SilverX emulsion for color holography

Introduction

Limited availability and particularly high cost of holographic plates intended for color reflection holography led us to continue the SilverCross project [1, 2] to develop holographic emulsion, suitable for large format hobby use. This requires emulsion with grain in 10 nm range and small Low Intensity Reciprocity Failure (LIRF) to allow long expositions in whole visible spectrum.

Material and apparatus

Deionized water	0.5 l
Gelatin Addox Colloida P	2.508 g
Silver Nitrate ($AgNO_3$)	8.7 mMol (1.479 g $AgNO_3$)
Potassium Halides (KHal)	9.285 mMol (1.05 g KBr + 0.077g KI)
Isocyanine solution 0.1 % in ethanol or methanol	3 ml
Pinacyanol solution 0.1 % in ethanol or methanol	3 ml
Syringes 20 ml	2 pieces
Hypodermic needle 1.2 × 40 mm	
Shortened hypodermic needle 1.2 × 10 mm	
Beaker 600 ml or plastic container	
Magnetic stirrer, optionally with heat plate	
Thermometer	
Plastic ice cubes bags or trays	
Glass plates of the same size as plastic ice cubes bags	3 pieces
Freezer	
Mechanical syringe discharger (optional, but recommended)	
Upper part of a 1.5 l PET bottle or a big funnel	2 pieces
Fine nylon mesh (ladies socks)	
Black plastic foil and / or aluminum foil	

Experimental procedure

1. Gelatin is soaked in 440 ml of deionized water for at least 2 hours at room temperature (20 °C). The gelatin solution is heated to 42 °C with constant stirring until the gelatin is completely dissolved.
2. The gelatin solution is then cooled to 32 °C with constant stirring.
3. The syringes are opened and charged with the silver and halides salts (one syringe with silver salt, the other syringe with halides, then closed and completely filled with deionized water (2 × 24 ml), carefully tilted to completely dissolve the salts and then cooled down to 0 °C. Put hypodermic needles onto the syringes. Be aware of any contact with silver nitrate! In contact with skin, you turn to black, if ingested you may completely turn blue and with contact with eyes you may blind forever!
4. Switch off light and switch on a red safety light. Increase stirring speed to maximum and continuously discharge syringes with the ice cold solutions of salts into stirred gelatin, see Fig. 1. The time of discharge should be between 60–90 s. Both syringes need to be discharged

simultaneously with equal rate through different length needles to different levels below gelatin surface. It is important to maintain the constant reaction speed and avoid the salts to come into contact before they are completely mixed with gelatin. This is important to avoid the AgX crystals to grow. It also helps to add dropwise a small amount (0.1 ml 0.1%) of isocyanine solution during precipitation process. Cyanine dyes are adsorbed on the surface of freshly created crystals and prevent recrystallization. These dyes are used later in spectral sensitization, and using them as a grain grow restrainer keeps the formulae simple. Freshly precipitated emulsion should be clear, only very slight opalization should be seen.

Fig. 1. Precipitation at maximum stirring, time to discharge the salts solution less than 90 s.

5. As soon as possible, the precipitated emulsion is filled into ice cubes bags and placed between pre-chilled glass plates, see Fig. 2. Pre-chilled ice cubes tray can be used. The sandwich is covered by aluminum foil or black plastic foil and placed for at least 24 hours into a freezer at temperature below –18 °C.

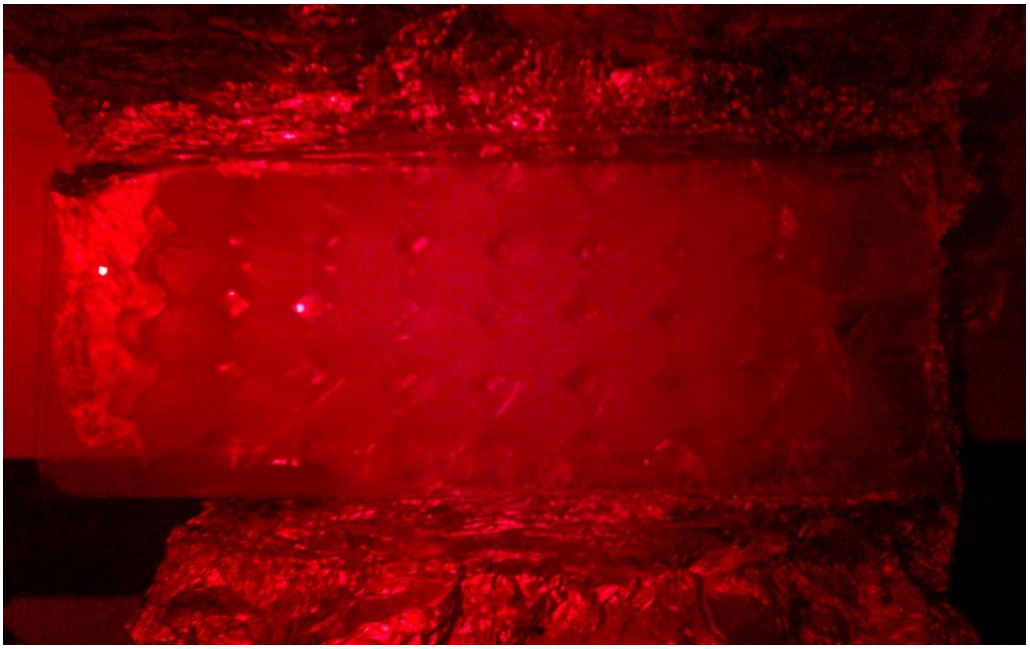

Fig. 2. Frozen precipitated emulsion in plastic ice cubes bags between glass plates.

