Making Analogue Colour Holograms In The Home Laboratory: Lessons From Failure And Success

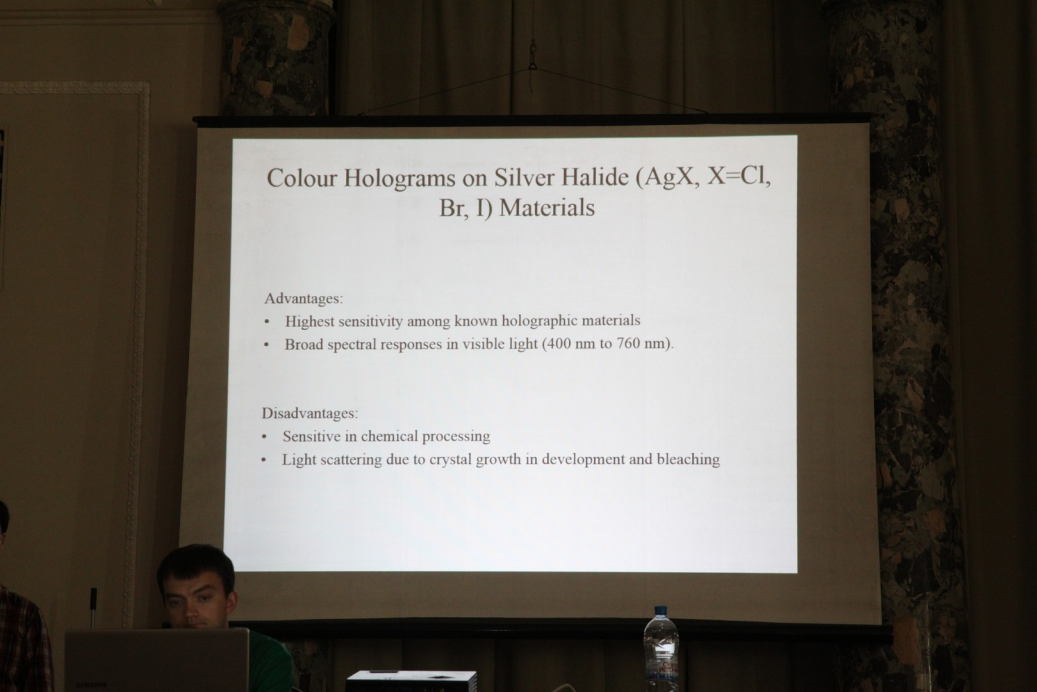
Quan Yuan, Ph.D

3D Holo Art Lab (www.3d-holo-art.com)
4-2-101 YanShangYuan XiErQi, Haidian District,
Beijing, China 100085
E-mail: products@3d-holo-art.com

ISDH 2015 July 2nd, 2015 St. Petersburg, Russia

Outline

- Colour Holograms based on AgX materials
- Review of published emulsion formulae and my experiment results
- Chemical processing of colour holograms
- Exposure calculation for balancing colour in Low Intensity Reciprocity Failure (LIRF) conditions


Colour Holograms on Silver Halide (AgX, X=Cl, Br, I) Materials
Advantages:
• Highest sensitivity among known holographic materials
• Broad spectral responses in visible light (400 nm to 760 nm).
Disadvantages:
• Sensitive in chemical processing
• Light scattering due to crystal growth in development and bleaching


Difficulties of Colour Holograms on Silver Halide Materials
• Relatively lower diffraction efficiency than monochromatic holograms
• More sensitive chemical processing than monochromatic holograms
• Difficult calculations for balancing exposures at different wavelengths, especially in low intensity reciprocity failure (LIRF) conditions
Michael Sheytsov

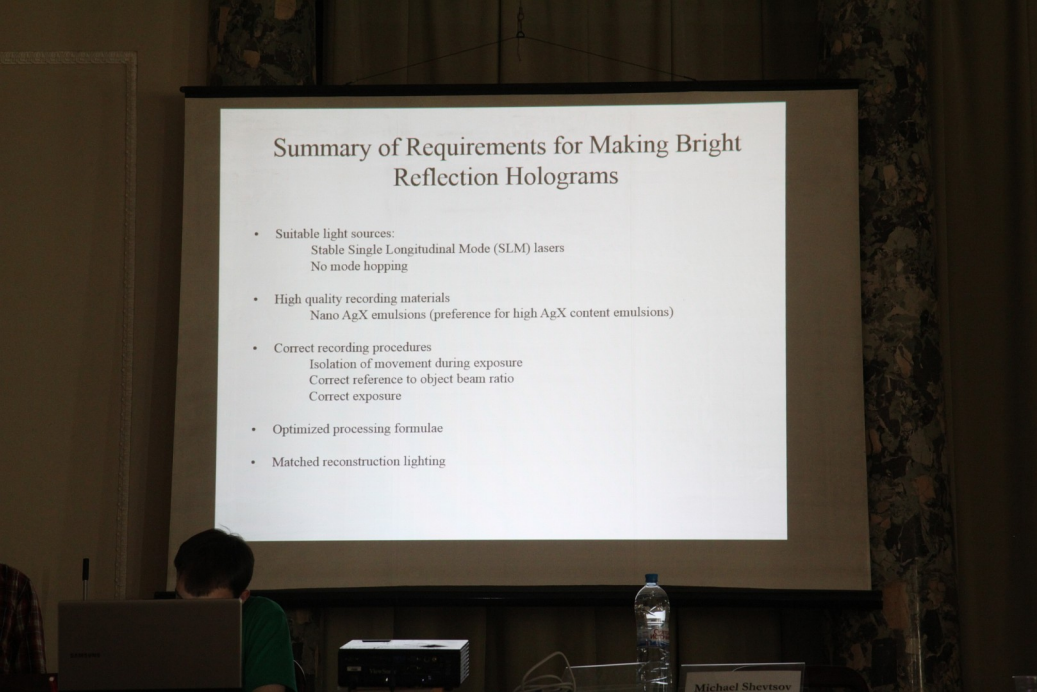
Criteria of High Quality Colour Holograms

