by three-stage chemical processing (bleaching, fixing and toning) have been obtained and analysed. It has been determined that the redox process $Fe^{II} \rightarrow Fe^{III}$ takes place here and, also, the image carriers are $Fe(OH)_2$, FeO(OH) and the corresponding coordination compounds with an Fe^{III} ion–organic ligand ratio of 1 : 3.

One of the most important problems in the modern chemical–photographic industry is known to be the world silver economy, because this industry consumes about one third of the silver produced in the world.[1] No doubt this situation will remain at least until the end of the twentieth century. One of the possible ways of solving this problem is to change from the use of silver as the photographic image carrier, to cheaper organic compounds, which are formed in the modern colour silver halide photography. However, such silverless images are very unstable to light and harsh conditions. It has been established[2–10] that chelate complexes of such 3d element ions as Ni^{II},[2,5,7,8,10] Co^{III} [2,4] and Cu^{II},[2,3,6,9] which exhibit highly intense absorptions in the visible spectrum, do not have this defect. However, from the practical point of view, the most suitable metal–organic compounds for the production of silverless photographic images are Fe^{II} and Fe^{III} complexes, because iron compounds are the cheapest and least scarce in comparison with analogous compounds of the other d-block elements.[11] Unfortunately, most Fe^{II} and Fe^{III} complexes have weak absorption in the visible spectrum, comparatively high solubility in water, or high kinetic lability. Because of these factors, iron compounds are essentially unfit for use as possible carriers of silverless photographic images. Nevertheless, it may be expected, based on coordination chemistry principles, that Fe^{II} or Fe^{III} complexes with 8-sulfanylquinoline and its derivatives (**I**; R = alkyl, aryl, Hal, sulfanyl, thioalkyl), might be suitable for the formation of silverless photographic images. This paper is devoted to determination of whether the above-mentioned complexes can be used as carriers of such images.



I

Experimental

RT-12 radiographic commercial film, intended for recording hard ionizing radiation and with a surface silver concentration of 15–20 g m^{-2} in the photographic layer, was used as the working material. This material was subjected to X-ray exposure (exposure dose varied from 0.1 to 5.0 Röntgen) followed by a standard chemical photographic treatment (development in D-19 methylhydroquinone developer and fixation in 25% aqueous sodium thiosulfate solution). As a result, initial silver images were obtained with absorbances (A^{Ag}) in the range 0.1–4.0 and silver concentrations in the gelatin layer of 0.1–7.0 (g Ag) m^{-2}. Then, the silver images were converted into silverless ones consisting of Fe^{III} complexes according to the following scheme:

Stage I:	bleaching in an aqueous solution containing iron(III) ammonium citrate	4.5 g l^{-1}
	tartaric acid	1.8 g l^{-1}
	potassium hexacyanoferrate(III)	4.0 g l^{-1}
	potassium dichromate	0.1 g l^{-1}
Stage II:	fixing in an aqueous solution containing sodium thiosulfate pentahydrate	250.0 g l^{-1}
Stage III:	toning in an aqueous solution containing the organic compound (8-sulfanylquinoline, 5-bromo-8-sulfanylquinoline or 5-thiomethyl-8-sulfanylquinoline) and an alkaline agent (NaOH or KOH)	

Stage I was continued until complete transformation of the silver contained in the initial image into silver hexacyanoferrate(II), $Ag_4[Fe(CN)_6]$ was achieved. Experimentally, this process was found to be completed within 15–20 min at 20 °C. In principle, the bleaching process can be realized by using a solution containing only iron(III) ammonium citrate, tartaric acid and potassium hexacyanoferrate(III), but at high absorbance values of the initial silver image ($A^{Ag} > 3$), the complete oxidation of free silver into $Ag_4[Fe(CN)_6]$ is observed only in photographic material samples characterized by insignificant hardening of the gelatin layer. In order to achieve both complete bleaching at $A^{Ag} > 3$ and significant hardening of the photographic material, a small quantity of potassium dichromate, $K_2Cr_2O_7$ (0.1 g l^{-1}), was added to the bleaching solution. Moreover, the temperature of this solution must not exceed 20 °C because the solution begins to decompose and loses its ability to oxidize elemental silver (the decomposing reaction is accompanied visually by the precipitation of a dark-blue insoluble product). Nevertheless, at temperatures below 20 °C, this bleaching solution is stable for a minimum of 5 days. Upon completion of stage I, the material was washed in running water for 5 min and treated with a 25% aqueous solution of $Na_2S_2O_3$ for 5 min at 20–25 °C to enable the transformation of the water-insoluble $Ag_4[Fe(CN)_6]$ present after stage I into a water-soluble thiosulfate complex which is then removed from the photographic layer. Upon the completion of stage II, the material was washed in running water for 5 min at 20–25 °C and stage III was performed. The concentration of the organic reagent in the toning solution of stage III was varied in the range

1.0×10^{-3} to 1.0×10^{-2} mol l^{-1} (*ca.* 1.0–10.0 g l^{-1}). The pH was maintained at 12.0 ± 0.1. This pH was chosen to avoid the deformation of the thin gelatin layer and its detachment from the polyethyleneterephthalate base, and to achieve the full conversion of the organic reagent into its ionized form, which results in an insoluble iron(II) or iron(III) complex. After the completion of stage III, the material was washed in running water for 15 min and dried for 2–3 h at room temperature.

