Black & White Film Processing
Some Investigations on the Kinematics of the ILFORD batch Film washing Procedure

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1 The Procedure recommended by Ilford and some Questions

According to the environmental protection issue Ilford has recommended a revised film washing procedure years ago. Instead of washing the film for 15 minutes with running water Ilford recommended to wash in a batch process:

Clean the tank with the film under running water and
Fill tank with fresh water, turn 5 times
refresh water, turn 10 times
refresh water, turn 20 times
and we have a film washed in **archive** quality

This procedure might in the first glance sound astonishing, if we compare the amount of water used in the traditional method to the amount we need now (15 - 45 l (Liter) vs. 1.5 l).

Some publications have shown, that the Ilford method results in very clean films, one of these is [1].

But for me some questions were still open and I haven't found any hints in previous publications:

a) Why does Ilford give turns instead of times, e.g. 15, 30, 60 seconds?

b) What is the (film surface) / (water volume) ratio for their procedure (1 135 / 500ml, 1 135/250 ml). What is to do when I have one 120 film or 2 120 films in my tank?

c) Can this procedure be improved or even more economized in terms of water spill or process time?

d) Does the procedure depend on the temperature?

2 A small Problem encountered with the Procedure

It is known that a very diluted solution of **Potassiumpermanganate** may be used as **test fluid for residual hypo**.

0.1g Potassiumpermanganate
1.0g Sodiumcarbonate
1.0l Demineralized Water

Mixed in a **volumetric equal ratio** with wash water the color should not change within two minutes. otherwise hypo is still present.

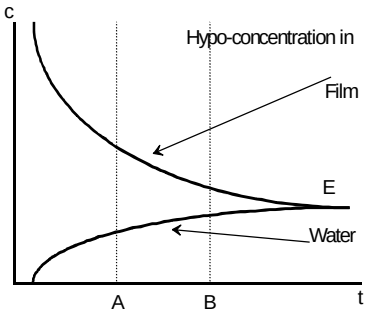
My first checks of the Ilford procedure were done with this test fluid:

After the first wash the tank was opened and the reel was taken out of the water with an empty test-tube in the left hand. The reel was held under 45° so that we have one deepest point where the water leaves the reel continuously. When this water flow discontinued and changed to droplets, the rest of the water was catched in the test-tube, the amount was 1-2ml. This water should have had the longest contact with the film hence containing the most hypo accessable. The level of water catched was marked on the test-tube. Then the test-tube was emptied and cleaned with some fresh water and filled with the same amount of test solution as I catched water from the reel. Then I processed the next steps of the washing procedure, checking the water after the step with the test solution the way descripted above. Usually there was no residual hypo shown after the second wash. The temperature of the wash water usually was ca. 20°.

Once I made an error and for the second wash I used water with approx. 25° with the result that the test fluid clearly showed residual hypo after the second wash with a film where it never occurred before with water of 20°. Is the **efficiency** of the washing process strongly **related to the water temperature?**

3 Washing and Physics

However, we have to take in account that the physical process we call 'washing' is not to be compared with washing clothes in a washing machine, we do not and we must not treat a film the same way as we do with laundry.
The removal of the hypo-ion-complex from the emulsion has something to do with **diffusion**. Therefore the **driving force** for the washing process we have in the tank is the **difference in concentration of hypo** in the **film emulsion** and the **surrounding water**. With the constant agitation as we apply with the Ilford procedure we remove constantly water enriched with hypo from the emulsion surface of the film. The maximum concentration difference is always established providing most efficient transfer of ions from the emulsion into the washing water. However, the speed slows down because the concentration difference with each ion leaving the emulsion is getting smaller until **equilibrium** is reached and the transfer stops. **Additional washing is absolutely useless**.



Some topics may be seen in the picture on the left, it is just typical. We see that the concentration in the film decreases much faster than the concentration in the water increases. No numbers are given. What is time A, where we may decide to change the water because the additional amount of hypo washed out until equilibrium E is reached, Or may we wait to time B? Is time B 2 or 10 (or whatever) times A?

It is quite interesting here that it is **theoretically enough to wash a film once**.

Here is a short cut calculation with rounded figures: A 135 film has an surface area of 600 cm², the emulsion thickness of a 400 film (APX400) is 10µm, which results in an emulsion volume of (600cm² x 10µm) = 0.000,000,6m³ = 0.000,6l (Liter). If our tank contains 0,5l, and we fully use this volume, the ratio **(Dilution factor)** is 0.5 / 0.0006 = **833**. I.e 1 / 833 of 500ml is the emulsion volume in 500ml liquid.

