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Instant colour photography: chemistry and UV stabilization

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An ultraviolet (UV) screening agent precursor, dinonylphenylisophthalate, applied as a component of a surface coating on instant colour positive photographic prints stabilizes the dyes that are used and prevents the fading of colour that otherwise occurs. It is believed that upon exposure to UV light the ester precursor rearranges *in situ* to form substituted benzophenones, which are effective UV screening agents. Eastman Kodak instant colour prints protected by this system successfully resisted prolonged exposure to high intensity UV light. Under the same conditions, unprotected controls showed extensive fading and other changes in colour. Extension of the general technology to prevent colour fading of dyes in other applications is foreseen.

1. Introduction

Instant colour photography is a useful innovation of modern chemistry. An instant colour print film is an integral unit with provisions for exposure, open-to-light development, and immediate viewing of the emerging image. The principles of optics and colour that apply to traditional colour photography apply to instant photography except that processing is automatic and dyes are not produced but are required to diffuse to the viewing area.

The positive colour images produced by instant photography are known to fade away and/or change colour substantially when exposed to sunlight or fluorescent light. This paper describes improvements obtained in the long-term performance of instant prints by use of a protective overcoating containing a plasticizing-type of ultraviolet (UV) absorber.

2. Chemistry of instant colour photography

In instant photographic materials of the type manufactured by the Eastman Kodak Company, dyes are attached to carriers that are immobile [1]. Cyan, magenta, and yellow-type "dye-releasers" are incorporated in the film associated with red-, green- and blue-sensitized silver halide layers, respectively. Diffusible dyes are released from their carriers in amounts that are inversely proportional to the amount of exposure. After exposure, a highly alkaline activator pouch is ruptured, spreading the activator between integral imaging receiver and cover sheets. Carbon present in the activator serves as one "wall" of the dark room; the other walls are provided by a spacer mask, the black opaque layer and the white opaque reflective layer. The developing agent in the activator fluid and the alkali (KOH) cause release of dyes from the "dye-releasers". Thus, the developing agent functions as an electron-transfer agent and supplies electrons to the silver halide emulsions. The agent is regenerated when its oxidized form extracts electrons from the "dye-releasers". No exposure causes release of all three cyan, magenta and yellow dyes which combine to form black in the image-receiving layer. Exposure to white results in no development and consequently no dye release. Exposure to red releases yellow and magenta dyes; to green, cyan and yellow dyes; to blue, cyan and magenta dyes. The dyes are immobilized in the image-receiving layer by interaction with a polymeric mordant (Fig. 1).

Instant colour photographic materials of the type made by the Polaroid Corporation, on the other hand, use "dye-developers", which are dyes

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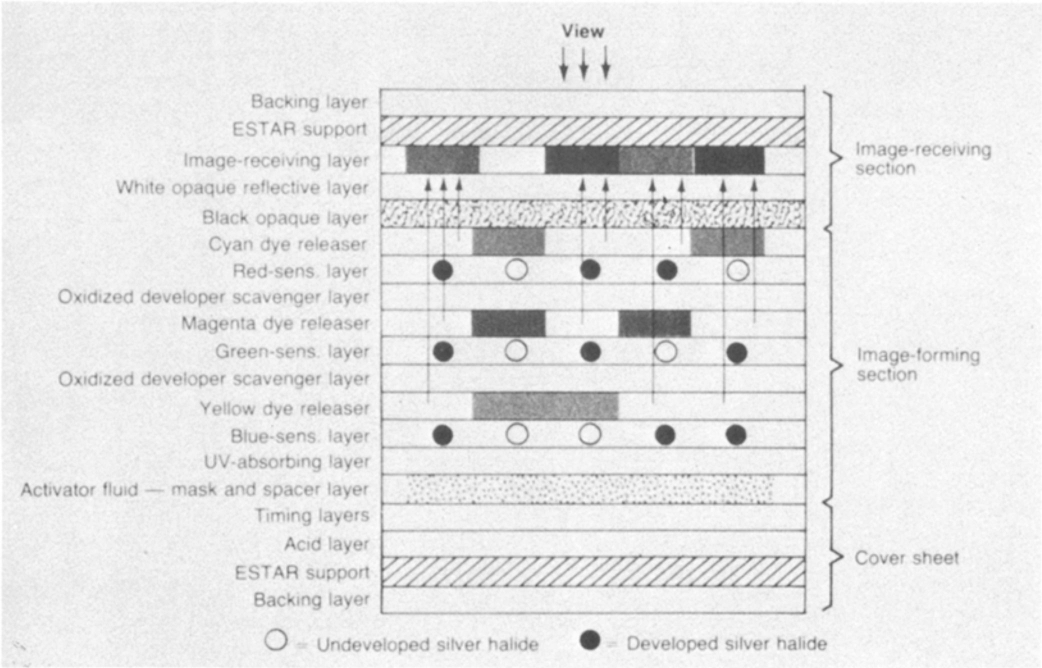


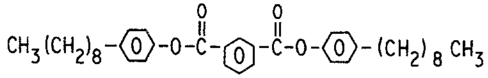
Figure 1 Processed Kodak instant print illustrated.

attached to the developing agents [2, 3]. Cyan, magenta and yellow "dye-developers" are incorporated into the photographic material in close association with the red-, green- and blue-sensitive silver halide emulsion layers. After exposure, the highly alkaline activator fluid spreads between the light-sensitive layers and the viewing layer. The activator dissolves with the "dye-developers", allowing them to diffuse within the light-sensitive layers. In exposed areas the "dye-developers", with the assistance of other agents also present, become oxidized to alkaline-insoluble quinonoid materials and move no further. In less exposed or unexposed areas the "dye-developers", diffuse to a receiver layer to form positive colour images. The photogrphic element consists of light-sensitive layers, dye-developer layers and spacer layers. Each "dye-developer" interacts with the layer sensitive to its complement. Thus, dyes that are complementary to the colour of the exposing light are immobilized in the developing areas, while the still mobile dyes in the less-exposed areas diffuse to a receiver to form a positive colour image (Fig. 2).

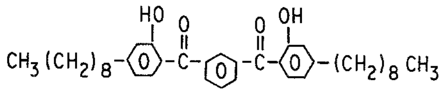
3. Chemistry of UV stabilizer

Much work has been done to find chemicals that can stabilize organic dyes against UV light [4–7]. However, the effectiveness of a given UV stabilizer varies considerably with the dyes to be stabilized as well as with other characteristics of the positive print viewing area. It is difficult to predict the degree of effectiveness of a stabilizer because some dyes (e.g., azo dyes) are more susceptible than others to UV light.

A number of ester-type UV stabilizers have been previously suggested for stabilization of polymeric materials [8–13]. In our work, dinonylphenylisophthalate was used to stabilize instant photographic prints [14]. Its chemical formula is as follows:



Dinonylphenylisophthalate has low absorption in the 290 to 400 nm wavelength range. After exposure to sunlight absorption in the 290 to 400 nm wavelength range it rearranges by the photo-Fries mechanism to become an actual UV absorber; namely, substituted benzophenones.



The precursor isophthalate ester is compatible with many polymers. In addition, because of the long-chain methylene groups, dinonylphenylisophthalate can also function as a plasticizer.

