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Thermally Developed Photographic Materials Based on Silver Organic Salts

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Analysis of patents, publications and our own experimental data concerning thermally developed photographic materials based on silver organic salts ($AgO_2C_xH_{2x-1}$, x = 10-22) makes it possible to outline the prospects of their future development as well as the trends in the scientific activity devoted to optimizing these materials. The study of the competing processes of the catalytic thermal development of silver carboxylates, in conjunction with the developing agents, and catalytic thermal degradation of silver carboxylates in the absence of developers, has revealed that radical reactions play a significant role in these processes. Because the formation of radicals adversely affect the stability of thermally developed materials we have found that it is very important to use developing agents that are inhibitors of radical processes. We have studied the effect of the composition and ingredient ratios in the photosensitive films on the sensitivity of thermally developed photographic papers (TDPP), both spectrally and chemically sensitized. The correlation between structure and the developing ability of reducing agents used in TDPP is established. The sensitivity of TDPP can be increased both through the modification of the light-sensitive composition with benzotriazolidophosphate and through increasing the efficiency of sulfur sensitization with amines. Also, boric acid is found to be an efficient crosslinking agent for the polymer binder in TDPP, polyvinylbutyral. In addition, high stability of TDPP can be achieved by using a reducing agent encapsulated within a polyvinylacetate caplet.

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Introduction

The growing demand for modern methods of recording information has stimulated improvements of not only traditional photographic materials but also has provided impetus for the creation and development of unorthodox silver containing photographic media. These latter materials have the advantage of being dry processed resulting in rapid development of the recorded information. Dry processed silver halide/carboxylate based imaging materials were given the appropriate name of “dry silver” many years ago. The history and up-to-date status regarding the preparation, development and preservation of black-and-white thermally developed photographic materials based on silver organic salts ($AgO_2C_xH_{2x-1}$, x = 10-22) has been previously reviewed.[1–4] The optimum combination of silver halides and silver organic salts made it possible to obtain relatively high sensitivity along with good shelf-life properties at room temperature.

The exact mechanism for formation of the latent image in thermally developed photomaterials based on silver salts remains controversial. Some authors[1] maintain the traditional viewpoint[3,4] that latent image (LI) formation occurs in analogous fashion in these materials and in conventional silver halide emulsions. More recently, evidence has been presented[2] that the silver halide component acts as a photocatalyst for the reduction of silver ions from the silver carboxylate phase. In either event, light absorption leads to nucleation of a silver(0) phase which is thermally amplified.

The resulting thermal development reaction takes place under short heating, 5-20 s, in the 110-160°C temperature range and may be expressed as follows.

$$\mathrm{RCOOAg + Red \xrightarrow[Ag^o_{LI}]{} Ag_{IM} + RCOOH + Ox} \qquad (1)$$

$$\mathrm{RCOOAg \xrightarrow[Ag^o_{LI}]{} Ag_{IM} + R\cdot + CO_2} \qquad (2)$$

The basis of the development process is the thermal catalytic transformation of silver organic salts with or without weak reducing agents (such as nonconjugated *bis*-phenols) according to these reactions.

Both reactions (1) and (2) contribute to the creation of the metallic silver image and provide information for understanding the actual mechanism of the processes involved. Potential routes to improved materials, based on these reactions, can be envisioned. For example, Eq. 2, well known for silver carboxylate systems,[5,6] suggests that the formation of the metallic silver image might be accomplished without reducing agents. However, it is important to keep in mind the need to use reducing agents not only for developing the silver halide and the silver organic salts but also for inhibiting the formation of hydrocarbon radicals, R·, resulting from catalytic thermolysis of silver carboxylate, Eq. 2.

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Radicals of the R-$CH_2CH_2\cdot$ type that are formed under thermal catalytic decomposition of silver carboxylates[5,6] can reasonably be expected to be stabilized in three ways, as shown below.

$$2\text{R-CH}_2\text{CH}_2\cdot \rightarrow \text{R-CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{-R} \quad (3)$$

$$\text{R-CH}_2\text{CH}_2\cdot \rightarrow \text{R}\cdot + \text{CH}_2\text{=CH}_2 \quad (4)$$

$$2\text{R-CH}_2\text{CH}_2\cdot \rightarrow \text{R-CH}_2\text{CH}_3 + \text{R-CH=CH}_2 \quad (5)$$

