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Examination of an Antifungal Agent for Use on Photographs

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Abstract

Japan experienced an unprecedented disaster in 2011, the Great East Japan Earthquake and Tsunami. Recovering and preserving family photographs was of critical concern for people who lost their families or homes in the disaster. As the very difficult recovery of photographs from the unimaginably vast amount of wreckage occurred, microbial deterioration in tsunami-damaged materials presented a serious problem. This study of an antifungal agent, Hokucide® R-150, introduces a new approach to fungal problems concerning photographic materials. Preventive measures are proposed which can be utilized in uncontrolled environments where mold outbreaks and infestations are difficult to restrain.

Introduction

The Great East Japan Earthquake and Tsunami in 2011 caused tremendous damage to photographs and documents. Recovery of these materials should ideally be carried out as soon as possible; however, the scale of this disaster was unprecedentedly vast, and many water-damaged personal objects, including photographs, were left untreated for months. For many of the disaster victims who lost their homes or families, photographs became irreplaceable treasures- the most important things to retrieve from their lost lives. Unfortunately, many photographs were found with microbial deterioration because of the delayed recovery, leading to dissolution of the gelatin binder and damage to the support, at times making it very difficult to conduct further conservation treatment. Controlling microbial deterioration is one of the keys to saving water-damaged photographs; however, in the case of a disaster such as was experienced in 2011, the immediate washing and drying or freezing of recovered photographs is impossible. This study evaluates the use of Hokucide® R-150 as an antifungal agent in an emergency response procedure. The goal is to investigate the effectiveness of the agent at preventing mold as well as how safe it is to use on photographs, in terms of not causing further damage.

About Hokucide® R-150

Hokucide® R-150 (Hokko Chemical Industry Co., Ltd, Japan, MSDS No: 7025-001) is an aqueous solution of chloromethylisothiazolinone (5-chloro-2-methyl-4-isothiazolin-3-one, CMIT, CAS#26172-55-4) and methylisothiazolinone (2-methyl-4-isothiazolin-3-one, MIT, CAS#2682-20-4). Hokucide® R-150 is widely used in the architectural industry as an antibacterial and antifungal agent for construction materials, adhesives, paints, coatings, paper, and silicone oil. It can control the germination of bacteria, fungi, algae and yeast. Its oral toxicity is LD_{50} (rat) > 2000mg/kg, and it has a pH of 3.0~4.0. in undiluted solution.

Hokucide® R-150 was selected by our collaborator, microbiologist Hideo Arai, who proved its antifungal capabilities when mixed with animal glue on a color painted surface of the main wooden building of the Kongoshoji Temple, an important national treasure in the Mie prefecture. Hokucide® R-150 has a history of being used in the photographic industry- it was added as a detergent to the final rinse during the development of gelatin silver prints, and it was also used to clean automatic film processing devices. This agent was selected for its aqueous, nonvolatile nature (which allows it to persist on photographs in nonideal environments) as well as its simplicity of preparation, availability and cost.

Effect of Hokucide® R-150 solution against fungi

The first step was to isolate the various fungi found on tsunami-damaged photographs and albums. *Stachybotrys* sp., *Penicillium* sp., *Trichoderma* sp., and *Aspergillus* sp. were identified as non-tonophilic fungi, and *Asp*. *penicilloides* was identified as an absolute tonophilic fungi. Sample photographs were then immersed in sea water and air-dried. The minimum inhibitory concentration of Hokucide® R-150 was obtained by inoculating and cultivating strains of non-tonophilic fungi (*Aspergillus niger*) and absolute tonophilic fungi (*Aspergillus penicilloides*, *Eurotium herbariorum*) on groups of paper disks treated with Hokucide® R-150 solution, and comparing the samples with untreated paper control disks. A surfactant is usually added to Hokucide® R-150 for even dispersion and reduction of surface tension. An aqueous solution of 1.0% Hokucide® R-150 was prepared, with 20% aqueous propylene glycol solution added as surfactant. The right halves of sample photographs were immersed in the solution and air dried. The standard strains of *Aspergillus niger*, *Aspergillus penicilloides*, *Eurotium herbariorum* were inoculated on the prints and cultivated at 94-100% RH and 25°C/77°F for 45 days. Ultraviolet images show that fungal growth was not found on the treated areas (Fig. 1b).

