

# Recording Material Selection

## Contents

- 1 Phase materials for HOE applications
- 2 Introduction
- 3 Basic phase diffracting structures
  - 3.1 Basic transmissive volume holographic gratings.
  - 3.2 Surface phase recordings.
- 4 Matching materials
  - 4.1 Silver-Halide in gelatin
  - 4.2 DCG (dichromated gelatin)
  - 4.3 DMP-128 photopolymer from Polaroid
  - 4.4 DuPont Photopolymers
  - 4.5 PVA and PVK
  - 4.6 Shipley Photo-resist
- 5 Relative material sensitivities
- 6 References

## Phase materials for HOE applications

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The choice of a phase recording material strongly affects the utility of the final recording. For display holograms properties like brightness, contrast, color range and color saturation might dominate and the choices are part art and part science. For HOEs, the extended range of properties that may require manipulation and the choices of materials to obtain each property in the required quantity, makes a working knowledge of what can be done extremely useful. This paper presents the fundamental properties of phase recordings and the fundamental properties of many phase materials so that a choice that will get a person from plan to product can be more readily made. Recipes are not given but references to recipes are and modifications or procedures that can modify a well-known material may be described. The object of this paper is to make the reader aware of both the strong functions of these materials and the weak or subtle properties so that a design may be reviewed for feasibility a little more thoroughly and hopefully the route to a functioning product will be shorter and less costly.

## Introduction

The phase recordings we will consider are the simple transmissive sinusoidal volume plane grating, the powered or focusing volume grating, the general reflective volume grating with the two special cases of a conformal reflection recording and a strong spherical wave recording and finally the large class of surface phase gratings so popular because of the supposed ease of

fabrication. We first identify as many of the properties of these phase structures as we can, then discuss the variations and mix of these properties that may be required in a well-functioning final copy. At this point we define the minimum performance required of the end product and then list some popular media to choose from. In order to make a good first choice we need to know the intrinsic properties of these materials and their limitations, strong and weak points, cost, availability and perhaps what would be termed their "nuisance factor". This last factor is the reason I end up with plenty of work to keep me busy. Very often the art gets in the way of the science, the recipe has too many variables, the learning curve is a little too long and the literature a little too short and probably ambiguous and contradictory. We will use unscaled illustrations as much as possible and keep things as simple as possible, steering clear of any exhaustive validations of claims made for different materials or the chemistry involved. The reference material can be used to satisfy these other needs. Only simple algebraic equations or approximations are used without formal justification.

## Basic phase diffracting structures

Each of the figures 1 through 5 represent a common spatial phase modulator. The simple plane grating covers a wide terrain, wide enough to include transmission display holograms made in bleached silver grain films which can be thought of as being made up of very many superposed plane gratings or as many tiny spatially multiplexed gratings. The reflective grating covers just about everything else that could be made but we have to consider the subtleties of various configurations and some special cases. Surface phase gratings are not just thin volume gratings, they have become a large class of optics themselves, referred to as diffractive optics (DOEs) and they enjoy considerable popularity at the present time. Some materials in common use today can be used to fabricate all of these diffraction structures, but none will cover all possible constructions within every class. Within the description of the properties of the HOE that is to be fabricated is the description of the material that will have to exist to make it. In most cases the material does exist and may be available in some form, but not always on the right substrate and in the right thickness. In real materials the direction that light transits through the HOE makes a difference, sometimes a large difference, the efficiency of a grating can actually be greater in one direction because of gradients in the modulation and holographic mirrors often reflect different spectra on each side with different intensities.

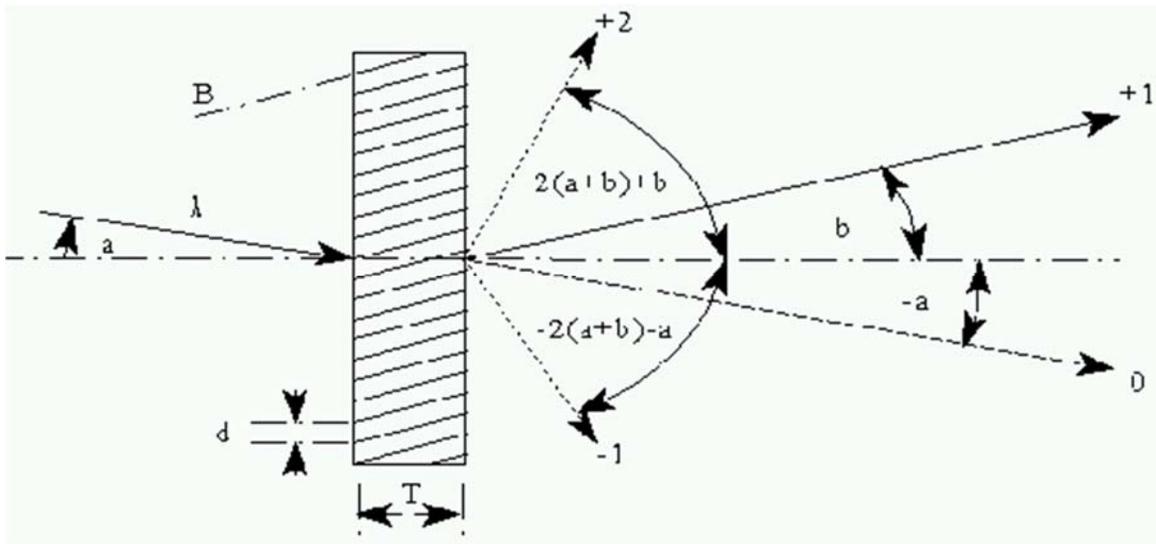
### Basic transmissive volume holographic gratings.

Fig 1. Depicts an edge view of a section of a plane grating of thickness ( $T$ ) of fringe spacing ( $d$ ), at the surface and of fringe tilt or Bragg tilt ( $B$ ). The fringes themselves are regions of high and low index ( $n$ ) with the differences referred to as ( $\Delta n$ ). The product of  $\Delta n T$  is the total modulation of the grating but the diffracted light in each order also depends on angles  $A$  and  $B$  and wavelength ( $\lambda$ ) which together define  $d$ . The change in index is usually not uniform through the film.