Visual aspects:

- High brightness
- High signal to noise (S/N) ratio
- No colour shift
- High colour saturation

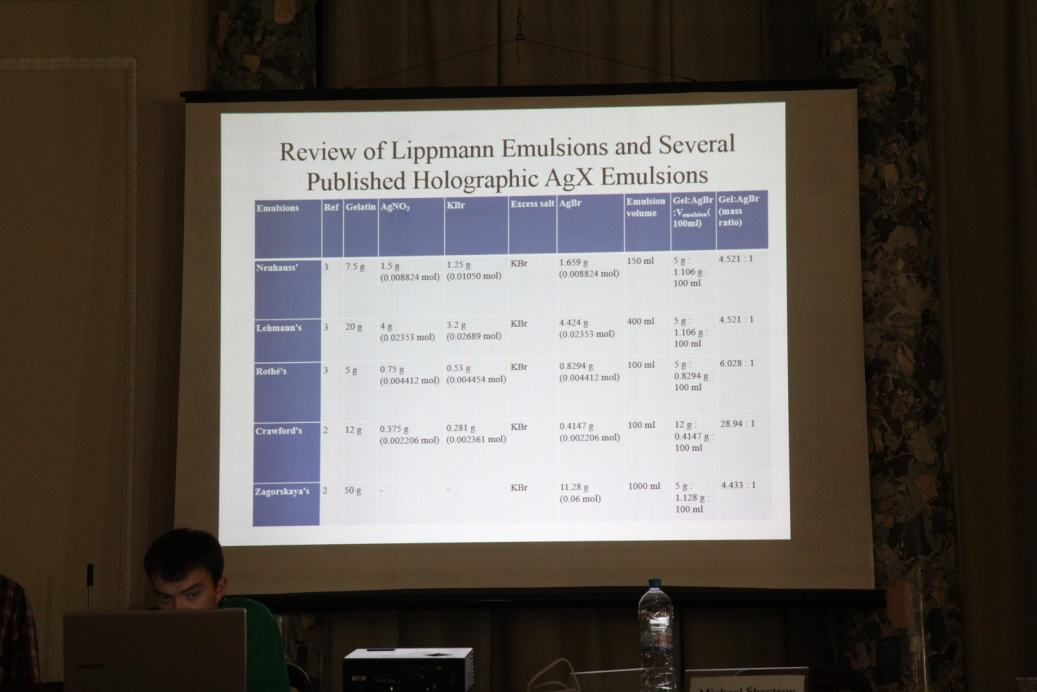
Meanings in physics:

- High diffraction efficiency (high index modulation)
- Low light scattering (small size of AgX crystals)
- Balancing exposures at different wavelengths and no emulsion shrinkage
- Narrow spectrum width of the reconstruction wavelengths (accurate Bragg planes)


Summary of Requirements for Making Bright Reflection Holograms
• Suitable light sources:
Stable Single Longitudinal Mode (SLM) lasers
No mode hopping
• High quality recording materials
Nano AgX emulsions (preference for high AgX content emulsions)
• Correct recording procedures
Isolation of movement during exposure
Correct reference to object beam ratio
Correct exposure
• Optimized processing formulae
• Matched reconstruction lighting

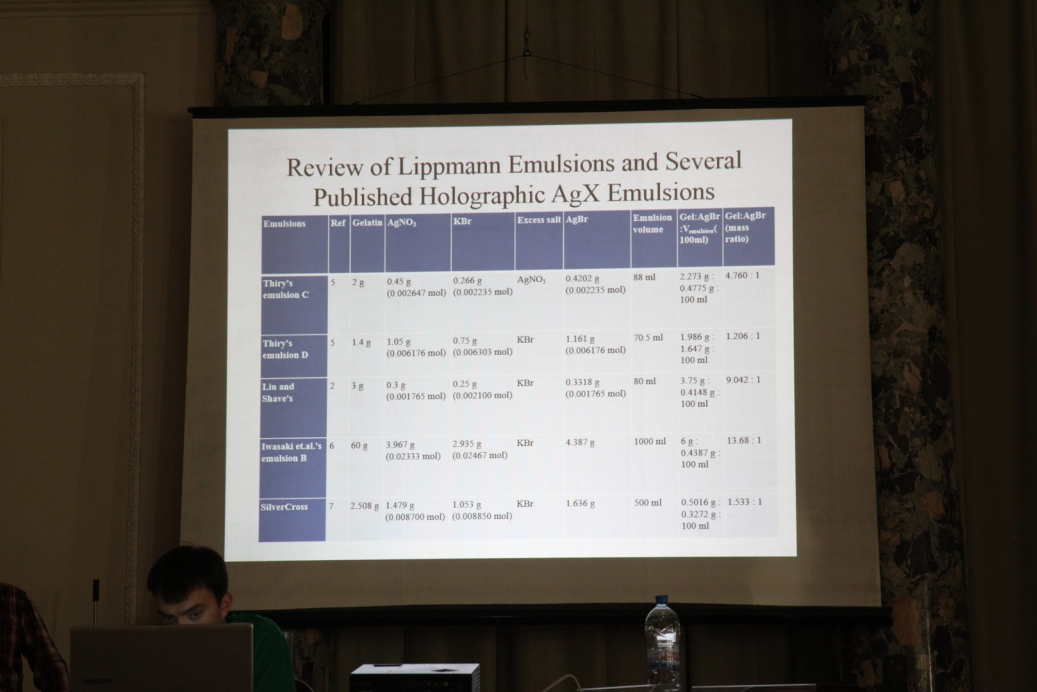
Review of Lippmann Emulsions and Several Published Holographic AgX Emulsions

