zerochrome-SbQ

A viable alternative to chromium salts in pigmented colloid printing

by Simone Simoncini and Kees Brandenburg

April 2023

Simone Simoncini and Kees Brandenburg explore a new non toxic method for pigment polymer printing.

About the authors

Simone Simoncini

I live in Italy and have been an amateur practitioner of alternative printing techniques since 2003. 59, I developed my first FP4 roll 48 years ago, I started in the alternative printing techniques field with iron based one (mainly kallitype) but as I aged I felt more and more keen to experiment more with painterly techniques such as gum dichromate, gumoil and Sury along with a little carbon transfer. All revolving around dichromate. So, I progressively became interested in finding ways to replace them, and here I am.

Here you can see some of my work: https://www.facebook.com/simone.simoncini.338

To drop a line: ssimoncini@gmail.com

Kees Brandenburg

I am a photographer and printer based in the Netherlands. I teach alternative printing techniques and work on exhibition projects with/for photographers and artists in my studio. My primary focus is on pigment colloid techniques, particularly carbon transfer, gum, casein, and similar methods. For over a decade, I have concentrated on non-toxic or less toxic processes and was an early adopter of Halvor Bjørngård's Chiba System with ferric ammonium citrate. I use DAS with gelatin for carbon transfer, casein, and polyvinylpyrrolidone (PVP) and experimented with riboflavin as a photo initiator with various colloids. I enjoy experimenting and researching to connect new and old knowledge for broader and richer ways of materializing the contemporary (mostly digital) photographic image. Since 2009, I have been hosting and maintaining the alt. photo mailing list.

polychrome.nl | workshops@polychrome.nl | zerochrome.org

Our motive

This article aims to share the results that the authors are having with a new method for pigment printing to be used as a serious alternative to dichromates and showing very interesting features in terms of stability, shelf life, absence of stain, light sensitivity.

Just for sake of simplicity, we named the process zerochrome-SbQ (short: Z-SbQ).

The process itself is about the same as gum or casein printing as the phases are the same: make sensitive pigmented mix, coat, expose, develop.

Simple, we don't want to be misleading. We think that there is value in historical research to keep the ancient processes alive but there is also value in applying safer and more advanced technology to our field of practice as it becomes available.

Historically, techniques based on a colloid holding a pigment and forming the image with the action of a photo cross linker has been generically described as "direct carbon", meaning that no transfer is involved, but we think that would be misleading too. So we prefer just to point out what we focused on, that is finding a non toxic alternative mix for direct pigment printing.

We would like to spend a few words about the meaning of innovation in our field of printing by hand using ancient techniques.

In 2017 dichromates were banned in the EU. To be more precise, their use has been restricted to severe regulation. Their use is illegal unless specifically authorized by the competent authority. No need to say that individuals do not fall in the category of those who can apply for such permits.

What we do, as researching artists, is not to improvise ourselves as alchemist apprentices. We just try to be smart and apply the best technology available in terms of toxicity, ease of use, shelf life, in a feasible way, to our printmaking.

Nor are we trying to mimic industrial printmaking, and just browsing through the referenced bibliography will make it clear that we are not actually "discovering" anything.

In this paper we focus on SbQ chemistry and its adaptation to our purposes. Indications about paper, paper sizing, pigments should be regarded as idea sharing rather than instructions. In order to fully exploit the concepts, it is good for the reader to have a fairly good knowledge of colloid printing techniques like gum bichromate, casein or carbon transfer. We do not cover anything specific about calibration, curves, negatives and so on because all of the principles still apply and some steps of one's workflow will definitely need to be adjusted.

After a century of chromium

When gum bichromate was invented in the late XIX century, only inorganic cross linkers such as dichromates were available as the whole field of polymer science was yet to come.

Chromium salts act on any kind of colloid, so for almost a century it has been the weapon of choice for a variety of techniques[1], both industrial and homemade.

Although very toxic, they are cheap, stable, work with virtually every crosslinkable substance (gum arabic, gelatin, casein and so on) and the process to obtain a sensitive mix is pretty straightforward. Measure, mix, coat, develop and your print is good to go.

In the past decades people like us printers were then playing around with these chemicals, relying on small quantities and thoughtful management to minimize health risk for ourselves and the environment.

Meanwhile, the printing industry has developed hundreds of different solutions to bind a pigment to paper, and a whole branch of chemistry is dedicated to the crosslinking of colloids. Specifically, how to use light to crosslink polymers either protein or polysaccharide based. It is hard to even summarize the huge variety of chemicals and techniques patented and/or referenced in polymer science and related fields' technical papers. UV sensitive photo initiators are not only seen in the printing world but are also widely used in electronic component and microchip lithographic production processes. In the medical world hydrogels with non-toxic photo initiators as riboflavin (vitamin B2) are used more and more. 3-D printers also work with UV hardening compounds. Bio based hydrogels can be 3-D printed and UV cured to replace body tissue.

But, as obvious, most of the techniques are far too elaborate and costly to even think about applying them "by hand". They are thoroughly thought to be industrial processes, on a large scale, in a tightly controlled environment and often using pieces of equipment specifically designed for a given purpose and to process large volumes (coating machines, mixing machines, drying cabinets and so on).

Among the dozens of photo initiators and photo crosslinkers available[2] the vast majority could never be of interest as "our" dichromate substitute because of

- toxicity: many are toxic. Maybe not as much as dichromates, but not to be handled in a friendly manner
- water insolubility: many are only soluble in organic solvents, and you don't want to replace dichromates with something to be diluted with toluene or chloroform, do you?
- availability: many are intended for large scale use and have a dedicated supply chain, so simply you don't have a place to order them and/or the potential supplier

[1] Still right before the Eu ban occurred in 2017, chromium salts were pushed by the printing industry as difficult to be replaced by non toxic alternatives. See ECHA opinion N° AFAO0000006524-74-02/F on replacing dichromates in the metal forming photoresists industry.

