Chapter

Emulsions, Photochemistry, and Processing Factors for Display Holograms

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Abstract

This article reviews the range of emulsions, photochemistry, and processing techniques that have been proposed and put into practice for the successful making of display holograms. It covers various types of media including gelatin-based emulsions and photopolymers (it focuses on the former) and considers external factors that affect the final results. This is a compact review of the history of the field but focuses on the range of easily available commercial emulsions, as well as certain accounts of how to make holographic emulsions from scratch. It considers various combinations of developer, bleach, and redeveloper, which have been used to achieve the best of various trade-offs for such factors as resolution, contrast, diffraction efficiency, clarity, color quality, blackest blacks, and resistance to printout. It describes a recent advance in hypersensitizing holographic emulsions.

Keywords: holograms, holographic emulsions, hologram processing, hologram exposure factors, hologram hypersensitizing

1. Introduction

Display holography at its birth was not worth a second glance. Dennis Gabor's first images to demonstrate his new principle of image recording with scattered light were of flat objects, two-dimensional text on transparent film [1]. His idea had grown out of a desire to find a way to make an X-ray microscope, in an era when focusing X-ray optics did not exist. He conceived a way to use monoenergetic (monochromatic) X-ray scattering off objects to interfere with directly delivered X-rays of the same wavelength to create an interference pattern that coded information of the object's transparency, texture, and disposition in space, which could be recorded, and, when viewed in similar illumination, reveal a reconstructed image of the object. At that time he not only lacked focusing optics but also a medium with sufficient resolution to record the tiny-scale interference pattern details. As a demonstration he chose to use a mercury vapor discharge tube as a source, filtered to pass just one spectrum line, and photographic film to record the hologram. The limited spectral purity of the source only permitted an exposure setup with the source, filter, transparency object, and film in a straight line. This arrangement provided an interference pattern of maximum scale, one possible to record on film of ordinary resolution. The view of the hologram image seen through the

hologram was a twin image centered on the light source. This is not a favorable view for display holography. However, it demonstrated that the principle was correct: an interference pattern can record details of the object, and its recording could reconstruct an image of the object when the viewing light is in the location that it occupied when the recording was made.

The game changed with the invention of lasers in 1961. Almost immediately, Leith and Upatnieks, who had been working on imaging from side-looking radar and had adopted a version of Gabor's invention to do so, realized that the laser's orders of magnitude better purity allowed an off-axis arrangement for the exposing setup and thus a view of the object without the light source mixed in [2]. They published an article with photos of the images they made with this technique, clearly demonstrating potential for realistic 3-D images that can be viewed without any optical aid [3].

Now, the production of suitable emulsions added a new requirement: it must resolve the interference pattern that, due to the change in beam geometry, became much finer, in certain respects, down to half (or less) of the wavelength of the laser light chosen. This requirement amounts to resolving at least 3000 lines per mm (lpmm) for red, 5000 lpmm for green, and at least 8,000 lpmm for blue. The grain size in the last case would need to be around 10–20 nm. These numbers contrast with resolutions of 75–150 lpmm for conventional films.

This can be done and in fact was demonstrated to be achievable back in the 1890s, by Lippmann [4, 5]. Lippmann created such an emulsion in pursuit of recording the interference pattern of ordinary light interfering with itself upon reflection at the surface of the emulsion, in contact with a mercury mirror. In principle it was the same as a reflection hologram, with full color but with no 3-D. It won him the Nobel Prize in Physics in 1908.

Ever since the work of Leith and Upatnieks, the search for emulsion materials, photochemistry, and processing has had the goals of making possible holograms with great brightness, color saturation, sharpness, contrast, clarity, minimum noise in the form of scattering, resistance to printout from further exposure to light, robustness of the emulsion in and after processing, and process safety. In these goals hides a fundamental conflict well known in ordinary photography: the inverse relationship between resolving power/grain size and sensitivity—the finer the grain, the less sensitive the emulsion. Many holographic emulsions have speeds that would lie in the range of ISO 1 or less.

