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Monitoring of Physical Development in the Silver Halide Diffusion Transfer Process with a Linear CCD

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In this paper, a linear CCD was used to detect the whole physical development process directly on the silver halide direct printing plate. The activity of the physical developing nuclei was also detected, and the influence of the ingredients of the working solution such as developer hydroquinone, silver complexing agent, and the environment such as pH, was evaluated. It was proved that the CCD technique was very successful in detecting the physical development process in the diffusion transfer reversal (DTR) system.

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Introduction

In silver halide diffusion transfer reversal (DTR) systems, the physical development process has attracted much attention because of its intensive application in lithographic printing plates and in instant photography.[1,2] Particularly, in recent years, many authors attempted to improve in or relating to a lithographic printing plate. However, in previous works, the physical development process and the activity of catalytic nuclei were studied manly in aqueous solution. For example, Levenson and Twist[3] reported the reduction of silver ion by hydroquinone on various colloidal nuclei followed continuously by measuring the optical density of the suspension. Kang et al.[4] detected the dynamics of the reaction of silver complexes and hydroquinone in solutions. The change of the concentration of silver can be observed by measuring characteristic absorption of silver at 410 nm, and the change can be used to indicate the activity of the developing nuclei. The results showed that the order of activity of nuclei was Ag > PdS > Pt > CoS. This was an indirect, and very slow way, to obtain the information. In addition, differences existed in solutions and on plates.

In this paper, a novel method for monitoring the silver precipitated in a physical developing process and the activity of catalytic nuclei has been achieved by means of a linear CCD. Because of the many characteristics of CCDs, such as: (1) linear response, (2) wide dynamic range, (3) low noise, (4) high sensitivity, and (5) wide spectral response, CCDs have been used in many scientific fields, research, and practical applications.[5–11] CCDs also provide digital results that facilitate computer handling of large amounts of data. Unlike a single diode, signals by CCD are obtained at the same time. CCDs can detect signals at very low light intensity. But CCDs rarely have been used in chemistry, especially in detecting the dynamics of chemical reaction in situ. In our paper, we first introduced a CCD into the determination of dynamics of physical development in photographic chemistry.[12–14] It is valuable to perform real-time measurements in the study of the physical development of a silver image

The approach we established for direct determination of the formation of metallic silver in the physical development process was used to measure reflected light from the plate surface with a linear CCD. The construction of the silver halide printing plate is illustrated in Fig. 1. While the exposed silver halide emulsion layer was put into the developing cell, which was filled with the developing solution, the latent image in the emulsion layer was developed and blackened. The unexposed AgX was dissolved through the action of the complexing agent. The silver complexes then transferred through diffusion onto the surface and under the catalysis of the physical developing nuclei precipitated in the form of metallic silver. As the development proceeded, the amount of metallic silver on the surface of the plate increased. Thus, the reflected light from the surface, for the given incident light, became stronger and stronger. The CCD was utilized to monitor the reflected light intensity from the plate. Because the reflected light intensity was proportional to the amount of metallic silver per unit area, the change of intensity could be used to represent the reaction process.

Experimental

Silver halide direct printing plates were in part made in our laboratory; others were 3M Onyx plates (made in the United States). The process for the plates made in our lab was as follows: First the double jet method was used

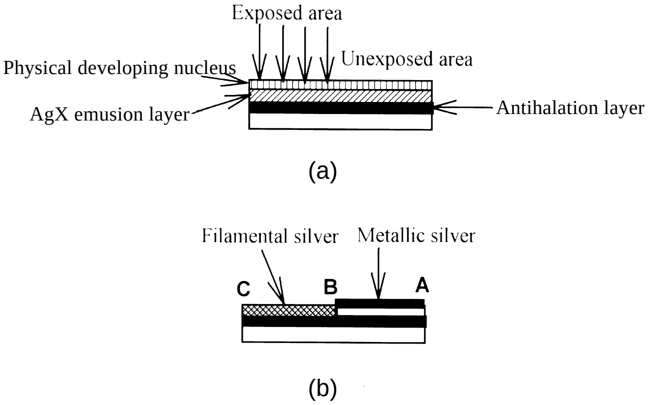

Figure 1. The cross-sectional structure of silver halide direct printing plates (a) before and (b) after development.

