A Toast to Nick Phillips

Ed Wesly

ABSTRACT

The art of holography requires bright holograms with good signal-to-noise ratios. The author profiles a man who pioneered techniques in silver-halide holographic material processing to make reflection holograms that are eminently viewable.

Silver-halide–based photographic materials were used to record the first holograms made by Gabor, Denisyuk, Leith and Upatnieks. These materials will probably remain useful in holography forever, due to their high sensitivity at all parts of the visible spectrum, in comparison to other available materials, which lag an order of magnitude or two behind in photon catching. Because of this, these silver-halide–based materials will continue to be the medium of choice for self-supporting holographic artists using small lasers.

In the beginning, holographic processing followed basic photographic darkroom conventions: develop, stop, fix, wash, add wetting agent, dry. But this procedure did not produce bright holograms, especially the reflection type, since the blackened, developed silver absorbed much more of the light than it diffracted. Bleaching techniques were suggested by Cathey in 1965 [1], and this resulted in a plethora of papers, many peddling not just the proverbial snake oil but also the use of toxic ferricyanides and mercuric chlorides.

A paper that remains a classic to this day is "An Advance in the Processing of Holograms", by N. J. Phillips and D. Porter [2]. They introduced the use of a concentrated photographic developer, Neofin Blue™, as a developer for pulsed holography. Neofin Blue™ is not only expensive but hard to obtain, so its use has been superseded by special formulations (such as my SM-6 [3]). More importantly, this paper introduced a relatively benign oxidizing agent, ferric nitrate, in a bleach used after fixing to rehalogenate the developed silver in the bright fringe areas of the holographic pattern into silver bromide (Formula 1). This bleach was gentle to the gelatin, avoiding the formation of noise due to surface relief, and it was observed that ferric nitrate also had hypo-clearing-agent capabilities. It also incorporated a desensitizing agent, phenosafranine, to eliminate printout, while also inhibiting grain growth to noisy levels. The ferric nitrate formula seems to still be the favorite bleach of white-light transmission holographers [4], such as Hans Bjelkhagen of Holicon, who prefers this over the simpler GP 431 formulation (Formula 2) for pulsed masters developed in Neofin Blue™ diluted 1:1.

Formula 1. Original Ferric Nitrate Formula

20	g	Glycerol
500	ml	Deionized Water
500	ml	Isopropyl Alcohol
300	mg	Phenosafranine
150	g	Ferric Nitrate
33	g	Potassium Bromide
1	liter	Water

Dilute 1 to 4 with water before use.
Bleaching time: One and a half times the time it takes to clear.
Temperature: 20° C
Agitation: Intermittent
For rehalogenation after fixing. This stock solution lasts indefinitely; working solution, about 1 week [23].

Phillips's next significant paper, "Advances in Holographic Bleaches" [5], introduced a new concept of bleaching to coincide with the introduction of Agfa's new line of improved Holotest™ emulsions [6] (Formula 2 and Formula 3). By rehalogenating the oxidized silver directly after development and skipping the fixing step, dramatic increases in brightness could be achieved. What is most remarkable about this process, and a tribute to Phillips's genius, is that conventional photographic wisdom would dictate that this type of system should not work!

Holographic plates initially contain a homogenous distribution of silver-bromide grains, and if all the developed silver were changed back into its original form, the plate would regain its virgin condition. In this condition, there would be no modulation of the incoming reconstructing light, since there would be nothing to differentiate where a bright fringe had been and where the dim ones had been. In reality, this process works really well, and the theory is that the developed grains migrate into the dim fringe areas as they are being rehalogenated. The bright fringe areas are represented by pure gelatin, and the dim fringe areas contain silver bromide, but the increase in modulable material in those areas increases efficiency. Since nothing leaves the emulsion—its elements are merely rearranged—the original thickness of the emulsion layer is preserved along with the spacing of the fringes during recording, so that it is possible not only to replay a reflection hologram with the laser that made it but to replace the hologram onto the object and generate real-time interferometric fringes with it.