It is striking that this challenge has existed in some form for the whole history of photography, the last 180 years, and that the generally best emulsion for meeting the challenge is some form of silver halide in gelatin, which has existed almost as long. Newer emulsions have come into existence that have proven useful for certain types and uses of holograms, but overall silver halides in gelatin still dominate display holography. This survey looks at some alternatives but is interested in versions of the latter, including some recent progress.

2. The range of emulsion types

In the history of holographic emulsions, silver halides in gelatin came first, as the dominating photo emulsion of the time. Then, dichromated gelatin, which was used in two old processes, carbon and gum bichromate, came into play in holography for uses that demanded the brightest possible images or greatest efficiency in focusing or diffracting light in holographic optical elements (HOEs). They are also used as master holograms for the production of mass market-reproduced holograms. The third class of materials, which includes photoresists and the possibly wide range of

photopolymers, came into use for HOEs and also for masters for the mass market. They are more physically robust than those in dichromated gelatin.

Unlike all the materials listed above, which have positive indices of refraction, there is a class of materials new to visible light photonics that has a negative index of refraction. This class of materials, now called metamaterials, has moderately distant roots in some research, going back as far as the nineteenth century, with seriously renewed work in the 1950s to control radiation at radio- and microwave wavelengths [6]. The materials are artificially constructed patterned dielectrics and mixed metals and dielectrics, with structural scale at or smaller than the wavelength in question. They have been constructed to investigate various possibilities that can be envisioned that are not open to ordinary, positive-index materials. The optical properties depend on the shape and spacing of the elements of the pattern, more than the intrinsic optical properties of the materials they are constructed of. Best known of the optical element ideas is the "invisibility cloak" (think of Harry Potter's invisibility cloak), a material that can bend light so that it hides any light from what it encloses and routes the light from the background around to the front. This has been demonstrated for single wavelengths, but it is likely to be a long time before such a material can be made that creates this functionality across the whole visible spectrum. Even with this single-frequency embodiment, such a cloak could have been used in evading detection at specified wavelengths from radar-like devices.

Nonetheless, work proceeds on creating metamaterial holograms. These have so far been the versions of HOEs rather than images of ordinary subjects, because the patterns are computed before being deposited on a surface, and such things as lenses and mirrors and diffraction gratings are both computationally and depositionally simple. Groups at Duke University have designed and made holograms that store two images in the same volume, independently viewable by illuminating the hologram with light polarized at the orientation the pattern was designed for [7]. A group at the University of Pennsylvania reports constructing a flexible metamaterial made of polydimethylsiloxane (PDMS) with embedded gold rods set in precise patterns. Three images were embedded by designing three patterns, which become separately viewable as the sheet is stretched and illuminated [8].

2.1 Information recording types and diffraction efficiencies

There are three types of information storage in holograms made in original exposures in photosensitive media. If the information is recorded as opacity and transparency patterns, this is termed an amplitude recording. If the information is in the form of patterns of varying index of refraction, this is termed a phase recording. Third, the information may be stored as microscopic surface relief patterns.

Diffraction efficiency, the ratio of the energy provided in the image to the energy incident on the hologram at its viewing, is a primary determinant of the image brightness. It has been shown theoretically that phase-only holograms as well as phase combined with surface relief can achieve diffraction efficiencies close to 100%. Amplitude holograms have been shown to be limited in diffraction efficiency to about 50%. Practice over the years, in the various media types and recording schemes, shows these theoretical estimates to be correct [9].

Copying holograms for small editions or mass production faces the same limits.

2.2 Photopolymer, photoresistive, and photothermoplastic emulsions

This category of materials is basically plastics, which by various mechanisms start as monomers and then respond to light exposure by changing to polymers.

2.2.1 Photoresists

These substances, rather varied in composition, upon exposure to blue or violet light become soluble or insoluble when soaked in an organic solvent. The coating rests on a substrate, and usually the coating thickness is fairly small, one to two microns. The exposures required are up to 100 mJ/cm^2 of emulsion. These materials can be used to generate master holograms for embossed replica holograms.

