

Development of Rapid Dry Photothermographic Materials with Water-base Emulsion Coating Method

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Abstract

The new system of the dry laser imager **DRYPIX-7000** and the dry photothermographic imaging film **DI-HL** has been developed as a new generation of dry imaging system for health imaging. The system has the highest specifications, amazingly rapid output of first print (65 seconds), the highest throughput (180 sheets per hour for 14 x 17-in), and the shortest start up time (15 minutes from power off condition). These features were achieved by the combination of the excellent technologies introduced in the new imaging film and the laser imager.

In **DI-HL**, new high-activity heat-developer and new heat-development accelerator were introduced in order to realize rapid processing and high throughput. Quite new yellow dye forming tone control agent was employed for excellent image tone reproduction. Image stabilizer, high purity silver behenate and new SBR latex binder were designed for image keeping stability. And the film is produced with water-base emulsion coating method, so much friendly to environment.

In **DRYPIX-7000** imaging apparatus, laser exposure and heat development are carried concurrently in order to realize high throughput.



Figure 1. Dry laser imager DRYPIX-7000 and photothermographic film DI-HL

Introduction

In recent years, digitalization of health imaging is proceeding rapidly by development and spread of health imaging technologies such as computed tomography (CT), nuclear magnetic resonance imaging (MRI), computed radiography (CR). These digital images were printed out to laser imagers connected to the network system in the hospital. On the other hand, increasing in concern over the global environment, importance of dry laser imagers are increasing further. This system does not use any chemical solutions for processing and does not put out any waste and residue. In 1995 the first dry imager and films were introduced from Minnesota Mining and Manufacturing Co., but the film was produced with a large amount of organic solvent. In this background dry laser imager **FM-DP L** and film **DI-AL** were released in 1999 from Fuji Film Medical Co., Ltd. The dry photothermographic film **DI-AL** is produced with water-base emulsion coating method.¹⁻³ This technology is much eco-friendly one that does not use a plenty of organic solvent in the manufacturing process.

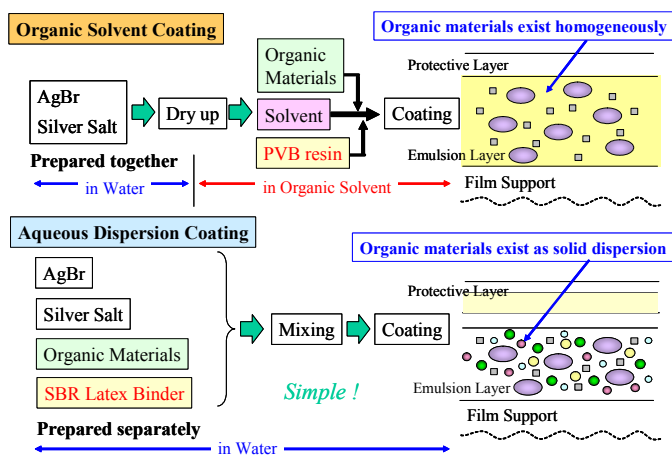


Figure 2. Manufacturing processes of solvent-base and water-base coated photothermographic films

FM-DP L system was highly regarded for high quality image, constancy of printing and easy operation, but recently demands on processing speed and image tone quality were increasing. Then we have developed the new system of the dry laser imager **DRYPIX-7000** and the dry imaging film **DI-HL**. In this presentation we will talk about organic chemical compounds introduced in **DI-HL** mainly.

Image forming mechanism of photothermographic materials

The image forming mechanism of the photothermographic materials was shown in Fig.3.⁴

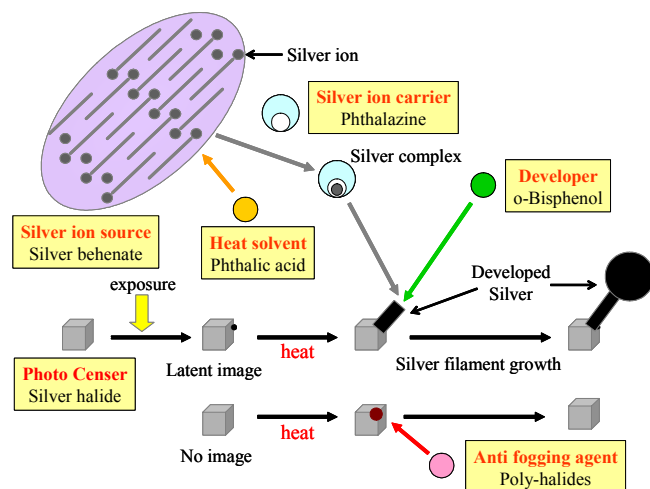


Figure 3. Image forming mechanism of photothermographic materials

First of all, latent images are formed on silver halide grains by laser exposure of the film. The film is heated about 120 °C, then silver behenate get mobility by phase transition. Silver ion is translated from silver behenate to phthalazine, and carried to the silver halide with latent image. Then silver ion is reduced to metal silver by heat-developer and silver filament is growing up there. Unexposed silver halide is not developed by the action of poly-halides anti fogging agent.

