12_04_17 v1.3

FORMATE AS A SENSITIVITY ENHANCER OF HOLOGRAPHIC EMULSIONS

William R. Alschuler
Science Faculty, School of Critical Studies, California Institute of the Arts
24700 McBean Parkway, Valencia, Ca. 91355 walschuler@calarts.edu

ABSTRACT

This paper reports experiments that confirm Belloni (2003) that pre-soaking a silver halide holographic emulsion in a dilute solution of the formate ion (HCO_2^-) will hypersensitize the emulsion by a factor of 5xs to 10xs, depending on the timing of development post-exposure. The quantum efficiency of the emulsion is effectively 1 in the first case. The extremely fine grain size of the holographic emulsion (Slavich PFG-01) is maintained and holographic image quality is excellent. When combined with a TEA pre-soak the expected TEA color shift is maintained.

1. INTRODUCTION

Some years ago Belloni (2002 *et seq.*)[1,2,3] and coauthors published a series of papers that showed how to significantly enhance photosensitivity in silver halide emulsions using an emulsion doping of formate. Some time later I asked if anyone had tried this technique for holographic emulsions, (Alschuler, 2005)[4]. This resulted in a brief exchange, and apparently then no one had tried it. Recently a search revealed no change in this situation and I decided to carry out simple tests to see if this process could enhance the photosensitivity of holographic emulsions.

2. THE SENSITIVITY EFFECT

Belloni (2002, 2003)[1,2] notes that the exposure to make a developable latent image grain requires about three atoms per silver cluster (AgBr) to be available to the chemical developer. To achieve this number, it is typical that 10 to 30 photons are required. This large number reflects the low quantum efficiency of the process, due to loss of excited electrons to direct recombination with holes in the silver halide. To eliminate this loss Belloni picked the formate ion, HCO_2^-, which is small and of the right ionic character to combine with the crystals. At a concentration of 10^{-6} molar of formate per mole of Ag^+, the enhancement is effectively a factor of 5 compared to normal if the exposed emulsion is developed immediately, and a factor of 10 if developed after a delay of about 15 minutes. The first gain is due to fast hole scavenging during exposure, the second to slow electron transfer to an additional silver cation from the formyl radical CO^-_2. The first step comes close to creating a quantum efficiency of the process of 1, and the second doubles that. Belloni (2003)[2] also states that the emulsions don't fog in the dark and that, key for holography, the grain size and resolution are unaffected.

3. EXPERIMENTAL

3.1 Initial Test and Photochemistry

To test these results out, I chose to use Slavich PFG-01, a popular red-sensitive holographic emulsion, which I use in my holography classes. The normal processing used for class is development in Kodak D-19 (equivalents now made by others than Kodak, such as Photographers' Formulary), bleaching in a ferric-EDTA re-halogenating bleach, the "No Patchy Haze," Wesly (1992)[5]*, and redevelopment in ascorbic acid (10gms/liter distilled water), rinsing after each step. With a 20mw HeNe laser illuminating a 4x5" plate, normal exposure time of 10-12 seconds yields a "negative" of O.D. (Optical Density) of about 1.2 to 2.0, estimated visually in transmission against a test chart and a strong final image for a wide range of objects, shot as white light Denisyuk holograms.

After a search of chemical supply houses, the most readily available formate molecule I have found is sodium formate, for example from Sigma-Aldrich # 107603-1KG (CAS 141-53-7), reagent grade.

I started by tray-soaking the plates in a one molar solution (68.01 gms sodium formate/liter of distilled water) for 30 seconds, in the dark, in analogy to the practice of pre-soaking holographic emulsions with triethanolamine (TEA) for pseudocolor imaging. The plate was squeegeed and blowdried before exposure.

This concentration of formate yielded a powdery deposit on the emulsion surface, detectable by touch when the emulsion was dry and wet. After drying, a 2-second exposure ($1/5^{th}$ normal) gave a successful image, with immediate development.

3.2 Usable Dilution to Avoid Powdery Deposit

After achieving good results from the reduced exposure and immediate development, the next step was to test at what dilution the formate hypersensitizing fails. Dilutions to 1/16 molar achieved the same success from the point of view of image quality and the powdery deposit mentioned above was absent at this modestly greater dilution.

*See the Appendix below.

4. RESULTS

4.1 Limiting Maximum Dilution with Immediate Development

Eventually dilution to 1/100 molar (0.6 gms/liter distilled) showed no or a slight drop in Optical Density (≈1.2-1.8) for the 2 second exposure (1/5th normal), and it therefore was judged that a concentration of 1/100 molar was perhaps a practical lower limit to the concentration of sodium formate that will achieve the desired image quality and hypersensitization.