It is common wisdom that the thicker the grating, the narrower is the angular bandwidth and the better is the suppression of higher orders, if they can exist. The other half of that assumption is that the value of  $\Delta n$  is small enough to make the product of  $\Delta n T$  just large enough to diffract all of the light. If in fact the product is 2 or 3 times that high, the grating will behave as a 3 or 4 times thinner grating. Materials that require wet processing almost always have a gradient in

index that can be very high, further reducing the effective thickness of the grating. Even real time recording materials, including photorefractive crystals have a gradient in index from absorption and behave as if they were much thinner than they are. The power lost to higher orders is proportional to  $\Delta n^2$  so if modulation is excessive then not only is a thick grating rendered thin but it may diffract most of the incident power into useless orders.

Another got cha' in dealing with thick gratings is the wandering Brag tilt B. Whenever wet processing is used there is a high probability that the original tilt made during exposure will play back at some other angle. In very thick gratings this error can exceed the angular bandwidth of the grating and render a non-uniform grating that is useless. Thick gratings made in low shrinkage photopolymers and photo cross linkers that require no processing seem to work well enough. If the intended use of the grating requires a thin structure with a broad angular and spectral response then the angles must be chosen so that higher orders cannot exist. This can begin when A and B both equal 30 degrees and the 2nd order becomes evanescent at 90 degrees (in air). The -1 order may still exist but is not entitled to receive much power at modulation levels near optimum for 99% diffraction efficiency (DE). When any of these gratings show excessive B error there is usually a pre exposure fix that can be done to compensate or a post processing bake down or swell up for each material. A special case of this grating is the total internal reflection (TIR) geometry that requires extreme control over fringe tilt error. It should also be remembered that TIR gratings will not diffract P polarized light very well or at all for the same reason that Brewster's angle works.



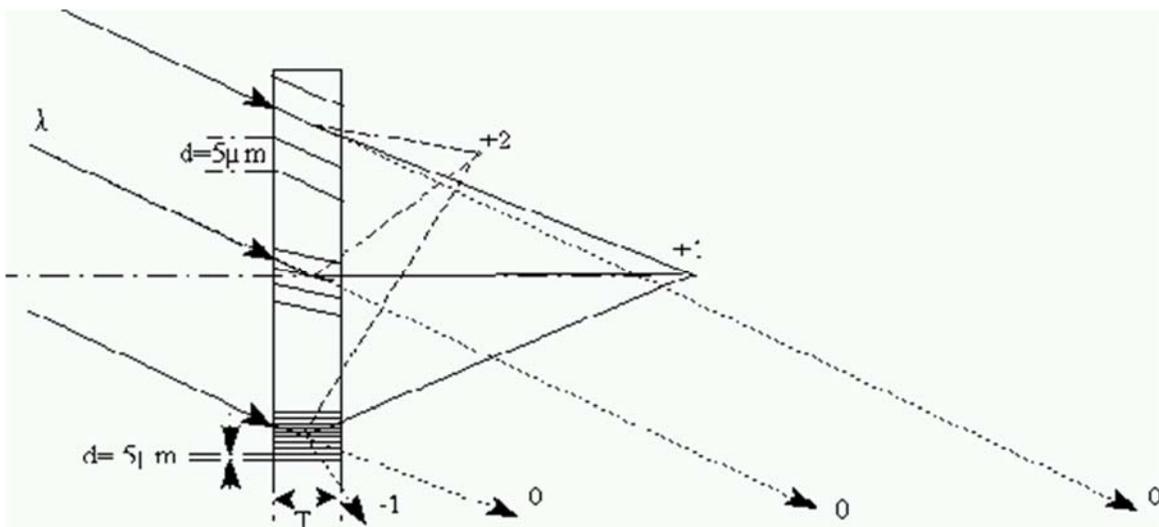
**Figure 1.** The simple plane volume phase grating with properties:

1.  $\sin a + \sin b = \lambda/d$
2. DE is proportional to  $\sin^2(\Delta n T)$  and to  $1/\lambda \cos a + \cos b$
3. Power lost to higher orders is proportional to  $\Delta n^2$
4. Fringe or Brag tilt B is proportional to T and n

Figure 2 shows a common variance on a plane grating, a grating with a spatially varying spatial frequency such that rays of a certain  $\lambda$  and a common input direction will be diffracted to a common point on the output side. We may have seen this in text books as an off axis equivalent lens which is generally assumed to be a practical application of holography. For the fast optic shown, the output could be a family of points, half of them virtual and half real and all related geometrically to the fundamental focal length. Note that from top to bottom the spatial frequency ( $f_0 = 1/d$ ) varies from very low, perhaps 200 l/mm to very high, perhaps 2000 l/mm. In the plane grating we only had to consider the modulation product of  $nT$  but now we have to add the term  $f_0$  which also modifies DE. Note also that higher orders are nearly impossible to suppress at the top of this HOE and are nonexistent at the bottom. How would you ever make this design work? What material could be used?

The difference in spatial frequencies could be compensated for in most materials by adjusting exposure energies in some way so that the lower end received less exposure and so create lower modulation than the top. This would solve the modulation balance except that now even more energy will be lost in the higher orders for only a small gain in the +1 because the losses at the top are proportional  $\Delta n^2$ , which just went up. Then perhaps the better fix is to try to keep  $n$  constant and vary the  $T$  from top to bottom such that the product of  $\Delta n T f_0$  is everywhere the same. Obviously you cannot buy such a material commercially so this special coating is very experimental. The processing will also have to be tailored because it is not likely that the thicker portions can be processed in the same time frames as the thinner portions. What about real time materials that saturate? Perhaps if available in liquid form, this HOE could be made.