In the water-base coated photothermographic materials, rate determining step is the earlier period of the silver cluster growth. To realize rapid processing, it is important how to accelerate the reduction of silver ion at the earlier period without increasing fog and degradation of image keeping stability.

Technologies introduced in DI-HL

Development acceleration technologies, image-tone control technologies and image stabilizing technologies have been developed for the photothermographic film **DI-HL**.

1) Development acceleration technologies

We developed a new reducing agent for heat-developer which is *o*-bisphenol compound with *tert*-alkyl groups at the 2,2'-position. This compound has high activity, and is able to reduce over 6-equivalent silver ions. We also

developed quite new naphthol compound as a development accelerator. This compound works as a strong reducing agent at the earlier period of the development process, and then works as an electron transfer intermediate from bisphenol developer to silver ion. Adding about 3 mol% of the accelerator against heat-developer, developing speed is amazingly accelerated as shown in Fig.3..

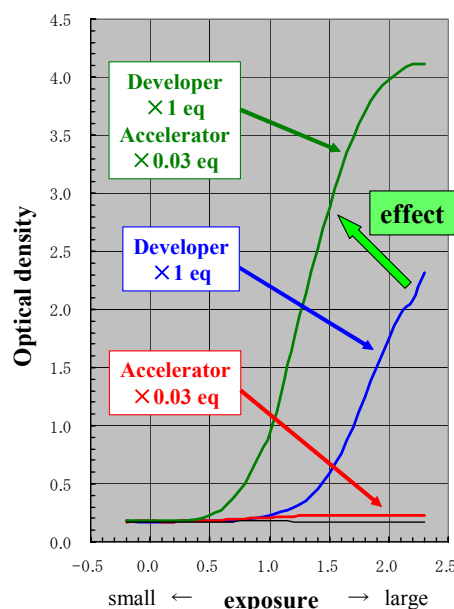


Figure 3. Effect of development accelerator

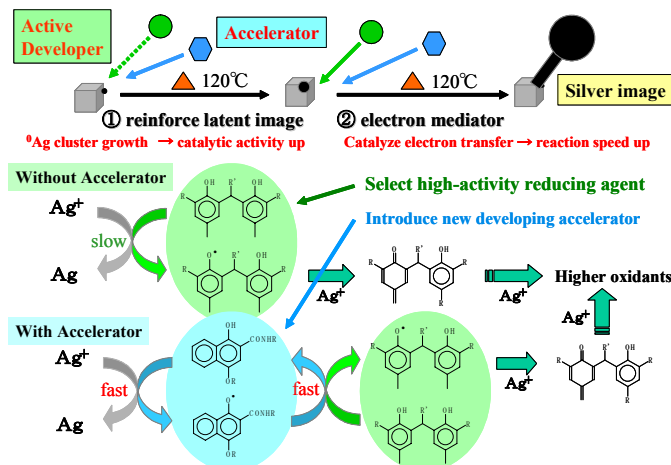


Figure 4. Mechanism of development acceleration

2) Image-tone control technologies

The color tone of the silver image depends on the size of the developed silver particles. In the photothermographic materials with water-base emulsion coated method, we can control the size of silver particles by changing the $\text{Na}^+/\text{NH}_4^+$ ratio. If Na^+ is increased the silver particles decrease the size, and spectral absorption of blue light region increases and red light region decreases. If NH_4^+ is increased the silver particles increase the size, and spectral absorption of blue light region decreases and red light region increases. We

can not increase both of the blue and the red absorption at once.

We found 2,2'-tert-alkyl-4,4'-methyl substituted o-bisphenol developer formed yellow dye during heat development at high density region. It reveals that two of one electron oxidized radicals are dimerized and oxidized to yellow dye. Furthermore we found p-bisphenol substituted with hindered alkyl groups at the 2,2',6,6'-position formed yellow dye at low density region. These compounds made us to control image tone as we like.