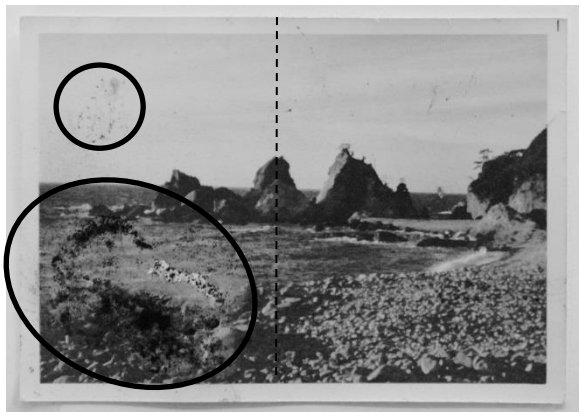

Fig. 1a (normal)

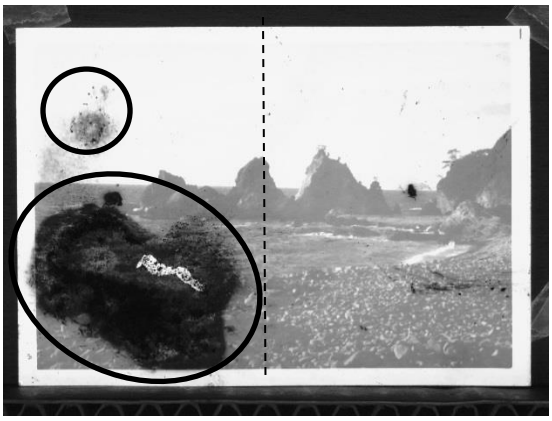

Fig. 1b (UV)

Fig. 1. Chromogenic color print on baryta paper from 1970. The right side of the photograph was treated with Hokucide® R-150 solution, while the left side where fungal growth is visible was untreated.

Effects of Hokucide® R-150 on photographs with Tween 80 as surfactant

The majority of the photographs damaged by the tsunami were gelatin silver prints and color prints on baryta paper and resin coated paper; however, cyanotype and albumen prints were tested also for completeness. Tween 80, a non-ionic surfactant which does not possess antifungal

activity, was chosen instead of propylene glycol to ascertain whether Hokucide® R-150 has any negative effects on photographs. Although the recommend concentration of Hokucide® R-150 is 1.0-2.0% according to the manufacturer, a maximum concentration of 3.0% was tested to examine the effect.

Samples tested (Fig. 2)

(1)Step tablet: cyanotype, albumen print, gelatin silver Developed-out Prints (DOP) on baryta paper, gelatin silver on Resin-coated (RC) paper.
(2)Macbeth Color Chart (chromogenic).
(3)Colloidal silver detector film.
(4)Old photographs: albumen print, gelatin silver Printed-out Prints (POP), gelatin silver DOP, chromogenic on baryta, chromogenic on RC.

Fig.2. Samples tested

Antifungal solution

1.5% Hokucide® R-150 with Tween 80 (1.5% w/v)
3.0% Hokucide® R-150 with Tween 80 (1.5% w/v)

Method

- Wash samples in distilled water.
- Immerse samples in solution: a) distilled water (control), b) distilled water with Tween 80 (1.5% w/v), c) 1.5% Hokucide® R-150 solution, d) 3.0% Hokucide® R-150 solution.
- Air dry.
- Set samples in stainless jigs and place into incubation chamber.

Observations

The transmission density of the colloidal silver detector film was measured using a densitometer (blue filter, TR924, Macbeth). Reflection density and colorimetric measurements of CIE L*a*b* values were measured using a spectrophotometer (Spectrolino GretagMacbeth). Four measurements were made: before and after immersion, and after 7 days and 14 days of accelerated aging. The incubator was set at 60°C/140°F and 86%RH for color materials, and 70°C/158°F and 86% RH for the rest. The corresponding color difference was calculated.