If we pour 500ml of fixer into the tank, which may contain 30g hypo ion (60g hypo ion per liter), we may get 36mg in the emulsion. With the first wash we may dilute that by 833 and have 43µg residual hypo in the emulsion. If we devide 43µg by the emulsion area we get 43µg/600cm² = 0.072µg/cm², which is a lot less than the usual 1.5µg/cm² residual hypo allowed for archival use.

But everybody knows that **one wash is not sufficient at all**. This is true to probable several reasons:

(A) The tank is not clean when the first wash water is entered, so the amount of hypo in the wash water is to a high degree raised by the liquid taken over from the previous bath and not by the contents in the emulsion. This in a high degree reduces the dilution factor of 833 derivated above.

(B) We are unable to reach in a resonable time or never the equilibrium point E, because the emulsion keeps the hypo-ions quite tight.

Consideration (A) leads me to the first rule to improve the standard Ilford recommendation:

Rule 1:

Reduce take-over from one wash batch to the next as much as possible.
Open the tank, sling water out and optionally wipe it out.
Sling water from tank cover and reel as much as possible.

4 How to measure

After the considerations in chapter 3 the problem to get some figures and numbers is to measure the contents of hypo either in the emulsion or the wash water. While it may be feasable to collect in a periodic time schedule a specimen of the wash water it will be very difficult to take from the reel a specimen of film after seconds 5, 7, 10, 14, .. Furthermore, I'm not a chemist nor do I have a laboratory available to make tedious analyses, so I decided not to follow this way.

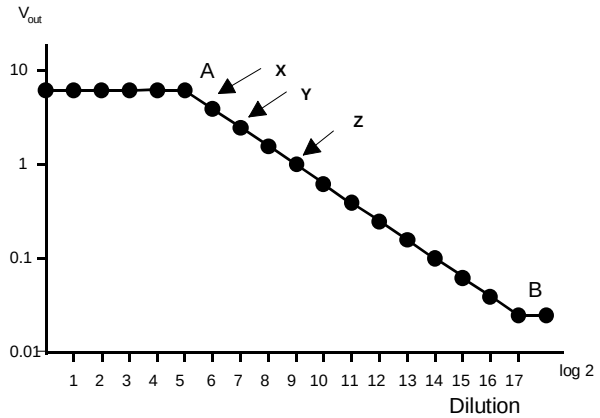
My approach to measure the kinetics of the washing process was quite different. The considerations of chapter 3 show that latest at the second wash we handle small concentrations. A very fast method of measurement of ion concentrations in water is the measurement of the electrical conductivity. Previous trials with normal mains water showed that after the second wash the conductivity is only controlled by the usual mineral constituents. So I decided to use demineralized water, where a high electrical resistance is really a quality mark for the pureness. The electrical conductivity was determined with an electronic device following a proposal in [2], but with several modifications. The voltage measured was transformed into PC-readable digital data and read together with data of a temperature sensor into a PC program which was used to collect, to interpret and to store the data.

It is clear that this method reacts on all ions leaving the emulsion, but there should be a stable ratio of hypo ions to the sum of ions. My aim was to find something about speed and not about absolute values.

To get a translation curve I've started with used fixer near its maximum capacity. The fixer used was one batch of an ammonium thiosulfate liquid rapid fixer (AGFA AGEFIX) 1+7 diluted, I don't believe there are significant differences between the rapid fixers offered by the major companies. So the found behaviour should be the same with other rapid fixers. The working solution was diluted 1 to 2 (50ml + 50ml), and from then devided by 2 by diluting it each time by 2:

Take 50 ml of the solution to a new bottle
Add 50 ml demin water to the new bottle
Mix and start again by dividing by 2.

Actually this is each time a dilution by two, so the dilutions are ½, ¼, 1/8, 1/16 and so forth, which is $1/2^n$ at the n-th step. When I used these stepped dilutions to calibrate my measuring devices I found a quite linear correlation (in logarithmic terms) to the dilution steps.