[2] See: Industrial Photoinitiators A Technical Guide, W. Arthur Green, CRC Press - Taylor and Francis Group, LLC 2010.

simply needs you to buy like fifty kilograms for a thousand euro and fifty lifetimes of use
- price: many are just too costly to be considered.

During the last few years, we both researched (although in a completely independent way) various substitutes and combinations of photo crosslinkers and colloids.

Mainly Diazo[3] and DAS[4] and their possible “companions” like gum arabic, casein, PVP[5], PVOH, chitosan and we both ventured in the more biocompatible chemicals like riboflavin, sodium benzoate and the like.

Although working perfectly in some respects (DAS has become the new standard for carbon printing for example) and promising in some others, some issues tend to stick around, like staining and sometimes low sensitivity. Staining is by far the main issue in direct alternative techniques[6].

In 2021, while searching for diazo related materials and other ideas possibly coming from the world of screen printing, Simone’s attention got caught by another promising chemical, SbQ.

By cross referencing info on printing industry products, patent information and research papers it showed as a serious candidate for replacing dichromate. At first, the volume of information to process led to putting the project aside, but at the end of 2022 there was an occasion to get another chance to analyze the process and get a deeper understanding of how it works.

---

[3] Benzenediazonium, 4-(phenylamino)-,sulfate (1:1), polymer with formaldehyde
[4] 4,4 ' - diazidostilbene -2,2' - disulfonic Acid Disodium Salt Tetrahydrate
[5] Polyvinylpyrrolidone
[6] referring here to gum, casein, “direct carbon” and generally speaking those which do not imply transfer of the image to a final, clean substrate.

SbQ and PVOH

SbQ stands for *N-methyl-4-(p-formylstyryl)pyridinium methylsulphate*. This intimidating name is just one of the many variants referenced in the scientific and technical papers. Its CAS number is: 74401-04-0. The acronym SbQ comes from: **S**til**b**azolium **Q**uaternized. SbQ was first engineered by Dr. Kunihiro Ichimura of the Japanese Research Institute for Polymers and Textiles and patented on behalf of the Japanese International Trade & Industry ministry at the same time[7]. Why do we like this one in particular?

Very simple. It is

- water soluble
- widely used in the silkscreen printing industry
- fairly cheap
- very sensitive to UV light close to the visible spectrum
- not a known carcinogenic/teratogenic agent like dichromates
- known to have long shelf life
- not needing special handling like, for example, diazo which has to be refrigerated
- known not to have dark reaction
- only slightly yellowish when in solution and leaving no visible stain behind
- the very low concentration of the SbQ groups leaves the PVOH virtually unchanged and makes it light sensitive

SbQ can transform polyvinyl alcohol (PVOH, also referred as PVA) to a light sensitive compound without changing its features.

PVOH is one of the most common polymers manufactured and its flexibility allows for the most diverse uses. Please note that the acronym PVA can be misleading sometimes as it is an acronym often also used for **P**oly**v**inyl **ac**etate (PVAc). These are two completely different things, even though they are related. Polyvinyl acetate is known as the white bookbinders and woodworking glue, and will not work here. Polyvinyl Alcohol is used in several clear glues. It is nontoxic and biocompatible. The glue you lick on the back of postage stamps is also made of polyvinyl alcohol. In its raw form it's shipped as white translucent grains. Brand names are Mowiol, Poval, among others.

For our tests we used a commonly available PVOH 4-88.
For those who are interested, the formula 4-88 means two things:

4 is the relative viscosity. The higher the number, the more viscous a solution of the polymer is at a given concentration. This plays a crucial role in our field, telling us how easy it is to coat with the given kind of PVOH.

88 refers to the degree of hydrolysis (or saponification). Without being too technical, the lower the number, the more soluble the PVOH is in cold water. And vice versa for higher numbers. You have to expect a reversed behavior in hot water. That is, a highly soluble PVOH in cold water (low hydrolysis grade) tends to gel when heat is applied. Vice versa for

[7] see bibliography, #2 and #3.

highly hydrolyzed PVOH (commonly referred as “fully hydrolyzed” when > 98%)[8]. We also tried different degrees of hydrolysis. Poval(™) 5-74 and 3-83, with similar results, the main difference being in how the emulsion spreads and flows on the paper. So, in case of poor results, it’s unlikely that PVOH is to blame.

[8] see Kurarai, Basic Physical properties of PVOH resin, 2022

The emulsion

SbQ is available as a powder, yellow and very soluble in water.
Unlike other chemicals that are just to be mixed into the colloid to make the sensitive emulsion, SbQ needs a chemical process to be bonded to the polymer that will become photosensitive itself by the bound styrylpyridinium groups.
The basic principle is that the mix needs time, agitation and an acid catalyst for the reaction to happen. It has a long shelf life when kept in the dark and is ready to use without any further processing.
So, if you want to experiment, it is useful to have a magnetic stirrer (not necessarily heated) and a scale able to measure at least 1/100 of a gram.

This is our basic recipe[9] for Z-SbQ emulsion:

PVOH 4-88 5g
SbQ 0,3g
85% Phosphoric acid 0,2g
Distilled water 100 ml

to neutralize the solution’s pH
Ammonia 28% 1 drop

Isopropyl alcohol 20 ml
Propylene glycol 30 ml

WARNING: while the other chemicals are fairly safe to handle, phosphoric acid is a powerful corrosive chemical used also as rust remover. Use gloves when handling it to avoid accidental spillage on hands, and wear protective glasses at all times.