Results

(1)Step tablet:
The reflection density change of immersed samples was similar compared to the control.
(2)Macbeth Color Chart:
The color difference (ΔE*ab) for samples in solutions a), c) and d) was between 0.53 and 0.92 before and after immersion, and 1.89-2.58 after 14 days; however, ΔE*ab for cyan in solution b) was higher than the rest (3.75, Table 1).
(3)Colloidal silver film:
There was a slight decrease in density (ΔTDb) for all samples after immersion. After 7 days and 14 days of artificial aging, those immersed in antifungal solution had a ΔTDb similar to the control. The concentration of Hokucide® R-150 did not affect the density change.

(4)Old photographs:

The readings were not as stable as for the step tablet, possibly because of the different history and level of deterioration of each photograph. There was no significant change in density or color difference before and after immersion; however, after 14 days of accelerated aging, all of the samples (including the control) showed a similar change in density and color difference with one exception: the old POP print in solution b) showed a significant loss of detail noticeable to the naked eye.

Due to the Tween 80 solution (without R-150) showing unsatisfactory results, an alternative surfactant had to be considered.

	Solution											
	a) Distilled water (control)			b) Distilled water + Tween 80			c)1.5% Hokucide® R-150+ Tween 80			d)3.0% Hokucide® R-150 + Tween 80		
Macbeth color chart	Cyan	Magenta	Yellow	C	M	Y	C	M	Y	C	M	Y
After immersion	0.92	0.69	0.63	0.85	0.90	0.63	0.72	0.72	0.63	0.60	0.70	0.53
7 days	1.30	2.34	1.31	1.46	1.93	1.28	1.40	2.01	2.00	1.75	2.02	1.61
14 days	1.89	2.47	1.98	**3.75**	2.41	2.06	1.99	2.38	2.58	2.40	2.14	2.54

Table 1. ΔE*ab for Macbeth Color Chart (chromogenic color print)

Choosing an alternative surfactant

Instead of Tween 80, four solutions commonly used in the film developing process were considered: Kodak Flexicolor Final Rinse, Kodak Ektacolor Prime LORR, Fuji Driwel K, and Kodak Photo-Flo. In order to obtain the minimum inhibitory concentrations for each surfactant, the following test was conducted.

Method

The conidia and spores of two fungal strains; *Aspergillus niger* (non-tonophilic fungi) and *Eurotium herbariorum* (absolute tonophilic fungi) were adhered onto paper disks inoculated in petri dishes of 1.25% malt agar (MA) media and MA media containing 40% sucrose. Then, solutions of 0.5%, 1.0%, 1.5%, and 2.0% Hokucide® R-150 with each of the four surfactants were dropped onto the paper disks. The petri dishes were incubated at 20-25°C (68-77°F) for 14 days. After 14 days, the dishes were observed, and the minimum inhibitory concentration was chosen to be 1.0-1.5%, depending on which surfactant was used. Solutions of the antifungal agent and surfactants were prepared, and colloidal silver detector films were immersed in them, dried, and placed in a chamber at 70°C/158°F and 86% RH. The transmission density was measured before and after immersion, and after 4 days, 7 days and 14 days of aging.

Results

Density changes (ΔTDb) for Kodak Flexicolor Final Rinse was 1.04, and for Kodak Ektacolor Prime LORR, it was 1.03 (Table 2). Color changes of colloidal silver films were clearly visible

(Fig. 3). TDb were minimal for Fuji Driwel K (-0.11) and for Kodak Photo-Flo (- 0.15), therefore these two surfactants were chosen for the next experiment.

Solution with Hokucide®R-150 (%)	Ref.	After immersion	After 4 days	After 7 days	After 14 days
Distilled water (1.5) control		-0.11	-0.08	-0.16	-0.02
Kodak Flexicolor (1.0)	A	-0.13	0.84	0.93	1.04
Kodak EktacolorLorr (1.5)	B	-0.13	0.77	0.85	1.03
Fuji Driwel K (1.5)	C	-0.11	-0.13	-0.17	-0.11
Kodak Photo-Flo (1.0)	D	-0.13	-0.13	-0.16	-0.15

Table 2. Colloidal silver film, change in transmission density (ΔTDb) compared to initial transmission density of 3.74.

