

**A yellow/green toner
for gelatin-based black and white silver prints
based on vanadium pentoxide**

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Introduction

Toning is a technique, used in black and white photography, to impart additional effect on an image, by adding color as one of the control parameters, besides lighting, contrast, graininess and composition.

Many recipes exist for toning black and white silver gelatin prints. The most well known ones are summarized here:

- sepia/brown by means of sulfide toning;
- deep blue by means of gold toning;
- brighter blue by means of iron / ferricyanide toning;
- red/brown by means of copper / ferricyanide toning;
- red/salmon by means of gold toning after sulfide toning;
- deep brown/purple by selenium toning.

This list encompasses the full spectrum between red hues and blue hues, together with brown hues. Effects, which are lacking are colors in the yellow/green range. There exist recipes for green toning, based on vanadium chloride. Is it really vanadium chloride what is meant? Whatever compound is meant, it is hard to obtain, does not keep well, and the resulting toner is not easily used (for an example of such a recipe see *The Darkroom Cookbook*, second edition, recipe 154).

In this article a toner is suggested, based on common chemicals, which are easy to obtain and inexpensive, and which allows a large range of colors to be generated in the full scale of bright lemon yellow to blue and all kinds of greens in between. A variation on this toner is presented, which extends the possible color range by inclusion of brown/sepia tones in the total mix of colors, which can be generated.

The first part of this article is about the preparation and use of the toner, the second part is about the chemistry of the toner and is an attempt to explain how this toner works. For people not interested in the chemistry, the second part of this article simply can be skipped. That information is not required for using the toner.

Starting point for all toners, presented in this article

All toners, presented in this article, assume a well fixed and rinsed silver gelatin print as starting point. The print may have been dried previously, but this is not required. It is wise, however, to make the print wet and have it soaked with water, before immersing it in the toner bath. The best results are obtained with fibre paper. RC paper tones OK, but dense parts obtain a certain metallic look, due to the relatively high acidity of the toner.

Required chemicals for all toners in this article

basic toner:	sodium hydroxide
basic toner:	dilute sulphuric acid (or hydrochloric acid), approximately 10% by weight
basic toner:	vanadium pentoxide
basic toner:	potassium ferricyanide
basic toner:	sodium thiosulfate (non-alkaline commercial fixer concentrate also is OK)
green extension:	ferric ammonium citrate
sepia extension:	sodium sulfide
sepia extension:	white vinegar (this is dilute acetic acid, approximately 4% by weight)

All chemicals from this list may be flushed down the drain when they have been used, except for the vanadium compounds. Vanadium compounds are not good for the environment and must be brought to an appropriate waste processing facility. The toner solution hence must be kept apart when it is exhausted.

Safety

Wear gloves when working with the toner solutions and do not immerse fingers in the liquids. Some people may show allergic reactions, when they are exposed to transition metal salts.

Potassium ferricyanide, sodium thiosulfate, vinegar and ferric ammonium citrate do not impose special risks. These are relatively non-toxic. Of course, the chemicals should not be ingested and it is important not to inhale dust and avoid getting these compounds in your eyes.

Sodium hydroxide is caustic. It attacks skin. If one comes in contact with this, immediately rinse with a lot of water until the greasy feeling has disappeared. Sodium hydroxide produces heat, when mixed with water and if it is mixed with a small volume of water, it may become hot.

Sodium sulfide also is caustic and besides this, it is poisonous, especially when it comes in contact with acids, because of the release of poisonous hydrogen sulfide. It has a very bad smell.

Vanadium pentoxide is toxic. The compound often is sold as a free flowing powder, which is not hygroscopic or sticky in any way, so dust from it can easily be formed. Be careful, be sure not to inhale any dust, when working with the dry powder. Use a good ventilation.

Dilute sulphuric acid is corrosive and attacks many things, including cloths and your skin. If this is spilled, immediately rinse with a lot of water, or even better, with sodium bicarbonate and water. Concentrated sulphuric acid is EXTREMELY corrosive. It eats everything, except glass and certain plastics, within seconds. Never get this on your skin! You will probably not have the time to rinse with water, before it really hurts you. When it comes in contact with cloths or paper, a hole is eaten in it within seconds. Besides this, concentrated sulphuric acid reacts with water, producing a lot of heat, sufficient to make the water boil and splatter. NEVER add water to the acid, always add acid to a large amount of water, while stirring continuously.

Hydrochloric acid is equally corrosive as dilute sulphuric acid of similar concentration. When the concentration of hydrochloric acid exceeds approximately 25% then it emits corrosive fumes, which should not be inhaled. Dilution of hydrochloric acid is best done by adding acid to water.

Concentrated (glacial) acetic acid is corrosive and has a very pungent odour. If this comes in contact with the skin, immediately rinse with a lot of water. Avoid inhaling of the pungent vapour. Glacial acetic acid must not be regarded as just a stronger vinegar. Handle this stuff with respect.

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Preparation and use of the toner

The toner uses a basic preparation, which is used as a component for all color variations. The basic preparation is mixed with other compounds in order to make a complete toner. Preparation of the basic preparation involves using fairly common chemicals, but requires more advanced chemical handling, performing some chemical reactions. Once the basic preparation is available, no special handling, other than simple mixing of chemicals is needed anymore.

The basic preparation of the toner, presented here, also uses a vanadium compound, but the compound, needed here, is easy to obtain and is cheap. The compound in question is vanadium pentoxide. This is used in ceramics for coloring purposes. It can be purchased at many ceramics supply houses for less than \$10 per 100 gram, enough for toning hundreds of 8 x 10" prints.

Some websites for obtaining vanadium pentoxide:

- www.standardceramic.com (USA, many places)
- www.creavisie.com (The Netherlands, ships to european destinations)
- <http://www.keramikos.nl> (The Netherlands)

Vanadium pentoxide keeps indefinitely, is not moisture/air sensitive, nor corrosive, but it is toxic.

The other chemicals, used for the toner, are fairly common in photography and can be obtained from a good supplier. A few suppliers are:

- www.artcraftchemicals.com (USA, ships many items worldwide)
- www.colba.net/~fotochem (Canada, ships many items worldwide)
- www.vanpuffelen.nl (The Netherlands, ships to european destinations)
- www.photoformulary.com (USA, carries dilute sulphuric acid, but only ships this in USA)

Sulphuric acid, as needed for the basic preparation, sometimes can be obtained locally, but often at higher concentration than 10%. Possible sources are drugstores and hardware stores.

Sulphuric acid can be substituted by hydrochloric acid of approximately the same concentration. In the Netherlands this can be bought at a convenient 10% concentration at many places. If 30% acid is used, then simply mix one part of acid with two parts of water, adding acid to the water.

The basic preparation

The following compounds are needed for the basic preparation (amounts are rough guidelines):

- 1 gram of vanadium pentoxide
- 3 grams of sodium hydroxide
- 125 ml of dilute (appr. 10%) sulphuric acid or 100 ml of 10% hydrochloric acid

Any multiple of all amounts given here can be deployed also, the process of preparation scales up without any problem. The toner is very forgiving for deviation from the amounts, mentioned here.

Add the sodium hydroxide to 75 ml of water and let all of the solid dissolve. Do not use less water or more sodium hydroxide. If the amount of sodium hydroxide, relative to the amount of water, is too high, then the liquid may become excessively hot. The ratio, given here, however is totally safe. The solution of sodium hydroxide only becomes a little warmer.

Add the vanadium pentoxide to the solution of sodium hydroxide and heat the liquid carefully, until the solid has dissolved (almost) completely. The liquid should be stirred now and then, while it is heated. If very pure vanadium pentoxide is used, then the liquid can be made completely clear and colorless. The vanadium pentoxide from ceramics supply stores, however, may contain a considerable amount of ammonium metavanadate and if this is the case, then a greyish flocculent precipitate may remain, which does only dissolve with great difficulty. This is of no concern and there is no need to dissolve all of the flocculent precipitate. It may be necessary to make the liquid quite hot, but it should not be necessary to boil the liquid.

Note: Do not heat the liquid in a metal can or cup, as this may result in spoiling the can or cup and contamination of the toner liquid. A good way of heating is to use an old glass teapot and put this on a hot plate or above a waxine light. Stirring must be done with a glass rod or plastic spoon.

Caution: If the vanadium pentoxide contains ammonium metavanadate, then there may be a noticeable smell of ammonia during the preparation,. If this is unpleasant, it is best to prepare the liquid outside or use good ventilation or a fume exhaust.

Caution: Be sure not to get in contact with the hot liquid.

While the liquid is still warm, slowly add 100 ml of 10% sulphuric acid or 75 ml of 10% hydrochloric acid. While adding the acid, stir the liquid. On adding the acid, the liquid first becomes yellow, then it becomes orange/red, but from a certain point it becomes lighter again. After all the acid is added, the liquid should be clear and yellow. Any flocculent precipitate should have been dissolved by now. If the liquid still looks somewhat orange, then add another 15 to 25 ml of dilute acid. Let this

liquid stand for a while, preferably in a long, tall bottle. If any solid particles settle at the bottom, then decant the clear yellow liquid and discard the small amount of liquid with the solid matter.

CAUTION (this only applies, when concentrated 95% sulphuric acid is used as a starting point): Preparing dilute sulphuric acid, 10% by weight, from concentrated acid must be done very carefully! For each 100 ml of water, use appr. 6 ml of concentrated acid. Never add the water to the acid, but add the acid --- slowly --- to the water, while stirring continuously. Even only 6 ml of acid in 100 ml of water gives a fairly hot liquid.

The clear yellow liquid must be completed to 250 ml with water and put aside. This is the basic preparation, which can be used for all toners in the subsequent part of this article. The basic preparation can be kept for a long time (at least many months, probably indefinitely).

A lemon-yellow toner or an olive-green toner

This is the simplest toner, which can be derived from the basic preparation. This toner also is the starting point for more advanced toners, which can be used for more interesting effects. It is wise, however, to first try the basic toner in order to get acquainted with the properties of this toner.

Required chemicals for this toner:

- potassium ferricyanide
- sodium thiosulfate (or any fresh commercial non-alkaline fixer)
- basic preparation (see above)

Dissolve one big spatula full of potassium ferricyanide in 50 ml of water and mix this with 50 ml of the basic preparation. This liquid must be diluted further to appr. 250 ml by adding 150 ml of water. This is a convenient amount of working solution for 5 x 7" prints. Double all amounts for 8 x 10" prints. The working solution is a clear bright yellow liquid. The exact amounts are not critical at all, not for the ferricyanide, nor for the toner solution. One spatula full probably is 200 to 300 mg.

The print must be immersed in the liquid and the tray with the print must be rocked/swirled continuously in order to have all parts of the print covered the same way (at least on average). The toner works slowly, but due to the low concentration there hardly is any staining of the highlights.

During toning, the black of the silver image turns into a muddy green and toning is complete if no black of the silver image exists anymore.

Take the print from the toner and rinse with water, until the water from the print does not appear yellow anymore. While rinsing, the image becomes much lighter and the muddy green color changes to a lighter brighter green. There may still be a slight yellow stain of the highlights.

Now there are two choices:

1. Rinse the print well, until white highlights are truly white and then let the print dry. Immediately after rinsing the print becomes very light, but much of its intensity is recovered within a few days, especially if kept in indirect day light. The final color is olive-green. The initial print must be somewhat darker than usual.
2. Refix the print in a plain hypo (sodium thiosulfate) solution, appr. one large tablespoon in 300 ml of water. It is also OK to use appr. 15 ml of a commercial fixer concentrate and mix this with 300 ml of water. The print becomes lemon-yellow and light. Any stains in the print are removed quickly and the white highlights become truly white. The fixing solution becomes light yellow and must be discarded after a few prints have been 'fixed' with it. The fixing solution cannot be kept. After refixing, the print must be rinsed well in order to remove all remaining chemicals. The initial print before toning must be much darker and more contrasty than usual. This is due to the mere fact, that yellow is a light color.

The mixed working solution for the lemon-yellow / olive-green toner can be kept safely for a few days without problems. In fact, it can be kept much longer than a few days, but it is a known fact, that ferricyanide very slowly decomposes in acidic solutions, containing several percents of free acid. One of the decomposition products may be hydrogen cyanide, an extremely poisonous volatile compound. In practice this decomposition product was not observed with any of the toners, but just to be on the safe side: don't keep the working solution for more than a few days! The basic preparation does not contain ferricyanide, so this warning does not apply for that.

The working solution turns green on storage and during use. If it is clearly green or when it has a blue precipitate on the bottom, then it must be discarded. A safe method of disposal is to add 50 ml of 5% household ammonia to each 250 ml of working solution and keep this mixture, until it is brought to a proper waste processing facility. When this is done, then there is absolutely no need to worry about formation of hydrogen cyanide, because the acid is neutralized by the ammonia.

A green toner

The lemon-yellow toner can be converted to a bright green toner, with one control parameter, which determines the color of the print. Any tone between the light yellow of the lemon-yellow toner and the bright blue of the familiar iron toners can be obtained.

Required chemicals for this toner:

- potassium ferricyanide
- ferric ammonium citrate
- sodium thiosulfate (or any fresh fixer)
- basic preparation (see above)

This toner can be prepared in the same way as the lemon-yellow toner, described above, with the addition of ferric ammonium citrate. Again, take 50 ml of the basic preparation, and make 50 ml of a solution of one big spatula full of potassium ferricyanide. Besides these, also make a solution of ferric ammonium citrate (both the brown and green version will do). A good starting point is to take the same amount as the potassium ferricyanide used (one spatula full). The ferric ammonium citrate must be dissolved in a third volume of 50 ml. All liquids can be mixed and completed to 250 ml with 100 ml of water. The resulting liquid is a golden yellow liquid.

The print must be immersed in the liquid and the tray with the print must be rocked/swirled continuously in order to have all parts of the print covered the same way (at least on average). This toner also works slowly. It is important to take the print from the solution, as soon as toning is complete in order to reduce staining.

During toning, the black of the silver image turns into pale grey/green/blue and toning is complete if no black of the silver image exists anymore.

Take the print from the toner and rinse with water, until the water from the print does not appear yellow anymore. While rinsing, the image becomes lighter and the pale hue disappears. The image becomes bluish. It is important to rinse well in order to remove most stain. After rinsing, the print must be refixed in a plain hypo solution or a diluted commercial fixer. The fixing solution becomes yellow again and must be discarded after use. While fixing, the print gets its final color. The more ferric ammonium citrate is used, the stronger the blue component in the final image. If just a pinch of ferric ammonium citrate is used, then lime-green colors can be obtained. Increasing the amount of ferric ammonium citrate, while leaving the other compounds the same, has the following effects:

- The color of the final image has a stronger blue component.
- The intensity of the final print increases.

This green toner may require some experimentation before the desired green color is obtained. It should not be committed to important prints before the required amount of ferric ammonium citrate is determined.

After refixing, the print should be washed well. Refixing already removes a lot of staining and the prints are remarkably clear in the highlights.

The mixed solution with ferric ammonium citrate can only be kept for a few hours and is exhausted fairly quickly. The more ferric ammonium citrate is added, the shorter the time that the mixed solution is stable. Each successive print has a stronger blue component, so if a series of prints is toned in a single bath, then the first prints are more green than the last ones. The last ones may look blue, compared to the first ones. So if a long series of prints must be toned and they must all have the same color, then one should work as follows:

- Prepare a large volume of toner working solution, however without the ferric ammonium citrate. This is solution 1.
- Prepare a large volume of ferric ammonium citrate solution. This is solution 2.
- For each few prints, mix solution 1 and solution 2 at the appropriate ratio, prior to toning the prints. Assure that each time, when a fresh final working solution is prepared, that the volume ratio of solution 1 and solution 2 is the same.

It is not wise to premix a large volume of toner working solution, with the ferric ammonium citrate already added. Although this assures that the concentration of all components of the toner is the same for all prints when fresh toner is taken frequently, the toning session may take so long, that the mixed solution has decomposed considerably already, when the last prints need to be toned. A decomposed solution is dark green or even dark blue, with a blue flocculent precipitate in it.

The green tones, produced with this toner, are real bright greens. One can obtain lime green, green like grass and bright blue/green. This is a large difference, compared to some iron-based toners, which are tweaked in order to get a greenish hue, but in reality only give greenish variations of blue.

A nice effect can be obtained, when the refixing stage is skipped and the print is rinsed thoroughly after it is taken from the toning bath. The image color tends to become a little darker/more intense and more olive-green. The change of color takes a few days when the picture is put in the light. In some cases this may give nice prints, but the effect is hard to predict and may require considerable experimentation.

Disposal of the green toner solution must be done in the same way as disposal of the yellow toner solution. Add 50 ml of 5% household ammonia to each 250 ml of working solution, if it is kept for a while, before it is brought to a waste processing facility.

Sepia toning with a green or yellow hue

Both the green toner and the lemon yellow toner can be combined with sulfide toning for producing nice toning effects. The complete tonal range from lemon yellow to green/blue can be mixed with sepia/brown from the familiar sulfide toning. This is no split toning, the tone of the image is the same on the entire print.

An ordinary sulfide bath is strongly alkaline and immediately would destroy the yellow, green and blue tones of the image. Sulfide toning, however, can also be done in acidic environments, due to the extreme low solubility of silver sulfide.

The sulfide bath can be made as follows:

- Take 150 ml of white vinegar (approximately 4% of acetic acid) and add 100 ml of water. One can also use glacial acetic acid (take 6 ml and mix with 250 ml of water).
- Add a spatula of sodium sulfide to this and dissolve the solid. The liquid may become a little milky. Do not use more than one spatula of sodium sulfide!

Caution: Use this bath outside if you don't want trouble with your house mates. The amount of sodium sulfide used in this bath is not so large that really dangerous concentrations of hydrogen sulfide can be formed, but the smell of the bath is really offensive, due to its acidic nature! Do not frequently use this bath in your darkroom, where photo paper is stored. The amount of hydrogen sulfide generated by this bath may be sufficient to produce noticeable fog on papers.

First tone the print in either the lemon-yellow toner or the green toner, as described above, but do not refix after toning. Rinse the toned print for a few minutes, until the stain in the highlights has disappeared. After rinsing, immerse the print in the vinegar/sulfide bath and rock/swirl the tray, such that all of the print is covered in the same way on average. The print slowly darkens, while it is in the tray and within a few minutes its final color is reached. The final color simply is due to 'mixing' brown/sepia and the color of the toner. Any green/sepia and yellow/sepia tones can be obtained. Some experimentation will give good insight in the tones, which can be achieved. After toning, the print should be rinsed thoroughly.

The sulfide bath cannot be kept and can only be used for a few prints. A spent sulfide bath can best be disposed of by flushing it through the toilet. This is environmentally acceptable.

The final color is not sensitive to the concentration of the sulfide and the acetic acid. Just keep the print in the bath, until no more change of color is observed anymore. The final color will also be the color of the dry print. These properties make the results of the process consistent.

Suggestions for further experimentation

The toner, presented here, in all its variations is a nice starting point, but it probably can be made better. At this place a few suggestions are given:

- If no refixing is used, use an inert colorless salt solution (e.g. sodium chloride or sulfate) at high concentration. This may even further reduce staining of the highlights, by replacing the staining ferricyanide by colorless compounds.
- If the sulfide variation is used, then the same may be tried, after toning, but before sulfiding.
- A two-stage toner, first toning in a copper toning, and afterwards toning in the vanadium toner, may result in orange tones, which are not achieved easily by other (known) toning methods. A problem may be the split toning effect. Light parts may become totally brick-red, while darker parts receive a mix of brick-red and yellow. The other way around, first toning in the vanadium toner and then in a copper toner, probably will not work. Copper toner requires a fairly high pH, resulting in destruction of the vanadium-yellow and the iron-blue.

Chemistry of the toner

This part of the article covers the chemistry of the toner and is of a more technical nature. Some knowledge of chemistry is required for understanding this part of the article.

Different types of toner

There exist different types of toner. The most common types are:

- gold toner
- bleach/redevelop toner
- metal/ferrocyanide toner

A gold toner works by replacing/covering the silver particles in the gelatin layer of the print by gold. Due to the very fine division of the gold, many colors can be achieved, most notably blue tints.

A bleach/redevelop toner works by bleaching the silver in the gelatin, converting it to an insoluble colorless or very pale compound in a first bath and converting this back to silver or a strongly colored silver compound in a second bath. The best known examples of this type of toner are sepia/sulfide toners and certain brown/selenium toners.

The last type of toner replaces the silver by a metal ferrocyanide compound. The vanadium toner, presented here, also is of this type, albeit a variation. Before going into details on the vanadium toner, first the general principle of the metal/ferrocyanide toner is presented here.

Chemistry of metal/ferrocyanide toner

A metal/ferrocyanide toner consists of three main compounds:

- a metal salt (e.g. the metal sulfate, the sulfate ion has no role in the working of the toner);
- a ferricyanide (usually potassium ferricyanide, as this is available commercially at reasonable price).
- a moderately strong chelating agent (e.g. citrate, oxalate, depends on choice of metal).

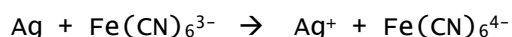
Generally, the metal cations and the ferricyanide anions cannot be in aqueous solution at the same time in high concentrations, because they form a precipitate under that condition. In order to overcome this problem, the chelating agent is added, in order to 'trap' the metal cations, such that the concentration of free ions is much lower and the solubility product of the metal-ferricyanide is not exceeded.

A fresh toner solution has the following active ionic species in solution:

- A metal cation, complexed by means of the chelating agent, notation $M^{n+}(\text{che}1)$, where M is the metallic species, (che1) denotes that the metallic species is complexed by the chelating agent and n is the charge of the free metal cation. The metal cation M^{n+} can be a simple ion, like Fe^{3+} or Cu^{2+} , but for vanadium and uranium this is a composite ion, namely VO^{2+} and UO_2^{2+} .
- The ferricyanide anion: $\text{Fe}(\text{CN})_6^{3-}$.
- A low concentration of solvated free metal cation: M^{n+} .
- Free chelating agent.

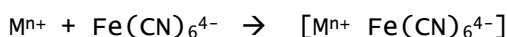
Besides the active species, there are so called spectator ions, which do not play an active role in the working of the toner. These are potassium ions, and other ions, brought into solution by dissolving the metal salt and the chelating agent. Possible examples are: sulfate, chloride, nitrate.

The basic principle of the toner is that the ferricyanide in the toner solution oxidizes metallic silver in the print (which is the black in the image), itself being reduced to ferrocyanide, $\text{Fe}(\text{CN})_6^{4-}$.



If no other compounds, but the ferricyanide were in solution, then part of the silver would remain in the gelatin as part of an insoluble silver ferrocyanide/ferricyanide compound, which is almost white. Another part would go in solution. This is what is observed if a print is immersed in a plain solution of potassium ferricyanide. The image is bleached to a very pale yellow/brown color, which is due to the formation of a complicated mixture of insoluble silver ferrocyanide and ferricyanide.

The free metal ions, present in the toner solution, do not precipitate with ferricyanide, but they do form a precipitate with the ferrocyanide formed on oxidation of the silver in the image, even at the low concentrations due to the chelating agent. I.e., the following reaction occurs (only a principal equation can be given, no exact equation):



Here the notation $[X Y]$ denotes an imprecisely specified insoluble compound, consisting mainly of X-cations and Y-anions and possibly other ions, like Ag^+ and K^+ . The precipitate is not a single well-defined chemical entity. The exact composition depends on the precise conditions. E.g., for M^{n+} equal to Cu^{2+} , the compound $[M^{n+} Fe(CN)_6^{4-}]$ will be mainly $Cu_2Fe(CN)_6$, but almost certainly, also potassium ions and silver ions will be incorporated in the precipitate.

The precipitate $[M^{n+} Fe(CN)_6^{4-}]$ is formed at the location of the black silver image. It is this precipitate, which is responsible for the color of the toned print. Where the original image is dark, a large amount of $[M^{n+} Fe(CN)_6^{4-}]$ is formed and the new color is intense. Where the original image is white, no precipitate is formed and the image still is white. In fact, the black of the silver image is replaced by the color of the $[M^{n+} Fe(CN)_6^{4-}]$.

The exact color of $[M^{n+} Fe(CN)_6^{4-}]$ depends mainly on M, but also on the precise conditions of toning and the precise composition of the toner solution. This variation in color is possible, because $[M^{n+} Fe(CN)_6^{4-}]$ is not a single well-defined compound.

The following colors can be achieved (among others) by mixing ferrocyanide and metal salts:

Cyan/blue to royal blue: $[Fe^{3+} Fe(CN)_6^{4-}]$
 Red, brick-red, brown/red: $[Cu^{2+} Fe(CN)_6^{4-}]$
 Lemon-yellow: $[VO^{2+} Fe(CN)_6^{4-}]$
 Brick-red: $[UO_2^{2+} Fe(CN)_6^{4-}]$
 Green: $[Co^{2+} Fe(CN)_6^{4-}]$

A metal/ferrocyanide toner can be prepared for a given metal if the following prerequisites are met:

- The difference between the solubility of the metal ferricyanide and the metal ferrocyanide should be sufficiently large, the ferricyanide being the more soluble compound.
- If the solubility of the metal ferricyanide is low, then there should exist a chelating agent, such that a reasonable concentration of the (mostly chelated) metal cation and the ferricyanide anion can be kept in solution simultaneously without precipitation.
- The metal ferrocyanide is colored sufficiently strongly.
- The metal ions are not easily oxidized by ferricyanide or reduced by ferrocyanide.

Only the copper and iron toners are prepared easily. The uranium toner also works well, but nowadays, uranium compounds cannot be purchased anymore (at least, not in the Netherlands). Cobalt toner is not easily prepared, because cobalt ferricyanide is highly insoluble. Vanadium toner can be prepared and recipes for that exist, but the required compound (vanadium chloride or vanadyl sulfate or chloride) is expensive and hard to obtain.

It is possible to prepare a solution of a vanadyl compound from vanadium pentoxide and some other common chemicals, but this requires a fair amount of chemistry. It can be done at home, but for the average photographer, the chemistry may be too involved. For the curious, however, at the end of the article an outline is presented, which can be used as a starting point.

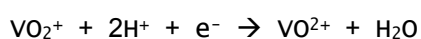
Vanadium-specific modification of basic metal/ferrocyanide toner

The toner, presented in this article, exploits a property, which only is exhibited by vanadium. In the standard scheme of the metal/ferrocyanide toners, the metal does not change oxidation state and hence, the metal species does not change. It is the difference between the metal ferricyanide and the metal ferrocyanide, which makes the toner possible. For vanadium, however, one can exploit a change of cationic species in order to make a suitable toner.

The standard vanadium toner exploits oxidation state +4 in the form of the vanadyl cation (VO^{2+}). In order to make such a toner, a vanadyl compound is required.

The toner, presented here, however, does not use the vanadyl cation as a starting point, but the so-called pervanadyl cation (VO_2^+).

Pervanadyl is a fairly strong oxidizer. The redox potential equals 1.0 V at pH = 0 for the following half-reaction:



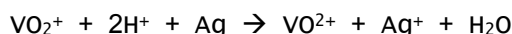
The pervanadyl ion is a sufficiently strong oxidizer for quick oxidation of metallic silver, but it is not capable of oxidizing chloride to chlorine, certainly not at the pH values at which it is deployed in the toner. This allows one to use hydrochloric acid instead of sulphuric acid.

Pervanadyl cations can coexist with ferricyanide anions in solution without the need of any chelating agent. Even at high concentration, no precipitate is formed. Pervanadyl cations only exist at low pH, hence the need of a relatively strongly acidic toner solution.

The basic yellow toner has the following active species in solution:

- Pervanadyl cations;
- Ferricyanide anions;
- Acid, in order to support the existence of pervanadyl.

When a print is immersed in the toner liquid, then the following reaction occurs:



As no chelating agent is present, the vanadyl cations, formed in the above reaction, immediately produce a dark green precipitate with the ferricyanide anions. The color of this was confirmed by means of a simple experiment by adding a vanadyl salt solution to a potassium ferricyanide solution. Besides the reaction, given immediately above, also some ferricyanide will be reduced to ferrocyanide. So, in practice, there probably will be a very complicated precipitate, containing vanadyl, ferricyanide, ferrocyanide and silver. On the toned image, this appears as the muddy green color. In terms of the [X Y] notation, a compound $[\text{VO}^{2+} \text{Fe}(\text{CN})_6^{3-}]$ is formed, together with $[\text{VO}^{2+} \text{Fe}(\text{CN})_6^{4-}]$, all in one precipitate. This precipitate apparently contains a considerable amount of silver, in the form of silver (I) cations, which is exploited in the sulfide toner variation.

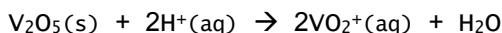
When the print is rinsed, then a fair amount of ferricyanide (and probably also of the silver) is removed, while all ferrocyanide is left behind. This causes the color of the print to shift from muddy green to a lighter brighter green. This also was confirmed by a simple experiment. Adding a vanadyl salt solution to a solution of potassium ferrocyanide produces a green/yellow precipitate.

When the print is refixed, then all silver is removed. This is complexed by the thiosulfate of the fixer and goes into solution as $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$. All remaining ferricyanide is reduced to ferrocyanide. The vanadyl is not affected. This causes the already lighter green precipitate to be converted to greenish yellow $[\text{VO}^{2+} \text{Fe}(\text{CN})_6^{4-}]$, which makes the print look bright lemon yellow.

Chemistry of preparation of the toner

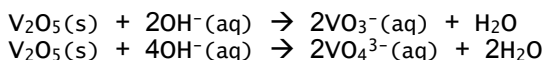
As vanadium pentoxide (V_2O_5) is the only vanadium compound, which is accessible at reasonable price for the public, this must be used to prepare the toner. The most obvious solution would be to make a vanadyl compound and use this as a basis for the toner. This, however, is not really easy, and an easier alternative is to use the properties of pervanadyl.

Vanadium pentoxide is only very sparingly soluble in water. It is a slightly amphoteric compound, but its acidic properties are more strongly developed than its basic properties. If one is very patient and is willing to boil and stir an acidic solution for many hours, then one can exploit the following (overly simplified) reaction for preparing a pervanadyl solution:



A more practical route to the pervanadyl cation is via an alkaline solution, which can be used to dissolve vanadium pentoxide quickly and then is acidified. The first step in the preparation is dissolving vanadium pentoxide in alkaline solution. In fact, the stronger the alkalinity of the solution, the better vanadium pentoxide dissolves in it.

When vanadium pentoxide is dissolved in alkaline solution, then the following reactions occur.



These equations are strong simplifications of what really happens. In reality, vanadium species in oxidation state +5 show very complicated behavior as function of pH and concentration. At high pH, vanadium forms many anionic species, the orthovanadate $\text{VO}_4^{3-}(\text{aq})$ being the extreme at the high end of the pH-scale. Protonated and subsequently dehydrated versions of this species can be formed easily, the metavanadate $\text{VO}_3^-(\text{aq})$ being only one possibility. The alkali metal and

ammonium orthovanadates are freely soluble. The metavanadates are only sparingly soluble, most notably the ammonium compound. This explains, why the presence of ammonium metavanadate in the commercial vanadium pentoxide causes the formation of a flocculent precipitate. This can be overcome, by using much more alkali when dissolving the vanadium pentoxide, but this has the disadvantage of the need of much more acid for making the liquid acidic.

The orthovanadate anion is colorless and the metavanadate anion also is practically colorless. On acidification of the liquid with the dissolved vanadium pentoxide, the orthovanadate and metavanadate species are protonated. These protonated anionic species condense to larger anionic species, containing multiple vanadium atoms in the +5 oxidation state. The exact composition of these anions is not known, but they can contain many vanadium atoms. The general formula of these anionic species is the following: $m\text{VO}_2^+ \cdot x\text{H}_2\text{O} \cdot y\text{OH}^- (\text{aq})$, $y > m$. The larger the value of m , the more intense the color and the larger the anion.

For decreasing pH (increasing amount of acid), the value of m increases and the ratio y/m decreases, approaching 1 from above. With increasing m , the liquid goes from colorless through yellow, ultimately going to orange/red. At a certain fairly acidic pH, m becomes so large, that macroscopic particles are formed. At this point, y/m equals 1 and a neutral species is formed, allowing precipitation. This precipitate has a general formula $m\text{V}_2\text{O}_5 \cdot z\text{H}_2\text{O}$, and can be regarded as hydrated vanadium pentoxide. This can be observed as an orange/red flocculent precipitate when the acid is added very carefully in small steps with constant stirring.

When even more acid is added, then the hydrated vanadium pentoxide is protonated further and y becomes less than m and cationic species are formed. At further decreasing pH, the large cations break down in smaller particles (m decreases again), finally resulting in single hydrated pervanadyl cations. So, from a certain point, the orange/red colour becomes less intense again on adding more acid, due to breakdown of large intensely coloured particles to smaller cationic species, with smaller number of vanadium atoms per particle. The extreme at the other end of the pH-scale is the light yellow pervanadyl $\text{VO}_2^+ (\text{aq})$ cation.

The scenario, described above, is the one exploited in the basic preparation of the toner. This basic preparation has as active component the pervanadyl cation (and almost certainly some condensed species, containing multiple vanadium atoms in a single cation), together with sodium cations from the sodium hydroxide, the acid's anion (sulfate or chloride) and excess of free acid.

Chemistry of extensions of the toner

Below, a short discussion is given of the chemistry behind the extensions of the basic toner, most notably the sulfide extension and the green-toning extension.

Sulfide extension

When the print is not refixed after rinsing, but put in a slightly acidic sulfide bath, then the remaining Ag^+ in the precipitate reacts with the sulfide to form the completely insoluble dark brown silver sulfide (Ag_2S), and the ferricyanide is reduced to ferrocyanide. Although most of the silver is removed by rinsing, sufficient is remaining to give the print a nice brown color, mixed with the yellow of the $[\text{VO}_2^+ \text{Fe}(\text{CN})_6^{4-}]$.

The sulfide bath may not be alkaline, otherwise the compound $[\text{VO}_2^+ \text{Fe}(\text{CN})_6^{4-}]$ is destroyed. This is a general property of all compounds $[\text{M}^{n+} \text{Fe}(\text{CN})_6^{4-}]$. This is why the sepia extension of the toner uses a solution of sodium sulfide in vinegar.

Green toning extension

The yellow color of $[\text{VO}_2^+ \text{Fe}(\text{CN})_6^{4-}]$, combined with the blue color of $[\text{Fe}^{3+} \text{Fe}(\text{CN})_6^{4-}]$ gives rise to nice green colors. There is a lucky coincidence that iron blue toning can be done at the low pH, needed to support the pervanadyl cations. The free anion Fe^{3+} does not form a precipitate with $\text{Fe}(\text{CN})_6^{3-}$ and hence can be kept in solution. However, these two ions do interact and form a brown compound, probably $\text{FeFe}(\text{CN})_6$, which remains dissolved in water. This compound is not very stable and within a few hours it decomposes, forming blue compounds of uncertain composition. This is why the mixed green toner working solution cannot be kept and even during a toning session it may decompose noticeably already, resulting in excessive staining.

When part of the iron is complexed, then the stability of the solution is increased somewhat and it remains stable at least during the toning session. When the iron (III) compound is ferric ammonium citrate (and probably the same holds for ferric ammonium oxalate, but no experiments were carried out with this), then the solution is sufficiently stable to be useful.

When a print is immersed in such a ferric / pervanadyl toner solution, then the standard chemistry of the iron/ferrocyanide toner and the specific pervanadyl chemistry are in effect at the same time, resulting in simultaneous formation of blue and yellow species. By adjusting the amount of iron (III) cations, relative to the amount of pervanadyl cations the entire tonal range from yellow to blue can be obtained.

Orange toning extension?

Combination with a copper toner for achieving bright orange colors is not as easy as combination with iron toner. The copper/ferrocyanide toner requires a much higher pH. Copper (II) cations can be complexed by many chelating agents, but these require high pH. One of the chelating agents, which works at sufficiently low pH to make the formation of $[\text{Cu}^{2+} \text{Fe}(\text{CN})_6^{4-}]$ possible is citrate, but even this requires a pH well above 7. Pervanadyl cations cannot exist at that pH.

It is expected that an orange toner can be made when a chelating agent for copper (II) cations is found, which is sufficiently effective at a pH, somewhere between 1 and 2.

No fixing of the toned print

When the print is rinsed well after toning, but not refixed, then it slowly turns darker, especially when exposed to daylight, until it has become olive green. The reason for this must be investigated further. Probably, the silver in the image is responsible for this behavior. The final color, however, appears to be stable. Once the final olive green color is reached, then the print does not change anymore, not in the dark, nor in the light.