Emulsions	Ref	Gelatin	$AgNO_3$	KBr	Excess salt	AgBr	Emulsion volume	Gel:AgBr :$V_{emulsion}$(100ml)	Gel:AgBr (mass ratio)
Lippmann's	2	4 g	0.75 g (0.004412 mol)	0.53 g (0.004454 mol)	KBr	0.8294 g (0.004412 mol)	100 ml	4 g : 0.8294 g : 100 ml	4.823 : 1
Valenta's	2	30 g	6 g (0.03529 mol)	5 g (0.04202 mol)	KBr	6.635 g (0.03529 mol)	600 ml	5 g : 1.106 g : 100 ml	4.521 : 1
Senior's	2	10 g	3 g (0.01765 mol)	2.1 g (0.01765 mol)	equal	3.318 g (0.01765 mol)	450 ml	2.222 g : 0.7373 g : 100 ml	3.014 : 1
Ives'	4	3 g	0.3 g (0.001765 mol)	0.25 g (0.002101 mol)	KBr	0.3318 g (0.001765 mol)	80 ml	3.75 g : 0.4148 g : 100 ml	9.041 : 1
Lumière's	3	20 g	5 g (0.02941 mol)	3.5 g (0.02941 mol)	equal	5.5295 g (0.02941 mol)	400 ml	5 g : 1.382 g : 100 ml	3.618 : 1



Review of Lippmann Emulsions and Several Published Holographic AgX Emulsions

Emulsions	Ref	Gelatin	$AgNO_3$	KBr	Excess salt	AgBr	Emulsion volume	Gel:AgBr :$V_{emulsion}$(100ml)	Gel:AgBr (mass ratio)
Neuhauss'	3	7.5 g	1.5 g (0.008824 mol)	1.25 g (0.01050 mol)	KBr	1.659 g (0.008824 mol)	150 ml	5 g : 1.106 g : 100 ml	4.521 : 1
Lehmann's	3	20 g	4 g (0.02353 mol)	3.2 g (0.02689 mol)	KBr	4.424 g (0.02353 mol)	400 ml	5 g : 1.106 g : 100 ml	4.521 : 1
Rothé's	3	5 g	0.75 g (0.004412 mol)	0.53 g (0.004454 mol)	KBr	0.8294 g (0.004412 mol)	100 ml	5 g : 0.8294 g : 100 ml	6.028 : 1
Crawford's	2	12 g	0.375 g (0.002206 mol)	0.281 g (0.002361 mol)	KBr	0.4147 g (0.002206 mol)	100 ml	12 g : 0.4147 g : 100 ml	28.94 : 1
Zagorskaya's	2	50 g	-	-	KBr	11.28 g (0.06 mol)	1000 ml	5 g : 1.128 g : 100 ml	4.433 : 1



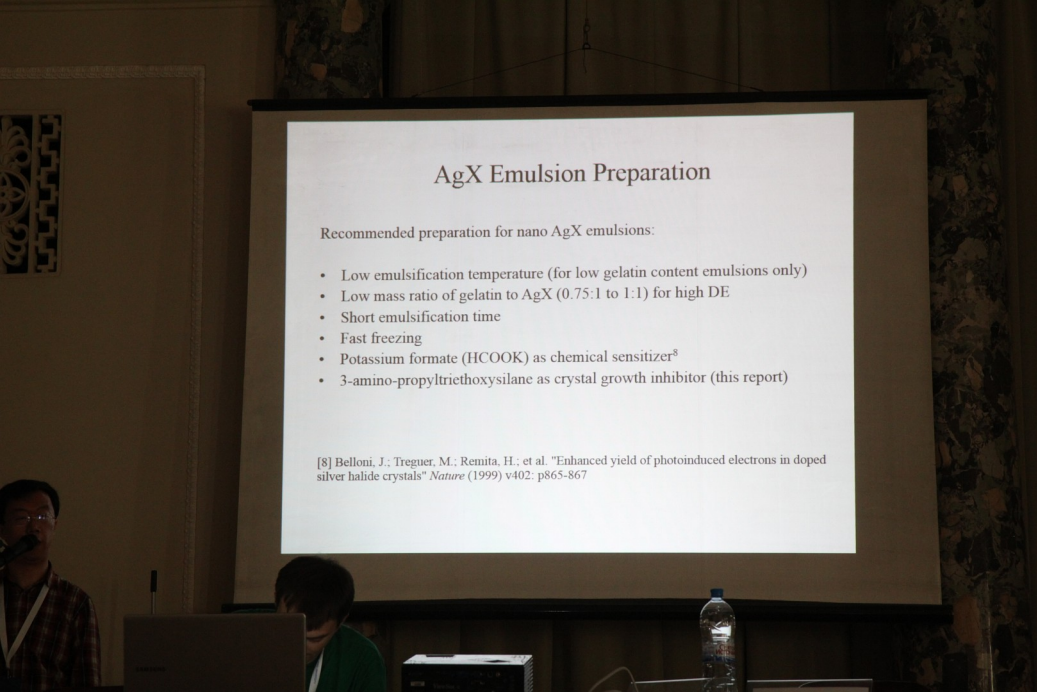
Review of Lippmann Emulsions and Several Published Holographic AgX Emulsions

