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ARCHIVAL PERMANENCE

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There has been a great deal written on the subject of archival stability or permanence of photographic materials. However because "archival" permanence implies that the prints and negatives will be stored under controlled, "archival" conditions such as those described in the relevant American standards 1, 2, 3. As this is often not possible most people are actually interested in optimum stability or permanence which simply means taking all the necessary precautions to ensure the longest possible life under typical conditions.

Obviously the requirements vary with different types of photographic material and for the purposes of this talk I have divided them into three groups:

1. Silver films and papers
2. Chromogenic films and papers (including XP1 400)
3. Silver dye bleach products, ie, CIBACHROME.

Starting with silver-image films and papers, it is most important that these are correctly processed if optimum stability is required. This means that the processed material should contain suitably low levels of retained silver compounds and thiosulphate, in other words, it should be properly fixed and washed.

Taking film first, proper fixing means not overworking the fixer. However, I have not been able to find any firm recommendations as to what this means in practice. I would suggest that a two bath fixer (I will be returning to this subject later) should be used and the fixing should be checked using the simple chemical test recommended in American National Standard ANSI PH1.41 1981 shown in Fig.1. It is not possible to measure these very low levels of residual chemicals without sophisticated analytical equipment. Fortunately it is a relatively simple matter to the required level and Table 2 shows a method which has been recommended by ILFORD for many years. Note that a non-hardening fixer is used which makes washing much easier and we would strongly recommend that hardener is not used.

Turning next to papers, the processing requirements for these are much more stringent for the following reasons:

1. The relatively fine grain images react more readily with residual chemicals
2. Any stains which do form are more severe because light passes through them twice
3. There is no scope for correcting any degradation at the printing stage.

Baryta/fibre base papers are still the main choice when making prints which are intended to have optimum permanence. These are, of course, much harder to wash because of the absorbent paper/card base. The structure of a typical fibre base paper is shown in Fig.2. As with film, proper fixing means not overworking the fixer and Table 3 shows the recommended maximum silver levels in the fixer. These can be checked using silver test papers (such as those manufactured by Merck) or by throughput. Note that both two bath fixation or a washaid make for a more efficient use of the fixer. Both the second fixing bath and the washaid act to 'flush out' the less soluble silver compounds which build up in a fix bath during use. The two bath system allows the rotation of the second bath to replace the first (up to five times or within a week). I would recommend that important prints be chemically checked as with film and the stain should be compared to that on a print which has been processed in two fresh fix baths.

There are no standards for residual thiosulphate in prints and instead processed samples are put through an accelerated aging test alongside a reference processed sample. The accelerated aging test and reference processing sequence are shown in Table 4. Obviously it would be very difficult for anyone outside the photographic industry to undertake this

sort of testing. This means that information is required from manufacturers regarding practical sequences which pass this very stringent test.

As far as I am aware only ILFORD has done so, with the so-called GALERIE washing sequence (4). When GALERIE was being researched it seemed opportune to investigate the fundamentals of fibre base paper processing. The key to an improved processing sequence proved to be the use of a rapid fixer (such as HYPAM) with a short fix time. Table 5 shows the full processing sequence which also makes use of the fixer and shorten wash times. Table 6 shows the effect of extending the fix time beyond 30 seconds.

It is probably worth describing what the consequences of not processing correctly actually are. Both the residual silver compounds and the residual thiosulphate will eventually react with the image silver to produce patches of brown silver sulphide, often with reduced density. It is worth noting that if prints are being made for optimum permanence then, ideally, they should be protected against atmospheric attack. This can be achieved using selenium or sulphide toners. These both provide an instant check on how well fixed and washed the prints are.