At first I doubted that this migration-diffusion mechanism would work, but its effectiveness was proven to me when I was making some extremely low frequency gratings.

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Formula 2. GP 431

150 g Ferric Nitrate (9-Hydrate)
30 g Potassium Bromide
0.3 g Phenosafranine (optional)
1 liter Water

Dilute 1 to 4 with water before use.
Bleaching time: One and a half times the time it takes to clear.
Temperature: 20° C
Agitation: Intermittent
The most enduring of the classic bleaches. The phenosafranine may need to be dissolved in an alcohol or in a bit of very hot water before being added to the stock solution.
This stock solution lasts indefinitely; working solution, about 1 week [24].

They had fringe spacing of about two line pairs per mm; these fringes are visible to the naked eye. I made my first exposure test, developed and bleached without fixing, and discovered almost no diffraction while the hologram was wet. It dried while I was 'interrogating' it with the undiverged laser beam, and I could see in the 'wood grain' caused by internal reflection between the two glass surfaces an excellent red Lippmann mirror. The process made a better hologram of the back of the glass than it did of the coarse interference system.

The simple grating had a fringe spacing of hundreds of microns. The reflection grating's spacing had fringes about 300 nm apart—half a wavelength of red light, or one-thousandth of the original size. If it were true that the silver grains were swimming from bright fringe to dim fringe as they rehalogenated, then this mechanism would be more effective in travelling short rather than long distances.

Developing-rehalogenating processes then have a lower limit of useful spatial frequency and do not reach their highest level of efficiency until about 1,000 lines per mm, as papers by Hariharan [7] and Ward [8] show. Benton had also predicted these effects when writing about his Intra-Emulsion Diffusion-Transfer (IEDT) processing [9], which shifts the unexposed silver grains that had been in the dim fringes over to the developing bright-fringe grains. But gratings with fringes so large that they are visible to the eye are extreme cases; certainly the process functions well on the size of fringes formed in the transmission mode by an object placed along the normal to the plate and a reference at 45° from the normal.

The lack of low spatial-frequency response aids in the suppression of intermodulation noise from the object's light interfering with itself. The fringes formed by points on the object are very widely spaced for points immediately next to each other, and are at their minimum for the interference caused by the extreme ends of the object, but rarely are these fringes as tiny as the reference-object fringes. The process tends to ignore these coarse noise fringes and to strengthen the more closely packed holographic ones. Bull's-eyes caused by dirt on the optics become less apparent on the developed-rehalogenated holograms, because the processing lowers their contrast. The same is true for the dreaded wood grain. It is strange to think of a holographic material's modulation-transfer function being at zero for the low spatial frequencies, then climbing to a peak in the thousands of line pairs per mm, and finally falling off. But silver-halide materials processed in this mode are not unique in this respect. Du Pont's OmniDex® family of photopolymers, which work by a diffusion mechanism, also exhibit this effect when used with products manufactured specifically for reflection or transmission work.

It is critical that the rehalogenation be performed in aqueous solutions in order for the diffusion of the silver to take place. If the developed holographic plate is rehalogenated by bromine vapor à la Thiry [10] or Graube [11], there can be no 'swimming' of silver bromide from one area to the other, which is necessary for the plate to return to its original consistency.

This subtle phenomenon can only occur with extremely fine-grained holographic or Lippmann-type emulsions. To illustrate how subtle Phillips's method is, not one of the researchers in Lippmann photography at the turn of the century, including some of the greatest minds in photographic research, ever attempted the simple experiment of rehalogenation in aqueous solutions. If they had, they could have solved one of the basic processing problems of Lippmann photography, that of retaining emulsion thickness to preserve color veracity. Most Lippmann photographers either developed to colloidal silver or developed, fixed and bleached in mercuric chloride and used some plumping agent in the emulsion to bring it back to its original thickness. Phillips's scheme rearranges all the modulable material in the layer, without losing any, so there is no shrinkage of the fringes to shorter wavelengths. It will be interesting to see if there will be any renewal of Lippmann experiments—other than those of Phillips himself—using these new processing techniques [12,13].

