The film development in the digital twilight

by

Georgy Bagdasarov

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THE MANIFEST OF FILM DEVELOPMENT

The present time is defined by wide range of available techniques a medias. However, such assumed diversity hide the ability to create a disparity. While some media and certain technologies are more preferred due to economical reasons or commercial and political reasons, the other medias and technologies are marginalized and pushed away beyond the general realm of interest of society. Nevertheless, there are a group of media and technique due to their so-called obsoleteness and inefficient are even denied or suppressed to ensure the domination of the main technology's paradigm. Calling the process of monopolization a “progress” has more in common with a brainwashing rather than with evolution or development of skills of mankind. Among the other processes which vanishing nowadays is craft of classical photography and the chemical development.

Actual paradigm of digital “here and now” can be imagined as a theoretical and technical problem which obstructs and limits the arsenal of artist who deals with an analog media. Par example the availability of tools and instruments and chemicals for the moment are very limited by market and law's regulation. The most serious problem in this situation is disappearance of knowledge and experience accumulated through years of history. There are tens or may be hundreds people scattered all around the world who's trying to collect and deposit important knowledges in photochemistry. May be it's a last opportunity to gather experience of the those who were the fathers of inventions and keep it out from oblivion.

Our aim is to sustain or in different cases even to resurrect the knowledges of the past, to try and to experiment so we can share the collected knowledges. Because of exhaustion of the photography market and reduced diversity of photographic techniques it's important to stay on or to reach the autonomy of the work. Time, place or even the

heart opened for the experiment could be among the other factors which can create an obstacle of imagined work. To reach or to hold the highest level of autonomy means to keep freedom of artistic medium and independence of market's temper. So that why we try to learn how to use the grains of misery which market can offer. So that why we try to stay on the way of inventions and construction our own tools and processes which hep us to reach the our aim.

First, we're gonna devote our energy to the basics of photochemical processes of development so we can later focus on alternatives. And the motivation to do it is based on:

1. contemporary situation of the politic of the market (the laws regulation which limit the buying of certain chemical substances due to drug restriction laws etc.) and in general the tendency to substitute analog mediums by digital.

2. We're curious to enter the realm of life sometime uncontrolled process which can give an impact to creative impulse

So we're going to deconstruct the process of photochemical development with a food ingredients, pharmacy products etc and instruments which can be reachable from home.

We would be happy to open the “black box” of process to any one who wants to create in freedom.

THE BASICS OF PHOTOCHEMICAL PROCESS OF DEVELOPMENT

The appearance of photographic image on the sensitive layer of the film is connected with the properties of Silver salts of halogenated acids. (AgBr Bromide of silver, AgCl chloride of silver and AgI iodide of silver). In the year 1667 Robert Bayle opened the darkening of chloride of silver. Although he mistakenly thought that the darkening is caused by air, but this moment is very important for the history of photochemical process. Finally in 1727 germane doctor Johann Heinrich Schulze and in 1757 Italian physicist Giacomo Batista Becaria defined that the darkening is caused by light. Shulze explored the wide range of other silver halides that have similar effect of light sensitivity or photo-sensitivity.

$$2AgX + hv = 2Ag + X_2$$

The big amount of light should act on photo-sensitive layer to get enough darkening which will create an image. This amount of light could be reached either by intensity of the light or by the longer time of exposure. Exactly this technique when the time of exposure can exceed hours was used by Jacques Luis Daguerre from 1831, and it used till nowadays in photographic experiments.

In 1840 William Henry Fox Talbot explored the other method when the time of exposure was reduced and final image appeared due the photochemical development of latent image in gallic acid. Thankfully to that invention the time of exposure was reduced thousands time and the sensitivity of the photographic emulsion was increased.

If after the exposure of the film by amount of light defined by film speed the rest of unexposed silver halides will be removed we will get the so called the latent image. This image is invisible by the human eye but it presents in the photographic emulsion. The

amount of light which exposed the film emulsion is too small so it can darken only small amount of silver grains.

The film processing in the developer can obtain a image with regular density. The chemical reaction of the development reduces silver halide to silver. Such reaction is much more faster around zones where presents the silver grain reduced by light during the exposure. This process can be explained briefly like that: after the exposure the film emulsion already has latent image as small grains of silver, there are more silver's atoms in the zones which were exposed with biggest amount of light than in the less exposed zones. After that when the film is soaked in the film developer the reduction of the silver is happening much more faster in a zones with more grains of silver (the bright part of the image) than in the dark part of the image. It needs more time to develop image or to reduce sliver in the dark parts of the image than in the bright parts.

