Photographic Images Obtained from Ni(II) Complexes with Dithiooxamide and $\textit{N},\textit{N}'$-Diphenyldithiooxamide

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Abstract

The formation processes of non-silver images in gelatin layers of silver halide photographic materials containing previously synthesized by two-stage chemical processing of a silver image, reactive matrix obtained from nickel hexacyan of errate (II) $\text{Ni}_2[\text{Fe(CN)}_6]$, upon the reactions with alkaline solutions of dithiooxamide and $\textit{N},\textit{N}'$-diphenyldithiooxamide. $D' = f(D_{Ag})$ relationships have been obtained and analyzed where $D'$ is density of a non-silver image formed on the basis of the initial silver image having $D_{Ag}$ density, for a wide range of agent concentrations in the solution and various durations of the processing stage. The chemism of the process involved was studied in detail, it was also determined that in the $\text{Ni}_2[\text{Fe(CH)}_6]$.-$\textit{N},\textit{N}'$-diphenyldithiooxamide system, the photographic image formed is substantially single-component, while in $\text{Ni}_2[\text{Fe(CN)}_6]$-dithiooxamide it is multicomponent. The possibility of practical applications of the process described for image application accompanied by complete silver removal from the layers was pointed out.

1. Introduction

One of the most important problems of modern silver halide photography is the substitution of silver constituting photographic images for other, less costly but available organic or inorganic compounds [1-3]. One of the possible ways of the transformation of the silver image into a non-silver one is the process where the image carriers are intensively coloured inorganic compounds, and first of all, coordination compounds of various metals. Taking into consideration a fairly high resistance of such compounds towards light and detrimental atmospheric attacks, it may also be expected that photographic images formed by the compounds of the given class will have similar properties.

Various Ni(II) complexes, being relatively cheap and chemically stable, characterized low by solubility are considered to be most promising carriers of photographic images. The most stable of them are the complexes with nitrogen-sulphur-containing organic compounds having two sulphur atoms associated with carbon $\alpha$- and $\beta$-atoms. Among them, of particular interest are dithiooxamide and $\textit{N},\textit{N}'$-diphenyldithiooxamide which are used in chemical analysis [4-6]. In the present paper, the process of their formation in thin gelatin layers of silver halide photographic materials, accompanied by the formation of photographic images is studied.

2. Experimental

In order to obtain photographic images, the commercial photographic film RT-5 on a transparent support was used, with a relatively high silver coverage (about 15-20 g·m$^{-2}$) on the photographic layer. Upon the exposure, the samples of this material were subjected to conventional chemical processing in D-19 methol-hydroquinone developer...
and in the 25% aqueous solution of sodium thiosulphate, this obtaining silver images with a wide range of optical densities (0, 1–4, 0) and high silver contents in the image (0–7 g·m⁻²). Then, the silver images were transformed into non-silver ones using nickel (II) coordination compounds as image carriers, according to the following scheme:

I. Processing in an aqueous solution containing (g·dm⁻³)
   - Nickel(II) chloride hexahydrate 15
   - Trisubstituted sodium citrate 88
   - Potassium hexacyanoferrate(III) 14

II. Processing in the 25% aqueous solution of sodium thiosulphate.

III. Processing in an aqueous solution containing an organic compound (dithiooxamide or its N,N'-diphenylderivatives) and alkaline agent (sodium or potassium hydroxide).

Operation (I) was performed until the completion of the transition of initial image silver into its chloride; the level of bleaching was visually controlled. It was determined experimentally that the process was completed within 20 min at 25°C. The selection of the solution for performing stage (I) was carried out according to the recommendations given in [7]. Upon the completion of stage (I), the material was washed in running water for 5 min and then processed in the 25% aqueous solution of sodium thiosulphate for 3 min at 25°C providing for the complete conversion of AgCl formed at stage (I) into the soluble silver-thiosulphate complex with its subsequent removal from the photographic layer, and again the material was washed in the running water for 5 min. Then stage (III) was performed varying its duration from 1 to 10 min at (20±0.1)°C. In the course of experiments of stage (III), solutions with a wide range concentrations of 10⁻³–10⁻¹ mol·dm⁻³ (about 0.1–10 g·dm⁻³) of dithiooxamide or N,N'-diphenyldithiooxamide were used; pH value was maintained constant and equal to 12.0±0.1. The selected pH value for conducting the experiments was conditioned by two factors: first, the possibility of a fairly complete conversion of dithiooxamide or its N,N'-derivatives into its ionized state that forms a complex with nickel (II) ions characterized by poor solubility, and, secondly, the preservation of a thin gelatin layer of the photographic material with its subsequent peeling of the polymeric support. Upon the completion of stage (III), the photographic layer was washed in the running water for 15 min and dried for 2–3 hours at room temperature (15–25°C).

