Controlling the effects of ultra-violet light on holographic emulsions

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Abstract

With a controlled UV light source, a variety of holographic processing regimens are tested for print-out. Density readings taken at selected intervals over a period of time allow us to examine optimum processing and post-processing techniques for display holograms.

Introduction

For many years holographers have noticed that finished holograms darken over a period of time. It is a dark, little secret and most agree it is a stumbling block for acceptance of holography as an art form by institutions and private collectors alike.

While concern with archival qualities has many aspects, there is reason to believe that gelatin and glass, properly preserved, will last indefinitely. Not only are there photographs over a hundred years old, but animal protein and glass fragments have been found intact in archeological digs. However, the light-sensitive properties of the holographic emulsion and its processing schema pose particular preservation problems. The phase modulation mechanism of silver halides reacts in the presence of what makes the hologram appear -- light, not only reconstruction sources, but also ambient lighting. This paper summarizes methods of minimizing the dreaded print-out. We exposed test samples to ultra-violet light because at short wavelengths, holographic emulsions retain greatest sensitivity.

Nature of print-out mechanism

Conventional photographic processing removes all unexposed, potentially active silver halides by using fixer. Holographers find that greater efficiency is achieved by using silver halides as a phase modulation material. Left in the emulsion are transparent silver halides with an index of refraction higher than the gelatin. But the action of the reconstruction and ambient light liberates the halogen from the silver halide crystal which is absorbed by some other substance nearby in the medium, leaving behind elemental silver in the form of finely divided clumps known as colloidal or red silver, or colloquially as print-out. Typically, silver bromide is left in the emulsion, but all three relevant silver halides ($AgCl$, $AgBr$, AgI) have their peak sensitivity between ultraviolet and violet light.

Experimental procedure

We irradiated emulsion samples of Agfa 8E75HD on glass and film. The low-intensity tests utilized a mercury vapor tanning lamp (GE Mazda 100 Watt bulb) at a distance of one meter, which gave us an effective broadband flux of 10 mW/cm^2. Sunlight is 100 mW/cm^2. Later, in the accelerated, high-intensity tests we used Argon laser light at 488 nm wavelength with a flux of 800 mW/cm^2.

Low Intensity Tests

In order to establish testing parameters, we ran a preliminary experiment with raw film uncovered and under plexiglass or glass. The difference in the short run was negligible, so all successive samples were directly exposed with the emulsion up without any covering to discount any humidity factors and to maximize use of the light. The 24 samples representing a cross-section of current processing schemes received controlled, continuous exposure for four months, totalling over 2500 hours.

As a baseline group, three pieces of raw film straight from the box were washed in water, methanol, or not at all. Raw film that had been wetted printed out much faster than film that had stayed dry, simply because a bath dissolves out excess bromine ions lurking in the emulsion since the manufacturing process. Although bromine post-baths have been recommended in the past to load the emulsion with a surplus of ions, we did not use this technique because fume hood facilities are rarely available to the average holographer.

For these tests we tried three different phase processing regimens: 1. Develop, fix, and rehalogenating bleach; 2. Develop and silver solvent bleach; 3. Develop and directly rehalogenate. Chart 1 shows the general trend of these schemes. A developed and fixed hologram (amplitude processing) was tested alongside these samples and did not change at all.

All density readings were taken with an X-Rite Model 331 black-and-white transmission densitometer. It is evident that there is an initial quick darkening, then a reversal lightening and apparent stabilization. We speculate that the solarization may reoccur to a lesser extent over a longer period of time, as the halides migrate to and fro in the emulsion.

In Chart 1 the graphed values represent an average of samples of holographic exposures, as the original density and printed out density depend on the amount of silver halide left in the emulsion. Since solvent bleaches and fixers remove material from the emulsion, it should come as no surprise that these processes print out less than develop-rehalogenate schemes which leave everything in the emulsion.

We looked in detail in Chart 2 at variations on the solvent bleaching scheme, namely the use of different developers and stain removers. The non-staining developer CWC2 has a lower initial density than the pyrogallol developed hologram, but their final print-out level is at about the same density.

The curious thing about the Pyrochrome-processed and S-13 stain-removed sample was that it darkened initially and then stabilized. This sample had been re-bleached and re-stain-removed after exposure to UV before beginning the tests. This leads to the possibility for future investigations about forced print-out and then re-bleaching.

Raw pieces of film and CWC2 processed holograms were subjected to three different types of post-baths in the search for the anti-print-out elixir. Chart 3 illustrates the results of unprocessed film samples treated with the solutions and exposed to the low intensity illumination.