The absorbances of the silverless images, $A°$, were measured by transmitted light, giving the relationships $A° = f(A^{Ag})$ ($A°$ is the absorbance of a silverless photographic image consisting of Fe^{III} chelates with 8-sulfanylquinoline, which was obtained by the above-mentioned procedure from the initial silver image with absorbance A^{Ag}). The absorbance measurements were performed with a Macbeth TD-504 densitometer (Kodak Co., USA). The curves of $A = f(A^{Ag})$ are shown in Fig. 1–4.

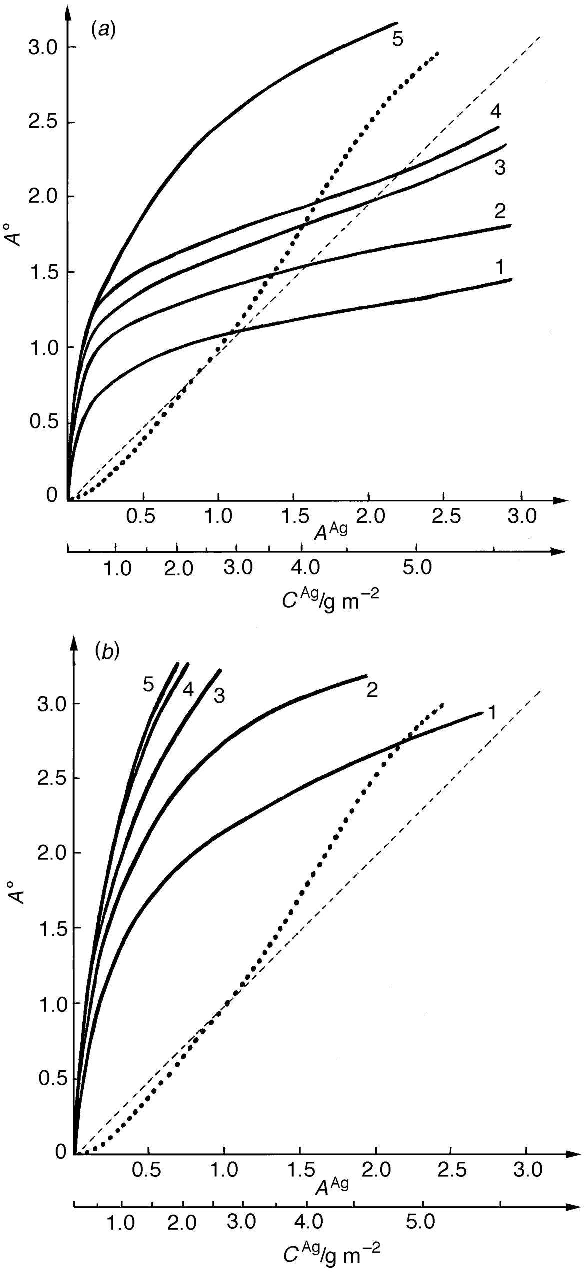


Fig. 1 $A° = f(A^{Ag})$ curves for silverless photographic images obtained in the $KFe[Fe(CN)_6]$–8-sulfanylquinoline system for the images formed at an organic compound concentration in the toning solution of 3.0×10^{-2} mol l^{-1} (*a*) and 6.0×10^{-2} mol l^{-1} (*b*) for toning stage durations of 1 min (curve 1), 2 min (2), 4 min (3), 6 min (4) and 10 min (5). The curves (– – –) and (···) represent the initial silver image and the image for $KFe[Fe(CN)_6]$, respectively. The absorbances were measured with a blue filter.