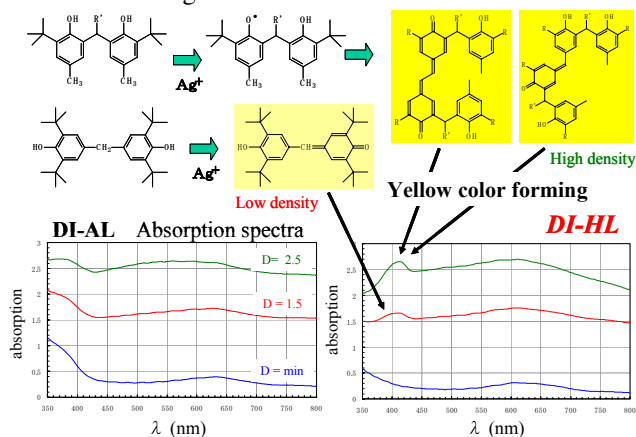


Figure 5. Yellow dye forming developer and tone controller

3) Image stabilizing technologies

Usually to use high activity developer degenerates image keeping stability. So we must develop the method to improve image keeping stability at the same time. We introduced three technologies in **DI-HL**, a new type of image stabilizer, high purity silver behenate, and improved SBR latex binder.

The image stabilizer is a triphenylphosphin oxide derivative, which makes the hydrogen-bonded complex with developer after heat-development, and thereby developer is inactivated. High purity silver behenate has a higher phase transition temperature and decrease silver ion supply in film keeping. The SBR latex is reduced the content of surfactant and inorganic salts as less as possible.