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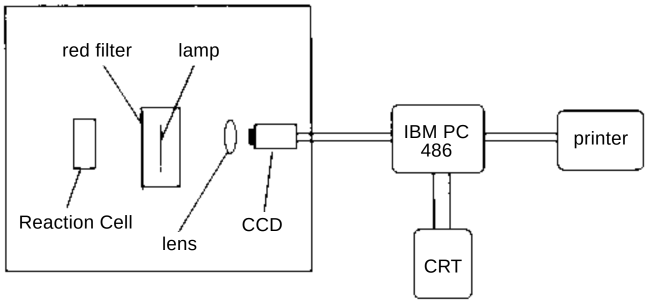

Figure 2. Schematic diagram for the experimental system.

to prepare 0.2- – 0.4-μm, cubic silver chloride emulsion. After chemical sensitization, the emulsion was coated on a paper base that was already coated with a black antihalation layer. Then the plate was stored at 40°C for 3 days. Finally, the physical developing nuclei were coated thereupon. The main ingredients of the developing solution were silver complexing agents ($Na_2S_2O_3$, KSCN), and developer (hydroquinone). The pH of our developer was 12 to 13. The CCD was a TCD102C made in Japan.

CCDs have a metal-oxide-semiconductor (MOS) structure that stores photogenerated charge carrier packets and CCDs are usually fabricated with a *P*-type material so that electrons are stored. The charge packets can be transferred by the controlled movement of potential Wells A MOS complifier is usually integrated on the chip to sense potential change. Then the data after integration are transferred to the computer and stored. In the experiment, the light signal rejected from the plate was first detected by a CCD, then was imported to the computer and stored. The schematic diagram of the experimental design is illustrated in Fig. 2. The developing cell containing working solution was thermostated. The plate was pretreated before the experiment with one part exposed to the light and the other part unexposed. The integrating time of this experiment was 197 ms, and the time interval was 500 ms. The linear light source was made in No. 117 factory, Beijing. Through most of the experiment, the incident light intensity remained unchanged, 13.9 lx at the developing area. This was detected by an EC&G Model 550-1. Through the change of the rejected intensity of metallic silver with CCD cells and the reacting time, the rate of physical developing process was obtained.

The preparation of the physical developing nuclei was carried out at 30°C. The reactant was first added into the medium, stirring at a speed of 500 to 1000 rpm. The precipitant was added dropwise into the solution. After 5 min, colloid nuclei were formed, then they were coated onto the plate very carefully.

In this experiment, 1-cm^2 plate after development was dissolved by HNO_3, and the solution was tested by silver atom absorption. The result showed that the reflected light intensity had a good linear relationship with the amount of metallic silver per cm^2 plate in our experiment as shown in Fig. 3. Therefore the reflected light intensity can be used to substitute the amount of metallic silver per cm^2 plate.

Results and Discussion

The Dynamics of Physical Development. In the experiment, the AgX on the exposed part was developed chemically into filamental silver, stayed in gelatin layer, and absorbed most of the incident light. Thus, the reflected intensity of the exposed part was very weak. The AgX on the unexposed part was dissolved by the silver complexing agent in the solution, then transferred onto the nuclei layer on the surface of the plate, and was developed into metallic silver (white color). By the physical development process, both the amount of metallic silver on the surface and the reflected intensity from the metallic silver increased. A three-dimensional plot of the change of the reflected intensity of metallic silver with CCD cells and reaction time can be obtained.[12] From this plot, the dynamic curve of the development process can be easily shown, as in Fig. 4. Note that with time, the reflected intensity of metallic silver first decreased and then increased rapidly. At last, the reflected intensity reached the highest point and remained unchanged. This means the completion of the physical developing process. The reason why at first the reflected intensity of metallic silver decreased may be the dissolving of yellow AgX that allows the antihalation layer to absorb more incident light. This needs further experiments to prove. From the dynamic curve, the maximum reflected intensity *I* from the plate and the average physical development rate *V* of the increase can be obtained. This can be shown in the following formula:

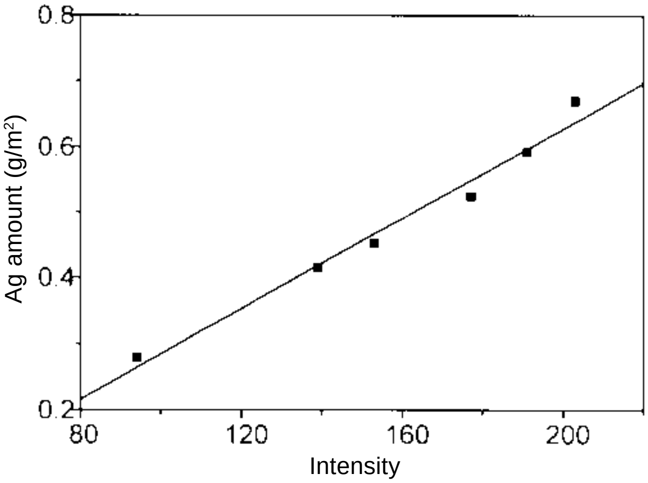

Figure 3. Demonstration of the linearity of the reflected light intensity (abscissa) with the amount of silver deposited in the physical development process (ordinate).

$$V = \Delta I/\Delta t = (I_2 - I_1)/(t_2 - t_1)$$

Because the average rate *V* and the rejected intensity were constant, the activity of the developing nuclei was determined and the quality of direct printing plates and the developing system were also determined. Given the linearity of reflected intensity with mass of silver reduced (Fig. 3), the maximum reflected intensity *I* of metallic silver was used to represent the amount of metallic silver per cm^2 plate after development.

Activity of Developing Nuclei. In the experiment, the developing nuclei were used as catalytic centers. There, the silver complexes were reduced into metallic silver. The activity of the developing nuclei directly influenced the quality and quantity of metallic silver. In the experiment, some metal-sulfide nuclei, such as PdS, Ag_2S, CoS, NiS, and Au_2S_3, and some metal nuclei, such as Au, Ag, Pd, and Pt, were chosen as the developing nuclei. Through the maximum reflected intensity *I* and the developing rate *V*, the activity of the physical development rate could be determined.

Metal-Sulfide Nuclei. *Various Metal-Sulfide Nuclei.* In the experiment, gelatin solution (0.05%) was used as the medium. The conditions of precipitation of metal-sulfide nuclei are shown in Table I. At 30°C, the reactant was

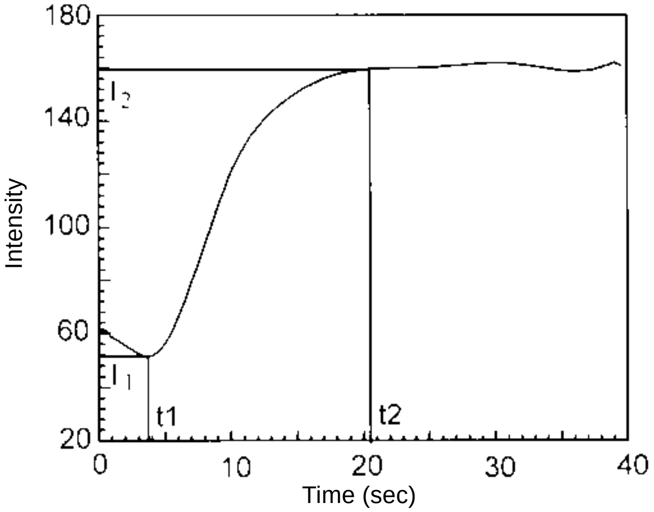

Figure 4. Dynamic curves of the physical development process.

added into the medium and stirred at the speed of 500 to 1000 rpm. Then the precipitant was dropped into the solution. After 5 min, colloid nuclei were formed. Then, they were coated on the plate very carefully. The dynamic curves of various metal-sulfide nuclei were obtained, as shown in Fig. 5(a). The developing rate *V* and the maximum reflected intensity *I* are shown in Table II. From Fig. 5(a) and Table II, it is apparent that the order of activity of metal-sulfide physical developing nuclei was:

$$\mathrm{PdS} > \mathrm{Ag_2S} > \mathrm{CoS} > \mathrm{NiS} > \mathrm{Au_2S_3}.$$

Of these metal-sulfide nuclei, the activity of PdS is the best.

The Influence of the Medium. The medium to support the nuclei is very important in our experiment. The medium provides protection for the nuclei to form colloidal nuclei and prevents precipitation. When the medium of the nuclei changed, the activity of the nuclei also changed. In the experiment, PdS was chosen as the nuclei to evaluate the influence of the medium, and the media were H_2O, gelatin solution (0.05%), and PVA solution (0.05%), respectively. The conditions were the same as in Table I. The dynamics in the various media are shown in Fig. 5(b). The developing rate *V* and the maximum reflected intensity *I* are shown in Table III. Note that the order of the activity of PdS nuclei in various media is:

$$\mathrm{PdS}\ (H_2O) > \mathrm{PdS}\ (\text{gelatin}) > \mathrm{PdS}\ (\text{PVA}).$$