Formula 3. GP 432

50 g Potassium Bromide
1.5 g Boric Acid
2 g p-Benzoquinone (PBQ) (add just before use)
1 liter Water

Dilute 1 to 4 with water before use.
Bleaching time: One and a half times the time it takes to clear.
Temperature: 20° C
Agitation: Intermittent [25]

The proof of the processing is in the holograms. Holograms processed using Phillips's method helped account for the success of the Light Fantastic gallery exhibitions in the late 1970s, which acquainted the general public with images that were extremely realistic, thanks to the high brightness and the black shadows made possible by the low signal-to-noise ratio. The second bleach mentioned in "Advances in Holographic Bleaches" [14] was adopted by John Kaufman [15], the dean of triethanolamine color control, in combination with the developer Kodak D-19, as his basic process. If not using Phillips's recipes verbatim, most workers have adopted his development-rehalogenation scheme.

The eradication of the fixing step also eliminated the characteristic odor of 'hypo' (thiosulfates), which has been the bane of photographic darkrooms since the days of Daguerre. It is an unpleasant smell for most people, and some are allergic to it. It is also unhealthy for bleached holograms, since it is a solvent for silver halides, which comprise the modulation ingredient in the holographic layer. Even the airborne particles that account for the smell are capable of ruining holograms.

Phillips has been criticized by the safety-conscious for having introduced an even nastier-smelling chemical, p-benzoquinone (PBQ) (Formula 3 and Formula 4), into which the developing agent hydroquinone oxidizes as it gets

Formula 4. PBQ #2

30 g Potassium Bromide
15 g Borax
2 g Potassium Dichromate
2 g p-Benzoquinone (PBQ) (add just before use)
1 liter Water

Bleaching time: One and a half times the time it takes to clear.
Temperature: 20° C
Agitation: Intermittent [26]

Formula 5. 'Benign' Ferric EDTA

ORIGINAL
30 g Ferric Sulfate
30 g di-Sodium EDTA
30 g Potassium Bromide
10 ml Sulfuric Acid (concentrated)
1 liter Water

REVISED
30 g Ferric Sodium-EDTA
30 g Potassium Bromide
30 g Sodium Bisulfate
1 liter Water

Bleaching time: One and a half times the time it takes to clear.
Temperature: 20° C
Agitation: Intermittent
Less hazardous to work with than PBQ. Either version of the recipe gives the same result; the choice depends on the availability of ingredients. Leaving the solution exposed to air (uncovered tray) will extend the lifetime of the oxidizer [27].

Formula 6. Nick's #5

PART A
60 g Sodium Sulfite
20 g Catechol
10 g Hydroquinone
10 g Potassium Bromide
1 liter Water

PART B
20 g Sodium Metaborate
120 g Sodium Carbonate
1 liter Water

Mix equal parts of A and B together before use.
Development time: 4–5 min
Temperature: 23° C ±1° C
Agitation: Constant
Primary recommendation for transmission holograms on Ilford green-sensitive materials, followed by a rehalogenating-diffusing bleach. Properly exposed plates will not show signs of development for 30 sec.

Part A lasts up to a month in a tightly stoppered bottle; Part B lasts indefinitely. The combined solutions last up to a day in a covered tray [28].

Formula 7. Nick's #6

PART A
10 g Pyrogallol
10 g Potassium Bromide
1 liter Water

PART B
20 g Sodium Metaborate
120 g Sodium Carbonate
1 liter Water
Developing time: 5 min
Temperature: 23° C ±1° C
Agitation: Constant
Primary recommendation for Ilford green-sensitive materials for same wavelength replay in the reflection mode when followed by a rehalogenating bleach. Ilford SP737T film and plates will work in this formula but at a loss of a stop in speed. A properly exposed plate will sit in this formula for 30 sec before any darkening appears.