6. Frozen emulsion is removed from ice bags and placed into upper parts of PET bottles with nylon mesh in the neck. Cover them and place them to darkness to thaw, see Fig. 3. It takes 6–8 hours for excess water to flow away while taking away reaction byproducts. During this process, the emulsion concentrates approximately five times.

Fig. 3. Thawing emulsion, it takes 6–8 hours in dark and cool place.

7. Crop the thawed emulsion before the temperature rises to 15 °C. Yield up to 100 g of the emulsion in a form of soft and almost clear jelly, see Fig. 4.

Fig. 4. Concentrated emulsion, yield up to 100 g.

8. Divide the emulsion to 8 g portions and freeze them again for storage. Alternatively you may proceed directly to next steps – sensitization, spectral sensitizing and finalizing.

Sensitization

Raw emulsion has very low sensitivity. Easy way to sensitize the emulsion is the reduction sensitizing by ascorbate. You can add the Na ascorbate (22 mg NaOH and 100 mg ascorbic acid) dissolved in small amount of water directly to the emulsion. Suitable amount is 15 mg per gram of emulsion, 1.5 g of the ascorbate per cropped yield. Drawback of the ascorbate sensitizing is limited shelf life of the plates. Hence, it may be useful sensitizing the plates directly before exposure by soaking them in 1 % Na-ascorbate solution, resulting in a slightly less sensitivity.

In both cases it is necessary to wash the plates in deionized water. Otherwise, the ascorbate sensitization results in strong blue shift due to shrinkage of the emulsion caused by the rather high amount of ascorbate dissolved in a developer.

Spectral Sensitizing

Heat fast the emulsion with stirring to melt it, around 40 °C. Add dropwise the solution of cyanine dyes in ethanol 0.03 ml (two drops) per gram of emulsion, 3 ml per entire batch. Pinacyanol itself creates panchromatic plates, but to obtain isopanchromatic emulsion, one must add isocyanine or quinaldine red otherwise sensitivity in green region is poor.

Substrate preparation

Suitable glass needs to be first cleaned by ordinary household detergent. Further cleaning can be done overnight soaking in nitric acid, or better 5 min in Cairo acid. These dangerous chemicals can be avoided using plasma treatment. Dielectric barrier discharge is excited by pulsed high voltage on glass surface create high reactive species from plain air, which burn every organic contamination. Then sublayer is applied, best adhesion promotion is created by applying 0.05% of (3-Aminopropyl)triethoxysilane in acetone. Apply by cotton swab in thin layer, less is better. After one hour unreacted silane needs to be washed by etanol or acetone.

Finalizing

Finalizing depends on coating method. Personally I skip this step and directly apply the emulsion on pre-subbed glass (silanized). Very thin layer of emulsion (around 0.01 – 0.02 g/cm^2) gives perfect results if it is formaldehyde pre-hardened after exposition, developed by GP2 developer and water washed. The plates can be fixed before final water wash to achieve blue shift, giving nice golden reconstruction, when exposed in red. This chemistry is excellent for monochrome and exceptionally stable, however not good in blue part of the spectrum due to strong absorption in colloidal silver. Also reconstruction replay is wide, due to thin layer, thus color saturation is weak. Thicker layer fail to be developed by GP2, due to mirror-like layer of metallic silver precipitate on emulsion surface, caused by excessive silver content. Dilution by adding more gelatin prevent this, but does not increase diffraction efficiency.

For color holography is needed to add a hardener, chromium(III) compound to the emulsion and coat thicker layer (up to 0.04 g/cm^2). Chromium(III) compound should be added in form of 0.1 M solution e.g. $KCr(SO_4)_2*12H_2O$ in concentration 0.5% - 1% of chromium relative to gelatin – approx. 300 mg of $KCr(SO_4)_2*12H_2O$ in 6 ml water to entire batch. After chromium hardener is added, the emulsion is applied to heated (30 °C) leveled glass. The plates are then cooled below 10 °C and let the emulsion to gel at least one hour. The plates are then rinsed twice (2x 5 min) in ice cold deionized water to remove unreacted ascorbate and chrome alum. Alternatively water wash can be done after drying, but longer washing time and agitating is recommended to eliminate blue shift. The plates are dried and aged at least 48 hours before exposition, due to time needed crosslinking of the gelatin by the chromium take place. Hardening is needed to preserve fine structure of fringes during development and bleaching and fasten the drying.

The development procedure should be performed by CW-C2 developer 1.5 – 2.5 minutes at 20 °C, with continuous agitation, followed by 1 minute water rinse. Longer developing time is only increasing noise, not diffraction efficiency. Then safe Brilland ferric bleach is applied, until clear and a minute longer. PBU bleaches are alternatives, namely PBU-ascorbic acid bleach is a choice, when blue shift is desired. The plate is rinsed 5 minutes in tap, followed two minutes rinse in deionized water with a suitable wetting agent. Finally the plates are slowly dried in vertical position.

References

[1] Bjelkhagen, H., Brotherton-Ratcliffe, D. **Ultra-Realistic Imaging: Advanced Techniques in Analogue and Digital Colour Holography**. 1st Edition. CRC Press, 2013. ISBN 978-1439827994.

[2] Bjelkhagen, H. I., Crosby, P. G., Green, D. P. M., Mirlis, E, Phillips, N. J. Fabrication of ultra-fine-grain silver halide recording material for color holography. **Proc SPIE Vol. 6912**, 691209 (2008). doi: 10.1117/12.765404