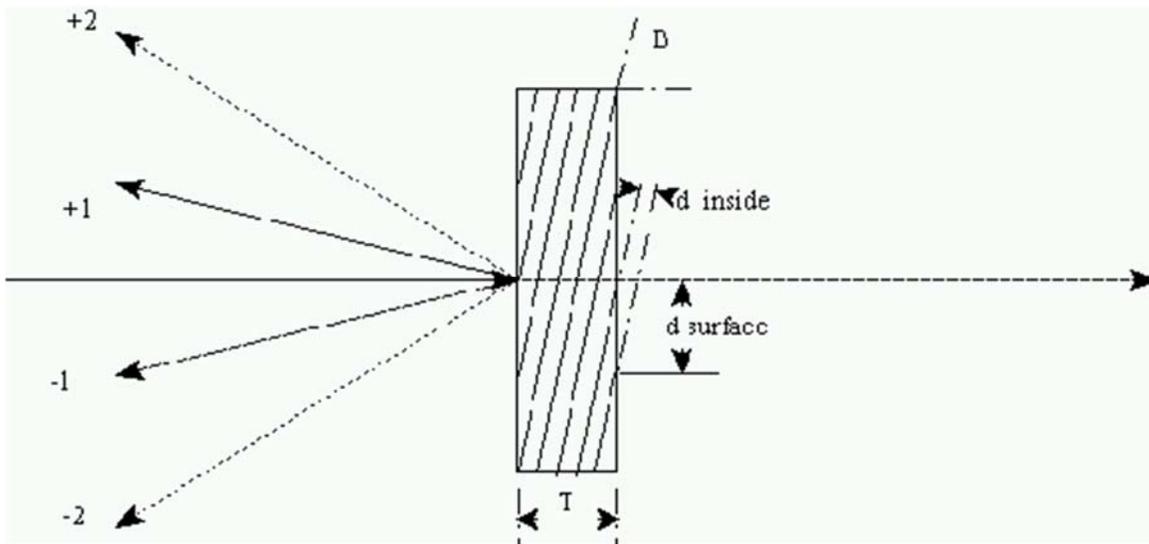
As the  $f\#$  goes to 2.5 or higher this lens becomes a fairly good performer in most materials, only the really fast  $f\#1$  and lower optics are an art to construct and are probably best made in pieces if possible. An on axis lens made in any volume material at any  $f\#$  will have a dead zone in the middle where almost no light can be diffracted because the spatial frequency falls to zero. One way around this dilemma is to work with a material that forms a surface phase structure at low spatial frequencies so that the HOE transitions from a surface phase HOE in the center to a thin and then thick phase HOE as the radial distance increases. A few materials will do this to some degree.



**Figure 2.** The case of a fast off axis focusing HOE with these additional properties:

1. DE varies from top to bottom if  $\Delta nT$  is a constant.
2. Bragg or fringe tilt error is typically not uniform.
3. Higher orders often rob power from regions of large d spacing such as near the top.
4. S + P (random polarization) efficiencies cannot be as high at the bottom as in the middle.

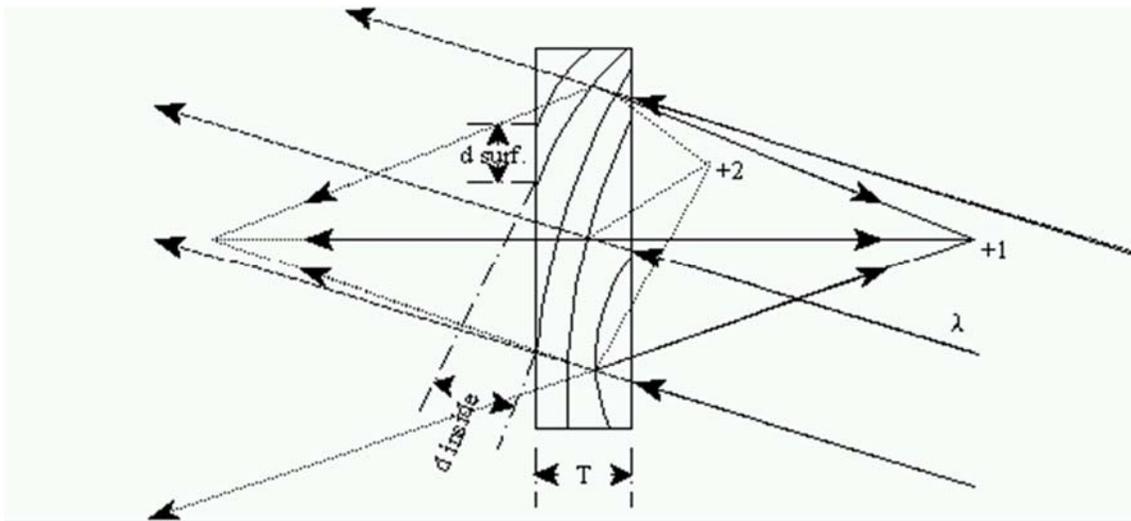
Figure 3 depicts a simple slanted reflection grating; if it were un-slanted we would call it a conformal mirror with about the same properties found in dielectric stack mirrors. All reflection HOEs share one advantage over all transmission HOEs, the efficiency just keeps going up with increasing modulation rather than cycling up and down. The suppression of higher orders is also better at high n but the fringe spacing is a new variable affecting color and fringe tilt and it is nearly impossible to record an off axis reflection HOE without also recording a fairly strong transmission HOE. The idea of suppressing the unwanted transmission HOE by somehow index matching it out is only wishful thinking. The plane where the fringes meet the substrate must necessarily contain the same periodic changes in index that makes the HOE efficient, so the only case where a transmission HOE is not formed is the special case of the conformal reflector. This effect is of course minimized in materials of low n that rely on significant T to get sufficient modulation. In an HUD design the surface grating produces serious flare light when flying at certain angles to the sun, for that reason alone, practically all holographic HUDs are conformal reflectors.



**Figure 3.** The simple reflection grating with the properties:

1. DE is proportional to  $\Delta nT$ .
2.  $\lambda$  is proportional to  $nT$  + any gradient in d spacing.
3.  $\Delta\lambda$  is proportional to  $\Delta n$  + any gradient in d spacing.
4. Surface grating strength is always non zero except for a conformal reflector.
5. power lost to -1 and higher orders is usually negligible even at high  $\Delta n$

Figure 4 is an illustration of a fast focusing reflection HOE. In this case the surface grating changes from high to low frequency but the reflection grating is more or less constant everywhere so that the efficiency is high everywhere. The efficiency falls off for P polarized light when the internal angle of diffraction or reflection approaches 90 degrees so if this is important to the design a denser material would be better than a less dense material. As the average  $n$  (roughly equivalent to density) of the film falls to low values the internal diffraction angles grow larger and account for many HOE failures. One of the errors this geometry is prone to is a variable fringe spacing and tilt induced by processing. Occasionally the distortion in the fringe structure is so large that constructive wave coupling fails and the HOE loses nearly all efficiency in spite of a large modulation level. Often the color is variable across the surface indicating a non-uniform internal  $d$  spacing or average  $n$ . Hoes exhibit more severe aberrations in the reflection mode compared to the transmission mode, much like conventional optics. The choice of materials and processes to control them is particularly important when designing reflection optics or reflection art work. Full color display films have to have the required sensitometric characteristics as well as true reconstruction characteristics and only a few do. There are none that do it all with high efficiency but that is not a show stopper for anything but multi-wavelength notch filters and such which can usually be made with some other material.