Transmission densities of photographic images obtained on the samples of the photographic material were measured; the measurements performed resulted in $D_v=f(D_{Ag})$ relationships where $D_{Ag}$ is the density of the initial silver image, $D_v$ is the density of a photographic image formed upon the chemical photographic processing of the present study from the silver image having $D_{Ag}$ density. These relationships are given Fig. 1–7. In these relationships also are given $C_{Ag}$ coordinate (where $C_{Ag}$ is the concentration of silver in g·m⁻² in initial silver image for the density $D_{Ag}$) which parallel of axis $D_{Ag}$ have been represented. The measurements were performed on Macbeth TD-504 Kodak Densitometer with an accuracy of ±2% (rel.). In Table 1 and 2 are given the photographic characteristics of images obtained from chelates nickel (II) with studied organic compounds.

3. Results

In view of data given in [8, 9], on the compositions of chemical compounds containing Ni (II) and a citrate anion (present in the solution of stage (I)), the following generalized equation can be given to describe stage (I) here H₄Ct is a citric acid,

$$6[Ni(HCt)₃]⁺ + 4[Fe(CN)₆]³⁻ + 4Ag + 4Cl⁻ \rightarrow 3Ni₂[Fe(CN)₆] + [Fe(CN)₆]³⁻ + 4AgCl + 18HCTs⁻ \tag{1}$$

Actually, here the well-known process of silver bleaching occurs with simultaneous precipitation of Ni (II) hexacyanoferrate (II) having poor solubility. In the course of stage (II) the transition of the bleached (AgCl) into its soluble form under the influence of sodium thiosulphate and its removal...
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Fig. 1 $D^* = f(D^{Ag})$ relationships for photographic images obtained in the Ni$_2$[Fe(CN)$_6$]-dithiooxamide system at dithiooxamide concentrations in the "toning" solution of $1.0 \times 10^{-3}$ mol dm$^{-3}$, for stage (III) durations 1 min (curve 1), 2 min (2), 4 min (3), 6 min (4) and 10 min (5) and processing in the 5% aqueous K$_2$S$_2$O$_7$ duration 30 s at 20°C. Optical densities were measured with yellow filter. Dashed curve represents the initial silver image.

Fig. 2 $D^* = f(D^{Ag})$ relationships for photographic images obtained in the Ni$_2$[Fe(CN)$_6$]-dithiooxamide system at dithiooxamide concentrations in the solution of $4.0 \times 10^{-3}$ mol dm$^{-3}$, for stage (III) durations 1 min (curve 1), 2 min (2), 4 min (3), 6 min (4) and 10 min (5) and processing in the 5% aqueous K$_2$S$_2$O$_7$ durations 30 sec at 20°C. Optical densities were measured with yellow filter. Dashed curve represents the initial silver image.

from the photographic layer to the solution is observed.

$$\text{AgCl} + 2\text{S}_2\text{O}_8^{2-} \rightarrow \text{[Ag(S}_2\text{O}_8\text{)]}^{3+} + \text{Cl}^- \tag{2}$$

As a result, in the thin gelatin layer of the photographic material only Ni$_2$[Fe(CN)$_6$] is present having a weak green-yellow colour. Special investigations showed that the process of Ni$_2$[Fe(CN)$_6$] formation is of non-catalytic character, and provided that stages (I) and (II) were fully completed, the amount of Ni$_2$[Fe(CN)$_6$] formed will be proportional to the amount of elemental silver originally present in the photographic layer. And, finally, stage (III) consist in the transformation of Ni$_2$[Fe(CN)$_6$] to a chelate complex. In case of the dithiooxamide the process of its formation can be described by the following probable generalized equation:

$\text{Ni}_2[\text{Fe(CN)}_6] + 4\text{OH}^- \rightarrow \text{H}_2\text{N}^-\dddot{\text{C}}\dddot{\text{C}}^-\text{NH}_2 + [\text{Fe(CN)}_6]^{4-} + 4\text{H}_2\text{O} \tag{3}$

The reaction results in the photographic image having a pink-violet colour (in the range of low ligand concentrations in the solution and at short (1–2) min) stage (III), its colour changes from yellow-green to cyan and, finally, to pink-violet. This phenomenon can be explained by the incomplete course of reaction (3) and the formation of Ni(II) compounds containing dithiooxamide and [Fe(CN)$_6$]$^{4-}$ anions. Such pink-violet image is characterized by a high transparency (compared to images) with an "intermediate"
colour, as well as intermediate images obtained from Ni₂[Fe(CN)₆]. Since it is Ni(II) chelate containing dithiooxamide that forms the resulting photographic image, it can be expected that stage (III) (called "toning" due to dyening of the photographic layer) must make the decisive contribution to the formation of optical characteristics. At the same time, if stage (III) were described by only a single generalized equation (3), monotonic increase of optical densities of nonsilver photographic images with the increase of the "toning" process should be expected. Experimental data, however, give evidence to the contrary: the expected state is observed at comparatively small (10⁻³–3·10⁻³ mol·dm⁻³) ligand concentrations in the toning solution, while at higher concentrations, with the increase of stage (III), optical densities pass their maximum, provided that the time required to reach the maximum as dithiooxamide concentration in the solution increase, is decreasing, and at concentrations of 3.5·10⁻² mol·dm⁻³ is less than 1 min. It is indicative of the fact that alongside with the formation of an insoluble Ni(II)-dithiooxamide complex, being a photographic image carrier, the decomposition of dithiooxamide is observed, and it can be explained by the formation of a soluble Ni(II) compound, according to the reaction (4) [10].

\[
\text{Ni}_2\text{S}_2\text{O}_7^2^- + 2\text{Ni}^2+ \rightarrow 2\text{Ni}_2\text{S}_2\text{O}_7^2^- + 4\text{OH}^- \quad (4)
\]
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In our case, the rate of reactions (3) and (4) is strongly affected by diffusion factors, and while dithiooxamide concentration in the photographic layer is relatively small, the accumulation of an insoluble complex is occurring; however, beginning with its certain limiting value, reaction (4) becomes predominant. The direct consequence of the above is that in areas with a relatively small amount of the originally present Ni$_2$[Fe(CN)$_6$] in the photographic layer (and, respectively, relatively low densities of the initial silver image), the non-silver image starts “dissolving” and the resulting optical density, having reached a certain limiting value, is found to decrease. At the same time, in areas where Ni$_2$[Fe(CN)$_6$] concentration is substantially high, a certain period of time is required for Ni(II) hexacyanoferrate (II) to transform into an insoluble complex, in order that reaction (4) could also proceed at an excessive dithiooxamide concentration for the destruction of the image. It may be expected that with the increase of dithiooxamide concentration in the toning solution, the period of stage (III) when the non-silver optical density is observed to increase, will become shorter; moreover, at a relatively high dithiooxamide concentration, the image fails to form. The phenomenon observed at dithiooxamide concentration in the solution of about 10$^{-1}$ mol·dm$^{-3}$ and more, confirms our conclusion.

