Security Printing: Towards Hologram Printing

Agate
SECURITY PRINTING: TOWARDS HOLOGRAM PRINTING

by

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SECURITY PRINTING: TOWARDS HOLOGRAM PRINTING

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Today we are facing many situations where the genuineness of the products and documents is questioned. Counterfeiting the original products has become a business of few people, which result in the degradation of quality of products, loss of money and loss of faith of end user. To prevent such malicious act, security features are added in the final product. Security printing is one of those methods that help in preventing counterfeit products and treachery. There are many different security features, which can be added in the security printing. Apart from those features, an embossed hologram is also included in prints to improve security features. However an embossed hologram is not a printed product.

In this Research for Master’s Thesis I worked on the possibility of reproducing a hologram by printing. Initially we had an idea of using Collotype printing process, which uses the same base materials as of the holographic recording plate i.e. a Dichromated Gelatin (DCG) layer on a glass plate. However, it was found that this method is not suitable for reproduction of holograms. Then another method was tested which uses surface relief properties of holograms generated in DCG. The results give us the hope of Printing a Hologram, which is generated by IR Laser.
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CHAPTER I

INTRODUCTION

Security printing is a process and workflow of printing high value documents in such a way that it becomes very difficult to counterfeit them [1]. In this process security is maintained at every step from creation of artwork through printing and distribution. All high value documents and printed products have security features in them, e.g. currency notes, property papers, government documents, bank documents, stamp papers, credit or debit cards, mark sheets and transcripts. Apart from these examples, security features are also included in the wrappers of branded products to prevent counterfeiting and thus protecting the image of a company [2].

To make the reproduction difficult, many features can be included in security printing. These features can be specialty paper with security threads and a specific composition [1,3]. In printing itself, the image can be printed using multiple printing technologies. Different sections of an image will have different characteristics depending upon the design and the printing process [4]. The machines used have high accuracy and are custom made. Inks used have special colors like dull colors, spot colors, and fluorescence. UV and IR reacting inks are also used to check authenticity under invisible wavelengths of light [3].

Apart from printed security features, one more security feature is used, a holographic tag [5]. A holographic tag contains a white light hologram (also known as rainbow hologram). This hologram does not come under actual printing, because it is an embossed image rather than a printed one.

In the following pages I will be talking about printing of holograms. Initially, a collotype printing process was suggested. Collotype is the printing process, which prints almost continuous tone images with the help of gelatin as an image carrier.
Gelatin is also used as the holographic image carrier. Hence this process was considered. After getting no positive results, a second process was considered. In this second approach, the surface relief obtained from the gelatin of holographic plate was used to hold the printing ink in recessed areas. The relief of gelatin, when gone leaves ink remaining on the plate surface. This ink is only present in image areas and can be transferred onto the substrate.
CHAPTER II

LITERATURE REVIEW

Hologram:

A hologram is a three-dimensional image recorded in two dimensions. In reality, the recorded image is in three dimensions, while the thickness of recording material is fairly low (a few microns [6]). We can assume it as two dimensional recording for general practical purposes.

Holography is regarded as recording of a three dimensional image on a photosensitive material using the phenomenon of interference of light [7-9]. In the process of recording a hologram, an object is placed in front of a recording medium and both the medium and the object are illuminated with a light source. The light falling directly on the medium and the light that is reflected from the object surface and falling on the medium combine to form an interference pattern. This interference pattern is recorded on the medium. When we develop and illuminate the recording medium with light, the interference pattern forms fringes (having different transparency or refractive index) that act as obstacles in the path of light. The result is diffraction of the light around the edges of the fringes and this diffracted light again interferes to form a wave front, which is the same as of the original object. Thus, we can see a 3-D object in the light.
'Destructive interference

Figure 1: Interference pattern: Generated by two coherent light beams in front of a substrate. The dark and bright fringes are visible at the interfering region. [7]

The main constraint on the recording of a hologram is the light source that is used [7-9]. As mentioned earlier, light waves interfere with each other to form constructive or destructive interference. If a white light source or any light source having more than one frequency is used for holography, it will create multiple interference patterns for each frequency in the light and overlap them. The result will be total exposure of the recording medium. To prevent such a thing, we need a monochromatic light source. One more requirement of the light source used in holography is the coherence of the waves. All the waves produced from the source should be coherent [7-9]. The above two requirements narrow the options, and the only known solution is a LASER. A laser has all the required qualities such as monochromatic output, coherence of waves till very long distances from the source. The output power of a laser can be adjusted according to requirements. In practice there are two types of lasers used for holography. One of them is a continuous output laser and the second one is a pulsed output laser [8]. In a continuous output laser, a beam of light is continuously emitted out of the source, while on the other hand a pulsed laser flashes with very high intensity for a very short period of time. The advantage of a pulsed laser is that we can have very high intensity light, which will
result in very short time of exposure. This is suitable, particularly in cases where an object cannot remain in one position for long time period.

A hologram is of two types; it could be either a transmission hologram or a reflection hologram [7-9]. A transmission hologram is the one in which the laser source and the recorded object are on the same side of the recording material. It is visible when the hologram is illuminated with the laser from one side and viewed through the hologram from the other side. In the case of a reflection hologram, it is exposed with the laser on one side of the recording medium and the object on the other side. These holograms can be viewed from the same side as laser exposure.

The diagrams given below (Figures 2-5) illustrate recording and viewing requirements for both the transmission and reflection holograms. The beam of laser that is reflected from the object is called the object beam, while the beam that falls directly on the plate is called the reference beam. After recording the hologram, the plate is developed and again placed in the same place where it was exposed. The original object and object beam are removed. The hologram is again exposed with the reference beam and then is viewed according to the instruction in the diagram. At this time a 3-D image of the original object can be viewed.
Figure 2 shows schematics of a setup for recording of Transmission hologram and Figure 3 guides how to view it.

Figure 2: Recording of transmission hologram. [10]
Figure 3: Viewing transmission hologram. [10]
Figure 4 is the schematic diagram to record a Reflection hologram and Figure 5 is schematic diagram to guide how to view it.

Figure 4: Recording of reflection hologram. [10]
Holograms can also be defined as amplitude modulation holograms or phase modulation holograms [7-9]. In amplitude modulation, the fringes created by exposure act as barriers to light. The dark fringes absorb the light falling on them, while the transparent ones let it pass through and diffract. On the other hand, a phase hologram is just a change in refractive index of the medium wherever a fringe is present. Thus, in a phase holograms, the entire incident light is available for image generation. The image is generated by diffraction of light due to a change in refractive index at the fringes.

A last differentiation of holograms can be made based on the fringe pattern created. If the fringes are generated on the surface of the substrate due to presence or absence of material, it is known as surface relief hologram. If the fringes are
generated inside the holographic material due to change in phase or amplitude, it is
called as volume hologram [7-9].

**Materials used as holographic medium:**
There are many photographic materials used in formation of holograms. But silver halide is the most famous among them, due to its efficiency and sensitivity [11].

**Silver halide:** It can be made sensitive to all frequencies of light. Because of its sensitivity, it takes a very short period of time for exposure. All other photographic materials have sensitivity far less then silver halide.

**Dichromated gelatin (DCG):** Potassium dichromate or ammonium dichromate is used as sensitizer in the gelatin [11,13]. Dyes can be used to increase the sensitivity to different frequencies of light. Still the red light sensitivity is low. The holograms formed are very efficient and are phase modulated volume holograms. But the gelatin is sensitive to moisture and expands on absorbing the moisture [11]. Hence, the fringe pattern gets disturbed. Therefore, a DCG hologram has to be covered by glass or transparent material to protect it from moisture.

**Photoresist:** A photoresist is a material that can become hard or soft after exposure [11,13]. Hence, it forms the holographic fringes in the form of surface relief. Such a material is UV sensitive and is used to manufacture embossed holograms.

**Photothermoplastic:** This material softens or hardens when heated or cooled. It is used for surface relief holograms. It has a photoconductive layer that discharges a charged surface where exposed to light. The remaining charged surface area generates a static electric field. Current is then passed through the conductive layer to heat up the thermoplastic. Heat softens the film and it gets deformed under the static electric field, thus creating surface relief [12,13].
**Photochromic material:** This is a recyclable material, changing its transmission spectrum as a response to appropriate wavelengths of light. It becomes dark when exposed to UV and is bleached when exposed to long wavelengths of light, such as IR. Photochromic material does not have grains in the layer and hence its resolution capacity is on the atomic level. It is not popular because of sensitivity and low storage time. It records a volume hologram [13].

**Photodichroics:** It is used to create switched and unswitched states of certain crystals. They absorb light of certain polarization only [13].

**Photorefractive crystals:** They are excellent for recording volume holograms. They have good resolution and sensitivity. Here the optical damage to the crystal is the key factor [13].

**White light transmission hologram:**

A white light transmission hologram (rainbow hologram) is one that can be viewed under white light. A transmission hologram, when illuminated with white light will diffract all the light frequencies and multiple images of the same object will form with different light frequencies [7-9]. The overall effect will be a blurred image. To avoid formation of such multiple images, we need to isolate a single light frequency while viewing. To do so, a narrow slit is placed in between the object and the recording material while generating a transmission hologram [9,12]. This slit will help in diffracting the different frequencies at different angles. So when we view this hologram under white light, it itself isolates the other frequencies of light by diffracting them in different angles. The result is formation of different images with different colors, but at different positions. Hence, from a particular angle, we can see only one image. In this procedure we need to compensate for the parallax of the image in the direction parallel to the slit. In practice, it has been studied and noticed that humans care about horizontal parallax more than vertical parallax. Hence, the slit
used for exposure is kept vertical. Thus, the hologram is formed by narrow vertical slits, which bear all the visible information about the object.

Figures 6 and 7 represent the recording and viewing concepts of rainbow (White light) hologram.

Figure 6: Recording of rainbow hologram. [10]
Modern techniques:

In modern life, a hologram can also be exposed by a computer guided laser source [9, 15]. A computer is used to guide two laser beams, which are used to expose the same spot of holographic material. Here the size of the beams is modulated to give the effect of a specific color. By using computer assistance, it is now possible to create a hologram with multiple layers. Also it is possible to generate a 3-D image from multiple 2-D images, which are fed to the computer. Though such images appear like holograms, in reality they are not holograms, because the image is formed of spots exposed by the laser [9]. There is no depth in the image like real holograms.

Embossed holograms:

Today, we can see many applications of holographic tags on products. These tags are embossed holograms. A white light hologram is exposed on a photopolymer material to get a surface relief pattern. This surface relief hologram is then silver
sprayed to make it conductive. This conductive surface is then used for nickel plating [9], which is then peeled off the surface. This nickel film contains the hologram in the form of surface relief, which is exactly opposite to the original hologram. Due to the softness of this nickel film, it cannot be used directly in further processing. Hence an electroplating method is used to create a new nickel master that is harder. This master is then used to produce its replicas by electroplating. These replicas are called shims [9], which are arranged in a grid and again electroplated to form hundreds of replicas. These replicated shims are inverted and hence they are again electroplated to form final shims in quantities of thousands. These final shims are known as Daughter Shims, while the others are Mother and Grandmother Shims, while going back step-by-step.

Finally, the step of mass production comes. All the daughter shims are on the same metal sheet. They are mounted on a cylinder. The next step is to emboss these holograms on the transparent polymer film, using the combined effect of heat and pressure. Heat provided to the polymer film causes it to raise its temperature above its glass transition temperature, while the pressure causes the holographic pattern to be embossed on the material by deforming it [9]. Then, the material is allowed to cool down before it is relieved from the image carrier/holographic shims.

These holograms are then metallized in vacuum to form a shinny mirror surface at the back of the hologram. This mirror surface reflects the light back when the hologram is viewed in light. Thus, the mirror acts as a light source to the hologram. This effect is necessary, because this hologram is in fact a transmission hologram [9].
Advantages of embossed holograms:
1. Cheap to manufacture
2. Easy handling
3. Forms a three dimensional image that is not easy to reproduce

Disadvantages:
1. Low efficiency of hologram because it is a surface relief pattern. The volume holograms are more efficient.
2. There is loss of depth in the image.
3. Loss of vertical parallax due to conversion in the white light hologram.
4. Can be counterfeited if proper procedure is followed.

• Why is it difficult to duplicate a hologram?

   The hologram is recorded as an effect of interference. Hence it reproduces the image in 3-D, exactly the same as the original one. Hence, it contains all visible details of the surface of the original. Holography is the phenomenon related to diffraction of light; hence it cannot be scanned and printed by any known techniques. The parallax in it cannot be copied with a scanner.

Counterfeiting:

Counterfeiting of embossed holograms is possible, due to the surface relief pattern created on the polymer film, which gets transferred onto the metal coating provided to act as a mirror. First, a hologram tag is removed from the product. Then, by a careful procedure, the polymer film is removed from the hologram. Now, a metal film with surface relief is exposed. This relief image can be used to emboss directly onto the aluminized polyester or PVC film to have counterfeit holograms. In the other method, this film is treated as a metal master to generate shims from it. These shims are used for mass production of counterfeit holograms. Sometimes photographic methods are used in which an image generated by holography is treated as the original image and a second hologram is recorded from it. From this second hologram, a third hologram can be recorded and then is used for counterfeiting [16].
Preventive measure:

To prevent counterfeiting, a hologram is glued to the product with a special process that causes the hologram to be torn apart into pieces if removed from the product [16].

Holographic fringes:

Holographic fringes are the obstacles to light that cause diffraction of light. During exposure, these fringes are formed by interference of two light waves. Hence by Bragg's theory, the thickness of a fringe can be about half the wavelength of light. Hence, the thickness of fringes can be about 200nm or less [9,11]. The resolution depends on the wavelength of light used and the angle at which the beams interfere. This equation is as follows [9,17]:

\[ 2d \sin(\theta/2) = \lambda \]  

where, \( d \) = fringe width,
\( \theta \) = angle between interfering beams,
\( \lambda \) = wavelength of light

If the wavelength is higher, wider fringes are obtained. The same applies also if the angle between two beams is wider.

The fringes are formed not only at the surface of the hologram, but also in the depth of the material. They form planes of fringes, which are called Bragg planes. The angle of the planes with the surface is half the angle between the object beam and the reference beam. To have high efficiency in surface relief holograms, it is necessary to have these fringes as vertical as possible. Hence the object beam and reference beam of laser should fall on the surface of holographic recording material at nearly 45°. The holographic fringes formed are in a sinusoidal form [18].

Printing of holograms:

Until now, there is no reference about printing of holograms. The obstacles in the process could be the size and the shape of the fringes. It is difficult to find a suitable process that will separate the image and non-image areas at a nanometer
scale. However, there is a process called Collotype printing, which could help in this case. This process is rarely used in commercial printing processes, due to its time consuming nature and low production capacity [19]. However, this is the only process that does not require screened images for printing.

**Collotype Printing:**

Collotype printing is an old process that prints nearly a continuous tone image [20-22]. The image carrier is a gelatin layer on a glass or metal surface. This layer is sensitized with potassium dichromate. Hence, it could be said that collotype uses DCG (Dichromated gelatin). DCG is sensitive to wavelengths below green light. Hence a UV, blue or at the max green colored light can be used to expose the DCG. The energy of photons is reduced as we move from UV to green wavelengths. Hence, the exposure time increases. Thus, UV light is preferred for rapid exposure [12,23].

The principle of imaging is that the DCG absorbs light and hardens in the exposed areas in proportion to the exposure [24]. A continuous tone negative is used for exposing the image. The next step is to wash the plate to remove dichromate from the gelatin. Finally we obtain gelatin that has been hardened in proportion to tones in the image. The plate is then dried.

This plate is then moisturized. The gelatin absorbs moisture in proportion to the hardness. Hence, the highlights will absorb more water, while shadows will absorb a negligible amount. When an oil-based ink is applied on the moist plate, the plate will hold the ink in proportion to its moistness. The dry portion will hold the maximum ink while the moist will hold a lower amount of ink. This inked image is then transferred onto the substrate [20-22].

The resolution of image printed with collotype is equivalent to around a 1250 lpi image [19].
Use of collotype for hologram printing:

A hologram requires a line resolution of around 5000 lines (fringes) per mm. So it looks like collotype printing has a lower resolution than required. However, here we must consider that the ink has pigments, which reduce the level of resolution. When we use a silver halide material to record the hologram, the silver halide grain size is around 10 to 50 nm. Hence the pigment size should be similar to this size [13,14]. Oil or a liquid polymer in pure form will have the higher resolution capacity because much smaller droplets can be formed with them. Oil or polymer printed with the collotype process will definitely have a small bulge at the center of droplet that will give it a shape that may be similar to sinusoidal curve. This will give the printed fringe a shape similar to sinusoidal fringe.

Figure 8: Groove profile in holographic grating. [18]

To let us use the principles of the collotype process, we must have a hologram that is made in DCG or the hologram must be in gelatin that is hardened at the fringes.
**Hardened gelatin holograms:**

A DCG coated glass plate can be used to expose a hologram that will have hard and soft gelatin fringes. An alternate way could be the use of a silver halide hologram and in the process of making, develop it followed by rinsing with water, bleaching in an acidic environment of ammonium or potassium dichromate, and rinsing with water, fixing and finally rinsing with water again. In this process, the bleaching will cause the oxidation of metallic silver. This oxidation process will reduce hexavalent chromium ions in liquid solution to trivalent ions. During this reduction process, the localized gelatin increases its cross-linking. The result is hardening of the gelatin [25]. The unexposed portions will have silver halide that will remain unbiased and so will the gelatin in its vicinity. The whole procedure will generate fringes with hard and soft gelatin. When completely dried, the hard and soft gelatin refractive indices are very different, which will create a phase-modulated hologram. Using the same plate as an image carrier can be used in the collotype printing technique.

**Printing:**

The Bragg planes in the hologram should be nearly perpendicular to the gelatin surface. The required fringe pattern in the hologram can be made only if the hologram is a transmission hologram. A transparent polymer film or substrate will be required, as the light needs to pass through the hologram. A hardened gelatin hologram works on the principle of change in refractive index at the fringes. Hence, a liquid polymer or oil can be used as the ink, which will have a different refractive index than the substrate after oxidation or polymerization (drying).

**Improved security:**

Success in printing a hologram, instead of embossing it, will make it difficult to reproduce by conventional techniques used for counterfeiting holograms. A printed hologram can be covered with a polymer film. Metallizing can be done to the
backside of the polymer film, which is supposed to act as a mirror. In this way, the metallized structure will not have the fringe pattern on it.
CHAPTER IV

RESEARCH WORK

As explained in the previous chapters, we need to consider oils or polymers as printing inks in the case of hologram reproduction by printing. We considered linseed oil as the ink for the same purpose and reason. But linseed oil has fatty acids and hence is slightly polar. Therefore hexadecane was considered in order to have the surface energy estimate of the gelatin surface, because it is non-polar.

Materials and equipment used:
1. PFG-04 (dichromated gelatin holographic) plate from Integraf L.L.C.
2. Raw and Boiled Linseed Oil.
3. n-Hexadecane
4. Glycerol, Ethylene Glycol
5. First Ten Angstrom (FTA), sessile drop test instrument for contact angle and surface energy measurement.
6. Imagesetter (Linotronic 530) and Offset lithographic Plate exposure unit (UV radiation).
7. Caron 6030 Caron CRS 101, Environment Test Chamber
8. Inverted Michroscope.
9. WYKO (White Light Interferometer) Microscope

Procedure to generate hardened gelatin area on the holographic plate:
The holographic plates used have dichromated gelatin as the photosensitive material on them. This material is sensitive to wavelengths below green light (~514 nm). Hence, it can be exposed to UV radiation to initiate the photochemical reaction.
However, in an actual holographic recording process it has to be exposed to a LASER.

For experimental purposes, we required large areas with hardened gelatin and hence the coherence of the light was not important. Thus, the UV radiation was used to expose the holographic plate. Masks were used to prevent exposure of unwanted areas of the gelatin. Two areas on the same plate can be obtained; one that is exposed to UV light, and the other that is not.

This plate is then washed in the safe light (red light) with deionized water so that the exposed dichromate will react with water molecules and during the conversion from hexavalent chromium ions to trivalent ions [14], the gelatin in their vicinity will crosslink. This will cause hardening of the gelatin in exposed areas. On the other hand, the unexposed dichromate will just dissolve in water and is removed. The whole process will generate hardened areas in exposed gelatin and soft areas in unexposed.

There will be a change in properties of hardened areas such as change in refractive index and change in water absorption capacity. The hardened areas will absorb much less water as compared with the unexposed gelatin.

Results:

Contact angle measurement and the surface energy estimate:

The gelatin is known as a hygroscopic material. However, it has hydrophobic heads, which are oriented towards its surface (in the case of thick films) and its hydrophilic tails are inside. Hence the drop of water does not spread over the gelatin surface [26]. Instead it beads over it. Water has very high contact angle with gelatin and this can be seen in the graph given below (Figure 9).

The surface energy of the moist gelatin can be estimated from the Owens-Wendt model [27]. For the same purpose, hexadecane was used. The surface tension of hexadecane is assumed to be 100% dispersive or in other words, it is non polar.
With the help of contact angle measurement with both the hardened and soft gelatin, the surface energy of gelatin can be estimated.

![Graph of contact angle of water on moist gelatin]

**Figure 9:** The contact angle of water with moist gelatin.

Table 1 given below gives the approximate values of contact angle after stabilization of liquid drop with gelatin surface.

**Table 1: Approximate contact angle of different liquids with moist gelatin surface.**

<table>
<thead>
<tr>
<th>Material</th>
<th>Average Contact angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hard Gelatin</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>2</td>
</tr>
<tr>
<td>Water</td>
<td>79</td>
</tr>
<tr>
<td>Linseed oil</td>
<td>27.5</td>
</tr>
<tr>
<td>50-50 mixture of raw and boiled linseed oil</td>
<td>30</td>
</tr>
</tbody>
</table>

From the surface energy estimates presented in Table 2 we can conclude that the oil or liquid polymer having surface tension less than 34 dynes/cm will be able to
spread over the gelatin surface. Also, we can conclude that there is no significant difference in surface energy between the moist hard gelatin and soft gelatin.

Table 2: The surface tension of hexadecane, water and surface energy of moist gelatin.

<table>
<thead>
<tr>
<th>Material</th>
<th>at 20°C</th>
<th>Surface Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>γ (dynes/cm)</td>
<td>γ^d (dynes/cm)</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>27.47</td>
<td>27.47</td>
</tr>
<tr>
<td>Water</td>
<td>72.8</td>
<td>21.8</td>
</tr>
<tr>
<td>Moist hard gelatin</td>
<td>34.44</td>
<td>27.45</td>
</tr>
<tr>
<td>Moist soft gelatin</td>
<td>33.99</td>
<td>27.45</td>
</tr>
</tbody>
</table>

where,

\( \gamma = \) total surface tension or surface energy,

\( \gamma^d = \) dispersive component of surface tension/energy

\( \gamma^p = \) polar component of surface tension/energy

As shown in table, approximately same contact angle of oil with two different areas on gelatin (hard and soft) makes it clear that there needs to be some kind of chemical mask on non-image areas (soft gelatin) to prevent them from accepting ink. The conventional collotype process says that we need to soak the gelatin plates in a mixture of 50% glycerol with water. A 30-minute or more soaking will make the plate water receptive at room temperature and 50% relative humidity (RH). This plate will now draw moisture from the atmosphere and will remain moist for a very long time. Soaked plates need to be blotted to remove excessive liquid from the surface. However, the plate surface should never be wiped, as it will remove the adsorbed glycerin.
Therefore, this procedure was carried out and the plates were kept in the Environment Test Chamber at room temperature and 90% RH. The higher level of humidity was maintained to have an excessive amount of water that will be absorbed by the plate. (At 50% RH, there was no water observed on the plates as well as there was no change in contact angle as it was measured without this treatment.) After some time, it was visually observed that there was presence of water on the plate. The soft area of gelatin had a very high amount of water, while the hard areas had a lesser amount. Also the water did not form a continuous layer, but was beaded on the surface.

Similar results were obtained with the use of ethylene glycol instead of glycerol.

Due to the presence of water on both areas, there will be difficulty in applying oil to only hardened areas of gelatin. Thus it seems that using a collotype process in this particular case is not feasible.

**New approach to the goal:**

The above data lead to the conclusion that it is not possible to avoid presence of water on the image areas of holographic plates, if we are trying to use the collotype printing process. Also, the contact angles measured with different conditions of gelatin and moisture show that the oils used cannot differentiate between image and non-image areas of the gelatin. Thus the collotype printing procedure fails in this particular case. Hence if we want to achieve the target of reproducing hologram, we need to find a different procedure.

With the observations from the experiments related to the above data, it was seen that the unexposed gelatin absorbs water in very high amounts and swells as compared with the exposed (hardened) gelatin. Hence, there is considerable change in the thickness of the gelatin in unexposed regions. For low-resolution images or a set of parallel lines with comparatively large gaps between them, we can feel the difference in thickness by touching them with fingers. This swollen gelatin will start to loose moisture as soon as it is exposed to the comparatively dry environment.
Thus, if we let the gelatin swell by immersing it in water and then expose it to air at regular room conditions, it will start to lose moisture and will gradually decrease in the thickness. After some time, it will completely lose water and shrink.

Using the above properties of gelatin we can now think about using the holographic plate as an image carrier that is similar to intaglio printing plate. When the gelatin swells in water, it will generate pockets or cells on its surface. These cells will be due to the exposed and hardened gelatin that cannot swell. Now we can think about filling the required ink in the cells formed.

**The details of the process:**

The tendency of moist gelatin is to lose moisture in the air as the time passes. This will cause automatic removal of walls of the cells because those will shrink by loosing water. As a result we can have ink revealed on the surface. It has been observed that as the walls of cells reduce, the ink (here oil) filled in the cells start spreading over the surface. The ink drop volume and the surface tension of ink will be in equilibrium when the drop will stop spreading.

Given below are schematic diagrams (Figures 10-14), which will illustrate this whole mechanism:

When we develop a DCG plate, it generates hardened and soft gelatin areas, which have variations in refractive index and the swelling ability in presence of water. Thus, if we immerse a developed DCG plate in water, it will absorb water and the gelatin will swell at different degrees according to its hardness. The soft gelatin will swell more, as shown in the Figure 10.
Figure 10: Gelatin layer soaked in water.

Thus we can form a surface relief on the DCG plate. The gaps between two swollen areas are like cells or channels on the intaglio plate. Then we can flood the whole plate with the ink that we have chosen. Here we used the mixture of 50% raw and 50% boiled linseed oil to have increased viscosity as compared to 100% raw linseed oil.

Figure 11: Gelatin layer flooded with oil (ink).
The next step is to wipe the excessive oil on the plate much like the doctor blade in the gravure printing process [28]. Care should be taken, because the gelatin is not hard enough to withstand the excessive pressure of wiping. I used a tissue paper to remove that oil. Here, we obtain a plate that looks like the illustration in Figure 12.

![Diagram of gelatin areas](image)

**Figure 12: Excessive oil is wiped; the cells hold the oil in them.**

Now that we have removed the excessive oil from the surface, the swollen areas of gelatin are now exposed to air. As the time passes, the swollen gelatin loses its moisture in air and becomes dry. In this process the thickness of gelatin continues to decrease and the oil from the cells or channels start coming out because the oil does not evaporate in air and its volume will remain the same. Figure 13 shows the intermediate state of drying of gelatin, while Figure 14 shows one of the last stages of drying.
From the above illustrations, it is clear that if we know the rate of moisture loss from the gelatin and the amount of ink spread once the cell walls start
diminishing, we can predict the ink coverage at any given time. The ink spread will depend on the surface tension of the ink as well as the volume of the cell. Finding the rate of ink spread will help in calculating the time at which the ink coverage is enough to have an impression.

Using the WYKO interference microscope, we tried to find out the difference in the thickness of gelatin after it was made moist. This will help in determining the amount of ink that each cell can hold. However the transparency of the gelatin film makes it difficult to have accurate readings. However we managed to obtain a few good readings and those readings say that for a gap of 20–40µm (exposed line), we get the difference in thickness in the range of 2–4µm (Figure 15).