Dilution is scaled logarithmic

	Dilution is by	
1	2	Upper limit reached
2	4	dto.
3	8	dto.
4	16	dto.
5	32	A = linear area starts
6	64	X = Mineral water (> 2 g ions/l)
7	128	Y = Evian type; mains water
8	256	
9	512	Z = Limit for Potass. Permang.
10	1024	
11	2048	
12	4096	
13	8192	
14	16384	
15	32768	
16	65536	
17	131072	B = Conductivity of demin water reached

It is clearly to be seen that the chosen method allows to look very much further into dilutions than the Potassium permanganate check mentioned above. We also see that the method has a horizon which is at a dilution of 1:130,000 roughly, which isn't the sugar cube in the Lake of Constance, but should be sensitive enough for issue here. A check at some points for temperature sensitivity showed that there is a dependency to the temperature of ~ 0.1 V/K, so the idea to take also the tempereature in account wasn't bad. It was

now a solvable task to write a PC-program (in BASIC), which beeps me to move the reels, to measure the voltage and the temperature, to give me the current values and which turned out after the first two films, to measure also in an exponential time schedule, which is after seconds 1, 1.4, 2, 2.8, 4, 5.6, 8, 11.2, 16, 22.4, 32, ... (real photographers know these numbers!), to reduce the number of data.

5 Preperations in the Tank, Sensor Placement, Pre-Checks

The ideal placement for the sensors would be somewhere in the vicinity of the film surface, but I did not dare to place something there to avoid the risk of damaging the films. Also I was not willing to drill holes into my good old faithful JOBO tank (23 years old) to glue in some cables. So I decided to place the sensors in two thin plastic tubes and to place the sensors in the centre cylinder of the reels. Washing was then done in an open tank, with the sensors in the center. Agitation was achieved by lifting the reels up and put them down into the wash water again. This was done in the first 10 seconds continously, then in a 3 sec interval. As a Pre-Check the tank with reels was used without film for 0.5h with 500ml demin water to see if any stains may influence the measurements, no significance was found.

6 What is to be expected

What we actually do with washing is presenting to the emulsion as clean as possible water to tempt the ions there to come out into the washing water. Literally spoken, it looks like they don't like each other and try to get the maximum distance to each other, thats why a lot of them leave the emulsion until the concentration in the emulsion and the washing water is (nearly) the same. This is called equilibrium and the end of all exchange processes. So what we should find are lines like the lower one in Pic 1. Equilibrium is reached when we have the flat direction (slope = 0).

When we measure the curves absolutely and plot them in the same diagram, the vertical distance from curve to curve will be smaller. That's shown in chapter four: we may dilutet from batch to batch by ½, 1/10, or whatever ratio, but we never may reach 0 with this method. When we may reduce the amount of hypo by 1/10 per 500ml fresh water, then the absolute values per wash are looking quite small:

1	Start	30	mg in the emulsion, working solution	50 µg/cm²
2	by 10	3	mg (i.e. 27 mg removed)	5 µg/cm²
3	by 10	0.3	mg (i.e. 2.7 mg removed)	0.5µg/cm²
4	by 10	0.03	mg (i.e. 0.27 mg removed)	0.5µg/cm²

etc. So if we calculate the ratio (removed hypo) / (used water), the ratio will be close to 0 very soon and it may turn out that an additional wash may only remove a few ions from the emulsion and therefore the gain (in terms on reducing hypo residuals in the emulsion) is reaching zero and additional wash is only a spill of water. But the correllation is surely not as linear as the above consideration is making believe.

7 Real Results

Tests were made with several 120-type films (FPX-4, APX 25. APX 100, AP(X) 400, NEOPAN 400) looking if there is any surprise. To say it here: there was no big surprise, but the impact of temperature on the results was not as much as I expected, I found no impact on the results in the temperature range of 20°C to 25°C.

One aim was to see if it possible to find the equilibrium points, because washing times should be shorter than the euilibrium time. Therefore I extended the time for each bath remarkable, either until over three subsequent measurements the conductivity stayed constant (=equilibrium), or 15 minutes where reached for the first tests. After a few trials I stopped measurements at 400 sec = 6.5 minutes, because there were no significant events between 6.5 min and 15 min.

As mentioned earlier after the usual fixing step (two times the clearing time) I first washed away the fixer bath with mains water for a few seconds before the first bath with demin water was done and observed. **Always** in the **first**, and **sometimes** also in the **second** wash, **equilibrium** was found after some time, and for the first batch this is reached after 10-15 seconds, i.e. very fast. OK to Ilford, the first 5 turns are OK, it is enough for the first batch.

Selected results are shown at the next page and here are some explaining words:

All plots show the dilution (or the concentration of ions in the wash water) versus time for each washing step. The highest curve is the first, and below we have the next washing steps. Saturation (Equilibrium) as expected (slope = 0) could be seen in Figs 1, 2 & 3.