This type of process recalls one of the two very earliest processes of photography: Niepce's 1827 process that employed Bitumen of Judea, coated onto a copper plate, as the photosensitive emulsion. Exposure to light caused it to polymerize and harden. Where it had not been exposed, when placed in a bath of oil of lavender, the Bitumen dissolved. The result was a relief plate that could be inked and run through a printing press.

2.2.2 Photothermoplastics

These materials typically have a multilayer structure that starts with a glass substrate; then a transparent conductive thin film, usually indium oxide; then copper contacts at the perimeter of the conductive layer; then a photoconductive layer, usually 2 microns thick; and finally on top is the thermoplastic layer, generally a fraction of micron thick, say three tenths of a micron. The surface of the thermoplastic is given a positive electric charge at its exposed surface; it is exposed to light, either blue or violet. This causes charges to migrate across the surface to form the pattern of exposure. A current is passed through the conductor to heat the thermoplastic, and it responds by forming a surface relief reproduction of the hologram interference pattern. The hologram is then ready for viewing. By heating the thermoplastic again, the charge redistributes itself to become uniform, the surface relief disappears, the image disappears, and the material is ready for use again [10].

2.2.3 Photopolymers

Photopolymers generally respond to exposure to light by polymerizing, and this generally results in changes to their density and thus their index of refraction that reproduces the interference pattern, mostly inside the emulsion. Photopolymers find a range of uses outside of holography, including some cyanoacrylate glues, bonding cement for glass, and UV-curing dental cements.

Holograms on photopolymers have a number of applications, most of which are not for display holography. These applications include security enhancement on credit cards and banknotes (so far the largest part of the market), occasionally for "flash" on packaging, makeup, trading cards, and large-volume replica images. They are also used for HOEs, such as for solar illumination control, concentrators for solar heat and photovoltaic collectors, optics for head-up displays and enhanced reality glasses, selective reflectors for laser protective glasses, optical computing, high-density optical data storage, and rapid pattern recognition.

For these as for all volume holograms, the larger the thickness, the narrower the wavelength bandwidths and also the narrower the viewing angles. In these properties volume holograms act as Bragg gratings. Narrow viewing angles are useful in many situations where holograms are used in HOEs, but usually not desirable for display holograms, where a wide audience is often a goal.

The active ingredient in the film is a photosensitive monomer that polymerizes to form the recording. The other components of a typical photopolymer film include binders (polymers that act to structure the film); photoinitiators, often

various sensitizing dyes, which begin the monomer polymerization; and plasticizers, which improve film flexibility.

The gross physical structure is usually in three parts: a cover sheet that can easily be peeled off, the active photopolymer layer, and a base sheet that normally remains attached after finishing the exposure. The base sheet optical properties must be paid attention to, specifically their transparency and amount of birefringence.

In use the cover sheet is first peeled off, and then the photopolymer side, which is sticky, is hand applied to a carefully cleaned glass sheet with the help of a roller. Care is taken to avoid and remove trapped air bubbles. Also, care is taken to be dust free, at least until the image is finished [11].

The photopolymerization process is usually described on a molecular scale as starting with the absorption of light by the sensitizing dyes and active monomers. Then, the dyes linked to the monomers or other initiators generate free radicals. The free radicals capture and combine the monomers into polymers. As the process proceeds, free monomers diffuse out of their original positions into the regions where the polymers are forming. Their arrival in that area and evacuation from their original sites create density variations that in turn give rise to the variations in the index of refraction that ultimately constitute the hologram [11]. For some compositions of film, there should be as short an interval of time between exposure and heat or UV treatment as possible to avoid reaction reversal and image fading.

Related to this last issue is the fact that one of a volume hologram's desirable properties is the ability to overlay multiple images in the same volume and then to view them separately. This is the basis for high-capacity holographic memory. In order to achieve the desired goal of as many stored images as possible with uniform optical quality, it is necessary to take into account the fact that each successive exposure will tend to overwrite the preceding ones, both modifying the earlier records and eventually using up all monomers and saturating the film. Generally, later records will be weaker than earlier ones. Self-absorption by earlier records will also affect laser beam intensity of later ones, also affecting the achieved diffraction efficiency. A strategy to deal with this can be devised in the form of an exposure schedule. Assuming a constant intensity per exposure, predetermined schedule ramps up the exposure in a slightly nonlinear fashion, so that the last exposure of 350 is four times the exposure of the first [12].