It is advisable to dissolve the SbQ in a little water as the tiny quantities left in the weighing container may lead to significant difference in concentration.

1. activate stirrer and make a 5% solution dissolving 5g of PVOH in 100 ml of distilled water. You can get by just measuring the two and adding the PVOH to the water.
2. add the SbQ powder dissolved in like 1cc of distilled water
3. add the phosphoric acid. You can go the same way as SbQ by dissolving it first in a little water.
4. cap the container with some plastic wrap to avoid evaporation and cover it with aluminum foil to keep in the dark

[9] Please note that a great deal of different variations are possible by varying PVOH type (partially and fully hydrolyzed, or a mix of the two) and the type of catalyst (sulfuric, sulphonic, phosphoric acid), but it goes far beyond the scope of this article. Should anyone be interested in experimenting, please refer to Photopolymer Design: Photocrosslinkable Styrylpyridinium substituted Vinyl Polymers with Absorption Maxima from 270 nm to 540 nm, Douglas G. Borden and Jack L. R. Williams, Makromol. Chem. 178,3035-3049 (1977) and United States Patent 4,272,620, Polyvinyl Alcohol-Styrylpyridinium photosensitive resins and method for manufacture thereof, Kunihiro Ichimura, Yokohama, Japan 1981.

5. let it go for 12 to 24 hours, as photosensitivity progressively increases while the reaction goes on.
6. neutralize the emulsion adding the ammonia[10] while slowly stirring
7. add the isopropyl alcohol and the propylene glycol while slowly stirring
8. put the emulsion in a light opaque container and label it. It is a good practice to note the formula and the process used.

Sensitivity increases over time[11], so it's a good idea to standardize and always allow it to stir for the same time span. but it does not seem to affect light sensitivity and those byproducts will be washed quite easily in final rinsing.

At this point the SbQ solution is ready, even though it still contains some byproducts such as excess SbQ and salts derived from the neutralization of the acid[12].

In order to obtain a higher purity emulsion, more proper methods are available but, as they involve precipitating the resin in acetone, vacuum filtering and washing with methanol mixed with little ammonia, followed by a second filtration, desiccation and resolubilization, we would say that they are not for the faint of heart[13]. A viable, simpler but still elaborate method is to purify the solution through the use of a mild base ion exchange resin[14]. In the latter, the resin absorbs the acid and must be then filtered out and "recharged" to be reused. Although we did not conduct extensive tests on shelf life, it should be quite remarkable.

The addition of isopropyl alcohol and propylene glycol are not strictly necessary but, as Kees thoroughly tested, they really help in coating uniform, fast drying layers with consistency and ease.

---

[10] When using 28% ammonia, beware that even a drop can lead to significant changes in pH. So one has to test how much ammonia is necessary for a given volume to reach the desired pH. It is advisable to have different concentrations like 28%, 14%, 7% to be able to put the right amount into the mix.

[11] "*The reaction solutions increase photosensitivity as the reaction proceeds. The progress of this reaction, therefore, can easily be traced measuring the degree of photosensitivity of the reaction solution.In either case, the solution obtained on completion of the reaction can be used, without purification as a photosensitive liquid of high sensitivity*" in United States Patent 4,272,620, Polyvinyl Alcohol-Styrylpyridinium photosensitive resins and method for manufacture thereof, Kunihiro Ichimura.

[12] For example, using ammonia will get ammonium phosphate, ammonium sulfate the like for other acids whether phosphoric, sulfuric or other acids were used as catalyst, accordingly.

[13] "*Desired purification of the resin is accomplished after completion of the reaction by pouring the resultant reaction mixture into a large volume of a non-solvent such as acetone, ethanol or dioxane or a coagulation bath containing such substance as sodium sulfate or potassium sulfate and thereby precipitating the photosensitive resin, separating the precipitated resin from a solvent or a bath and washing the separated resin with alcohol. Thorough removal of the trace of the acid used as the catalyst is attained by washing the resin with alcohol containing a small amount of ammonia or giving the resin repeated reprecipitation*", in United States Patent 4,272,620, Polyvinyl Alcohol - Styrylpyridinium photosensitive resins and method for manufacture thereof, Kunihiro Ichimura.

[14] "*In the reaction mixture, 2.5 g of Amberlite IR-45 was added…then…the pH of the mixture was checked to be neutral and then the mixture was filtered…to obtain a light-yellowish polymer aqueous solution*" in Polyvinyl alcohol base photosensitive resin, photosensitive composition, and method for pattern formation using the same, EP-0-779-553-B1, European Patent Specification, 1996, Synthesis Example #2.

The whole process is to be done in dim warm light. The emulsion is to be stored in the dark, so opaque bottles or vases work best.

Fine tuning and variations

The idea presented in this paper can be regarded as a general workflow developed to have a good balance between ease of process, cost and effectiveness. We are not presenting a number of alternatives because it would be confusing. For those interested, relevant material is referenced in the bibliography.

Some options are worth noting, though, as hints for further research.

It is possible to use a cationic exchange resin[15] instead of an acid catalyst[16] and just filter out the resin at the end of the reaction. This would leave a ready salt-free, pH neutral compound behind, and the resin can be eventually recharged according to the product's specifications.

A different emulsion with a percentage of fully hydrolyzed PVOH could help increase the water resistance and be used only as a clear layer to avoid mixing while brushing on. In this case, the unexposed pigmented layer should dissolve at room temperature, then raising the development bath temperature should dissolve the clear layer underneath making it easier to achieve pure whites.