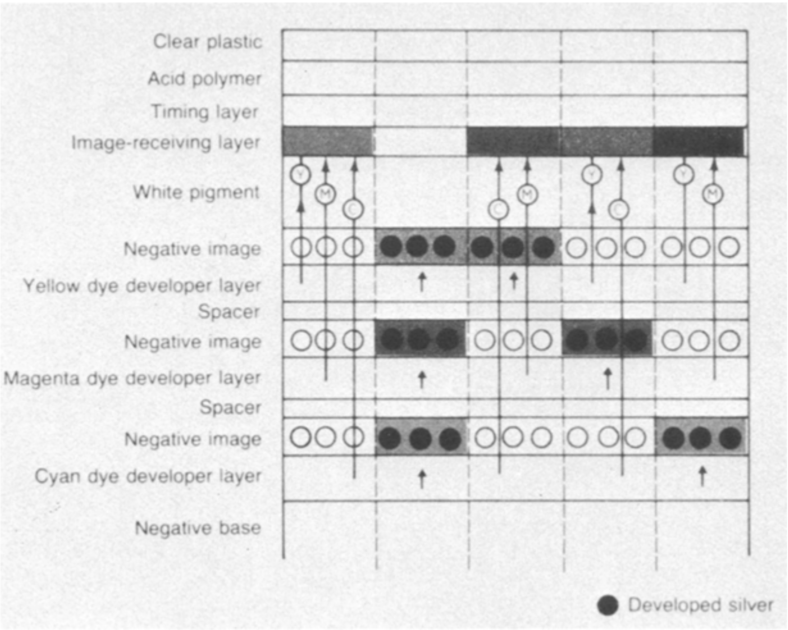


Figure 2 Processed Polaroid print illustrated.

4. Experimental procedure

4.1. Preparation of instant colour prints

Approximately 7.5 cm x 10 cm instant colour photographic prints in which the image-forming dyes were essentially monoazo derivatives of enolic couplers (e.g., benzylazo-1-naphthols and benzylazo-5-pyrazolones) were developed. All the prints were prepared identically by self-development of a commercially available (Eastman Kodak) instant colour film. The film was exposed by photographing a display board on which were mounted eight 7.5 cm x 10.3 cm colour chips substantially covering the visible spectrum.

4.2. Vehicle and coating preparation

The criteria considered in the selection of the vehicles for the stabilizing coating were high optical clarity, water-white colour, adhesion to the instant print substrate, resistance to moisture and good solubility. Cellulose acetate (40% acetyl content) and coating-grade polymethylmethacrylate were found to be suitable vehicles for this application. Two overprint varnishes (OPV I and OPV II) were prepared according to formulations indicated in Table I. The resulting solutions were optically clear and did not require filtration.

4.3. Varnishing and testing

The OPVs were applied to the prints by a knife in thicknesses ranging from 0.025 to 0.05 mm. The solvent was removed by evaporation. The fading test was an accelerated exposure using a UV lamp (Sunlighter IV Ultraviolet Test Console of Test-Lab Apparatus Co., Amherst, New Hampshire) in which the prints were arranged on a flat, 43 cm diameter turntable rotating 14 cm away from a single-bulb source of UV light (290 to 350 nm) of sufficient intensity so that about 24 h of exposure would simulate one year of exposure to natural sunlight in Florida. The air temperature inside the cabinet containing the turntable and the UV light source was maintained at 60° C. The prints were located on the turntable so that each received equal exposure to UV light. One uncoated (control) and two coated (by OPV I and II) prints were tested for 170 h in the Sunlighter.

5. Results

The results of 70 h of continuous exposure in the Sunlighter of the prints are shown in Table II. The "fading coefficient" is the per cent of the original

TABLE I OPV formulations

	Formula	
	OPV I	OPV II
Partially hydrolysed cellulose acetate (40% acetyl content)	13.0	–
Tetrahydrofuran (THF)	85.0	75.0
Dinonylphenylisophthalate	2.0	2.0
Polymethylmethacrylate (coating grade)	–	23.0

