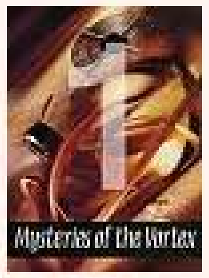

Mysteries Of The Vortex (Part One)

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A Practicum On Print Washing

As anyone reading this will be aware, washing black-and-white film and paper after developing and fixing is necessary to remove both unused fixer and complex silver/thiosulphate compounds produced during fixing. It's easy to regard the washing phase as the tedious postscript to the processing cycle, but perhaps it's time to review the washing and fixing stage in the light of recent research and, in many geographic areas, the increasingly pressing need for water conservation. Although the nature of fibre base (FB) paper demands higher washing standards than those required for film and RC materials, I believe we tend to grossly over-specify on FB washing and that by controlling factors within the washing and fixing steps we can waste less time and water.

"Archival" standards

The term "archival" applied to photographic prints has been so overused that authorities are now shy of it and the LE (life expectancy) factor is being adopted as an assessment of potential longevity. Aside from deterioration caused by storage and display, the principal factor controlling longevity in fibre based paper is the residual thiosulphate level, expressed in weight relative to unit area. The easiest to comprehend is grams per square meter, but those working in the field think in terms of micrograms per square centimetre (ug/cm2). One microgram is one millionth of a gram. The conversion is simple:

0.01grams per square meter = 1 microgram per square centimetre.

The standards accepted for archival or high LE are not yet fixed but are well defined. Ilford has an in-house standard of 0.7 mg/cm2 but discussion among all manufactures continues; a recommended upper limit of 1.5 to 2 mg/cm2 is likely to be the eventual recommendation for safe storage.

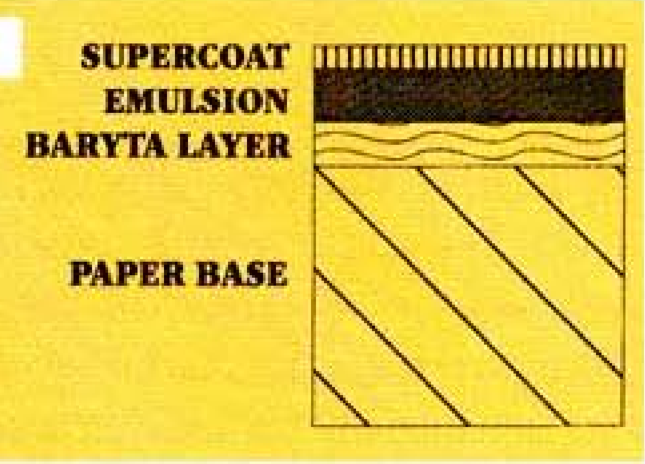
The cornerstone of basic thiosulphate testing in the home darkroom is the HT-2 reagent, which can be used with a Kodak Hypo Estimator to get a reasonable evaluation of thiosulphate content. The HT-2 is not accurate with very low levels of thiosulphate; for those, more complex procedures must be used. Until recently this was the "Methylene Blue" test from the ANSI standard. All the major manufacturers are now using the iodide amylase test, due to be published soon in a new standard.

Definitions

Figure 1 shows the structure of fibre-base paper. While film and RC materials are relatively easy to wash because processing solutions only penetrate the emulsion, the porous base of traditional paper accepts chemicals readily. Washing can be looked upon as three distinct phases that proceed simultaneously:

1. Salts in the base of the emulsion diffuse towards the surface of the paper.
2. The salts diffuse into fresh water at the paper surface.
3. This water then is replaced using agitation and/or water flow.

Figure 1.



An interesting hypothetical way of looking at washing is to think of an 8 x 10 print that can, theoretically at least be archivally washed in only 300 ml of water. Assuming a fibre-base paper 0.03cm thick, a print of this size will have a total volume of approximately 15ml. This print, removed from the fixer is permeated by thiosulphate throughout the base, baryta and emulsion layers. With a 15 ml dose of fresh water, and sufficient time for the thiosulphate content in the print and fresh water to equalise, the thiosulphate content has been reduced to half its initial level with this single washing step – using a minimal amount of water. Repeating this process ten times reduces the hypo level to one thousandth of its initial value; repeating it 20 times will reduce it to one millionth. All using only 300 ml of water! This dramatically illustrates that the exchange of water is a significant factor in washing.