It appears the formate presoak slightly shrinks the emulsion as the developed image is visually slightly more red than the image with normal processing and no presoak.:

4.2 Formate and Delayed development

Trials of delayed development were held with the same formate concentration. These confirmed that an exposure time of 1/10th normal (1 sec.) yielded a usable but slightly lower Optical Density (≈ 0.8) than the trials above, if development was delayed at least 15 minutes after exposure. The high image quality was maintained under this procedure.

4.3 Formate Combined with TEA

TEA is often used to create pseudocolor in holograms, by presoaking in it, which swells the emulsion. Rinseout before development shrinks it back and shifts the reconstruction color to shorter wavelengths. A test shot was prepared for which a plate was first soaked in 1/100 molar formate, dried, and then one third of the plate was soaked for 30 seconds in TEA, and dried, at a TEA concentration that provides a strong green color without the formate. This plate was exposed for 2 seconds. Processing began a few minutes after exposure, so the expected speed gain was a factor of 5. The plate was first rinsed for 2 minutes to remove the TEA and then developed normally (see above). Dividing the plate into two zones for pre-treatment allowed side-by-side comparison of the results. The TEA-treated section had its normal green color and an O.D. perhaps slightly higher than the untreated part (1.2 vs 1.0?). This is not unexpected, since though TEA by itself normally gives a speed gain of a factor of about 2, the formate is providing a quantum efficiency of about 1, so there is little room for improvement. Note that the literature leaves the TEA speed gain largely unexplained, and also that s simple distilled water presoak will also give about a factor of 2 speed gain, and that this is also unexplained.

4.4 Shelf Life Of Sodium Formate Solution

No visual change was observed nor any change in performance for the formate solution stored at room temperature in a plastic bottle in the dark for over a month.

4.5 Shelf Life Of Sodium Formate Presoaked Emulsion

No apparent change to plate appearance or any surface deposit was found to have occurred in 1/100th molar formate-presoaked plates stored refrigerated at 40°F for a month when examined under a safelight, and the image results from a 2 second exposure of this plate were as described above.

4.6 Shelf Life of Exposed Sodium Formate Presoaked Emulsion
No test was made to see if formate pre-exposure had any effect on the longevity of the latent image after exposure. No exposed plates were stored for long delays before development.

4.7 Safety Of Sodium Formate
This chemical is rated as potentially irritating from bodily contact and with potential chronic exposure (see http://datasheets.scbt.com/sc-203385.pdf) .[6]

5. CONCLUSIONS

The sodium formate (1/100 molar) presoaked images on Slavich PFG-01 emulsions were visually the equal of those shot without the formate. In transmission the visually estimated optical density was in the range 1.2 to 1.8 for very bright images, after development in D-19, and then ferric-EDTA bleach, and ascorbic acid redevelopment. The speed gain of ≈5xs for immediate development and ≈10xs for 15 minutes-delayed-development in Belloni's communications are confirmed.

The formate presoak by itself appears to shrink the emulsion thickness slightly, as the final color after redevelopment (see above) is visually a slightly deeper red than the final color after normal processing without the sodium formate.

ACKNOWLEDGEMENT

I wish to thank Jacqueline Belloni for helpful discussions.

APPENDIX

Photochemistry

FORMATE PRESOAK
Sodium Formate 0.6 grams
Water to make 1 litre (1/100th molar)

DEVELOPER
KODAK D-19 and its current replacements, equivalent compositions.
It contains:
Metol 2.0 gram
Sodium sulphite (anhydrous) 90.0 grams
Hydroquinone 8.0 grams
Sodium Carbonate 52.5 gms or (monohydrated) 52.5 gms
Potassium Bromide 5.0 grams
Water to make 1 litre.

Available From Photographer's Formulary or Bostick & Sullivan

*BLEACH
Wesly (1992) gives the "No Patchy Haze" bleach as:
12 gm ferric sulfate
12 gm di-sodium EDTA
30 gm potassium bromide
50m gm sodium bisulfate
1 liter distilled water

REDEVELOPER
10 gm ascorbic acid
1 liter distilled water.

This is the standard photochemistry sequence used in my holography classes, chosen for good effectiveness in image quality and relatively good safety.

REFERENCES

[1] Belloni, J. (2002). The role of silver clusters in photography. C.R. Phys. 3, 381–390.

[2] Belloni, J. (2003). Photography: enhancing sensitivity by silver-halide crystal doping. Radiation Physics and Chemistry, v **67,** pp.291-296
Also at http://pagesperso.lcp.u-psud.fr/belloni/

[3] Belloni, J. (2003). Private communication.

[4] Alschuler, W.R. (2005, Dec 30) PFG-03C Processing. Holography Forum.org. http://www.holographyforum.org/forum/viewtopic.php?f=30&t=5282&p=43182&hilit=Formate#p43182

[5] Wesly, E. (1992) "A Toast to Nick Phillips." Leonardo, v.25, no.5, pp. 439-442

[6] http://datasheets.scbt.com/sc-203385.pdf