Conclusion

In this article a toning solution is presented for making prints in the full tonal range from yellow to blue, using common chemicals only. The toner has been tried in practice and gives promising results. Some tuning may be necessary and results might have to be more precise, but the mechanism presented here is believed to be a good starting point for interesting toner solutions, for which the preparation and use is feasible for every photo enthusiast with some experience in basic darkroom techniques.

The mechanism, presented here, may well be extended with other well-known mechanisms, but in order to do so, more investigations are needed.

Materials, used as basis for this article

All results, described in this article, are achieved with the following materials:

Paper:

- Ilford Multigrade Fibre based paper, developed in home-brew Kodak D-72.
- Ilford Muligrade RC paper, developed in home-brew Kodak D-72.

Chemicals:

- The hydrochloric acid and sulphuric acid used in the experiments are both technical grade.
- The vanadium pentoxide used is technical grade, greyish brown/yellow powder. The greyish brown color probably is due to the presence of ammonium metavanadate.
- The sodium hydroxide used in the experiments is technical grade, so called 'gootsteen ontstopper', the dutch variation of standard commercial drain cleaners.
- The brown ferric ammonium citrate, used in the green toner, is so called Ph.Ned. quality. This is a high quality chemical, used in pharmacy.
- The green ferric ammonium citrate, also used for preparing green toner, was obtained from www.artcraftchemicals.com and works equally well as the brown variation.
- The potassium ferricyanide, used in the experiments, is from www.artcraftchemicals.com. This is standard photographic quality, suitable for all photographic processes, which require this compound.
- The sodium sulfide, used in the experiments, is technical grade, yellow flakes of approximate composition $\text{Na}_2\text{S} \cdot 3\text{H}_2\text{O}$, obtained locally.
- The vinegar used is simple white household vinegar.
- The sodium thiosulfate is standard photo grade 'hypo', purchased at www.vanpuffelen.nl.

Equipment:

- Determining the weight of chemicals was not done very accurately (1 gram could be measured at appr. $\pm 25\%$). A simple balance, used for weighing letters up to 60 grams was used. So, the amounts, given in the article, must be regarded as a reasonable guideline, not as values, carved in stone.
- Heating was done in simple glassware and a waxine candle light was used for heating.
- Other utensils used during the experiments are standard darkroom equipment, like trays, measurement beakers, mixing bowls, etc.

Further reading

The Darkroom Cookbook, second edition, *Steven G. Anchell*, 2000, ISBN 0-240-80423-6.

This is a very nice book, which contains an amazing number of photographic recipes, many of which indeed produce very good results.

General Inorganic Chemistry, *J.A. Duffy*, 1966, printed by Spottiswoode, Ballantyne and Co. Ltd., Colchester, Great Britain.

Contains a lot of general information about inorganic chemistry, in such a way that the subject is accessible for an amateur. Unfortunately, this book may be hard to get, it is not printed anymore.

Appendix: preparation of vanadyl compounds

As stated in the article above, it is also possible to prepare vanadyl compounds and use these for preparing a standard vanadyl/ferrocyanide toner. Preparation of vanadyl compounds, such that they can be used for preparing a toner, requires some caution and must be done outside.

The following process must be regarded as a guideline. Personal experimentation and tuning of the process is encouraged.

The following can be done inside:

- Prepare a pervanadyl solution, such as outlined in the basic preparation with dilute hydrochloric acid.
- Make the liquid a little bit more acidic by adding some extra acid.
- Dilute the liquid to appr. 200 ml with water.

The next step must be done outside or a good fume hood must be used! Standard kitchen/home ventilation is not sufficient!

Keep the liquid quite warm (not hot) and add solid potassium or sodium metabisulfite in small amounts, each time swirling the liquid. A lot of sulphur dioxide will be produced and although most of this will react to form the vanadyl, a substantial amount of sulphur dioxide escapes from the liquid. This is the reason why this step must be done outside. Sulphur dioxide is very pungent! The optimum temperature of the liquid must be determined by experiment. If the liquid is too cold, then the reaction proceeds slowly and it is hard to see how much of the pervanadyl is converted to vanadyl already. If the liquid is too hot, then too much of the sulphur dioxide escapes from the liquid as a gas.

For each amount of metabisulfite added, part of the yellow pervanadyl is converted to bright blue vanadyl. This conversion is not instantaneous, it may take a few tens of seconds. The liquid turns from yellow to deep blue, while more and more metabisulfite is added. When the liquid is bright blue, with no greenish hue anymore, then the reaction is completed.

The following step is to boil the liquid for a few minutes, blowing away the air above the liquid frequently while it is boiling. This step must also be done outside. This boiling is necessary in order to expell any excess sulphur dioxide from the liquid. It is very important that no sulphur dioxide remains present in the liquid, as this makes the liquid unsuitable for preparation of a vanadium toner. If the volume of the liquid contracts too much, due to loss of water vapor, then some hot water may be added in order to keep the volume the same.

The blue liquid, thus obtained, can be used as a substitute for solution C of recipe number 154 of the darkroom cookbook, second edition. The recipe calls for 2 g of vanadium chloride. Probably a hydrated form of vanadyl chloride is meant, as vanadium chloride is either very sensitive to oxidation (for vanadium (II) and vanadium (III) chloride, both are very deliquescent solids), or exceedingly prone to hydrolysis, due to air humidity (vanadium (IV) chloride, a brown fuming liquid). A solution, prepared from 1 gram of vanadium pentoxide probably contains more vanadyl than the recipe calls for. Experimentation for best results is necessary.