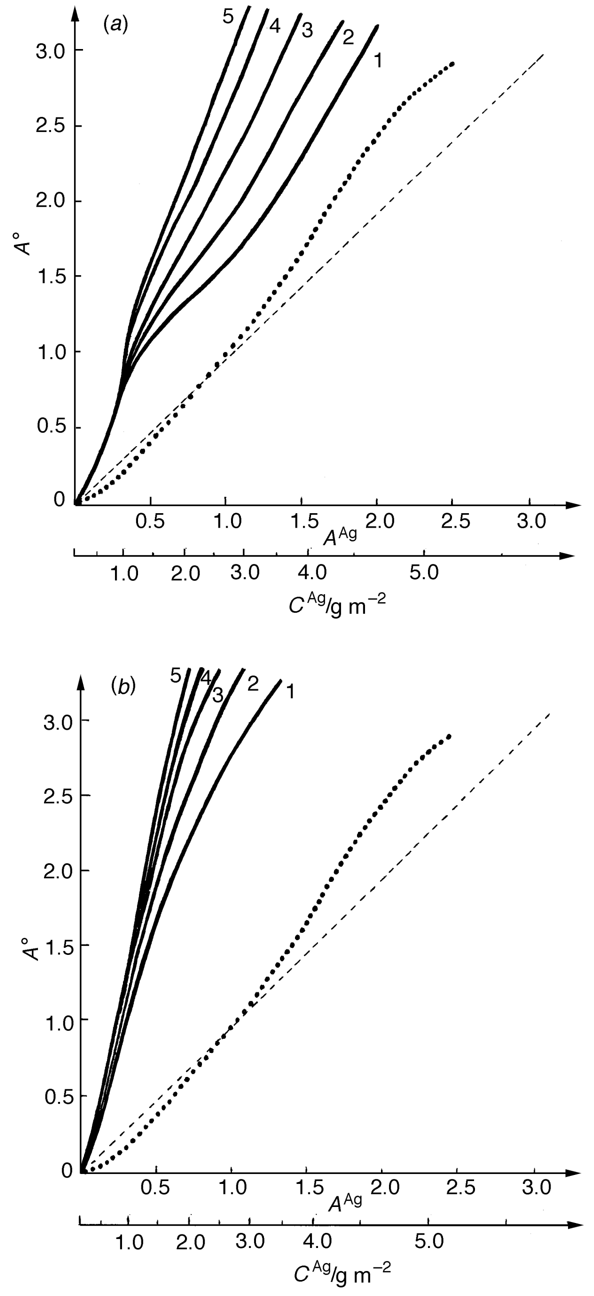


Fig. 2 $A° = f(A^{Ag})$ curves for silverless photographic images obtained in the $KFe[Fe(CN)_6]$–5-thiomethyl-8-sulfanylquinoline system for the images formed at an organic compound concentration of 2.5×10^{-2} mol l^{-1} (*a*) and 5.0×10^{-2} mol l^{-1} (*b*) for toning stage durations of 1 min (curve 1), 2 min (2), 4 min (3), 6 min (4) and 10 min (5). The curves (– – –) and (···) represent the initial silver image and the image for $KFe[Fe(CN)_6]$, respectively. The absorbances were measured with a blue filter.

Results and Discussion

Taking into account the compositions of chemical compounds containing Iron(III) citrate and tartrate anions (present in the stage I solution)[12] as well as the fact that only mixed iron(III) potassium hexacyanoferrate(II) [or its structural equivalent, iron(II) potassium hexacyanoferrate(III)] are known, stage I may be described by the following general eqn. (1), where H_3Ct and H_3Tr are citric and tartaric acids, respectively:

$$4[Fe(CN)_6]^{3-} + 4Ag + 3K^+ + 2Fe_2(Ct)(Tr) \rightarrow 3KFe[Fe(CN)_6] + Ag_4[Fe(CN)_6] + [Fe(Tr)_2]^{3-} + 2Ct^{3-} \quad (1)$$