**Figure 4.** The very fast non conformal reflection HOE with the properties:

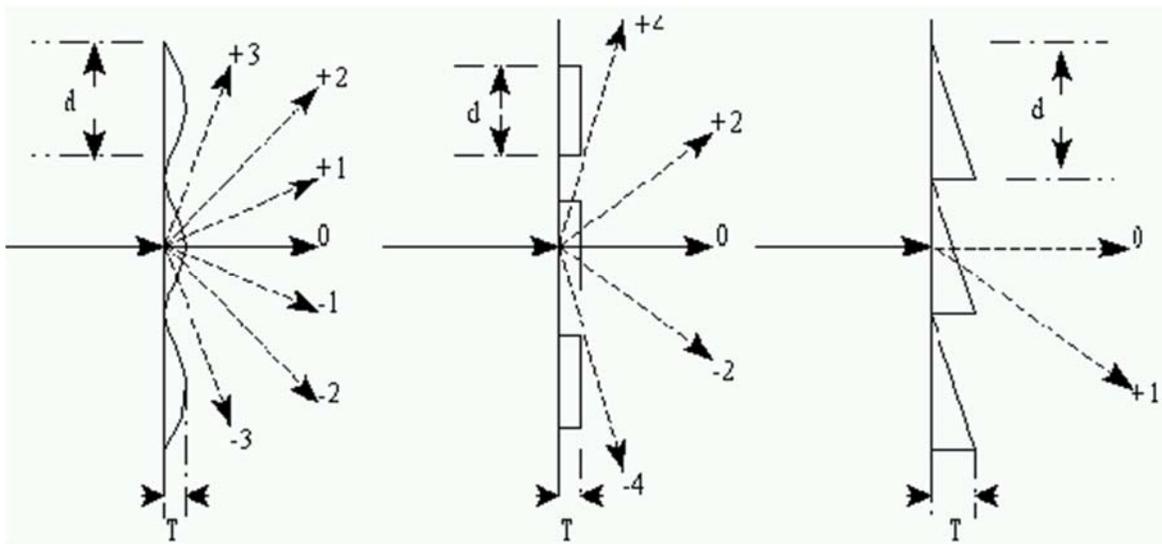
1. DE is proportional to  $\Delta n T$
2.  $\lambda$  may vary with position from process induced distortions.
3. Surface grating can be very intense, producing a "transflection hologram."
4. Higher orders are suppressed much better than in transmission equivalent with mirror backing.

### Surface phase recordings.

Figure 5 is a representation of the surface profiles common to diffractive optics, each has been recorded in one or more phase materials and copied in many more phase materials. The single biggest advantage of surface phase structures is that they can be replicated in a dozen or more

ways that do not involve the use of lasers. In fact many are made as originals without laser light or at least without interference effects. Since they can often be made optically with lasers we have to consider them and mention the common materials with their properties and uses. The three most common surface profiles are shown as sinusoidal, square and saw tooth. The sinusoidal are natural continuous phase interference patterns, the square waves could be made by interfering a lot of odd harmonics in phase but are better copied from masks generated in typeset machines or on chrome masks exposed to E-beams. The saw tooth is deeper and is sort of the equivalent to a single side band transmitter with a suppressed carrier. This shape or its interferometric equivalent which appears more rounded is the only one that puts nearly all the light into one order. An exception to this is the deep square or sinusoidal grating that is high enough in spatial frequency to have no possible higher orders and is deep enough to have some volume type wave coupled interaction that results in high efficiency.

The saw tooth shape has long been machined into materials to form blazed gratings for spectroscopy and now diamond turned blazed zone plates have become common on plastic lenses where the hybrid is effectively color corrected and has reduced spherical aberration. The blazed zone plate may also be made with a single exposure through a gray scale mask in photoresist, in some photopolymers and with lesser performance in silver grain and DCG films. It is also made in the stepped mask manner where a multilevel stair case approximation to a blaze is achieved by using from 2 to 4 masks in sequence to expose the resist. This method is limited by mask resolution and alignment and by the wavelength of light used. If the grey scale mask or its binary equivalent can be used then it is only a one step exposure limited only by the mask resolution. This general class of optics includes binary optics, embossed rainbow holograms, embossed full parallax holograms, Kino forms and all other DOEs that are not volume HOEs (VHOES).



**Figure 5.** The general surface phase structure with the properties:

1. Angular bandwidth ( $\Delta\theta$ ) is much larger than in volume holograms or VHOEs.
2. Power distribution in higher orders is a strong function of fringe shape and depth  $T$ .

3.  $T$  is roughly equivalent to  $\Delta n$  and depends on  $n$ , except for metalized reflective shapes where air is the phase shifter.
4. Computer generated DOEs, lithographic or machined, are now common and practical, HOEs still rule at high  $f_0$ , (pun intended).

## Matching materials

The broadest class of phase recording materials would fill a book or two so we only want to consider generic silver grain films, DCG, Polaroid photopolymers, DuPont photopolymers, PVA, PVK and Shipley photo-resist. Reference texts and papers are listed in the bibliography for recipes and other details. The new book edited by Hans Bjelkagen entitled Holographic Recording Materials is the most comprehensive single source for valuable practical material information. It is a milestone series containing 676 previously published papers covering all but PVK and PVA. Many of the papers listed separately in my bibliography are in his book.