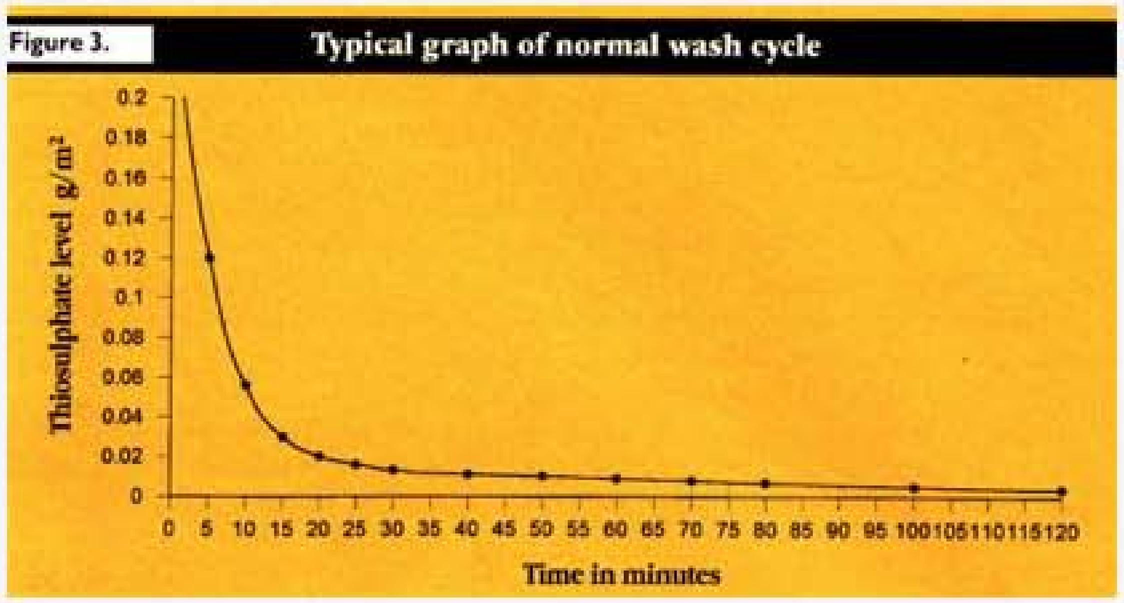
However, this approach might take a long time. This hypothetical model ignores the influences of agitation quality, which may vary considerably; the effect of washing in an enclosed tank of continuously running water; the retarding of the process by slow diffusion of hypo through the paper structure; and the problem of paper retained by the paper structure. How, then, can this idealised approach be most closely met in practice?

Diffusion and related issues

In Practice, the exponential decrease illustrated above works reasonably well for the first minutes of the wash, but slows progressively as the thiosulphate level in the paper drops. Looking at it from a more practical angle, the events that occur from the start of the wash cycle are not so linear.

First, a high level of fixer is sluiced from the surface and adjacent paper layers, resulting in a very rapid drop in thiosulphate level. This takes place within the first few minutes. Next, normal diffusion proceeds and a fairly linear progressive decrease in thiosulphate level dominate over the next half hour or so. However, getting out the very last trace of thiosulphate takes much longer. Thiosulphate and their silver complexes are larger molecules, which are prevented by friction from washing easily out of the paper structure.

The dense layer of baryta in commercially manufactured photographic paper seems to be especially significant in slowing thiosulphate removal. I observed this firsthand when doing some tests on washing emulsion hand-coated onto 300 g/m2 Cranes Parchment paper. This achieved a level of 0.015 g/m2 thiosulphate (using HT-2 testing) after only 10 minutes, faster than double weight baryta paper. It is virtually impossible to remove all thiosulphate from a paper, even with a wash duration of several hours, but this is possibly not a drawback (see "Desirable level of residual thiosulphate")
The three stages of washing mentioned earlier, it should be stressed, are not three consecutive steps, but are effects happening concurrently. The net result is a graph of thiosulphate content declining with wash time taking the general shape shown in Figure 3.



