RAD 409: RADIOGRAPHIC PHOTOGRAPHY AND IMAGING II

THE DEVELOPER

The features of a developer for use in automatic processing are not easy to define. However, it is possible to generalize and it is suggested that students familiarize themselves with sensitometry, where they will find definitions of the terms used in this section.

1. All conventional radiographic emulsions are subject contrast amplifiers when correctly processed. They have an average gradient that is greater than 1, usually between 1.8 and 3.5. The chemistry of the emulsion and the developer are arranged so that these limits are available over a wide range of different conditions. Many people are of the opinion that x-ray developers are 'high contrast'. This is a vague term, as the comparison used to determine 'high' is often not specified.
2. X-ray developers are considered to be high speed, and have the ability to produce an image in approximately 20 seconds, thereby enabling 90 second processing cycle. This speed is mainly due to working at high temperatures, but unfortunately this tends to increase the base + fog level of the film. In an attempt to reduce this, a move to 2 and 3 minute processing cycle would have to be made.
3. A base + fog level of less than 0.2 is desirable, but this is problematic due to the reasons outlined above.
4. A developer must produce a maximum density of between 3.0 and 4.0.
5. A developer must contain additives that allow the emulsion to be transported through high speed, high temperature roller processing.
6. A developer must contain additives that absorb detrimental by-products of the developer action as well as guarding against auto-oxidation and the non-uniform nature of water supplies. This allows solutions to be used for long periods without excessive maintenance or replenishment.
7. Concentrated solutions of the developer must store for long periods in a wide range of conditions without undesirable effects.
8. Chemicals must be as non-hazardous as possible, to conform with the health and safety regulations, and be simple to use.

Functions of a Developer

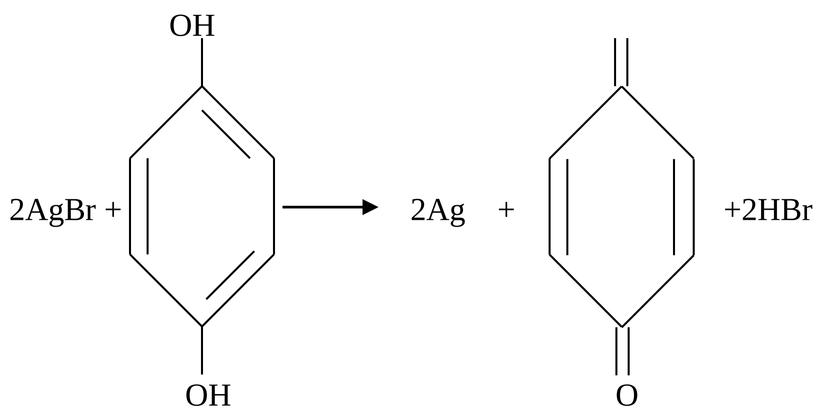
For a chemical to be considered a developer it must possess two main properties namely conversion and selectivity.

1. ***Conversion***

The chemical must be able to precipitate metallic silver from the silver salts of bromide, chloride and iodide or combinations of these salts (figure 2).

The most common silver halide in x-ray emulsions is silver bromide (AgBr). This is normally mixed with a small proportion of silver iodide (AgI) to produce an emulsion with the desired characteristics. The ratio is of the order of 96% AgBr to 4% AgI. Figure 2 shows the reaction that occurs when AgBr is placed in a developing agent. The developer reduces the AgBr to metallic silver and itself becomes oxidized, therefore developers are reducing agents. It can be seen that the desirable reaction has occurred. However, two by-products have also been formed, both of which adversely affect further development and must be combatted by other agents. The developing agent donates electrons to the AgBr crystal during the reduction process.

Development



Reduction ⟶ Oxidation

Silver bromide + Hydroquinone ⟶ Silver + Quinone + Hydrogen bromide

Figure 2: The chemical action of developer on silver bromide (Simplified)

2. ***Selectivity***

This is the ability of a developing agent to differentiate between exposed silver halide and unexposed silver halide, changing only the exposed crystals to metallic silver.

Many chemicals are able to reduce AgBr to metallic silver but few have the property of selectivity. It is an unfortunate fact that even those used as developing agents are not completely selective. In practice, therefore, developers reduce exposed AgBr quicker than unexposed AgBr. This differential ability can be evaluated and is called the selectivity ratio. It is the difference in the rate between the development of exposed and unexposed grains of silver bromide. The ratio is high in selective developers and low in unselective developers. Again, there are additions which may be made to developer solutions to try and improve this ratio. Examination of published data reveals that in general terms, highly selective developers are slow acting whereas unselective developers are fast. In practice, a trade-off exists between speed and selectivity.

3. ***Amplification gain***

It is this feature of the film, latent image and developer system that makes photography, as we know it, a viable proposition. Amplification gain is a measure of the extent to which the developer increases the initial effect of exposure on the silver halide grains. Many experiments have been carried out to assess the numerical value of this, giving results ranging from 10^6 to 10^{12}. However, the most widely accepted value seems to be 10^9.

Ag + development = Amplification gain of 10^9

The photographic process is the only process known at this time which gives gains of this order. A close rival is a heat transfer process (Diazo), having a gain factor of about 10^3. To put this value in perspective, a hi-fi system giving amplification of 10^9 would produce approximately 200, 000 W. An average domestic system gives -about 20-30 W.

Due to the relatively high cost of silver-based recording systems, large amounts of money have been spent trying to find alternatives that approach this enormous gain factor, with little success.

DEVELOPING SOLUTIONS IN THE AUTOMATIC PROCESSOR

Introduction

Automatic processing developers have special features that make them quite different from manual processing solutions. It is important therefore not to infer similar properties, and to realize that, due to advancements in technology, certain substances are given traditional names that are not strictly accurate in chemical definition.

In the following sections, reference will be made to machine tank developer and developer replenishes. These should be considered as separate entities, and care should be taken to state which is being considered.

The major differences between the two are shown in table 2. In general, most have a pH in the range 9.6-10.6.

Constituents

The constituents of developer replenisher and machine tank developer are shown in table 2. It is important to remember that:

Developer replenisher + Starter solution = Machine tank developer.

Table 2: The constituents of developer

	Developer replenisher	Machine tank
1.	Developing agent(s)	
2.	Preservative	
3.	Accelerator	
4.	Restrainer	
5.	Buffer	
6.	Sequestering agent	+ 9. Starter solution
7.	Solvent	
8.	Other additions:	
	Hardening agent	
	Wetting agent	
	Anti-frothant	
	Fungicide	

The need for replenishment

As previously stated, certain by-products of development affect its activity, and as development proceeds the developing agent is used up, its concentration falls, and the developer becomes less active (exhausted). In a practical situation this would necessitate frequent changing of the developer to maintain consistent results, both from the image and the machine / mechanical point of view. In order to obviate this, a certain amount of replenisher is added to the machine tank every time a film is fed into the machine. The replenisher replaces the exhausted developer and maintains the concentration of the other active components at the correct levels. It also maintains the physical quantity of the solution in the tank. The principal factors affecting developer replenishment are:

1. Area of film processed
2. Average density of the film
3. Silver content of the film
4. Maximum density required
5. Thickness of the emulsion
6. Single or duplitised coating
7. Processor work load

8. Amount of aerial oxidation.

Note: Many of the factors listed above are related to each other and decided by the film chemistry. However, knowledge of this data is essential to correctly replenish solutions, even though the manufacturer freely provides this information in the form of recommended replenishment rates.

Replenishment in most processors is usually governed by an average rate per length of film (for developer, the average rate is 40-60 ml for every 35 cm). This means that large films are actually receiving slight under-replenishment, whereas small film sizes receive over-replenishment, the net effect being that over an average working day, replenishment is correct. However, most modern machines are capable of assessing actual film size and therefore replenish according to area. Some advanced processors also calculate average density as well as area, giving even more accurate replenishment. This is achieved by a suitably programmed microprocessor (i.e. computer) which will also monitor all other automatic processor functions.

Starter solution

In theory, once correctly set, replenishment could continue indefinitely; but emulsion flaking and dirt accumulation in the developer tank necessitate regular cleaning.

After draining and cleaning the main tank, fresh developer replenisher is added to fill the tank to the recommended level. If the rollers were replaced and a film developed, it would exhibit all the features shown in figure 3.

The change in the characteristic curve is due to the high activity of replenisher. If films are still processed through this solution, its activity will eventually fall and balance at the correct level. This is due to the increase in bromine ion (Br^-) concentration and depression of the pH value, both of which are caused by development (figure 3). To enable immediate use of the processor, ***starter*** solution is added to the machine tank. ***This is a restrainer solution which adds weak acid and Br^- ions, therefore depressing activity to the required level before films are processed***.

Starter solution is usually supplied separately, a certain quantity being added for every mixed litre of solution in the machine tank. However, some manufacturers supply the developer, which just requires mixing with water, whilst replenisher is available separately.

Key:

1. ↑ Base + fog
2. ↓ Average gradient
3. Apparent ↑ in speed
4. Small ↑ D max

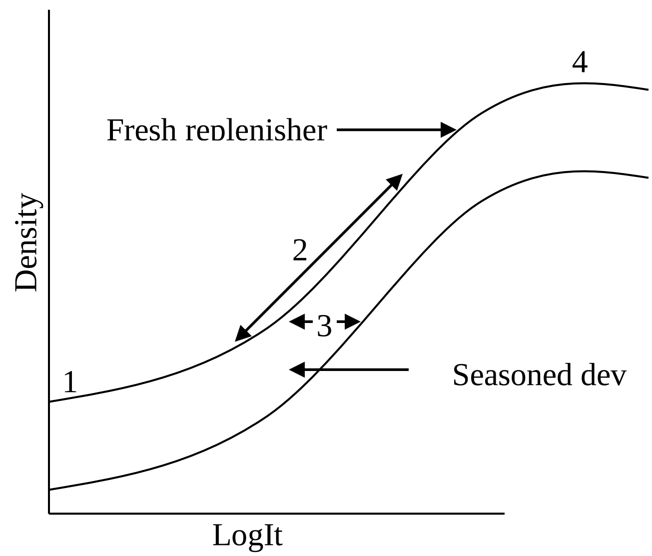


Figure 3: The effect of processing a film in replenisher as compared to "seasoned developer".

Developing agents

There are two principal agents used in automatic processor developers:

- phenidone (P) and
- hydroquinone (Q).

P and Q are not used separately but in combination to produce a phenidone-hydroquinone (PQ)-type developer. Using two agents in combination produces considerable advantages, which will become apparent (see figure 4).

Combining agents in this way enables the manufacturer to control base fog, contrast, speed, etc., as well as making full use of the super additive effect. Correct replenishment removes most of the problems experienced with a PQ combination.

Superadditivity and regeneration

This is another almost unique effect of the photographic process. It is an advantage that arises when using agents in combination. ***Superadditivity may be described as the combined activities of two developing agents in the same solution which is greater than the sum of their separate activities***. This is illustrated in figure 4.

It is still not completely clear how this mechanism functions, although it is believed to be due to:

1. The relative size of the ionized form of the developing agents in the early stages of their effect on the sensitized AgBr crystal.
2. Hydroquinone developers that contain sulphite (of which radiographic developers are a good example) form a first oxidation product of hydroquinone called hydroquinone monosulphonate. In the presence of phenidone this forms a super additive system of great power.
3. Regeneration — in this reaction the first oxidation product of phenidone reacts with hydroquinone to yield ordinary phenidone. This means that the concentration of the most active ingredient is kept high, thus assisting the left shift shown in figure 4.

Table 3: Characteristics of different developing agents

Developing agent	Characteristics
Common name: Phenidone (P) Chemical name: 1-phenyl 3-pyrazolidone Discovered by: Ilford Labs, 1940 Main modern use: General use	1. High speed 2. Low selectivity 3. Low Contrast 4. Only 10-15% compared with Q to give similar activity 5. Activity not so dependent on Br^- concentration 6. Liquid concentrate
Common name: Hydroquinone (Q) Chemical name: Para-dihydroxybenzene Discovered by: Sir W de W Abney, 1880 Main modern use: Graphic arts	1. High contrast 2. Slow speed 3. High selectivity 4. Susceptible to auto-oxidation 5. Activity very dependent on temperature and pH
Phenidone hydroquinone (PQ)	1. High speed 2. Higher contrast than Q 3. Low auto-oxidation rate 4. Not excessively Br^- ion dependent 5. Susceptible to pH variations 6. Temperature dependent 7. Superadditivity 8. Liquid concentrate 9. Less likely to cause dermatitis 10. Long shelf life

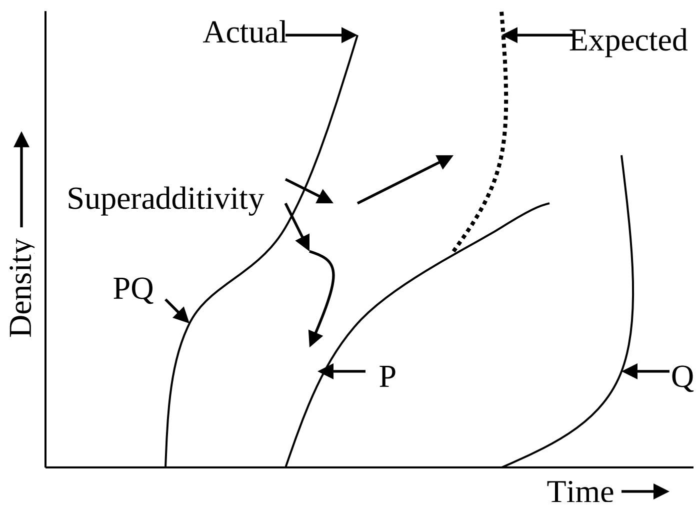


Figure 4: Diagrammatic representation of superadditivity.

Advantages of phenidone-hydroquinone (PQ) developers

PQ developers have certain advantages, so much so that they are the only ones used for radiographic processing. This is because they:

- have a more efficient superadditivity system
- have a greater regeneration effect
- are relatively cheap
- can be made as liquid concentrates
- have a long shelf life
- have a long working life are
- more active at equivalent pH values
- enable the easy control of replenishment
- are not susceptible to bromide ion concentrations
- are less likely to cause contact dermatitis
- are less likely to cause staining on clothes or hands
- do not tend to have an unacceptable odour after prolonged use.

Preservative

Developer activity is reduced by oxidation. This oxidation takes place in two ways:

1. Normal development action (Figure 2)
2. Aerial or auto-oxidation.

Developing agents + Oxygen $\longrightarrow$ Oxidized developing agents + OH^- ions

The problem is aerial oxidation; if not reduced to a minimum, it soon produces coloured insoluble products which depress, and would eventually destroy, the activity of the developer. To reduce this aerial oxidation to an acceptable level, various forms of sulphite can be added to the developer solution.

Preserving Agent

The most common agent used in automatic processing developers is potassium metabisulphite. This is used, especially in liquid concentrate developers, because of its high solubility and greater preserving efficiency compared to other preserving agents (such as sodium sulphite).

Function

The active 'ingredient' is the sulphite ion. This forms sulphonates with early oxidation products. These sulphonates are colourless and inert and have two properties:

- They slow down formation of discoloured products
- They discourage oxidation.

A highly simplified view of how this works is to imagine that the sulphite combines with dissolved oxygen, in the developer solution and at the surface of the developer, to produce the sulphonates in solution. However, in practice it is not as simple as this, as it is not a case of preferential absorption of oxygen by the preserving agent

Potassium metabisulphite is acidic. This is peculiar, as it was stated earlier that developers were alkaline and very pH-dependent. However, this acidity is more than compensated for by the addition of sufficient alkali to counteract its effect.

Aerial oxidation is kept to a minimum in automatic processing by a combination of the following five methods:

1. High preservative level in the developer;
2. Floating lid in the developer replenisher ' tank to reduce the surface area of the developer in contact with the air;
3. Closely fitting rollers, again to reduce surface area in contact with the air;
4. Deep narrow tanks in the processor so that the surface area to volume is kept as small as possible;
5. Totally enclosed replenisher tanks when using automatic chemical mixers.

Accelerator

As established previously, developers are very pH dependent and must be alkaline to work effectively and produce the desired result. Unfortunately, neither hydroquinone nor phenidone are particularly alkaline, and if simply dissolved in water do not produce a working developer. Both agents require an activator to stimulate their developing properties. This activator is called the ***accelerator***; it is alkali, which is added to the developer solution. By varying the amount of accelerator present, the activity of the developer is closely controlled.

Accelerating Agent

Automatic processing developers are considered to be highly active and therefore have a high amount of accelerator present. The agent used is either sodium or potassium hydroxide. Both these agents are strongly alkaline and are particularly useful in high contrast developers containing hydroquinone, as their high solubility makes them ideal for production as liquid concentrates.

Function

The accelerator controls developer activity by assuring correct pH value. It affects contrast and speed so that, in balance with other agents in the developer, the desired image quality is produced.

Restrainer (Anti-foggant)

As stated previously, restrainer is added to replenisher to produce machine tank developer when starting the machine from 'dry'. In this case it is known as starter solution. However, restrainer is also present in normally prepared developer replenisher where it may be called an anti-foggant. It is therefore good practice to consider starter solution as additional restrainer.

Restraining Agent

There are two principal types of restraining agent in use:

• Inorganic restrainers, e.g. potassium bromide;

• Organic restrainers, e.g. benzotriazole.

Developer replenisher uses an organic benzotriazole-type restrainer. This is principally because of two main factors:

1. Organic restrainers appear to be capable of restraining base + fog with little or no effect on film speed. This is not true of inorganic restrainers, which are occasionally deliberately used to control film speed during processing.
2. With high speed developers, the amount of inorganic restrainer required to keep 'fog' within acceptable limits would be such that image staining may occur, as potassium bromide in large quantities is a silver bromide solvent.

Because of these qualities it is common to find organic benzotriazole used in developer replenisher, and potassium bromide 'plus acetic acid used in starter solution.

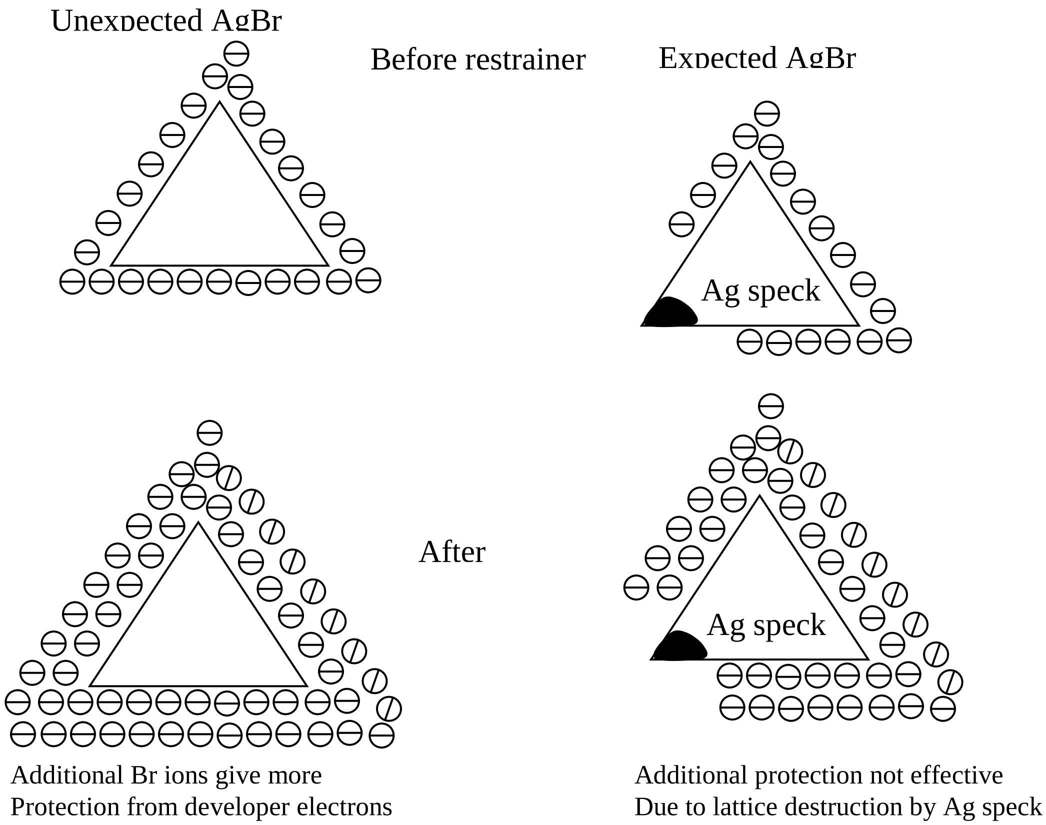


Figure 5: The effect of restrainer on silver bromide crystals.

Function

The function of the restrainer is to improve the selectivity of the developer, ensuring low fog and high image contrast. Its action is to increase the effective bromine ion barrier that exists around silver bromide crystals. The barrier is increased around both exposed and unexposed crystals. However, exposed crystals have some crystal lattice destruction where the protection is useless (figure 5).

The amount of restrainer provided in developer is sufficient to give adequate protection of the crystals when the replenisher is used in the conventional manner. When starter is added (it will be recalled that there is some acetic acid present in this solution, as well as potassium bromide) this depresses the pH of the replenisher, thereby giving the correct activity. The potassium bromide provides the small additional amount of restrainer to give correct selectivity.

Buffer

If figure 2 is studied, it will be noticed that the development process releases bromine ions from the silver bromide complexes within the emulsion and hydrogen ions from the developing agent, due to the donation of electrons from, in this case, the hydroxyl groups in hydroquinone. These combine to form hydrogen bromide, but as this occurs in an aqueous solution it becomes hydrobromic acid. This by-product will depress the pH value of the developer solution and take it away from its ideal level. As previously discussed, this would affect the activity of the developer and if allowed to persist would render the developer useless.

Buffering Agent

A buffer is normally a solution of weak acid and alkali compounds, and in the automatic processor is usually something like boric acid and sodium hydroxide.

Function

A buffer is 'a solution the hydrogen ion concentration of which, and hence its acidity or alkalinity, is practically unchanged by dilution, and which resists a change in pH on the addition of acid or alkali. In simple terms, in the case of developers, it can be considered that this is achieved by the absorption of the hydrogen ions before they combine with the bromine ions. In fact the actual effect of the hydrobromic acid is limited by the equilibrium concentrations that are allowed by the equilibrium equation. This limits the number of free hydrogen and bromine ions available and therefore the amount of acid produced. It is interesting to note at this stage that a buffer helps maintain pH and therefore activity by absorbing harmful by-products of development action, whilst the preservative maintains activity by absorbing products of auto-oxidation.

Sequestering agent

This addition is used to counter the problems that may occur if hard water is used to make up developer solutions. It prevents the precipitation of calcium sludge which would otherwise show up as chalky deposits on the dry film or cause 'scaling of the developer tank. The scaling would be somewhat similar to lime scale found in domestic kettles.

The calcium sludge is caused by a reaction that takes place between the calcium and magnesium salts present in the water supply and the sodium sulphite compounds in the developer. Under normal conditions this does not present a problem as caustic alkali developers (i.e. X-ray developers) do not suffer from calcium precipitation. However, extremes do occur and sufficient sequestering agent is added to cope with even the hardest water supplies.

The Sequestering Agent

Sodium salt of ethylene diamine tetra-acetic acid (EDTA sodium salt)is used.

Function

The function of this agent is to soften hard water supplies, thus preventing precipitation of the calcium and magnesium salts onto the surface of the film. This is achieved by transforming the calcium and magnesium salts into soluble complexes. These complexes are inert to the sulphite components of the solution and, as a result, do not precipitate out.

Solvent

The solvent used in the photographic process is almost always water and normal tap water is more than adequate for use with conventional X-ray developers and has two often quoted advantages, relatively low cost and availability.

There is also an advantage that arises because of a very useful coincidence. It is a fact that all the salts produced in the photographic process, with only one exception, are soluble in water. This removes the need for any intermediate steps to remove deleterious by-products that complicate many other processes. Unfortunately, there is one problem with using available water supplies.

Disadvantage

The water supply is not constant in character.

There are various problems associated with the non-constant nature of domestic and industrial water supplies. Table 4 itemizes the major problem areas.

The most significant practical precaution that can be taken is the use of filtered water in the preparation of solutions. It can be quite alarming to see the amount of foreign material present in a filter that has been in use for even a short time.

Table 4: Problems associated with water supplied

Problem	**Indication**	**Solution**
Hard water	Excessive calcium + magnesium salts, Chalky deposits on film	Sequestering agent: Sufficient included for hardest water supplies
Excessive iron + copper content	Can cause fogging + oxidize developer (usually from copper pipes used to supply water to processor	All specifications for installation of automatic processors now include the use of plastic pipes
Suspended solid matter	Particles of grit, dirt, etc., scratching of film in processor	Use of filtered water supply for mixing chemicals, usually from output side of water panel.
Fluoride and chlorides	Added at water treatment works to control bacteria content	No photographic effects in concentrations usually present.

Other Additions

It is the so-called other additions that principally distinguish developers for automatic processing and those for manual processing. However, commercially available solutions differ very little whether for manual or automatic processing, and as these additional chemicals provide significant improvements to both manual and automatic processing situations, examination of actual formulae will probably reveal little difference between the two. There are four principal other additions:

1. Hardening agent
2. Wetting agent
3. Anfi-frothant
4. Fungicide.

Hardening agent

Probably the worst situation in which to place the photographic emulsion (especially the gelatine used as the suspension agent for the silver bromide) is a warm aqueous alkaline solution. Developer is an excellent example of such a solution. The high temperatures in use can cause excessive swelling and softening of the emulsion, by encouraging water absorption. By controlling this effect the hardener reduces to a minimum the following problems:

- Chances of mechanical damage (e.g. scratching) due to roller transport
- Non-transportation, due to the film being too 'thick' to pass through the rollers
- Sticking of films in the crossover assembly due to the soft gelatine adhering to dry crossover rollers
- Sticking of the film in the fixer and / or wash racks.

Various hardening agents are in common use, e.g. certain aldehydes and sulphates. However, all modern emulsions are pre-hardened as part of the manufacturing process and this greatly assists in the protection of the film in high temperature roller transportation.

Wetting agent

This is added to stimulate uniform development by reducing the surface tension between the developing solution and the film emulsion. It allows easy penetration of the developer into the emulsion, which would otherwise prove difficult (in the short period spent in the developer tank in automatic processing), due to the presence of hardener.

Some developer formulations may not contain this agent, as emulsions do contain a proportion of wetting agent added during manufacture. Most agents are detergent-based derivatives and because of this an additional inclusion is needed to combat problems that may arise due to the agent's basic property of foaming.

Anti-frothant

The automatic processor relies, for replenishment and recirculation, on the use of pumps. These pumps deliver developer under some pressure to the main tank. This pressured delivery, and the action of the rollers, provides a very important feature of the automatic processor, that of constant agitation. However, this raises the problem of foaming and frothing, mainly due to the presence of the wetting agent. Therefore, an anti-foaming agent is included to reduce foaming, which if allowed to occur would contaminate the inside of the processor.

Fungicide

The developer tank of the automatic processor provides ideal conditions for the growth and multiplication of certain strains of fungi. It provides a continuous and uniformly warm moist area within which is a good deal of suitable food, in the form of gelatine which is stripped off the surface of the film during transportation through the rollers. This removal of the emulsion is unfortunate but is taken into account in film and processor design.

Fungi growth can also take place within the various lines transporting fluids in the processor (especially in the wash tank and pipes), causing blockage and incorrect flow. It usually has the appearance of a slightly opaque strand-like slime.

The addition of fungicide usually controls this growth, but in extreme cases it may persist. This necessitates the complete drainage and cleaning of tanks and lines with a powerful fungicide, to remove this growth and any spores that may be present.

The advent of the first generation of cold water processors exacerbated this situation, as the low water throughput (about 1.5 l/min, compared to about 14 l/min in tempered water processors) caused great problems; many processors had to be converted back to mixed water machines. Second generation (so-called total cold water processors) solved this problem by recirculating the water at higher pressures but still using only about 1.5 l/min from the main supply.

Starter Solution

As stated previously, this is added to developer replenisher to produce machine tank developer, when starting the processor from 'dry'. It has two main functions:

1. It depresses the pH of the developer, therefore reducing the activity of the solution.
2. It adds bromine ions to the solution, thereby restraining the action of the developing agents on the unexposed AgBr grains (i.e. increases selectivity).

The amount to add is critical, as under- or over-addition greatly affects the developer's characteristics and therefore affects final image quality. It is usually supplied in a separate bottle, with instructions to add so many millilitres per mixed litre of developer in the machine tank.

Agents

Usually potassium bromide plus acetic acid.

Commercial Preparations of Developer

Developer chemical available from manufacturers is normally supplied as a liquid concentrate to make up so many mixed litres, and sometimes packed containing three parts, A, B and C. Each of the three parts comprises various items of the final developer that, for chemical reasons, need to be kept apart until working developer is required. It is not possible to be specific about the constituents of each part (as exact formulations are normally trade secrets). However, generalizations can be made to illustrate actual solutions. Table 5 is an indication of the contents of developer solutions, if packed as three separate parts.

Never bring part B into direct contact with water; always dilute the solution with part A. This is important, as phenidone is insoluble in water and is kept in solution by the fact that it is mixed with diethylene glycol. Direct mixing with water that does not contain part A will cause the phenidone to precipitate out. Unfortunately this process is irreversible.

Table 5: Developer constituents in commercial preparations

Part	Danger	Content
A	Causes burns	Developing agent (hydroguinone) Preservative (Sulphite) Butter + accelerator (alkali – hydroxide)
B	Causes burns	Developing agent (phenidone) Solvent for phenidone (diethylene glycol) Restrainer (acetic acid + bensotriazole) Restrainer (potassium bromide)
C	Irritant	Hardener (glutaraldehyde) Acetic acid

NB: It is possible to purchase developer which does not contain glutaraldehyde and also where diethylene glycol has been replaced with monopropylene glycol.

Mixing

Developer should be mixed carefully, with due regard to the fact that both parts A and B can cause burns and part C is an irritant. Suitable protective clothing should be worn in the form of gloves, aprons, etc. This is particularly relevant not only for reasons of personal safety, but also because of the health and safety regulations.

Before mixing the replenisher, check the volume remaining in the replenisher tank and ensure that there is "sufficient space to accept the additional solution. Then:

1. Add the volume of water stated in the instructions.
2. Add slowly the whole of parts A, B and C in order, with continuous stirring.
3. Continue stirring for at least 2 minutes to give a uniform mixture.

Stirring is very important, as it prevent the formation of insoluble precipitates. It is also *a* wise precaution to use separate stirring rods for developer and fixer, as even small amounts of contamination may be detrimental

Automatic chemical mixers

The use of automatic chemical mixers is advisable in order to minimize the handling of chemicals by the operator. The chemicals are supplied in bottles with foil tops, and therefore the cap is removed and the bottle is up-ended onto the mixer. The foil top is then pierced allowing the chemicals to enter the machine. A measured quantity of water at the correct temperature is mixed with the chemicals, the force of the water being such that it ensures the even distribution of the chemical throughout the solution.

The advantages of automatic chemical mixers are:

- Reduction in chemical handling
- Even mixing
- Correct temperature of the chemicals
- Reduction in splashing and as the chemicals are mixed in a closed unit
- A reduction in chemical fumes.

It is important that anyone using one of these machines is trained in the correct use of the particular equipment being used, if only to prevent developer being added to the fixer and vice versa.

Low Temperature Chemistry

The normal range of temperatures within which developers operate can conveniently be divided into two sections. These are so-called high and low temperature, and their ranges are only relevant when considering radiographic processing (table 6).

The advent of the demand for low temperature chemistry posed many problems for the designers of chemical systems, as it was still necessary to retain the same total processing cycles (i.e 90 seconds, 2 minutes, etc.) which meant staying with short developing times and also retaining the same image quality.

The main problem was that of processing the film at lower temperatures for the same time, but still producing the same maximum density, contrast, speed and base fog levels. In order to achieve this, three principal alterations have been made in the production of low temperature chemistry. These are:

1. Higher concentration of hydroquinone

2. Different restrainer
3. Higher concentration of preservative.

The increase in the hydroquinone level provides the higher activity needed at lower temperatures to give the required densities. Unfortunately hydroquinone is more susceptible to aerial oxidation and therefore requires a higher concentration of preservative. The higher pH, caused again by the large amount of hydroquinone, also has an adverse effect on the usual restrainers, requiring a change in this agent as well. The advantage of low temperature chemistry is in the much lower running costs.

Table 6: Temperature ranges

Division	Temperature	Normal pH
High temperature Chemistry	31 ^{o}C - 39 ^{o}C	9.6*
Low temperature Chemistry	25 ^{o}C - 33 ^{o}C	10.00*

NB: * Actual value depends on the manufacturer

Points to Always Remember (Summary)

1. For a chemical to be useful as a developer it must possess two main properties: conversion and selectivity. It must be able to convert exposed silver bromide to metallic silver whilst leaving unexposed silver bromide relatively unchanged.
2. The amplification gain of the silver + developer system is of the order of 10^9.
3. Developers for automatic processing have special features that distinguish them from their manual counterparts, and although it is possible to use auto-process developers in a manual situation it is usually not possible to do the reverse. The developer and the replenisher have different properties and pH values, e.g. pH developer 10.00, pH replenisher 10.30. But they are related by the fact that:

   Developer replenisher + starter = machine tank developer

4. Developer replenisher is a very important solution, mainly because it is used to maintain constant solution activity and quantity. There are many factors affecting the degree of replenishment required.
5. Starter solution must be added to replenisher when initially filling the main developer tank. This is because it has two important effects. Firstly, it increases the bromine ion concentration; secondly, it depresses the pH to the correct value, enabling immediate use of the processor to give correct film quality.
6. A typical developer comprises many agents. Table 7 shows the general names of these agents, their probable chemical composition and their functions.
7. Commercial developer preparations may be supplied in three parts. These can be hazardous if handled incorrectly and must be kept apart for complex chemical

reasons (see table 5). Ideally an automatic chemical mixer should be used. If chemicals are mixed manually they should be mixed carefully, with suitable precautions, according to the manufacturer's instructions and always with continuous stirring.

8. 'Low' temperature; chemistry differs from 'high' temperature chemistry in that it has a higher hydroquinone concentration, a different restrainer and a higher preservative concentration.

9. The constituents of developer can easily be remembered by using the mnemonic 'SOAPRADS':

S — Solvent
O — Other additions
A — Alkali buffer
P — Preservative
R — Restrainer
A — Accelerator
D — Developing agents
S — Sequestering agent.

Table 7: Developer constituents: probable composition and function

S/N	General name	Chemical used	Function
1	Developing agents	Phenidone plus hydroquinone	Selective conversion, AgBr (exposed) to metallic silver. Also possesses the feature of superadditivity.
2	Preservative	Potassium metabisulphite	Reduces aerial oxide to a minimum
3	Accelerator	Sodium or potassium hydroxide	Gives the developer its pH value, therefore ensuring correct activity.
4	Restrainer (Anti-foggant)	Organic: benzotriazole, Inorganic: potassium bromide	Improves developer selectivity, therefore reduces fog level.
5	Buffer	Boric acid + sodium hydroxide	Maintains pH within defined limits and therefore activity of developer constant
6	Sequestering agent	EDTA sodium salt	Softens hard water
7	Solvent	Water	Acts as solvent for all chemicals and by-products of developer action.