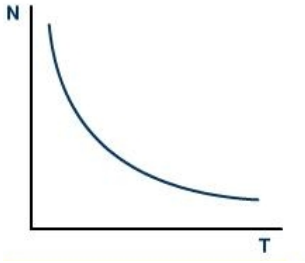


Image 1

The process of reduction of silver in the zones with the highest intensity of exposure are finished first. This process can be illustrated by the graph (Image 1), where N is a intensity of exposure or amount of light which exposed silver halides and T is a time of development needed to reduce silver halide to silver. According to the graph if the process of development is stopped before regulated time the resulted image will be visible but with less details in the shadows and with the less density. So it will be hard to use such image for projection or for the printing.

THE FILM DEVELOPER'S COMPONENTS

Different types of film processes like the processes for black and white negative, reversal positive or the processes for colour development are started with the development of the latent image. So the first step in any of those processes is to obtain black and white image of the negative which consists of reduced silver grains. The next steps of any photochemical processes are based on the quality of such image. In this case the understanding of the film developer's components is the key to get know photochemical process in general.

Developer can consists of the variety of chemical substances which define the result of final image. The developer can have different complex function, like the anti-veil function, gelatin hardening or colour development like in the case of colour process and so on, except the main one which is the reduction of silver halide. So here we will focus on the basic components of the film developer which lead to the reduction of the silver halide to silver which creates the negative image.

Three basic substances of the film developer are the developing agent, the alkali or the base and the preservative or sodium sulfite. First two substances are essential for the process of reduction of silver, the third one keeps the developer from degradation.

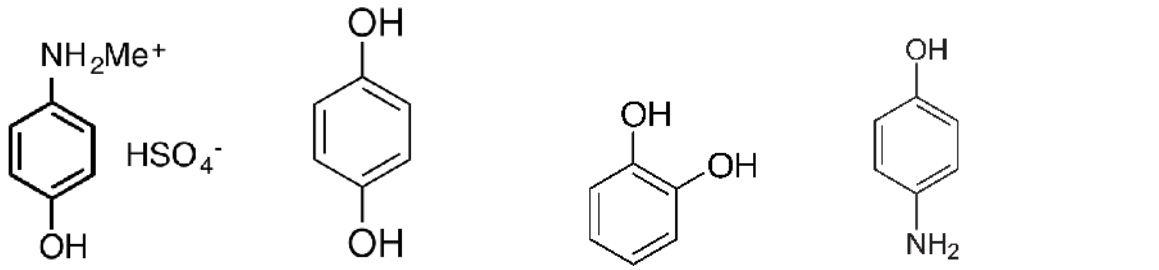
THE DEVELOPING AGENT

Benzene's derivatives

The developing agent is the main substance of the film developer. Such chemical is responsible for the creation of the negative out of latent image. The developing agent is a certain type of active oxidants it means that kind of substances which has possibility to easily donate electrons to silver halide so to “extract” the silver out of one. Because of that if we leave unexposed film which almost has no grains of silver in the developer for very long time we will get complete black film. It means that developer reduced all silver halide in the film emulsion to silver grains. That why in the case of the exposed film it's important to stop the process of development at the right moment to get useful negative.

There are non-organic as well as organic development agents. Among non-organic chemical which can be used as development agent are salt of vanadium, titanium chloride ($TiCl_3$), hydrazine etc. Most of those non-organic chemicals are very toxic and some of them are unstable, that was the reason why such chemical were not broadly used. In this text we won't focus on them because of such limitation as well as because of the their inaccessibility.

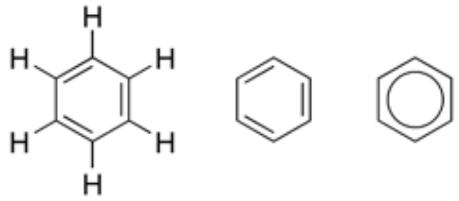
When we check molecular structure of wide used the development agent like a metol, hydroquinone, p-Aminophenol (well known under trade mark as “Rodinal”) or pyrocatechol (image 2) even without deep knowledges in chemistry we can see certain similarity of the structure. Most of them consist of the ring and “branches” of radicals.



Metol *hydroquinon* *pyrocatechol* *P-Aminophenol („Rodinal“)*

Image 2

Such ring is called benzene's ring which means that most of organic development agents are derivatives of benzene C_6H_6 (obr. 2) .



