Contents

The first version of this article was put into the public of the Internet in 1998. It is and was interesting to look occasionally for the traces and the echos in the web. Here are the most common misunderstandings:

- This paper can't prove that the Ilford washing instruction leads to films of archival purity under all conditions. But the conclusion is that there are very rapidly conditions reached, where washing can be stopped. Subsequent washing is just a waste of water without any decrease of hypo concentration in the film. (A statement about archival purity would only be possible if the residual hypo content would have been really determined, which is beyond my ability).
- This paper does **not say, that the Ilford method can just be used as published by Ilford**. In my opinion the instruction is too rough and does not consider available water volume per film.

The summary of my experiences and my recommendations are:

- **The results are valid for rapid fixer only!** (basis: ammonium thiosulfate)
- Consider the **water to film ratio**:
  1 film in ½ l water can be washed faster and with less water than 2 films in the same tank volume.
- After finishing the fixer step **rinse your open tank** with the film(s) in it and the cover for cleaning the equipment from any residuals of fixer. For this rinse I usually use ½ l of water, pour it into the open tank, shake this tank, and pour then the water from the tank through the upper part of the tank and the cover. This is the first step of my recommendations below for minimising take over, and I do this so automatically that I had forgotten to mention it in previous releases of this paper.
- Use for **1 film 4 x 500 ml water** for washing in **5, 10, 20, 40** turns (continuous turning) after each water exchange.
- Use for **2 films 8 x 500 ml water** for washing in **5, 7, 10, 14, 20, 28, 40, 56** turns, i. e. double the amount of water and increase the time.
- **Reduce the take over to a minimum**: Open the tank for changing the water, remove the reels (do not remove the film form the reels, because wet film is very vulnerable), dry the tank, sling away from the film-reel as much water as possible, and the start the next washing sequence.
- **Take care that your fingers** are at least as wet as the equipment. Fixer usually has to be removed from the fingers as from the film, so take care that your fingers have really contact with the water when you pour each batch away.
- Fixer is "**infectious**" for me during film washing. After funnelling the fixer back into the bottle, this bottle is closed and not touched during the whole washing procedure, as all other equipment which might have been "infected" with fixer like measuring jugs, rags or sponges
- I have used **de-mineralised water** for washing and measuring. No recommendation for using it generally!

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 washing 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 (should) have a film washed in **archive** quality

This procedure sounds in the first glance astonishing, if we compare the amount of water used in the traditional method to the amount we need now (15 - 45 l (Litres) < > 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 x 135 / **500** ml, 1 x 135 / **250** ml).
What is to do when I have **one** 120 film **or two** 120 films in my tank?

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

d) Is the procedure temperature dependent?

2. A small Problem encountered with the Procedure

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

0.1 g	Potassium-permanganate
1.0 g	Sodium-carbonate
1.0 l	De-mineralised Water

Mixed in a **volumetric equal ratio** with wash water the colour should not change within two minutes. Otherwise hypo is still present. (See the sketch in chapt 4 for the limits of this test)

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

A test-tube was used as test equipment.

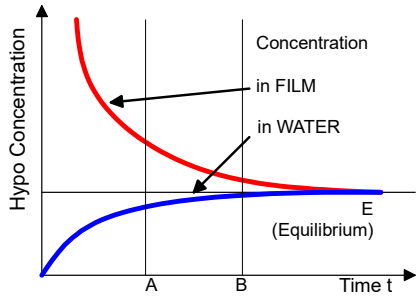
After the first wash the tank was opened and the reel was lifted out of the water. An empty test-tube was held in the left hand for immediate use. The reel was held under 45° so that we have one low point where the water leaves continuously the reel. When the steady water flow discontinued and changed to droplets, the rest of the water was caught in the test-tube, the amount was 1 - 2 ml. This water had the longest contact with the film hence containing the most hypo accessible. The level of water caught 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 caught 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 described above. Usually there was no residual hypo shown after the second wash. The temperature of the wash water usually was app. 20°C.

Once I made an error and for the second wash I used water with app. 25°C 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 (!, not chemical) process we call 'washing' has nothing in common with washing laundry in a washing machine, we do not and we must not treat a film the same way as we do it 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.



Subsequent time for washing is absolutely useless.