Fig. 1 and 2. show results with the same type of film. While in Fig. 1 the washing method of Ilford was simulated by just exchanging the water in the tank, in Fig 2 the reels were slinged dry as much as possible and the tank was wiped out before the next step. It can be clearly seen that reducing the take-over from one bath to the next has a significant effect on the efficiency on the washing process. While in Fig.1 we need 3 bathes to come to the horizon of my measuring method, we have in Fig. 2 the same or better result after 2 bathes.

Fig. 3 and 4 show interesting results of a presoaking time of 10 min. After fixing and a cleanment under running water the films were left for approx. 10 min in a waterbath without any movement. Then the test washing procedure was started. The influence of the presoaking bath is evident. However, I do not recommend it because the fixers during the presoaking bath are of relativ high concentration and may damage the developed silver picture. If possible I will do some additional measurements if a soaking bath after the second or third wash may have a similar impact on the results. NEOPAN may be taken as representative of T-type emulsion films as also KODAKs Txx films. The results without soaking bath give the recommendation to wash these types of film perhaps two batches more than more traditional emulsions, this was also found in [1].

Fig. 5 and 6 proof the efficiency of the Ilford method: The films were washed with demin water in the given timeframe in the closed tank turning the tank continuously, with reduced take-over and then put into the measuring arrangement. In my opinion the films have left the regular bathes clean.

I give the following recommendations as conclusion:

1) Dry the the equipment between the single washing steps, reduce take-over to a minimum.

2) Use: 5 10 20 40 seconds for washing 1 film in ½ l (or 1 pint) of water (* 2)
5 7 10 14 20 18 40 seconds for washing 2 films in ½ l (or 1 pint) of water
I.e. use 2 times the water for 2 films as for 1 film (* 1.4)

3) If in doubt, the efficiency may be slighly improved by increasing the times

4) The movement of the tank is continuously in the given time frames.

5) T-grain films may need two batches more than others and/or longer times, e.g.
5 13 30 75 (* 2.5) or 5 8 13 20 30 50 75 (* 1.6)

Thanks to my daughter Hannah for checking the publication.