There are a number of treatments that can improve one or more aspects of the washing process, including improvements in agitation and the use of washing aids – and especially, in the control of fixing time.

Leave it out

The purpose of most of the time, water and energy spent in the washing stage is to remove thiosulphate from the paper base, where it never fulfilled any function in the first place. Although it can certainly be removed, why not look at ways of limiting the uptake of fixer in the paper?

Major research by Ilford culminated in the 1981 publication of their archival processing sequence, based on careful control of the quality and timing of the fixing stage. The sequence uses remarkably short washing times, enabled by using a very short fixing time in concentrated ammonium thiosulphate fixer. Originally 30 seconds, this short fixing step prevents the fixing agent from penetrating significantly into the core of the paper. The paper can then be well washed using a pre-rinse, hypo clearing, and a final short wash. The thiosulphate level achievable using the Ilford sequence is, on average, 0.2 ug/cm2 (.002 g/m2), comparable with the ANSI archival standard. This is exceptionally good, way below the levels detectable with the HT-2 test, and heading for a point at which it is beyond the capability of the laboratory Methylene Blue test to detect. In practice, results may be modified by the wash water hardness, but will usually be well within any reasonable standards for archival processing.
The original Ilford archival sequence, with all processing times at 20C (68F) is:

1. FIXING (Ilford Universal Rapid Fixer 1 + 3): 30 seconds
2. FIRST WASH (Good supply of fresh running water): 5 minutes
3. HYPO CLEARING RINSE (Ilford Galerie Washaid 1 = 4): 10 minutes
4. FINAL WASH (Good supply of fresh running water): 5 minutes

The significance of the short fixing time is seen when looking at the levels of residual thiosulphate in the paper as the fixing time is increased. There is relatively little rise up to 60 seconds, with levels increasing significantly thereafter.

Code:

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Fixing time        Micrograms
in seconds     Thiosulphate per sq.cm.
    30              0.14
    60              0.16
   120              0.60
   240              1.00
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The 30 second time, although ideal, is difficult to apply while ensuring good coverage of all areas of larger prints. Ilford now recommends 60 seconds as optimal, because it allows more control without significantly increasing retained thiosulphate levels (0.16 Vs. 0.14 ug/cm2)

While the results from using this sequence are unquestionable, it flies in the face of traditional techniques, which have always tended towards an attitude of "more fixing is better fixing". Although all the steps are short, they must be controlled accurately, and the fixer capacity must be monitored carefully – both of which involve considerable attention. Having an assistant to carry out the processing is one answer. The washing steps don't seem suited to a washer designed for conventional long washes; the entire sequence is probably best done in trays, where short washes can be carried out with good agitation, dumping the tray contents several times during washing.

On the other hand, the fixing step is the only real critical step of the Ilford Archival Processing Sequence. The hypo clear and wash stages have been optimised by Ilford for minimum residual thiosulphate in the shortest time, using the least water. These can be adjusted considerably – there is no reason why a more extended wash should not be used. Perhaps the basic problem is that Ilford presents the sequence as a package, but the rigid requirements needed to follow their steps create practical problems in use. Photographers may also be unwilling to substitute materials, lacking in confidence that other processing chemicals will not work as well as the chemicals Ilford recommends. Another problem is that many photographers cannot easily test the effectiveness of the short fixation on other makes and brands of papers. However, the Ilford archival processing sequence is the best and most efficient way to reduce residual thiosulphate in FB papers.