The first bath was a 2.5 gram per litre solution of potassium iodide, (KI) as suggested by Ilford, Ltd., which changes the AgBr in the emulsion to AgI. Of all the silver halides, AgI has the highest resistance to printout, while AgCl darkens the quickest and was used as the active ingredient in the early "photogenic drawings" of Fox Talbot in the second third of the nineteenth century. Photochromic effects were definitely slower on these samples of plates when compared to the AgBr emulsion.

There are two disadvantages to the AgBr to AgI conversion. The first is cosmetic; the yellow stain of the KI produces a sometimes unpalatable color cast to the finished hologram. The substitution of the larger iodine atom for each bromine one causes the grains to grow in size with an attendant increase in scatter and hence the signal to noise ratio decreases.

Chemicals which would destroy the silver halide's inherent sensitivity to actinic radiation are available in the form of desensitizing dyes. Another type of bath used was a 50-50 mix of water and isopropyl alcohol with 300 milligrams of phenosafranine added to it.

The desensitizing power of phenosafranine and other safranine compounds was discovered by Lüppo-Cramer at the turn of the century. By treating an exposed photographic plate in a dilute solution of the violet-red dye, its development could be inspected in roomlight of moderate intensity. The mechanism of desensitization involves the trapping of the photoelectrons by the dye in competition with the trapping carried out by the sensitivity centers in the silver halide crystals themselves which leads to their eventual reduction in print-out. Since there is a finite amount of these traps depending on the concentration of the dye in the emulsion their usefulness may eventually be overwhelmed.

We restricted our research to only one type of desensitizer at one concentration. Other dyes, like pinacryptol yellow and green or even more exotic ones could be tried, but their cost is high. Some of these dyes stain the gelatin and phenosafranine merely imparts a slight pink cast. One of our samples was dried immediately after immersion in the dye bath, another rinsed in alcohol after the treatment, and a third was washed 5 minutes in running water. The staining decreased in the above order, however the net density changes were the same for all.

The last post-processing scheme we tried involves a novel approach described by Nick Philips in holosphere[1]. Immersion of the hologram in an acid bath to combat print-out makes perfect sense when one considers that inside the "Photo-Grey" type sunglasses live a population of extremely small (finer-grained than our holographic plates even!) silver halide grains in an acid environment. Sunlight darkens them, and when the stress is removed the environment allows them to return to the clear state.

The original article was unclear as to whether to use diluted or undiluted Kodak Indicator Stop Bath. We tried both stock solution and the recommended 1:31 dilution. The full-strength solution protected against print-out even if there was a rinse after the bath. With the diluted stop bath, washing after this step seemed to allow more print-out but it finally solarized to be back in line with the unwashed sample. Certainly, it would be best to let this be the final bath with some Photo-Flo added to it. But further tests are necessary to determine the long-term effect of an acid environment on the gelatin itself. A pleasant side effect of this treatment is the bleaching or destruction of the bluish sensitizing dye that comes with the emulsion, giving the cleanest holograms of all the samples.

High Intensity Tests

Given the results of the low-intensity tests, we decided to boost the flux to mimic extremely long exposure doses. We interrogated the hologram with a very slightly diverged beam to give 800 mW/cm^2 in the blue to the emulsion. We used 488 nm line of the Argon laser since the silver bromide is still sensitive to that wavelength. These results were markedly different than the low-intensity long duration exposures, creating a situation analogous to that of high versus low intensity reciprocity failure.

We monitored the intensity of the beam passing through the grating with a Newport Corporation Model 820 Power Meter, and Chart 4 is a strip chart recording of the typical darkening curve given by output of the instrument. The chart appears to be upside down; this is because of the silly circuit of this device. The absence of light on its detector produces an output voltage to the recorder of about a volt; more light produces less of an output signal, contrary to all the other meters we have had experience with. Common sense would dictate that more light would get more voltage out of the unit.

Chart 4 shows that the reaction is rapid at first and then decelerates since the new density has a self-masking effect. It also does not appear to reverse the way that the low intensity exposures did. The samples receiving 10 mW/cm^2 for over 2500 hours received over 90,000 $Joules/cm^2$ of energy, while those interrogated by the laser received about 9600 J/cm^2 in twenty minutes. (We use interrogate here in the bright light spy movie sense of the word.) Although the samples received about ten times as much in the low intensity case, the density change was nowhere near as dramatic as the high intensity photon bombardment. It would appear that the rate of printout is a function of the intensity of the irradiating source and may be particularly relevant for holographers working with strong lasers at short wavelengths, e.g. mastering for photo-resist.