The next topic is R.C. papers which, as I have already implied, are not normally the first choice for optimum permanence. This is because a great deal has been said or written about the alleged impermanence of prints on R.C. papers and I hope here to separate fact from fiction. Fig.3 shows the construction of a typical R.C. paper, as you can see it differs from a fibre base paper in that the paper is laminated on both sides with polyethylene and the face polyethylene contains the pigment Titanium Dioxide. Because polyethylene lamination renders the base virtually impermeable it becomes very easy to wash out the residual thiosulphate and a two minute wash reduces the thiosulphate to optimum levels. As R.C. papers are very easy to wash and no more difficult to fix than fibre base papers (which they are not) there must be some other problems which have generated the adverse criticism. There have in fact been two problems with the permanence of R.C. prints. The first of these is called "cracking" and this occurs on prints displayed in daylight (5). This problem is caused by a reaction between ultra-violet radiation and the Titanium dioxide pigment. The pigment TiO₂ is converted to Ti₂O₃ plus a very reactive Oxygen atom, which then oxidises the polyethylene making it much more brittle. Then the normal expansion and contraction of the emulsion layer with variations in humidity causes both the polyethylene and emulsion layers to crack, ultimately, destroying the print. Obviously what was required was some form of antioxidant and after

extensive testing, both accelerated and 'real-time', both Kodak and ILFORD (independently) have switched to coating on base containing antioxidant. Kodak are projecting a life of at least 100 years before the appearance of the first crack under normal display conditions. None of the testing done by ILFORD has produced any cracking on the improved R.C. papers even though slight cracking has been induced on fibre base papers. It is probable that similar improvements have been, or will be, made by other manufacturers. Interestingly this effect seems to be catalysed by silver and so is not a problem with colour papers.

The second problem has proved to be more intractable and has been variously described as image fading, oxidative fading and 'bronzing' (6,7). Once again this is a problem when prints are displayed and atmospheric pollutants are able to react with the image silver. This converts some of the image silver to silver ions which are able to migrate through the emulsion layer. These are then either photo-reduced to metallic silver or converted to silver sulphide and often form on the surface of the print where they act as a silver mirror. Otherwise the effect takes the form of orange stains with reduced density. To the untrained eye the effect looks very similar to the sulphiding of the image caused when prints are not properly washed. However, sulphiding is not very likely to occur on R.C. prints because they are very easy to wash. If there is any doubt then the two effects can be distinguished by putting a spot of developer on the stain which will darken if it has been caused by oxidative fading. Among the many pollutants which can cause these problems are Nitrogen dioxides (from car exhausts) or peroxides (from drying gloss paints or in hairdressers).

It seems a reasonable question to ask why R.C. papers should be much more prone to this problem. There seem to be two elements to this, both related to the absorbency of the fibre base. The fibre base means that any atmospheric pollutants are not confined to the image layer and when silver ions are formed they are able to diffuse into the paper base where they will be much more difficult to see.

Table 7 shows what can be done to prevent this problem. Toning, which converts the silver image to less reactive compounds, is inconvenient because it involves extra processing steps and invariably results in some image colour change. Nevertheless toning, particularly selenium, is very effective and should be used on any prints intended for long term display. Silver image stabilisers require an additional processing step but do not cause image colour changes. Protective laquering will change the appearance of the prints and polyethylene containers can only be used to protect prints

in store. That leaves the improved design of sensitised materials and this is the approach being used by ILFORD. Extensive research together with accelerated testing has led to an understanding of the factors in product design which influence this problem and the intention is to ensure that future ILFORD products will perform much better in this respect.

Next I want to move on to chromogenic films and papers where the image dyes are formed by colour development. It has only been since the advent of these that there has been concern about the permanence of colour images because early colour processes such as Finlaycolour, Autochrome, Dye Transfer and Carbro gave very permanent images.

The reasons for their relatively poor permanence are as follows:

1. The number of dyes which can be formed by colour development is limited and many have poor stability
2. All chromogenic films (except Kodachrome) and papers contain unreacted couplers which are a potential source of image degradation.

Table 8 shows the protected 'life' of images on various Kodak colour films in dark storage. This information was unofficially 'leaked' by sources within Eastman Kodak in 1978 and did much to promote the current concern about colour image permanence. In fairness I should emphasise that a .1 density loss from a density of 1.0 in one of more dyes does not represent the life of an image and is, in fact, the smallest difference that most untrained observers would detect on direct comparison to an unfaded original. In addition these figures, like most data on image permanence, are derived from accelerated aging tests and, as such, are extrapolations with all that that implies. Even taking this rather pessimistic view then all is not lost because the reactions involved are very dependant on temperature on temperature as can be seen in Table 9. Although dark stability, as discussed above, is most important for colour negative and slide films there is, with the latter, the additional problem of light stability. Although there is very little information published on this aspect it has been stated that a Kodachrome transparency can show noticeable dye loss in highlight areas with as little as a half-hour of intermittent projection. Incorporated coupler films such as Fujichrome and Ektachrome are approximately three times more stable to light and projection.