The formation of saturated hydrocarbon products, via Eq. 3, may be expected to be benign in thermally developed materials, but the formation of unsaturated products, Eqs. 4 and 5, might become a destabilizing factor. It has been observed, for example, that the presence of silver based unsaturated carboxylic acids salts has an adverse effect on the stability of thermally developed photographic materials.[7] To avoid unsaturated compounds bulky phenols and non-conjugated *bis*-phenols are preferred as weak reducing agents because they do not reduce silver salts at room temperature but can effectively inhibit the radical processes that might result from the silver organic salt decomposition.[1–4]

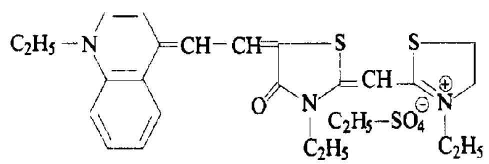
In this article we report the results of the investigation of the principal approaches to the creation of a thermally developed photographic paper composition based on silver organic salts. As part of this work, the specific points related to the preparation and development of TDPP are discussed.

Experimental

The synthesis of silver stearate was carried out by the standard double exchange reaction between sodium stearate and silver nitrate:

$$C_{17}H_{35}COONa + AgNO_3 \rightarrow C_{17}H_{35}COOAg + NaNO_3$$

Phthalimide and stearic acid were obtained as the "pure" grade (>97%) from Khimkombinant, Kazan. Polyvinylbutyral was obtained from Russian sources meeting GOST No 9439-73 standard in which the monomer mass percent is ~2% acetate, 45-48% butyral and the remainder alcohol. Photopaper samples were made in the following way. A ball mill 1/3 filled with porcelan balls (8 mm diameter) was charged with 7.8 g silver stearate, 5.6 g stearic acid, 1.8 g phthalimide and 3% solution of polyvinylbutyral in isopropyl alcohol to obtain 100 mL of total volume. After milling (rotation speed of 52 rpm), the dispersion was poured into a hermetically sealable container in which a 4% solution of KBr in water and alcohol mixture (1:1) was then added (in a quantity to achieve a AgBr:AgSt ratio of 1:4) along with a 10% solution of polyvinylbutyral (PVB) in isopropyl alcohol (50 mL). The vessel was stirred at 52 rpm under non-actinic light (light filter with λ_{max} = 585 nm). The AgBr formation process lasted 90 min. Then a reducing agent (developer) solution of 2,2′-methylene-*bis*-(4-methyl-6-tert-butylphenol) was added. In the case of spectrally sensitized materials, before adding the reducing agent, 0.04% alcohol solution of panchromatic dye, having the following structure, obtained commercially ("Svema" company in Shostka, Ukraine), was added:



The sensitization process lasted 15 min.

The effect of benzotriazolidophosphate was investigated by its addition at the TDPP emulsion preparation stage in amounts of 200 mg per mole Ag.

For structural characterization of the reaction product between silver stearate and potassium bromide in the AgSt + KBr + PVB system (molar ratio KBr:AgSt = 1:10) a comparison was made of X-ray diffraction patterns of the above composition and a reference AgSt + AgBr + PVB mixture. The electron-microscope analyses were made using JSM-350F scanning microscope (JEOL Company, Japan) and electron transmitting microscopes Jemb-10 and PEM (Electron Company, Sumy, Russia). The diffraction patterns of the samples studied were obtained using DRON-3 X-ray diffractometer by the reflection method and Bragg-Bretano focusing. The crystal sizes were also determined with the DRON-3 X-ray diffractometer.

The thermally developed compositions were coated on paper base with a polymer coating (a latex based on a copolymer of vinyl chloride and vinylidene chloride), the metallic silver content being 0.6 ± 0.1 g/m². The TDPP material was dried at 20 ± 5°C. The development process was carried out by the dry thermal method by heating the paper base side at 115 ± 0.5°C for 7 ± 1 s. The developing apparatus was comprised of a metallic cylinder with a heated glass surface. The image optical densities (D_{max}, D_0) were measured using a DO-1M densitometer. Determination of material film sensitivity was carried out in a manner typical for ordinary black and white photographic papers (through an optical density step wedge at 0.1 density steps) with a 2850 degree color temperature lamp, according to GOST 10752-79. The maximum sensitivity was determined in the kinetic experiments from the dependence of sensitivity versus development time.

Results and Discussion

A systematic study of various methods of silver stearate (AgSt, x = 18 in $AgO_2C_xH_{2x-1}$) preparations were carried out. The influence of micro- and macro-additives on the AgSt properties and the efficiency of its aqueous preparation made it possible to optimize the preparation procedure. In addition, the preparation carried out in the presence of other metal stearates (Ca^{++}, Zn^{++}, Cu^{++}), stearic acid, polyvinylbutyral and cadmium nitrate was investigated.