With the laser beam we were also able to measure the intensity of the first order diffracted beam in samples of HOE's which we sacrificed. Chart 5 shows the ratio of the intensity of both output beams as compared to their original throughput. Efficiency drops faster than the attenuation of the light.

Chart 6 shows the darkening of gratings processed in CWC2 developer with its PBQ bleach, one without any post-bath as a control and three others with each one of the postbaths mentioned before. It certainly pays to use one of these solutions rather than not to use any at all.

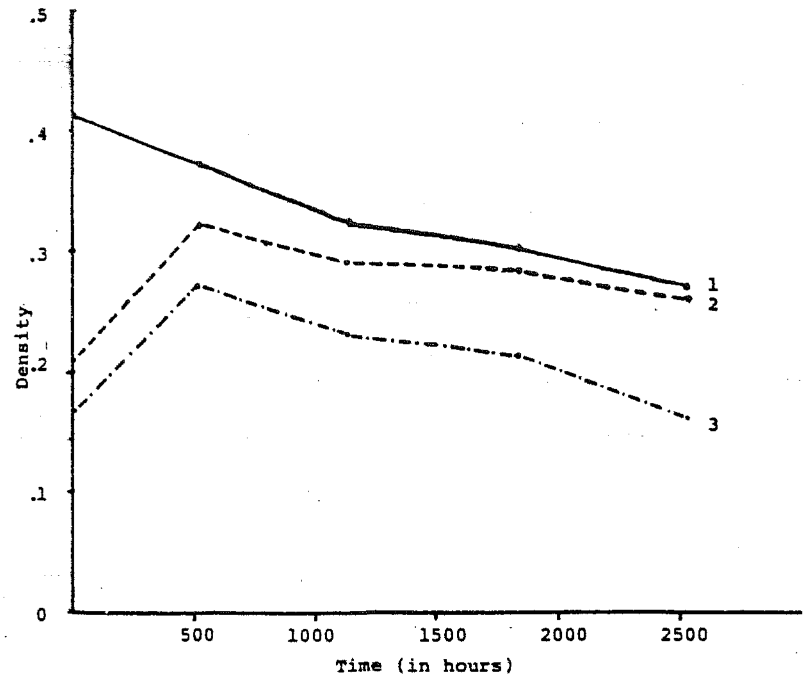
Closing

A darkened transmission hologram can be heartbreaking, but printing out a reflection can be beneficial! Some practitioners do expose their processed Lippmann holograms to UV sources until they get a color to the plate similar to that of Russian emulsions, whose red color comes from the extremely small grains formed by their solution-physical developers. The darkening agent proposed by Jeff Blythe[2] also seems to produce the same effect, which increases signal-to-noise ratio since white-light scatter is reduced!

This is only one aspect, though a significant one, of the panoply of potential problems for archival holographic methods. Others include base life, adherence of emulsion to base, shrinking of triacetate over time, processing variables, micro-organic growths, pre-soaking sensitizing agents, epoxies and laminants, image contrast and efficiency over time. Conventional photographic and cinematographic wisdom recommends storage conditions that permit outgassing of the emulsion and a relative humidity of 47 to 51%. We hope that these questions will be noted and addressed by manufacturers and users alike.

We would recommend full washing to remove all the organic agents left behind by the processing baths. It seems that any one of the post baths we investigated is better than none at all; none are perfect. It would be best not to laminate the emulsion to anything permanently so that the hologram can be rebleached and recovered. It may be advisable to mount plates so that air can circulate around them for outgassing.

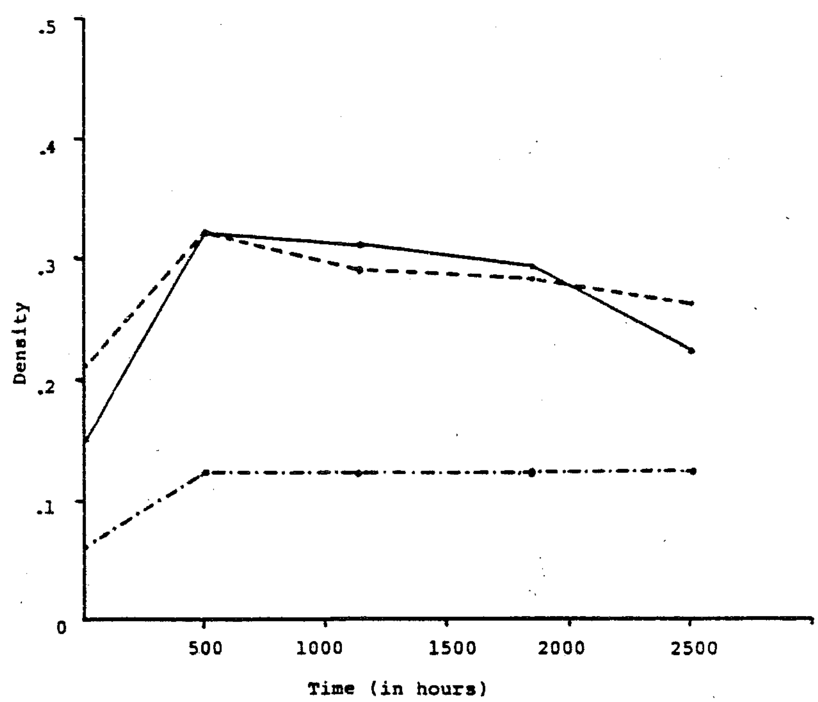
We look forward to results of a long-term study of print-out and encourage other user groups so that optimum procedures can adopted as soon as possible to preserve the integrity of the holograpers' arduous efforts.