Turning next to XP1 400 which is ILFORD's chromogenic monochrome film. As with colour negative films the principal concern with XP1 is dark stability and this has been evaluated using accelerated ageing tests. The same 10%

dye loss criterion is employed as in the Kodak data shown earlier and Table 10 shows the 'life' of the three image dyes. Although the cyan dye is most fugitive this is present for cosmetic reasons and only the yellow and magenta dyes are used when making prints (principally the yellow dye). So we can tentatively claim a life of 50 years for an XPI negative under normal storage conditions even with this very stringent test. However as more severe dye losses could still be compensated for a changing print contrast a longer life seems probable even under normal storage conditions. Also if the storage temperature is reduced as described earlier it might be possible to claim (not altogether seriously) a 'life' of 800 years.

Finally I should like to discuss colour print materials with particular reference to CIBACHROME. This is, of course, not a chromogenic product and is renowned for offering excellent dark stability (8). Table 11 shows the result of an accelerated aging test comparing the dark stability of CIBACHROME with a Kodak Dye-Transfer print. The changes on both papers are too small to allow extrapolation and Kodak have tentatively suggested a 300 year life for Dye Transfer prints. Fig.4 shows how much more stable CIBACHROME is than conventional chromogenic papers under the same conditions. Before I leave the subject of dark fading of colour prints I would like to comment on the claimed 100 year life of prints made on Konica's SR colour paper. This illustrates some of the points I have been making because they have assumed storage at 24 degrees Centigrade and 60% relative humidity (described as typical album storage conditions) and they project a 30% dye loss.

With colour print materials light stability is very important because these are often used by display purposes. Early chromogenic papers had very poor light stability but in recent years substantial improvements have been made by the use of improved couplers (particularly the yellow) the incorporation of UV absorbing additions to the emulsion and base, and magenta dye stabilisers (9). All of this has led to colour papers which are slightly superior in light stability to both CIBACHROME and Kodak Dye Transfer prints. Fortunately for CIBACHROME users this is not the last word on light stability because recent research by ILFORD has shown that it is possible to further improve the light stability of CIBACHROME by laminating the surface with adhesive polyester or polypropylene foils.

This technique works because it prevents the penetration of moisture but is far less effective with chromogenic products which are already well protected against moisture. Fig.5 shows a comparison of light fading with and without a polyester foil for CIBACHROME and atypical chromogenic papers.

References

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FIGURE 1 ANSI PH1.41 1981 RESIDUAL SILVER COMPOUND TEST

FILM SHOULD BE SPOTTED (BOTH SIDES) WITH A 0.2% SOLUTION OF SODIUM SULPHIDE. THE AREA TREATED SHOULD SHOW NO MORE THAN A BARELY PERCEPTIBLE TINT.

TABLE 1
MAXIMUM PERMISSIBLE CONCENTRATION OF RESIDUAL THIOSULPHATE (ISO 4331-1977)

FINE-GRAIN COPYING, DUPLICATING AND PRINTING FILMS	0.7µg/cm ²
MEDIUM GRAIN CONTINUOUS-TONE CAMERA FILMS	2µg/cm ²

TABLE 2 WASHING FILM TO ARCHIVAL STANDARDS

1. PROCESS YOUR FILM IN A SPIRAL TANK.
2. FIX IT, USING A NON-HARDENING FIXER SUCH AS ILFORD HYPAM.
3. AFTER FIXATION, FILL THE TANK WITH WATER AT THE SAME TEMPERATURE AS THE PROCESSING SOLUTIONS AND INVERT IT FIVE TIMES
4. DRAIN THE WATER AWAY AND REFILL. INVERT THE TANK TEN TIMES.
5. DRAIN AND REFILL IT FOR THE THIRD TIME AND INVERT THE TANK TWENTY TIMES.

