

On the Role of Microcrystalline Silver Bromide in the Development Process of Photothermally Developed Materials of the “Dry Silver” Type

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Abstract

A model is proposed for the role of a silver bromide and silver carboxylate epitax in thermally developed photographic materials (TDPM) of the “Dry Silver” type. The model proposes that the epitax acts as a form of an insulator with the carboxylic acid in the polyvinylbutyral layer. This type of insulating lattice has the ability to acquire a stable negative charge resulting from the reaction of the photolytic bromide with the silver carboxylate of the epitax. The proposed model is based on a wide range of data now available including the investigation of the electrochemical properties of the silver bromide and silver carboxylate dispersions, the effect of pre-exposure heating on the TDPM photographic properties, the use of existing concepts regarding the role of the components in the “Dry Silver” type thermally developed photographic materials, the morphology of the silver halide formed from silver carboxylate, and the morphology of the silver particles formed upon reduction during thermal development.

Introduction

The latent image in the light exposed silver bromide microcrystals in thermally developed photographic materials (TDPM) is visualized by thermally induced reduction of the silver source (typically silver carboxylate) with a developer [1]. In order to increase the reactivity of the organic silver compounds, “toners” are added to the film which can form various complexes with silver ions [2]. It is normally assumed that the development process in TDPM is similar to the “physical” development process in aqueous processed photographic materials [3]. However, the results of many investigations [4-6] do not fit this scheme very well since only in a few cases do the developed silver particles exhibit the spherical shape characteristic of physical development [3].

The object of the current work is to propose and verify a model of the TDPM development process in which the silver bromide microcrystals not only form the latent image centers but also accelerate the delivery of the organic silver compounds to the reduction reaction zone. The proposed model is based on previous investigations of the light sensitive component formation process [5], the

development kinetics [7], the morphology of the epitaxial interface observed in certain microcrystals of silver carboxylates and silver bromide [8], the morphology of the developed silver [4] and the effect of preheating on the TDPM sensitometry [9].

Results and Discussion

Upon light exposure the silver bromide microcrystals form latent image centers of Ag^0 and bromide ions [10]. It is assumed here that the separation of the photolytic silver is at the interface between the AgBr and silver carboxylate where the epitax has been observed in certain cases [11]. The bromide, as highly mobile Br^- ions, can exchange with the carboxylate to form silver bromide and carboxylate. The probability of this reaction is greatest at the interface between the AgBr and silver carboxylate phases where silver ions are located. Since the carboxylate ions are poorly mobile a negative charge can accumulate during development and localize a negative charge at the interface of the AgBr/Ag-carboxylate epitax. The charge can be neutralized during heating in the resulting pseudo-melt of various components such as carboxylic acid, toners, silver carboxylate, and polyvinylbutyral. However, at the initial stages the charge may influence the development process by accelerating the delivery of positively charged silver compounds, presumably such as $[\text{AgPHZ}]_2^{2+}$ [12, 13], to the latent image centers. Verification of the proposed mechanism was carried out by comparison of the results of three types of TDPM, “*in situ*”, “*ex situ*” and AgBr-free films. Upon photolysis the silver stearate decomposes to form metallic silver (latent image centers), carbon dioxide and paraffin (St-St) [14] but not a negative charge. The photolytic silver is in the form of colloidal particles, the growth of which inhibits the release of paraffin. Electron microscope investigation of these samples show that the AgBr-free samples develop significantly slower than the films containing silver bromide. Based on these data and earlier results of the investigation of the processes occurring in TDPM [4, 7-9], the following model for the development process in TDPM is proposed.

Exposure of the TDPM results in photolysis of the silver bromide to form metallic silver and bromide ions. The metallic silver is the latent image center at the interface between AgBr and silver carboxylate. There the bromide

ions displace the carboxylate from the silver carboxylate generating a negative charge. On heating the photolayer the PVB viscosity decreases, the carboxylic acid and the developer melt, and the dissociation of the silver carboxylate increases. Positively charged toner complexes of the silver carboxylates are attracted to the negative charge of the AgBr/Ag-carboxylate epitax. The melting of the carboxylic acid and the formation of silver complexes create the conditions for neutralization of the charge at the epitax. The ionic silver is reduced to nano-sized metallic silver crystals, aggregating as the carboxylic acid is eliminated. The release of carboxylic acids and toners during development increase the reactivity of the silver carboxylate and decrease the reduction potential at the expense of the developer.

Conclusions

Based on a wide range of data now available, a model is proposed for the role of a AgBr/Ag-carboxylate epitax in TDPM. It acts as a form of an insulator in the carboxylic acid in the polyvinylbutyral layer. This insulator has the ability to acquire a stable negative charge resulting from the reaction of the photolytic bromide with the silver carboxylate of the epitax. The proposed model accounts for existing concepts regarding the role of the components in TDPM, the morphology of the silver halide formed from silver carboxylate, and the morphology of the silver particles formed.

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