### Silver-Halide in gelatin

By far the most popular materials to work in are products from Agfa, Kodak and a handful of smaller producers around the world. Some are panchromatic, some have extremely fine grains, all are comparatively fast and a few have been made to work in the near IR. They are the first choice of most artists because of the sensitivity to commonly available lasers of all colors and because they may be repeatedly exposed and processed to produce the widest range of visual effects. The upper range of  $n$  is on the order of .1 and the grain size varies from a low of about 10 nm to over 100 nm. Grains are a significant source of scatter and therefore produce noise in the recordings, especially at short wavelengths. This is a major consideration for most applications and for all but the smallest grain films. Just about any HOE and some DOEs may be made in silver films but they will rarely be optimized for any enough properties and if they are bleached to get the highest efficiency then other sources of noise begin contributing and grain size may grow as well. A well worked out plan for a product may utilize the speed and panchromatic properties to produce a master HOE that can then be contact copied into a material with appropriate final properties. These films can be left as clean amplitude holograms or converted to "no silver halide in gelatin" (SHG) with simple chemistry and the resultant optic will be free from scatter caused by the grains of silver. The SHG masters are especially good when copying in the blue region where the lower  $n$  works well and silver grains often produce excessive noise.

A good example is the making of a HOE like figure 2 that must perform well at 680 nm. If it were made at any other wavelength than 680 it would play back with aberrations so we either have to precompensate for those aberrations or make a master at 680 nm. Both Agfa and Kodak make films that are sensitive to 680 nm and that can also readily be processed into SHG masters with a simple weak chrome bleach followed by a fix and some hot alcohol baths. Then the master can be copied at 488 into DCG or a suitable photopolymer or the much slower photo-resist. Display masters may also be made this way, taking advantage of the speed of silver (as low as  $3 \mu\text{j}/\text{cm}^2$ ) and then creating a photo-resist sub master in a more stable set up using 442 nm light. Contact copies of even a weak hologram can be very bright when transferred to DCG provided that the ratio of reference to object light is no less than 10:1 at the bright points and the scatter from all sources is very low. We highly recommend this general procedure for any

exposures that have to be made at wavelengths longer than 514 nm to about 750 nm. Diode lasers can easily be made to operate in a single mode for long enough to make a good recording and Ion lasers or cadmium lasers can do all the copying.

## **DCG (dichromated gelatin)**

By far the most versatile of the phase materials, DCG in its simplest form can be used to create almost any type of HOE as long as the exposure is allowed to be done at blue green or shorter wavelengths. A few people have even made good quality HOEs with dye sensitized DCG aka DSDCG, using krypton red or big HeNe lasers. The disadvantage there is the low sensitivity of the material and low availability of strong red sources. DSDCG may require from 50 to 1000  $\text{mj}/\text{cm}^2$  @ 647 nm while DCG can be used with as little as 4  $\text{mj}/\text{cm}^2$  @ 442 nm to about 100  $\text{mj}/\text{cm}^2$  @ 514 nm. In general all the photopolymers and all the photo cross linkers are at least 1000 times less sensitive than silver halide products. We are fortunate that low scatter can be had from both mediums or else copying from one to the other would be useless. The intrinsic noise from a highly efficient DCG HOE of moderate thickness in the 5 to 8 micron range is 1 or 2%, a very low number. The sources of noise can be controlled to that level for simple grating like structures but surface noise from dirty beams, intermodulation noise found in multi-beam or diffuse object recordings, dust on and in the film and nonlinearity noise through the bulk can all contribute to the best of the materials and not all noise sources can be eliminated.

The two greatest advantages of using DCG are the intrinsic low scatter, (if hardened sufficiently), and the tolerance for many reprocessing or post processing steps to fine tune the end product. The biggest disadvantage is that you have to devote time and space to a clean coating facility and the end product is extremely sensitive to high humidity. Some products require a careful tailoring of the thickness and juggling of the sensitizer and in those cases the requirement to coat your own is a big advantage. We work with standardized mixtures and coating methods that produce 5, 8, 10 and 25 micron thick coatings that have been sufficient to make almost any HOE for the visible and near IR regions, from 450 to 1500 nm.

When the material is used without much hardening it produces hazy holograms that exhibit broad spectral and angular bands but as it is hardened it also narrows and at some point it crosses into the no scatter zone quite suddenly, with no attendant change in other properties. This point is where even unexposed gelatin can no longer be dissolved out with warm water, leaving scattering centers behind. At all levels of hardness the  $\Delta n T$  near the surface can be pushed to .25 but as in most other media that number cannot be extrapolated to thicker films. Films as thick as 100 microns have been made and processed but they behave no differently than 50 micron films which in turn behave thicker than 25 micron films but have a  $\Delta n T$  product that is actually lower than what is achievable at 25 microns. We think 25 to 30 microns is about the practical limit for HOEs made in DCG, which means notch filters made in DCG can trade off bandwidth for density up to that thickness but top out at a  $\Delta n T$  product of about 2.5, no matter how thick or thin the film is. DMP-128 from Polaroid tops out at about 2 also, bleached silver film is about .7, PVA is about .8 after wet processing and DuPont products go to at least to 1.

DCG has been used successfully with all the basic configurations, including the surface relief structures. For spatial frequencies below 500  $1/\text{mm}$  DCG and silver halide films both form a form

more efficient surface relief profile. This works best with softer gelatin and in silver film it is enhanced by repeated bleach and develop steps. In DCG the effect is enhanced by using thick film and a longer soak in a .86 SG alcohol and water mixture before final dehydration in straight alcohol. Fixing after the first processing can improve the gel hardness without destroying the relief image and then the gel can be used as an embossing master with solvent softened plastics. Hardened silver halide films work about as well.

The problems related to non-uniform spatial frequencies or just non uniform exposures can be fixed if they are only off by 10 or 20% by post processing DCG in baths of hot soapy water and in fixer where areas that require more modulation are dipped in hot water and areas that are too well done can be brought down with fixer. Local zones may be repeatedly painted with fixer or a 5% solution of TEA and then reprocessed in water and alcohol to balance out the plate. If an area is known to be over exposed before processing, it may be effectively unexposed with an ordinary incandescent light bulb held close to it for a few minutes. All of these manipulation methods are experimental and the rules are loose and vary greatly from thick to thin in time and intensity. Baking at about 150 C will cause the gelatin to densify and if tilted fringes are present they will appear to lay down, baking also makes the gel much more stable and a little less hygroscopic. While it is still hot a glass cap or at least an epoxy coating can be applied without trapping too much moisture in the film. Trapped moisture can become active upon heating and cause the gel to collapse here and there and everywhere. Mysterious color shifts in capped reflection holograms can be explained by the action of trapped moisture and lack of 150 bake down.