One of the earliest and most important commercial families of photopolymers for holography was developed by E. I. duPont. It started with HRF-700, and now there are later versions, which are stable; have an index of refraction modulation of 0.06, which is quite high; and can be made in thicknesses up to 100 microns [11].

Dupont distributed film samples to the wider holographic community, including those who made display holograms, for a number of years, but eventually changed its policy and restricted distribution to a select "approved" list, which is now basically limited to companies using the films for mass production [13].

There are safety issues that can occur with the acrylate monomers that are often used in these films and specifically in Dupont's films. After exposure the films are UV and heat cured. Though most monomer content will typically have been converted to polymers in the exposure and UV after-exposure, the latter step can generate some acrylate monomer vapors. Therefore, curing ovens should be ventilated to the outdoors. If the vapor condenses indoors on surfaces, including the skin, it will be an oily liquid and should be removed as quickly as possible. Handwashing with soap and water is recommended at every shift. This and other directives can be found in Dupont's literature on handling their films [14].

Polaroid developed and for a time marketed a high-quality photopolymer that was available in thicknesses up to 1 mm [15]. It was discontinued when Polaroid went into bankruptcy.

There are two more recent developments in photopolymers that are worth noting.

The first is a relatively new film family by Bayer, trademarked Bayfol HX. It was supplied at least initially at 16 microns thickness, requires no postexposure heat treatment, and has an index modulation of 0.030 at the exposure wavelengths of 633, 532, and 473 nm. Typical exposure energies are 18, 25, and 30 mJ, respectively [16, 17]. It has been supplied as a four-layer film. The first is a removable cover film, the second the photopolymer, the third the substrate, and the last another removable cover film. The substrates have included low-birefringence polycarbonate and polyethylene terephthalate.

The photopolymer is a two-chemistry composite. The first is the matrix precursors, which get cross-linked during manufacturing and thereby form a matrix that provides stability. The second is the photosensitive part of the film and includes the absorbers (dyes), the initiators, and the monomers. The unexposed film can be stored and shipped (in the dark) if kept at reasonably temperature-stable conditions. During exposure the image forms. After sufficient exposure to the lasers, the film is photo-cured to bleach out the absorbers and improve transparency. No heat treatment is needed. Bayer claims that with the two "independent" photochemistries, each can be separately optimized to allow for various quality requirements.

The second development is that recently Liti Holographics entered the market with photopolymer-based kits for home and school holography and also as a supplier of large holographic images for advertising. The film is marketed for home and school use as C-RT20 in 2 × 3 inch and 4 × 5 inch sizes in packets of 6–20. The commercial services also include offers to professional photographers for add-on services for portrait photography. They promise saturated color, large view zones (120°), 7 seconds of animation, and forward projecting (i.e., real) images [18–20]. This film develops as it is exposed, so that the image slowly comes into view (in early photographic terminology, it "prints out"). It requires no further processing. The fact that this film is self-developing and requires no chemical processing is a definite plus in terms of safety, especially for home and educational uses.

The active film is specified as being 16 microns thick with a 50 micron ®cover sheet and a 1.8 mm substrate. It claims diffraction efficiencies of 99% and to be panchromatic, requiring exposures of 20, 30, and 50 mJ/cm^2 at 635, 532, and 450 nm, respectively. It is optional to post expose the film to white light that will bleach out remaining monomers and improve clarity [21].

2.2.3.1 Photopolymer holographic applications to augmented reality displays

In recent reports various applications of photopolymer holograms to augmented reality displays are described. In one design a hologram is used to provide a selectively reflecting optical element for use in eyeglass-type head-up 2-D displays [22]. The hologram is constructed as a selectively reflecting hologram, designed to create a view directly in front of the eyes, using various locations and types of illumination geometries. These include straightforward down looking informational screens, such as LCDs, and also embedding the holoscreen in a larger edge-illuminated slab, so that the projected image arrives by repeated total internal reflection at the holoscreen, which then reflects it out of the slab to the eye.