Structure of benzene (for simplicity is showed as hexagon)

Image 3

The position of radicals -OH or NH_2 defines the property to reduce silver halide to silver. Most of those benzene's derivatives have property of development agent with an exception of such derivatives which has radicals at meta position (Image 4). So to get know if the random substance has a property to be the development agent is enough to check the molecular structure of such chemical.

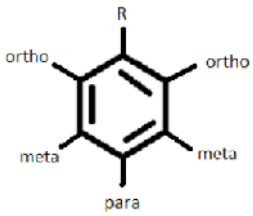


Image 4

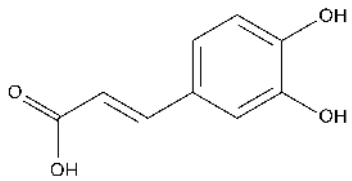
The properties of the development agent defines not only the position of radical but also the type of radical. The substances which can reduce silver halide to silver should have the radicals which can donate a electron[1] to the chemical reaction of reduction.

[1] The properties of radical to be donors of electron as well define their position on benzene ring. Only donors can be

Donors of electron are radicals of hydroxide group -OH and amino group $-NH_2$, -NHR, $-NR_1R_2$[2]

For understanding of that principle we can check the molecular structure of hydroquinone (Image 2). Hydroquinone has two radical of hydroxide group -OH which are placed at para position of benzene ring. Such structure is defines development agent according to was said above. In case of P-Aminophenol, there are radicals of hydroxide group -OH and amino group $-NH_2$, which are placed at para position. Pyrocatechol has two radical of hydroxide group -OH but in that case they are placed at ortho position.

So now we can explore the properties of development agent for example in coffee, which is essential part of Caffenol developers. It mistakenly supposed by so many film lovers that the development agent of coffee is caffeine but in that case caffeic acid is the substance which has the property of development agent.



Caffeic acid

Image 5.

If we check the molecular structure of caffeic acid (Image 5) we'll see that it has the long branch of radicals at the benzene ring plus two radical of hydroxide group -OH which are placed at ortho position. Such condition is enough for the caffeic acid to be the development agent.

Caffeic acid is one of the effective development agents. It can be found in many fruits, plants and so on. Except the coffee it can be found in wine, in beer where it occurs as the products of fermentation. It could be interesting that for example there are bigger concentration of caffeic acid in thyme, peppermint than in coffee. And the winner in the

placed on ortho and para position of benzene ring. (Image 4)

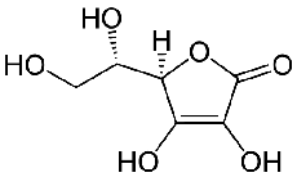
[2] Bijelkhagen, Hans I. Silver-Halide Recording Materials: for Holography and Their Processing. Second Edition, Springer-Verlag Berlin Heidelberg 1995 p.118

competition of concentration of caffeic acid is aronia or chokeberry.

Benzene derivatives which have properties of development agent we can found in the huge amount in the forest and meadows, in the garden and kitchen, in the mushrooms, potatoes, beer etc. We just have with open eyes to look for benzene derivatives with the radicals of hydroxide and amino group on ortho or para positions. One day it can happen that someone in the complicated web of molecular structure will meet benzene ring with electron donors which can release the silver from the bound of halide and will bring from the darkness to the light the photographic image. That someone will extend the list of the unknown photographic developers.

Kendall-Pelz rule

Caffenol-C developer except the coffee include also Vitamin C or ascorbic acid which also has the properties of development agent. Such properties of ascorbic acid are well known since 60s years of XX century. The property of ascorbic acid to reduce silver halide to silver was opened even early. However, when we check the molecular structure of ascorbic acid (image 6) we'll notice that it doesn't look as benzene derivative.



Ascorbic acid

Image 6

In that case there should be explained another rule defines the properties of chemical substance to develop a latent image. That rule is called Kendall-Pelz rule and it spreads on the widest class of developing agents, where benzene derivatives are only one type of such substances. According to Kendall-Pelz rule the molecule of developing agent defined

as:

a-(A=C)n-b[3]

C is carbon atom,

a,b are radicals OH, $-NH_2$, -NHR, $-NR_1R_2$

A is carbon atom C in case of Kendall developing agent

or nitrogen atom N in case of Pelz developing agent.

number **n** define number of C=C (carbon-carbon) or C=N (carbon-nitrogen) double bonds between **a** and **b** radicals.

In the molecule of ascorbic acid occurs such structure OH-(C=C)-OH, which defines that it's developing agent of Kendall type with hydroxide radicals on both sides.