If a non-silver image of the present study is processed in an acid solution with pH 2–4 (sulphuric, acetic, hydrochloric acids, potassium pyrosulphate, etc.), the colour of the image will immediately change from pink-violet for blue. This fact was first was recorded by one of the authors of the present paper in [11], however, it wasn’t discussed in detail since then, although in [12] we have shown the possibility of using this process for manufacturing of the so called “blue
slides”. It is noteworthy that the process of the colour change in the non-silver image is irreversible (i.e. the blue colour does not change for pink-violet upon the reaction with alkaline solutions). As a result of colour transformation, the non-silver and fog densities are observed to decrease to some extent compared to those for the pink-violet image (through its light-sensitivity and contrast remain substantially unchanged); the general shape of $D_{N}=f(D_{Ag})$ kinetic curves at the fixed dithiooxamide concentration for various durations of stages (III) remains the same as in case of the non-silver pink-violet image. Here, a bathochromic shift of absorption band maximum from 580 to 640 nm in the absorption spectrum of the photographic image is observed; spectral characteristics of the blue photographic image correspond to those of polymeric Ni(II)-dithiooxamide complex having Ni(II) ion/dithiooxamide ratio equal to 1:2 [5]. The above circumstances as well as the irreversible character of colour transformation in the photographic image are indicative of reaction (5) in the course of which a stiff-structured chain polymer is formed in thin gelatin layer.

$$\text{Fig. 7} \quad D_{N}=f(D_{Ag}) \text{ relationships for photographic images obtained in the Ni}_2[\text{Fe(CN)}_6]_2 N,N'-\text{diphenyldithiooxamide system at N,N'-diphenyldithiooxamide concentrations in the solution } 3.0 \cdot 10^{-2} \text{ mol} \cdot \text{dm}^{-3}, \text{for stage (III) durations 1 min (curve 1), 2 min (2), 4 min (3), 6 min (4) and 10 min (5) at } 20^\circ C. \text{ Optical densities were measured with blue filter with transmission maximum at } 450 \text{ nm. Dashed curve represents the initial silver image.}$$

It should be noted here with that the photographic image formed in the region of low ($\sim 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$) dithiooxamide concentrations and for short (1–2 min) toning process (yellow-green or cyan) does not change its colour during “acidification”, compared to the pink-violet photographic image. Similar property is observed in the images formed upon the processing with solutions containing high ($3.0 \cdot 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ and more) dithiooxamide concentrations in the region of high densities of the initial silver image (i.e. in region of comparatively) high Ni$_2[\text{Fe(CN)}_6]$ concentrations in the photographic gelatin layer. In both cases, the above peculiarity of the photographic image may also be interpreted as a result of the formation of stiff-structure Ni (II) dithiooxamide compounds

$$\text{forms at low dithiooxamide concentrations}$$
The given set experimental data allows one to make a conclusion that the formation process of photographic images in the gelatin layer where coordination compounds of Ni(II)-dithiooxamide are used as carriers, has rather a complex character and is accompanied by the formation of at least five

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n chains

in the solution) and (forms at high dithiooxamide concentration in the solution). \( D^\nu = f(D^{45}) \) and its equivalent \( D^\nu = f(C^{45}) \) experimental relationships of formation processing of the photographic images obtained from "blues" Ni(III)-chelate with dithiooxamide in Fig. 1–4 have been represented.
Table 2 The photographic characteristics of images obtained from chelates Ni(II)
with \(N,N'\)-diphenyl dithiooxamide

<table>
<thead>
<tr>
<th>(N,N')-diphenyl dithiooxamide concentration in solution, mol·dm(^{-3})</th>
<th>Toning stage duration, min</th>
<th>Photographic Sensitivity, (S_{0.85}), Röntgen(^{-1})</th>
<th>Photographic Sensitivity, (S_{2.00}), Röntgen(^{-1})</th>
<th>Contrast coefficient, (\bar{g})</th>
<th>Fog density, (D_0)</th>
<th>Filter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>(1.2 \times 10^{-2})</td>
<td>1</td>
<td>7.0</td>
<td>—</td>
<td>—</td>
<td>0.10</td>
<td>Green with transmission maximum at 540 nm</td>
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<tr>
<td></td>
<td>2</td>
<td>12.5</td>
<td>2.6</td>
<td>2.0</td>
<td>0.12</td>
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<tr>
<td></td>
<td>4</td>
<td>16.0</td>
<td>5.0</td>
<td>2.9</td>
<td>0.12</td>
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<td></td>
<td>6</td>
<td>19.5</td>
<td>7.0</td>
<td>3.3</td>
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<td></td>
<td>10</td>
<td>23.0</td>
<td>10.0</td>
<td>3.9</td>
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<tr>
<td>(3.0 \times 10^{-2})</td>
<td>1</td>
<td>0.7</td>
<td>—</td>
<td>—</td>
<td>0.08</td>
<td>Blue with transmission maximum at 450 nm</td>
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<td></td>
<td>2</td>
<td>2.5</td>
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<td>7.3</td>
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<td>(1.2 \times 10^{-2})</td>
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<td>2</td>
<td>8.5</td>
<td>1.8</td>
<td>1.4</td>
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<td>18.5</td>
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<td>3.7</td>
<td>0.12</td>
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For initial silver-halogenide materials:

\(S_{0.85}=6.0\) Röntgen\(^{-1}\), \(\bar{g}=3.0\), \(S_{2.00}=2.0\) Röntgen\(^{-1}\), \(D_0=0.09\).

Different complexes one of which is water soluble. The situation, however, changes abruptly, if instead of dithiooxamide, its \(N,N'\)-diphenyl derivate is used. In this case, photographic optical densities are found to increase monotonically with the increase of both the toning reaction, and the organic compounds concentration in the toning solution, at least for the time-concentration conditions of stage (III) in the present paper. The resulting photographic image has a red-violet colour and \(\lambda_{\text{max}}=510\) nm, this value coincides with maximum position in absorption spectrum of 1:2 Ni(II)-\(N,N'\)-diphenyl dithiooxamide complex [5, 13, 14]. Unlike the photographic image, formed by Ni\(_2\)[Fe(CN)\(_5\)]-dithiooxamide system, the image obtained with Ni(II)-\(N,N'\)-diphenyl dithiooxamide does not show any change in optical densities or its colour upon the reaction with acid solutions. It can thus be assumed that in this case the image is formed by compound having Ni(II) ion/\(N,N'\)-diphenyl dithiooxamide ratio equal to 1:2, according to the generalized equation (6).

\[
\text{Ni}_2[\text{Fe(CN)}_6]+4\text{OH}^--\xrightarrow{\text{HN}}\text{HN}--\text{C}--\text{C}--\text{NH}--\text{HN}--\xrightarrow{\text{S}}\text{HN}--\text{S}--\text{Ni}--\text{S}--\text{HN}--\text{S}--\text{Ni}--\text{S}--\text{HN}--\frac{+[\text{Fe(CN)}_6]^{3+}}{4\text{H}_2\text{O}}
\]
The lack of an organic compound with regard to Ni$_2$[Fe(CN)$_6$] results in the possible formation of a complex containing both N,N'-diphenyldithiooxamide and [Fe(CN)$_6$]$^{4-}$ anion rendering the photographic image orange-yellow which is especially noticeable in the region of high initial densities $D_{Ag}$. The structure of this complex is similar to that of Ni(II) dithiooxamide compound. At the same time, when the lack of an organic agent is not observed, spectral characteristics of the photographic image are found to be independent of time-concentration conditions of stage (III). The constant increase of the photographic densities combined with the increase of both stage (III), and the concentration of N,N'-diphenyl substituted dithiooxamide in the solution, makes one to assume that the formation of any other complexes (both soluble and insoluble), except the above mentioned ones, does not take place in the Ni[Fe(CN)$_6$]-N,N'-diphenyldithiooxamide system. $D_{Ag} = f(D_{Ag}^{4-})$ and its equivalent $D_{Ag} = f(C_{Ag})$ experimental kinetic curves of formation processing of the photographic images obtained from Ni(II) chelates with N,N'-diphenyldithiooxamide, in Fig. 5–7 have been represented.

As an important fact, it should be noted that in most cases photographic image densities exceed those for initial silver image, provided that it is possible to vary the sensitivity and contrast of the processed photographic material in a wide range, by varying both the nature of an organic compound and the time-concentrations of stage (III) (Table 1, 2). Under such circumstances, the improvement in characteristics, as a rule, is not accompanied by any noticeable increase in the fog density (in case of Ni$_2$[Fe(CN)$_6$]-dithiooxamide, the fog level can even be decreased compared to that of the initial silver image). Photographic processing involving the transformation of the silver image is rather simple for implementation and does not produce any defects on the photographic material. The process Ni$_2$[Fe(CN)$_6$]-dithiooxamide described here can also be used for the production of the “blue slides” [12].

References