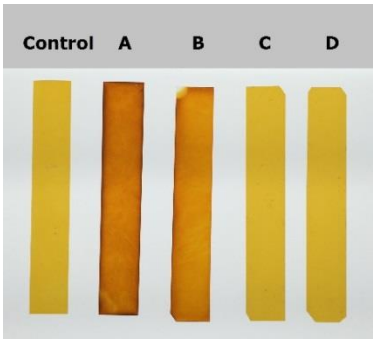

Fig.3. Colloidal silver film after 14 days.

Influence of Hokucide® R-150 solution on photographs using Fuji Driwel K and Kodak Photo-Flo as surfactants

Samples tested
(1)Step tablet: albumen print, gelatin silver POP, gelatin silver DOP on baryta.
(2)Resolution chart: albumen print, gelatin silver POP, gelatin silver DOP on baryta.
(3)Macbeth Color Chart (chromogenic), CMY, and WGB (white, grey, black) were measured.
Resolution charts were added to the samples in order to observe any changes.

Antifungal solution
1.5% Hokucide® R-150 with Fuji Driwel K (1% v/v)
1.0% Hokucide® R-150 with Kodak Photo-Flo (0.5% v/v)

Method
- Wash samples in distilled water.
- Immerse samples in solutions.
- Air dry.
- Set samples in stainless jigs and place into incubation chamber.

Observations
Reflection density and colorimetric measurements of CIE L*a*b* values were measured using a spectrophotometer (Spectrolino GretagMacbeth). Four measurements were made: before and after immersion, and after 7 days and 14 days of accelerated aging. The incubator was set at 60°C/140°F and 86%RH for color materials, and 70°C/158°F and 86% RH for the rest. The

corresponding color difference was calculated. Resolution charts were viewed four times under an optical microscope (100x magnification): before and after immersion, and after 7 days and 14 days of accelerated aging.

Results

(1)Step tablet:

The reflection density change values for immersed samples were similar to the control except for POP, which had a slight change in the middle tone area after accelerated aging (Fig. 4, middle).

(2)Resolution chart:

Images were compared using an optical microscope, and no loss of detail was observed from before immersion to after accelerated aging.

(3)Macbeth Color Chart:

There was a slight change of color (ΔE*ab) in magenta (+2.44) and a yellow stain in white (+3.55) for the Photo-Flo solution samples, but all other ΔE*ab values remained between 0.19 and 1.02 (Table 3).

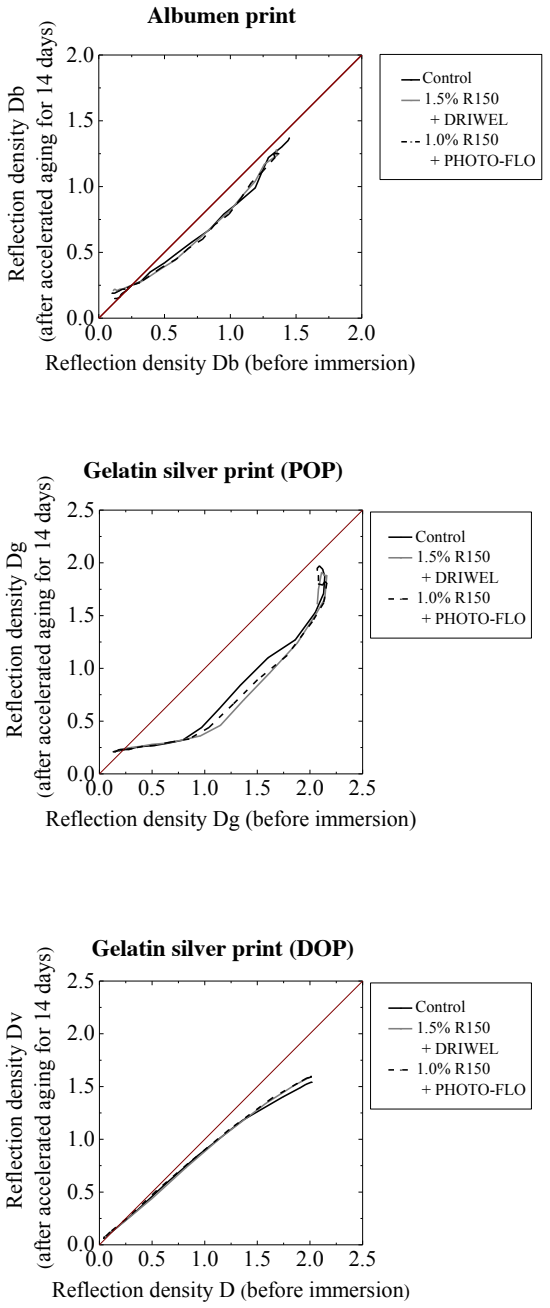

Fig. 4. Reflection density change (step tablet).