When we examine from that point of view well known developing agents based on benzene derivatives, it will show us that most of them are Kendall type developers with n=3 carbon-carbon double bonds (C=C) represented by benzene ring. We can write well known developing agents in the way showing us such properties according to Kendall-Pelz rule. Par example, hydroqinone will look like a $HO-(C=C)_3-OH$, p-aminophenol $OH-(C=C)_3-NH_2$ (image 2).

There are three non-organic developing agents according to Kendall-Pelz rule which has zero double bonds (n=0) like a peroxide (HO-OH), hydroxylamine ($HO-NH_2$) a hydrazine (NH_2-NH_2). Oxidizing properties of those substances are too strong which often brings to fogging of the emulsion. Because of such properties some of them are used for the “chemical exposure” or fogging in reversible processes or for amplification of the effect of colour development.

[3] Williams, Scot The Chemistry of Developers and the Development Process In The Focal Encyclopedia of Photography 4th edition Taylor&Francis 2007 p.657

ALKALI

Next important component of the developer is base. The process of the development take place in solution with pH greater that 7 (pH>7), which means in the solution with alkalinity. During the development process the silver halides a reduced into silver and halogen acid. Appearance of such acid in the reaction reduce pH of the solution so makes it acidic which slows down or stops the process of the development most rigorously in the places of th emulsion where development occurs. So, if we leave the film to develop in the solution containing just a developing agent, the reduction of silver will slow down or will stop in the more exposed zones than in the less exposed zones due to acidity of the local environment. So after the long period of the development we can obtain non-contrast negative with a weak details.

The amount of alkalinity of the solution influences the speed or energy of the reaction. The development in the strong alkaline solution brings to appearance of hard contrast image. The result of weak alkaline developer is usually less contrast image with balanced highlights and shadows. The other property of strong alkalinity solution is the creation of the big size grains of the image.

The selection of the base is defined by:

1) the acidity of the developing agent (to start the development process the solution should have pH>7)

2) the desired gradation or gamma of the resulted negative (bigger or lesser contrast of the image, the size of the grains)

According to alkalinity of the solution the bases are classified on three types: strong, medium and weak bases.

Among the weak bases we can find sodium bicarbonate $NaHCO_3$ or baking soda,

borax $Na_2B_4O_7$, sodium sulfite Na_2SO_3.

Medium alkalinity bases are alkali carbonates like sodium carbonate Na_2CO_3 or washing soda or potassium carbonate K_2CO_3.

Strong alkali are sodium hydroxide NaOH and potassium hydroxide KOH.

SODIUM SULFITE

The other important component of the film developer is Sodium sulfite Na_2SO_3. The developing agent is a strong oxidant which means that one reacts with oxygen and decompose into inactive for development process' chemicals. It's very important to protect developing agent from oxidation before the reaction of development. One of the function of sodium sulfite is to protect developing agent from oxidation because of the certain amount of oxygen are dissolved in the water[4]. That why sometime sodium sulfite is called “oxygen scavenger”. Sodium sulfite reacts with the oxygen in the water more actively than developing agent. So such property of the sodium sulfite is the wide spread in the food industry where sodium sulfite is used as the preservative.

Another important function of sodium sulfite is to react with the products of the reaction of development. During such reaction developing agent due to reduction of silver halide is decomposed on inactive substances, which has no developing properties. It says that developer is exhausting. Sodium sulfite can react with those by-products of the reaction and recover them back into the substances with the properties of the developing agent. Most by-products of the developing agents of Kendall's type has possibility to be regenerated by sodium sulfite.

The next property of sodium sulfite is to dissolve silver halides, so it works as a weak fixer. This is mostly used in the development process to protect negative image from creation of big size grains. Such property appears when the concentration of sodium sulfite is more than 5% of entire solution.

The property of sodium sulfite as a weak alkali is used in in some fine grain developers. So some fine grain developers consists only of developing agent and sodium sulfite. In such cases sodium sulfite has several functions. It protects developing agent from oxidizing by oxygen, regenerates developing agent during the development process,

[4] From 0.14 to 0.5 g of sodium sulfite is enough to de-oxidize water

works as a weak alkali to obtain less contrast negative and as a weak fixer protects from creation of big grains. Nevertheless such developers can process only in the case of non-acidic developing agent with a strong potential of Redox.

The quantity of sodium sulfite in the developer is between 3 and 125 g per litre of entire solution. The concentration of the sodium sulfite is defined by several factors:

highest alkalinity of the solution

lesser amount of developing agent

highest temperature of the development

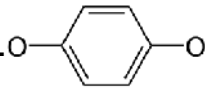
longer expiration of solution

If the concentration of sodium sulfite is too high it can dissolve silver halides due to weak fixer's properties of that substance.

THE CHEMICAL PROCESSES OF THE DEVELOPMENT

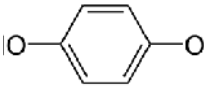
So now, when we know the basic components of the developer, we can explain the chemical reaction of the development. In our case the developer will consist of hydroquinone as a developing agent, sodium hydroxide as an alkali and sodium sulfite

+ 2AgBr = 2Ag +



2HBr +

In the beginning of the reaction hydroquinone  as a developing agent reduces Silver bromide AgBr to silver Ag and Hydrobromic acid.

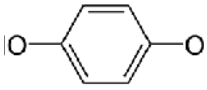
Hydroquinone is reduced to benzoquinone 

One of the final products of the reaction Hydrobromic acid decrease pH and creates acidic solution. To continue the reaction the obtained acid has to neutralize by alkali.

$2HBr + 2NaOH = 2NaBr + H_2O$

Sodium hydroxide is a strong alkali so it neutralize Hydrobromic acid to water and inactive salt of sodium. After that equation the reaction keep going.

Benzoquinone as another by-product of the first reaction has benzene ring, however it doesn't have the properties of the developing agent. Benzoquinone has -O radicals in the right position but as we know such radicals has no effect according to Kendall-Pelz rule. In the next phase benzoqinone has function to regenerate to hydroquinone in the reaction with dissolved in the water H_2O sodium sulfite Na_2SO_3.



$+ Na_2SO_3 + H_2O = Na_2SO_4 +$

Sodium sulfite reduces inefficient benzoquinone back to hydroquinone and oxidizes to sodium sulfate Na_2SO_4**.** Regenerated hydroquinone can again join the following

reaction of reduction of silver halide.

There are more complexes reaction are happening during the development of the film in the real situation. Par example Sodium bromide NaBr as a alkaline halide has possibility to react with the silver grains so it can slow down the entire reaction a bit. sodium sulfite can exhaust faster in the reaction with benzoquinone in the case of high alkalinity of the solution and as a result of such reaction produces others inactive substances. That's the reason why the high alkalinity developers have to contain bigger amount of sodium sulfite.

The presence of two strong oxidants like a sodium sulfite and developing agent in the same solution increases activeness of their oxidation. The stronger oxidant react with oxygen intensively in the presence of other oxidant than alone. In most cases sodium sulfite behaves as a stronger oxidant.

However, there are some developing agents which are more active oxidizers than sodium sulfite. Oxidation properties of such developing agents are increasing in the presence of sodium sulfite which can lead to the degradation of the developer much faster than without sodium sulfite.

The properties of the components and their interaction are very important for the creating the final recipe of the developer. Such knowledges can help to understand the photochemical processes of film development and to control the behaviour of the film developer.

THE PREPARATION OF THE DEVELOPER

The water is the basic substance not only for the life but also for the preparation of the developer. There are so-called “dry” developers on the waterless basis which exist as a powder or as a creme. The water is the optimal substance for the exploration of the developing properties of different ingredients.

Water has several functions in the developer. First, water can swell gelatin where are

placed silver halides and by this function water “opens up” gelatin for the fusion of active chemicals from the developer. Second, water is optimal solvent for the developer's ingredients as well as for the products of the reaction, but it doesn't dissolve the silver which stays in the photographic emulsion. While searching for the developing agent it's very important to pay attention on the amount of solubility of such developing agent in the water. Third, water transports dissolved active substances to the silver halides and drains the products of the reaction out of the emulsion.

The ideal solvent is distiled water due to absence of the dissolved substances which can have effect on the development's process. So distiled water is widely used to research the developers in the chemical labs, but in our case the boiled and filtered tap water is enough.

The procedure of preparation of the developer is always the same. In the beginning the developing agent has to be dissolved in the water with small amount of sodium sulfite. It was already mentioned that 0.14 to 0.5g of sodium sulfite is sufficient to get rid off the oxygen in the water. Then the rest of sodium sulfite is added to the water. Followed addition of a base can activate oxidant's properties of the solution so it's necessary to protect developing agent from oxidation by atmospheric oxygen. The base is dissolved as the last ingredient and the final solution reaches pH level recommended by the properties of the developer.

For exploring the different kind of developing agents, or researching Redox potential of developing agent, is sufficient to prepare developer which consist of developing agent and medium alkali. The base with medium alkalinity which is easy to get is sodium carbonate.

Sodium carbonate can be found for example in the washing soda where it appears as a decahydrate of sodium carbonate. However we have to think of that amount of sodium carbonate in decahydrate of sodium carbonate is lesser than in pure sodium carbonate. In the case of using washing soda we always add 2.7 times more of washing soda than prescriptive quantity of pure sodium carbonate in the recipe.

The other source of sodium carbonate is baking soda. The baking soda has to be heated 10-15min in the oven or on the pan. Cation, the reaction of transformation of baking soda to sodium carbonate is very active and produces small geyser like fountains in the powder, so it's important to close the lid of the container and from time to time control. When the micro-eruptions stop it means that baking soda is transformed to sodium carbonate. The amount of the resulted sodium carbonate is always lesser than the amount of baking soda in the beginning of the reaction. To obtain 1 part of sodium carbonate is necessary to use 1.6 part of baking soda.

The source of the developing agent could be plants, food or medicaments. The starting point in the mining of the developing agent is to check chemical composition of researched object. It's important to find out if researched object contains substance which has Redox potential and according to Kendall-Pelz rule looks like developing agent. To get know that is sufficient to check molecular structure of encountered substance in the encyclopedia. Then it's important to check the concentration of such substance in the researched product. And the last step is find out in the description of the substance the solubility in the water or in alcohol.

While finding out the amount of effective substance in the certain plant it's good to

know if the other plants contains the same substance. It happens often that the same substance occurs in the different plants, some of them have larger concentration than the other. For example caffeic acid can be found in the significant bigger concentration in the thyme or mint than in coffee itself.

There are several ways how to extract developing agent out of the plant. If the substance is soluble in the water and doesn't decompose when heated up to 103°C (217°F) then we'll have to prepare by boiling or cooking in the water during several minutes the hot infusion of the plant. If the substance is soluble in the water but it's not heat resistive then the developing agent can be extracted during 20hrs up to 1 week by cold infusion in the water.

In the case when researched substance is not or bad soluble in the water the alcohol solution has to be used as a solvent. Due to flammability of the alcohol the extraction of the developing agent from the plant has to be made without heating. There is a possibility to combine both water and alcohol for cold extraction. Also it's possible to use cheap alcohol beverages (like a cheap vodka, schnapps or some other similar beverages) when the one doesn't contain colour, aroma or other additives.

For the preparation of the developer it's necessary to dilute the extraction with the water when developing agent is extracted by pure alcohol. The developing process can't occur in the pure alcohol solution cause alcohol doesn't swell up gelatin and most bases are almost insoluble in the pure alcohol.

As it was mentioned before, to activate the developing agent it's important to make alkaline solution. In the case of the developing agents with lesser Redox potential it's necessary to obtain alkalinity of the solution pH around 9-10 with the help of medium alkaline base. Very useful tool for researching of the developing agent is a simple pH-meter for the pool which easy to get. This simple tool has sufficient definition to measure pH of the entire solution in home situation. If there is no way to measure the pH of the

solution we can add 40-70g[5] of sodium carbonate or 100-200g of washing soda per litre of the solution which is enough for the reaction to start.

[5] Barchet, Hans-Martin Chemie photographischer Prozesse, Akademie-Verlag, Berlin, 1965 s.120

THE SPEED OF THE REACTION AND THE SUPERADDITIVITY EFFECT

The speed of the chemical reaction of the photographic development is defined by several factors. For example the ISO speed of the film and type of the film emulsion, temperature of the development, the activity of agitation of the development all these factor can lead us to certain results. So the time of the development could be changed by such factors.

In the case of home brewed developer determination of the time of the development of the researched developing agent can be made by several experiments. The required temperature for every experiment can be 20°C/ 68°F and should be constant for every experiment. The same is agitation of the developer. First, we have to find out the activity of the developing agent and to confirm the theoretical hypothesis of the researched developing agent. We have to soak the film completely exposed by light into the prepared developer and wait until it will get visible dark. If the there is a darkening of the film occurs it means that the researched substance has the properties of the developing agent. The time of the darkening of the soaked film has to be measured. The entire operation can be made under not direct light which helps to control the result of the experiment.

To obtain the approximate time of the development $\mathbf{t_n}$ we have to multiply by 7 the resulted time of the darkening of the film from the first experiment. The next experiment can help to come closer to the right development time. We have to expose film in the camera using the values of the light meter for the right ISO speed of the film. To do that we have to shot a standard grey test table or the scenery with full range of shadows and highlights. Better to make several shots of the same object so to get the 15cm of the film strip. In the completely darkness then we have to make two cuts of the film to have three strips which are still slightly joined together. Then the film has to be developed in the darkness.