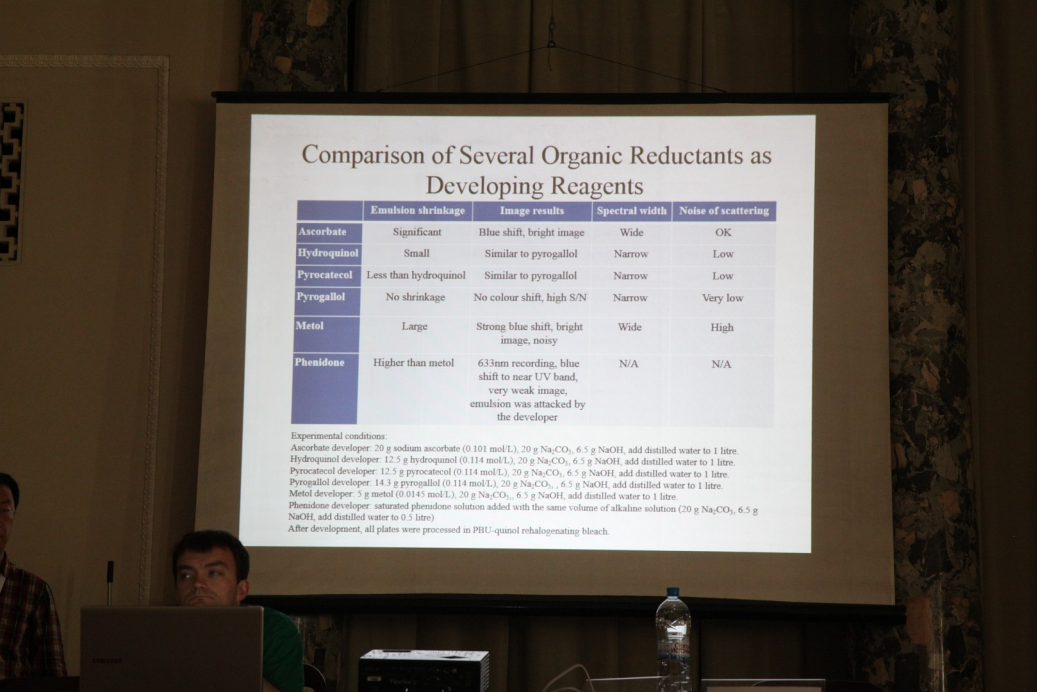
Emulsions	Ref	Gelatin	$AgNO_3$	KBr	Excess salt	AgBr	Emulsion volume	Gel:AgBr :$V_{emulsion}$(100ml)	Gel:AgBr (mass ratio)
Thiry's emulsion C	5	2 g	0.45 g (0.002647 mol)	0.266 g (0.002235 mol)	$AgNO_3$	0.4202 g (0.002235 mol)	88 ml	2.273 g : 0.4775 g : 100 ml	4.760 : 1
Thiry's emulsion D	5	1.4 g	1.05 g (0.006176 mol)	0.75 g (0.006303 mol)	KBr	1.161 g (0.006176 mol)	70.5 ml	1.986 g : 1.641 g : 100 ml	1.206 : 1
Liu and Shave's	2	3 g	0.3 g (0.001765 mol)	0.25 g (0.002100 mol)	KBr	0.3318 g (0.001765 mol)	80 ml	3.75 g : 0.4148 g : 100 ml	9.042 : 1
Iwasaki et.al.'s emulsion B	6	60 g	3.967 g (0.02333 mol)	2.935 g (0.02467 mol)	KBr	4.387 g	1000 ml	6 g : 0.4387 g : 100 ml	13.68 : 1
SilverCross	7	2.508 g	1.479 g (0.008700 mol)	1.053 g (0.008850 mol)	KBr	1.636 g	500 ml	0.5016 g : 0.3272 g : 100 ml	1.533 : 1

AgX Emulsion Experiments

Comparison of different emulsions and their holographic image results:

#	Gelatin	AgBr	Emulsion volume	Emulsification temperature	Freezing method	Holographic image results	Notes
1	1 g	0.2 g	20 ml	40 °C	fast	very weak	
2	0.5 g	0.2 g	20 ml	40 °C	fast	weak	
3	0.25 g	0.2 g	20 ml	40 °C	fast	good	
4	0.2 g	0.2 g	20 ml	40 °C	fast	good	high fog
5	0.1 g	0.145 g	~18 ml	40 °C	fast	good	high fog
6	0.2 g	0.2 g	80 ml	40 °C	fast	very good	
7	0.2 g	0.2 g	80 ml	40 °C	slow	no image	coarse grain
8	0.25 g	0.2 g	80 ml	20 °C	fast	good	
9	0.15 g	0.2 g	80 ml	20 °C	fast	no image	coarse grain generated during drying process
10	0.15 g +0.15 g PVA	0.2 g	80 ml	20 °C	slow	no image	could not get homogeneous coating
11	0.15g PVA (no gelatin)	0.2 g	80 ml	20 °C	slow	N/A	difficult to wash, desalt and concentrate
12	0.15 g, (1×10^{-2}:1 methionine: AgBr molar ratio)	0.2 g	20 ml	20 °C	slow	weak	high fog


AgX Emulsion Preparation
Recommended preparation for nano AgX emulsions:
• Low emulsification temperature (for low gelatin content emulsions only)
• Low mass ratio of gelatin to AgX (0.75:1 to 1:1) for high DE
• Short emulsification time
• Fast freezing
• Potassium formate (HCOOK) as chemical sensitizer[8]
• 3-amino-propyltriethoxysilane as crystal growth inhibitor (this report)
[8] Belloni, J.; Treguer, M.; Remita, H.; et al. "Enhanced yield of photoinduced electrons in doped silver halide crystals" *Nature* (1999) v402: p865-867