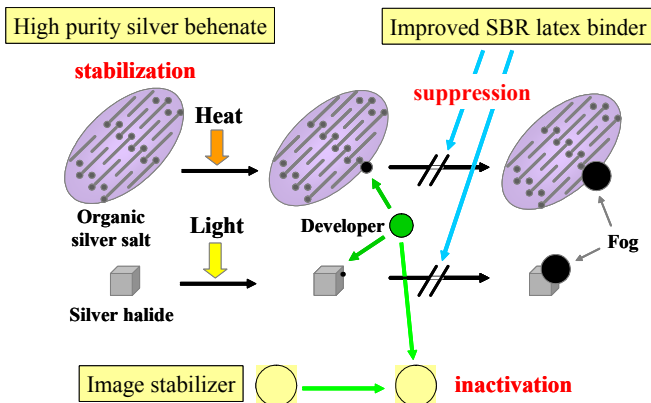


Figure 6. Image stabilizing technologies

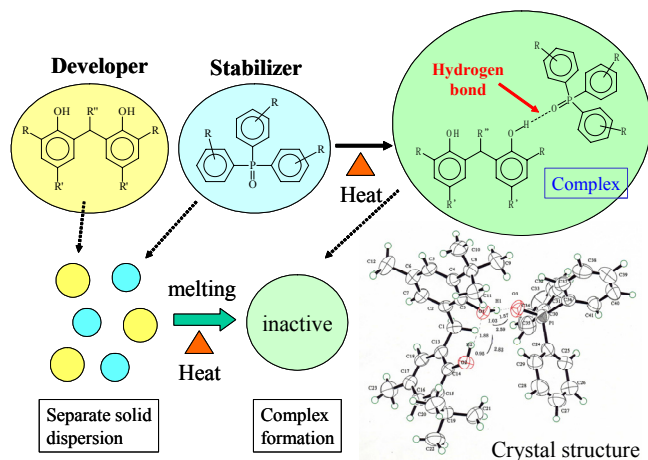


Figure 7. Mechanism of phosphin oxide image stabilizer

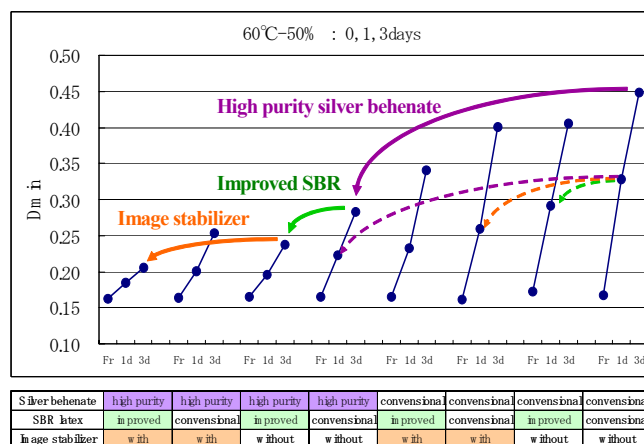


Figure 8. Combination effect of image stabilizing technologies

DI-HL

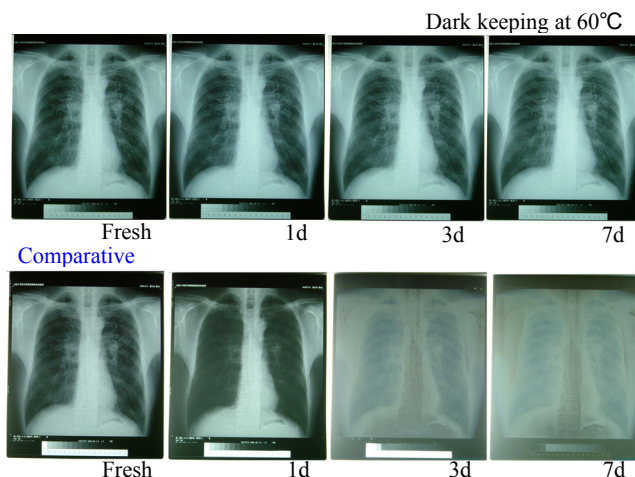


Figure 9. Dark keeping stability of DI-HL and comparative organic solvent-base photothermographic materials

Combination of these technologies we can realize both of the developing ability and keeping stability.

Advancement in dry imager *DRYPIX-7000*

In order to shorten the processing time we change the inner layout of apparatus shown in Fig.10. In this layout the film transfer pass is very short and exposure part and developing part is placed closely. In this apparatus heat development begin from the top of the film sheet before the exposure does not finish the end of the sheet. The time table of the developing process is shown in Fig.11.

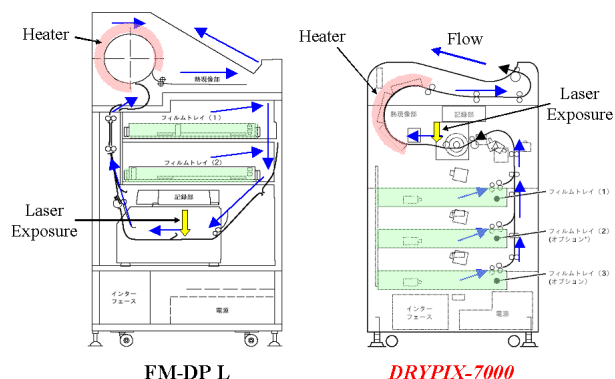


Figure 10. Internal structure of the dry imagers

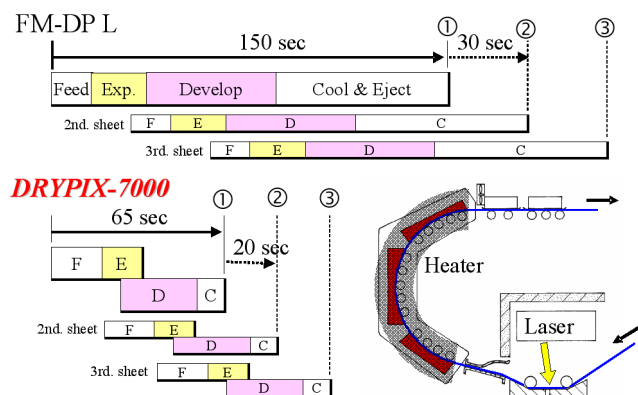


Figure 11. Processing time table and laser-heater layout

Conclusion

We developed the system of dry laser imager *DRYPIX-7000* and new photothermographic material *DI-HL*. Combination of the new imager and film, we can get high quality diagnosis image with high productivity.

Table 1. System performance of dry imagers and films

Imager Film	<i>DRYPIX-7000</i> <i>DI-HL</i>	FM-DP L DI-AL
Continuous processing rate (14x17 inch sheets/hour)	180 sheets	130 sheets
Time for first print output (seconds)	65 sec	150 sec
Time for rising from power off condition (minutes)	15 min	30 min
Imager volume (m ³)	0.62 m ³	0.78 m ³
Imager weight (kg)	203 kg	250 kg

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Biography

Yasuhiro Yoshioka was born in 1955 in Tokyo Japan. In 1980 he was graduated from the graduated course of chemistry division of The University of Tokyo, and obtained a degree of Master of Science. In the same year, he joined Ashigara Research Laboratories of Fuji Photo Film Co., Ltd.