Comparison of density over time for holograms processed in three different types of regimes

- —1. Developer, rehalogenating bleach: CWC2 with PBQ
- --2. Developer, silver solvent bleach: Pyrochrome
- ·—3. Developer, fix, rehalogenating bleach: D-19, fix, $FeNO_3$

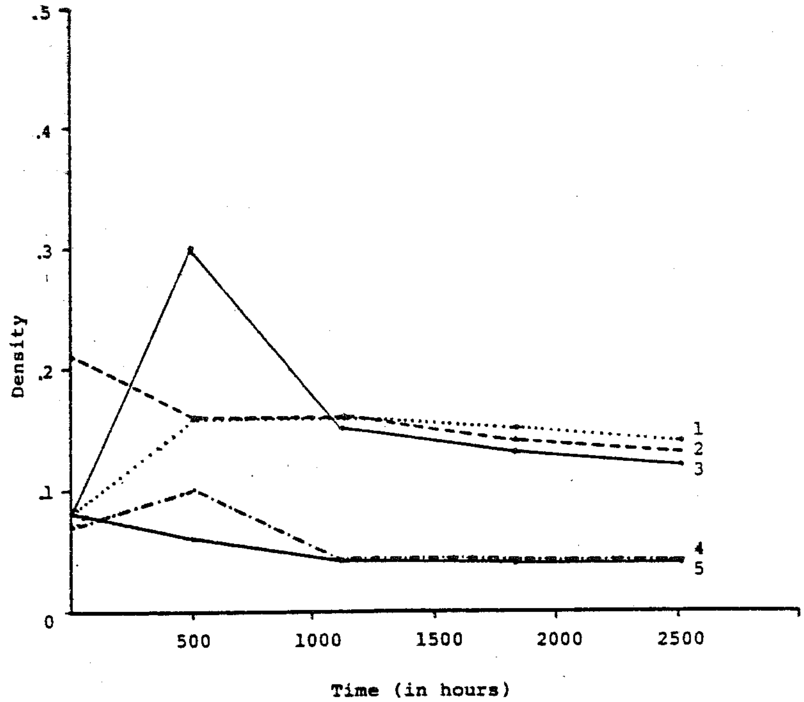
Chart 1



Comparison of Density over Time for Holograms Processed in Three Different Variations on the Solvent Bleach System

- --1. Pyrochrome
- —2. CWC2 with chrome bleach
- ·-·3. Pyrochrome with stain remover S13