FIGURE 2

SECTION THROUGH A TYPICAL FIBRE BASE PAPER (Not to Scale)



SUGGESTED MAXIMUM PERMISSIBLE CONCENTRATIONS OF SILVER

(BARYTA PAPER)

- COMMERCIAL PROCESSING - SINGLE BATH UPTO 2 G/LITRE (40 PRINTS : 20.3 X 25.4CM)
- ARCHIVAL PROCESSING - SINGLE BATH UPTO 0.5G/LITRE (10 PRINTS : 20.3 X 25.4CM)
- FIRST BATH (OF 2) UPTO 2G/LITRE
 - SINGLE BATH USED WITH WASHAID UPTO 2G/LITRE

TABLE 3

TABLE 4

ANSI PH4.32-P1974 - REFERENCE PROCESSING SEQUENCE

DEVELOPER	TIME (AS RECOMMENDED)	TEMPERATURE
ANSI STOP BATH	10 SECONDS	20°C ± 1.1°C
ANSI FIX BATH	5 MINUTES	
ANSI FIX BATH	5 MINUTES	
WASH	30 MINUTES	
ANSI HYPO ELIMINATOR (PEROXIDE-AMMONIA)	5 MINUTES	
1% SOLUTION SODIUM SULPHITE	2 MINUTES	
WASH	20 MINUTES	

ACCELERATED AGING TEST - 30 DAYS AT 37.8°C ± 1.1°C AND 94% ± 4% R.H.

ARCHIVAL PROCESSING SEQUENCE FOR ILFOBROM GALERIE

FIXING	HYPAM (1+4) CONSTANT AGITATION HARDENER IS NOT RECOMMENDED	30 SECONDS
FIRST WASH	GOOD SUPPLY OF FRESH, RUNNING WATER	5 MINUTES
RINSE	GALERIE WASHAID (1+4) INTERMITTENT AGITATION	10 MINUTES
FINAL WASH	GOOD SUPPLY OF FRESH, RUNNING WATER	5 MINUTES

ALL PROCESSING TIMES ARE AT 20°C

TABLE 5

TABLE 6

EFFECT OF FIXING TIME ON RESIDUAL THIOSULPHATE LEVELS

FIXING TIME (SECONDS) HYPAM (1+4) AT 20°C	- 30	60	120	240
RESIDUAL THIOSULPHATE $\mu\text{g}/\text{cm}^2$	- 0.14	0.16	0.60	1.00

SECTION THROUGH A TYPICAL RC PAPER (Not to Scale)

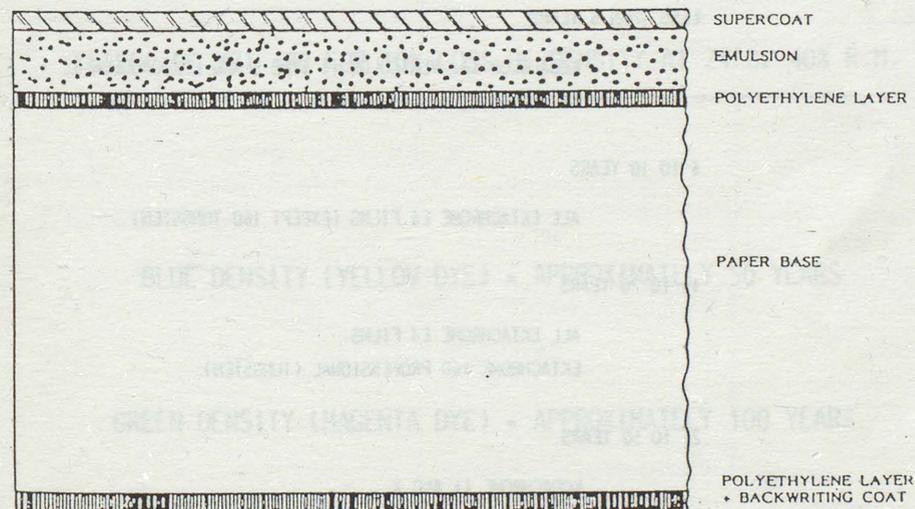


FIGURE 3

TABLE 7

PREVENTIVE MEASURES AGAINST OXIDATIVE FADING

1. TONING (SELENIUM, SULPHIDE AND GOLD).
2. AFTER TREATMENT WITH IMAGE STABILIZER (AGFA SISTAN, FUJI Ag GARD, TETENAL STABINAL).
3. PROTECTIVE LACQUERING.
4. STORAGE IN POLYETHYLENE CONTAINERS.
5. IMPROVED DESIGN OF SENSITIZED MATERIALS.