Tray life of the combined solutions is about 15 min. Part A lasts 2 to 3 days in a full stoppered bottle, but Part B lasts indefinitely [29].

spent in the process of reducing silver-bromide crystals into elemental silver. It is certainly a problematic powder to mix. Its very fine dust inflames the sinuses and dries out the eyes. Certainly, personal air masks with organic filters help, and some workers have made spare shower stalls into fume hoods to control the hazard [16]. PBQ takes a very long time to dissolve, and the bleach has a covered tray life of a few hours. It cannot be left uncovered, as this causes it to oxidize into uselessness even more quickly. More importantly, even the solution reeks. Because of these drawbacks, Phillips formulated a rehalogenation/diffusion bleach based around ferric Ethylene Diamine Tetra-Acetic acid (EDTA) as the oxidizing agent (Formula 5). Ferric EDTA is the oxidizing agent commonly used in color photographic processes because it is ecologically benign [17].

When Ilford introduced a new blue-green–sensitive silver-halide holographic recording material in 1988, Phillips eliminated its problem of splash marks (Formula 6 and Formula 7) [18]. The plates were developing splotchily because the solution did not penetrate the entire coating evenly and simultaneously, and the developer darkened some areas more than others. By using a restrainer in the developer to delay developing activity for about 30 sec after immersion (until the light-sensitive coating was totally saturated with developer), much more even development was achieved.

Phillips's next processing publication [19] fine-tuned the ferric EDTA formula with a 'No Patchy Haze' version of this bleach, which cuts down local variations in surface scatter (Formula 8). But the paper "Bridging the Gap between Soviet and Western Holography", which he delivered in Budapest, Hungary, for the celebration of the 90th birthday of Dennis Gabor, introduced the greatest improvement in the processing of holographic materials since the invention of PBQ [20].

After having been impressed by the high signal-to-noise ratio of Russian colloidally developed silver-halide materials in 1979, Phillips tried processing Agfa Holotest™ materials in Russian-style developers. These solutions reduce the exposed silver-halide crystals into red silver, which gets its color from its small, compact grains. Black silver, which is the typical product of development, is composed of long, filamentary strands. The colloidal type of developer works very well with the Russian-style materials with their extremely tiny grains, which are about a third of the diameter of those in Agfa plates. Since scatter is proportional to the fourth power of diameter, Russian plates have less than 1% of the scatter of Western ones. Because of these small grains, Russian plates look as clear as glass, since they do not have the large scattering sites that give a soft, ground-glass look to the Western plates. There is less haze in recording and in replay, contributing to blacker shadows, which add significantly to the apparent solidity of the holographed object. However, since sensitivity is proportional to the third power of diameter, Russian materials need almost 100 times the exposure of Western plates.

When the Agfa plates did not respond well to the single-step colloidal developers, and because he was getting such high efficiency with black-silver development followed by rehalogenating bleaches, Phillips changed the rehalogenated silver bromide into colloidal silver, using a highly diluted developer. In this process, the plate is exposed to light to the saturation point but not enough to cause solarization or to the point of printing out. It is then immersed in the weak developer formula without any agitation. The weak developer breaks down the large, highly scattering silver bromide into little rocks of colloidal silver. This creates an appreciable increase in signal-to-noise ratio, so much so that the true-color holograms that I made with red 633 nm, green 515 nm and blue 476 nm on a single Agfa Holotest™ 8E75HD [21] would not have worked at all if not for this trick. The blue image would have been buried in the blue scatter noise of the Agfa emulsion.

The original colloidal developing formula, which I had dubbed in the beginning 'Reddeveloper', a pun on red developer and redeveloper, and which I now call the 'Blood Bath' because of the characteristic dried-blood color of the finished plate, had six ingredients (Formula 9). But in a slightly

Formula 8. 'No Patchy Haze'

12 g Ferric Sulfat
12 g di-Sodium EDTA
30 g Potassium Bromide
50 g Sodium Bisulfate
1 liter Water

Bleaching time: The time it takes to clear plus 1 min (the total bleaching time is usually in excess of 6 min).
Temperature: 20° C
Agitation: None
A slow, diluted Ferric EDTA bleach that eliminates nonuniform scattering patches throughout the emulsion. The key to success is to avoid the urge to agitate, as this process can take up to 15 min to clear a well-exposed plate [30].

