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An Update on the Stability of B+W Resin Coated Papers*

Sarah S. Wagner**

Introduction

In recent years, there has been renewed concern about the image stability of current black and white resin coated (RC) photographic papers. It had appeared that manufacturers had "solved" some of the known RC problems by the early 1980s, especially resin cracking **(1)**. Henry Wilhelm reported extensively on RC image stability problems in his 1993 book and recommended against their use due to problems with their image stability **(2)**. From 1996 to 1998, the fine art photographer Ctein (pronounced KaTyne) has published articles expressing concern about the image stability of RC papers when displayed **(3,4,5,6)**. This article reviews the RC issues, provides an update on recently published concerns, and recommends some preservation steps.

RC characteristics and its problems--cracking and image stability

RC papers consist of a paper core coated on both sides with a thin polyethylene (PE) plastic. The polyethylene on the emulsion side is pigmented with titanium dioxide to provide opacity and whiteness. After their introduction in the early 1960's, RC papers quickly replaced traditional fiber paper prints for both color and black-and-white photos (although many fine art photographers continue to print on black-and-white fiber paper). Their primary advantages were the ability for rapid machine processing, due to the reduced need for lengthy washing, and their reduced cost, both for materials and for processing. Secondary factors included a lack of curl, improved wet strength, dimensional stability, and handling durability.

Two stability problems quickly became apparent after the introduction of RC papers and have been discussed widely in the literature. The first problem was cracking of the polyethylene, referred to as resin cracking by the manufacturers. Resin cracking results as the polyethylene polymer is oxidized, leading to chain scission, breakdown of the polymer, and embrittlement of the PE layer. Oxidation eventually causes the emulsion to crack leading to a disfiguring, crazed surface. Resin cracking may also result from thermal degradation, thermal cycling, and environmental stress such as solvent exposure **(7)**. The second problem was the formation of red spots and silver mirroring in image areas. Red spot formation and mirroring result from cyclical oxidation and reduction reactions that lead to the formation of ionic silver, its migration to the emulsion surface during humid conditions, and finally its reduction to metallic colloidal silver on the emulsion surface in high density areas. Diffuse migration of silver also can result in an overall yellowing in low-density areas. A localized version of the reaction creates red spots or redox blemishes -- the particle size formed is such that it appears red in reflected light.

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Silver mirroring caused by true image deterioration should not be confused with a visual change peculiar to glossy RC papers that is not due to deterioration: prints that are air-dried, or dried by hand held dryers, may develop a shiny metallic surface sheen in image areas **(2)**. This sheen, sometimes referred to as veiling or blooming, looks somewhat like silver mirroring in raking light.

Deterioration mechanisms

The manufacturers **(7)** quickly realized that the deterioration reactions of the resin and silver were accelerated by the presence of TiO_2 pigment in the polyethylene and its reaction with light to form free radicals.

The TiO_2 free radical mechanism is well-documented **(7, 8)** :

$H_2O + O_2$ $[TiO_2] \rightarrow$ UV (480nm) $\rightarrow$ $^{\bullet}OH$ radical + $^{\bullet}HO_2$ radical
$^{\bullet}HO_2 + [TiO_2]$ [UV]$\rightarrow$ $^{\bullet}OH$ radical and $^{\bullet}O$ singlet oxygen radical
$2\ TiO_2$ [UV]$\rightarrow$ $Ti_2O_3{-}O^{\bullet}$ Titanium tetra-oxide free radical

These free radicals react with the polyethylene resin through other well documented mechanisms leading to chain scission of the polymer, increased brittleness, and resin cracking **(7, 8)** :

$3^{\bullet}HO + 3^{\bullet}HO_2 + 2CH$--PE Resin $\rightarrow 2CO_2 + 5H_2O$ + PE-Resin–$O^{\bullet}$

In addition, any of the free radical byproducts can also oxidize the silver. In the process, the morphology of the filamentary silver is changed to a colloidal form visible as any combination of metallic sheen (silver mirroring), red spots, image discoloration or fading, for example:

$Ag + {}^{\bullet}O$ or $^{\bullet}OH$ radical $\rightarrow Ag^{+}O + H_2O$
$Ag + Ag^{+}O \dashrightarrow Ag_2O$
$Ag_2O \rightarrow$ [UV/vis blue light]$\rightarrow 2Ag$

There are two forms of titanium dioxide -- the rutile and the anatase forms. The rutile form is now used by the photo industry, because it is far less photo-reactive than the anatase form. However, anatase can be present as a contaminant in minute quantities. A 'bad batch" of TiO_2 with larger than usual amounts of anatase contamination could adversely affect a product line.

Stabilization of RC

The resin cracking problem has been reduced by the incorporation of stabilizers, anti-oxidants, and peroxide- or oxidant- scavengers. By 1979, Kodak had patented a proprietary process that incorporated the stabilizer into the paper core where it could diffuse over long periods through the PE to counteract the effects of the generated oxidants. This reservoir of stabilizer was expected to provide protection from resin cracking for long periods, even during display **(7)**. Around the time that Kodak made this breakthrough, other major manufacturers soon followed. For example, Ilford patented a process in which a proprietary stabilizer (a hindered amine) was incorporated in the resin layer. **(9)**

The TiO_2 pigment itself can be stabilized. According to Valente and Butler **(10)**, TiO_2 is now stabilized prior to use as a pigment in almost all plastics through inorganic and organic surface treatments that both facilitate particle dispersion and retard reactions with the plastic matrix by coating the pigment particle. This coating acts as a barrier between the pigment particle and components within the plastic matrix with which it might react during photo-oxidation. The stabilizer may also act as a barrier between the particle and UV light. The most common stabilizer is aluminum oxide, Al_2O_3. Glycols, amines, siloxanes and phosphated fatty acids may also be used as stabilizers and dispersion aids.

Because of the incorporation of anti-oxidants, scavengers, and/or stabilizers in the polyethylene resin (or paper core), it now tends to take decades for resin cracking to appear even after continuous display in UV-containing light (at least in papers made by major manufacturers that utilize these processes). The image stability problem has been far more difficult to solve. And while mirroring and red spots still occur, as described above, there are continuing reports of other visual changes such as the appearance of an overall bronzing discoloration to the surface, and yellowing or pinking.

Other causes of image stability problems

The nature of the support

The image deterioration mechanism appears to be far more complex than just the light-induced TiO_2 free radical mechanism, and includes many variables. Externally generated chemical contaminants from numerous sources (e.g., matboard, enclosures, polluted air) also play a role, as they do with all photographic images **(11)**. Although the gelatin emulsion can be a good barrier to contaminants below a relative humidity (RH) of 40%, it's permeability to contaminants and internally migrating ionic silver increases as the RH goes above 50%-60%. As seen in the chemical reactions above, water itself plays a role in the TiO_2 free radical mechanism. According to Reilly **(12)**, "without the presence of water, even the most aggressive pollutants don't have much effect on silver."

It has been thought that fiber paper is either more resistant to image oxidation than RC or better at masking the effect in the initial stages of deterioration **(13)**. This is probably because the paper and baryta layer act as absorbent "sinks" for external contaminants or internally generated oxidative by-products of any reactions, thereby keeping those chemicals away from the emulsion and the image **(14)**. Due to the PE barrier, oxidized silver in RC papers can only migrate to the emulsion surface where it is visible as image deterioration once it re-deposits as metallic silver or undergoes further reaction in its ionic state. The PE coating in RC has no absorbent sink capabilities. There is no absorbent baryta layer and the paper core is inconsequential as a sink for reactants because it is encapsulated between the PE layers. Papers with thinner emulsions may possibly offer faster permeability of contaminants and provide a quicker route to the surface for migrating ionic silver. Some RC papers have thinner emulsions and use about 20% less silver than fiber papers **(15)**. A current Ilford technical data sheet states that "atmospheric pollutants can affect any black and white photograph, but those printed on resin coated papers are most susceptible." **(16)**

Possible interactions with optical brighteners

At the PMG 1999 Winter Meeting Peter Roth, a retired Polaroid scientist, presented information on the manufacturing and preservation issues of RC prints. He mentioned that some image changes may also be due to the interaction of oxidants with the optical brighteners found in the emulsion of modern RC papers (and almost all fiber papers) or the degradation of brighteners themselves **(17)**. Titanium dioxide absorbs light in the same region where optical brighteners re-emit (480nm). Degradation products of free radical reactions can attack stilbene-based optical brighteners, and other optical brightener dyes, causing them to break down and result in a color shift. Exposure to UV-containing light causes rapid optical brightener "exhaustion" within months after which the molecules no longer fluoresce, and the print appears less of a brilliant white and more yellow. This yellowing affect would occur overall and be most noticeable in the highlights.

Picture frame effect

Wilhelm and Ctein note that freshly processed prints that are immediately framed seem to suffer image deterioration more than "older" prints that are later framed (the "picture frame effect"). It is possible that residual processing chemicals are a contributing factor, also. Framing itself could trap contaminants and free radicals in the print or frame, keeping them close to the image surface and slowing down diffusion rates so that reactants have time to react with each other. In fact, the same phenomenon can occur in color chromogenic prints and affect the yellow dye **(18)**. Framing itself introduces many variables -- poor quality matboards inside frames can act as sources of harmful contaminants while high quality matboard can act as a protective sink for oxidants. However, the author has seen image deterioration on both new and old black-and-white RC prints recently displayed without glazing, albeit in a public space having both bright light levels (fluorescent or sunlight) and presumed exposure to moderate levels of pollutants.

RC concerns recently published by Wilhelm and Ctein

Wilhelm feels that if the deterioration occurs, it happens within 6-12 months of display, and all within 2 to 3 years **(19)**. If there is no evidence of image deterioration by then, the print in question is probably "resistant". Wilhelm suspects that the light is the main culprit and does not feel that the "bronzing" and red spots happen in the dark. The effect can be unpredictable even with the same paper. Prints with slightly higher residual hypo levels might be less susceptible, possibly due to protective toning of the silver by the residual sulfur from the hypo. Just as too much residual hypo can cause degradation, too "clean" a print may make the image less stable (for this reason, ANSI raised the residual hypo levels on films a number of years ago).