In the second, a 3-D see-through screen is achieved by a conversion of Lippmann's 1908 [23] idea of an integral photograph lenslet array to a holographic version. The original idea achieved a 3-D view of a scene by photographing it through a fly's eye lens array with the recording emulsion at the back focal plane of the array. After development and reversal to a positive, it was replaced behind the array and viewed through the array. The lenslets each provided their own views

of the scene, which in total gave full parallax, both horizontal and vertical, for the viewer. In Lippmann's time producing such an array was not simple, and he apparently only got one custom-made example with which he confirmed his idea.

The new version [24] converts a lens array to a photopolymer hologram of the reflection or Denisyuk type to take advantage both of the transparency of the medium, which allows see-through views of the world beyond, and of the angular and wavelength selectivity of the hologram, which is a "thick" Bragg-angle reflector that is very wavelength selective, when illuminated with ordinary incoherent light. (Transmission-type holograms also work, but are not wavelength selective.) Illuminated at the reference beam angle, the diffraction efficiency can easily be 30%, but at the same time, the transmission through the holographic array is up around 90%. Using R, G, and B lasers to record the array, it will render full-color images, assuming the wavelengths are well chosen.

When the reference beam is replaced by a projected view of information, for example, projected from a spatial light modulator, the array forms the reflected and focused image through which the world is seen. The illumination angle can be chosen to use the phase-reversed version of the hologram. This avoids the problem of reversed depth perspective in the real image (pseudoscopy) and gives an orthoscopic version in a virtual image.

Various schemes for multiplexing 2-D and 3-D images are also explored, as are schemes for enlarging the image viewing zone. To implement large screens, which run into problems of high required laser powers and large optical systems to project the array, it is suggested that the array be constructed by mosaicking smaller arrays side by side on the polymer, and the reference beam can be diverging, instead of a collimated parallel beam.

Among the various applications, it seems that in principle the screen could be very large and allow projection of 3-D images in a Pepper's Ghost arrangement for large audiences. However, there likely would be practical difficulties.

2.2.4 An exotic potential development

A holographic recording material that apparently can be switched on and off by application of an electric current is mentioned in Ref. [25] by Bob Hess. It is described as "Holographic Polymer Dispersed Liquid Crystal (HPLDC) produced by SBG Labs (formerly DigiLens, formerly Retinal Displays)." At least one use already in production is for augmented reality helmet optics according to the DigiLens website, and there it is described as a switchable Bragg grating [26]. The grating structure is synthesized according to the optical element functionality desired.

2.2.5 A very exotic, distinctive (and tasty) family of surface relief holographic media

Back in 1997, after there was publicly available experience with photopolymers and dichromated gelatin that recorded surface relief images of the hologram interference patterns that allowed development of mass replication of master holograms, an entrepreneur experimented with and eventually succeeded in impressing a surface relief hologram on the surface of chocolate bars. To do this he started with a metal shim, made from a conventional relief master hologram, and used it to stamp copies in the chocolate. He had to find the right chocolate rigidity to record and retain the patterns, as is also needed, but perhaps less difficult to achieve in making conventional plastic copies [27]. Of course, the image quality would suffer if the chocolate went through a long enough experience of high enough temperature or was pressed down upon or rubbed in handling. This market was revisited more recently and expanded to include hard candies in addition to chocolate [28].

2.3 Photochromic materials

Photochromic materials generally darken on exposure to light. They are usually responsive to blue or UV wavelengths. Their most distinctive characteristic is that the photoreaction taking place is completely reversible, so that they make possible materials for erasable holographic memories or repeat nondestructive testing using holographic interferometry. They have been demonstrated mostly in glass doped with silver halides. These materials have essentially unlimited resolution, as the photosensitive molecules are distributed evenly throughout, not as crystals or long-chain polymers or monomers. Against this advantage there is the problem that the image decays with time, lasting perhaps 10 minutes at room temperature, though it can be slowed down by refrigeration. They are also sensitive only in the blue and UV, and not to longer wavelengths. The exposure technique began with illumination by white light, which darkened the glass uniformly, then exposure to the laser light, which selectively bleached the glass where the exposure intensity was greatest. If left alone after that, the glass gradually lightened to transparency. The image could be speed-cleared and readied for re-exposure by another white light illumination. In the 1960s I experimented using photochromic glass used for darkenable sunglasses, supplied by Corning, to make holograms. This worked in that I recorded holographic images, but the extreme insensitivity to red laser light forced 5-minute exposures with an unwidened 5 mW beam. The viewing of the reconstructed image, by laser light, will also bleach out the image, though that too could be slowed by refrigerating the sample.