Metal Physical Developing Nuclei. With this method using a linear CCD, the activity of metal nuclei also was detected. The formation conditions of metal nuclei are shown in Table I. The dynamics of the physical development process under the catalysis of metal nuclei is shown in Fig. 5(c). Because the reflected intensity of metallic silver was out of the detecting limit of the CCD, the incident light intensity was reduced to 7.80 lx at the developing area. The maximum reflected intensity *I* and the physical development rate of various metal nuclei are shown in Table IV. Note that the order of the activity of metal nuclei is:

$$\mathrm{Au} > \mathrm{Ag} > \mathrm{Pd} > \mathrm{Pt}.$$

The Influence of the Ingredients of the Working Solution on the Physical Development Rate. ***The Influence of the Developer.*** In the physical development process, hydroquinone (HQ) was used as the developer. When silver complexes were transferred onto the surface

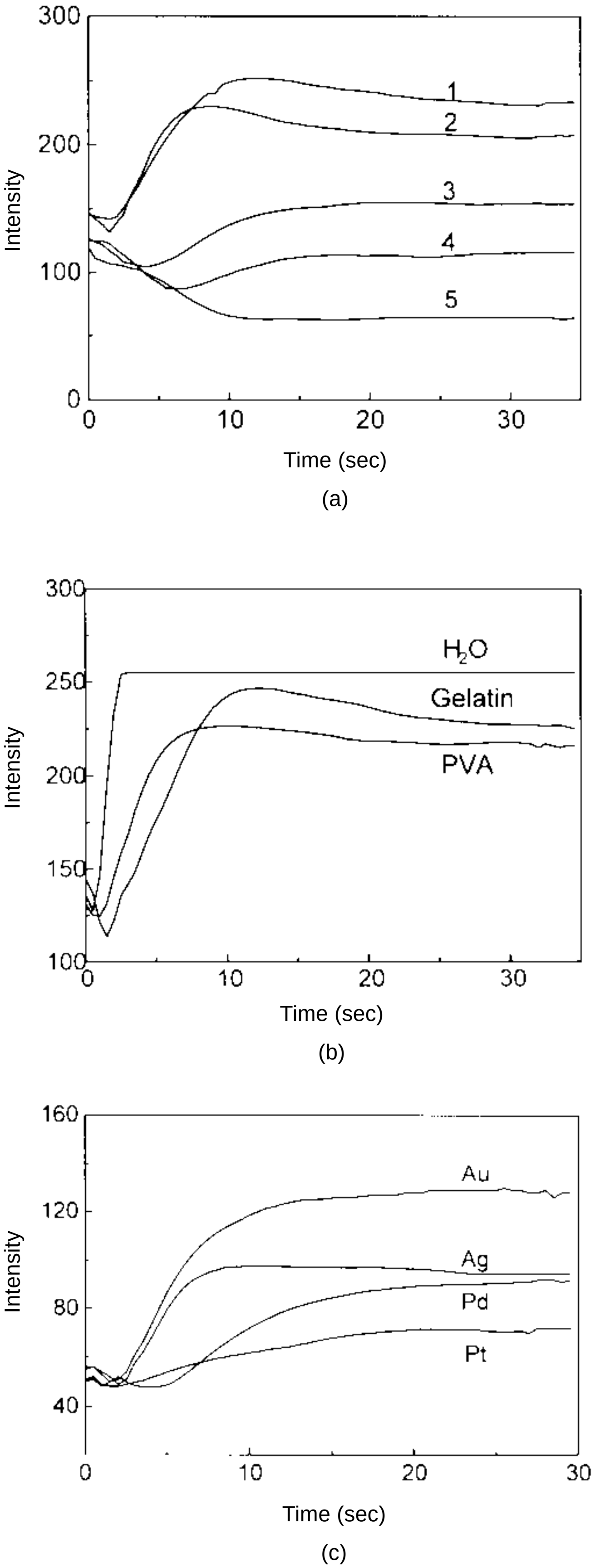

Figure 5. Dynamic curves of the physical development process: (a) catalyzed by various developing nuclei, metal sulfide nuclei; (b) catalyzed by PdS under the preparation in various media; (c) catalyzed by various developing nuclei, metal nuclei.