AFTER KOLZ, MODERN PHOTOGRAPHIC PAPERS B.J.P. 127: 316-319 (1980)

"LIFE" OF VARIOUS KODAK COLOUR PRODUCTS AT 20°C, 40% R.H. FOR DENSITY

LOSS OF 0.1 FROM A DENSITY OF 1.0 IN ONE OR MORE DYES

LESS THAN 6 YEARS

KODACOLOR II, VERICOLOR II TYPE S AND L KODACOLOR X,
EKTACOLOR TYPE S AND L.

6 TO 10 YEARS

ALL EKTACHROME E6 FILMS (EXCEPT 160 TUNGSTEN)

11 TO 20 YEARS

ALL EKTACHROME E4 FILMS
EKTACHROME 160 PROFESSIONAL (TUNGSTEN)

21 TO 50 YEARS

KODACHROME II AND X

MORE THAN 50 YEARS

KODACHROME 25 AND 64

TABLE 8

TABLE 9

INFLUENCE OF TEMPERATURE ON FADING OF CHROMOGENIC-TYPE FILM IMAGE DYES AT 40% R.H.

STORAGE TEMPERATURE	RELATIVE STORAGE TIME FOR EQUAL DYE FADING
24°C	x1
19°C	x2
12°C	x5
7°C	x10
-10°C	x100
-26°C	x1000

"LIFE" OF XP1 400 FOR 10% LOSS OF DENSITY AT 24°C, 40% R.H.