The sensitivity to moisture is not the only drawback to using DCG. It will easily distort in thick films and in large area recordings in thin films it is very difficult to process uniformly. The processing leaves the fringe planes at slightly random positions and usually the film expands so that the fringes stand up while the bulk  $n$  goes down. In gratings made at near 64 degrees in and out for either reflection or transmission the diffraction efficiency for incident P polarized light is near zero, because  $n$  has dropped to about 1.3. Unless you were building a polarization separator you would not find this desirable. In fact the low  $n$  means that the difference between S and P efficiencies is always larger than in more dense media. DMP-128 also has a low average  $n$  for about the same reason; the  $\Delta n$  is created by producing low density voids in the film during dehydration, much like the making of aerogels.

### **DMP-128 photopolymer from Polaroid**

This film has enjoyed success as a flexible film used for great looking reflection and transmission display holograms. It is also useful for making high density reflectors and because of the unique open structure it can be filled with liquid crystals to make disappearing HOEs and DFB lasers and narrowband filters. It is easier to stabilize than DCG and has about the same high modulation in films of 7 to 15 microns. All of the wet processed films seem to work best in the thickness range of from 5 to 15 microns, probably owing to limited diffusion rates in DCG and in DMP-128. This material is used mostly with red light but can be made panchromatic more easily than DCG and is much more sensitive, requiring only about 25 mj/cm<sup>2</sup> to fully expose.

This material is saturate able, once the polymerizable material is used up, the effects of exposure are nil. This is a great advantage in production because over exposure has almost no

effect, except to maybe compress the contrast range a little. This is true of all the migratory photopolymer systems, including all of DuPont's photopolymer products. The light used to expose the hologram need not be perfectly uniform to get a uniform copy. The ratio of the reference to object wave is the primary determinant of how much modulation an area will have after an over exposure. It is a sort of self "dodging" film with a hard limit on modulation related to beam ratio. This implies that to get maximum performance a reflection or transmission master has to be as bright in its hot spots as the reference.

One disadvantage of this material is that it is on a substrate that has a higher index than the unexposed film so that all recordings have a mirror in them and the film is not generally available in liquid form as of this writing. Environmental controls are important at the exposure station, because the film has to be activated by a fairly precise percentage of water or it will produce noisy holograms. The low average  $n$  may be a disadvantage for some HOES and the material tends to shrink during or after processing and needs to be babied a little to get it to reconstruct with perfect fidelity. The display holograms are the best and brightest among the mass produced products and last a very long time.

Polaroid has announced the introduction of another photopolymer that also has a high  $n$  but needs no wet processing and therefore is much more suitable for precision HOE making. It will be a great boon to some of us if they market the film as DuPont does, coated and in liquid form. I don't have a clue about how it is used or how well it performs. Photopolymers, because of the dynamics of monomer migration, may make pretty poor sequential hologram recordings, each successive shot adds noise to the previous shot, and if angles are not changed sufficiently between shots in a real time material then more than one recording will be made at a time as previous recordings reconstruct and rerecord with new ones. Latent image recordings do not have this problem and some real time materials do not have migration occurring. The little things can get you.

## **DuPont Photopolymers**

These are all real time recording materials with migration of monomer. They work as is or may be enhanced with post exposure baking and with the addition of a monomer to swell them to a thicker state. Swelling shifts playback color and angle in reflection holograms. The sensitivity of some films is down to a few  $\text{mj}/\text{cm}^2$  but as with DMP-128 they cannot be over exposed. Some films are panchromatic and good full color holograms can be made in them. The available  $\Delta n$  is about .06 on a good day in the best of films so to get good brightness the films are over 8 microns thick, more typically about 20 microns. They play back with smaller bandwidths but look clear in about any light. The normal backing is Mylar and is birefringent causing some problems with production and making it difficult to make HOEs with high integrity. The liquid film has been made available so that it can go on glass and then good quality HOEs are possible. A very large number of display holograms have been produced in this material, which is sold in sheets and rolls with machines to expose and process it.

The limited modulation prevents this material from being used in some tasks, but it is a big plus for others. When high angular selectivity or a narrow notch filter is needed it is the material of choice, especially if you can get coatings of 50 microns or more. Optical memories have been

made with it and could flourish. We made diffraction limited gratings with it. The dye never bleaches all the way out of some of their films so it is useless at short wavelengths, as is DCG and PVK. Most if not all holographic recording materials naturally absorb strongly in the UV region both long and shortwave.

One of DuPont's materials forms an excellent embossed surface upon exposure and is great for copying binary or possibly shaded masks. The shading may copy with poor linearity depending on light intensities, spatial frequencies and migration rates and distances, all considerations that could spoil your day. We copied a binary mask in non-embossing material and found that it was self-guiding because of the real time formation of the higher index light fringes. The first light through the slits forms a guide for the rest and the usual diffractive spreading does not occur and the copied HOE is excellent except for the plastic substrate it is usually on. This is very easily used material, and stores for years in a fridge.

## **PVA and PVK**

PVA (polyvinyl alcohol) has been dichromated and used as a real time material fixed with heat for many years. It is easy to get, mix, coat and use this way. It is also possible to enhance the modulation greatly by dipping it in water and alcohol, similar to DCG processes. It can also serve as a binder for a monomer and act more like other photopolymers. In its dichromated form it is a photo cross linker like DCG and as such has no migration but the latent image in PVA is many times better than the latent image in DCG. Images and HOES are easily seen as they form in films as thin as 5 microns. The integrity of the recordings is very high with very little damage done by overwriting multiple times. As a cross linker it is not a saturate able media and can be overexposed, however it requires about a 100 mJ/cm<sup>2</sup> to form a strong recording and about 1000 more to begin to undo it.

One disadvantage is that it does not adhere well to glass or plastic which makes it a perfect candidate for a transfer hologram. It is possible to form a conformal mirror in it on flat glass or plastic in a production environment and then lift it off and transfer it to a spherical surface in another off line process. It is soluble in water and unstable at high humidity but it may be possible to stabilize chemically by converting at least some of its molecules back into polyvinyl acetate or by adding crosslinking agents to a last bath. Borax is used to crosslink PVA and form "slime", baking a wet processed PVA hologram causes it to return to its original latent image state and stabilizes it somewhat against moisture. Other uses include protecting and cleaning optics and it is a common mold release agent.

PVK (polyvinyl carbazole) is not soluble in water but dissolves in chloroform and in sensitized by halogens to become a photo cross linker. It is processed in xylene and hexanes or a mono bath of miscible but differentially volatile solvents. It should only be used where maximum resistance to water is needed. It will work well in 5 micron layers, has a short shelf life and a high  $\Delta n$  but is hard to process uniformly. It is sensitive to blue green light and requires only a few mJ/cm<sup>2</sup>. It requires the use of noxious chemicals, some of which are known carcinogens.

PVK is also a commonly used photoconductor which could be used to form relief holograms in thermoplastics and for light intensifiers. If used for holography it has to be sensitized at the same

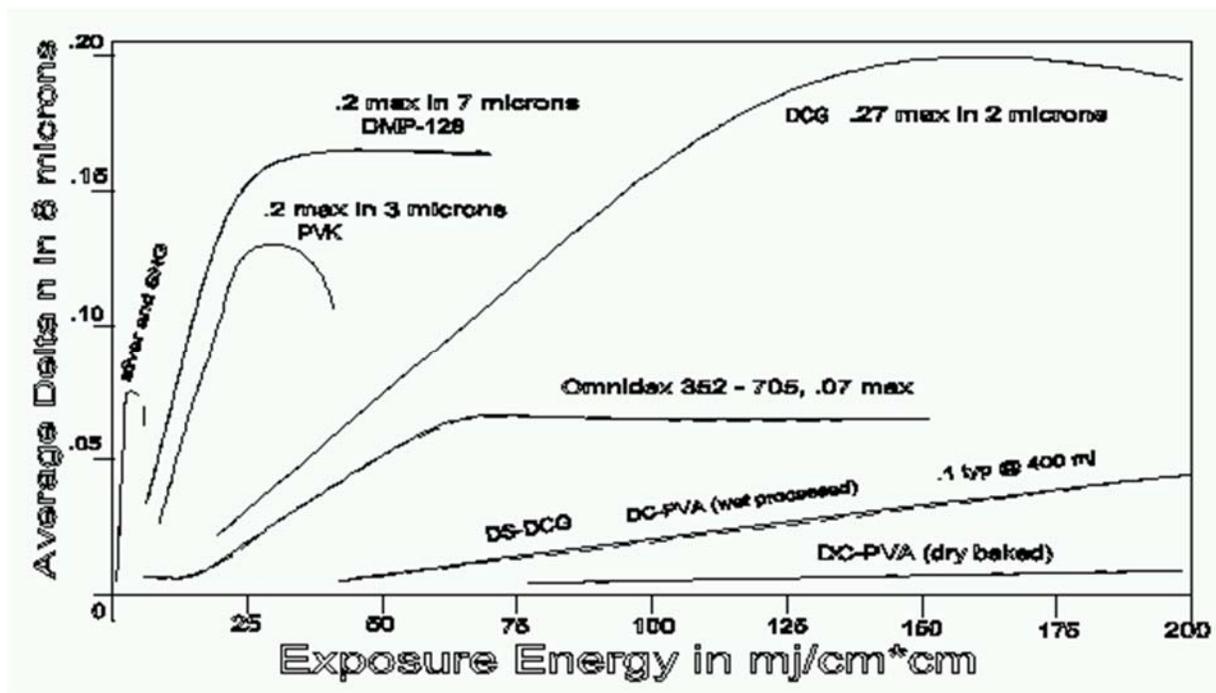
time it is dissolved or it will not work, the fastest sensitizer is carbon tetra iodide and it is extremely unstable.

## **Shipley Photo-resist**

Many of us use this as a standard for embossing masters. It can be obtained on plates commercially from several sources, has a long shelf life, and reasonable sensitivity to blue and UV light. We have jars of material that are 20 years old and still work about as well as they ever did. This is the most common material used to make binary optics from metal masks and it is easily metalized for production of embossing shims. We make masters from epoxy molds lifted from the resist and then mold copies in other epoxies and plastics. It is possible to make features as deep as 4 or 5 microns with little effort and resist masters may be directly converted to glass masters with reactive ion etching or with diluted HF. Some people are able to get very high aspect ratios in it and form high frequency high efficiency gratings in it. The integrity of the recording is rarely compromised in processing, but very high frequency gratings may close over at the top if there are exposed to common organic solvent fumes. Resist is user friendly and you never have to even dim the lights while working with it.

All surface phase DOEs and HOEs are readily made in this material. It is often advisable to make a clean master in DCG to copy from because the exposures for reasonable sizes copies can run from several minutes to an hour, during which time a contact copy on three legs may not move but most optical setups of any size will. The required exposure is on the order of  $2000 \text{ mJ/cm}^2 @ 488 \text{ nm}$ . Clean glass and primers and bake outs are sometimes necessary to keep the resist on the glass and since most resists used are positive, exposure to UV after processing will break bonds and leave the material prone to falling off when you least want it to. There is a lot more to be said about designs and materials but no more room or time to say it.

## **Relative material sensitivities**



## References

1. H. Kogelnik, "Coupled wave theory for thick hologram gratings" *Bell Syst Tech J.* **48**:2909-2947 (1969)
2. T. K. Gaylord and M. G. Moharam, "Analysis and applications of Optical Diffraction by Gratings" *Proc. of IEEE*, **73**, (5) (May 1985).
3. J.N. Cederquist and J.R. Fienup, "Analytic Design of Optimum Holographic Optical Elements" *J Opt Soc Am A***4**:699-705 (April 1987)
4. E. Hasman and A.A. Friesem, "Analytic Optimization for Holographic Optical Elements". *J Opt Soc Am A***6**:62-72 (Jan 1989)
5. F. T. S. Yu. "Effect of Emulsion Thickness Variations on Wavefront Reconstruction". *App Optics***10**:1324-1328 (June 1971)
6. R. D. Rallison "Incoherent Multifocus Hololens design and fabrication", *Proc. SPIE* **1183**:663-668 (1989)
7. M. Chang and N. George, "Holographic Dielectric Grating; Theory and Practice" bibliog diags *Ap Optics***9**:713-719 (March 1970)
8. T.K. Gaylord and F. K. Tittel, "Angular Selectivity of Lithium Niobate Volume Holograms", *J. App Phys* **44**: 4771-4773 (Oct 1973)
9. J.N. Latta, "Computer-Based Analysis of Hologram Imagery and Aberrations", *Ap Optics* **10**:599-618 (Mar 1971)
10. Y. Amitai et al "Holographic Elements with High Efficiency and Low Aberrations for Helmet Displays", *Appl Opt* **28**:3405-3416 (Aug 15 1989)
11. Y. Ono and N. Nishida "Holographic Zone Plates for f0 and Collimating Lenses", *Appl Opt* **25**:794-797 (Mar. 1986)
12. J.R. Fienup "Iterative Method Applied to Image Reconstruction and to Computer-Generated Holograms", *Opt Eng* **19**:297-305 (May 1980)