Varying the SbQ proportion and the acid used one can produce a less or more sensitive emulsion.

---

[15] A simple description of what a cationic ion exchange resin is: "*The strongly acidic cation exchange resins are bead-like products which have a sulfonic acid group in the cross-linked styrene frame.The sulfonic acid group (-HSO3) is the exchange group and behaves like a strong acid, dissociating to (-SO3)- and H+ even in acidic solutions, not to mention in alkaline solutions.*" - Mitsubishi Chem. Corp.l https://www.m-chemical.co.jp/en/products/departments/mcc/ion/product/1201064_8072.html
[16] Korean patent KR20010107288A - Manufacturing method of Photosensitive Polymeric Resin

Process tips

The use of SbQ is not new in industrial printing, but, to the extent of our knowledge, it is in our field. Although intuitive, it is worth remembering that, for the process not to be a chem test every time, we need the chemicals to work with some tolerance and sustain a degree of flexibility, as we cannot implement or even mimic the exactness that could be standard elsewhere.
So let’s examine the procedure and the limits of our tests along with some suggestions for further research.

Paper and sizing

Generally speaking smooth paper works best as texture tends to bring out unwanted random large dots that are quite difficult to remove bringing no harm to the image.The process is quite sensitive to differences in paper sizing. Sizing is all about adhesion and managing stain.

Good news is that this process **often does not need** a sizing layer, at least in the way that is often referred to. Not for adhesion, because PVOH has much better adhesion properties than gum, nor for stain managing as we are just about to describe.

Kees had a real breakthrough in the process development when he thought to leverage on a property of PVOH dried film called water resistance. To make a long story short, you can coat a layer, let it dry in the dark and then coat another one on top without having the underlying layer mix with the new one. It will eventually mix if one really goes for it brushing over and over, but the resistance is enough for the printer to coat the new layer fairly easily.

With gum arabic you cannot do that because the dried gum film will melt so fast that you’ll end up with a messy sticky goo under your brush. PVOH makes it possible.

When you coat the pigmented layer on top of the clear one what will happen is that you are going to expose the two layers together. In the dark areas, the two layers will both stick to the paper. In the highlights the two layers will wash away together in development giving you perfect white, as the pigment never touched the paper surface. Again, do not expect to brush really hard for ten minutes and still get perfect whites. And, as a final note on the matter, the reader should be advised that the overall result **does** depend on the paper in use. Papers with rough surfaces, for example, tend to accumulate PVOH in micro zones across the sheet giving poorer results than smooth ones.

A really interesting workflow we tested is the combined use of PVAc size and PVOH clear layer. Below a description of the workflow.

1) Size the paper with a diluted PVAc solution. Gamblin Size™ diluted 1+2 to 1+4 depending on the paper at hand can be used as reference. Let it dry.
2) Once dried, put a clear Z-SbQ layer and let it dry.

3) Coat the pigmented layer on top of the clear one, as mentioned earlier.
4) Expose.
5) Develop; development should happen quite quickly, leaving almost no stain or none at all.
6) As development is finished, dip the print in a very diluted PVAc size solution. Gamblin Size™ 1+10 can be used as reference[17]. Hang the print to dry.
7) Repeat steps from 2 to 6 for the other layers.

We have been able to get very interesting results using this technique in terms of lack of stain and contrast.

Mixing pigments

Put the pigment of choice in a small bowl and add just some drops of emulsion. Mix them in to obtain an homogeneous mix. Add the emulsion while stirring. Usually, with pH neutral emulsion, this step is fairly straightforward.

Coating and exposing

Proper way of coating will depend on the type of PVOH in use and the concentration of the emulsion. We have been using a low viscosity type as reference but we encourage the reader to experiment.
Smoothness of coating is greatly helped by the addition of isopropyl alcohol and a plasticizer like glycerin or propylene glycol to the mix as shown in the recipe.
Drying is quite fast and coating can occur long before exposure, as there is no dark reaction[18]. This in turn can be useful when giving workshops to have some of the material ready.

Z-SbQ is much faster than dichromate. Actual sensitivity depends on a number of factors, but it is roughly tenfold higher. We both experimented using UV sources, but it should be ok to use led light sources or halogen.

Just to give you an idea, Simone has a standard time of 7 to 14 minutes printing gum dichromate with his old plate burner, equipped with 1200W Philips suntan lamp. During the tests, the attained speed of some of the batches allowed for exposures as short as 15 seconds with an average of 120 seconds. Kees found out that his standard equipment (Eskofot 245 FFP metal halide plate burner) is way too powerful and prefers to use a simple 395nm LED floodlight above the vacuum frame in order to more easily manage exposure. A bank of UV fluorescent tubes was usable but also resulted in very short times, like 20 seconds.

---

[17] Depending on pigment concentration and brushing habits, it could be necessary to increase PVAc concentration. It is however possible, as shown in the examples below, to obtain very neat results.
[18] The ability of certain sensitizers, notably dichromates, to crosslink a colloid in the absence of light.

Developing and rinsing

Generally speaking, development is carried out in water at room temperature. Polyvinyl alcohol, having a much greater adhesive power than gum, tends to be trickier to remove, resulting, normally, in a thin veiled stain in the highlights.

This is where Kees' intuition kicks in. Veil can be overcome to a great extent by using a clear coat before each pigmented layer, as described above, because the unexposed emulsion will protect the highlights from having pigment sticking to the substrate.

As a result, almost all of the unexposed emulsion can be washed away through a little shaking in the water. Thin layers can develop fully in a time as short as 30 seconds.

Fine tuning can be easily done by using a fine spray, by gently brushing or pouring water on the print.