Comparison of Several Organic Reductants as Developing Reagents

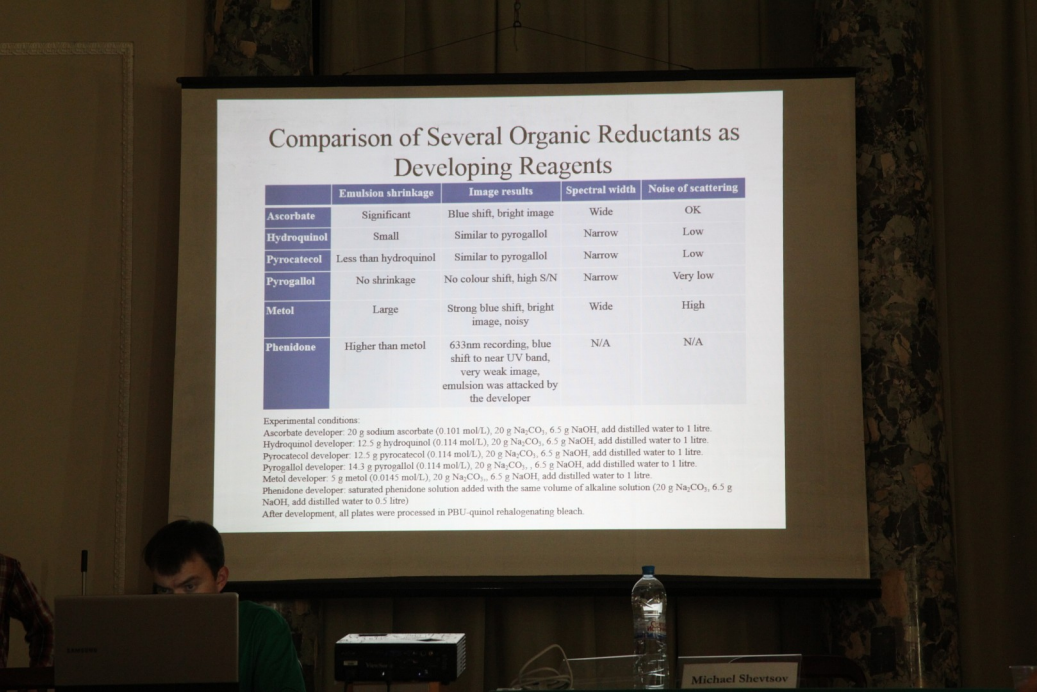
	Emulsion shrinkage	Image results	Spectral width	Noise of scattering
Ascorbate	Significant	Blue shift, bright image	Wide	OK
Hydroquinol	Small	Similar to pyrogallol	Narrow	Low
Pyrocatecol	Less than hydroquinol	Similar to pyrogallol	Narrow	Low
Pyrogallol	No shrinkage	No colour shift, high S/N	Narrow	Very low
Metol	Large	Strong blue shift, bright image, noisy	Wide	High
Phenidone	Higher than metol	633nm recording, blue shift to near UV band, very weak image, emulsion was attacked by the developer	N/A	N/A

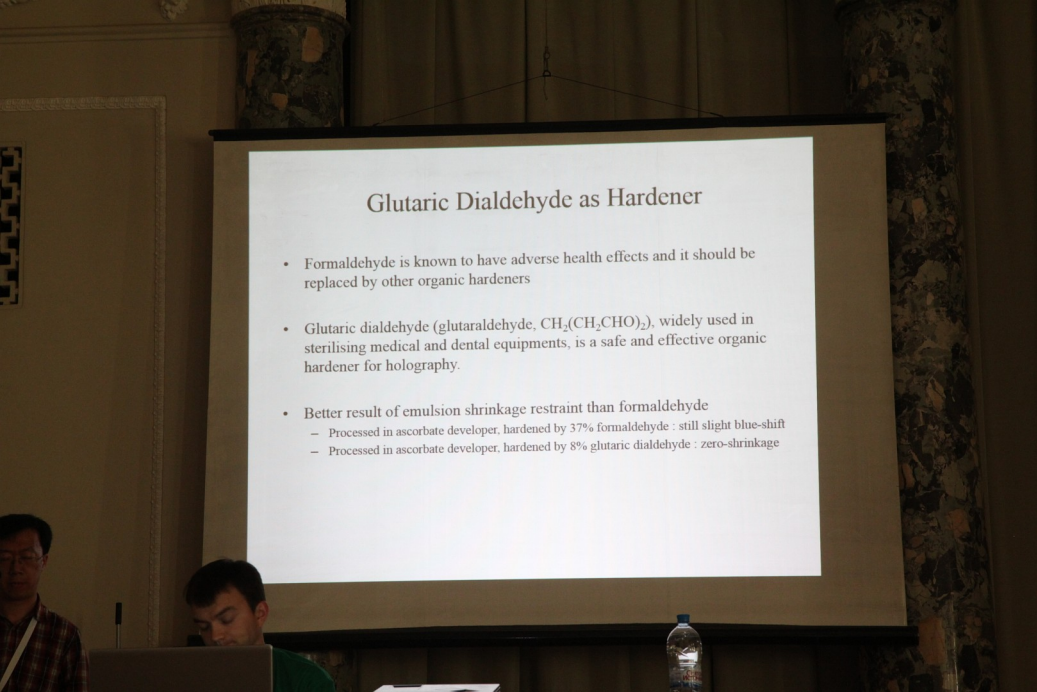
Experimental conditions:
Ascorbate developer: 20 g sodium ascorbate (0.101 mol/L), 20 g Na_2CO_3, 6.5 g NaOH, add distilled water to 1 litre.
Hydroquinol developer: 12.5 g hydroquinol (0.114 mol/L), 20 g Na_2CO_3, 6.5 g NaOH, add distilled water to 1 litre.
Pyrocatecol developer: 12.5 g pyrocatecol (0.114 mol/L), 20 g Na_2CO_3, 6.5 g NaOH, add distilled water to 1 litre.
Pyrogallol developer: 14.3 g pyrogallol (0.114 mol/L), 20 g Na_2CO_3, 6.5 g NaOH, add distilled water to 1 litre.
Metol developer: 5 g metol (0.0145 mol/L), 20 g Na_2CO_3, 6.5 g NaOH, add distilled water to 1 litre.
Phenidone developer: saturated phenidone solution added with the same volume of alkaline solution (20 g Na_2CO_3, 6.5 g NaOH, add distilled water to 0.5 litre)
After development, all plates were processed in PBU-quinol rehalogenating bleach.