Solution		After immersion	After 7 days	After 14 days
Control	C		0.77	0.80
	M		1.45	1.01
	Y		0.78	0.68
	W		1.23	1.58
	G		0.39	0.33
	B		0.26	0.24
Distilled water + Hokucide®R-150	C	0.21	0.69	0.71
	M	0.29	1.56	1.09
	Y	0.19	0.65	0.61
	W	0.16	1.08	1.50
	G	0.37	0.45	0.51
	B	0.35	0.51	0.35
Kodak Photo Flo + Hokucide®R-150	C	0.39	0.67	0.94
	M	0.81	**2.59**	**2.44**
	Y	0.34	1.10	1.02
	W	0.10	**2.85**	**3.55**
	G	0.15	0.69	0.64
	B	0.57	0.57	0.16
Fuji Driwel K + Hokucide®R-150	C	0.19	0.90	0.98
	M	0.58	1.03	0.72
	Y	0.03	1.34	0.61
	W	0.33	1.09	1.44
	G	0.20	0.35	0.19
	B	0.16	0.40	0.48

Table 3. ΔE*ab for Chromogenic color print.

Antifungal Effect: Spray and Soak

The 2011 disaster in Japan resulted in a widespread loss of basic infrastructure. The water supply was interrupted and some towns and cities experienced a shortage of supplies for several weeks. It is therefore important to find a way in which this agent can be used effectively with a limited water supply. Thus, the antifungal effect of Hokucide® R-150 applied via simple spraying (as opposed to the more water-intensive immersion) was evaluated.

Method

Silver gelatin DOP samples were first washed, then cut and placed in petri dishes. Solutions were prepared with Fuji Driwel K (1.5% Hokucide® R-150) and Kodak Photo-Flo (1.0% Hokucide® R-150). Four groups of prints were prepared: a) control, b) sprayed with solution, c) immersed in solution, and d) immersed in tap water. Spores of fungal strains *Aspergillus niger* and *Eurotium herbariorum* were adhered onto two paper disks per print. The petri dishes with the *Aspergillus niger* strain were placed in a chamber at 27°C/80°F and 100%RH for 9 weeks until fungal growth was detected. The petri dishes with the *Eurotium herbariorum* were placed in a chamber

at 27°C/80°F and 90%RH for 9 weeks, but fungal growth did not occur in the control; therefore, a 1.25% malt solution including 40% sucrose was added to the paper disks as a nutrient, and incubation was continued. After 17 weeks, fungal growth was detected in the control.

*Result*s

There was slightly more fungal growth with the sprayed samples compared to those immersed in the antifungal solution; however, compared to the control and tap water groups, the growth was significantly less and slower. This experiment proves that, to conserve water, spraying can be an effective application method for suppressing fungal growth.

Conclusion

Following the Great East Japan Earthquake and Tsunami of 2011, it was extremely difficult to save damaged photographs from further deterioration. Many prior studies have focused on preventive measures and controlling the environment in order to prevent mold (because of the delicate and complicated nature of photographic materials), rather than direct treatment. However, this study suggests a method to be considered in preventing a mold outbreak. The results confirm that Hokucide® R-150 solution with a surfactant (Fuji Driwel K or Kodak Photo-Flo) can suppress microbial damage to photographs, and furthermore, does not show any significant negative impact on the photographic materials after accelerated aging. The solution is simple to make, easy to use, and can be sprayed on, which will of great benefit when treating large numbers of objects during emergency recovery when washing or immediate drying is difficult. In ongoing research, we are evaluating the use of Hokucide® R-150 with ethanol or isopropyl alcohol as a substitute for the surfactants, as they are becoming more difficult to obtain as a result of the decline of film photography.

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