13. M.R. Latta and R.V. Pole "Design Techniques for Forming 488-nm Holographic lenses with Reconstruction at 633 nm", *App Opt* **18**:2418-2421 (July 15 1979)
14. E. Wihardjo, et al "Compensation of Wavelength-Shift Aberrations in an off-axis Holographic Zone Plate", *Opt Eng* **25**:871-874 (July 1986)
15. *Holographic Optics: Design & Applications*. Cindrich, ed. *SPIE press* (1988).
16. R.C. Fairchild and J.R. Fienup, "Computer Originated Aspheric Holographic Optical Elements", *Opt Eng* **21**:133-140 (Jan/Feb 1982)
17. D. A. Winick, "Thick Phase Holograms", Environmental Research institute of Michigan, Level, (January 1981).
18. L. Solymar & D.J. Cooke, *Volume Holography and Volume Gratings*, Academic Press, (1981).
19. Felix P. Shvartsman and Moshe Oren, "Photo-lithographic imaging of computer generated holographic optical elements" *Proc. SPIE* **1555**:71-78, (1991).
20. A.J. Lee and D. P. Casasent, "Computer-Generated Hologram Recording Using a Laser Printer", *Appl Opt* **26**:136-138 (Jan 1 1987)
21. Steven M. Arnold, "Desktop computer encoding of electron-beam written holograms" *Proc. SPIE* **884**:23-27 1988.
22. R. D. Rallison, "Wavelength compensation by time reverse ray tracing", *Proc. SPIE* **2404**: 217-225 (1995)
23. G. D. Mintz, D.K. Morland & W.M. Boerner, "Holographic Simulation of Parabolic Mirrors", *Applied Optics*, **14** (3):564-570 (March 1975).
24. Hans Dieter Tholl "Polarization properties of volume phase gratings", *Optical Engineering*, **34**(10)2879-2885 (Oct 1995)
25. W. S. Colburn & B. J. Chang "Holographic Combiners for Head-Up Displays", *Technical Report AFAL-TR-77-110* (Jan 1977).
26. Ryszard Gajewski "Holographic Technology for Solar Energy Concentration" *Technical Report No. 87-1479* (July 1984).
27. Jose R. Margarinos & Daniel J Coleman "Holographic Mirrors" *Proc. SPIE* **523**:203-218 (1985).
28. Richard D. Rallison, "Holographic Optical Elements (HOES) in Dichromated Gelatin (DCG)", *Proc. SPIE* **523**:292-295 (1985).
29. Jon D. Masso "Multilayer Thin Film Simulation of Volume Holograms" *Proc. SPIE* **883**:68-72 (1988).
30. H. M. Smith, *Holographic Recording Materials* Springer Verlag, 1977
31. H. I. Bjelkhagen, *Silver-Halide Recording Materials for Holography*, Springer Verlag, 1995
32. R. D. Rallison, "Materials for Volume Phase Holographic Notch Filters" SBIR #A 86-68 Final Report, U.S. Army CECOM, Ft. Monmouth, N.J. Aug.(1987)
33. T. A. Shankoff, "Phase holograms in dichromated gelatin" *Appl. Opt.* **7**:2101-2105 (1968)
34. Hans I Bjelkhagen, *Holographic Recording Materials*, SPIE publications, 1996.
35. R. D. Rallison "Survey of properties of volume holographic materials", *Proc. SPIE* **1051**:68-75 (1989)
36. J. L. Salter and M. F. Loeffler, "Comparison of dichromated gelatin and DuPont HRF-700 photopolymer as media for holographic notch filters" *Proc. SPIE* **1555**:268-278 (July 1991)

37. R.A. Bartolini, "Characteristics of Relief Phase Holograms Recorded in Photoresists" *App Optics* **13**:129-139 (Jan 1974)
38. Tung H. Jeong, *Proceedings of the International Symposium on display holography*, Vol I (1983)
39. Tung H. Jeong, *Proceedings of the International Symposium on display holography* Vol II (1986)
40. D.J. Lanteigne and T.D. Hudson, "The DMP-128 Holographic Cookbook" Technical Report RD-RE-86-14 U.S. Army Missile Command, Nov. 1986.
41. J. C. Kirsch, D. J. Lanteigne and Don Gregory, "An investigation into DMP-128 Holographic Recording Material" Technical report RD-RE-87-1 U.S. Army Missile Command, Feb 1987.
42. D.H. Close and A. Graube, "Materials for Holographic Optical Elements", Technical Report AFML-TR-73-267, Oct. 1973.
43. B.J. Chang, "Post Processing of Developed Dichromated Gelatin Holograms", *Opt Comm*, **17** (3): 270-271 (June 1976).
44. T. Kubota, T. Ose, M. Sasake and K. Honda "Hologram Formation with Red Light in Methylene Blue Sensitized Dichromated Gelatin" *Applied Optics*, **15**(2):556-558 (Feb. 1976).
45. S.P. McGrew, "Color Control in Dichromated Gelatin Reflection Holograms", *Proc. SPIE* **215**:24-31 (1980).
46. R. T Ingwall, M Troll and W. T. Vetterling "Properties of Reflection Holograms Recorded in Polaroid's DMP-128 Plotopolymer" *Proc SPIE* **747**:67-73 (1987).
47. R. D. Rallison, "Control of DCG and non-silver holographic materials" *Proc SPIE* **1600**: 26-37 (1991).