Modified PBU Bleach for Lower Scattering Processing

Cupric sulphate, pentahydrate ($CuSO_4 \cdot 5H_2O$)	1 g
or Ferric sulphate ($Fe_2(SO_4)_3$)	1 g
Potassium persulfate ($K_2S_2O_8$)	10 g
Citric acid ($C_6H_8O_7$)	50 g
Potassium bromide (KBr)	10 g
Add distilled water to	1 L

Half amount of KBr of the original PBU bleach (20 g per litre) was used in this bleach, and cupric sulphate ($CuSO_4 \cdot 5H_2O$) or ferric sulphate ($Fe_2(SO_4)_3$) was added but there was no quinol or metol. In this modified bleach, when quinol or metol is missing, cupric sulphate or ferric sulphate is important, or the bleaching rate would be very slow, indicating the catalysing effect of those salts. Low KBr concentration in the rehalogenating bleach is helpful in getting small size AgBr crystals for low scattering holograms.


Comparison of Several Organic Reductants as Developing Reagents
Emulsion shrinkage
Image results
Spectral width
Noise of scattering
Ascorbate
Significant
Blue shift, bright image
Wide
OK
Hydroquinol
Small
Similar to pyrogallol
Narrow
Low
Pyrocatecol
Less than hydroquinol
Similar to pyrogallol
Narrow
Low
Pyrogallol
No shrinkage
No colour shift, high S/N
Narrow
Very low
Metol
Large
Strong blue shift, bright image, noisy
Wide
High
Phenidone
Higher than metol
633nm recording, blue shift to near UV band, very weak image, emulsion was attacked by the developer
N/A
N/A
Experimental conditions:
Ascorbate developer: 20 g sodium ascorbate (0.101 mol/L), 20 g Na_2CO_3, 6.5 g NaOH, add distilled water to 1 litre.
Hydroquinol developer: 12.5 g hydroquinol (0.114 mol/L), 20 g Na_2CO_3, 6.5 g NaOH, add distilled water to 1 litre.
Pyrocatecol developer: 12.5 g pyrocatecol (0.114 mol/L), 20 g Na_2CO_3, 6.5 g NaOH, add distilled water to 1 litre.
Pyrogallol developer: 14.3 g pyrogallol (0.114 mol/L), 20 g Na_2CO_3, , 6.5 g NaOH, add distilled water to 1 litre.
Metol developer: 5 g metol (0.0145 mol/L), 20 g Na_2CO_3, 6.5 g NaOH, add distilled water to 1 litre.
Phenidone developer: saturated phenidone solution added with the same volume of alkaline solution (20 g Na_2CO_3, 6.5 g NaOH, add distilled water to 0.5 litre)
After development, all plates were processed in PHU-quinol rehalogenating bleach.
Michael Shevtsov


Glutaric Dialdehyde as Hardener
• Formaldehyde is known to have adverse health effects and it should be replaced by other organic hardeners
• Glutaric dialdehyde (glutaraldehyde, $CH_2(CH_2CHO)_2$), widely used in sterilising medical and dental equipments, is a safe and effective organic hardener for holography.
• Better result of emulsion shrinkage restraint than formaldehyde
– Processed in ascorbate developer, hardened by 37% formaldehyde : still slight blue-shift
– Processed in ascorbate developer, hardened by 8% glutaric dialdehyde : zero-shrinkage

Comparison of Different Processing for Colour Holograms

Developers	Advantages	Disadvantages	Notes
Lumière developer	No colour shift in 60 seconds processing Simple High DE	Colloidal silver in red to brown colour, rendering red hue in colour holograms	No bleaching needed
Ascorbate developer + glutaric dialdehyde hardener	No emulsion shrinkage Almost colourless High DE	Higher scattering than pyrogallol developer	Followed by PBU bleaching
Pyrogallol developer	No emulsion shrinkage Low scattering High DE	The tanning product of pyrogallol shows yellow-brown colour	Followed by PBU bleaching

Bleaches	Advantages	Disadvantages	Notes
Rehalogenating bleach (PBU-quinol, PBU-metol)	No emulsion shrinkage	Crystal growth during bleaching	Extended bleaching results in scattering
Reversal bleach ($Cr_2O_7^{2-}$, or MnO_4^- with H_2SO_4)	Very low scattering Almost no crystal growth during bleaching	Emulsion shrinkage occurs (even if emulsion is hardened by glutaric dialdehyde or in pyrogallol development)	Chemical attack to the tanning product of pyrogallol and cross-linked gelatin hardened by glutaric dialdehyde

Re-examination of Beer-Lambert Law and Hurter-Driffield curve (H&D curve)