In order to reduce the content of silver ions in the stock solution, to improve filtration of the final product and to optimize the photographic characteristics of TDPP, the influence of small amounts of bivalent metal stearates (Ca^{++}, Zn^{++}, Cd^{++}, Cu^{++}), free stearic acid and polyvinylbutyral on the silver stearate qualities was studied.[8] Table I shows data which demonstrate the influence of bivalent metal stearates [MSt_2] contained in the silver stearate on the TDPP photographic characteristics.

TABLE I. Effect of MSt_2 (% of AgSt) upon the Photographic Characteristics of TDPP.

	M	[$MeSt_2$], %	S	D_{max}	D_{min}
1	—	—	1.00	1.50	0.23
2	Cu	10	0.80	1.50	0.29
3	Zn	8	1.50	1.60	0.32
4	Zn	10	1.30	1.55	0.18
5	Ca	3	1.40	1.60	0.24
6	Ca	5	1.50	1.55	0.20
7	Ca	8	1.70	1.55	0.20

TABLE II. Effect of Microadditives (MA) on the Photographic Characteristics of TDPP Based on AgSt

	MA	% MA of AgSt	S	D_{max}	D_{min}
1	—	—	1.0	1.35	0.20
2	$Na_2S_2O_3$	0.1	1.6	1.30	0.16
3	$Na_2S_2O_3$	1.0	1.1	1.40	0.16
4	$Cu(St)_2$	0.1	1.5	1.45	0.38
5	$Cu(St)_2$	1.0	0.6	0.90	0.30
6	$Cu(St)_2$	10.0	0.7	1.30	0.28
7	$Cd(St)_2$	0.1	1.7	1.60	0.24
8	$Cd(St)_2$	1.0	1.7	1.60	0.37
9	HSt (pH 3)	—	1.6	1.40	0.24
10	PVB	5.0	1.4	1.37	0.23

TABLE III. Effect of Bromide Cation on the Main Sensitometry Properties of TDPP. MBr_n/AgSt (mol/molAg) = 0.25.

	MBr_n	S	Lg	D_{max}	D_{min}
1	$FeBr_2$	0.001	1.7	1.2	0.3
2	$CuBr_2$	0.010	1.2	0.9	0.2
3	NH_4Br	0.04-0.06	1.0-1.1	1.0	0.1
4	$CdBr_2$	0.06-0.07	1.1-1.2	1.2	0.2
5	NBS*	0.01-0.03	1.1	1.0	0.1
6	LiBr	0.06-0.08	1.5	1.4	0.1
7	KBr	0.07-0.09	1.5	1.4	0.1

* N-Bromosuccinimide

The effect of microquantities of Cu^{++} and Cd^{++} stearic acid salts, polyvinylbutyral and $Na_2S_2O_3$ on the photographic characteristics of TDPP based on silver stearate are shown in Table II.

From these data it can be seen that addition of preset quantities of calcium and zinc stearates into silver stearate does not adversely affect the photographic characteristics of TDPP. Furthermore, addition of certain microadditives actually results in improving some photographic characteristics of the material as compared to the reference (sample 1). Cadmium stearate, for example, proved to be the most effective in improving the photographic speed of the paper.

The influence of the dispersion characteristics of silver carboxylates on the photographic properties of thermally developed papers was investigated by electronic and optical microscopy. The silver bromide synthesis was carried out during the synthesis of the photosensitive composition by bromination of the silver organic salt (AgSt) via the scheme shown below.

$$C_{17}H_{35}COOAg + MBr \longrightarrow AgBr + C_{17}H_{35}COOM$$

The use of different brominating agents significantly affects the size of silver bromide microcrystals and hence the initial sensitivity of a material and adsorption processes including spectral sensitization. The best results with respect to the majority of characteristics were achieved with lithium and potassium bromide brominating agents. Table III shows the influence of the bromide cation nature on the photographic characteristics of the TDPP (non-sensitized).

As can be seen from Table III, LiBr and KBr provide the best photographic properties of a source of bromide for the formation of silver bromide in TDPP.

We have also studied the influence of the ratio of silver organic salts and silver halide on the photographic characteristics of the material as well as the photostability of the background of the developed image. Both spectrally sensitized and non-sensitized systems were investigated. The most effective ratio of inorganic to organic silver salts for the preparation of thermally developed paper is 1:4 (see below). The figures show the data which confirm the expediency of using AgBr and AgSt in TDPP in the 1:4 ratio.