Some topics may be seen in the picture (1) on the left, it is just a typical representation. We see that the concentration in the film decreases in a higher rate than the concentration in the water increases. I can't give any values for that. Is it time **A** where we might decide to change the water? Is it better to invest the double time **B** because we can wash out a small additional amount of hypo. The closer we come to the equilibrium point **E** the smaller is the additional efficiency..

It is in this context quite interesting that it is **theoretically enough to wash a film once**

Here is a short cut calculation with rounded figures: A 135/36 film has a surface area of 600 cm², the emulsion thickness of an ASA 400 film (APX400) is 10 µm, which results in an emulsion volume of (600cm² x 10µm) = 0.000,000,6 m³ = 0.000,6 l (Litre). If our tank contains 0,5 l, and we fully use this volume, the ratio **(Dilution factor)** is 0.5 / 0.0006 = **833**. I.e. 1 / 833 of 500 ml is the emulsion volume in 500 ml liquid.

However, according to measurements of Mark Torzynski [3] the real volume of the emulsion is 2 ml, which would mean that the possible dilution is 0.5 / 0.002 = 250 only. Dry / wet = 3.33!

When we pour 500 ml of fixer into a tank, and the fixer may contain 30 g hypo ion (60 g hypo ion per litre), we may get 36 mg in the emulsion. With the first wash we may dilute that by 833 and have 43 µg residual hypo in the emulsion. If we divide 43 µg by the emulsion area we get 43 µg / 600 cm² = 0.072 µg / cm², a number significantly smaller than the usual 1.5 µg / cm² residual hypo allowed for archival use. Even: 0.072 x 3.33 = 0.24 is < 1,5µg/cm².!

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 by 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 derived above.

(B) We are unable to reach in a reasonable 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 is the determination of some real values. How to measure the contents of hypo either in the emulsion or the wash water? While it may be feasible to collect in a periodic time schedule a specimen of the wash water it will be very difficult to take from the reel a test piece of film after seconds 5, 7, 10, 14, .. Furthermore, I'm not a chemist (but a chemical engineer) nor do I have the chemistry and a laboratory available for performing accurate analysis for hypo contents of the film. Such I decided not to go this way.

My approach for measuring the kinetics of the washing process was quite different. The considerations of chapter 4 show that latest at the second wash we operate with small concentrations. A very fast method of measurement of ion concentrations in water is the measurement of the electrical conductivity.

Previous trials with normal tap water proofed that after the second wash the conductivity is only controlled by the usual mineral constituents of tap water. So I decided to use de-mineralised 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.

For achieving 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.

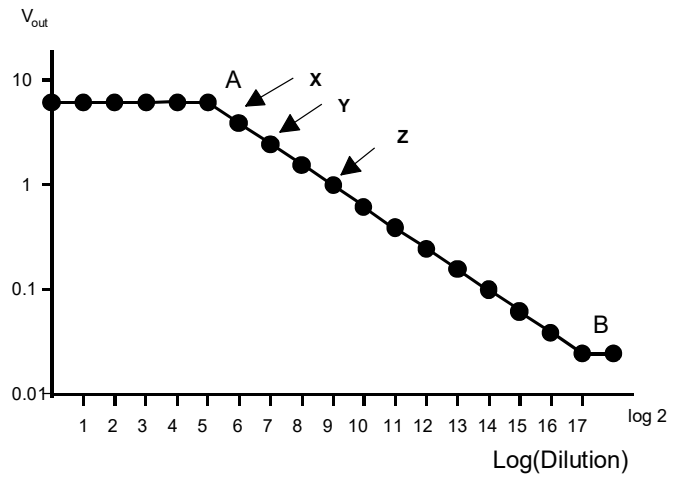
The working solution was diluted 1 to 2 (50ml + 50ml), and from then divided by 2 by diluting it each time by 2:

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

Actually this is each time a dilution by 2, 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.

It is clearly to be seen below 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 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 temperature in account wasn't bad. It was now a solvable task to write a PC-program which controls the washing process: it beeps me to move the reels, it measures the voltage and the temperature, it displays the current values. After the first two films I decided to measure 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!) for reducing the number of data recorded.

As a check the conductivity of a mineral water with high mineral content (> 2g/l), and tab water (which I call Evian type water) with low mineral content, was determined. Also I checked at which dilution the sensitivity of the permanganate test was reached, i.e. when did the colour no longer change.