When the time of the development will reach the 60% of approximate time of the development $\mathbf{t_n}$ from the first experiment one strip of the film has to be separated and immediately soaked in the fixer. We have to continue the development until it will reach approximate time of the development $\mathbf{t_n}$ then separate the second strip and again immediately soak in the fixer. Then repeat the same operation with the rest of the film with the time of the development will reach 150% of approximate time of the development $\mathbf{t_n}$.

When the film is fixed we have to compare three resulted strips to check which one has the better density and gradation of the negative. The proper time of the development can be interpolated from the results of that experiment.

$\mathbf{t_1 = 0.6 * t_n}$

$\mathbf{t_2 = t_n}$

$\mathbf{t_3 = 1.5 * t_n}$

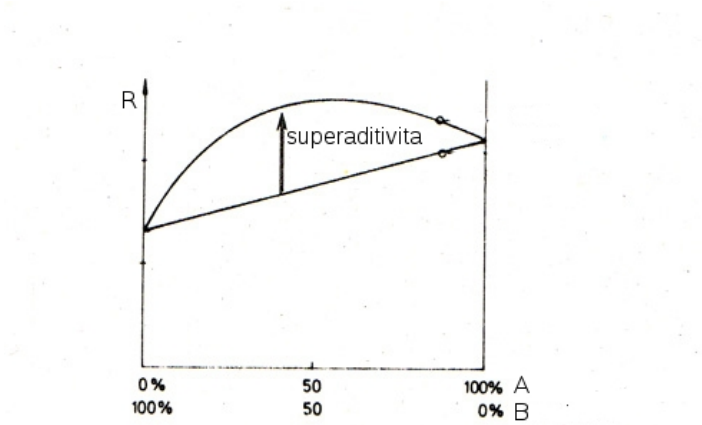
t1, t2, t3 are times for the development of three strips, t_n is the time of the development from the first experiment

During the experimenting with the developers based on the natural developing agents can occur that the reaction is too slow and it leads to longer times of the development sometime even longer than 30min. It's related to the weak Redox potential of the developing agent. Addition of the second developing agent can speed up the reaction, will shorter the time of the development and will increase the effectiveness of the developer. In some cases, developers without preservatives can degrade within 30-40min, so it will exhaust earlier than can develop film.

One of the wide used ingredient which is added to the natural developers is ascorbic acid (Vitamin C). 6 to 15g of Vitamin C per litre of the developer can make the time of the development short enough sometime even half shorter than with one developing agent.

There are many commercial developers which use two developing agents instead of

one like a metol-hydroquinone MQ-developers or phenidone-hydroquinone PQ-developers. The increased effectiveness of such developers is based on the effect of superadditivity. Each of the developing agents has own limited effectiveness and can develop the film during certain time defined by Redox potential of the developing agents. When both of those substances are mixed together the resulted activity of the solution is higher than theirs Redox potentials.(image 7).



Superadditivity. R – speed of the reaction, A – the amount of the first developing agent, B – the amount of the second developing agent

Image 7

The superadditivity effect is defined by the type of the developing agent according to Kendall-Pelz rule. The superadditivity occurs when the first substance is Kendall type developing agent with hydroxide radicals -OH and the second substance is both Kendal or Pelz type developing agent but it has contain both hydroxide -OH and amino $-NH_2$, -NHR or $-NR_1R_2$ radicals. The important regulation is that hydroxide radical should occur in both developing agents[6].

During the process of the development the developing agent with amino radical reacts first and the second developing agent of Kendall type regenerates the first oxidized substance by hydroxide radicals.

The supperadditivity results not only a speed up of the process but also helps to limit the fast exhausting of the developer due to mutual regeneration.

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[6] Mason, Leslie Frederick Alfred Photographic Processing Chemistry, Focal Press, London, 1975 s.29 s.103

PARODINAL

The other way of the research of the developing properties of the substances encountered in the nature is the synthesis of the developing agent out of existing products. The investigation in that area is characterized by detailed analysis of the researched substance and deep knowledges in the chemistry.

One of the example of such way of investigation could be the preparation of the developer similar to the one well known under the trade name Rodinal. The developing agent of Rodinal is p-aminophenol can be obtained by synthesis of analgetic acetaminophen which basic substance of paracetamol, paralen etc.

The comparison of the molecular structure of p-aminophenol (left) and acetaminophen (right)

Image 8

It is well known that p-aminophenol (the dev.agent of Rodinal) is commonly used in pharmaceutical industry synthesize acetaminophen for production of paracetamol[7]. There is possibility to make a reverse reaction to reduce acetaminophen to p-aminophenol in the strong alkalinity. To synthesize p-aminophenol it's necessary to use strong alkaline base like sodium hydroxide.

The crystals of sodium hydroxide is commonly used as home chemical to clear the drain. Sodium hydroxide is a strong alkali and can burn the skin, so it's important to caution manipulate with it and to use rubber gloves. The big quantity of paracetamol is toxic and can evoke liver dysfunction which is the other reason to use rubber gloves during

[7] Viz Ellis, Frank Paracetamol: a curriculum resource. Cambridge: Royal Society of Chemistry. 2002 ISBN 0-85404-375-6. p.12

that preparation. More information about toxicity of paracetamol can be obtained in the pharmacy.

To prepare developer out of paracetamol we need:

15g of acetaminophen (30 pills of paracetamol or similar product)

250 ml of water

50g of sodium sulfite

20g of sodium hydroxide

The best source of acetaminophen is a paracetamol's capsules. The capsule of paracetamol has to be opened with care so we can use the powder which is inside. The easiest way to dissolve that powder in the hot water because acetaminophen is hardly soluble in the water. When the powder is completely dissolved let's cool the water to the room temperature and then will add sodium sulfite. The sodium sulfite protects the oxidation of p-aminophenol which will be obtained in the following reaction. Slowly add sodium hydroxide (lye) while stirring the solution until entire amount of lye is dissolved. The dissolving reaction of sodium hydroxide should handled with care because such reaction is very active and can heat the solution. When the solution is prepared, pour one in the bottle with the dark glass, tightly close and leave in the darkness for the next 3-7 days. It's very important to keep the bottle without air because oxygen i the air can contaminate the developer.

The synthesis of p-aminophenol is very slow. During those days the solution will change the colour from yellow to brownish and purple. A week later prepared developer will have the properties of Rodinal.

In the case that there is no possibility to get capsules of paracetamol, the pills can be used as well. Grind the pills to the powder and then dissolve in the hot water. After the powder is dissolved filter the solution through the fabric to eliminate the precipitated starch and other ingredients of the pills. The follow the same instruction as to preparation and

synthesis of p-aminophenol.

Because acetaminophen is better soluble in the alcohol sometime it's easy to use one to dissolve the powder made out of pills. Then filter the solution and leave it outside under the direct light of the sun to evaporate alcohol. After evaporation what will stay in the glass is the pinkish crystals of pure acetaminophen which could be used as pure powder from the capsules.

That developer has the shelf life of 3 months so it makes sense to prepare the bigger amount of the developer for the future uses. The time of the development and dilution are exactly the same as in the Rodinal's case. That's the reason why such developer is called Parodinal.

COOKBOOK OF DEVELOPERS

Here we introduce some examples of preparation of organic and plant developers. The approximately quantity of ingredients response to the development of the film under 20°C/ 68°F. The concentration can be adapted to the needs and aims of every user. The unit which is used in the recipes is a teaspoon (tsp)

Coffee developer

Dissolve in the 1 litre of water in the following order:

Instant coffee 7-12 tsp

Sodium carbonate 5-2.5 tsp (or washing soda 13-7 tsp)

Vitamin C 1-3 tsp

Time of development is 15min, temperature is 20°C/ 68°F

Potato developer

Cook 6-7 medium sized potatoes in 1 litre of water. Potatoes can be used latter in the dinner. Add 7tsp of washing soda to the cooled water. Time of development: 30min at temperature 20°C/ 68°F. To speed up the process add 2 tsp of Vitamin C. In that case time of development is 10-12min at temperature 20°C/ 68°F.

Sumac tree (Rhus typhina) developer

Prepare the extraction of sumac tree in the 250ml water-alcohol solvent (the ratio of alcohol to water is 1:5) and leave for the night. In the next bottle dissolve 6-7 tsp of washing soda. When the extract of sumac tree is ready filter it through coffee filter and then mix both solution. Time of development: 12-15 min at temperature 20°C/ 68°F.

Conifer bark developer

Grind the bark of the tree and boil with the water in the ratio 1:2. Filter cooled solution through coffee filter and add 11 tsp of washing soda plus 1 tsp of Vitamin C. Time of development: 8-11 min at temperature 20°C/ 68°F.

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