2.4 Dichromated gelatin emulsions

Dichromated gelatin was one of the earliest alternatives developed to silver halide gelatin and gained favor because it recorded phase holograms directly by both very large index of refraction modulations, up in the range of 0.05, and strong surface distortions, yielding very high diffraction efficiencies and very bright images. The surface distortions can be copied onto metal that in turn could make the metal shim for stamping plastic copies. The internal transparency is excellent and the scattering noise is low. The majority of the "novelty" holograms, such as glasses with holographic eyes and keychain fobs, were mastered with or actually directly sold as sealed dichromates.

Saxby [29] gives reasonably detailed instructions for coating glass plates with DCG emulsion by three different methods:

1. Pouring along the top edge of a standing plate

2. Using a Meyer Bar to draw the emulsion across the plate while it lies horizontally

3. Spin coating the plate while pouring the emulsion on it from its center out to the edges

Gelatin can be sensitized by being premixed with dichromate (ammonium dichromate, $(NH_4)_2Cr_2o_7$) or by dipping a gelatin-coated plate into a dichromate solution.

If plates are not pre-hardened before exposure, they will tend to dissolve during processing. But this is a somewhat delicate task, because if the emulsion is too hard, then the refractive index modulation and the diffraction efficiency will be suppressed, and also scattering will increase.

The natural sensitivity of dichromated emulsion is to the blue and UV. As a result the laser that has been most used is likely the argon ion laser operating at

488 nm. Dichromate can be sensitized reasonably well to longer wavelengths by the addition of dyes. Normal exposures will be up to 100+ mJ/cm^2. It is possible to drive the diffraction efficiency to 100%, but if exposure continues, saturation can drive it down again even if the index modulation increases beyond 0.05.

Dichromated gelatin is normally processed by fixing, bathing in water, then drying by immersion in successively more concentrated baths of isopropyl alcohol in water, and finishing with 100% alcohol. After processing the emulsion must be sealed to prevent further contact with moisture, to preserve the image. This is a common practice if the image is intended for display, and not for copying. In the latter case, the surface relief is reproduced in a metal coating (a "shim") and used to stamp or injection mold the copies.

One of the pioneers of the use of DCG for display holograms and optical elements, Richard Rallison, has a good reference list [30].

2.4.1 A possible alternative DCG finishing technique

An alternative mode of finishing dichromated gelatin holograms might exist. In 1905 Lippmann commented [31], referring to his interference color photographic process, which works on the principle of a reflection hologram: "the question arose in my mind whether this transitory effect of moisture could not be permanently replaced by that of a solid, stable body."

"I soaked the plate in a solution of potassium iodide instead of in pure water. On drying, the colors were visible, though feebly so. The potassium iodide thus remained in the film, unequally distributed between maxima and minima of interference. On proceeding to pour over the dry iodized film a solution of silver nitrate (20%), the colors became extremely brilliant, and, on drying the plate, lost none of their striking character." The images were so bright that when viewed in transmission, instead of reflection, the complementary colors could be seen, and they were also brilliant. It remains to be seen whether images on emulsions processed like this remain stable or fade (blacken) due to printout.

2.5 Silver halide gelatin emulsions

Silver halide emulsions are still the most favored variety for display holograms. This is because they can be easily sensitized across the visible spectrum and are more sensitive than any of the alternatives (typically requiring exposures of 1 mJ/cm^2 or less), thus permitting the use of shorter exposures and lower power, less expensive lasers. They can also be processed to give low scattering noise and high diffraction efficiency. They are happy living unsealed in normal environments, in contrast to DCG emulsions, but less mechanically robust than photopolymers.