TABLE II Results of UV stabilization of instant prints

Original colour in prints	Control (no stabilization)		OPV I		OPV II	
	Final colour	Fading coefficient (%)	Final colour	Fading coefficient (%)	Final colour	Fading coefficient (%)
Dark beige	Light ivory	90	No change	5	No change	5
Maroon	Light beige	90	No change	10	Slightly brownish maroon	20
Olive green	Light ivory	80	No change	5	No change	10
Dark rose	Light ivory	80	Medium rose	15	Orangy rose	20
Yellow	Light pale yellow	95	No change	0	No change	0
Dark red	Light ivory	95	Medium-dark red	10	Medium-dark red	5
Purple	White	95	No change	10	No change	10
Blue	Light brown	80	No change	5	No change	5

colour in the print; a completely faded colour (essentially white) would be characterized by a 100% "fading coefficient". All colours faded almost completely in the uncoated colour prints after 70 h of UV exposure. The OPV I- and II-coated prints, however, remained colourfast, the former being slightly better than the latter. Indeed, Kodak prints protected by OPV I and OPV II were stable even after 170 h exposure to UV in the Sunlighter (Fig. 3).

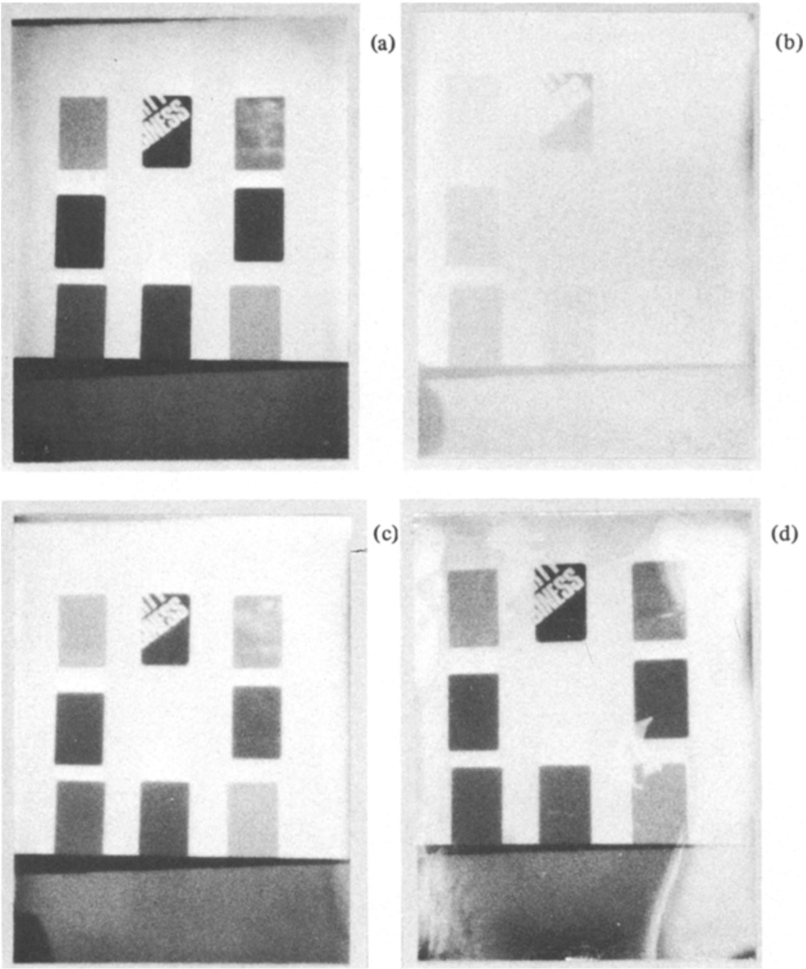


Figure 3 Kodak prints protected by OPV I and OPV II as well as control. (a) Exposed to UV for 0 h, (b) exposed to UV for 70 h, (c) OPV I protected; exposed for 170 h, (d) OPV II protected; exposed for 170 h.

6. Conclusions

Our work showed that dinonylphenylisophthalate provided an unexpectedly high degree of improvement in stability of Kodak instant photographs against undesirable UV light effects such as colour fading and colour drift. Similar results can be expected if the stabilizer is incorporated in an external or internal coating on photographic film prior to its exposure in a camera. Other dye-containing articles that can be stabilized by dinonylphenylisophthalate are textile fibre and fabrics, wall coverings, extruded thermoplastics and art work (e.g., paintings).

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