Ctein became concerned when some of his own well-processed RC prints on Agfa paper underwent image deterioration while on display **(3-6)**. He undertook his own set of experiments to look at the bronzing/silvering in RC prints, including papers by other manufacturers besides Agfa. His research shows that all major manufacturers' papers seem to develop the problem. Ctein carefully made inert acrylic frames to hold the photographs so that part of the print would be inside the frame and part outside. One set was exposed to light, one was kept in the same room in the dark. In addition, samples were also prepared with toning regimens of selenium and

Sistan (an Agfa proprietary post-processing treatment whose main ingredient is potassium thiocyanate) and similarly exposed to dark or light. None of the toned samples developed bronzing nor did any of the dark-kept samples. Of the light-exposed samples that were not toned, only the framed part of the photo developed bronzing.

Ctein's preliminary research seems to substantiate Wilhelm's recent assertions **(2)** that all RC prints suffer light-induced image deterioration (exacerbated by framing) which is only prevented through toning procedures that convert the silver image to a more stable compound. Unfortunately, because toning is not feasible in standard machine processors and has to be done afterwards as a separate tray step, most RC prints have not been toned.

History of recommendations for stability
Protective toning (or silver conversion) of all black-and-white papers has been recommended for years in popular photographic journals by various proponents of 'archival processing', by ANSI and ISO standards, by independent consultants and researchers such as Wilhelm **(20)**, and by manufacturers in their product literature **(21, 22, 23)**. Treatments have included gold, selenium, polysulfides (e.g., Kodak's Polytoner), Agfa's Sistan or Fuji's Ag-Guard (a proprietary formula).

Development of a test method for light induced deterioration
The complexity and unpredictability of the RC image problem and the variables involved in any display situation have compounded the difficulties in pinpointing an accurate, reproduceable, and predictive light exposure stability test. The ANSI/ISO Paper Stability Committee continues to investigate test methods that could screen papers for susceptibility to light-induced image deterioration (e.g., a picture frame test or equivalent). A standardized image stability test involving display could help manufacturers improve their product and allow independent testing labs to test and compare papers. In the meantime, the paper stability standard is in the draft stage and should be published within a few years. This standard will include test methods to evaluate the stability of fiber and RC papers in dark storage based on physical and chemical properties (resin cracking, tensile energy absorption, levels of residual silver and thiosulfate).

Recommendations
Conservators and custodians of photo collections usually have very little information on papers used by photographers, other than a possible manufacturer imprint on the back. Such information might not even be helpful if all black-and-white RC papers are susceptible to light induced image deterioration, as postulated by Ctein and Wilhelm. A display option that deserves investigation is the use of matboards that incorporate chemical scavengers in the paper -- this type of matboard might act as a beneficial sink for contaminants that exacerbate the "picture frame effect." Likewise, sealed framing that ensures a stable RH of 30-40% deserves further investigation as it might slow the formation of free radicals and limit the permeability of the emulsion.

Contemporary photographers who prefer to print on black-and-white RC should be encouraged to tone their prints. Until there is better understanding of light induced deterioration, it also may be helpful for photographers to take a cautious approach to display, by avoiding immediate framing and display of untoned freshly processed prints and by using UV-filtering glazing.

At institutions, the same cautious approach would apply to valuable prints. Display of untoned freshly printed photographs probably should be avoided, unless the photographer is willing to replace prints that might become damaged or tone the prints prior to display. As to display, most exhibition lighting or glazing carefully filters out the UV component that is most active in initiating the TiO_2 mechanism. However, near UV may also be harmful and should be avoided. The use of UV-filtered light or glazing will also increase the longevity of the optical brightener, but unfortunately it also will mitigate the fluorescing effect dependent on UV absorption. The prints will appear less white under these conditions as a result.

For research institutions requiring reference prints that for the most part will be in dark storage, RC papers are probably still preferable to fiber papers due to physical stability in handling, lack of curl or cockling, and low cost compared to archivally processed and toned fiber paper. If the storage location is in a polluted building or city, then these reference prints could be toned as a post-processing treatment as an added precaution. Sleeving in polyester also might help reduce image oxidation in the dark in polluted areas. Wilhelm says he has not seen image deterioration in stacks of prints except those areas exposed to light and air at the edges or on top **(19)**. Sleeving file prints might replicate the dynamics of the stack situation by reducing the availability of oxygen and contaminants to the emulsion surface. The author has rarely seen image deterioration in well-processed black-and-white file prints on RC base that have been stored and housed in acceptable conditions.

As with all types of photographs, one should:
1) use only non-reactive enclosures, matboards and containers that conform to the ANSI standard IT9.16 (ISO 18916) *Photographic Activity Test* and the ANSI standard IT9.2 (ISO 18902) *Filing Enclosures and Storage Containers*;
2) ensure proper storage conditions that conform to ANSI 9.20 (ISO 18920) *Processed Reflection Prints -- Storage Practices* (defining temperature, RH and pollutant levels); and
3) display according to commonly accepted museum standards that limit light exposure.

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