In practice, no real rinsing is needed after development is finished. Just a quick immersion in clean water, enough to make sure the diluted pigment in the development bath washes away completely.

Breadcrumbs

As the polymer chemistry behind our work is very complex, one has to bear in mind that small variations can have an impact on the final result, either for the good or for the bad. During our research a number of hypotheses were put to test to find what we thought is the optimum mix.

The dismissed “Rheological team”

We noticed that the standard Z-SbQ emulsion is very light sensitive but also has a little tendency to stain pigment in the highlights.

At first we noticed that mixing in a coworking colloid that stays unsensitized can help the clearing work. There were many possible candidates available that we called “Rheological Team”. Our heroes were gum arabic, xanthan gum, polyvinylpyrrolidone (PVP), Aquazol™, Laponite-JS™, polyethylene glycol (PEG), monopropylene glycol, Aerosil 380™ and plain sugar.

All these components, among many others on the market, can be effectively used to modify the rheological properties of the mix. That is, how it flows, how much it is water resistant, how easily it brittles after drying, and so on[19].

Simone kicked off with mixing in gum arabic, one part with four parts emulsion and got better clearing behavior. This coworking colloid principle might also work with other processes. The co-worker raises the solubility of the light sensitive colloid while leaving its active crosslinking untouched. There is a sweet spot between the two components where the unwanted attraction of paper fibers and cross linked molecules is eliminated without highlight loss.

Following this line of thought Kees carried out a number of experiments on the other candidates. Although his research was useful, he discovered that a simple change in the process[20] was way more effective in managing stain than any of the coworking colloid mix he had tested. So the coworking colloid principle is definitely something that could prove useful in certain scenarios to modify the emulsion behavior, but not a mandatory part of the process. Finally we found out that using a liquid that has the best spreading capacity should be leading. Looking at airbrush medium recipes got us in the right direction. These are used to dilute acrylic paint to use it with an airbrush. Most contain water, propylene glycol and or isopropanol. As seen before[21] a mixture of 2 parts isopropanol, 3 parts monopropylene glycol and 10 parts water is a good start. The reader should be aware that these proportions have to be tuned according to the paper sizing method as different sizing mixes can have different affinity with isopropanol and the emulsion could be absorbed by the paper, leading to stain. In those cases, try a lower mix like 1+1+10.

---

[19] Ref.: Handbook of water-soluble gums and resins, 24-8, R.L.Davidson, McGraw-Hill, 1980.
[20] Referring here to the interleaving clear sensitive layer before each pigmented one.
[21] Ref.: chapter “The emulsion”.

Managing pH

It is quite important to adjust the pH of the solution. We experimented with ammonia and magnesium oxide. Both work well. We preferred ammonia in our standard recipe for practical reasons such as no need of filtering out residue.

In principle, other alkali could be used. Beware that some, namely the salts of boric acid, will lead almost immediately to the formation of hydrogels through chemical crosslink (kids know this as “slime”), while other, for example sodium hydroxide if using in combination with sulfuric acid as catalyst, can lead to formation of a salt solution (in this case sodium sulfate) that can cause the emulsion to precipitate.

Sometimes, especially when one tries to increase the SbQ ratio, the emulsion becomes more sensitive to pH changes and the addition of alkali can lead to cloudiness as neutral pH is approached or crossed over from acidic to alkaline. Should it be the case, it can be useful to dilute the alkali agent like, for example, diluting 28% ammonia 1+1 with distilled water. A smoother increase in pH can help avoid the problem.

Sizing

We did our tests mostly on gelatin sized and glutaraldehyde hardened paper. So there is room for testing with other sizing materials and options like polyvinyl acetates or acrylates and even the very same Z-SbQ emulsion.

There is often a misconception about sizing paper. We don’t actually see unsized paper unless you specifically go to a local papermaker and order a batch of unsized hand made paper. The actually unsized paper will act like a sponge and is quite useless in alternative photography. We should talk about factory sized paper and custom sized paper.
All commercially available papers are sized to some extent, using either gelatin or some synthetic material. So, the right question to ask is *“do I need **additional** size for my process/paper combo?”*. The reasons to do so may be quite a few. For example, in carbon transfer printing the receiving surface must be prepped depending on what transfer is in order (gelatin, albumin etc). In general terms, sizing is needed to avoid excessive absorption of chemicals in the paper fibers. But never assume that it is necessary.
Although, as stated above, one can often avoid sizing the paper in this process, we tested the emulsion on different papers and different sizes. In the following table we summarize the main results.

Size	Sizing notes	Pros	Cons
Z-SbQ	A clear layer of the emulsion is coated on paper and left to dry. The paper is then exposed for two or three times the standard exposure to ensure complete polymerisation	Good clearing of highlights Usually no need for spray or brush development	Sometimes one layer is not enough to completely size the paper.

Gelatin + White Acrylic paint	A variety of combinations is possible. A viable formulation is to make a 3% gelatin solution and add the same weight of white acrylic paint (or gesso).	Smooth surface, good adhesion	A little prone to staining depending on the acrylic used
PVAc Gamblin[22]	As a reference, dilute Gamblin size 1+2, coat the paper.and let it dry.	Ease of treatment Speedy process	Paper acquires a plasticky feeling, not always welcome.
AKD[23]	AKD is available as Aquapel. Make a 1% suspension in water. Soak the paper for two to five minutes. Dry. Hot press the treated paper.	Usually one of the best sizing method available	Although widely used in the papermaking industry, maybe not available off-the-shelf even among chemicals' dealers
Pure Acrylic	A combination of different acrylic mediums can be used together with a white acrylic paint.	Ease of treatment No toxic hardeners involved Suitable for customization Definitely to be considered having in the toolbox	Different combinations lead to very good or very poor results, depending on a number of factors.