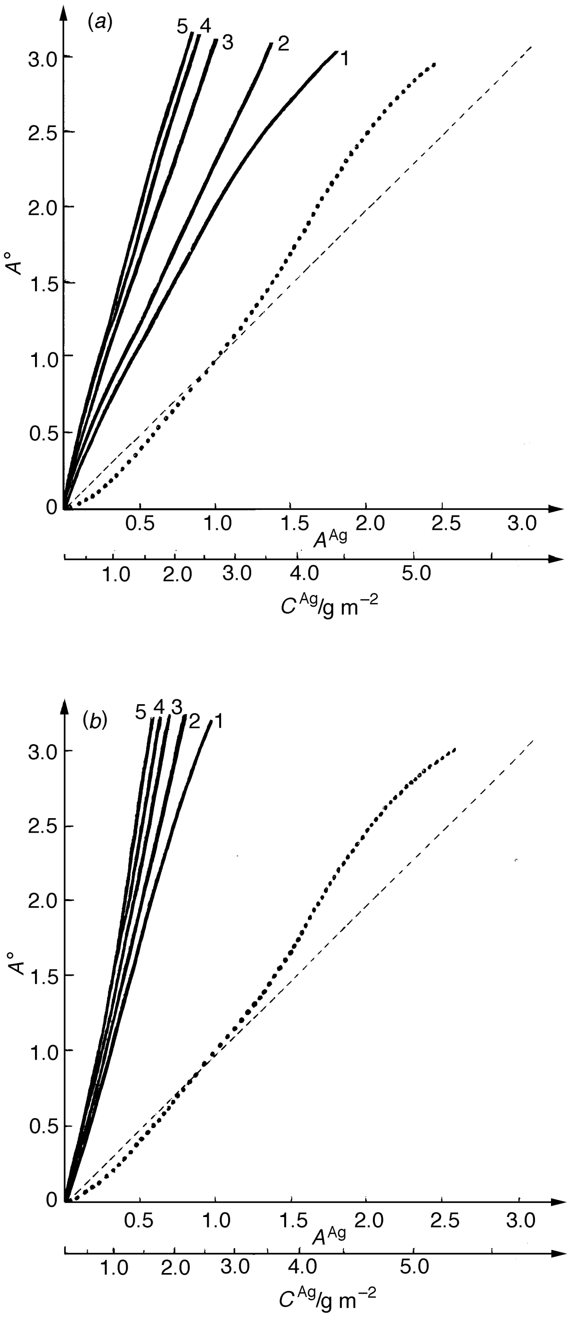


Fig. 3 $A°=f(A^{Ag})$ curves for silverless photographic images obtained in the $KFe[Fe(CN)_6]$–5-bromo-8-sulfanylquinoline system for the images formed at an organic compound concentration in the toning solution of 2.5×10^{-2} mol l^{-1} (*a*) and 5.0×10^{-2} mol l^{-1} (*b*) for toning stage durations of 1 min (curve 1), 2 min (2), 4 min (3), 6 min (4) and 10 min (5). The curves (– – –) and (···) represent the initial silver image and the image for $KFe[Fe(CN)_6]$, respectively. The absorbances were measured with a blue filter.

Stage II involves the conversion of silver(I) hexacyanoferrate(II) into a soluble silver(I) complex according to reaction (2), and its subsequent removal from the photographic layer into solution

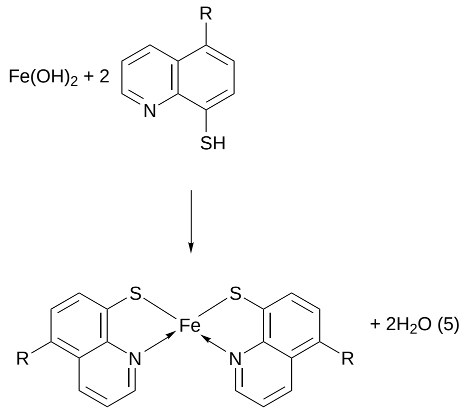
$$Ag_4[Fe(CN)_6]+8S_2O_3^{2-}\rightarrow4[Ag(S_2O_3)_2]^{3-}+[Fe(CN)_6]^{4-} \quad (2)$$

Finally, stage III consists of the formation of the silverless image, the carrier of which is an iron chelate complex. In addition to these processes, alkaline degradation of $KFe[Fe(CN)_6]$ will take place according to reactions (3) and (4) before the Fe^{II}–ligand complexing process begins:

$$KFe[Fe(CN)_6]+3OH^-\rightarrow FeO(OH)+[Fe(CN)_6]^{4-}+K^++H_2O \quad (3)$$

$$KFe[Fe(CN)_6]+2OH^-\rightarrow Fe(OH)_2+[Fe(CN)_6]^{3-}+K^+ \quad (4)$$

$Fe(OH)_2$ can then react with the 8-sulfanylquinolines to form a complex:



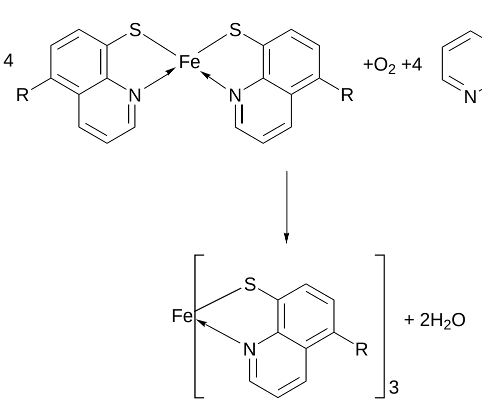
It is expected, however, that if the silverless image formation process in stage III is described only by reactions (3)–(5), the absorbance values for the silverless images, $A°$, will increase monotonically with the duration of stage III, and with the organic reagent concentration in the toning solution. At relatively low concentrations, the absorbances of the silverless image with increasing time will decrease {this circumstance is connected with the alkaline degradation of $KFe[Fe(CN)_6]$ and with the formation of slightly coloured hydroxo complexes of iron(II,III)}, and then increase owing to the complexation of Fe^{II} with the ligand. The character of the $A°=f(A^{Ag})$ relationship is fully consistent with this conclusion and resembles the characters of analogous dependences for silverless images consisting of an Ni^{II} chelate with 8-sulfanylquinoline where, according to ref. 10, only one complex with an Ni^{II} ion–ligand ratio of 1:2 is formed. An unusual feature of the silverless photographic images resulting from stages I–III is that they are red with various tinges of the 8-sulfanylquinoline studied (orange–red in the case of 8-sulfanylquinoline and pink–red in the cases of 5-bromo- and 5-thiomethyl-8-sulfanylquinoline). This colour is non-typical for Fe^{II} complexes with N,S-donor organic ligands.[11] The absorption spectra of these images in the visible spectrum region are shown in Fig. 5. According to ref. 13, this colour and the absorption spectra are indicative of Fe^{III} chelates with various 8-sulfanylquinolines whereas Fe^{II} chelates with these ligands are black or green–black. Mathematical processing of the $A°=f(A^{Ag})$ kinetic curves, according to the procedure described in ref. 14, showed that the addition of three molecules of each of these ligands took place in the process of silverless image formation over the range of A^{Ag} values studied. Two ligand molecules would be expected by taking into account only eqn. (5). Finally, the substances with red–grey–brown (8-sulfanylquinoline), grey–brown (5-bromo-8-sulfanylquinoline) and dark red (5-thiomethyl-8-sulfanylquinoline) colour may be isolated from the gelatin layer by enzymolysis (*e.g. Bazillus mesentericus*). According to chemical analysis data, these substances have FeL_3 stoichiometry where L^- is the deprotonated form of the corresponding 8-sulfanylquinoline [calc. for FeL_3 stoichiometric compositions ($FeC_{27}N_3S_3H_{18}$, $FeC_{27}N_3S_3H_{15}Br_2$, $FeC_{30}N_3S_6H_{24}$): Fe 10.45, 7.24, 8.31; C 60.45, 41.92, 53.41; N 7.83, 5.43, 6.23; H 3.36, 1.94, 3.56; found: Fe 10.0, 6.9, 8.2; C 59.7, 41.3, 53.0; N 7.1, 5.1, 6.0; H 3.4, 1.6, 3.4%]. By taking into account all these circumstances, and that the photographic layer and toning solution are in permanent contact with air oxygen which is known to be a strong oxidizer, it may be concluded

Table 1 The photographic characteristics of silverless images consisting of Fe^{III} chelates with 8-sulfanylquinoline

				characteristics		
ligand conc.[a]/mol l^{-1}	t^b/min	$S_{0.85}{}^c$	$S_{2.00}{}^c$	g^d	$D_0{}^e$	filter
1.2×10^{-2}	1	—	—	—	0.13	green with transmission maximum at 540 nm
	2	—	—	—	0.20	
	4	—	—	—	0.22	
	6	0.1	—	—	0.27	
	10	0.4	—	—	0.30	
3.0×10^{-2}	1	0.5	—	—	0.19	
	2	0.7	—	—	0.31	
	4	4.5	—	—	0.38	
	6	6.5	0.4	—	0.42	
	10	24	1.8	1.0	0.44	
6.0×10^{-2}	1	19	0.4	0.7	0.28	
	2	40	2.5	0.9	0.34	
	4	50	8.0	1.5	0.39	
	6	54	13.0	2.2	0.47	
	10	58	14.5	2.4	0.57	
1.2×10^{-2}	1	—	—	—	0.19	blue with transmission maximum at 450 nm
	2	—	—	—	0.25	
	4	—	—	—	0.29	
	6	0.2	—	—	0.37	
	10	0.9	—	—	0.42	
3.0×10^{-2}	1	7.0	0.2	1.0	0.27	
	2	14.0	0.3	1.1	0.37	
	4	26	1.5	1.2	0.50	
	6	34	2.1	1.3	0.52	
	10	40	7.2	1.5	0.60	
6.0×10^{-2}	1	44	6.5	1.2	0.44	
	2	100	13	1.4	0.47	
	4	140	18	1.6	0.52	
	6	145	25	1.9	0.62	
	10	150	26	2.0	0.66	
initial silver image	—	9.0	3.0	3.5	0.10	

[a] Concentration of ligand in the toning solution. [b] Toning stage duration. [c] Photographic sensitivity (in Röntgen^{-1}). [d] Contrast coefficient. [e] Fog density.

that redox process (6) takes place at the formation of silverless images consisting of iron chelates with 8-sulfanylquinolines, together with reactions (3)–(5).