The gold standard for consideration of silver halide gelatin techniques is still Bjelkhagen's 1993 book [9], followed closely by more recent texts [10, 32]. The complications and considerations are numerous, but the practice has encompassed a large range of materials and processing, and many approaches allow good control of results, including color control, low noise, and high diffraction efficiency.

2.5.1 Developers

There is a very long list of developers that have been tried for holography. The most successful ones have involved one or more of the historically important developers such as metol, hydroquinone, pyrogallol, amidol, and ascorbic acid.

Development occurs in two basic ways, sometimes in combination. The first way involves reduction of the silver halide crystals that contain excited electrons created

by absorbing photons and that constitute the latent image specks. The developer reduces these to form metallic silver, and the specks agglomerate to form grains. This is termed chemical development and amplifies the creation speed of the silver grains by a factor over 100,000 times. The second way uses the developer to carry silver in solution to deposit on the latent specks. These form the latent image, and a fix is used to remove unexposed silver halide. The development continues to deposit more silver on the specks. This is a rather slow process but can result in very fine grains, often called colloidal, which can decrease the light scattering and photosensitivity and thus the proclivity to printout from further exposure to light. When development is complete, the result is an amplitude hologram.

The most widely used developer formula is the one formerly issued by Kodak as D-19. It has been widely used because it gives consistently good clarity and brightness with most emulsions, is easy to use and prepare, and is one of the safest of the possibilities. It is hydroquinone (8 g)-based, with metol (2 g), sodium sulfite (90 g), sodium carbonate (52.5 g), and potassium bromide (5 g) mixed in distilled water (1 liter). It also has excellent keeping qualities.

2.5.2 Fixing

It is conventional in photography to fix the developed image by dissolving all unexposed silver halide crystals, so that further exposure to light does not darken them. This is the role of "hypo," which was discovered by Sir John Herschel at the beginning of photography in 1839. However, many fixers (including that one) shrink the emulsion as they remove the halide crystals. Fixers are used in some silver halide holography practices, but for reflection holograms, this will create a color shift to the blue. This has led to strategies that omit fixer. Desensitizers can be used in place of fixers for transmission holograms [9].

2.5.3 Bleaches

To convert an amplitude hologram to a phase hologram, and thereby achieve diffraction efficiencies in the range of 70–90%, the usual tactic is to bleach the emulsion. There is a large range of bleaches too. They are principally of two types: rehalogenating and reversal. Reversal bleaches convert the silver grains to soluble complexes that are removed from the emulsion, leaving behind the unexposed silver halide crystals, which had not been removed by fixing. This leaves voids where the silver was removed and some shrinkage. For reflection holograms this leads to color shifts, as mentioned above, but has little effect on transmission holograms. Rehalogenating bleaches recombine the developed silver with the halides. If the emulsion was fixed first, this will also result in shrinkage and color shift from the fix step. If there is no fixing, this will leave the thickness unchanged. The image contrast will receive a big boost as the image becomes transparent and is converted to a phase hologram. The migration of the silver causes voids, and this leads to some scattering, which creates a milky haze that is exposure dependent. One of the various formulas that gives good results and is relatively safe is due to Ed Wesly. It consists of ferric sulfate (12 gms), disodium EDTA (12 gms), potassium bromide (30 gms), and sodium bisulfate (50 gms), to make up to 1 liter of distilled water. It keeps very well.

2.5.4 Redevelopers

The bleached emulsion can be put through developer again. One choice is to use a developer that is slow and yields smaller and more spherical silver grains, of the colloidal type referred to above. This will reduce the scattering caused by the bleach

step and can yield clear images with excellent contrast and brightness. A very simple developer for this purpose can be made by dissolving 10 gms of ascorbic acid in 1 liter of distilled water. It has a long shelf life and is safe. Soaking the bleached plate in this solution while illuminating it with a white light source will gradually darken the plate to a brown-red tone, after which it can be rinsed and dried. If the white fog is still present, it can be redeveloped again. The smaller grains are also less prone to printout.