- Beer-Lambert law: Absorbance (Abs or OD)=$\varepsilon \cdot l \cdot c$, while ε is the extinction coefficient of specific particles, l is the optical path, c is the concentration of the particles.
  - ε is for pure substance, for total absorbance of mixtures: Abs=$\sum_{i=1}^{n} \varepsilon_i \cdot l \cdot c_i$
  - Particles: atoms, molecules, nano-particles

- Hurter-Driffield curve: empirical curve based on traditional black & white photography

Re-examination of Beer-Lambert Law and Hurter-Driffield curve (H&D curve)

Derivation of OD v.s. logH for an ideal mono-dispersed AgX emulsion in Non-HIRF and Non-LIRF conditions:

$Abs = \varepsilon \cdot l \cdot c$

Concentration of exposed AgX crystals (it must be mono dispersed!) in emulsion: $c = k_1 \cdot I \cdot T$,

while I is laser intensity, T is the exposure time, k_1 is a coefficient.

Assumption: exposure is not reaching the limit or the thickness of emulsion is large enough.

$Abs = \varepsilon \cdot l \cdot c = \varepsilon \cdot l \cdot k_1 \cdot I \cdot T = (\varepsilon \cdot l \cdot k_1) \cdot I \cdot T = k_2 \cdot I \cdot T$

$OD = Abs = k_2 \cdot I \cdot T = k_2 \cdot H$

$H = 10^{logH}$ $(logH = \log_{10} H)$

$OD = k_2 \cdot I \cdot T = k_2 \cdot 10^{logH}$ OD is an exponential function of logH !

Deviation of Beer-Lambert law in Hurter-Driffield curve:

For Hurter–Driffield curve (H–D curve) in the linear region:

$OD = \gamma \cdot logH + N$, γ is the slope of the characteristic curve, N is a negative value

$OD = \gamma \cdot logH + N = \gamma \cdot logI + \gamma \cdot logT + N$

The reasons for deviation of Beer-Lambert law in traditional black & white photography

- Non-mono dispersed AgX emulsion: mixture of AgX crystals of different sizes, non-homogenous media
- Limited thickness of the emulsion

Schwarzschild's Law in Traditional AgX Photography and the Form in Holography

Schwarzschild's Law[9]: empirical law in traditional black & white photography (Non-mono dispersed emulsion for astronomy photography plates, long before the invention of Tabular AgX emulsion)

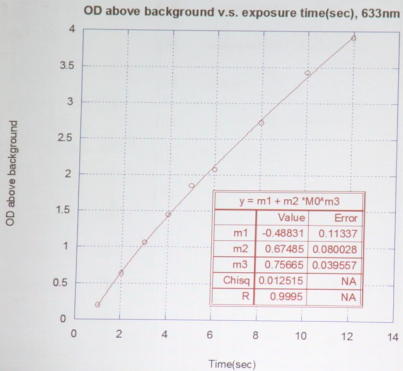
$H=I\cdot T^{p}$, p is the Schwarzschild coefficient, $p \approx 0.86$

[9] Schwarzschild, K "On the Deviations From The Law of Reciprocity For Bromide Of Silver Gelatine" *Astrophysical Journal* Vol.11, p89, (1900)

Assumptions for exposure of holographic emulsions in LIRF conditions:

- Mono-dispersed AgX crystals
- Concentration of exposed AgX crystals in the emulsion in LIRF conditions: $c=k_1\cdot I\cdot T^{b}$, while I is laser intensity, T is the exposure time, k_1 is a coefficient, b is an empirical coefficient similar to the Schwarzschild coefficient.
- $OD=Abs=\varepsilon\cdot l\cdot c=\varepsilon\cdot l\cdot k_1\cdot I\cdot T^{b}=(\varepsilon\cdot l\cdot k_1)\cdot I\cdot T^{b}=k_2\cdot I\cdot T^{b}$ $(0<b<1)$

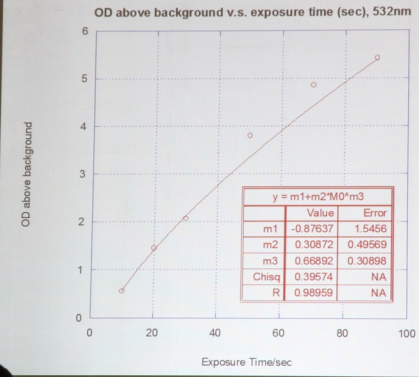
Let's fit the curve to see if b is a constant?



y = m1 + m2 *M0^m3		
	Value	Error
m1	-0.48831	0.11337
m2	0.67485	0.080028
m3	0.75665	0.039557
Chisq	0.012515	NA
R	0.9995	NA

- Red-sensitive plate
- He-Ne laser intensity: 53.7μW/0.636cm^2
- Ascorbate developer, 2 minutes
- No bleaching
- No fixing
- Black filament silver
- OD measured at 650 nm

- $OD=k_2 \cdot I \cdot T^b$
- b=m3=0.756±0.039
- b is a constant!



- Red-sensitive plate
- 532nm DPSS laser intensity: 88.0μW/0.636cm^2
- Ascorbate developer, 2 minutes
- No bleaching
- No fixing
- Black filament silver
- OD measured at 650 nm

- $OD=k_2 \cdot I \cdot T^b$
- b=m3=0.67±0.31
- b is a constant!