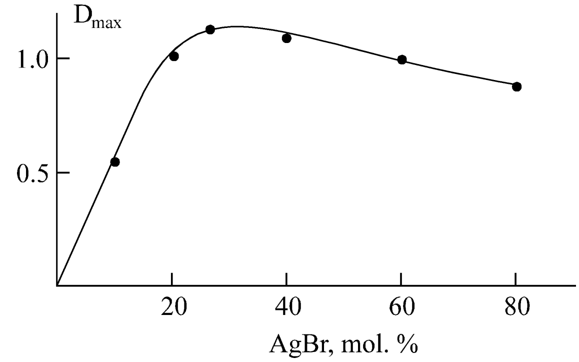


Figure 1. The relationship between the change in optical density of spectrally non-sensitized TDPP and the ratio of silver salts.

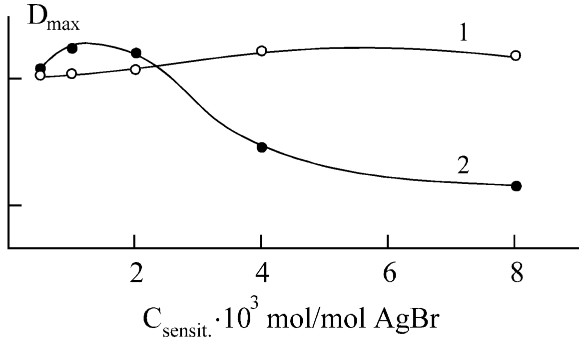


Figure 2. The relationship between the spectral sensitizer concentration and TDPP optical density. 1- 20 mol% AgBr; 2- 40 mol% AgBr

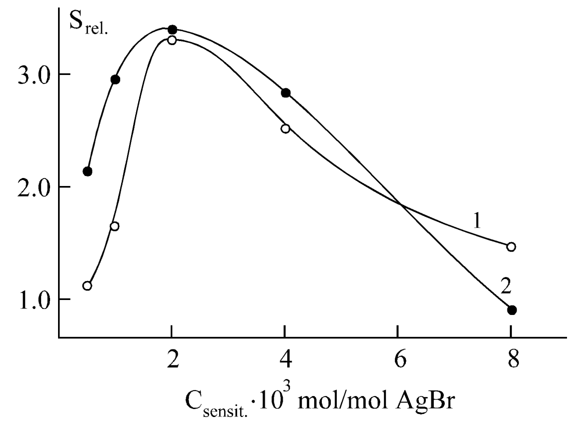


Figure 3. The relationship between the spectral sensitizer concentration and TDPP relative light sensitivity (S_{rel}).

In Fig.1, for example, the maximum optical density of spectrally non-sensitized TDPP is reached when AgBr/AgSt ratio is within the range 1:4 - 1:1.5.

Shown in Figs. 2 and 3 are the relationships between the spectral sensitizer concentration and relative light sensitivity (S_{rel}) and optical density (D_{max}), respectively.

TABLE IV. Photographic Characteristics of TDPP, Benzotriazolidophosphate Introduced at Different Stages of Emulsion Preparation

	At the beginning			10 min. later			20 min. later			Reference		
	S	D_{max}	D_o	S	D_{max}	D_o	S	D_{max}	D_o	S	D_{max}	D_o
1	0.50	0.45	0.10	0.65	0.62	0.11	0.57	0.55	0.11	0.45	0.32	0.09
2	0.45	0.39	0.10	0.57	0.47	0.10	0.57	0.53	0.10	0.45	0.35	0.10
3	0.50	0.45	0.12	0.65	0.60	0.12	0.50	0.49	0.10	0.35	0.31	0.11
Avg.	0.48	0.43	0.11	0.62	0.56	0.11	0.55	0.52	0.10	0.42	0.33	0.10

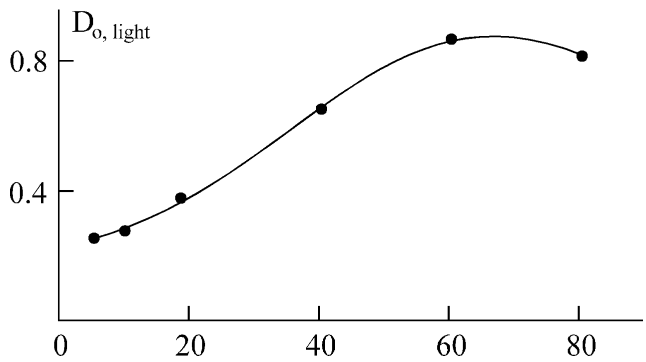
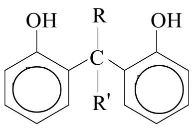


Figure 4. The relationship between the light induced fog and the proportion of silver salt in TDPP.