Formula 9. Reddeveloper #1

10 g Sodium Sulfite (anhydrous)
5 g Hydroquinone
10 g Ascorbic Acid
23 g Potassium Phosphate (mono)
30 g Sodium Carbonate
1 liter Distilled Water

Dilute 1 part developer to 40 parts distilled water, otherwise there will be patchiness in the final hologram.
Re-expose plate to ultraviolet or visible light and develop for 5 min with the lights on [31].

Formula 10. Reddeveloper #2

10 g Ascorbic Acid
1 liter Distilled Water

Re-expose plate to ultraviolet or visible light and develop for 4 min with the lights on [32].

later version of the formula Phillips had introduced in his paper "Bridging the Gap between Soviet and Western Holography" [22], he simplified the step to a simple 1% solution of ascorbic acid (Formula 10). This is quite remarkable, as there is no alkali to provide the proper pH to activate the developing agent, and the bath runs at a pH of about 3. Again, this goes against the grain of conventional wisdom.

Not only does this increase the signal-to-noise ratio of the Agfa and Ilford plates to a level comparable to that of Russian-style materials, it also prevents printout. Colloidal silver is fully oxidized, like the black silver in conventional black-and-white photographic negatives and prints, and will not change on its own, as an unstable silver halide will. Holographers looking for that 'hologram-as-a-crystal-clear-window' effect might be daunted by the red color of the emulsion, which unfortunately filters out a bit of the blue and green end of the spectrum. Then again, they may take comfort in the fact that the hologram will be archival and will not change its color over time.

Currently Phillips and Bjelkhagen are researching new formulations of bleaches that create PBQ in the solution by oxidizing hydroquinone with potassium persulfate. PBQ as an oxidizer has advantages over the others, especially regarding efficacy: 2 grams per liter of PBQ does the same job in the same amount of time as 30 grams of ferric EDTA, ferric nitrate, potassium ferricyanide, mercuric chloride or copper sulfate. It also tans, or hardens, the gelatin, preventing the shrinkage that often occurs with the other oxidizers, especially ferric EDTA. Their formula, which they have dubbed Phillips-Bjelkhagen Ultimate (PBU), does not require the nasty ordeal of dealing with powder PBQ, yet it works identically.

I propose a toast to Nick Phillips, the gentleman who has done the most in inspiring us all in the creation of high-quality reflection holograms, and who has thrown off the bondage of his 'commercial ties' to holographic business to give us the knowledge to get the best possible results from holographic materials, so that the medium can progress.

Who knows what may follow—a special monobath, with a developing agent that changes the silver bromide into black silver but whose spent by-product oxidizes the developed silver so that it can be rehalogenated and diffused back to a silver-bromide phase hologram and in which the by-product of the oxidizer then becomes a weak developing agent that changes the silver bromide into a colloidal silver? That would be nice. But if that does not happen, surely the legacy of Phillips will include the perfection of the processing of holograms.

References and Notes

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16. The West coast holographer Robert Hess's apartment when he lived in Silicon Valley circa 1985.

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23. For the source of Formula 1, see Phillips and Porter [2] p. 631.

24. For the source of Formula 2, see Phillips et al. [5]; and Agfa-Gevaert Technical Information Bulletin 21.7271(480).

25. For the source of Formula 3, see [24].

26. For the source of Formula 4, see Phillips et al. [5] p. 120.

27. For the source of Formula 5, see Phillips [17] p. 21.

28. For the source of Formula 6, see Phillips [18] p. 35.

29. For the source of Formula 7, see Phillips [18] p. 35.

30. For the source of Formula 8, see Phillips [19].

31. For the source of Formula 9, see Phillips [20].

32. For the source of Formula 10, see Phillips [22].