Agitation

That hypo is heavier than water is the hoariest old chestnut around as far as print washing is concerned. It is used as a selling point by manufacturers whose washers use a downward flow system. A solution of hypo is higher in density than water alone – barely. And if you lower a print straight from the fixer into the washer, you will see flow patterns as the fixer drains down from the surface of the paper. Left alone, however, the fixer will eventually diffuse evenly into the water. Introduce any turbulence into the wash water, and diffusion is quick and complete. And, once in solution, fixer cannot separate itself from the water and "sink" anywhere. If you mixed fixer and water in a bottle and left the bottle on a shelf for months, would you return to find the fixer on the bottom and the water on the top, separated from each other like milk and cream? Obviously not, and this can't happen in your print washer either.

Let's now forget for a moment about the rest of the water in the tank. The significant part of the process takes place in the thin layer of water at the boundary between the print surface and the wash water. The rest of the water in the tank merely acts as a reservoir to absorb the hypo diffusing into this layer. However, the rapid removal and replacement of water in this interface layer is fundamental. Paper in a still tank will wash by diffusion alone – eventually – but the strong concentration of hypo in the interface will greatly impede the process. Some degree of agitation is necessary to shift the layer of water at the print surface regularly. This can be assisted mechanically, but usually the simplest solution is providing a good flow-through.
Although a reasonable level of water flow is necessary, excessive flow may waste water and excessive turbulence may work against the washing process. For example, Nova tested an experimental 5-slot 12 x 16 unit running at 6 litres per minute through 3mm jets – a very high volume of flow-through. The unit washed no faster, and the vortex created by this high throughput significantly retarded the washing rate in the central areas of the prints (Figure 4). As the water rate was reduced first to four and then to two litres per minutes, and the jet sized to 2.2 mm, an optimum flow rate was reached. This seems to suggest that any extreme turbulence in a washer of this type is as likely to create problems as it is to solve them. The ideal must be a smooth sweeping of all areas of the print.

If agitation due to water flow is inadequate, supplementary mechanical agitation might help. The SaltHill washer can have an aquarium pump connected to the air input of its multiple venture chambers. This maintains or increases agitation turbulence while at the same time allowing for the reduction of water flow. This appears to be a unique feature. One budget priced washer places prints in a rack, which is supposed to be given an occasional nudge by a hydraulic piston to move it within the chamber. Anything that relies upon water pressure to mechanically actuate it is likely to be temperamental, and this is no exception.

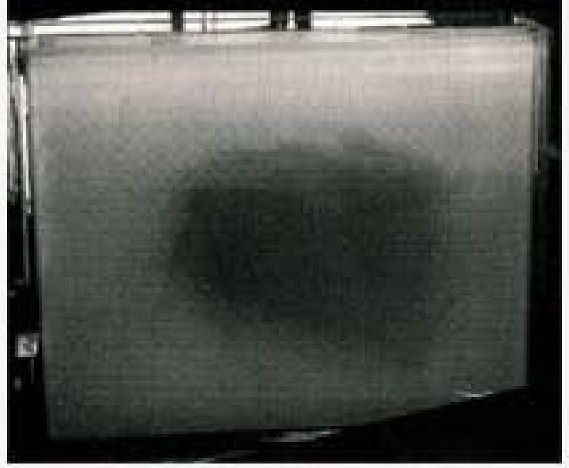

Figure 4. Dye introduced to show the effect of overturbulence in a Nova washer — a 12×16" unit with 3mm jets running at 6 liters/min. The poor exchange in the central area severely retards the washing rate.

Effect of effluent fix in the wash tank

If a dump/refill system is not used, effluent thiosulphate in the water is being progressively diluted as the wash proceeds. Dilute fixer in the wash water is usually cited as being a major factor controlling wash quality. It is commonly stated that effluent fixer held within the wash chamber or cell is a serious retarding factor to further washing, and that is why most washers are designed to use a high rate of flow-through.

The second part of this article includes some practical tests examining the effect of the presence of effluent thiosulphate. The results show little effect on the rate of diffusion of thiosulphate from the paper in the early to mid stages of the wash, and that is only when the concentration of thiosulphate within the paper is at a very low level that the retarding effect becomes significant. By this stage an "archival" level should have already have been reached. As will be discussed below, thiosulphate retained within the washer is blamed as a significant factor when the dominant one is the quality of the agitation at the surface of the paper.