TABLE I. Precipitation Conditions of Various Developing Nuclei: Metal, metal-sulfide

Nuclei	Reactant	Concentration	Precipitant	Concentration	Medium	Concentration
PdS	$PdCl_2$	0.024 mol/L, 2 mL	Na_2S	0.042 mol/L, 2 mL	gelatin	0.05%, 20 mL
PdS	$PdCl_2$	0.024 mol/L, 2 mL	Na_2S	0.042 mol/L, 2 mL	PVA	0.05%, 20 mL
PdS	$PdCl_2$	0.024 mol/L, 2 mL	Na_2S	0.042 mol/L, 2 mL	H_20	20 mL
Ag_2S	$AgN0_3$	0.06 mol/L, 2 mL	Na_2S	0.042 mol/L, 2 mL	gelatin	0.05%, 20 mL
CoS	$Co(NO_3)_2$	0.01 mol/L, 4 mL	Na_2S	0.042 mol/L, 2 mL	gelatin	0.05%, 20 mL
NiS	$Ni(NO_3)_2$	0.01 mol/L, 2 mL	Na_2S	0.042 mol/L, 2 mL	gelatin	0.05%, 20 mL
Au_2S_3	$AuCl_3$	0.01 mol/L, 2 mL	Na_2S	0.042 mol/L, 2 mL	gelatin	0.05%, 20 mL
Au	$AuCl_3$	0.011 mol/L, 2 mL	KBH_4	0.185 mol/L, 2 mL	gelatin	0.05%, 20 mL
Ag	$AgNO_3$	0.06 mol/L 2 mL	KBH_4	0.185 mol/L, 2 mL	gelatin	0.05%, 20 mL
Pd	$PdCl_2$	0.024 mol/L, 2 mL	KBH_4	0.185 mol/L, 2 mL	gelatin	0.05%, 20 mL
Pt	H_2PtCl_6	0.024 mol/L, 2 mL	KBH_4	0.185 mol/L, 2 mL	gelatin	0.05%, 20 mL

TABLE II. The Maximum Reflected Intensity of Metallic Silver and the Average Physical Development Rate at Increasing Period *V* under Catalysis of Various Metal Sulfide Nuclei

	PdS	Ag_2S	CoS	NiS	Au_2S_3
I	234	206	154	116	64
V	12.04	14	3.23	2.35	0.29

TABLE III. The Maximum Reflected Intensity of Metallic Silver and the Average Physical Development Rate at Increasing Period *V* Under the Catalysis of Various Metal-Sulfide Nuclei

	PdS (H_2O)	PdS (gelatin)	PdS (PVA)
I	254	228	218
V	63	13.79	15.23

TABLE VI. Maximum Reflected Intensity of Metallic Silver and Average Physical Development Rate at Increasing Period *V* under the Catalysis of Metal Nuclei

	Au	Ag	Pd	Pt
I	129	97	90	72
V	7.2	7.83	2.63	1.28

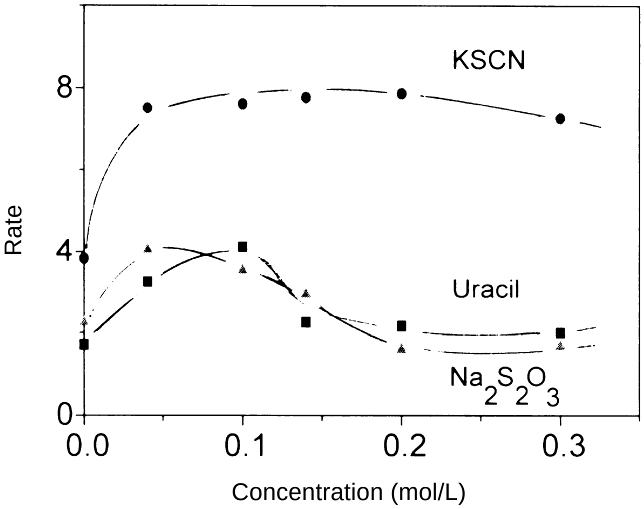

Figure 6. Influences of hydroquinone concentration on the physical development rate.

of the plate, under the catalysis of physically developing nuclei they were reduced by HQ into metallic silver. The kinetic curve of the physical development process with concentration was obtained when uracil was used as the silver complexing agent. It was shown that the concentration of HQ influences the physical development rate *V*. With concentration of 0.1 mol/L, the rate was the maximum when uracil was used as the silver complexing agent as shown in Fig. 6. When the complexing agent was changed to KSCN, the rate was low without HQ in the solutions. After HQ was added into the working solution, it was shown that the concentration of HQ did not influence the rate seriously. When $Na_2S_2O_3$ was used as the complexing agent instead of KSCN, it was seen that with increase of HQ concentration when the concentration was lower than 0.04 mol/L, the physical development rate increased. However, when the HQ concentration was higher than 0.04 mol/L, the physical development rate increased with the concentration. Figure 6 shows the physical development rate is influenced not only by the concentration of HQ, but also by different silver complexing agents. The differences between these three complexing agents may be the constant of their silver complexes.

The Influence of the Concentration of the Silver Complexing Agent. In the DTR process, AgX in an unexposed area was dissolved by the silver complexing agent, transferred onto the nuclei layer of the plate surface, and developed physically. Therefore, the complexing rate influences the rate of physical development directly. In this paper, we used KSCN and $Na_2S_2O_3$ as the complexing agents. The result is shown in Fig. 7. With increase of the concentration of KSCN, the physical development rate increases rapidly and has a good linear relationship with the concentration of KSCN. This is similar to the linear relationship between the reflected intensity of metallic silver and the concentration of KSCN.[12] But the influence of the concentration of $Na_2S_2O_3$ was not like that. The optimum was when the concentration of $Na_2S_2O_3$ was 0.063 mol/L. When the concentration was low, the physical development rate increased. When the concentration was higher than 0.063 mol/L, the physical development rate decreased.

The reason may be explained by reference to the complexation constants of silver complexes. Under the experimental conditions, the complexes were mainly $[Ag(SCN)_2]^{-1}$ (constant $k = 1.67 \times 10^8$), $[Ag(SCN)_3]^{-2}$ ($k = 5.6 \times 10^9$), and $[Ag(S_2O_3)_2]^{-3}$ ($k = 2.85 \times 10^{13}$) (Ref. 1). The $[Ag(SCN)_2]^{-1}$ and $[Ag(SCN)_3]^{-2}$ were easily reduced by hydroquinone. The $[Ag(S_2O_3)_2]^{-3}$ was first dissociated into free Ag^+ and $S_2O_3^{2-}$, then Ag^+ was reduced. The higher the complexation constant, the more difficult the complex to be reduced. Also because $[Ag(S_2O_3)_2]^{-3}$ was chemically absorbed on the surface of the developing nuclei, the static electronic repulsion made hydroquinone far away from the nuclei, thus reducing the development rate.

Conclusions

We used a linear CCD to detect the physical development process directly and in situ. We proved the CCD usable in physical development in the DTR process. The activity of developing nuclei and influences of the ingredients of the working solution also were detected.

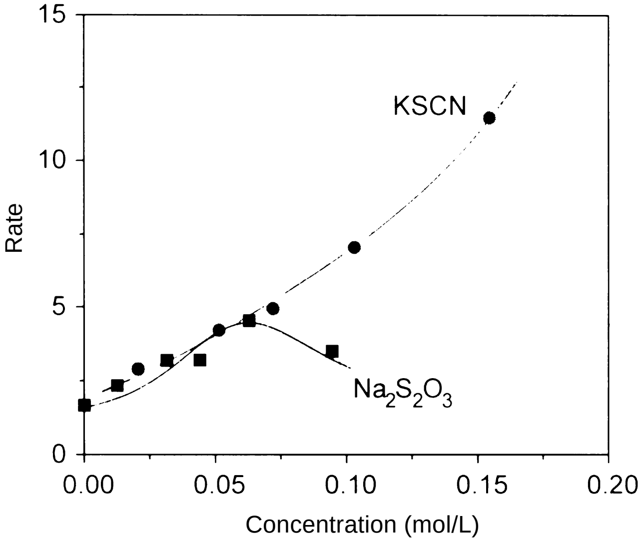

Figure 7. Influence of the concentration of various silver complexing agents on the physical development rate.

The results show:

1. Under identical conditions, the order of the activity of developing nuclei is PdS > Ag_2S > CoS > NiS > Au_2S_3 for metal-sulfide nuclei and Au > Ag > Pd > Pt for metal nuclei.
2. The medium that protects the nuclei from precipitating seriously influenced the activity of the nuclei.

Further work will be needed to improve this method, and further studies must be made to detect the influence of other conditions on the activity of developing nuclei. The CCD was found to be useful in detecting the physical development process in the DTR system. We foresee that CCDs will be used more widely in the chemical research area to detect the change of light and color.

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