(6)

As can be seen from eqn. (6), the FeL_3 chelates are formed in the photolayer from $Fe(OH)_2$, but not from FeO(OH) or another iron(III) compound arising during the $KFe[Fe(CN)_6]$ degradation process. This conclusion is corroborated by the fact that no iron chelate silverless image is formed upon treatment of the photolayer containing only FeO(OH) as the image carrier {a photographic layer with this carrier may be obtained readily *via* treatment of a photolayer containing $KFe[Fe(CN)_6]$ within an alkaline solution of hydrogen peroxide, H_2O_2}. It should be noted, however, that at low concentrations of the organic reagents in the toning solution ($<10^{-5}$ mol l^{-1}), a deep yellow substance is formed; according to chemical analysis data this is a mixture of $Fe(OH)_2$ and FeO(OH). In addition, mathematical treatment of the $A^\circ = f(A^{Ag})$ kinetic curves, by the method described in ref. 14, at such low concentrations of organic reagents, degradation of $KFe[Fe(CN)_6]$ does not occur at all. These circumstances are evidence that at the iron chelate silverless image formation the alkaline degradation of $KFe[Fe(CN)_6]$ takes place before the start of the complexing process.

The photographic characteristics of silverless images consisting of Fe^{III} chelates with 8-sulfanylquinoline, 5-bromo-8-sulfanylquinoline and 5-thiomethyl-8-sulfanylquinoline are shown in Tables 1–3. As can be seen, in most cases, the formation of silverless images of Fe^{III} chelates with these organic ligands is accompanied by a considerable increase of the photographic sensitivities ($S_{0.85}$ and $S_{2.00}$) in comparison with the initial silver images. This image-amplification effect is more pronounced when the absorbances are measured with a blue light filter. Note that the photographic characteristics of silverless images consisting of iron(III) chelates with 5-bromo-8-sulfanylquinoline and 5-thiomethyl-8-sulfanylquinoline are extremely similar under the similar concentration–time conditions of stage III (see Tables 2 and 3), while the photographic characteristics of silverless images of Fe^{III} chelate with non-substituted 8-sulfanylquinoline are significantly different (Table 1. For example, higher fog densities are found for Fe^{III}–8-sulfanylquinoline silverless images. Also, it is significant that the dependence of the absorbance of the silverless image on the toning stage duration and, especially, on the organic reagent concentration in the toning solution, is most pronounced for the Fe^{III}–8-sulfanylquinoline chelate. The causes of these differences have not yet been determined. However, they may be related to the lower molecular mass and size of 8-sulfanylquinoline in comparison to those of the 5-substituted derivatives studied, thus diffusion into gelatin is easier. As a

Table 2 The photographic characteristics of silverless images consisting of Fe^{III} chelates with 5-bromo-8-sulfanylquinoline

				characteristics		
ligand conc./mol l^{-1}	t/min	$S_{0.85}$	$S_{2.00}$	g	D_0	filter
1.2×10^{-2}	1	13.0	8.0	4.0	0.08	green with transmission maximum at 540 nm
	2	7.8	5.5	4.9	0.09	
	4	11.0	4.8	4.1	0.10	
	6	13.5	5.2	4.4	0.11	
	10	20	5.5	4.3	0.11	
2.5×10^{-2}	1	12.0	4.0	2.8	0.09	
	2	17.5	6.0	3.4	0.10	
	4	22	8.5	3.4	0.10	
	6	40	9.3	3.4	0.12	
	10	42	10.0	3.4	0.13	
5.0×10^{-2}	1	29	9.5	3.2	0.11	
	2	35	12.0	3.5	0.12	
	4	42	14.0	3.5	0.13	
	6	47	17.0	3.5	0.13	
	10	51	18.5	3.5	0.14	
1.2×10^{-2}	1	8.5	4.3	4.4	0.09	blue with transmission maximum at 450 nm
	2	10.0	5.1	4.5	0.10	
	4	16.0	5.3	3.9	0.10	
	6	25	6.7	3.6	0.11	
	10	36	8.0	3.1	0.12	
2.5×10^{-2}	1	22	7.0	3.5	0.12	
	2	30	8.5	3.5	0.14	
	4	55	13.0	3.3	0.15	
	6	60	17.0	3.3	0.16	
	10	64	17.5	3.3	0.17	
5.0×10^{-2}	1	47	15.0	3.3	0.16	
	2	57	18.0	3.5	0.16	
	4	62	20	3.6	0.16	
	6	68	22	3.7	0.17	
	10	70	25	3.9	0.20	
initial silver image	—	10.0	4.0	3.5	0.09	