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; tab water (low mineral cont.)
8	256	
9	512	Z = Limit for Potassium Permanganate.
10	1024	
11	2048	
12	4096	
13	8192	
14	16384	
15	32768	
16	65536	
17	131072	B = Conductivity of demin water reached

5. Preparations 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 for avoiding 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 centre. Agitation was achieved by lifting the reels up and put them down into the wash water. This was done in the first 10 seconds continuously, then in a 3 sec interval. As a Pre-Check the tank with reels was used without film for 0.5 h with 500ml de-min water to see if any stains may influence the measurements, no evidence was found.

6. What is to be expected

What we actually do with washing is presenting to the emulsion water as clean as possible to tempt the ions to move into the washing water. As a picture: it looks like they don't like each other and try to get the maximum distance to each other, that's 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 5: we may dilute from batch to batch by ½, 1/10, or whatever ratio, but we never may reach 0 with this method. When we might reduce the amount of hypo by 1/10 per 500 ml 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)	0.5	µg/cm²
4	by 10	0.03	mg (i.e. 0.27 mg removed)	0.05	µg/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 correlation 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. At the outset: 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. It must be repeated that after fixing a short rinse was performed for cleaning equipment and film.

One aim was to see if it possible to find the equilibrium points, because washing times should be shorter than the equilibrium 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 tab water for a few seconds before the first bath with de-min 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 on the end of this paper 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 slung 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 batches to arrive at the horizon of my measuring method, we have in Fig. 2 the same or better result after 2 batches.

Fig. 3 and 4 show interesting results of a pre-soaking time of 10 min. After fixing and a rinse under running water the films were left for approx. 10 min in a water without any movement. Then the test washing procedure was started. The influence of the pre-soaking bath is evident. However, I do not recommend it because the fixers during the pre-soaking bath are of relative high concentration and may damage the developed silver picture.

The results without soaking bath give the recommendation to wash T-Grain type of films 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 equipment between the single washing steps, reduce take-over to a minimum.

2) Use: 5 10 20 40 seconds or turns for washing 1 film in ½ l (or 1 pint) of water (* 2)
5 7 10 14 20 28 40 (56) seconds or turns 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 slightly improved by increasing the times or turns

4) The agitation of the tank is <u>continuously</u> 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)

Sometimes I think the pink dye of Kodak TMX/TMY, Fuji NEOPAN, Ilford Delta and others can be used as a wash-ing status indicator: As long as the film has even the smallest pink hue, washing is not completed and must be con-tinued.

8. Washing Prints

I've been asked frequently what are my recommendations for washing prints?

Here they are:

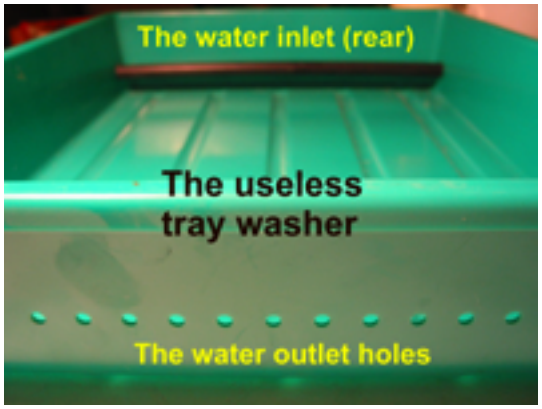
Fibre paper:

I follow the recommendation of AGFA: a bath of 2% Sodium-carbonate (Soda) is used to open the fibres of the paper. Then my prints are washed in a Kaiser tray where the incoming water is guided in a way that the water together with the prints is continuously rotated. After some time (10 - 15 min) I catch a print (18x24cm), hold it on one corner, wait until the continuous water stream at the opposite edge turns to droplets and catch now the water for a potassium permanganate test as depicted in above. In case no colour change is observed a give additional 10 minutes, if colour is changing, I repeat the test every 5 minutes until colour change does not occur. Since I follow this procedure I haven't found any problems with my prints even when they are exposed to daylight for years.

RC-paper:

RC-Paper is too stiff to be washed together with fibre based paper.
A few sheets RC paper obstruct the movement in the tray completely.

So I acquired a special RC paper washer: A usual 30 x 40 cm tray, with a tube at the one end, where several small holes distribute water into the tray, and a row of holes in the tray at the other end as water outlet. After a while I found that the amount a water spilled was large, compared with the amount of water used per surface area of a film. And this amount of water should be even less. because the thickness of a RC paper emulsion is much less than of a film emulsion.