Washing by exchanges

Translating the "300 ml archival wash" method into practice is to wash prints use a tray with a moderate volume of fresh water, agitating thoroughly, then dumping the water completely and replacing it at regular intervals. Many people use this as a pre-wash technique anyway, and it's extremely efficient. In a test by David Vestal, a single 8" x 10" double-weight print was washed to a point where it showed no trace of hypo (using the HT-2 test) after only three 20-minute baths in 500 ml of water. SaltHill engineers found that the most efficient wash that they could achieve was a single print in their Vortex washing tray, a pre-rinse device. A single print in a tray with a Kodak tray siphon also achieves an excellent wash with good efficiency.

These techniques become impractical, and too labour intensive, when many prints are involved. Methods of efficiently washing larger numbers of large-sized prints had to be found. This, not the quality of the wash, is what led to the invention of the so called "archival" washers.

Water exchange relative to tank volume

In the real world, total dump and replacement washes become impractical where large numbers of prints are concerned. Although it's possible to dump quickly, the refill time makes the method impractical unless supercharged plumbing arrangements are made. The Salthill archival washer appears to be the exception to the rule – David Katchel's review of the unit states that its rapid dump/fill feature is unique among archival washers. I have yet to see or use one, as they are not distributed in the UK.

A 16 x 20 13-slot Nova tank has a volume of about 50 litres; with a typical throughput of a 4-5 litres/minute there is a refill time of 10 - 12.5 minutes, and the print will be uncovered for most of this time. (Additionally, washing action might be different at the bottom and the top of the print.) Sinks, as opposed to slotted washers, do exist to perform this type of wash efficiently. In the UK, the Epic brand has a 100 litre wash sink that dumps, using a siphon of the type utilised in men's' toilets. Water filling can be extremely rapid. The only problem is that the high forces involved in filling and dumping are stressful to large prints. The kinked and corrugated prints I've seen emerge from such washers would never be described as "fine".

A washing tank has a relatively high volume compared to the volume of prints being washed in it – for example, a 16 x 20 washer may contain 50 litres of water. Washing a volume of about 750 ml paper when fully loaded. An average water throughput is about 5 litres per minute, which will result in a volume equivalent to about 12 exchanges during a two hour period. This does not mean that in 10 minutes from the start of washing the washer contains fresh water, or even 30 minutes later. Diffused thiosulphate is only gradually being transferred out of the tank, and a certain amount remains right to the end of the wash. To offset any effects on diffusion, and to improve agitation, the economical solution is to reduce the tank volume.

When using spray washing this is taken to the extreme. I tested this when investigating washing emulsions applied to ceramic surfaces. The water from a shower head was passed over the ceramic surface for 10 seconds per minutes, draining into a sink. Consequently the water volume present at the surface of the vertically washed piece approached zero. Efficiency was compared to a control specimen continually washed in a dish using a Kodak tray siphon. There was no practical difference between the qualities of washing of the two methods, from which we can infer that as long as a film of fresh water is present at the surface of the material for salts to diffuse into, washing will proceed effectively. Regular replacement of the water film by passing the shower head across it ensured this. Although not tested, it seems a reasonable inference that continual spray washing will be more effective than tank washing; this is confirmed by Neblette, and it is a washing technique used in some rapid access film processing systems.

From dye injection tests, it is evident that a higher volume of water in the compartment serves to act as a reservoir, slowing down water exchange. An individual cell or compartment in an archival washer can be effectively doubled in size to check this effect by removing one divider and blocking one inlet jet. The dye persists longer, illustrating that the hypo level in the water persists at a higher concentration. The traditional view is that the washing rate is retarded by thiosulphate build-up, and while tests such as David Vestal's washer review show a slower wash rate in larger volume tanks, could the dominant effect be due to inferior agitation? All I can conclude for sure is that, for a given water flow, larger cell volume does not help. Extrapolating this principal means that a cell containing virtually no water is the most efficient, with the ideal being complete total water exchange at regular intervals, or possibly washing with continual laminar flow. Reducing the internal cell capacity to a safe minimum is the nearest way of approaching this in a constant flow washer. SaltHill follows this principle; the cell width of their washers is 1 cm. Nova opted for a cell width of 1.5cm on their 13 slot washers and this seems to be a good optimum. The print is not too difficult to insert, and there is sufficient capacity to induce an efficient sweeping water action.

Further controls in washing

Pre-Rinsing:

Introducing a print straight from the fixer directly into the washer is not helpful. You begin the wash having dumped a load of fixer into the compartment that wasn't even in the paper structure to start with. If you can pre-rinse even briefly prior to washing, you avoid filling the cell with concentrated fixer, thus cutting the steepest part off the washing curve and easily ten minutes off your time. You can adopt part of the special Ilford sequence and employ a five minute pre-rinse, followed by hypo clearing and the main wash. A water saving pre-rinse bath is easily set up when using most archival washers simply by using the overflow from the washer.

Hypo Clearing:

The importance of hypo-clearing agent as a wash aid cannot be over-stressed. It is inexpensive, environmentally harmless, and its use results in lower levels of residual thiosulphate than can be achieved by washing alone, as well as a considerable saving in water. In addition to the thiosulphate displacement, wash aids help reverse the mordanting of thiosulphate in the image silver that takes place when aluminium hardeners are used, and help remove the sparingly soluble silver thiosulphate complexes that cannot be removed by washing alone. A further attribute is that cold-water washing is more effective after the use of hypo clear. Both the Kodak product and Ilford Galerie Washaid are similar. The Ilford product is slightly more alkaline, which should improve its efficiency marginally, and it contains agents to balance it for hard water. A number of other brands exist, including Heico Perma Wash. For scratch mixers, a 2% solution of sodium sulphite (about a heaped teaspoon in a litre of water – measurement accuracy is not critical) works well.

Hypo Eliminator:

Hypo eliminator is frequently confused with hypo clearing agents. It is a completely different substance, performing a different function. Hypo eliminator is a mixture of ammonia and hydrogen peroxide, prepared immediately before use. Whereas hypo clear acts by displacement, hypo eliminator actually breaks thiosulphate down by oxidising it into soluble sulphates that are more readily removed. Until the 1980's, the use of hypo eliminator was recommended for the ultimate in archival work, and was included as a benchmark in the ANSI standard. Current thinking is that the cure is worse than the disease, as it weakens the paper structure and may have long term effects on image stability. Hypo eliminator is no longer recommended.

Other considerations

Water hardness:

An area that is seldom considered in relation to washing is the relationship between the degree of water softness, or hardness and washing time. Many salts – some of which are contained in hard tap water act as hypo clearing agents. Their carbonate and bi-carbonate ions operate in an ion exchange reaction that speeds the washing process. Pure water such as distilled water, the "softest" possible water is surprisingly relatively poor at washing. This effect was investigated by Kodak in tests at its plants in Harrow and Manchester UK on washing motion picture film, which has a hardened emulsion less easily washed than conventional camera film. In reaching a good commercial thiosulphate level, tap water washed 20 times more quickly than deionised water. Moreover, the harder Harrow water washed at 5 times the rate of the softer Manchester water. Remember that this large variation will be much smaller when washing papers processed without hardeners. The effect of water hardness on wash quality is so geographically specific that it is impossible to make recommendations other than to test your washing with HT-2.

Contaminants in tap water:

There are many reasons besides saving water for avoiding long wet times for FB prints. Excessive wet times may leach brighteners, weaken the structure of the paper, affect dimensional consistency, or cause the emulsion to lift off the paper or chip at the edges. But there is another good reason to avoid long wet times.

Ralph Steiner, in an unpublished treatise on print washing, observes that during extremely long washes his prints actually picked up contaminants from his water supply. His washes lasting two hours produced cleaner prints than test washes he performed lasting 12 hours or more. This factor is also too closely tied to local water supplies to generalise about, but avoiding potential contamination from unknown substances in your water is another good reason to increase the efficiency of the wash and to minimise both the length of the wash and the amount of water used.

Paper base weight:

Most fibre papers are what is termed double weight (240 grams per square metre). Single weight (140 g/m2) papers are still available from a few manufactures. There are also several heavier weight papers, including Kodak Elite and Forte Museum, which use a 300 g/m2 base. From my own tests it appears that the base washes faster than the emulsion, and consequently, no allowance need be made for heavier base papers. There are no published recommendations for increased washing time to allow for 300g density, but if in doubt, a 10% increase over the wash time used for 240g/m2 papers would seem an adequate precaution. This is another reason for testing the wash quality of your own preferred papers with HT-2.

Hardeners:

The use of hardening fixers in paper processing is recommended by Ansel Adams in his classic text The Print, and this has encouraged their enthusiastic use. However, there is no point in using a hardening agent in the fixer unless it's for a particular purpose, such as preventing the print from sticking to the blanket of a glazer during heat drying, or when processing at high temperatures. The bottleneck in washing is the rate of thiosulphate diffusion from the emulsion side; this is further aggravated by the presence of a thin, hardened gelatine super-coating. Using a hardening agent tends to "trap" thiosulphate within the emulsion layer by compacting the emulsion, making it more difficult to wash efficiently, and preventing washing to an optimum level. If you use a hardener, it is virtually mandatory that you also use a wash aid. Doubling the wash time when employing hardeners is the rule of thumb, but an HT-2 test really is required.

Effect of low temperatures on washing time:

Low wash temperature wash results in compacted emulsion, which washes more slowly. Ilford suggests a straightforward doubling of washing time when the temperature is below 10C. A temperature lower than 3 – 4C is rarely encountered in water coming through ground pipes. The use of hypo clearing agent mitigates considerably the problems caused by using cold water.

Fixer silver level:

Under-fixed prints can be washed well and have most of the fixer removed, but they still won't be stable, tending to "print out" on exposure to light, producing staining. Another cause of instability in fully washed prints is that the fixer silver level may have been too high, and thiosulphate and fixation by-products may be bonded on to the silver structure of the paper. These won't wash out with any amount of washing, and are likely to be revealed by a yellowing in the print highlights when exposed to light for any length of time. Rather than test the paper for retained silver, the simplest measure is a preventative one; monitor the capacity of the fixing bath(s), or use silver estimating paper to check the build up of silver in the fixing bath(s). A colour change on the estimating paper is compared with a reference chart that gives the silver level. A level of 2 grams per litre is recommended by Ilford whether fixing in single or twin baths for "commercial" work, but the practical minimum is 0.5 g/litre when working to archival standards. This equals roughly 40 8 x 10 prints per litre for commercial, 10 8 x 10 prints per litre for archival work. Two bath fixing is recommended for archival work; this allows the first bath to be loaded up to 2g/litre, while the second bath is maintained at the 0.5g/litre or below.

Desirable level of residual thiosulphate:

In the early 80's it was established that a certain (small) level of thiosulphate retained in the emulsion and base actually stabilised the image, by preventing or reducing image oxidation. This is extremely convenient, and means there is no longer any reason to agonise over the remaining 0.01 grams per square metre of thiosulphate remaining after an archival wash (it is also another reason why hypo eliminator is not needed). However, the discussion has quieted since then. Fuji has been the main proponent of the beneficial effects of the trace level, but their work has been mainly on microfilms. Recent work by Ilford on RC papers failed to show a similar stabilising effect. A standard for the recommended retained thiosulphate level should arrive eventually, but a significant amount of work is still required. Ilford's opinion is that a level of around 0.015 – 0.02 g/m2 (0.15 – 0.2 ug/cm2) is likely to be adopted. A rider to the issue is that this thiosulphate level is beneficial only when the image is to be displayed. If the print is for archival use – meaning that it will be stored predominantly in darkness – the lowest possible level of thiosulphate is preferred.