The above regime, of D-19 developer, ferric EDTA rehalogenating bleach, and ascorbic acid redeveloper, is simple and reliably gives good results for reflection and transmission holograms. Other combinations can give better results in some cases but are mostly more dangerous, and the solutions keep less well. Often, a very last step is a soak in a wetting agent, such as Photo-Flo, which can add protection against printout.

2.5.5 Hypersensitizers and color-shift treatments (pre-exposure)

There are several methods that have been developed to hypersensitize silver halide emulsions. All three enhance sensitivity without enlarging grain size or reducing resolution. These are:

1. Pre-exposure soak in water

2. Pre-exposure soak in triethanolamine (TEA)

3. Pre-exposure soak in formate

The first two are long known to holographers. The third was recently published.

Of the first two, a simple dip of 30 seconds into distilled water followed by drying will enhance sensitivity by about a factor of 2. This effect has a shelf life of perhaps a day. The pre-exposure dip into TEA solutions followed by drying likely has a shelf life of several months. It also achieves a speed gain of about a factor of 2, without affecting resolution, though careful technique is needed if streak-free results are desired.

TEA is well known to holographers primarily for its ability to shift the color of the final result in reflection holograms. This occurs because TEA swells the emulsion. The normal interference layered fringe pattern, with spacing of ½ the laser wavelength, is recorded. Then, when the TEA is rinsed out, before development, the emulsion shrinks back, and after development and drying, the layer spacing shrinks to yield image reconstruction at a shorter wavelength. The amount of swelling effect is controlled by a combination of dip time and TEA concentration in water. The range of colors accessible by this technique is from the laser color to the bluest visible color.

There is also a post-development color-shift treatment by soaking the emulsion in a swelling agent, frequently the chemical sorbitol. This will shift the color from the laser color to colors to the red of that.

The third type of hypersensitization treatment was recently published [33]. It builds on an invention by Belloni and her coworkers that employs a pre-exposure soak in a solution of formate in water. Tests showed that a dilution of 1/100 molar would give the desired effect and leave no residue on the emulsion. The emulsion is soaked for 30 seconds to a minute and then dried. It is then exposed and developed normally. However, there is a peculiarity to the way the effect works. The speed gain is maximized by delaying development by 10–15 minutes after the exposure. With that delay, the speed gain is 10×s. If the development is done immediately

after exposure, the speed gain is only a factor of 5. This converts emulsions of silver halide from requiring three or four photons per latent silver halide molecule to needing only one, a quantum efficiency of 1. There is a very slight color shift to the red, which means there was a very slight swelling of the emulsion due to the treatment.

This hypersensitizer was tested only on one holographic emulsion (Slavich PFG-01), with one developer (D-19), and for a continuous exposure, though it should in theory work for all other silver halide emulsions. It was not tested in conjunction with a pulsed laser exposure. There is evidence that latent images made by pulsed exposures fade more rapidly than by continuous exposure [9]. This leaves to open a question: will the formate pretreatment be less effective for pulsed exposures due to their tendency to rapid fading, or will it be more effective as it will slow down the rate of fading? This remains to be tested.

3. Conclusions

In this review we have looked at a range of processes and media for making high-quality holograms and some of the associated history.

The last 50 years has seen the market for holograms grow in certain commercial sectors. These have exerted pressure to develop master holographic emulsions for mass market uses such as security markers and HOEs. There have been many experiments tried, and recently two photopolymers, one by Bayer and one by Liti, have appeared. They have improved stability, improved resistance to shrinkage and color shifts, and in the case of Liti are completely self-developing, in analogy to the very old photographic printing-out processes.

Metamaterials appear to be in the process of revolutionizing holography, as well as optics in general. There will be a great deal of work done in order to commercialize them, and their primary application is likely to be for HOEs.

Display holography has not seen the market growth of other applications, despite efforts by artists and entrepreneurs, and there have not been big resources devoted to them. The most recent advance is a method of presoaking silver halide emulsions with a formate solution, which hypersensitizes them by a factor of 5–10×'s. This can allow shorter exposures, making vibration less of an issue, or allow the making of larger area images using lasers of modest power output. It can be possible to have similar effects for a wide range of photochemistries.

Conflict of interest

The author declares no conflict of interest.

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