Figure 4 shows the dependence of fog ($D_{0,ef}$) on the ratio of silver salts in TDPP. Comparing the data given in Figs. 2 through 4 it can be concluded that the optimal ratio between AgBr and AgSt is 1:4.

In order to prevent non-selective reduction of silver during thermal development, low-activity reducing agents such as monophenols, *bis*-phenols and other phenolic developers are used.[1–4] The relationship between the structure of the monophenol developers, and non-conjugated *bis*-phenols, and their reducing activity in the process of thermal development is discussed below. We have found that, other conditions being equal, the incorporation of donor substituents into the reducing agent molecule increases developability while the incorporation of acceptor substituents decreases the developability of the corresponding derivative. In the case of non-conjugated *bis*-phenols having hindered phenoxy groups of the general formula

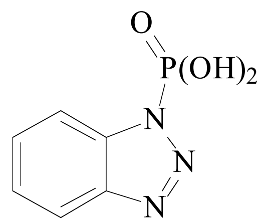


where R and R' are bulky radicals, low activity as developing agents is observed.

One of the urgent tasks in improving thermally developed photomaterials is increasing their light-sensitivity. Because silver bromide is used in TDPP the possibility of improving the light-sensitivity of photomaterials by taking advantage of known technology for the modification of the AgBr crystals and by optimization of their sulfur sensitization. In order to study the effect of AgBr crystal modification and sulfur sensitization of thermally developed photopapers on their photographic properties, both spectrally-sensitized and non-sensitized samples were investigated.

From the X-ray results, the KBr in the AgSt + KBr + PVB system was found to react completely to form normal AgBr crystals, ranging in size from 0.01 to 0.3 μm. The average microcrystal size, from the X-ray data, is 400Å. The AgBr crystals were observed by TEM to form mostly on the surface of the AgSt crystals. TEM analysis of the dried AgSt + KBr + PVB composition revealed cubic crystals (*100*) which are clearly observed as they are non-transparent to the electron beam of the electron microscope. These results are similar to the observations made by others regarding the formation of AgBr in an *in situ* AgBr reaction process.[9] At the same time both clusters and agglomerates of small (0.01 μm) crystals and larger polycrystals (0.3 μm) were observed. The growth of the AgBr crystals takes place mostly on the surface of AgSt crystals (the latter being relatively transparent to the electron beam of the microscope).

The effect of benzotriazolidophosphate, shown below, which can modify the AgX microcrystal surface during emulsification,[10] on the light-sensitivity (S) of thermally developed photopapers is of great interest. First, the time from the beginning of the emulsion preparation to the time the modifier was added was determined at which the optimum photographic TDPP characteristics were obtained. The data in Table IV show that the introduction of benzotriazolidophosphate 10 min after the beginning of the emulsion preparation is the most effective. Then, the optimum concentration of modifier at the TDPP emulsification stage (10 min after the beginning of the emulsification) was determined at which the best photographic characteristics are achieved.



From the data in Table V it can be seen that the optimum concentration of the benzotriazolidophosphate is 230 mg/g at.Ag.

Another route to increase the TDPP light-sensitivity is to optimize the process of sulfur chemical sensitization. Previously[11] sulfur sensitization was shown to be effective in the case of AgX materials containing gelatin as a binding agent, due to the fact that gelatin amino groups assist the nucleophilic sulfur substitution in sulfur based chemical sensitizers.[12] Sulfur sensitizers form the sulfide anion according to the scheme shown below for thiourea:

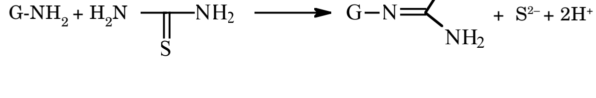


TABLE V. Photographic Characteristics of TDPP at Different Concentrations of Benzotriazolidophosphate, mg/mole Ag Added 10 min After Beginning of Emulsification