One has to be prepared to experiment a bit in this field, as usual in alternative techniques.

[22] Gamblin makes a neutral pH polyvinyl acetate sizing. It is quite possible to dilute normal PVAc glue to a similar level and add ammonia to neutralize the pH. A rule of thumb is that normal PVAc glue is seven times denser than Gamblin size.

[23] Alkyl Ketene Dimer. It is a very popular sizing agent in industrial papermaking, both for internal and surface size, and the molecule is a dimer, meaning that it is made up of two monomers, an hydrophilic and an hydrophobic one. The molecule works by attaching itself with its hydrophilic "end" to the paper fibers. By doing this, it exposes its hydrophobic side to the surface. Heating reinforces the bond, so the usual treatment is soaking the paper in the AKD suspension, let it dry and then heat press the treated sheet.

Suppliers

All the chemicals cited in the paper are commonly available from a variety of sources, including various e-commerce platforms, with the exception of SbQ.

Although it can be ordered from major chemical companies, the price tag is normally higher there than in the printing industry supply chain.

We got ours from Zhejiang Rongsheng Tech Co.,Ltd in Quzhou City, Zhejiang Province, China , whose website is https://www.rsemulsion.com/ .

This company, whose representatives are very friendly and responsive, manufactures the powdered SbQ compound, which use has been outlined in the paper, as well as a premixed emulsion, which is a base further making of silkscreen emulsion, so it's a semi-ready product, normally supplied to other companies that makes silk screen emulsions for that specific market, so, normally, as part of large B2B agreements.

This emulsion is very viscous so it has to be diluted with distilled water or preferably the mix proposed in the chapter ***The emulsion.***

Suggested dilution is 1 part of semi ready emulsion with nine parts of the diluting mix. Expect some differences, mainly in speed of emulsion. The semi ready emulsion is very fast.

Conclusions

Our goal was not to find a one-shoe-fits-all solution for pigment printing, nor are we stating that the combination we experimented works in every condition. We are using a bit of imagination to map a well known and well established chemical mix into a hand crafted process it was **not** engineered for. Alas, there are some constraints we have to work with.

We think that there are some conspicuous advantages:

- non toxic or, at least, a level of toxicity that falls far from dichromate
- one shot light sensitive mix
- long shelf life of the resin
- no dark reaction leading to long shelf life of sensitized sheets
- high sensitivity leading to short time exposures
- sensitive to UV and near visible light spectrum, leading to potential use of a wider range of light sources
- no stain from sensitizer
- no need for lengthy wash process as there is no chemical residue to be removed[24] giving what we think are prints with a good permanence..

As always, there are some drawbacks:

- chemicals not as commonly available as dichromate (where is still legal)
- cost is not prohibitive but a tad higher than gum dichromate, both for raw materials and time needed
- the SbQ resin need some work to get ready
- contrast is not as manageable by changing the composition of the resin as it is with dichromate

As a final note, we do think that we successfully found a way to adapt an already available technology to our field.

Obviously there is room for improvement so feel free to share your findings should you decide to give this method a go.

Happy printing!

[24] For example, PVOH can be crosslinked with iron salts too, but it is quite common sense that removal of chemicals is always trickier than not having to.

Gallery - Simone

Figure #1 - Cecina river #1

One layer of forest green, hand painted with (mostly) iridescent watercolors and dry pigments, a clear layer to fix pigments and a last very light layer of indanthrone blue to deepen the shadows and the water. It is printed on plywood sized with acrylic gesso and zinc white. It is interesting because it is quite evident how SbQ can be used even in multiple layers without staining. Please note that no clearing bath has been used, and final rinsing was minimum, just a minute or so in cold water.

Figure #2 - Cecina river #2

This is printed with the same negative as above. One layer, The Wet Print© Black pigment. again, no stain coming from SbQ. Only a little fog to be removed with a touch of spray development. To be further optimized through a combination of a co-working colloid and paper sizing. This is printed on old Magnani Acquerello 600gsm, sized with a mix of gelatin and white acrylic paint.