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Fig. 1

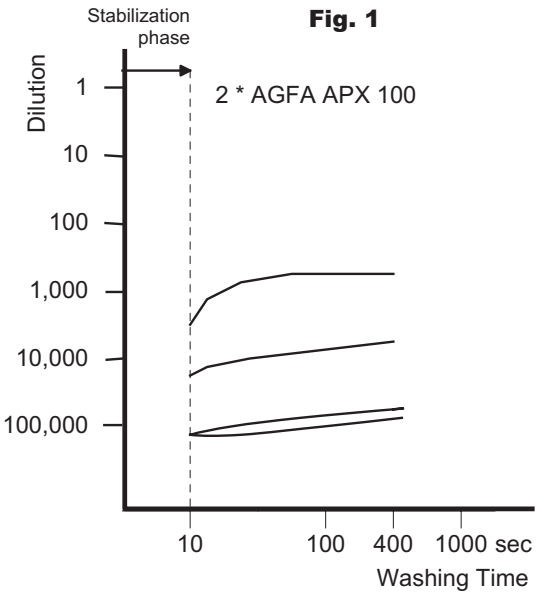


Fig. 2

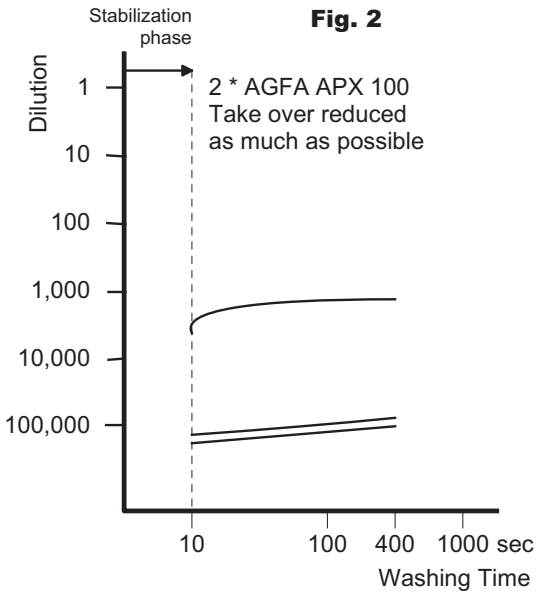


Fig. 3

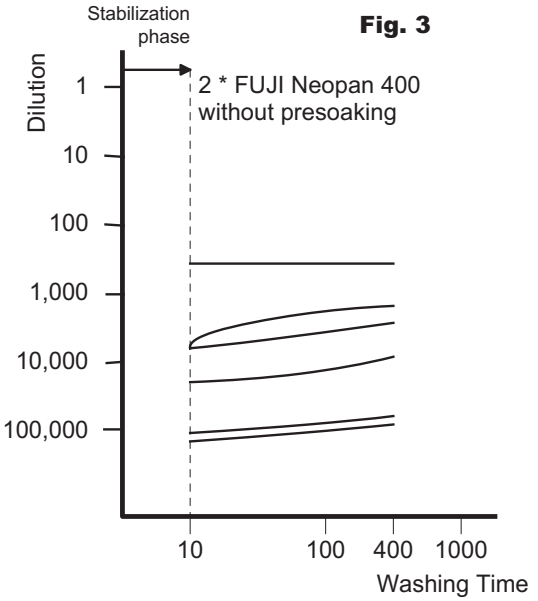


Fig. 4

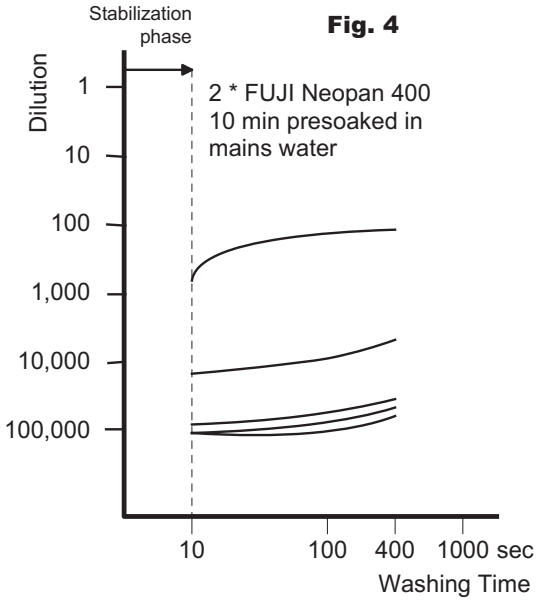


Fig. 5

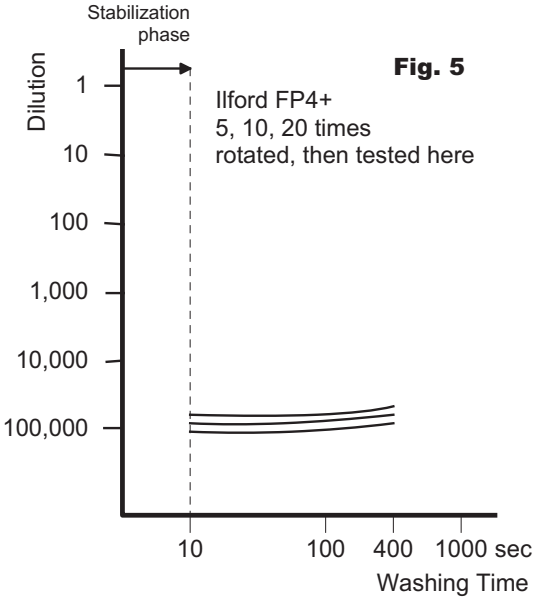
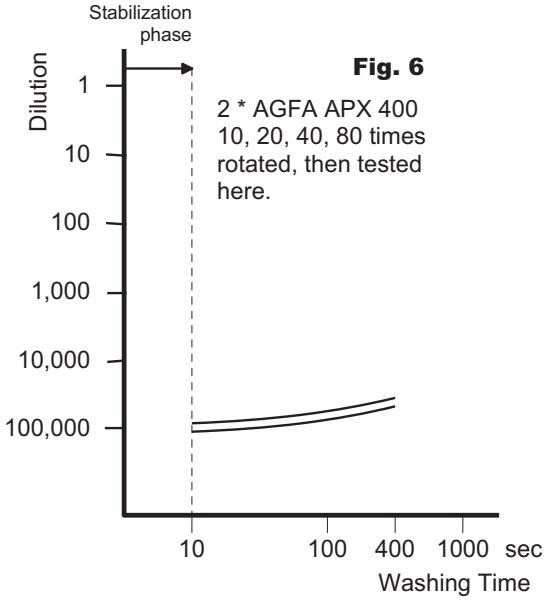


Fig. 6



[1] D. Findeisen: Volles Rohr?
Wässern von SW-Filmen
Photo Hobby Labor 1/90 p. 18

[2] J. Vaessen: Conductance Meter,
Elektor Electronics magazine (UK), May 1991, p 46

Leitwertmesser Elektor (Germany) Sept 1991 Pg. 62: