Sustainable Plant Proteins as a Less-toxic Alternative to the Gum-bichromate Process

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In this article, I am going to explain how one can use plant proteins, iron salts, pigments and a small amount of hydrogen peroxide as developer, to make prints that share aesthetic similarities to gum bichromate prints.

First, a little history…
Gum bichromate printing provides the artist or printmaker the opportunity to make colour prints by hand. The invention by Alphonse Poitevin of France in 1850, was popularized in the pictorialism movement of the late 1800s. Unfortunately, one of its key ingredients: dichromate (historically called bichromate) can be harmful to life. This concern had me searching for safer alternatives starting in 2009. My first find was a 1952 British patent publication by the Autotype Company[i], describing that a combination of iron salts and gelatin, with a peroxide development, will photo-harden. In addition, I came across a research paper about the CHIBA SYSTEM, published in 2007 by Halvor Björngård and Hiroyuki Kobayashi[ii]. Their techniques for carbon and gum-like prints, use the same peroxide hardening mechanism and was developed to provide a safer alternative to traditional carbon and gum printing. Since 2009, I have used this approach experimentally in my own alt-process practice, working with fish gelatin, casein, and occasionally whey.

More recently in 2023, I wondered about the use of plant proteins and whether they could be used to replace animal-sourced proteins. One of the difficulties is in the plant protein's insolubility, often producing gummy or turbid slurries when mixed into water. I did more research and came across the lupin bean, which is a niche legume product in North America, better known in other countries. It is high in protein and low in carbohydrates and fat. I was also successful in making prints using other proteins such as soy and wheat. The lupin bean[iii] however, provides for a relatively straight forward extraction, which I will describe below.

Principle of Extraction

The majority of practical plant proteins are sourced from the seeds. These are

referred to as storage proteins, providing the germinating plant with much needed early nutrition. For the most part, these are the sources that I am investigating due to their excellent availability. However, most of these proteins are soluble only in alkaline conditions and cannot be practically utilized in their native form at the pH that iron salts function, as used in the CHIBA system. Fortunately, with lupin, much of the protein is soluble at this lower pH, while those of soy, or wheat tend to precipitate. To extract the protein, the ground plant material must be made alkaline allowing for increased dissolution, then filtered or decanted, and finally precipitated at low pH. This precipitation point is called the isoelectric point of the protein and is often between pH 4 and 5. This acts in a similar fashion to the extraction of casein from milk, where the casein protein curds precipitate upon acidification.

Materials for Lupin Extraction

Ground plant flour has a limited shelf life due to oxidation and enzyme action. It is best to use within one year of purchase, or it will not print well. Flour can be frozen for long term storage. Use fresh flour!

100g yellow or white lupin flour
2.5 g sodium carbonate (washing soda)
1 litre tap, or distilled water
120 ml 5% acetic acid (household white vinegar)
(sodium bicarbonate or ammonia solution)

1 tall vessel to hold 1.5 litres (a cylinder style vase is ideal)
pH paper or otherwise for measurements around pH 4-5, and 6-7

Technique

It is important to only use gentle stirring. While the lupin beans are low in fat, they do contain approximately 5% by weight, variable by cultivar, climate. Vigorous or extended stirring will produce a cloudier protein solution in the end, possibly due to emulsified fat. It is only necessary to stir at the start and briefly a second time. No additional stirring will dissolve out any more protein.

1) Measure out 1 litre of room temperature water and pour into the vase

2) Add 5 g sodium carbonate to the water in vase and stir until dissolved

3) Pour all of the lupin flour into the vase and stir gently with a tall spoon or paddle for several minutes until all clumps are dispersed, leave for 1 hour

4) Stir gently once more just until the settled portion mixes back into the entire volume

5) Cover Top, and leave for about 18 hours undisturbed at room temperature

Recently stirred and left to settle

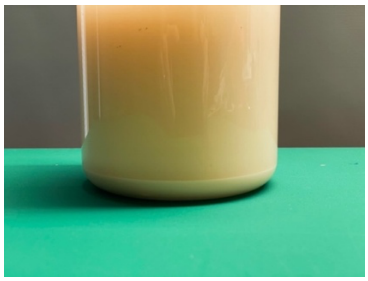
Extraction

1) After about 18 hrs, you will see a clearly defined translucent amber layer sitting above the solids. Siphon this off (the supernatant) and KEEP IT, discarding the fiber, undissolved protein, and fat at the bottom, which can be composted as is.

After 18 hrs settling

2) Add household vinegar slowly with stirring (you may not need all 120 ml), until the pH drops down to about 4.5-5. This is the isoelectric point. Leave to settle for up to 6 hrs but it may settle in as little as 2.

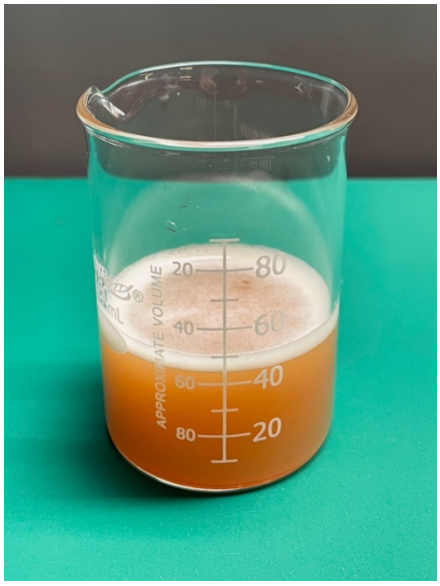
Vinegar addition complete



Settling has started

3) After settling, pour out the top layer and discard it this time, keeping the gummy precipitate that has settled to the bottom. This precipitated protein will stick to itself and the bottom, so no need to siphon, just invert the vessel

4) Add household ammonia **(Do not breathe it!)** dropwise into the gummy mass in the vase while stirring, until all has re-dissolved. An alternative is sodium bicarbonate, but it will foam up some. Either should be added in slow additions. Check for a pH of 6-7 occasionally. If you go too far alkaline, add a few drops of vinegar while stirring. Final solution strength should be about 20-25% w/v. It should be a sticky, gummy material when drying on your finger, similar in texture to diluted gum arabic solution.



Protein extraction complete

In this example, about 45 ml of a 25% solution was recovered. Given the 36% protein content of the flour, 31% of the total protein ended up in the beaker. Losses are from the decanting, and insoluble protein loss at the mild extraction pH. Some improvement can be had by using a greater starting volume of water (2 litres).

As mentioned for use with the CHIBA system, the pH should not be alkaline (set for pH 6-7) as it will weaken the print density, or there will be none at all. If too acidic, it will curdle the lupin protein, so keep it in this range. In addition, most pigments disperse better closer to neutral pH. To preserve the extract, divide into plastic film canisters or similar, in 10 ml portions and freeze. Freeze/thaws have no effect on performance. I have used frozen extract after18 mos, and it performs well.

Pigments, Emulsion speed

For pigments, I prefer dispersions for cost and convenience. Some of these can stain paper highlights, just as the watercolour tubes do. The Wet Print in Spain sells purpose-made pastes which clear well. I also use dispersions and pastes from Kama and Kremer -tested by trial and error. The downside to watercolour tubes other than cost, are the additives. Gum Arabic for instance is the most used binder in practically all of them, but it does not harden in the CHIBA system and can weaken the print if the manufacturer is cheap with the pigment load, and you have to overload your emulsion. Some pigments from one manufacturer will work much better than that same pigment from another. Look for pigments rated as low staining. Visit Bruce MacEvoy's handprint.com web site[iv] for comparisons of watercolour pigments incl staining, lightfastness etc…Exposures are typically about twice as fast as classic cyanotype, but highly variable by applied coating thickness and pigment choice.

A Typical Emulsion

For small prints:

1 ml lupin extract 25% w/v (as above)
*1 ml ferric ammonium citrate (FAC) (green) 20% w/v
pigment to taste -test on a paper scrap dried and unexposed to see if the pigment clears well

(*Note: I used Photographer's Formulary FAC, as the pH is about 6, so not too acidic. If your FAC solution is very acidic i.e. less than 6, you may need to alkalize it slightly. I have also found that some pigments may destabilize on FAC addition, in which case, you can use 0.75 ml instead. Using too little may not properly harden the print- you may need to adjust with testing)

For larger prints, it is usually necessary to dilute further with water and reduce the pigment load. The reason being is that a large piece takes more time to brush and without further dilution, the emulsion will set up prematurely.

Paper Use and Emulsion Application

I use 100% cotton-based papers for permanent work. They have better archival properties, and do not expand and shrink to the degree of those based on wood pulp. I am currently using Hahnemühle Platinium Rag. This is a 300 gsm 100% cotton paper. For basic testing, I use Canson XL watercolour paper for economic reasons. This student-grade paper is given extra size to facilitate paint lift. XL factory sizing stays put in multiple soaks but has a noticeably rougher texture and cockling on dry down. I prefer to use only the factory size and do not add any additional sizing. Papers with factory size and some tooth such as Platinum Rag work best. Pre-soaking the paper and letting it dry will also increase tooth.

If I anticipate multiple coatings in registration, I pre-shrink it with a soak in room temperature water for about 20 minutes. Hot water can remove size, while others can tolerate higher temps. Japanese washi paper is interesting. I can get excellent highlight clearing by reducing the pigment load to about 1/3 vs western papers. Washi papers have very little size so they will soak up a lot of emulsion.

For laydown I use a synthetic bristle brush with taklon fibres. Once I have the coat laid down, I smooth it with a hake brush, first in the opposing direction of the synthetic's brush marks. Brush coating is a skill that comes with practice. The key is to be able to complete brushing in a short amount of time while watching to ensure that the entire printable area is covered evenly. Hang to dry once the sheen has left

the paper. Dry room air is best for coating and drying as it reduces the staining of highlights.

Developing

1) Develop in water with hydrogen peroxide to a final strength of 0.3 -0.5%. Insufficient or excess peroxide (above 1%) can cause poor or non-development. Tap water may contain impurities that increase highlight staining. Use distilled if in doubt. If the print is stubborn to clear, a pinch of sodium bicarbonate may be added to the water per litre.

2) Slide print into developer in one even push or hold the two corners and pull it down under; this is unique and critical with CHIBA. A brief pause in this motion may lead to a white development line on your image, necessitating post-touch ups! Gentle rocking of the tray or pulling the print up a few times will suffice. Development occurs in a minute or two.

The CHIBA lupin emulsion is quite fragile, so brush development is not recommended unless you wish to completely remove a feature. A non-aerated water stream can be utilized at its very lowest flow, to assist with highlight clearing etc… A brief dip in a second tray will remove most of the lingering pigments. When hung to dry, there may be a small amounts of pigment run-off, so always leave a sufficient margin, keeping the stain outside of the print area.

Iron Removal after Print Completion

A 2% w/v solution of citric acid in water is used to remove most of the iron. Soak for 5 mins, and rinse for 20 mins in plain water. This should only be done when the print is complete and dry.

Exhibition

In my solo exhibition in May, 2024, I worked lupin, soy, and wheat into my print series of SW Saskatchewan, Canada. These other proteins require modification, a topic for a future article. https://propellerartgallery.com/exhibitions/sun-smoke-sky-and-grass-peter-friedrichsen/

Future Work

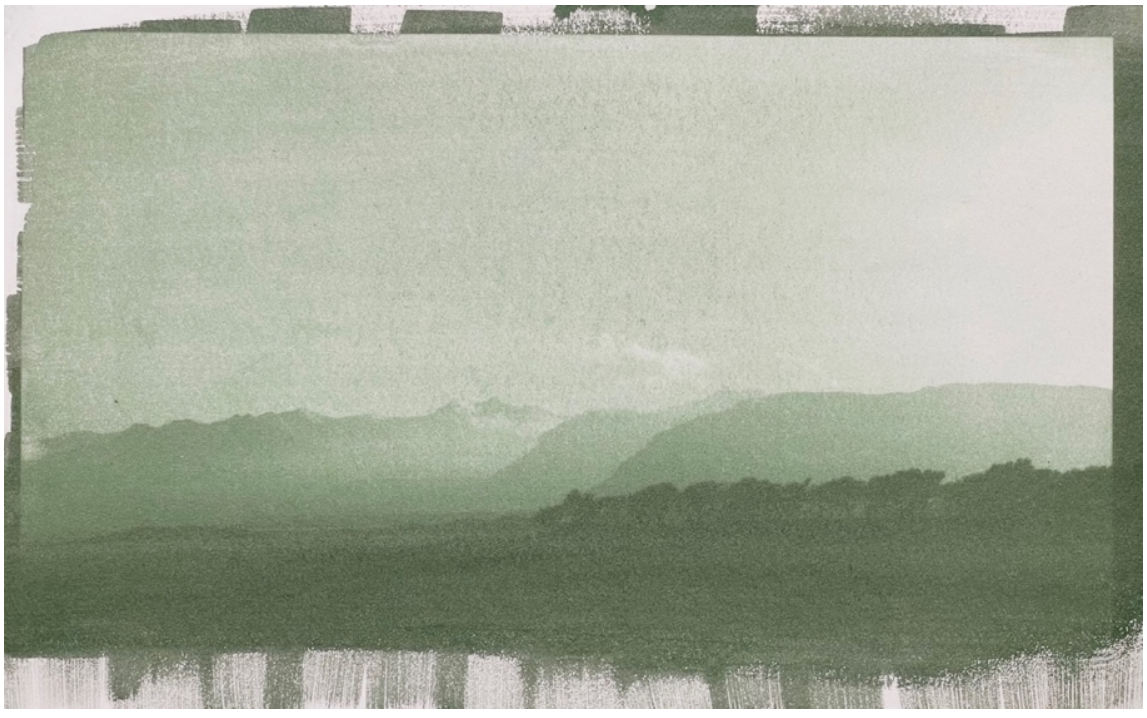
Plant proteins in printmaking are mostly unexplored, and I believe that they have plenty of potential. Not only is it a step towards sustainability, but also in terms of performance. Already, I have seen some remarkable properties that very well may help to expand the alt toolbox in a more sustainable, safe, and effective way.

Biography

Peter Friedrichsen is a Toronto-based photographer and alternative process printmaker known for his experimental approach and minimalist aesthetic in image making. His work reinterprets historical photographic printing techniques, exploring how materials, surfaces, and processes shape the interpretation of the image.

He is an active member of the alternative process printmaking community, with a focus on sustainable methods. His work has been exhibited locally and internationally, and has been featured in several articles and book publications within the alternative photography community. As a current member and past Chair of Propeller Art Gallery, he remains actively involved in Toronto's arts community.

Images of several of my lupin prints

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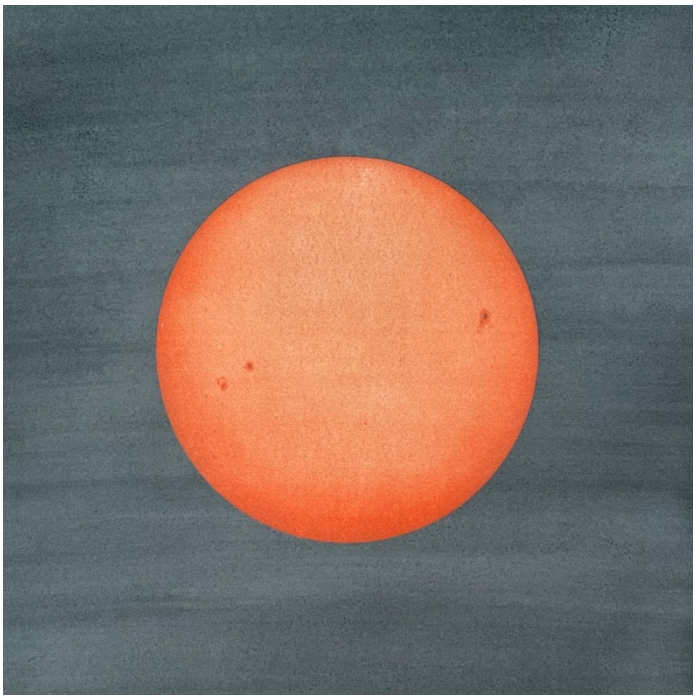

Sun, Smoke, Sky, and Grass Exhibition. All prints based on plant proteins of lupin, wheat, or soy

Bibliography

1. [i] British Patent 665649 Frank William Sharp, Autotype Company: Improvements in photographic films and processes for producing stencils therewith

2. [ii] Halvor Björngård and Hiroyuki Kobayashi J. Soc. Photogr. Sci. Technol. Japan. (2007) Vol.70 No.2: 106-112

3. [iii] Shrestha, S., Hag, L. V. T., Haritos, V. S., & Dhital, S. (2021). Lupin proteins: structure, isolation and application. *Trends in Food Science and Technology*, 116, 928-939. https://doi.org/10.1016/j.tifs.2021.08.035

4. [iv] Bruce MacEvoy's Handprint website: https://handprint.com/HP/WCL/water.html