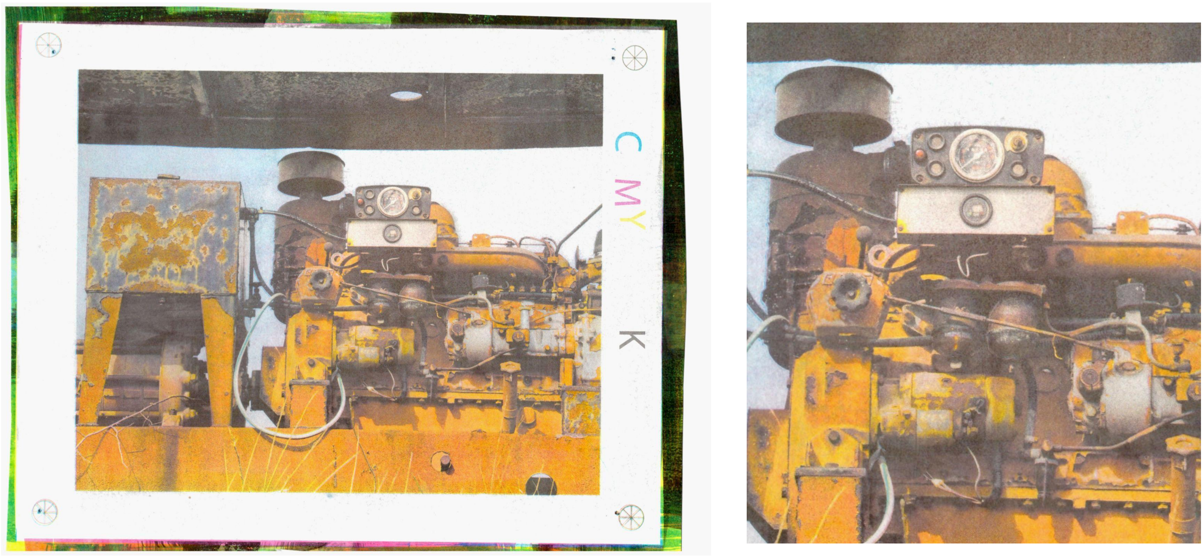

Figure #3 - Rusting Pump Motor
Four layers, CMYK. Printed on the back of Arches Platine using The Wet Print™ color pastes. Note that “on the back” means using a scrap kallitype print. Clear layer before each pigmented one. There is actually some stain on the border coming from too much black pigment in the final layer, the scanner did some clearing of its own. Overall result is good, nevertheless.

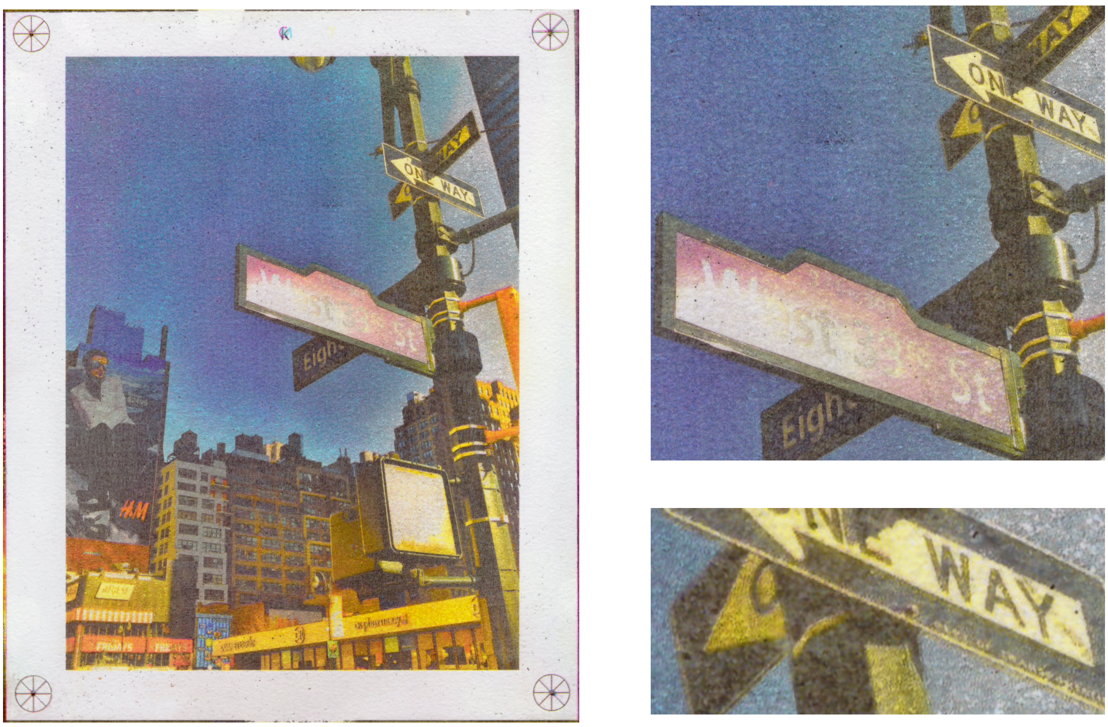

Figure #4 - Manhattan Street
Four layers, CMYK. Printed on the back of Arches Platine using The Wet Print™ color pastes. In this one I used the method of PVAc sizing plus a clear emulsion layer before each

pigmented one. Please note that the print is 20x25cm and the small writing on the sign is readable. In this picture whites are **really** good.

1 2 3 4

Figure #5 - Patches
From left to right, test patches printed on Fabriano Pittura, unsized. Fabriano Pittura is a pretty hard surface paper, 50% cotton with a rather heavy texture. Definitely not the easiest nor the prettiest to print upon. But in this case it does serve the purpose of showing the effect of clear layering underneath the pigmented layer and the effect of a little spray development in refining the highlights.
From left to right : 1) NO clear layer and NO spray; 2) NO clear layer and spray dev.; 3) clear layer, NO spray; 4) clear layer AND spray.

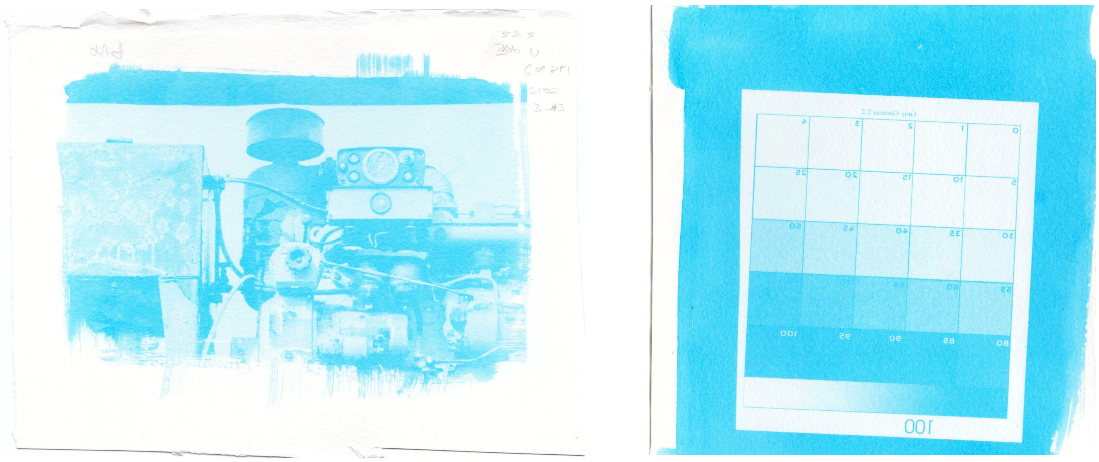

Figure #6 - Thin layer advantages
From left to right, this is a test small print I made with the leftover of a cyan mix. I had just about one cc of emulsion so I brushed it over a piece of PVAc+clear emulsion sized scrap paper (back of Arches Platine) trying to cover as much paper as I could. It really was exciting to see that development was almost immediate (30 seconds) leaving no traces of stain whatsoever.