Holographic Exposure Calculations in Low Intensity Reciprocity Failure (LIRF) conditions

- Obtaining characteristic constants for the emulsion at your recording wavelengths:

$$OD_{633nm}=k_{633nm}\cdot I_{633nm}\cdot T_{633nm}^{\ b}+c_{633nm} \qquad b\approx 0.7$$

$$OD_{532nm}=k_{532nm}\cdot I_{633nm}\cdot T_{532nm}^{\ b}+c_{532nm} \qquad b\approx 0.7$$

$$OD_{\lambda}=k_{\lambda}\cdot I_{\lambda}\cdot T_{\lambda}^{\ b}+c_{\lambda} \qquad \text{b is wavelength-independent}$$

- For balancing exposure at 532 nm and 633 nm, set a target monochromatic OD for both wavelengths, for example $OD_{633nm}=OD_{532nm}=2.5$.
- Measure the laser intensities at 532 nm and 633 nm
- Calculate the exposure time at your wavelengths:

$$T_{\lambda}=\left(\frac{OD_{\lambda}-c_{\lambda}}{k_{\lambda}\cdot I_{\lambda}}\right)^{\frac{1}{b}}$$

How To Make Colour Holograms Using Non-panchromatic AgX Materials?

- Panchromatic AgX emulsion has different spectral responses at different wavelengths too!
- Colour holograms can be made using red-sensitive AgX materials (but need longer time or higher laser power for exposures in green and blue)
- For unknown AgX HOLOGRAPHIC emulsions (monochromatic or panchromatic):
  - Fit the curves of OD v.s. T and get the values of b, k and c at all recording wavelengths (633nm, 532nm, 473nm)
  - Measure the laser intensity (reference + object) for each wavelength
  - Calculate the exposure time of each wavelength
  - Recording
  - Zero-shrinkage processing

References

[1] Bjelkhagen, H.I.; Brotherton-Ratcliffe, D. , Ultra-Realistic Imaging: Advanced Techniques in Analogue and Digital Colour Holography, CRC Press (2013), p147

[2] Bjelkhagen, H. I. "Silver halide emulsions for Lippmann photography and holography" *Proc. SPIE* Vol. 1600, pp. 44-59 (1991)

[3] Bjelkhagen, H.I.; Brotherton-Ratcliffe, D. , *Ultra-Realistic Imaging: Advanced Techniques in Analogue and Digital Colour Holography*, CRC Press (2013), p49-53

[4] Ives, H. E. "An experimental study of the Lippmann color photograph" *Astrophysical Journal* Vol. 27, p325-352, (1908)

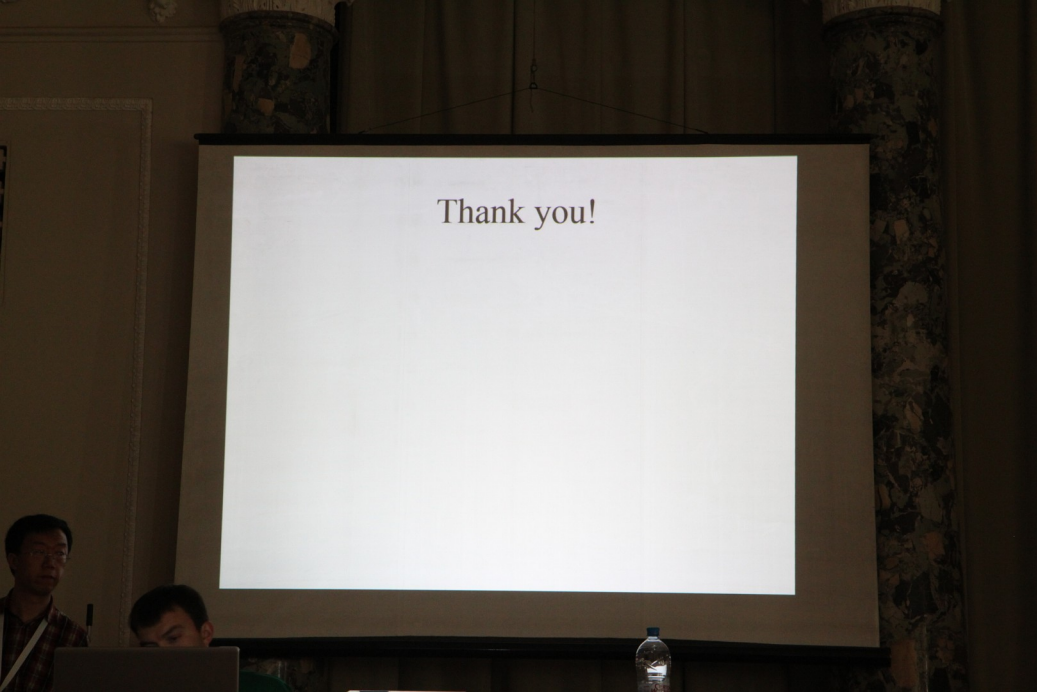
[5] Thury, H. "Preparation and Properties of Ultra-fine Grain AgBr Emulsions" *The Journal of Photographic Science* Vol. 35, p150-154, (1987)

[6] Iwasaki, M.; Kubota, T.; Tanaka, T., "Preparation of New Ultra-Fine-Grain Emulsion for holography" *The Journal of Photographic Science* Vol.41(3) p112-113 (1993)

[7] Bjelkhagen, H.I.; Brotherton-Ratcliffe, D. , *Ultra-Realistic Imaging: Advanced Techniques in Analogue and Digital Colour Holography*, CRC Press (2013), p106

[8] Belloni, J.; Treguer, M.; Remita, H.; et al. "Enhanced yield of photoinduced electrons in doped silver halide crystals" *Nature* Vol.402, p865-867, (1999)

[9] Schwarzschild, K "On the Deviations From The Law of Reciprocity For Bromide Of Silver Gelatine" *Astrophysical Journal* Vol.11, p89, (1900)


Thank you!