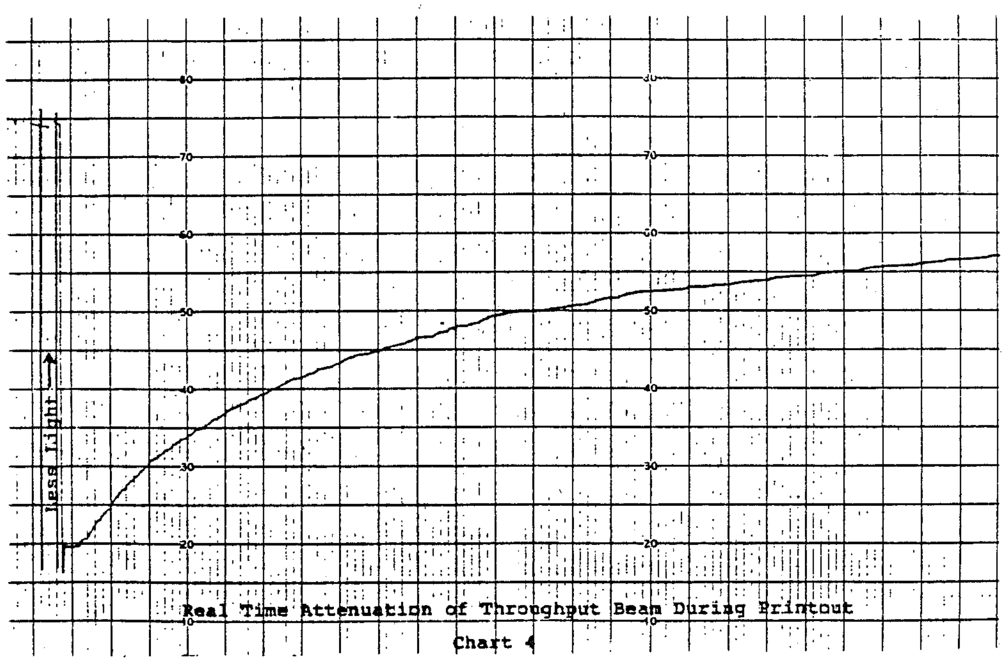
Chart 2



Comparison of Density over Time for Unprocessed Films Subjected to Different Anti-print-out Post-baths

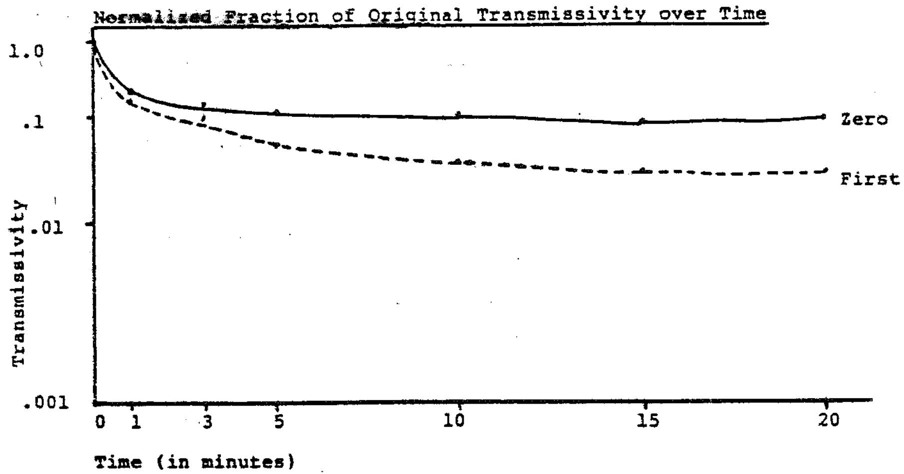
- ····· 1. KI
- - - 2. Phenosafranine
- —— 3. Washed film
- ·—· 4. Diluted stop
- —— 5. Untreated film - control

Chart 3



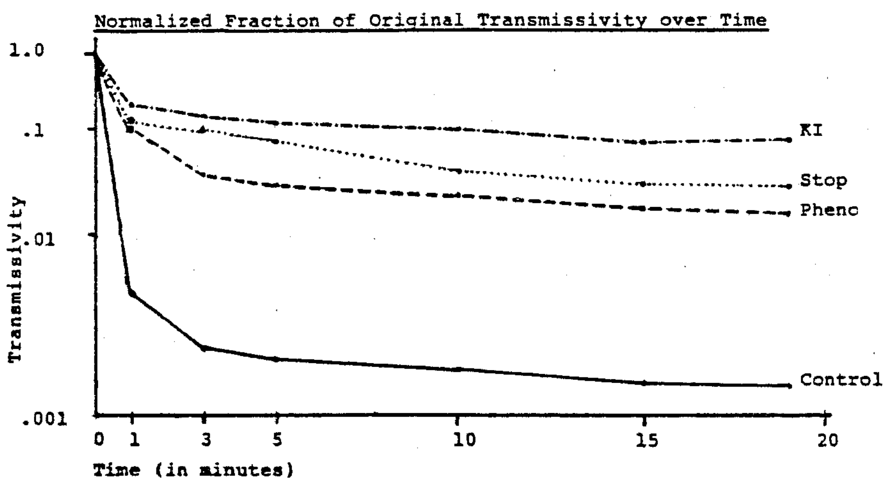
Real Time Attenuation of Throughput Beam During Printout

Chart 4



Relationship of Zero and First Orders of Diffraction.
The first order loses intensity twice as fast as the zero order.

Chart 5



Comparison of CWC2 with PBQ processed plates with different types of anti-printout post-baths & control.

Chart 6

References

1. N.J. Phillips, "Benign Bleaching for Healthy Holography," holosphere, Volume 14, No. 4, p. 21 (1986).
2. J. Blythe, "Notes on Processing Holograms with Solvent Bleach," Proceedings of the International Symposium on Display Holography, Volume II, p. 325 (1985).