Gallery - Kees

Figure #1 - one layer with an extra clear sublayer
First test with the extra clear (sensitive) layer under the pigmented layer.

Figure #2 - the rheological team
Dilute mixes of several compounds in water, all at a specific gravity of around 1.
Best performers are: water/alcohol/glycerin and water/propylene glycol/alcohol.

Figure #3 - exposure setup
Led floodlight above the vacuum frame. Fortunately the Eskofot vacuum frame can be turned exposure side up. With the built-in UV turned off the frame can be used with other light sources. The light-integrator does not work, so exposures had to be timed.

Bibliography

1 - **Photopolymer Design: Photocrosslinkable Styrylpyridinium substituted Vinyl Polymers with Absorption Maxima from 270 nm to 540 nm**, Douglas G. Borden and Jack L. R. Williams, Makromol. Chem. 178,3035-3049 (1977), Research Laboratories, Eastman Kodak Company, Rochester, New York 14650. USA. ,1976

2 - **United States Patent 4,272,620, Polyvinyl Alcohol-Styrylpyridinium photosensitive resins and method for manufacture thereof**, Kunihiro Ichimura, Yokohama, Japan 1981

3 - **Preparation of Water-Soluble Photoresist Derived from Poly(viny1 Alcohol)**, KUNIHIRO ICHIMURA, Research Institute for Polymers and Textiles, 1-1-4 Yatabe-Higashi, Tsukuba, Ibaraki 305, Japan 1981

4 - **Preparation and Characteristics of Photocrosslinkable Poly(viny1 Alcohol)**, KUNIHIRO ICHIMURA and SHOJI WATANABE, Research Institute for Polymers and Textiles, 1-1-4 Yatabe-Higashi, Tsukuba, Ibaraki 305,Japan 1982

5 - **Photocrosslinking behavior of poly(vinyl alcohol)s with pendent styrylpyridinium or styrylquinolinium groups**, Kunihiro Ichimura Research Institute for Polymers and Textiles, Yatabe-Higashi, Tsukuba, Ibaraki 305, Japan, 1987

6 - **Photocrosslinking reactions of stilbazolium salts**. Cockburn, Eleanor Stewart, Doctoral thesis, City, University of London, 1992

7 - **Photocrosslinkable Poly(vinyl alcohols): Preparation, Properties and Applications**, Kunihiro Ichimura, HCR Reviews , Vol. 3, p419-441, John Wiley & Sons, Inc, 1996

8 - **Polyvinyl alcohol base photosensitive resin, photosensitive composition, and method for pattern formation using the same**, EP-0-779-553-B1, European Patent Specification, 1996

9 - **Hydrocarbon Resins**, R. Mildenberg, M. Zander, G. Collin, VCH Publishers. Inc., New York, NY (USA) 1997

10- **Lithographic Resists**,in Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 15, John Wiley & Sons, Inc.1999

11 - **Hydrocolloid Applications Gum technology in the food and other industries**, A. Nussinovitch, The Hebrew University of Jerusalem - Faculty of Agricultural, Food and Environmental Quality Sciences - Institute of Biochemistry, Food Science and Nutrition, Chapman & Hall, 1997

12 - **Industrial Photoinitiators A Technical Guide**, W. Arthur Green, CRC Press - Taylor and Francis Group, LLC 2010

13 - **Photoinitiators for Polymer Synthesis Scope, Reactivity and Efficiency**, Prof. Jean Pierre Fouassier et others. Wiley-VCH Verlag GmbH & Co. KGaA. 2012

14 - **Revisit to the Photocrosslinking Behavior of PVA-SbQ as a Water-Soluble Photopolymer with Anomalously Low Contents of Quaternized Stilbazole Side Chains** Kunihiro Ichimura, Shuji Iwata, Shin'ya Mochizuki, Mamoru Ohmi, Daisaku Adachi R&D Center, Murakami

Corporation, 8-39-2 Miyama, Funabashi, Chiba 274-0072, Japan in journal of Polymer science 2/2012

15 - **ECHA/RAC/SEAC: Opinion N° AFA-O-0000006524-74-02/F**, European Chemical Agency, 2016

16 - **Evaluating alternative crosslinking agents in poly(vinyl alcohol) hydrogels membranes**, Audie Thompson and others, Journal of Polymer Science, Vol 1 Issue 2 2018

17 - **Basic Physical Properties of PVOH Resin**, Kuraray Corp., 2022

18 - **Handbook of water-soluble gums and resins, Robert L. Davidson**, McGraw-Hill 1980.

19 - **Korean Patent KR20010107288A** - Manufacturing method of Photosensitive Polymeric Resin, Yisoon Park, Daegu

20 - **Mitsubishi Chemical Group** - Strongly Acidic Cation Exchange Resins https://www.m-chemical.co.jp/en/products/departments/mcc/ion/product/1201064_8072.html