	0, Reference		115		172		230		287		345	
	S	D_{max}	S	D_{max}	S	D_{max}	S	D_{max}	S	D_{max}	S	D_{max}
1	0.75	0.51	0.75	0.51	0.82	0.63	0.92	0.65	0.82	0.65	0.82	0.63
2	0.50	0.49	0.75	0.52	0.82	0.60	1.05	0.70	0.82	0.61	0.75	0.55
3	0.65	0.50	0.65	0.50	0.92	0.69	0.92	0.68	0.82	0.64	0.82	0.60
Ave.	0.63	0.50	0.72	0.51	0.85	0.64	0.96	0.68	0.82	0.63	0.80	0.59

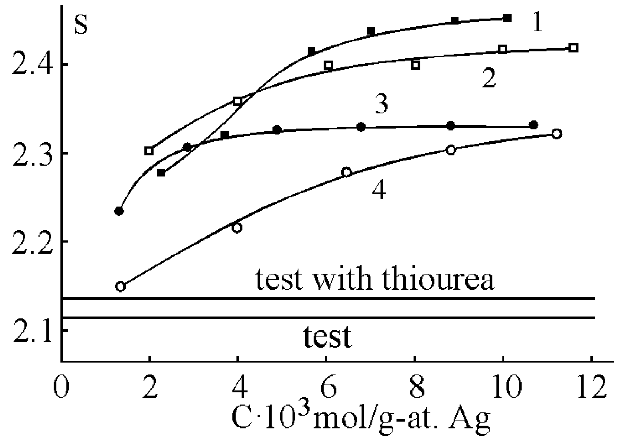


Figure 5. Dependence of TDPP sensitivity upon the concentration of amine added at the chemical sensitization stage with thiourea. 1 - diethylamine, 2 - n-butylamine, 3 - ethanolamine, 4 - diethanolamine.

This reaction explains the formation of Ag_2S impurity centers on AgX microcrystals.

With TDPP made in the absence of gelatin, sulfur sensitization is not effective,[13] thus, amines were added to the TDPP in order to improve the efficiency of TDPP sulfur sensitization. Amines should act as nucleophilic agents in the formulation in place of the gelatin amino groups. Figure 5 shows the relationship between TDPP sensitivity and the concentration of amines added.

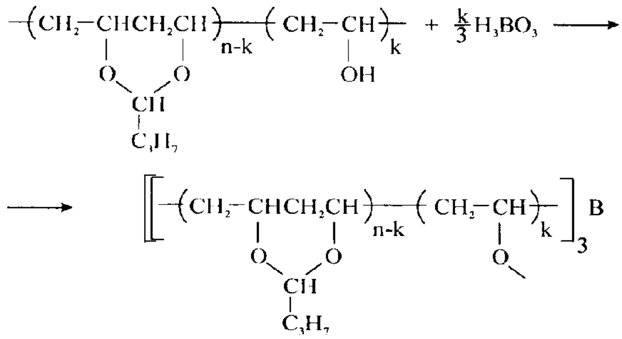
As can be seen from Fig. 5, the effectiveness of TDPP sulfur sensitization depends on the basicity of the amine added at the chemical sensitization stage. Thus, from these results we conclude that TDPP sensitivity can be increased both through modification of the light-sensitive composition with benzotriazolidophosphate and through increasing the effectiveness of sulfur sensitization with amines.

Because the formulations of actual thermally developed systems are more complex than the model systems described above the specific features of their spectral sensitization were also studied. The adsorption of the dyes in the thermally developed materials suggest that they primarily adsorb on the silver halide. This fact probably explains some of the similarity in mechanisms of the spectral sensitization of thermally developed materials and traditional silver halide materials.

Using compounds possessing bromine accepting properties in the photosensitive layers is of particular significance in thermally developed materials that utilize polyvinylbutyral as the binder. The most efficient compounds of this type are succinimide, phthalimide and compounds possessing the guanidine group.

For better practical characteristics of thermally developed materials the problem of isolation of the developing agents from the photosensitive composition, for improved print stability, was also solved. The developing agents were incorporated into the protective layer of polyvinylbutyral in the form of caplets enclosed in a vinylacetate-ethylene copolymer shell. This approach allowed the material aging to slow, thereby increasing the maximum image optical density and photostability.

Finally, to obtain better mechanical properties of thermally developed photographic papers, including higher adhesion of the photosensitive polyvinylbutyral layer to paper, the polyvinylbutyral layer was crosslinked with boric acid, as illustrated by the following reaction.



The incorporation of boric acid into the protective layer (added immediately prior to coating) now makes it possible to thermally develop the material from this side of the film.

Conclusions

The optimization of silver stearate preparation methods for thermally developed photographic papers and routes to improving their photographic and physical-mechanical properties are shown.

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