To check for small water supply (2 l/min) the movement and the distribution of the water in the tray I threw two or three Potassium permanganate crystals into the water. I saw that at these low speed the flow was just at the surface of the water in the tray, but at the bottom, where usually the prints are located when washed, practically no water movement occurs. So this tray used as a print washer is badly designed and useless because it fails completely its task: Providing as much fresh water to the print as possible.

As a conclusion today I wash my RC prints completely separate from the fibre prints. When I start washing them, each print is individually rinsed under running tab water, which is running quite slow (app. 0.2 - 0.3 l/min) just to remove the water loaded with hypo. Then the prints are collected in a tray with fresh water and stacked one above the other. For this I use an 18 x 24 cm tray with app. 1 l water in. After a while (app 30s) I start the same procedure, i.e. each sheet is hold individually under slow running fresh water and put into another tray with fresh water. The main principle is to follow what I have found for film washing: **reduce the amount of take over as much as possible** .

Before I transfer the last sheet into the next tray I examine it with the Potassium permanganate test as depicted above. As long as I can observe a colour change I proceed. When the colour change is no longer visible, I give two additional wash batches. It is astonishing how small the number of batches is: for 20 18x24cm prints usually 4-5 batches are sufficient.

After all, my recommendation is to check the efficiency of washing and control it as described. All other rules (apply exact times and temperatures, specific agitation, and what ever ...) do not work reliable.

Contact: Use e-mail: photo+[at_sign]+suessbrich.info

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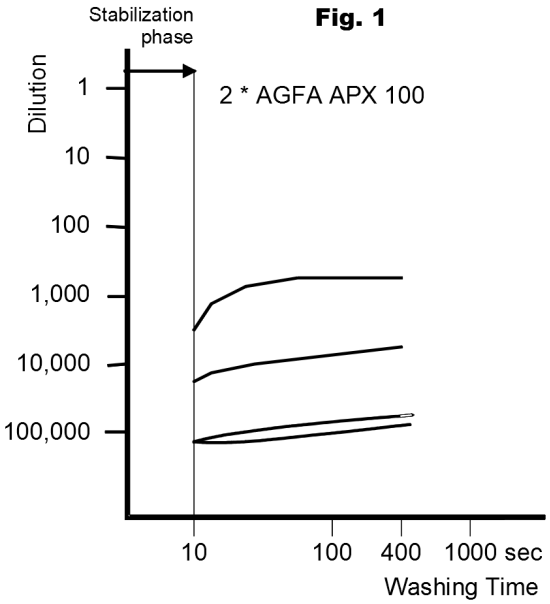
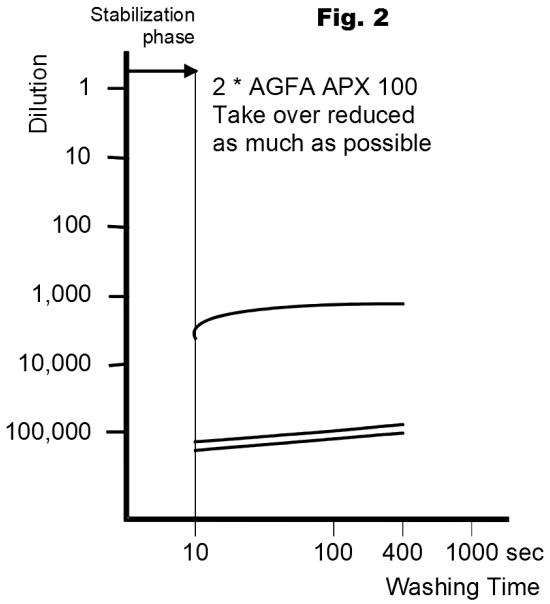
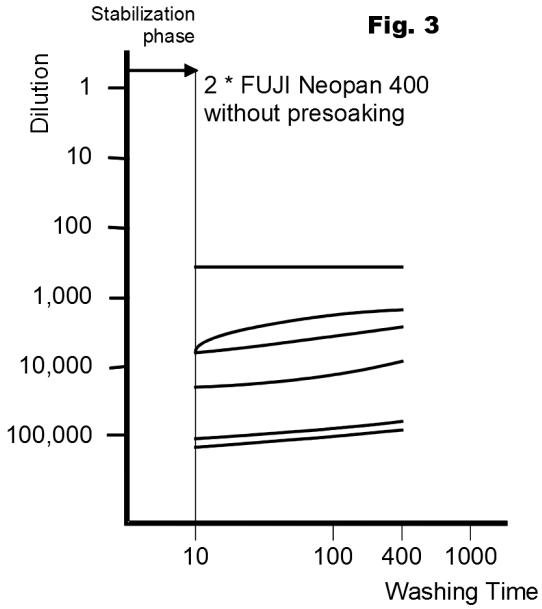
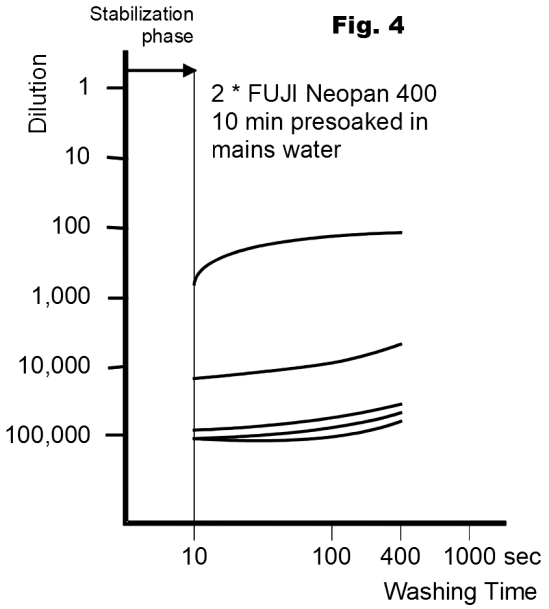
Bauanleitung Chemikalienwaage: http://www.suessbrich.info/foto/duka/waage/waage2.html

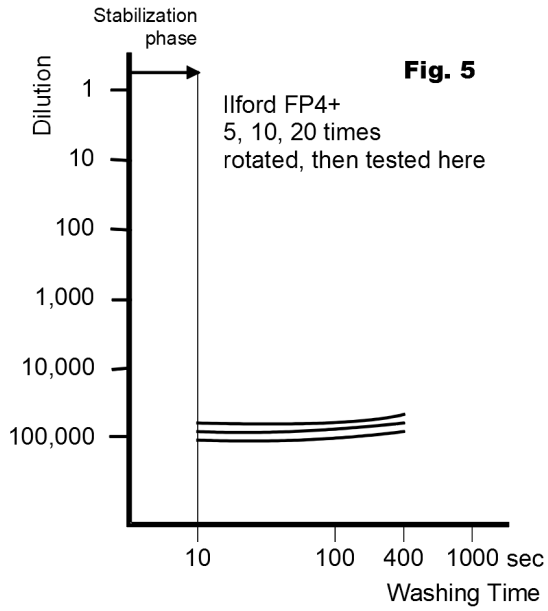
9. Results as diagrams

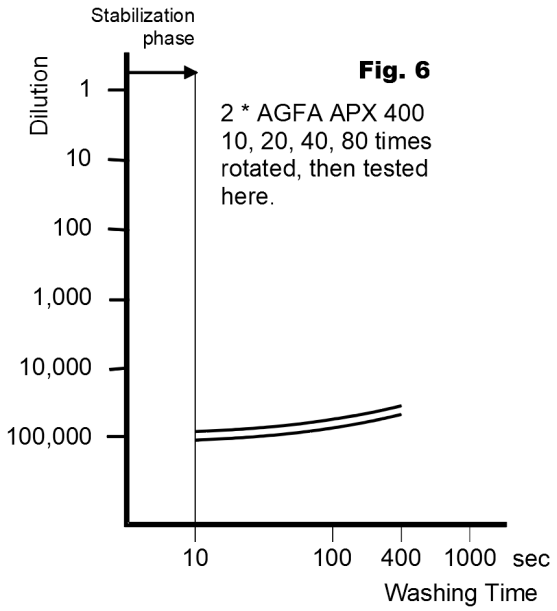












10. Literature:

[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:

[3] M, Torzynski: Comments on the paper “see title above”, October 2004
http://www.largeformatphotography.info/unicolor/com_rolf.txt
Remark: These comments refer to Version 1.0