Table 3 The photographic characteristics of silverless images consisting of Fe^{III} chelates with 5-thiomethyl-8-sulfanylquinoline

				characteristics		
ligand conc./mol l^{-1}	t/min	$S_{0.85}$	$S_{2.00}$	g	D_0	filter
1.2×10^{-2}	1	16.0	7.0	4.3	0.08	green with transmission maximum at 540 nm
	2	9.5	5.3	5.0	0.10	
	4	12.0	5.0	4.2	0.11	
	6	17.0	5.5	4.5	0.12	
	10	27	5.8	3.8	0.13	
2.5×10^{-2}	1	15	3.6	3.2	0.09	
	2	24	7.2	3.1	0.11	
	4	45	10.0	2.9	0.11	
	6	54	12.0	2.8	0.12	
	10	60	14.5	2.7	0.13	
5.0×10^{-2}	1	45	12.0	2.4	0.15	
	2	75	16.0	2.5	0.16	
	4	80	23	2.6	0.16	
	6	82	25	2.9	0.16	
	10	85	27	3.1	0.17	
1.2×10^{-2}	1	11.5	5.0	4.4	0.09	blue with transmission maximum at 450 nm
	2	13.0	5.5	4.5	0.10	
	4	21	6.5	4.0	0.11	
	6	31	7.2	3.5	0.12	
	10	43	9.3	2.9	0.13	
2.5×10^{-2}	1	41	7.1	2.6	0.10	
	2	50	10.0	2.6	0.11	
	4	57	12.5	2.9	0.12	
	6	63	17.0	2.9	0.12	
	10	69	19.0	3.1	0.13	
5.0×10^{-2}	1	63	18.0	2.4	0.22	
	2	85	24	2.5	0.23	
	4	90	28	2.9	0.24	
	6	95	32	3.3	0.24	
	10	100	35	3.5	0.24	
initial silver image	—	11.0	4.0	3.5	0.09	

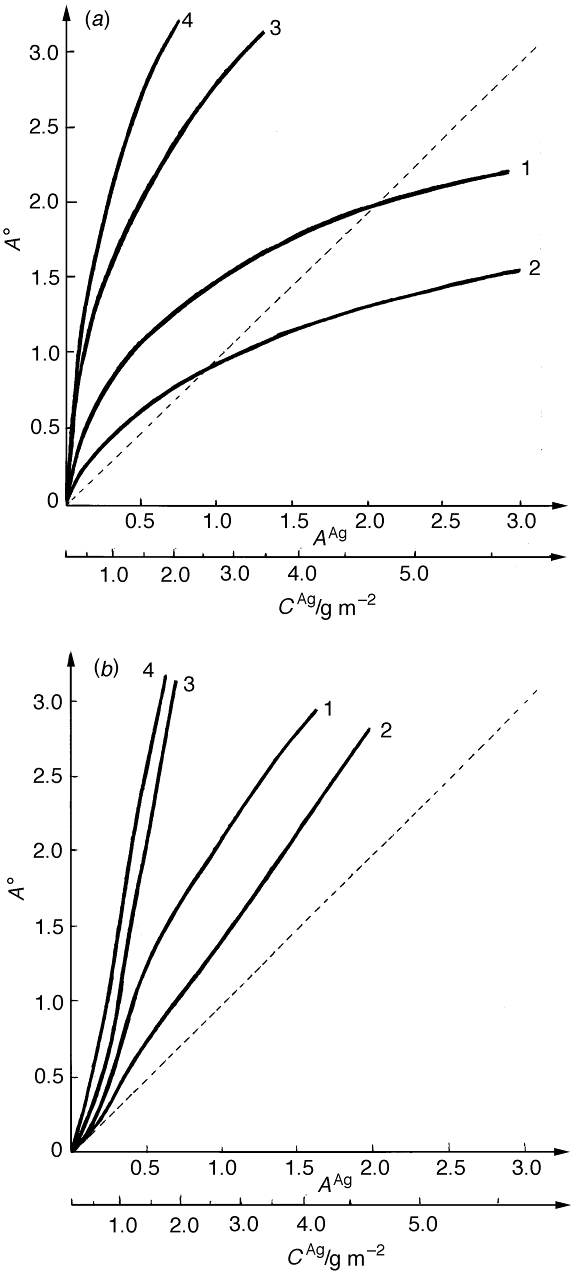


Fig. 4 $A^{\circ}=f(A^{\mathrm{Ag}})$ curves for silverless photographic images obtained in the $\mathrm{KFe[Fe(CN)_6]}$–8-sulfanylquinoline system for the images formed at an organic compound concentration of 6.0×10^{-2} mol $\mathrm{l^{-1}}$ and a toning stage duration of 10 min at 20 °C (*a*), and for silverless images obtained in the $\mathrm{KFe[Fe(CN)_6]}$–5-thiomethyl-8-sulfanylquinoline system for an organic compound concentration of 5.0×10^{-2} mol $\mathrm{l^{-1}}$ and a toning stage duration of 10 min at 20 °C (*b*) measured with yellow (curve 1), red (2), green (3) and blue (4) filters. The dashed curve (– – –) represents the initial silver image.

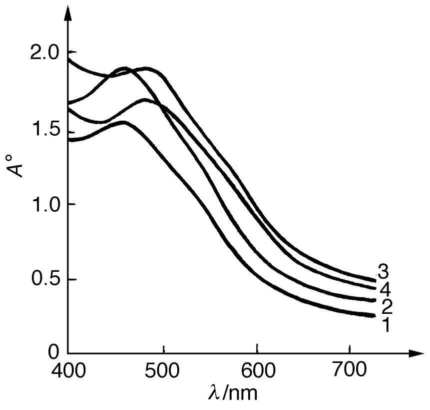


Fig. 5 The spectral characteristics of gelatin layers with silverless photographic images obtained from $\mathrm{Fe^{III}}$ chelate complexes with 8-sulfanylquinoline (for a ligand concentration in the solution $C_{\mathrm{L}}{}^{0}=1.2\times10^{-2}$ mol $\mathrm{l^{-1}}$, initial silver concentration in the gelatin layer, $C^{\mathrm{Ag}}=0.90$ g $\mathrm{m^{-2}}$, toning stage duration $t=4$ min (curve 1); at $C_{\mathrm{L}}{}^{0}=3.0\times10^{-2}$ mol $\mathrm{l^{-1}}$, $C^{\mathrm{Ag}}=0.80$ g $\mathrm{m^{-2}}$, $t=6$ min (curve 2); and of gelatin layers with silverless images obtained from $\mathrm{Fe^{III}}$ chelate complexes with 5-thiomethyl-8-sulfanylquinoline at $C_{\mathrm{L}}{}^{0}=1.2\times10^{-2}$ mol $\mathrm{l^{-1}}$, $C^{\mathrm{Ag}}=2.20$ g $\mathrm{m^{-2}}$, $t=2$ min (curve 3), at $C_{\mathrm{L}}{}^{0}=2.5\times10^{-2}$ mol $\mathrm{l^{-1}}$, $C^{\mathrm{Ag}}=0.90$ g $\mathrm{m^{-2}}$, $t=10$ min (curve 4)

result, in the non-exposed areas of the initial photomaterial where the $\mathrm{KFe[Fe(CN)_6]}$ concentration is very low and the alkaline destruction process is completed earlier than on the exposed areas, the interaction of the products of this destruction with non-substituted 8-sulfanylquinoline starts earlier than for the 5-substituted derivatives and proceeds at a higher rate. This is why the concentration of the $\mathrm{Fe^{III}}$ chelate with 8-sulfanylquinoline at any time will be higher than the concentration of the $\mathrm{Fe^{III}}$ chelate with 5-bromo-8-sulfanylquinoline or 5-thiomethyl-8-sulfanylquinoline (at the same molar concentrations of these ligands in the toning solution). The molar absorption coefficients of all the 8-sulfanylquinolines of iron(III) considered here in the visible spectrum are similar,[13] and therefore it may be expected that absorbances at non-exposed areas (low fog density) for silverless images of $\mathrm{Fe^{III}}$ chelates with 8-sulfanylquinoline ought to be higher than those for silverless images of $\mathrm{Fe^{III}}$ chelates with 5-bromo- or 5-thiomethyl-8-sulfanylquinoline. Perhaps the dependence of the photographic characteristics of silverless images on the ligand concentration in the toning solution, which was most marked for the silverless image of the $\mathrm{Fe^{III}}$ chelate with 8-sulfanylquinoline (see Table 1), should be connected with an analogous cause.

Our investigations of image stability showed that, after storage at 50 ± 1 °C in air for one month, at 25 ± 1 °C in $\mathrm{NO_2}$, $\mathrm{SO_2}$ or $\mathrm{H_2S}$ atmosphere for 15 days, and also upon storage at 20–30 °C in air with exposure to sun for more than 5 years, the absorbances A of the above-mentioned silverless images were changed by no more than 10% in comparison with the absorbances of the corresponding 'fresh' images. In this connection, it can be affirmed that the silverless images consisting of $\mathrm{Fe^{III}}$ chelates with 8-sulfanylquinoline, 5-bromo- and 5-thiomethyl-8-sulfanylquinoline are stable to the influence of UV and visible radiation and to the influence of aggressive agents of the environment. The 'sharpness' of all the above-mentioned silverless images is practically identical to that of the initial silver image (for the photographic material used here, it is 200 $\mathrm{mm^{-1}}$ in the case of the silver image, whereas for the silverless images studied, it is 185–205 $\mathrm{mm^{-1}}$).

Conclusions

The data presented show that the absorbances of silverless images consisting of iron(III) chelates with the 8-sulfanylquinolines studied generally exceed the absorbances of the initial silver image, as measured with green or blue light filters. This allows the technologies described to be recommended for amplification of photographic images (in particular for small A^{Ag} values). In addition, these technologies may be realized for the toning of silver images to various tints of red. Also, it should be noted that these silverless images are very stable to the influence of radiation and aggressive agents of the environment.

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