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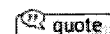
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Author	Message
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### < Ferric Gum Process

**pgum**

Posted: Tue Oct 19, 2010 12:50 am



Has anyone made attempts at replicating the Michael Andrews process noted on the page

<http://www.alternativephotography.com/wp/processes/gum-bichromates/ferric-gum-process>

Joined: 19 Oct 2010  
Posts: 52

I attempted this technique by applying 25% ferric chloride soln to Fabriano hot pressed watercolour paper both as it is out of the box, and after acidifying and drying using acetic acid to remove the calcium carbonate buffers.

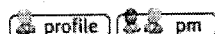
Results:

The ferric chloride was not rendered light sensitive on either of the papers. It appears that the cellulose is not enough to render it sensitive. The addition of a quantity of citric acid did sensitize it since, after 5 mins exposure to a UV lamp, the exposed areas were noticeably bleached. I proceeded to apply a gum/pigment mix. The gum was a 30% soln gum arabic in water + phthalo blue.

The gum seemed to gel on contact so there was quite a bit of streakiness. A positive image was observed but it was extremely feeble and the quality of the print was awful, as it was mottled, streaky and faint.

Has anyone else given this technique a shot?

[Back to top](#)



**Botanic88**

Posted: Tue Oct 19, 2010 9:18 am



Firstly I should say that I am the person who wrote this article: Michael Andrews and Botanic88 are one and the same!

Joined: 14 Aug 2010  
Posts: 50

You say that the process failed in two respects: the ferric chloride was not light-sensitive, so you modified it and then it failed to harden the gum. May I start with the second difficulty?

In my experience the hardening of the gum is very reliable provided one gets unmodified ferric chloride onto the paper (although a little hydrochloric acid may be added if necessary). Indeed the image is so robust that the excess gum can easily be swept off without damaging it. Adding citric acid (or acetates) will weaken the image. However one can add some potassium oxalate without weakening the image too much (it may become too weak to survive washing if too much oxalate is added).

So the real difficulty is to get ferric chloride onto the paper without modifying it too much and without allowing the paper to hydrolyse it to ferric hydroxide. In the past I used artists' sketch pads or Basildon Bond writing paper without any trouble and I still have a 25 year old sketch pad that works! I guess one may need to use a paper intended for working with iron salts now.

Then there is the question of making ferric chloride light-sensitive. I never had much difficulty with this. It could take a long exposure if the solution was strong and under certain circumstances the salt would hydrolyse before the end of a very long exposure.

I suspect that the manufacturer's sizing in the paper made the salt light-sensitive. I know for certain that gelatine does the same. However adding some potassium oxalate to the ferric chloride will certainly make it more light-sensitive.


I hope that your initial difficulties will not deter people from trying this process. It should work fine provided one has the right paper and learns how the chemicals behave. The real problem lies with clearing the iron compounds from the final print but that is another matter!

Back to top

 [profile](#)  [pm](#)

**pgum**

📅 Posted: Tue Oct 19, 2010 5:59 pm

 [quote](#)

Joined: 19 Oct 2010  
Posts: 52

OK. Michael, I think the key to yours working is due to the gelatin size as you suspect. I believe this because the Fabriano paper I use is sized with something called AKD (Alkyl Ketene Dimer) and this is an inert wax like substance added to the paper pulp with the pressing of the pulp done afterwards. It works quite well as a gum printing size but probably does not lend the sensitivity to the ferric chloride.

My next two experiments will be to

- 1 attempt to size the paper with gelatin
- 2 add potassium oxalate or perhaps sodium oxalate because I have oxalic acid and can make it easily. I suspect that both should work


I'll post these results next week and if all goes well, move on to the iron staining problem that seems to be where you sit.

Back to top

 [profile](#)  [pm](#)

**Botanic88**

📅 Posted: Wed Oct 20, 2010 2:14 pm

 [quote](#)

Joined: 14 Aug 2010  
Posts: 50

I am really pleased that you are giving this process a trial. 😊

You may also like to look at my second article about Ferric Gum.

<http://www.alternativephotography.com/wp/processes/gum-bichromates/mechanism-ferric-gum-process>

Can I provide some tips to increase the chances of achieving a decent print first time?

Sizing the paper should achieve three ends. It must make the ferric chloride light-sensitive. It must also form a suitable 'binder' to hold the chemical (simply putting ferric chloride on a sheet of glass certainly doesn't work properly with the gum). It must also allow the chemical to diffuse easily into the gum. So I guess that the sizing needs to be a thin yet coherent film and one that will withstand the acidity of ferric chloride without hydrolysing it.

I would recommend testing the gum-hardening aspect before tackling the light-sensitivity question. This can be done simply by making some marks with ferric chloride on the paper and drying them, preferably using varying amounts of the chemical. Then the gum should be applied (with or without pigment). This would allow one to see what strength of chemical is required in the full process. It would also ensure that this aspect of the process is working well, before worrying about exposure times, etc.

This initial test would also allow one to try varying amounts of potassium oxalate. Oxalate increases light-sensitivity but it also decreases the tendency of the ferric salts to be hydrolysed. The latter helps preserve the chemical on the paper but it is not so good for getting a robust image in the gum. The gum is only hardened by the formation of ferric hydroxide!

Finally it is best to make the gum reasonably concentrated. It should be thin enough to brush (or push with a finger!) across the paper but there is no point in having it any thinner.

Good luck! 😊

[Back to top](#)



**Frank Gorga**

Posted: Sun Oct 24, 2010 9:48 pm



Joined: 24 Oct 2010  
Posts: 4

Hello pgum and Michael,

I, too, have been experimenting with the "ferric gum" process. I'll summarize my results thus far here.

I have been using ferric chloride solutions between 0.5 M and 2 M; you'll need to forgive me with regard to the units of concentration, I make my living as a chemistry professor. Anyway, 1.0 M is about 15% (w/v)... i.e. 15 g / 100 mL.

My gum solution is 14 g / 40 mL final volume... i.e. I dissolve 14 g in about 20 mL of water and bring the final volume to 40 mL after the gum has dissolved.

I add pigment to the gum at a rate of about a 1 cm "bead" as it comes from the tube to 5 mL of gum.

For my initial experiments, I used Fabriano Acquarello paper with no pre-treatment of any kind.

I found that coating this paper with ferric chloride, allowing it to air dry and brushing on gum/pigment caused the gum/pigment to become "fixed" to the paper... just as Michael suggested in might!!!

To test light sensitivity, I exposed a sheet of coated paper to sunlight under a positive transparency using a hinged back frame so I could check the progress occasionally. After about an hour in bright sun, a weak image could be seen due to the sun bleaching the iron salt. Applying (by brushing) gum/pigment to this paper and washing away the excess under warm running water resulted in an image that was not half-bad for the first attempt!!!

Playing with the concentration of ferric chloride gave the expected variation... doubling the concentration gave a darker image and halving the concentration gave a lighter image... all with nominally the same exposure (i.e. 1 hour in the sun, on a partly cloudy day).

All of the exposures have an orange-ish background, presumably due to ferrous salts... more on this in a moment.

So much for the successes... now for the failures!

I tried exposures as above except that I exposed under the artificial UV source ( a home-made box with fluorescent tubes made for keeping reptiles) that I use for cyanotypes without success... no image was seen with a one hour exposure.

Adding a bit of tartaric acid to the ferric chloride seems to increase the sensitivity to light while decreasing the density of the shadows. Thus this may allow exposures under the artificial light source. I'll need to explore this further as this was my last experiment of the series and I was both rushed and tired.

I have also tried coating Fabriano Aristico paper with ferric chloride and found that it does not fix gum/pigment. Thus, I may be seeing the "sizing problem" you both speak of.

I have also tried (without success) a number of things to reduce the orange-ish background. Since the color of the background is reminiscent of ferrous salts, I decided to try things that I thought would solubilize ferrous iron... as I said before, I am a chemist, but my specialty is biochemistry not inorganic chemistry, so I am really outside of the realm of my expertise here.

Anyway, the basic experiment was to coat paper (the Acquarello) with ferric chloride (1 M) and allow to air dry. Then I painted on a bit of gum/pigment and washed off any that did not immediately fix; most of the paper was kept free of gum/pigment. These samples were then placed in a bath of different solutions for about 10 min with gentle agitation. Some of samples were treated fresh (i.e. directly after washing in running water) and others were allowed to air dry before re-soaking.

I tried soaking in a 1:1 mix of vinegar (acetic acid) and water, knowing that iron salts tend to be more soluble

in acid solution that in basic solution. I tried treatment with 0.1 M disodium EDTA; EDTA forms complexes many metal ions and thereby solubilizes them. Lastly, I tried 1 M ascorbic acid, knowing that ascorbic acid can reduce ferrous iron to ferric iron which is more soluble.

None of these treatments were successful... there was little if any change in the intensity of the background and in many cases, the previously fixed pigment/gum started to wash away. Immersing a sample in plain water overnight did not cause the fixed pigment gum to wash away nor did it affect the background staining.

To summarize, I've had mixed results! But I'm still interested enough to keep experimenting as time permits.

I'll try to get the couple of successes scanned in the next few days and post them on my blog.

Lastly, I'll just say that if this technique can be worked out it will be a very useful addition to the world of alternative processes. I have only done a bit of gum printing but I stopped doing it completely because I can not personally justify the use of highly toxic chromate compounds in the pursuit of art... the environmental costs are just too high.

Regards,

--- Frank

Frank Gorga  
[www.gorga.org/blog](http://www.gorga.org/blog)

Back to top



pgum

Posted: Mon Oct 25, 2010 2:45 am



Frank, Michael

Joined: 19 Oct 2010  
Posts: 52

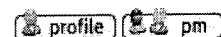
It was interesting to read of Franks experiments. These results will certainly help with my experiments. I would not have expected the long exposure that was necessary. I will keep this in mind for my tests.

The orange stain sounds like a challenge. Another compound to try may be sodium sulfite. I know it is a powerful reducer but I do try to avoid it because I do not like the fumes it gives off when dissolved in water (Sulfur Dioxide) albeit this is minimized in cold water. Dilute HCl or H2SO4 is another option, however I am aware that some pigments may be damaged by this highly acidic environment.

On the topic of gum printing and the use of chromate/dichromate, an effective alternative I have had success with is the use of ferric ammonium citrate instead of dichromate and casein instead of gum arabic. This method differs somewhat but is very low in toxicity and has good exposure sensitivity and is also a negative working process like the traditional gum dichromate. I discussed my methods and results on the alt-photo listserv last spring. Others have made attempts using iron compounds and gum with mixed results. Search there to see what was done if you wish to go this route. It is a whole other topic and not fit for this thread.

Peter Friedrichsen

Back to top



Botanic88

Posted: Mon Oct 25, 2010 10:13 am



I have also done a little experiment in the last couple of days, but let me indulge in a bit of (not entirely relevant) preamble first.

Joined: 14 Aug 2010  
Posts: 50

I enjoyed your attention to measurement Frank. Indeed I have a homemade weighing balance that weighs one or two grains of sugar, but in terms of this process I tend to chuck stuff in, more or less judiciously (like Jamie Oliver I suppose)!

I suspected that Pgum might be the very same Peter who commented on my article and mentioned the so-called Poitevin Process. In my reply to your comment I suggested that that process might contain a hidden subtlety.

Briefly Poitevin seemed to think that a gelatine and ferric chloride mix is both light-sensitive and hardened at the same time. My experience suggests otherwise. It is true that acidified ferric chloride can be added to gelatine or gum and it will be light-sensitive. It is also true that when the result is washed in water it will become hardened. However my experience suggests that it is the washing that completes the hardening process. Ferric chloride as such does not in itself harden colloids but the moment it is hydrolysed it does. Well that is my opinion!

Now to my little experiment. I used some modern artists sketch (cartridge) paper. I bathed two pieces in very dilute acids overnight (less than 1% I guess). Then I washed them for about 15 minutes and let them dry. The two acid were HCL and oxalic acid.

The paper bathed in oxalic acid ended up with powder on its surface (insoluble calcium oxalate I suppose).

The paper bathed in HCL took ferric chloride and maintained it in a bright yellow (ferric chloride) state with no change observed after an hour. The paper bathed in oxalic acid began to turn brown (ferric hydroxide) within the same time period.

Both papers allowed gum to harden on the ferric chloride but the paper bathed in HCL produced the best result. It was also possible to get hardened gum with some untreated paper but it was very thin. This confirms your experience Frank.

I also exposed the papers to sunlight under an old surform blade (my methods are cruder than yours)! The paper bathed in HCL only bleached very slightly after an hour of intermittent sunlight. This confirms your experience Peter. However the paper bathed in oxalic acid bleached significantly more (due to calcium oxalate left hanging about I suppose).

In terms of speed, in the past one variation of the process has given me a good image in about 7 seconds of sunlight and also an image in 45 minutes exposure to a 35mm transparency projected from an ordinary slide projector with the image enlarged to about 7 inches. So speed is not going to be a problem with this process! These increases in speed involve oxalates. The reason I kept to simple ferric chloride in my article was that I felt it would be best to begin with the simplest version of the process.

Finally I come to the problem of the orange coloured stuff in the background you both mention. I am a little puzzled by your experiences here. I get brown stains in the background and within the hardened gum itself and I assume this is ferric hydroxide. I don't get anything orange. Also I thought that ferrous salts tend to be greenish (eg ferrous sulphate).

Anyway I am very pleased that you are both taking this process seriously. May it become the success it could never manage to be 25 years ago when I worked alone without the resources of the wonderful Web!

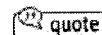
Michael Andrews

Back to top



Frank Gorga

Posted: Mon Oct 25, 2010 8:00 pm



Thanks to both of you for the additional information and the encouragement.

Joined: 24 Oct 2010  
Posts: 4

I have posted scans of my best results to date on my blog at: <http://gorga.org/blog/?p=339>

As for the background, I thought that is may be iron (III) oxide (i.e. ferrous oxide, commonly know as rust) it certainly has the right color!

Additionally, it seems to appear spontaneously as coated paper sits around in the dark but exposed to air... in other words the same color appeared on a piece of coated paper that I accidentally left in the cupboard for

a few days. (This piece of "old" paper did not fix gum/pigment and was not photosensitive.)

Also, my reading of the CRC Handbook suggests that iron (III) chloride can be either "dark yellow-red" or "brown-yellow" in its crystalline form, depending on its state of hydration. So, I can also easily imagine these might show as orange-ish when coated on paper.

I'll try sulfite when I get a chance. Looking at the solubility of both iron (II) and iron (III) salts in water, it looks like the nitrates of both forms are, by far, the most soluble... so maybe I'll also try washing with sodium nitrate or nitric acid.

I'll report back again as soon as I have a chance for further experiments in all areas (i.e. orange backgrounds / sizing / photosensitivity)... if only the day job did not keep interfering! ☺

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Frank Gorga


[www.gorga.org/blog](http://www.gorga.org/blog)

 [profile](#)  [pm](#)  [www](#)

Back to top

**pgum**

☐ Posted: Tue Oct 26, 2010 2:43 am

 [quote](#)

Frank,

Joined: 19 Oct 2010  
Posts: 52



I was impressed to see the scans of your experiments. The 1.0M print looks pretty good for such early stage experimentation. What is most interesting is the apparent wide scale of the reproduction- that is what I was hoping to see.

I noticed that you had mentioned that your UV light source did not generate enough of an exposure. I'm wondering if the light spectra is shifted out of UV and into the visible spectrum with this Ferric Chloride or perhaps the sun's warmth is accelerating the reaction.

Michael,

Yes, It was I who made the reference to Poitevin's process. Your theory regarding the hardening by hydrolysis sounds interesting. I am wondering if it is this action that is causing difficulty with Franks attempts to remove the residual iron. Perhaps the hardening requires the iron hydroxide to be available, and if it is washed out, the gum goes back to its more fluid state, causing image loss.


Peter Friedrichsen

 [profile](#)  [pm](#)

Back to top

**Botanic88**

☐ Posted: Tue Oct 26, 2010 11:11 am

 [quote](#)

When you said your initial attempts were not half bad I never guessed you meant that good, Frank!

Joined: 14 Aug 2010  
Posts: 50

If this process gets saved from oblivion, where it was headed, I think it will be largely due to your print! Without this early success many people may have been put off.

And the same may be said for the underlying mechanism which I have called crys-gelling. This could even have applications outside photography.

<http://www.alternativephotography.com/wp/processes/gum-bichromates/mechanism-ferric-gum-process>

So I am very grateful to you!

One minor matter: You refer to iron(III) oxide as ferrous, and you talk of ferrous elsewhere when I think you mean ferric. This has been confusing me. Surely iron (III) is ferric!

So now we all seem to agree that the ferric hydroxide/oxide stain is the main problem. Other questions like

exposure speeds, spectra and the possible need to size the paper won't matter if we cannot solve this staining problem.

Unless I am mistaken the hardening of the gum is due to ferric hydroxide. Therefore any attempt to remove this chemical would destroy the image unless we can fix the image in some additional way first.

One solution that works is to use gelatine instead of gum. Then the stain is easy to remove after the gelatine has set thoroughly. I have removed it with oxalic acid in the past but I think EDTA also works under certain conditions. My images with gelatine are not as good as with gum but this problem could well be solved. However my strong preference is to make the process work with gum!

Another solution is to clear the print in a mixture of alcohol (iso-propanol) and water plus oxalic acid or whatever. The mixture would need to be about 70% to 30%. I dare say that some extravagant Victorians might have chosen this route but I'm not keen on it!

Another solution might be to cross-link the image using persulphate. This is mentioned as a 'dark reaction' in the CHIBA system. I have done a little work with this idea so far, but not got there yet.

So on with the work!

Finally I tried to find the stuff you mentioned at alt-photo (listserv) Peter, but without success. Please can you give me a link to it? My concentration is on our present process but anything concerning iron salts and colloids is grist to the mill!

Michael

[Back to top](#)



Display posts from previous: All Posts Oldest First Go

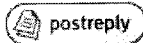
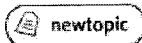
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[View next topic](#)

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Page **1** of **15**  
Goto page **1**, **2**, **3** ... **13**, **14**, **15** [Next](#)

**AlternativePhotography.com Forum Index > All other processes**



Jump to: All other processes Go

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2



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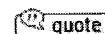
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Author	Message
--------	---------

< Ferric Gum Process

pgum

Posted: Tue Oct 26, 2010 12:40 pm



Michael,

Joined: 19 Oct 2010  
Posts: 52

In regards to the listserv, here is a link to my response in a thread started by Sam Wang re alternative sensitizers.

<http://lists.altphotolist.org/pipermail/alt-photo-process-list/2010-April/001419.html>

In the post there is a link to some sample prints. Several of these use casein while others use a modified gelatin. The thread goes into details of what modifications were required to make the process work.

I am still waiting for the sun to show up here in Toronto but the forecast does not look to good in the near term. I would prefer to do tests using this light source so that I can at least eliminate one more variable and then hope to replicate Frank's results.

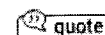
Peter Friedrichsen

Back to top



pgum

Posted: Wed Oct 27, 2010 11:13 pm



Ferric gum test print results

Joined: 19 Oct 2010  
Posts: 52

I have attempted to make some more prints with this process. You can see three test prints which have been scanned and are viewable at:

<http://picasaweb.google.ca/pgfriedrichsen/FerricGumProcess#>  
(Prints are from left to right starting with test print 1)

All prints made on Arches Aquarelle Hot Press Watercolor paper.

Note on Pigment: I recently edited this post to add in the fact that the pigment I used was lampblack (raw powder) mixed into a 30% w/vol solution of gum arabic. The amount of pigment I added was done by eyeing the density of the mix since my weigh scale does not accurately measure such small amounts of a light and fluffy pigment such as lampblack.

Test Print 1

Sensitizer:

- 1 ml ferric chloride 42 degree baume (approx 60% w/vol)
- 1 ml ferric ammonium oxalate 20% w/vol
- 3 ml distilled water w/2 drops 99% isopropyl alcohol

sensitizer brushed over three times by hand

Exposure 45 minutes under UVA lamp



washed in smooth non-aerated cold water stream for about 6 minutes

#### Test Print 2

##### Sensitizer:

2 ml ferric chloride 42 degree baume  
1 ml ferric ammonium oxalate 20% w/vol  
9 ml distilled water w/2 drops 99% isopropyl alcohol

sensitizer brushed over three times by hand

Exposure 60minutes under UVA lamp

washed in smooth non-aerated cold water stream for about 6 minutes

#### Test Print 3

##### Sensitizer:

2 ml ferric chloride 42 degree baume  
1 ml ferric ammonium oxalate 20% w/vol  
9 ml distilled water w/2 drops 99% isopropyl alcohol

sensitizer brushed over three times by hand

Exposure 75 minutes under UVA lamp

washed in smooth non-aerated cold water stream for about 6 minutes

#### Test Print 4 -Iron removal

A strip of 20% potassium dichromate was "painted onto the middle of this junk image (from a previously underexposed test print. The print was dried, then exposed to UVA for 20 minutes, washed in dilute sulfite to remove dichromate stain, then sodium bisulfate 2% soln w/vol for about 10 minutes (soak) All other parts of the image dissolved off except the dichromate hardened strip, but there was a small amount of blistering in a couple of dense regions. Iron stains were effectively removed.

#### My comments

i found that the oxalate addition increased sensitivity but too much reduces density. Using only ferric chloride produced a very dark image at 60 mins and I believe that 90 mins may be sufficient. It is something else to try.

The prints show a fairly good range of blacks. The step wedges show about 10 steps but may not be as apparent in the scanned prints as I see them. There is some horizontal banding which I attribute to brush overlap. It seems that the overlapped area results in a more dense region. I think it would be interesting to dip the print face down into a tray of gum/pigment for a minute or so, as I think this may give a nice even coat.


#### Iron removal

I tried a number of acids and sulfite in an attempt to remove the iron. Unfortunately as Frank had mentioned, the image dissolves. I had success with post hardening the gum using dichromate and this was only a proof of concept. I now think that a post hardening step of glyoxal and an acid wash after hardening would remove the iron as it did for my test print. Unfortunately I do not have any glyoxal to try. Formaldehyde or gluteraldehyde can be used but I don't have these either and they do require good ventilation.

Peter Friedrichsen


*Last edited by pgum on Thu Oct 28, 2010 5:38 pm; edited 1 time in total*

Back to top

 [profile](#)  [pm](#)

**Botanic88**

📅 Posted: Thu Oct 28, 2010 1:50 pm

 [quote](#)

Joined: 14 Aug 2010  
Posts: 50

Once again I am very impressed by these early results. 😊  
I am not a photographer and the process was originally intended for another field of printmaking. So hardly any proper photographic prints have ever been made with it!

Re. your suggestion for dipping the exposed print into gum, may I suggest an alternative? If one could pull an elongated puddle of gum across the print in a slow continuous motion it would avoid any horizontal marks whilst retaining the frugality of the process. One thing I like about the process is that it uses (and wastes) less pigment and colloid compared with Carbon Prints, for example. However if you intend to print in batches then dipping would make sense!

Re. your ideas for fixing the print before clearing the stain, I also don't have any glyoxal (is it known to harden gum arabic?) I used to have some formalin but I'm not keen on it. I almost certainly tried this latter chemical myself in the past, so I guess it may not work.

Meanwhile, leaving the question of background stain for a moment, I did another small experiment yesterday that makes me think that the 'modern' paper problem is just about solved.

I am guessing that my 'modern' bog-standard Daler artists sketch paper is sized with AKD and buffered with chalk. I bathed a piece of this paper in a very dilute HCL bath for 2 hours (in my earlier post you may remember that I did the same and left it overnight). The concentration was about 1 part in 1000. Then I washed the paper and let it dry.

I diluted some ferric chloride and added a small amount of potassium oxalate (probably something like 10 milligrams in 2 mL). Then I coated a small piece of my acid-treated paper and a similar piece of 25 year old paper with this sensitiser and dried them. I exposed both pieces side by side for about 30 minutes in sunlight (intermittent and sun low in the sky in UK). When gum was put on both pieces the results were very similar.

I am fairly certain that my 'modern' paper is not gelatine sized, because it is the same paper that showed almost no light-sensitivity with just ferric chloride alone the other day. Therefore the light-sensitivity it showed in the current experiment must be entirely due to the oxalate.(as I would have expected).

From this experiment I conclude that many 'modern' papers are likely to work with this process, though some would require an acid pre-treatment to remove buffers. Also sizing the paper to obtain light-sensitivity is not essential because the oxalate will do the job instead.


If this hypothesis is correct then it should also be possible to make Fabriano Aristico paper work by the use of acid pre-treatment and adding oxalate to the sensitiser. Frank found this paper didn't work at all when he used it out of the box. I wonder if either of you would like to try this because I don't have any Fabriano paper at all!

Back to top

 [profile](#)  [pm](#)

**pgum**

📅 Posted: Thu Oct 28, 2010 10:34 pm

 [quote](#)

Joined: 19 Oct 2010  
Posts: 52

A few comments:

Re. pulling a puddle

This is something to try. I would expect that one would only have one stroke of it and could not go back over. A glass rod may do the trick.

Re. Fixing the print

I don't have any information to support the assumption that glyoxal would harden the gum. I do know that gelatin and some starches are hardened by it. There are a number of alternative print makers using glyoxal in their sizing operation and involving gelatin as the size.

If the gum can be hardened, the iron can be removed. I scanned a print of the results of print number one cleared of iron, again as proof of concept (same link as before). The print was coated with potassium dichromate, then chemically reduced (rather than using UV light) to harden the gum. The bath used for the reduction and clearing was a mix of ascorbic acid and sodium bisulfate. I hope we can find a simpler way!

The print smeared somewhat when the dichromate was applied and is apparent as horizontal streaks. A slight loss of density occurred, but this is to be expected with all the soaking and washing.

Re. Paper compatibility

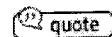
I'll give it a try with the Fabriano Artistic. I will try one HCl acidified and one unaltered and do them together to see what happens.

Back to top



**pgum**

Posted: Fri Oct 29, 2010 4:57 pm



I made a print using the Fabriano paper both without and with acid pre-treatment

Joined: 19 Oct 2010  
Posts: 52

I placed one of the papers in a 0.5% HCl solution for about two hours, then removed it and hung it to dry overnight. I treated the leftover solution with a little sodium carbonate and a white precipitate formed so I guess that confirms a calcium carbonate buffer. The other paper was used right out of the box.

The untreated paper (Print 5) printed very poorly. The sensitizer dried to an orange hue so it is likely reacting with the carbonate.

The treated paper (Print 6) printed reasonably well. The sensitizer dried as a lemony yellow coat. It seemed a bit underexposed as the image is a little too dense. It seemed to be slightly less light-sensitive than those made with Arches (BTW the Arches is gelatin sized).

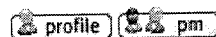
The mottled appearance is another issue. I have also seen this when gum printing on this paper, although not to this extent.

View the prints at:

<http://picasaweb.google.com/pgfriedrichsen/FerricGumProcess#>

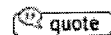
Michael, your hunch seems to be correct.

Back to top



**Botanic88**

Posted: Sat Oct 30, 2010 10:28 am



Peter, thanks for the link to your work with casein. I read the whole thread with interest.

Joined: 14 Aug 2010  
Posts: 50

Back to Ferric Gum. Your latest results prove the effectiveness of secondary hardening before clearing the stain. It's a pity that dichromate is so unpleasant whilst being the best chemical for fixing colloids! Anyway I feel sure we can solve this stain issue between us, although I would put my money on people like you and Frank who have much more chemical knowledge than me!

Thank you also for testing my hypothesis regarding the use of 'modern' papers.

You say my hunch seems correct. Hunch, what hunch? But seriously nearly everything I have ever done on the process has relied on hunches. Indeed the initial invention was made despite an almost complete lack of chemical knowledge about what was going on. 🧐

Anyway here is another hunch to contemplate when you want a change from the stain problem.

I have always thought that the oxalate in the sensitiser punches above its weight. If the ferric chloride and the potassium ferric oxalate are reduced by sunlight separately then the oxalate part should finish long before the ferric chloride part.

This doesn't seem to happen, which suggests that the two 'systems' may be interacting. My last reported experiment suggests this strongly because the light-sensitivity was provided almost entirely by the small amount of oxalate present.

I'm aware that my measurements are not very accurate. For example when I said there was about 10 milligrams of potassium oxalate in 2 mL of sensitiser I made this measurement *post hoc* in order to give you some idea of the quantities. I remembered how much stuff I had used, as judged by eye, so I reproduced the same amounts and then measured them. But even if my figures are 100% out there is still something funny going on. According to my figures the potassium oxalate was roughly 0.5% w/v whilst the ferric chloride would have been about 15% w/v.

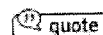
So my hunch is as follows. When the 'ferric oxalate' complex is reduced by sunlight the resulting ferrous oxalate is either not complexed or, if it is then it is pulled apart in the presence of ferric ions because the 'ferric oxalate' complex is stronger in some sense. Of course I have no idea if this is correct! But if it is then the oxalate would be recycled to generate more 'ferric oxalate' complex. Consequently one part of oxalate would effectively act like three parts after recycling.

Back to top



**pgum**

Posted: Mon Nov 01, 2010 2:38 am



Joined: 19 Oct 2010  
Posts: 52

The casein/gelatin work was great to learn from and it has good potential as a negative working process without toxic chemicals. It may even play a part here at some point because casein can be made insoluble on an as needed basis by pH adjustment but that is another direction. Of course, it has the same problem as that of gum bichromate in that thick gum/colloid coats cause very short scale prints.

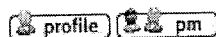
For now, it would be nice to try to understand a little more of what is going on. Is it ferrous hydroxide or ferrous chloride or something else that is hardening the gum? Is the oxalate recycled in some type of catalytic cycle as you suggest? Why does it take 60 mins for an exposure when ferric ammonium oxalate (or citrate) can be made to generate a gum "bichromate" type print in 3-4 mins using casein or gelatin and a peroxide developer?

Some of these questions will likely go unanswered with the limited resources available but through a few more experiments perhaps the right key(s) may be found to unlock the potential. I see a number of potential uses from a carbon printing alternative to photogravure, hopefully as alternative techniques that avoid the use of toxic chemicals.

One area that I did not have a chance to experiment with is the effect of resident time of the pigment/gum sitting on the sensitized paper before it is rinsed off. Does this affect the outcome of the resulting print? Further, what about the thickness of the coating? How do we know when we have applied enough?

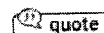
Peter

Back to top



**Botanic88**

Posted: Mon Nov 01, 2010 2:26 pm



Joined: 14 Aug 2010  
Posts: 50

I agree with you Peter about getting to understand the process in order to realise its potential.

My position is a little difficult in that I worked on the process (and two variations) for a number of years, a long time ago. So I have lots of experience but my basic knowledge of chemistry is sparse and shaky! So I don't want to undermine our progress by declaring that such and such is definitely true or untrue.

However I can answer some of your questions with near certainty!

No ferrous salt is involved in hardening the gum. This must be so because ferric chloride works before anything is exposed to sunlight.

Ferric chloride does not in itself harden the gum. If it did then the gum would be hardened when a ferric chloride and gum mixture is acidified with HCL just sufficiently to convert any ferric hydroxide to the chloride.

I always understood that ferric hydroxide coagulates the gum because the former is colloidal (especially when it is first formed) and two colloids with opposite charges do coagulate. I'm not completely certain that this is the mechanism here, but it seems likely. The image washes away if the pH is increased beyond 7, which suggests that electrical charges have something to do with it.

Re. the long exposure times: I think the simple answer is that ferric chloride together with an organic material like gelatine is just not as light-sensitive as ferric oxalate or ferric tartarate complexes etc.

However it will be possible to shorten the exposure times considerably. One way will be to increase the amount of oxalate used and another will be to lessen the amount of ferric chloride that is 'wasted' in producing stains.

Re. leaving the gum 'resident' on the exposed print: My experience tells me that the image is hardened in a few seconds or less. So there is nothing to be gained by leaving the gum in place for a long time before washing. Anyway this is true for the way we are currently working. If we were to change the acidity levels in the sensitiser and/or the gum then it might be otherwise!

Re. the thickness of the gum one applies. I always apply plenty and then sweep the excess back into the container for future use. One could try applying it very thinly and then applying some more on top. In principle this might harden the gum onto the brush but this has never happened to me. On the other hand it might produce some interesting effects if the second coat was a different colour!


I intend to go in two directions when I get round to it. One will be to continue trying to use peroxide or persulphate to produce secondary hardening, so that we can remove the stain. The other will be to test just how little oxalate is required to make a print equivalent to one made with 25 year old paper.

[Back to top](#)

 [profile](#)  [pm](#)

**pgum**

📅 Posted: Wed Nov 03, 2010 3:08 am

 [quote](#)

Michael,

Joined: 19 Oct 2010  
Posts: 52

Actually I was aware that no ferrous salt is involved. I was actually thinking about the another process -the iron + peroxide hardening mechanism when I wrote that.

A few comments on the use of that system

In that system, I found that gum, casein, or gelatin are all hardened or cross-linked when in the presence of a ferrous salt when it transitions (oxidized) to the ferric state. This works for gum arabic but if you attempt to make a print using for instance, ferric ammonium citrate, expose it and then bathe it in say a 0.5% bath of hydrogen peroxide, it will not stay on the print unlike casein or gelatin.

In another test I mixed a ferrous salt with a gum arabic solution and then dropped in some dilute hydrogen peroxide and the gum hardened. It appears to me that gum simply takes a few more milliseconds? or so to harden and by then it has already softened from the immersion and started to lift.

Halvor Bjoerngaard (Chiba system) mentions the problem with gum not hardening but does not give a reason why. His solution is the use of persulfate in the sensitizer. I think this causes the hardening as it is exposed (as with dichromate), so there is no effect of the gum being slow to harden. Also worth mentioning is that a ferrous salt/colloid mix applied to paper will harden overnight as the ferrous will oxidize via oxygen in the air, hardening the colloid in the process. Further, the hardening is quite effective and the prints made

from this system are resistant to dilute acids and water immersion, somewhat reminiscent of dichromate hardened colloids.

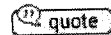
For our usage, it may be possible to bathe the print in a ferrous salt solution and then into a weak peroxide bath in order to perform the requisite hardening of the print. The ferrous salt would have to have a near neutral pH so the ferric hydroxide is not dissolved out. The print may also need to dry before the final acid wash.

Back to top



Botanic88

Posted: Wed Nov 03, 2010 11:46 am



Peter

Joined: 14 Aug 2010  
Posts: 50

I have been scouring the Web recently and it seems to me that there are essentially two ways to harden a colloid.

One way is to crosslink the colloid. This seems to be how dichromates work and also how peroxide or persulphate works when catalysed by ferrous ions (Chiba - free radical polymerisation).

The second way is to coagulate the colloid with an oppositely charged colloidal substance. I think this is how the alums work, as well as ferric chloride. I suspect they work by hydrolysis, which is why they are sensitive to pH levels. (Another example of this second way can occur when two incompatible colloids are mixed!)

When you are using ferrous salts with peroxide or persulphate I suspect that both kinds of hardening occur at the same time! The crosslinking referred to in the Chiba system obviously occurs but ferric ions are also being produced. The latter hydrolyse and harden the gum (because ferric hydroxide can be colloidal).

I have carried out the test you mention.

**Quote:**

In another test I mixed a ferrous salt with a gum arabic solution and then dropped in some dilute hydrogen peroxide and the gum hardened. It appears to me that gum simply takes a few more milliseconds? or so to harden and by then it has already softened from the immersion and started to lift.

I think that 'double hardening' accounts for these results. The ferric hydroxide hardening will happen almost instantaneously whilst the polymerisation will be slower.

Currently AlternativePhotography is the only forum I post to. So if you want to check out these assumptions by posting them on another site, that would be fine! ☺

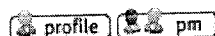
Returning to one of your earlier posts - you thought about trying glyoxal. I have found some evidence that suggests it might work.

<http://www.usask.ca/lists/alt-photo-process/2005/may05/0309.htm>

I found a number of threads with posts by Katherine Thayer. One suggested that a single drop hardened the gum too much! Another that it could give the gum a sugary or crystalline texture.

But it seems to me that it would be worthwhile to give glyoxal a try. Would you like to try it or shall I (no point in us both wasting money if it is no good at all)?

Michael



Back to top


Display posts from previous:


All times are GMT

[View next topic](#)  
[View previous topic](#)

Page **2** of **15**  
Goto page [Previous](#) [1](#), [2](#), [3](#), ... [13](#), [14](#), [15](#) [Next](#)

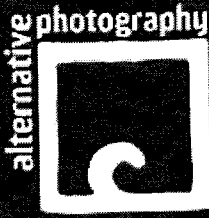
**AlternativePhotography.com Forum Index > All other processes**

 [newtopic](#)

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< Ferric Gum Process

pgum

Posted: Wed Nov 03, 2010 11:19 pm

quote

Michael,

Joined: 19 Oct 2010  
Posts: 52

I received a price from a local supplier of small chemical quantities and they quoted me \$60.00 cdn for 100 ml of glyoxal 40%...how outrageous! I think it was a get lost price!. I may try to shop around but selection is very limited. I do know that prices from suppliers in the US put it around \$9.00, so right now it is out of reach. Perhaps you have better access.

As far as the hydrolysis goes, I don't think it is occurring when using ferric ammonium citrate in the Chiba system. I say this because I am aware that the citrate is a strong chelator. Even in mildly alkaline conditions, this salt will not precipitate hydroxide. If it is mixed with gum and dried as the ferric salt, it will completely wash out without leaving any residual iron in both unexposed and exposed areas but will still harden these colloids after peroxide immersion. Before peroxide immersion (which is when I would expect the hydrolysis to appear), there is a minimal photo-effect.

Peter

Back to top

profile pm

Botanic88

Posted: Fri Nov 05, 2010 11:44 am

quote

Peter

Joined: 14 Aug 2010  
Posts: 50

I tried to buy some glyoxal in the UK yesterday but suppliers will only deal with registered companies not working from residential addresses! Eventually I may have to buy some from Korea/Japan on a site included on ebay, but it is over £20 (500gm minimum quantity) which is rather a lot for something that may not work at all!

Meanwhile I have e-mailed Katherine Thayer who posted stuff about glyoxal and gum back in 2004. I hope she may be able to give us more information.

From your latest post I guess you have tried the Chiba system using gum and persulphate. How robust is the hardened gum in this process? Halvor seems to suggest it's not very robust.

From the Chiba System 2007

"The gelatine layer is, after clearing, relatively strong and consistent. The polymerized gum is less strong than the gelatine, leaving it for extended periods in water will dissolve the print."

Apart from a lack of strength, the idea of adding even more stain by bathing in ferrous sulphate followed by peroxide strikes me as less than elegant, but I will try it!

Another possibility might be to use the ferric hydroxide that is already there. This ought not to work but Halvor mentions a 'dark reaction' which should only involve ferric salts.

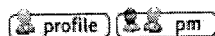
Something connected with this possibility: I discovered something strange a few weeks ago. I had soaked a 'ferric hydroxide gum' image in peroxide (and probaly some EDTA) and left it around damp. After some hours



the hydroxide started turning light green! This suggests that the ferric hydroxide was being changed to a ferrous salt (not impossible - see Fenton's Reaction). The gum had also hardened but it was rather lumpy and not nearly as good as our ferric hydroxide hardened gum.

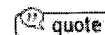
Michael

[Back to top](#)



**pgum**

Posted: Fri Nov 05, 2010 9:49 pm



Michael,

Joined: 19 Oct 2010  
Posts: 52

I may yet try to obtain some glyoxal from a US company (\$8.95/100ml). Ill see what they charge for shipping.

If I recall correctly, I found that the hardened gum in the Chiba system did not dissolve off of the print to any noticeable amount after about 1 hr immersion. I did not try for any longer. I think this would probably suffice for this technique. It may be a good idea to make a print and soak it to confirm this.

Re ferrous baths

I had best results with dilute ferrous acetate. I found that my ferrous sulfate washed the gum off. It may be something to do with the acidity of this salt but you should see what you get because my ferrous sulfate is a solution and it has additional acid to keep it from oxidizing.

What I did:

-3 min soak in about a 1% soln of ferrous acetate after the print was developed and still wet.

-hang to dry for a couple of hours

wash in 5% acetic acid (white vinegar) with about 0.5% hydrogen peroxide for a bout 5 mins with gentle rocking. I used vinegar because other stronger acids including sodium bisulfate were still too aggressive towards the gum although they did a better job of clearing the iron

The peroxide aids iron removal and ensures that any Fe2 gets oxidized.

Results

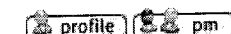
By eye only I would say that about 2/3 of the iron was washed out. Longer soaks in the final bath causes gum losses. A similar print not treated was also run through the final wash bath and the gum was pretty well washed out in a couple of minutes, so it is harder after the treatment but still not as hard as dichromate gum which can sit in strong bisulfate for hours without loss according to a test I did.

If the iron that is there can be used, that would be best but I am not sure if there is enough there or how to make it active without dissolving it out, although perhaps that is what you achieved by leaving it for several hours in the peroxide. Maybe a long peroxide soak, then hung up to dry would harden the gum.

Another option may be to add some type of additive to the initial gum/ ferric chloride mix but that may be another can of worms to be left for another day.

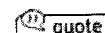
Peter

[Back to top](#)



**Botanic88**

Posted: Sun Nov 07, 2010 2:33 pm



Peter

Thanks for various bits of information. I feel more confident pursuing the peroxide/persulphate route now

Joined: 14 Aug 2010  
Posts: 50

you tell me that the product from Chiba/gum is reasonably washable. So I am doing a test as I write!

I prepared five pairs of ferric hardened gum images. After drying I soaked these in various strengths of ferrous sulphate soln (no problems here; your ferrous sulphate was probably too acid as you thought). I dried these to a fair extent. Then I put one of each pair into peroxide (roughly 1%) and the other of each pair into persulphate (10% or less). They are getting a good long soaking in these baths now. Later I will wash and dry them and tomorrow I will try to clear them (probably in slightly acidified EDTA).

The fact that ferric citrate can go to pH 7 without hydrolysis may well prove useful.

I have looked at Halvor's thesis on Chiba again and I note that he doesn't mention the reverse chemical reaction, by which peroxide reduces ferric salts to ferrous as well as oxidising ferrous to ferric. However articles on Fenton's reagent clearly state this fact. They treat ferrous sulphate as a catalyst in such reactions.

Halvor mentions the possibility that catalysis might be involved in connection with the 'dark' reaction. If it is then it would mean that a little iron would go a long way!

Finally, Katherine Thayer got back to me but she has no further information on glyoxal and gum. She cannot believe that our process actually works but that is another matter! After seeing a print (either yours or Frank's) she admits something must be going on!

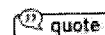
Michael

Back to top



pgum

Posted: Mon Nov 08, 2010 3:16 am



Michael,

I am looking forward to hearing about these test results.

If your test prints can withstand the ferrous sulfate, that is encouraging. How long did you soak them and at what strength?

I didn't explain my choice of ferrous acetate. I used it because: 1- the pH is not too low ( I measured around 5.0), and I could make it easily by heating some steel wool and vinegar in a pot for a couple of ours. It is also very readily oxidized which is good for this project. It is odd in that, as the solution absorbs oxygen at the surface, a dark garnet coloured crust forms as crystals that eventually fall to the bottom of the container suggesting that the ferric salt is poorly soluble. If ferrous sulfate works for the task, all the better.

Re Fentons reaction, or reagent. Potassium ferricyanide makes a sensitive test for ferrous ion (blue precipitate), so it may be useful if you wanted to test for it while the peroxide is acting on it. I do have some of this salt which I use for making cyanotypes.

Hopefully this secondary iron treatment will suffice, but I guess we will soon find out with your tests. I agree that the added iron soak is inelegant but it is a very safe technique in terms of toxicity. Having said this, I will test glyoxal hopefully in a week or so, since I purchased some from the US. I picked up a couple more items that have floated on my wish list for years, so the shipping becomes a little more worthwhile.

P.S.

I did read that post you had linked to written by Katherine Thayer, and that was something that pushed me further to want to try glyoxal. I believe that her notes and comments are pretty trustworthy as she seems to have plenty of experience in working with gum. In fact her web site is a great resource and I think in fact one of the best resources that I am aware of for gum printers who wish to learn and better yet, understand the process. I have referred to it many times in the past.

Peter

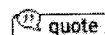
Joined: 19 Oct 2010  
Posts: 52

[Back to top](#)



**Botanic88**

Posted: Mon Nov 08, 2010 11:20 am



Peter

Joined: 14 Aug 2010  
Posts: 50

My ferrous sulphate ranged between roughly 10% and 1% (volume of crystals to water) as judged by eye. I bathed each sample for about 10 mins but the salt would have continued to diffuse through the gum during the lengthy drying time.

Everything went fine when I bathed each sample in peroxide or persulphate for about 1 hour. Then I washed the samples and left them to dry. Then things started to go wrong, even though I had added nothing to remove the stain yet!

It seemed to me that the gum was pretty swelled and it was taking a long time to shrink and dry. In retrospect I have seen this before, after using peroxide/persulphate. Anyway I think there is less gum this morning than there was originally, especially in the samples where the strongest ferrous sulphate soln was used.

So I have come up with another speculation 🤔  
Perhaps the gum is being polymerised whilst it is in its swelled state and this prevents it losing water readily and ultimately it weakens the gum. In the Chiba system the gum is polymerised in its shrunken 'dry' state.

So my next step will be to copy the Chiba system more faithfully and in particular to create the 'dark' reaction in the dried gum. I may use some citric acid to make ferric citrate from ferric hydroxide as I don't have any ammonium ferric citrate.

I'm very pleased you are getting some glyoxal. From Katherine Thayer's posts I gather she simply mixed it with some pigmented gum and brushed it onto some paper. Then she dried it and later washed it and it was insoluble!

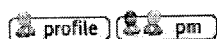
I have also seen something recently about glyoxal being used in the past in paper making. It was used to harden the binder that holds the manufacturer's pigments onto the paper. Apparently glyoxal has now been replaced by a zirconium salt because the glyoxal doesn't work with buffered paper. It prefers a slightly acid environment (like ours!)

Katherine Thayer seems keen to continue the conversation. I am tempted to ask her to repeat her earlier experiment with glyoxal and gum and to give the results a really prolonged wash to see what happens.

Also I have now subscribed to the Alt-Photo list and I am tempted to ask people how alums harden gelatine and to suggest that the same mechanism could be happening with ferric chloride and gum.

Michael

[Back to top](#)



**pgum**

Posted: Mon Nov 08, 2010 10:04 pm



Michael,

Joined: 19 Oct 2010  
Posts: 52

I know that the hardening in the peroxide/persulfate in the bath when using casein or gelatin only takes a few seconds to act ( a few seconds longer with gum I speculate, but still very fast). It may be worthwhile to just drop the print in for 30 seconds or so, then hang to dry. Somehow I recall some type of reversal going on with prolonged soaks at least when I used casein or gelatin.

The other option is to just let the print dry overnight after the ferrous treatment. I believe (at least with ferrous acetate) that the air will oxidize the ferrous while it hangs (the paper should darken to a dark tan) and may act like the peroxide without having to soak it, then go straight to the iron wash out.

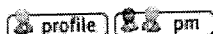
Another thing that might be worth trying is to exclude the whole ferric chloride component and mix some

ferrous sulfate with fresh gum/pigment, paint it on to paper and let it dry overnight , then dip one in water and the other in peroxide/hang to dry and check for hardness in the final iron wash.

As far as alum goes, I am not sure myself how it works but I did try using potassium alum in some washes with the ferric gum process, but at least with my particular concoction, it did not seem to help with keeping the gum on the paper.

Peter

[Back to top](#)



**Botanic88**

Posted: Tue Nov 09, 2010 11:30 am



Peter

Joined: 14 Aug 2010  
Posts: 50

I cleared the ferric stain from my earlier test pieces this morning and they sort of worked, in that some of the gum survived the EDTA + a little oxalic acid and all the stain was cleared. But the cleared gum is very fragile so I'm not convinced yet.

The reason for the lengthy peroxide bath was that Halvor soaked his Chiba Carbon prints for 30 minutes. Presumably his gelatine coatings were much thicker than his gum prints. Our process should also be able to deal with fairly thick gum images eventually.

So polymerisation (as used in Chiba) does seem to work in the context of gum that has been already hardened using ferric chloride. But the fragility of the polymerised gum worries me.

I have set up a small test piece with some ferric chloride and tartaric acid mixed into gum and then roughly 10% persulphate mixed in as well. This is brushed onto paper. So I'm hoping it will polymerise by the 'dark' reaction (together with some reduction of the ferric tartarate by ambient light). It is as near as I can get to Chiba with stuff I've got at hand!

Katherine Thayer said she would test some glyoxal for me. Just to repeat the experiment she did 6 years ago and see how long the hardened gum will survive in water and how much it will swell.

If glyoxal gives a more robust hardening it will certainly be a relief! I hope you will be able to try it soon. I have looked at its properties and it is a strong reducing agent. This could be really good for us or really bad! Also it is 'incompatible' with iron salts but I cannot find out what it actually does with them (apart from reducing ferric to ferrous no doubt).

Michael

[Back to top](#)



**pgum**

Posted: Wed Nov 10, 2010 12:33 am



Michael,

Joined: 19 Oct 2010  
Posts: 52

At best, I found the secondary iron treatments to "sort of work" as you say. One thing I noticed was blistering in dense areas, and pieces of gum sloughed off in bits. It makes sense that these bits did get crosslinked because they are still in a gelled state in my acid wash bath.

My main concern right now is whether going from an initial physical crosslink with the ferric hydroxide to a chemical one with a post treatment has a negative effect on adhesion in general, or is it specific to the iron-peroxide/persulfate method.

If I get a chance, I will try a post dichromate crosslink on a dense print and watch it a little more closely in the acid bath to see if any problems surface.


Peter

[Back to top](#)

 [profile](#)  [pm](#)

**Botanic88**

Posted: Wed Nov 10, 2010 3:10 pm

 [quote](#)

Peter

Joined: 14 Aug 2010  
Posts: 50

Okay, it's possible that peroxide/persulphate fixing will turn out to be inadequate, although I've not given up entirely on it!

Testing your 'chemically reduced dichromate' again is an excellent idea. Dichromates are annoyingly good!

When your glyoxal arrives I guess it will be quick to get some idea of its potential, especially if it has no chance of working!

If glyoxal turns out to be useless, where would you like to go next (assuming you are happy to stay with the process)? From my past experience the directions we could take are as follows:

(1) Stick with dichromate. How harmful to the environment would this be? If we have a dilute solution and only soak well washed prints in it, couldn't we use the same solution for a very long time? And wouldn't all the dichromate on the prints get reduced to chromium (III) compounds?

(2) Explore a 'negative working' version of the process. This uses considerably more oxalate and it has much shorter exposures. The iron stain is much reduced, with little or none in the highlights. This version is tricky to get right but I think careful measurement would make it reliable. Currently it uses small amounts of dichromate but it may be possible to replace these with peroxide/persulphate. It involves two kinds of fixing at the same time, so peroxide/persulphate might work here.

(3) Push the basic process to its limits in terms of efficiency. This would involve doing things with acid levels (and possibly buffers) both in the sensitiser and in the gum. The more we make the ferric chloride do useful work the less stain there would be (but it would never be zero).

(4) Try other colloids. Ferric chloride fixes gelatine but it is not so robust as with gum. My results in the past have been less sharp than with gum, but I think this was partly caused whilst dissolving away the unhardened gelatine. It could be corrected I think. Then there is casein!

(5) Continue work with the basic process by looking for another way to fix the gum prior to clearing the iron stain.

This forward planning is not intended to mean that I want to give up on clearing the stain in the basic process. Hey, glyoxal may even work! But I would like to know where you would like to go, if anywhere, if we continue to come up against a brick wall.

Michael

[Back to top](#)

 [profile](#)  [pm](#)


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[View next topic](#)  
[View previous topic](#)

Page 3 of 15  
Goto page [Previous](#) [1](#), [2](#), [3](#), [4](#) ... [13](#), [14](#), [15](#) [Next](#)

[AlternativePhotography.com Forum Index](#) > [All other processes](#)

 [newtopic](#)

 [postreply](#)

Jump to: [All other processes](#) [Go](#)

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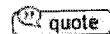
Author

Message

< Ferric Gum Process

pgum

Posted: Thu Nov 11, 2010 12:03 am



Joined: 19 Oct 2010  
Posts: 52

Michael,

I tested the following:

- 1-Gum arabic- dichromate hardening treatment
- 2-Gelatin using ferrous salt /peroxide hardening treatment

Dichromate

- bathed in a 1% dichromate bath for about 5 minutes
- hung to dry
- exposed to UV for 1 hr ( usually 5 mins with my uv and gum bichromate printing)
- rinsed
- acid wash in dilute sodium bisulfate

All of the visible iron was removed in about 2 minutes with gentle rocking. After about 8 mins, very fine insoluble flakes broke off of the heavily exposed areas. The smallness of these bits probably indicates strong crosslinking. Larger sloughing would occur if the gum was much softer. There was ample time to remove the iron but it still indicates an issue with adhesion which makes me uncomfortable. It would be a shame to have a dried print that starts to flake years down the road due to temp/humidity cycling.

Gelatin

20% w/v warmed gelatin was mixed with Ivory black and applied to an exposed ferric chloride print, then...

- rinsed in water just warm enough to melt off the excess and clear the print
- hung to dry
- bathe in 1% ferrous citrate (not acetate as previous tests) for about 2 minutes
- bathe in 1% H<sub>2</sub>O<sub>2</sub> for about 1 minute while print is still wet from ferrous treatment
- hang to dry
- acid wash in dilute sodium bisulfate

The print showed good density -comparable to gum but a bit more mottled. It withstood the acid wash even after a one hour soak. I then ran it under a warm stream of water (about 35 C) for about 1/2 minute and it lost very little density and no flaking occurred. A parallel print was subjected to the same steps without the ferrous treatment and it slowly lost density in the acid wash and upon rinsing in a stream of water, it was ruined.

I know that the iron-peroxide system is very effective with gelatin because I have made prints with this system before (Chiba). Further I also know that gelatin films are much tougher than gum, as gum films are fairly brittle. These two properties likely account for the success. Further, it may be possible to skip the drying step from the initial washed print to the ferrous bath. This is all very encouraging to me. 😊

On the other hand, I don't really enjoy working with heated gelatine as it tends to make for a lumpy coating. I also find that the coating properties in terms of flow etc are inferior to gum. Fish gelatin may be an option

as it is liquid at RT, or one can hydrolyse pig gelatin with some pineapple enzyme or alkali/acid and heat. I have done this before but you have to be careful going too far.

As far as looking ahead, I am not there yet. I have not been able to match the scale range and print density of this process in one go using the gum bichromate process, so it will be made to work.


Peter

[Back to top](#)

 [profile](#)  [pm](#)

**Botanic88**

📅 Posted: Thu Nov 11, 2010 2:00 pm

 [quote](#)

Peter

Joined: 14 Aug 2010  
Posts: 50

Firstly I get the feeling that you are well motivated to continue with this process 😊

I have had bits of image flaking off before, but not with most of my stuff, which is over 25 years old. It might happen because the 'fixing' doesn't work so well across the gum/paper interface but I suspect the real reason is as follows.

The iron stain that you see in the highlights also occurs under the gum in the other areas. If this stain is a thin layer of iron compound then clearing it would also detach the gum. If this is true then it could be solved by reducing the amount of stain deposited on the paper in the first place. Alternatively it could be solved in a more complicated way by sizing the paper so that the stain is held within the size. Fortunately most of the improvements we are likely to make to the basic process also happen to reduce the amounts of stain.

So you have tried the process with gelatine. I completely agree with your preference for gum but in the end it could just be so much simpler to use gelatine! In the past I also thought about trying to make gelatine liquid at room temperature, but I had no idea how to do it. So I was interested when I read your reference to bromelain in your casein post. I have also come across stuff about a Norland product (which is a kind of fish gelatine I think) but it is not sold in the UK.

I have done the process with gelatine in the past. The gelatine behaved very much like you described when you did it without any secondary hardening. However you may have produced sharper prints than me because you did some things differently.

In the past I could always clear my gelatine prints by letting the gelatine set thoroughly and doing the clearing in cold water. However this probably made them fluffy due to extra swelling. I guess there would be simpler ways than using the 'Chiba mechanism' to prevent this swelling, if we do decide to go down the gelatine route.


Michael

[Back to top](#)

 [profile](#)  [pm](#)

**pgum**

📅 Posted: Fri Nov 12, 2010 2:20 am

 [quote](#)

Michael,

Joined: 19 Oct 2010  
Posts: 52

Regarding your adhesion hypothesis:

I was thinking along the same lines however it doesn't explain the excellent adhesion of re-crosslinked gelatine after one hour in an acidic bath.

One thing I did notice is that the gum thickens almost instantaneously as it is applied, yet the gelatine seems to act a little more slowly. I think it may be that the gum does not have enough time to sink in and hardens more on top of the paper whereas the gelatine has time to sink deeper and slip under and around the paper fibers to find some "tooth". A little more acidity in the sensitizer may help here if this is the case.

It will be interesting to see how all of this plays out with multiple coats, if this is at all possible. The gum



bichromate process gives each layer plenty of time to sink into the paper and also, to bond with successive ones, so it may win on this one. We will see.

On another note, I found that the gelatine image can be strengthened if it is soaked in an alkaline bath rather than water. Oddly, such an alkaline bath weakens those made with gum.

Looks like glyoxal will be available Monday.

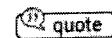
Peter

[Back to top](#)



**Botanic88**

Posted: Fri Nov 12, 2010 2:23 pm



Peter

Joined: 14 Aug 2010  
Posts: 50

Okay, the adhesion problem requires some more understanding. I hadn't noticed the difference in fixing times between gum and gelatine in the past, probably because I used to work with either one or other colloid quite separately. So, well noticed 😊

Re. multiple coats. It is certainly possible to use them. Each coat seems to act like a size for the next one. However I think it may lead to some strange (interesting) effects. The ferric chloride is likely to diffuse into the moving gum at different rates, depending on whether it is held in the paper surface or in one of the earlier coats of gum. Also the sensitiser may get less exposure when it is in areas of darkly pigmented gum.

Re. the effect of pH on the strength of the hardened colloid. In the past I always found that ferric hardened gum withstood soaking overnight, provided the water was slightly acidic (normally it was because the acid remaining in the print made it so). This is why I wasn't surprised when Frank said his test pieces remained intact next morning. However I have also found that changing the water many times can make the print less stable. This is one reason why I thought the hardening was essentially 'electrostatic'. So I don't find it odd that the hardened gum is weakened by dilute alkali.

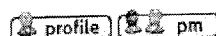
However two of Katherine Thayer's extended family of scientists are doubtful that colloidal charges would have enough energy to achieve the hardening effect. One of them thinks the hardening may be more like crosslinking with dichromate.

So I need to know what you mean when you say the gelatine is strengthened by alkali. Do you mean that the 'cold set' gelatine is strengthened or are you thinking that the 'ferric bond' itself is being strengthened?

Finally it is good that the glyoxal is going to arrive! Can you try one thing for me? Can you simply add some glyoxal to some gum and try to discover when the crosslinking is effectively happening. Does the glyoxal harden the gum gradually over time, or does it only harden it when the gum has dried out?

Michael

[Back to top](#)



**pgum**

Posted: Fri Nov 12, 2010 7:36 pm



Michael,

Joined: 19 Oct 2010  
Posts: 52

The print after being coated with gelatine, was immersed in a warm sodium bicarbonate solution and the result was more gelatine and pigment adhering to the paper. My first thought is that the alkalinity increases the amount of hydrolysis before some of the ferric chloride gets dissolved out, but this is little more than a guess. Why do the gum and gelatine behave oppositely? For now, I will leave this effect alone and work on the iron removal problem.

I am still doubtful on the speculation of a chemical-type crosslink. The evidence of loss of the coagulum of gum when the iron is dissolved out suggests something physical. If the crosslink was due to a chemical change in the gum, simple dissolution of the iron in the acid wash bath or with EDTA should not undo the

linkage I would suspect. As far as I know, a chemical crosslink can be broken by other chemical reactions or use of enzymes but I don't see anything like that happening in the final wash.

When I have the glyoxal, I will test it mixed with gum at varying proportions and note how it changes over time.

Here is an interesting link on the use of alum in paper sizing. It think this may help us to understand this process.

<http://www.wovepaper.co.uk/alumessay3.html>

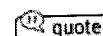
Peter

Back to top



**Botanic88**

Posted: Sat Nov 13, 2010 3:54 pm



Joined: 14 Aug 2010  
Posts: 50

Peter

Thanks for the link. I will look at it more carefully when I have time. Also I am not going to forget the adhesion problem. I can see this may be more important than I had thought.

Re. alkalinity and the odd difference between gum and gelatine. Is it possible that the gelatine is not actually being made alkaline? The sodium bicarbonate could be reacting with the HCL that is around, and being converted to NaCl plus carbonic acid!

Re. the 'bond' involved when gum is fixed by ferric chloride. As you know I tend to agree with you on this, but there are these scientist saying they think it is likely to be crosslinking.

I have written down some evidence which supports the idea that the fixing at least coincides with the formation of colloidal ferric hydroxide. I will e-mail it to Katherine Thayer in the hope that her family of scientists might think more about the matter. Here is the evidence:-

If ferric chloride solution is added to 'liquid' gum arabic, then the gum is fixed so that it's no longer liquid and it becomes insoluble in water. Colloidal ferric hydroxide also appears to form when the ferric chloride solution is added to the gum.

According to my experience the fixing of the gum pretty much coincides with the formation of the colloidal ferric hydroxide. This coincidence doesn't mean that the fixing is caused by any surface charges on the two colloids but it is tempting to think it might be!

My evidence for the coincidence between the formation of colloidal ferric hydroxide and the fixing of the gum is as follows.

Some 'liquid' gum is mixed in a glass vessel such that it is viscous but still pourable. Fairly strong ferric chloride solution is added, a few drops at a time. The ferric chloride permeates the gum, which takes on a rich translucent brown colour. This looks like colloidal ferric hydroxide to me. The result is that the gum ceases to be liquid and sticky. Sometimes it is possible to take the gum out and drop it on a hard floor, whereupon it bounces like a rubber ball.

Dilute hydrochloric acid is slowly added to some fixed gum which has been formed in the above manner. The gum becomes liquid at the point when the last of the brown colour disappears. If the gum is then thrown into water it turns brown and it is fixed again.

Alkali is added to some fresh 'liquid' gum and then ferric chloride solution is added. The result is a more opaque brown, which doesn't appear colloidal. In this case the gum is either poorly fixed or not fixed at all.

If gum is fixed and translucent then it seems to be stable in water more or less indefinitely, provided the pH is below 7. However it can weaken slowly if the pH is above 7.

One more piece of evidence. If the ferric chloride solution is brushed onto paper and dried and then 'liquid' gum is brushed over it, the gum gets fixed in the same way as it does when no paper is involved. However if hydrochloric acid is added to the 'liquid' gum before it is brushed on, then the result is a little different. The fixing appears to occur before the formation of the translucent brown colour. Furthermore it is possible to add just enough acid so that the fixing occurs without any brown colour appearing, or only appearing after several seconds. If more acid is added then no fixing occurs. This marginal result is interesting. Is there some colloidal ferric hydroxide there but not enough to see?

Michael

Back to top



pgum

Posted: Tue Nov 16, 2010 6:45 pm



Michael,

I used an excess of bicarbonate so I suspect that the bath was in an alkaline state.

It may be that the salts produced in the gelatine print alkaline bath are having some effect. What also complicates this is the charge of both the hydroxide and gelatine which changes with pH. I know that the gelatine I am using is food grade and is made by acid hydrolysis. The charge on it is negative above pH 7-8, and positive below. The ferric hydroxide also has a pH dependent charge, being positive below pH 7.5. The charge weakens for a range above this so perhaps this explains the loss of coagulation with gum arabic.

I have also learned that ferric chloride is used in water treatment where it aggregates organic matter as it hydrolyses to ferric hydroxide. Your evidence still seems to suggest a colloid hardening.

I am not sure if the hydroxide colloid can be invisible and still harden the gum.

Glyoxal

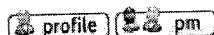
I started a few tests with glyoxal and a few prints have been bathed in a 1% solution for about 5 minutes and then hung up to air dry for a few hours.

Gum-glyoxal test

I placed three drops of glyoxal 40% solution into 5ml of a 30% gum solution. So far, after 4 hours, the gum remains liquid but on the sidewall with the interface to air the gum is showing a gelling effect. I am not sure whether it needs oxygen to react, or if it is just the dry down at the edge that is causing this. I will know soon enough. I will post more on all of this shortly.

Peter

Back to top



Botanic88

Posted: Wed Nov 17, 2010 12:04 pm



Peter

Joined: 14 Aug 2010  
Posts: 50

Okay, lots of directions to go in but not all in one e-mail! I read the article about alum and paper from your link more thoroughly, but more about that later.

Katherine Thayer has been testing glyoxal and gum in various ways. She already uses glyoxal but she needed to buy some ferric chloride. I will read all her e-mails again and post my summary of her results.

However you may find two results immediately useful. Firstly she couldn't get the glyoxal to fix gum as well as it had done years ago. She suspected that her current gum is not 'proper' in some way. But she has now made the basic 'glyoxal fixing' work (with a different shipment of gum I think). You may need to be aware of this in case your gum doesn't fix well, even when no 'ferric fixing' has been involved.

Secondly the 'glyoxal fixing' either needs time to work or it may be quicker if the 'glyoxal and gum' are dried out. So it won't surprise you to learn that the glyoxal can be added to the gum before they are brushed onto the ferric chloride. Obviously the soft gum has to be washed away without any intermediate drying in this situation, and it's not clear whether the glyoxal also diffuses out from the 'ferric fixed' part of the image during the wash.

Now to your discussion about alkalinity and in particular the acidity and iso-electric points of the gum or gelatine. To be honest I wasn't even aware that the 'supermarket' food gelatine was made by acid processing and therefore has a high iso-electric point. I must research stuff better in future! I think this might help to explain some of the different behaviours of gum and gelatine, because their iso-electric points are wildly different.

However, after reading more stuff I am now torn between the 'ferric fixing' being a matter of 'opposite charges' or whether it involves some kind of crosslinking.

If it involves crosslinking then it is not as stable against acids and alkalis as the crosslinking that results from the reduction of dichromate. But I think 'ferric fixing' could well be analogous to alum hardening and if one involves crosslinking then so would the other.

One factor in my thinking is that I had assumed in the past that hydrolysis of ferric chloride always resulted in ferric hydroxide but this is not necessarily so. It seems that the brown colour in ferric chloride solutions comes from 'hydrated' ions but not hydroxide.

Another factor in my thinking concerns with the way ferric chloride visibly changes gum, especially when the gum is made more acidic. I've mentioned this before. The fixing happens first and then the image becomes brown over the next few seconds.

In the past I reasoned that 'excess' ferric hydroxide was being produced. But if this was true it should be possible to get thicker gum reliefs by lessening the production of this 'excess' ferric hydroxide (e.g. by acidifying the gum more). But I simply could not make this happen. The thickness of the relief seems wholly dependent on the concentration of the ferric chloride.



So maybe no ferric hydroxide is produced! Then there would be no 'excess' hydroxide! It could be that the ferric 'hydrates' crosslink the gum and that they then turn from one variety (and colour) to another without destroying the crosslinks. I think I read somewhere that the chromium ion changes from valency 6 through to 5 and eventually to 3 when dichromate crosslinking occurs.

However the fact that 'ferric fixing' is so affected by pH does seem to favour the 'opposite charges' hypothesis! Do we know how much alum hardening is affected by changes in pH after the hardening has been done?

Good luck with your glyoxal 😊


Michael

[Back to top](#)

 [profile](#)  [pm](#)

**pgum**

📅 Posted: Wed Nov 17, 2010 9:43 pm

 [quote](#)

Michael

Joined: 19 Oct 2010  
Posts: 52

The gum I use is mixed up from powder which is about a year old from the purchase date and I mixed the current batch of solution about three days ago. The gum is from a company that uses it to make tube watercolour paints and looks to be good quality. It has a slight tan colour in solution and has an almost edible aroma. I have noticed that after several months, this solution can acquire a slight sour smell but this is not the case with this batch. This is not to say that this gum is good for this process but I am assuming that it is for now.

First Run Results with Glyoxal

The gum/glyoxal mix in a bottle still remains liquid after about 30 hours. The sides still have hardened gum.

After the initial water development and dry down, the prints were bathed in a 0.4% glyoxal solution for 5 minutes, then hung to dry. The prints were then bathed in a 1% w/v sodium bisulfate solution for removal of iron. Prints that were acid bathed within a few hours of being dried, did not survive well. The gum started to dissolve out immediately.

Prints that were dried overnight (about 18 hours) showed better resistance. They were bathed for about 5 minutes in the acid bath, with gentle rocking without any noticeable loss of gum. This was not possible with the ferrous/peroxide treatment of before and I had resorted to using acetic acid because they were so vulnerable. I then washed the prints in a tray of cold water for about 5 minutes, with gentle rocking and they withstood the rinse well. They were hung up to dry but some comet like streaks were evident emanating from heavy shadow regions indicating some dissolution. The slight gloss in the gum areas was smooth without any noticeable change in texture from the original untreated print (before the glyoxal and acid bath).

I then placed one of these still wet prints in water, and another back in the acid bath. After about 10 minutes, the gum started to wash off and not just peeling off but actually dissolving. The same result occurred in water but this took longer -about 15 minutes. I then tried a prolonged bathing on treated dried prints, and the gum eventually started to dissolve.



It is possible that the crosslinking is insufficient with a 0.4% bath. Literature I have found suggests a range of 1-3% for gelatine and I believe many gum printers use 2% in sizing. I will have a couple more prints to test tomorrow after bathing them in a 1% and 2% solution, so we will see if this improves things. Also, for comparison, a few gelatine prints will be hardened with these glyoxal strengths.

FYI The gelatine prints I am making are using a dilute sodium bicarbonate bath as it significantly strengthens the image. If the bicarbonate is added directly to the gelatine, no image results. I guess we need the ferric chloride to diffuse into the gelatine before the bicarbonate acts.

I also found an interesting trick to keep the gelatine liquid at RT. The addition of calcium chloride serves the purpose well. The amount of chloride I am using is a 20% w/v in a solution of 20% w/v gelatine in water. Even at 10 deg C, the gelatine remains liquid. Not sure if the 20% chloride is excessive, I just started at that point. The chloride salt also seems to have a strengthening effect. From what I gather, strong salt solutions seem to stimulate coagulation, so perhaps that is what is happening here.

Peter

[Back to top](#)

 [profile](#)  [pm](#)

**Botanic88**

Posted: Thu Nov 18, 2010 2:05 pm

 [quote](#)

Peter

Joined: 14 Aug 2010  
Posts: 50

This is looking good 

Let me get some 'housekeeping' things out of the way first.

Katherine Thayer wants to post a summary of her results and thoughts herself. Although she can read this thread she cannot post to it for some reason. So I will put her summary in one of my posts when it arrives.

I have decided to keep both the 'opposite charges' and the 'crosslinking' hypotheses in my head together until we get a definite answer. So I may add comments in brackets about the meaning of any particular observation for each of these hypotheses. This will help me to judge how well each hypothesis fits our observations.

Re. the gum. My gum is at least 35 years old! It is mostly in knobby extrusions and it includes bits of vegetation! So I think we can safely say that virtually any gum arabic can be fixed by ferric chloride. Being fixed by glyoxal may be a different matter.

**Quote:**

The gelatine prints I am making are using a dilute sodium bicarbonate bath as it significantly strengthens the image. If the bicarbonate is added directly to the gelatine, no image results. I guess we need the ferric chloride to diffuse into the gelatine before the bicarbonate acts.

I have always found that adding alkali to gum in order to help make the colloidal ferric hydroxide doesn't work. If a colloid is indeed formed then it only fixes the gum if the gum itself is involved in making the colloid (by some kind of 'buffering' action). It doesn't surprise me that the same kind of thing applies with gelatine. But adding the bicarbonate to a gelatine image afterwards sounds good.

**Quote:**


I also found an interesting trick to keep the gelatine liquid at RT. The addition of calcium chloride serves the purpose well. The amount of chloride I am using is a 20% w/v in a solution of 20% w/v gelatine in water. Even at 10 deg C, the gelatine remains liquid.

I used to have some calcium chloride and I added it to gum sometimes (along with goodness knows what else - I was clutching at straws). I think this gave me a really thick image on one occasion, but it got spoiled and I never managed to repeat it. Or it might just have been a delusion!

**Quote:**

The prints were then bathed in a 1% w/v sodium bisulfate solution for removal of iron.

Are you saying this is a simple and relatively gentle way to remove the iron compounds? It sounds good.

And now to the main point 

Your results from bathing 'ferric fixed' prints in glyoxal seem to say that the 'glyoxal fixing' works and that it can hold the image in place even when the iron compounds are removed. Furthermore I get the impression that the longer the glyoxal is left in place before the iron is removed, the better.

Is this correct? If so then I would be quite happy to leave a good print for several days before finally clearing the iron stains!

Michael

[Back to top](#)

 [profile](#)  [pm](#)


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Page 4 of 15  
Goto page [Previous](#) [1](#), [2](#), [3](#), [4](#), [5](#) ... [13](#), [14](#), [15](#) [Next](#)

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< Ferric Gum Process

Botanic88

Posted: Thu Nov 18, 2010 3:56 pm



Joined: 14 Aug 2010  
Posts: 50

Here is Katherine Thayer's summary of her work on this process so far.

Greetings folks,

When Michael approached me with questions about glyoxal, he sent me a link to this discussion along with links to his two articles about ferric gum on the alternativephotograph site, and I've been watching the discussion out of the corner of my eye while I've been conducting parallel investigations. I would join the discussion myself, except that for some reason my system has always had some incompatibility with that site and I am unable to register and post there, so I've asked Michael to post this for me.

As Michael has suggested, my first effort at replicating my brief earlier (5-6 years ago) experiments at hardening gum with glyoxal, per his request, was not successful in that even though with increasing time from mixing and brushing the glyoxal and gum, it took longer for the gum to dissolve off the paper, the gum did always eventually dissolve. This happened even though I used more glyoxal (10 drops/5ml gum) than I had used before, to be sure of hardening. The longest time to dissolution of the gum layer was one hour, after four hours elapsed drying time, which seemed to be the most hardening I could get with that mixture; another sample that dried for 24 hours also completely dissolved after an hour of soaking.

I have suspected for some time that the gum I've been using for the last 3-4 years may be partly or wholly acacia seyal rather than acacia senegal, because it behaves differently from the gums I've used before. As a result of gum marketing strategies by a government-owned gum marketing consortium in Sudan, the price of acacia senegal has skyrocketed in the last few years and many gum distributors marketing powdered or liquid gum have been substituting acacia seyal for gum senegal. Gum seyal has different properties, for example it's dextrorotary rather than levorotary and is brittle when brushed out and dried. I haven't been able to confirm my suspicion with my supplier, but this gum does behave very much as acacia seyal is described in the literature. So my first thought was that the difference between my observations with gum/ glyoxal several years ago and last weekend might be a result of a difference in the gum.

At any rate, when I redid the experiment using 15 drops glyoxal/5 ml gum (the same gum that I suspect of being acacia seyal) the gum hardened quite well, as long as some time (30 minutes at least) was allowed to elapse between brushing the gum-glyoxal mix on the paper and putting it in the water. However, I was using paper sized for gum printing for my experiments, and the glyoxal-hardened gum invariably failed to adhere to the sized surface, flaking off in insoluble chunks (insoluble in either cold or hot water) as soon as the paper entered the water. But that's a paper issue, not a hardening issue.

Looking at Peter's results, I would agree that more glyoxal in the glyoxal wash might be beneficial.

(BTW, colloids in solution don't behave the same chemically as colloids in the form of dried films, so I would caution against drawing conclusions about one type from experiments on the other type.)

I live in the Pacific Northwest, where last year's rainy season lasted til July and this year's started in September, so there has only been one brief period since I've been corresponding with Michael that there was enough sun to do an exposure in sunlight. When the sun came out unexpectedly, I ran to look for the one positive-on-film that I knew I had, but couldn't find it right away. Worried that I was going to lose the sun, I exposed a negative instead. I used only ferric chloride; I don't have the other chemicals that might

speed up the process. It took about half an hour in direct sunlight for the ferric chloride in the margins of the paper to bleach to white. I found, as others have reported, that the gum dragged and streaked when being brushed onto large areas of unexposed ferric chloride, so I ended up with a lot of streaks in the dark background of the negative image. However, I was surprised to find that I got little or none of the iron stain that has been described; the exposed areas (white on the print) were white, with maybe a slight reddish tint in one or two parts, but nothing I'd be concerned about; it was quite inconspicuous in the print. So that's a mystery to me, why I wouldn't get this iron stain; at any rate if all these prints came out like the two I did this week, there would be no reason to worry about keeping the ferric-gum image from dissolving when clearing the iron stain, because there wasn't any stain to clear. This was on Arches bright white paper, sized for gum printing with glyoxal- hardened gelatin.

While that negative was exposing, I found the positive I'd been looking for and exposed that, but the image is a very high-key image, (eggs on a white table) and since the tones are very pale, the positive was not dense enough to block exposure to the areas that shouldn't have been exposed. Also, the sun had dimmed by then and it took around two hours for the ferric chloride to bleach to white. At any rate it was an utterly unsuccessful print; the thin positive had allowed too much exposure to all areas so that there was insufficient fixing of the gum in the image areas (in other words insufficient unexposed, unreacted ferric chloride to fix the gum in areas where there should be tone). There was also severe mottling, speckling, blotching throughout the image, even though the print was on the same sized paper as the other one, which didn't have this mottling throughout the print. But again, no iron stain.

I'm too busy at the moment to put these up on a web page, but when I can, I'll send the link.

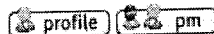
I have been somewhat skeptical about the colloidal ferric hydroxide explanation for the fixing of the gum, and my skepticism has been supported by conversations with chemists in my extended family. Maybe more about that later.

It's an interesting process. I haven't seen anything to convince me yet that it has the potential of being an improvement over gum, but as Michael keeps telling me, it's early days for the process.

Have enjoyed eavesdropping on your discussions; keep up the good work,

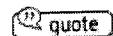
Katharine Thayer

[Back to top](#)



**pgum**

Posted: Fri Nov 19, 2010 3:22 am



Greetings Katherine,

Joined: 19 Oct 2010  
Posts: 52

Your feedback and testing is a great addition to our experiments. I hope you will be able to do a little more experimenting as the sun and time permit.

I have been able to make some very interesting monochrome prints with this process. They have good scale range, good Dmax, excellent detail and virtually no staining, something I could not get with a one coat gum. I didn't get all of that on the first few attempts as you are probably aware. Laying the pigmented gum is still experimental for me and I am hoping it can handle multiple coats but that is an unknown right now.

One thing that works for me is to apply an excess of the pigmented gum and brush over twice. Something else I tried was dipping and that did a very good job but it may be impractical. Spray is another option especially since the dichromate is absent. As Michael mentioned, some type of puddle pusher may also do the job. There is a new set of variables with this process and we really haven't explored many of them other than a few small adjustments to the sensitizer and the testing of a few different paper types.

Gum:

I did not know that there are two types of gum, so your information has been a help. After reading this, I dug out an old pair of polarizing filters (from a 3d movie show some time ago) and placed a glass container (It has parallel walls an inch apart) of gum solution in between. I shone a light through the gum solution and found that it rotated the minimum of light counterclockwise by a few degrees, I would guess. I then tried just



plain water and there was no rotation, and finally dextrose, which gave a strong clockwise rotation. I guess the conclusion is that there is senegal in this gum but of course with my jury rigged setup, there is no way to get accurate rotation measurements and further, I don't have the necessary optical data on these gums.

The fact that you have been able to make the gum completely insoluble is encouraging. One thing you may want to check is the age of the glyoxal. It will slowly loose its strength and go acidic as it absorbs oxygen. Shelf life says 6 months unopened.

Regarding your lack of an iron stain, here are some possibilities:

I have noticed a lack of stain when I have added extra acidity to the sensitizer or have acidified the paper previously to eliminate buffers. So perhaps, what may be happening is that the glyoxal in your sized paper has been converted to glyoxylic acid. I believe that this is an oxidation byproduct of glyoxal after it has been exposed to air for some time. One think you may not see is the stain hiding under the shadow areas of the pigment since that is where it tends to predominate. It may alter the hue of a low pigment load mix and of course the iron may be no good for paper in the long run although iron in an insoluble form may very well be inert and not cause harm. If the sensitizer can be adjusted to reduce the stain to a minimum, perhaps it can be left on the paper especially if the first gum/pigment layer can withstand a second/third coat of sensitizer without involving a hardener. It is something else to try.

Peter Friedrichsen

=====

Michael,

The calcium chloride used was hanging around for use as a winter ice melter. Table salt may also do the job but I haven't tried it. It certainly would help to preserve the gelatine but I am not sure if it will keep it liquefied as the calcium salt does.



The bisulfate works very well. I find that all visible stains are gone within about 3 minutes but it takes about 6 or 7 to dissolve out the stain hiding under the gum/pigment at least for my particular method. It can be purchased as a pool or spa pH reducer for about \$10/kg and is relatively pure without other additives and not so acidic as to being caustic.

With the low concentration of a 0.4% bath, I found that it did take many hours to get hard enough. I suspect that the crosslinking only goes as long as there are molecular groups to crosslink. The glyoxal however does not stay active for very long from what I have read (when exposed to oxygen). So, at 0.4% is the glyoxal finished after 16 hours or can it still do more work? I don't know. From what I have read, a bath of glyoxal may last a day or so left exposed to the air, but of course there are all sorts of other variables involved when gum is mixed in and it dries on paper. I would think that a higher concentration would move things along at a faster pace although Katherine's experience with 10 drops/5ml gum showed no greater hardening after 4 hours.

I hope to post my results for a few more glyoxal runs at higher concentrations, tomorrow, time permitting.

Peter

[Back to top](#)

 [profile](#)  [pm](#)

**Botanic88**

📅 Posted: Fri Nov 19, 2010 10:38 am

 [quote](#)

Katherine

Joined: 14 Aug 2010  
Posts: 50

Re. your lack of stain, my experience supports Peter's idea that the staining is (partly) dependent on the acid level of the sensitizer.

In the beginning before I used oxalates, I had two tricks to reduce the stain. Firstly I added a little hydrochloric acid to the sensitizer. I couldn't add much because it damaged the writing paper I was working with at the time.

I also discovered another trick that seems counter-intuitive. I discovered that leaving ferric chloride coated paper open to indoor light made it useable for longer than keeping the paper in the dark! With this in mind I would allow some light to enter through the back of the paper during long exposures. This resulted in more substantial dark areas and less stain.

My explanation for this goes as follows. When ferric chloride is reduced it produces acid or 'acid type stuff'. This is sufficient to prevent much of the stain forming. More importantly this acid is produced gradually during a long exposure, so it cannot just disappear into the paper or the air or wherever it goes when one only relies on the original amounts of acid in the sensitiser.

I wouldn't recommend using these tricks any more. Oxalates and some extra acid in the sensitiser renders them obsolete. I only mention them because I think they help to explain why you got very little stain.



Peter

I forgot to mention something regarding the use of calcium chloride. This is obvious but I'll say it anyway! If you continue using oxalates then there is a danger of forming insoluble calcium oxalate. However this substance is only totally insoluble at neutral pH so it may not be a problem!

Re. glyoxal becoming ineffective (or less effective) either in the print or during storage, wouldn't it be possible to give the print a second glyoxal bath?

I appreciate that using second baths and waiting for lengthy periods is not ideal. But in the long run I see the ability to remove all the stain as something that needs to be possible but that may not always be required. If we can provide a really reliable method of stain removal then people can choose whether or not to remove the stains, long after the print has been made if necessary.

Michael

 [profile](#)  [pm](#)

[Back to top](#)

**Katharine Thayer**

Posted: Fri Nov 19, 2010 3:04 pm

 [quote](#)

Joined: 19 Nov 2010  
Posts: 44

Well, look at this.. I had repeatedly tried registering by clicking "Register" and ran into problems every time; apparently the trick, if you want to register, is not to click the "Register" tab but to click "Start Chatting Now." Who knew?

**Iron stain:** Okay, I'll buy that the no staining could be due to extra acid in the sensitizer, because both Michael and my brother in law told me that I'd need to add a little HCl to the ferric chloride to get it to dissolve, and I had these great big hunks of the stuff in the water (yes, I should have crushed them first, but I couldn't remember where I'd put my mortar and pestle). My brother in law had cautioned me not to use too much HCl, "a couple of drops might be enough" but I had added a couple of fairly goodsized glugs by the time I got it all dissolved.

But the sensitizer seems to work well this way, so why not just add a little acid to start with?

I appreciate that the areas under the gum might be stained, in fact I've seen a stain when I was experimenting last weekend with making marks on paper with ferric chloride and gum and then washing it for various periods of time. Under a couple of conditions bits of the gum flaked or wore off after extended washing (3 or 5 hours) or under treatment with ammonia, and left a yellowish stain underneath. But I'm puzzled... we don't know enough about the mechanisms, but surely the stain on the unexposed areas where the ferric chloride has remained unreacted by light isn't going to be the same chemical compound as the stain where light has changed the ferric chloride into something else? Or am I not understanding where the stain occurs? My impression from looking at the prints online was that the problematic stain (visually, I mean, not archivally) is in the areas that were more exposed.

**Age of glyoxal:** That was one of my first thoughts when I was trying to think of reasons why the hardening wasn't working as well as it used to, that the glyoxal might lose strength over time. If it does, maybe it's not the gum that's the problem at all. I've had this glyoxal for at least four years, maybe longer, and who knows

how long it was sitting on the shelf at the suppliers before that. But if it does lose strength, then they shouldn't sell it in such big bottles, because you use such a small amount of it for most purposes. At any rate, using more of it seems to do the trick.

**Other glyoxal issues:** I brushed some fairly concentrated glyoxal over part of a ferric gum print last night, to sit overnight and then treat with various agents today. Since I don't have stain to remove, I won't be able to tell whether the agents remove stain, but I may be able to tell whether the glyoxal protects the fixed gum from being dissolved by the agent.

One thing I found interesting: the gum resisted the glyoxal mightily at first; it just beaded up on the surface, and I had to brush and brush and brush for several minutes until it started "taking" the liquid. When it did, I thought it lightened the gum a little, but I'll have to see it after it's dried to be sure of that.

I wouldn't be concerned with the glyoxal changing over time once the gum is hardened, if that's what Michael was asking; once the crosslinking has occurred, the material should be stable.

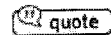
Katharine

[Back to top](#)



**pgum**

Posted: Fri Nov 19, 2010 6:06 pm



I completed some tests with glyoxal. To summarize (details below), I was unable to keep the gum from dissolving in all cases, however more glyoxal= a longer soak time before it starts to dissolve out. 😊

Joined: 19 Oct 2010  
Posts: 52

In the first run, I placed a test strip with the different glyoxal strengths in each of four spice bottles containing the acid bath, and then in the second run, with the acid bath for 5 minutes, then washed out and replaced with water (after a short water rinse of each strip). The strips for each %glyoxal test were from pairs, so they were processed in the same way. The 4% and 8% strips had the glyoxal treated yesterday, and the 1% and 2% strengths were from the day before.

Below are the results:

Acid bath is a 1% w/v soln of sodium bisulfate

glyoxal bath strength-----time to image breakup (minutes)

(%)	-----	(test 1-acid only)	---	(test 2-acid then rinse)
1	-----	10	-----	15
2	-----	35	-----	30
4	-----	50	-----	40
8	-----	80	-----	45

I don't know why the image is now more vulnerable in the water. Perhaps it is the tap water, since mine is slightly alkaline -about pH 7.3

I should add that the 4% and especially 8% glyoxal baths were starting to attack the gum on treatment, and causing pigment smear and some loss during drip dry. It is either the acidity (as glyoxal is naturally acidic), or its reducing power converting ferric to ferrous, or something else! For another test, I will try a water soak skipping the acid to see if the prints hold up.

I tried one approach to make an actual photographic gum print using a 2% glyoxal bath for 5 mins and dried overnight, then 5 mins in acid, 5 mins in a water rinse then hung to dry. The print looks very good. All visible iron was removed and it dried down without any visible loss or dislodging of gum. It has plenty of detail with good whites and strong blacks, but overall a little underexposed (a few shadows are blocked up). The key here is that it dried sufficiently before it would have started to dissolve.

It all seems a bit nerve wracking to have to race against time while risking a precious print. I would also find that the 4 and 8% baths could burn through quite a bit of glyoxal, on larger prints especially if each coating (on multicoat) needs post hardening. At this point, I really think that the image should be "permanently"

fixed. It looks like some modification to the bath or a different hardening agent needs to be sought.

Other side tests:

#### Gelatine

A side test I did with a gelatine print using a 1% glyoxal bath for 5 minutes and left overnight, showed that even after 24hrs in water (post iron removal in the acid), the print showed no loss. I even placed it afterwards, under warm running water and it did not loose coating.

It sounds like gelatine would have great potential however I have been unhappy with the test prints. Now they do show excellent density with lamp black, but the scale is very jumpy going from black to white in short order, reminiscent of too thick a coat of gum in a gum bichromate print. Of course some adjustments to technique or sensitizer/paper may improve things. I used a 10% w/v gelatine strength.

#### Chromium Sulfate

I wanted to try a chrome salt (not dichromate). I don't have chrome alum so I had to resort to reducing some potassium dichromate with a little potassium metabisulfite til the solution went green, as this green form is, from what I understand, the type which actually does the crosslinking. I bathed two test prints in this crude bath (of very roughly 1%) for 5 mins. One I rinsed thoroughly, then they were hung to dry for an hour. Once dry, I placed them in the acid bath and then a water soak and after about 16 hours, the image is still very intact. There were a few flaky bits lost but very very little. The flaked bits did not re-dissolved in the water in opposition to glyoxal where all tests showed the gum to dissolve.

I would like to avoid the use of chromium compounds if possible. I don't really want the chromium compound dripping off of the prints and leaving a residue. Of course based on the test above, it may be certainly possible to rinse it before drying, but then I have yet another bath to deal with. I am not sure why there is such a difference but I do know that gum has a small amount of protein and perhaps it is just that component that gets hardened with glyoxal.

Katherine,

I think that the light is reducing the ferric to a ferrous salt. The ferrous form will quickly get reoxidized to a ferric form after the rinse but while it is in the ferrous form, it should be more soluble because most ferrous salts are more soluble than their ferric counterparts and they don't seem to get bound to the gum at the paper surface. I am speculating somewhat on this.

Peter


*Last edited by pgum on Sat Nov 20, 2010 2:57 am; edited 2 times in total*

[Back to top](#)

 [profile](#)  [pm](#)


**Frank Gorga**

📅 Posted: Sat Nov 20, 2010 1:48 am

 [quote](#)

Wow!

Joined: 24 Oct 2010  
Posts: 4

So much activity... I feel like a complete laggard! I hate it when my day job interferes with my art making!  


I checked in here this afternoon, to see what was new in anticipation of having some time this weekend to work on the ferric gum process and found this amazing amount of activity and progress.

Peter's prints look pretty good in my view and I am glad to see a new recruit to the effort.

I have spent most of the evening reading though all of the posts. Although it will take me some time to digest it all and figure out what area I can best help with, I do have a bit of information that I can add regarding glyoxal based on my (bio)chemical background.

What I am reading about needing relatively high concentrations of glyoxal and relatively long times for reaction of gum compared to gelatin is very consistent with the organic chemistry.

Gum is a polymer of sugars which are rich in hydroxyl groups but which do not have much other "functionality". Gelatin (and albumin) are both proteins which, in addition to hydroxyl groups, have a much larger range of functionality; most germane to this discussion is that they contain amino groups (amines). The rate of reaction of amines with aldehydes (such as glyoxal) is much larger than the rate of reaction of alcohols (hydroxyl groups) with aldehydes. Thus the results you are seeing are what one expects from the chemistry of cross-linking as I understand it.

By the way, at some point someone (Peter, maybe?) mentions that glyoxal can be oxidized to glycolic acid... another name for glycolic acid is oxalic acid. Keeping stocks of glyoxal tightly sealed and cold (i.e. 4 deg. C) will prolong their life, as will repackaging it into smaller bottles so that the exposure to oxygen is minimized. (Every time you open the bottle you let in another "dose" of oxygen.)

I'm not sure that any of this "theoretical" knowledge will help with the practical chemistry but I thought that I would throw it out any way.

I'll report back if I actually get some time to experiment this weekend.

Regards,

--- Frank

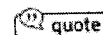
Frank Gorga  
[www.gorga.org/blog](http://www.gorga.org/blog)

Back to top



pgum

Posted: Sat Nov 20, 2010 3:35 am



Hi Frank,

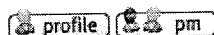
Your input has already made me think of an additional possible reason for the difficulty with the gum and acid baths.

If gum is predominantly a polymer of sugars (as I believe starch and cellulose are), then the acidic bath may be hydrolyzing the recently crosslinked molecules. In other words one step forward with the glyoxal, and one step back with the acid hydrolysis. I guess this could be put to test with a non acidic bath. Would one of the EDTA salts remove the iron (post glyoxal) without acidification in order to see if this may be the case? Or can we reduce all of the iron to the ferrous form and rinse it out without acidification?

If it is acid hydrolysis that is having a negative effect, then I would be more inclined to think that the odds seem greater that there could be a chemical crosslink with the iron but it is getting undone by hydrolysis. Some type of chemical crosslink was suggested by a relative of Katherine's who works in a scientific field.

Peter

Back to top



Katharine Thayer

Posted: Sat Nov 20, 2010 2:09 pm



A clarification re the comment of my relative the physical chemist:

When I asked him about this, I didn't understand the basics of the process; somehow I'd missed two important facts: (1) that the photochemical reaction is not part of the image-formation mechanism, and (2) that it's a positive working process. So he was assuming (since I was assuming) that a photochemical reaction was involved in the fixing of the gum, when he responded:

Joined: 19 Nov 2010  
Posts: 44

"Ferric ion like chromate is an oxidizing agent and may form a ferrous ester. If so, the ferrous ester is less stable than the chromate ester. In the chromate case, the image comes from cross linking of the gum. I would guess that this is also true in the ferric case. I doubt that a ferric colloid would be effective. Colloids often have surface charges, but I doubt that they would hold the gum together with sufficient binding energy."

The first sentence may also be true in the absence of light; I don't know enough about the chemistry any more to be able to judge that, but I wanted to make clear that in this case, he was assuming that the reduction of the iron is happening as a result of photoactivity, and that's why he described it as analogous to the crosslinking of gum by  $\text{HCrO}_4^-$ , the active ion in the crosslinking of irradiated dichromated gum.

At any rate, it seems possible to me that what he described may well be what is happening in the photochemical part of this process; some iron ion is crosslinking elements in the paper or size to form a resist to the gum. Frank, any thoughts on that?

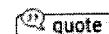
Katharine

[Back to top](#)

 [profile](#)  [pm](#)  [www](#)

**Botanic88**

Posted: Sat Nov 20, 2010 4:15 pm

 [quote](#)

Hi all

Joined: 14 Aug 2010  
Posts: 50

That looks like a pretty thorough test of glyoxal and 'ferric fixed' gum Peter! The results don't rule out glyoxal completely but taken with Frank's information about glyoxal being inherently less good with gum than with gelatine, it does cast some doubt on the possibility that glyoxal could be a really reliable way to fix gum once the 'ferric fixing' has been removed. ☹️

Coincidentally I intended to buy some glyoxal this morning, only to discover that the one source I had discovered (on-line from Korea/Japan) is no longer available.

Please can someone put me straight about  $\text{Cr(VI)}$  and  $\text{Cr(III)}$  ions.

(1) Are the environmental concerns the same with both?

(2) Is the fixing (crosslinking) of gum likely to be the same with both? Dichromate seems so reliable and resistant to acids etc. but I have read that chrome alum is fairly fussy about pH levels.



I would really welcome some facts about these things. 😊

I have just read on Wikipedia that chromium (III) chloride on its own is very slow to react, dissolve in water and form ligands, etc but it does so very fast in the presence of tiny amounts of chromium (II) ion.

I am wondering if the way you made your chromium (III) ions would have produced this bit of extra chromium (II) Peter. I have got some chromium (III) chloride but I never got it to do much in the past. It may have been this bit of catalysis that was missing!


Michael

[Back to top](#)

 [profile](#)  [pm](#)

**Katharine Thayer**

Posted: Sat Nov 20, 2010 4:52 pm

 [quote](#)

Joined: 19 Nov 2010  
Posts: 44

While I'm passing on comments from scientists in my family, I may as well include the comments of my brother in law the analytical chemist, who is also skeptical of the colloidal ferric hydroxide explanation for the "fixing" of the gum. He says metal ions tend to glom onto organics like everything, and iron is especially good at this, and while he hasn't suggested or proposed a specific mechanism, says he'd bet money that the fixed gum is rendered "fixed" by the formation of a bond between an iron ion in the ferric chloride solution and something in the gum. He says he thinks it's unlikely that ferric hydroxide is being formed, and he wouldn't find that an attractive explanation anyway, because ferric hydroxide wouldn't form nearly as strong a bond with the gum as the ferric ion itself would, and from my observations so far, I'd say that we're talking about a fairly strong bond. However, I would need to know more about what happens with the gum. In dichromate hardening of gum, there's an electron transfer between the gum and the chromium; I suppose

there must be something like that happening here, if this is what's going on.

When I did my first experiments with this, going by the explanation that this isn't really a bond but an attraction of some sort (well, I suppose if you want to get technical that's all any bonds are, the difference being the strength of the attraction, but I digress) I expected the ferric-fixed gum to be quite fragile, easily dissolved and easily disturbed, and was surprised to find this not the case. Unlike the hardened gum layer in the traditional gum process, the fixed gum couldn't be removed by rubbing or scratching while it was still in the wash. A hardened dichromated gum image can be ruined by even a touch before the hardened gum is dried, and continues to lighten when left to soak, while the ferric fixed gum did not change density over many hours of soaking (I cut some in half and left half soaking, then put them back together when dried, and you really can't see a difference). I don't have a lot of likely agents for dissolving the gum, but 5% acetic acid did not soften or dissolve the ferric-fixed gum. Ammonia did soften the ferric fixed gum if applied while the gum was still in the wash, but did not seem to affect it when dried; there was no color difference between a portion that was dipped in ammonia for several minutes and the adjacent area. I know that ammonia does lighten still-wet dichromate-hardened gum, since I sometimes use it to chemically hurry up development in shadow areas that aren't opening up fast enough to suit me, but I've never had any reason to try it on a dry gum print, so I don't know about that. I'm aware that ammonia isn't something that would be used to remove the iron stain, but I was just trying to get a feel for the stability of the ferric-fixed gum in general, compared to dichromate-hardened gum, my initial impression being that the ferric-fixed gum seems quite sturdy.

Katharine

[Back to top](#)

 [profile](#)  [pm](#)  [www](#)

Display posts from previous: All Posts Oldest First Go


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[View next topic](#)  
[View previous topic](#)

Page **5** of **15**  
Goto page [Previous](#) [1](#), [2](#), [3](#), [4](#), [5](#), [6](#) ... [13](#), [14](#), [15](#) [Next](#)

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Message

< Ferric Gum Process

Katharine Thayer

Posted: Sat Nov 20, 2010 5:53 pm

quote

Joined: 19 Nov 2010  
Posts: 44

Sorry, don't mean to be monopolizing the thread, but just saw Michael's question about Cr(VI) vs Cr(III). Answers:

No, the environmental (or health) concerns are not the same for the two species of Cr.

No, Cr(III) does not bond gum in the same way Cr(VI) does, although we don't have a perfect idea of how Cr(III) reacts with gum any more than we have a perfect idea of how Cr(VI) reacts with gum. We know that for Cr(VI) anyway, the mechanism is probably different for gelatin than for gum, but we have to extrapolate from research on dichromated PVA, since there's no research actually done on dichromated gum. But since, as Frank said, the active groups in gum are mainly -OH groups, just as in PVA, we feel somewhat comfortable assuming that dichromated gum works more like dichromated PVA than like dichromated gelatin. By the same token, the mechanism for chrome alum with gelatin has been described, but we don't know if the same mechanism holds for chrome alum and gum.

katharine

Back to top

profile pm www

Katharine Thayer

Posted: Sat Nov 20, 2010 7:15 pm

quote

Joined: 19 Nov 2010  
Posts: 44

**Some rough results: acid over glyoxal over ferric gum**

I applied dilute HCl and citric acid across the band of glyoxal-treated ferric gum that I prepared two nights ago, and found that while the dilute HCl wiped the ferric gum completely off the paper in the untreated part, it left the gum largely unfazed in the glyoxal-treated part. It did slightly fade its color, but did not soften or dissolve the gum at all. Whether the glyoxal would also keep the acid from clearing the stain, I have no idea.

As for glyoxal disturbing the gum and pigment, as Peter observed, I did not see any smearing, running or softening of the gum by the glyoxal either during application or any other time. (Perhaps that's because his glyoxal is fresh and mine isn't.) I used 10 drops of glyoxal in 5 ml water, which I determined was equivalent to 80 drops from this particular dropper. The glyoxal stock solution is 40%, so if my arithmetic is correct that comes out to 5% glyoxal.

I also used citric acid, which seemed to change the color of the gum slightly but equally across glyoxal and non-glyoxal-treated areas. But I ruined the effect by spilling HCl on it, which promptly cleared the gum off the non-glyoxaled area and left the gum on the glyoxaled area, so if I upload this, what you'll be seeing is an HCl effect in both cases; I'd need to do the citric over again to show an accurate picture of the effect of citric acid on glyoxaled vs nonglyoxaled ferric gum.

I put up a quick page here:

<http://www.pacificr.com/~kthayer/html/ferricgum.html>

Back to top

profile pm www

pgum

Posted: Sun Nov 21, 2010 12:50 am

quote

Joined: 19 Oct 2010  
Posts: 52

Katherine,

Do you have any information on the length of time that the test print had been subjected to the dilute HCl and Citric acid? I should mention that I did try one test on Friday with a 2% v/v glyoxal treated print bathed in 0.3% v/v HCl. The result was that the dilute HCl caused the gum to wash off roughly 30 minutes after immersion. I have not tried citric acid since using the glyoxal.

I have found a fairly detailed note about the effect of chromates on gum as it relates to early photographic print making in 1879. The author suggests that chrome alum mixed with gum will become insoluble after it has dried. The article is in a very old journal (British Journal of Photography) found on google books. Find the link below:

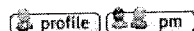
<http://books.google.ca/books?id=-p0QAAAAQAAJ&pg=PA461&dq=chrome+%22gum+arabic%22>



22&hl=en&ei=QZ7kTlr5OdGQnwe25Jz4BQ&sa=X&oi=book\_result&ct=result&resnum=5&ved=0CEkQ6AEwBA#v=onepage&q=chrome%20%22gum%20arabic%22&f=true

Peter

Back to top



Katharine Thayer

Posted: Sun Nov 21, 2010 1:55 am



Joined: 19 Nov 2010  
Posts: 44

Hmm, perhaps I didn't make myself clear about chrome alum. I don't think there's any doubt that chrome alum hardens gum, but I thought someone was asking about the *mechanism* for that hardening, and I was just saying that although the mechanism for gelatin and chrome alum has been well described -- it involves the formation of a ring structure between two ionized carboxyl groups, with a sulfate group in the middle and OHs and Crs around the ring--we don't know for sure that the same mechanism holds for chrome alum and gum. Thanks for the link, but the old journals/books are obsolete as far as any useful understanding of the chemistry of our processes; chemistry, and specifically colloid chemistry, has moved far from the understanding that was available then. They were pretty much making it up as they went along (I especially like "This fact, which I discovered, I explained to myself as being caused by the formation of 'chromous oxide metagumate'" --my single quotes) so their observations, while historically interesting and entertaining, are not very useful or helpful toward furthering our current understanding of chemical mechanisms.

The acid was only on the gum for a few minutes before the gum completely dissolved, but only where there was no glyoxal. I didn't leave the acid on after that but rinsed it off at that point; does it need to stay on for a period of time? How long did your glyoxal "cure" before putting the acid on it? As for the concentration of my HCl, I didn't make up a new solution; I was using some that was already mixed that I'd been using to clean mortar off some stone walls I built this summer, that I wanted to use up. Rough guess, I'd say the solution was around 2%.

Back to top



pgum

Posted: Sun Nov 21, 2010 3:21 am



Joined: 19 Oct 2010  
Posts: 52

Katherine,

Michael's second part to his question:

"(2) Is the fixing (crosslinking) of gum likely to be the same with both? Dichromate seems so reliable and resistant to acids etc. but I have read that chrome alum is fairly fussy about pH levels"

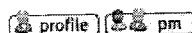
I think Michael was wondering (other than the pH sensitivity question of chrome alum) if in fact CrIII is able to make gum as resistant to acids as CrVI. The linked journal article does provide the observation that chrome alum (CrIII) hardened gum is very resistant to boiling water, alkali and muriatic acid, so hopefully this archaic article provides us with some optimism in regards to the potential of CrIIIs such as chrome alum as a powerful gum hardening bath alternative.

In regards to the length of time to remove the iron, the only detailed testing I did was with the bisulfate bath of 1%. In that case it was about 5 minutes to remove any visible stains although there were some vestiges of stain remaining under the gum in the most dense areas. I didn't do any detailed tests with HCl except to observe that the visible stains were removed in about 3 minutes in a 0.3% solution of HCl.

Oh yes, I forgot to mention that the cure time for the HCl test was about 32 hours post glyoxal treatment.

Peter

Back to top



Botanic88

Posted: Sun Nov 21, 2010 11:02 am



Joined: 14 Aug 2010  
Posts: 50

Hi all

The main question I want to ask concerns Peter's use of chromium sulfate.

#### Quote:

I wanted to try a chrome salt (not dichromate). I don't have chrome alum so I had to resort to reducing some potassium dichromate with a little potassium metabisulfite til the solution went green, as this green form is, from what I understand, the type which actually does the crosslinking. I bathed two test prints in this crude bath (of very roughly 1%) for 5 mins. One I rinsed thoroughly, then they were hung to dry for an hour. Once dry, I placed them in the acid bath and then a water soak and after about 16 hours, the image is still very intact. There were a few flaky bits lost but very very little. The flaked bits did not re-dissolved in the water in opposition to glyoxal where all tests showed the gum to dissolve.


If I understand this correctly you started with a gum image fixed with iron(III) and you fixed it in addition with chromium(III). Then you dried the image. Then you removed the iron(III) with sodium bisulfate (I presume) but the chromium(III) fixing was left intact.

If this describes what happened accurately I find it doubly intriguing.

(1) The idea that one trivalent metal ion seemed to find additional places in the gum to attach to (assuming the crosslinking hypothesis). I suppose the second metal ion might have replaced the first, possibly.

(2) The idea that the 'acid' seemed to remove the iron(III) whilst leaving the chromium(III) in place. Is it possible that the chromium(III) became very unreactive once all traces of chromium(II) had been removed (in accordance with the stuff in the wikipedia article I referred to yesterday)?

I would appreciate some feedback on this. Does it correspond to what you actually did Peter? Is it plausible in terms of chemistry?

Now to some other things 

**Quote:**

I don't really want the chromium compound dripping off of the prints and leaving a residue.

Can you tell me more about this residue or 'stain'. I haven't done a lot with chromium salts so I would like to know whether this something that happens with chromium(III) but not with dichromates, for example?

Re. the mechanisms behind dichromate and chrome alum hardening. Yes I did want to get some idea about the difference in mechanism between these two kinds of hardening. I thought that the chemicals end up as chromium(III) even in dichromate hardening. So what is the difference? Is it something to do with the route the reactions take, I imagine?

Re. The environmental impact of chromium(III) compounds. If they are relatively harmless (compared with chromium(VI) why don't people just reduce the more harmful species before disposal?

**Quote:**



The rate of reaction of amines with aldehydes (such as glyoxal) is much larger than the rate of reaction of alcohols (hydroxyl groups) with aldehydes. Thus the results you are seeing are what one expects from the chemistry of cross-linking as I understand it.

Are you just saying that the rate of reaction is much slower, Frank? Or are you saying that the eventual crosslinking is not likely to be so good?


Re. The fact that glyoxal oxidises to oxalic acid (even though it sometimes has another name) makes it unsurprising that stronger solutions dissolve a 'ferric fixed' image. I have always found that oxalic acid is very efficient at removing the ferric stain and fixing and all!


Michael

[Back to top](#)

 [profile](#)  [8:28 pm](#)

**Katharine Thayer**

 Posted: Sun Nov 21, 2010 5:17 pm

 [quote](#)

Oh dear, I was determined to have little to say today, but there's so much I want to respond to... I'm also worried about Frank not ever being able to catch up, if I write too much, and we need him. So I'll try to pick out a couple of things where I think I can add something and try to make it as brief as possible, but there's so much to say.

Joined: 19 Nov 2010  
Posts: 44

**Mechanisms of Cr(VI) vs Cr(III)**

**CrVI:** First let's dispose of the idea, still unfortunately current in photographic circles, that goes back to Eder 1869, I believe, that the dichromate reduces to chromium oxide (CrIII) (the green stuff) which forms a complex with the gum. One of the things we know for sure is that that's not what's happening. (I could say a lot more about why we know that, but I'm trying to keep this brief. A short and partial answer is that when that was written, they didn't yet know about how things dissociate into ions in aqueous solution, much less about photochemistry.)

Then there's the question of whether CrVI reduces to CrIII ions that complex somehow with the gum. This is the conventional wisdom, but there's little to no actual evidence to back it up, and some reasons to question it, and at any rate the latest research, on dichromated PVA (which we hope with fingers crossed behind our backs works similarly to dichromated gum), seems to show clearly

that within any reasonable exposure period (any exposure that provides complete hardening of the PVA), the Cr(VI) reduces only to Cr(V) which crosslinks the PVA. The evidence for this is thorough and convincing. Out of my own curiosity, before I was aware of that body of research, I coated mylar sheets with unpigmented gum, exposed them, washed them well and then scraped off the clean hardened gum with a razor blade and sent the scrapings to my brother in law for analysis; the analysis showed that the hardened gum definitely contained chromium, but it was definitely not Cr(III). So our analyses seem to provide some limited confirmation for the more thorough body of research done by a large group in Canada, at least to the extent that it's not Cr(III) that's involved in the polymer matrix. If anyone is interested in learning more about that research, the key papers, IMO, are these, in increasing order of relevance and importance:

Mannivannan, Gurusamy et al. J. Phys Chem 1993, 97: 7228-7233 "Primary Processes of Cr(VI) : Dichromated PVA"

Pizzocaro, C et al. J Photochemistry and Photobiology A: Chemistry 2002, 151: 221-228 "Dichromated PVA: key role of chromium (V) in the properties of the photosensitive material"

Bolte, Michele et al, 2005 conference proceedings of SPIE vol 5742 (I bought this from SPIE as soon as it was available from them, but I would bet that it's been long since published somewhere) "Hologram formation reconsidered in dichromated PVA: polymer crosslinking around chromium (V)"

[Later edit:] I should add for anyone who's familiar with the oxidation states of chromium that a possible reason for the conventional wisdom that Cr(VI) must reduce to Cr(III) is that Cr(V) and Cr(IV) are unstable in water, so perhaps it's generally been believed, without evidence, that no stable states exist between Cr(VI) and Cr(III) in dichromated colloid films as well, therefore Cr has to go to III before it can complex with anything. However, the Bolte group has demonstrated quite convincingly, to me and to my chemist consultants, that Cr(V) is stable in dichromated PVA film, and that it does indeed form the polymer.]


Well, that's the end of my available time. I didn't get far on my list of things I wanted to say something about; I didn't even get to Cr(III) yet. Later,  
Katharine

Back to top

 [profile](#)  [pm](#)  [www](#)

pgum

Posted: Sun Nov 21, 2010 9:07 pm

 [quote](#)

Katherine,

This is very interesting.

Joined: 19 Oct 2010  
Posts: 52

Somehow I am now thinking that the crude Cr(III) that I made by reducing dichromate may in fact be going up to Cr(V) in the gum while it hung on my line to dry for an hour. Possibly it absorbs oxygen from the air and changes to this form fixing the gum or does it need oxygen at all?. The funny thing was that the gum had no additional resistance until it was completely dry. Let me explain: I was hoping that I did not have to go through another dry down so I went right from the chromium to the bisulfate but this failed. I wonder if this Cr(V) mechanism may also help to explain why chrome alum was mentioned as a hardener only after it had dried with the gum.

I don't believe that any trace of dichromate (if there was any) in my crude chromium bath was responsible for the hardening because I did not expose it to light, and only one hour had passed before it was hardened.

I don't think it is too risky to consider the valence as potentially getting promoted up as well, not just down. I know Fe<sup>2+</sup> and Fe<sup>3+</sup> can bounce back and forth in a "ping pong" fashion with peroxide and out in nature in oxygenated water systems containing natural iron.

Now to answer Michael's questions

The print had the iron removed with the bisulfate after fixing with the chromium brew. Yes, the chrome fixing left the print intact.

In terms of chromium compounds dripping off the print, It is just an outcome of bathing the print in such a bath and not rinsing. It seems possible that it could be rinsed before hanging because the chromium seems to still do its job even if the print has been rinsed with water prior to drying; that was my experience.

I didn't see much of a stain from the chromium bath. In fact I have seen stronger staining from overexposed gum bichromates.

In regards to environmental impact, from what I have gathered, the Cr(VI) compounds are more toxic, however the Cr(III)s still are not completely safe. My one other concern with the chromium compound is their future availability, especially to those who lack manufacturing facilities which can remove residues. I have heard of some individuals in Europe (I don't recall the country(s), who are unable to obtain any dichromates. I see that day on the horizon!

Peter

*Last edited by pgum on Mon Nov 22, 2010 9:23 pm; edited 1 time in total*

[Back to top](#)

[profile](#) [pm](#)

**Katharine Thayer**

Posted: Sun Nov 21, 2010 10:13 pm

[quote](#)

Joined: 19 Nov 2010  
Posts: 44

Hi, Peter, I don't see any reason to think that CrIII ions don't bind with gum as CrIII, and much reason to assume they do, just not by the same mechanism by which Cr(VI) reacts with gum. The research that shows that Cr(VI) in the presence of PVA (or gum) and UV radiation is reduced only to Cr(V) before crosslinking the PVA has no bearing on the very different mechanism by which CrIII might bind with PVA, or with gum. We know that CrIII readily forms complexes with all sorts of things, organic and inorganic, so I can't think of good reasons why it would need or want to change oxidation states in order to do this, or what would cause it to do so, although maybe Frank has some ideas.  
Katharine

[Back to top](#)

[profile](#) [pm](#) [www](#)

**pgum**

Posted: Mon Nov 22, 2010 3:27 am

[quote](#)

Joined: 19 Oct 2010  
Posts: 52

Katherine,

OK. That sounds reasonable, but does anyone know why the gum is not hardened until after it is dry (with the CrIII form)? Do you know of any article references that may explain this effect?

The other surprise I found was that the gum would get crosslinked upon drying even if it had been well rinsed after being in the CrIII bath for 5 minutes. There must be some reaction going on immediately which is not apparent by plain observation.

If these two properties are true (I should try to repeat those results), then it may be possible to place a few drops of a CrIII compound into the sensitizer or gum/pigment mix before being applied to the paper assuming some compatibility with Fe2 and Fe3, FeCl3 and whatever else ends up in there.

Peter

[Back to top](#)

[profile](#) [pm](#)

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[View next topic](#)  
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Page 6 of 15  
Goto page [Previous](#) 1, 2, 3 ... 5, 6, 7 ... 13, 14, 15 [Next](#)

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