BLUE DENSITY (YELLOW DYE) = APPROXIMATELY 50 YEARS

GREEN DENSITY (MAGENTA DYE) = APPROXIMATELY 100 YEARS

RED DENSITY (CYAN DYE) - APPROXIMATELY 30 YEARS

TABLE 10

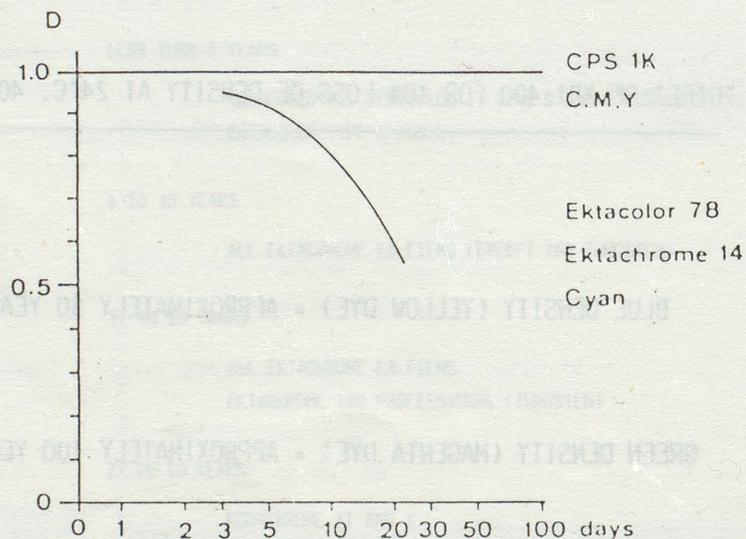
TABLE 11

DARK STABILITY, CIBACHROME, KODAK DYE TRANSFER

TEST CONDITION 77°C, 40% R.H., 112 DAYS

INITIAL DENSITY $D = 1$ KODAK DYE-TRANSFER $\Delta D = -0.08(Y)$ CIBACHROME II DELUXE $\Delta D = \pm 0.02 (Y,M,C)$

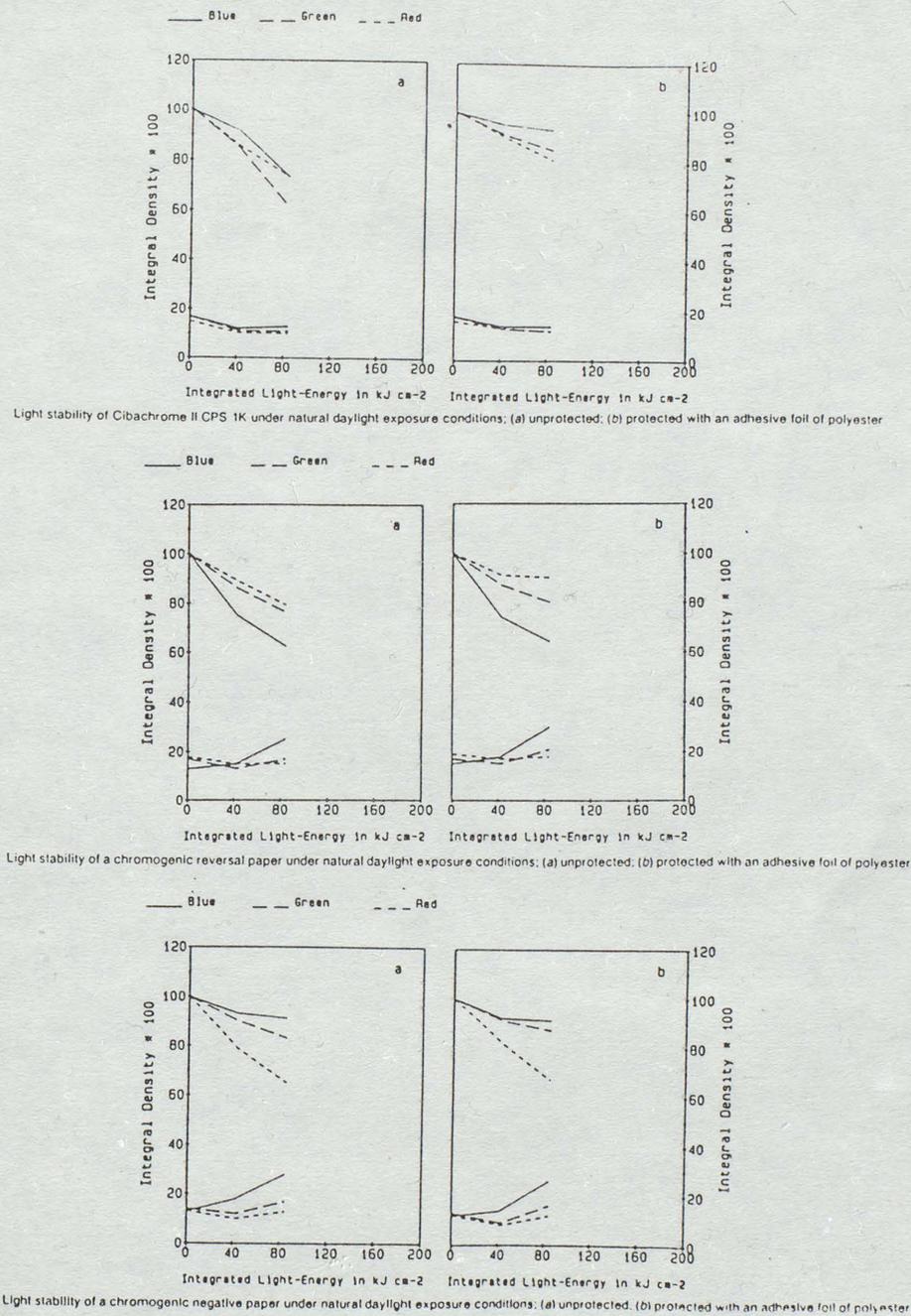
DMIN = UNCHANGED



Dark-fading of Cibachrome II De Luxe Print (CPS 1K) and two chromogenic papers at 77°C/40% RH. D = optical density, C = cyan, M = magenta, Y = yellow.

FIGURE 4

FIGURE 5



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