The gaps and lines on the gelatin surface were generated by exposure through a film negative generated with the imagesetter. The imagesetter has the capability to expose the 2 pixel wide lines and generate 2 pixel wide gaps at the 2540 lpi resolution. This resolution is possible at exposure intensity of 325 exposure units and also it gives acceptable density, which is over 4. This was found by exposing the line patterns with variable intensity of exposure.

Figure 15 A: The 2-D plot of WYKO measurements. (on plate; exposed lines are about 40µm wide and unexposed are about 30µm wide)
Figure 15 B: The 3-D plot of WYKO measurements. (on plate: exposed lines are about 40µm wide and unexposed are about 30µm wide)
Given below (Figures 16-19) are a few images of the swollen gelatin lines. As the gelatin is translucent and it is hard to measure the line thickness on gelatin, the average thickness of lines was measured. For these calculations, first the microscope was focused on the top of swollen gelatin lines and then it was focused on the bottom of the unswollen or hardened gelatin lines.

Figure 16: The swollen gelatin (unexposed); focused on the top. (distances in mm)
Figure 17: The swollen gelatin (unexposed); focused on the bottom. (distances in mm)

Figure 18: The unswollen gelatin (exposed or hardened); focused on the top. (distances in mm)
Figure 19: The unswollen gelatin (exposed or hardened); focused on the bottom.
(distances in mm)

From the average of all readings the hardened or exposed lines had the average thickness of $40\mu m$ while the unexposed lines had $30\mu m$. 
The image below is captured after filling the oil (50-50 mixture of raw and boiled linseed oil) into the cells or groves formed in the swollen gelatin. After about 35 minutes the surface of gelatin appeared dry. However it cannot be said that the gelatin had lost all its moisture. The measurements in the image are measuring the line thickness of oil while the portion between two oil lines is the dry gelatin.

Figure 20: The oil from unexposed or hardened gelatin lines. (distances in mm)

The measurements of oil line thickness averages to about 42µm which when compared to the line measurements indicate that there is spreading of oil over the gelatin surface.

All these readings just show that there will be spreading of ink/oil once the gelatin dries. We need to have more data to predict the spreading percentage.

The above images show that it is possible to generate a surface relief structure on DCG and then use it as an image base for printing. The ink/oil that remains on the surface of gelatin can be transferred to transparent polymer film with impression. The impression pressure required will have to be determined by experiments.
Print trial:

A simple trial was taken to check if it is possible to transfer the ink/oil from such plates on to the transparent polymer film with impression. The image shown in the Figure 21 indicates that it is possible. Here the inked plate was just pressed on the polymer film with hand. However, research will be required to determine the exact impression pressure and the type of polymer for the substrate.

Figure 21: The oil transferred from the inked gelatin plate onto the polymer film by hand impression.

Conclusions:

The initial approach of this research was to determine the possibility to print a hologram with the help of the collotype printing process. For the same purpose, contact angle measurements were done. The collotype process requires masking of non-image areas with water so that oil based ink will adhere with very low or no percentage. However, the holography is somehow similar to a binary process. There are fringes recorded on the hologram, which means that there is no gradation. The ink should be either present or not at a particular area. The results of the glycerol or
ethylene glycol treated plates show that water was present on the both image and non-image areas with different amounts. Of course, the non-image areas (soft gelatin) had higher amounts of water, but the image areas (hardened gelatin) too had water on them. Also the discontinuity of water layer suggests that the ink (oil) may be applied on the areas covered by water. Thus, it leads to the conclusion that it is not possible to reproduce the hologram with the collotype printing process.

The second approach towards printing of a hologram seems quite promising. Here the primary principle is to convert a DCG hologram into a surface relief structure by letting it swell in water. This surface relief structure can be used as an intaglio plate. If this image carrier is filled with ink in the cells and groves, we can transfer this ink to the substrate by impression. The way to do this is to wait till the surface relief of gelatin is diminished by moisture loss in the air. The observations say that more than 35 minutes of air exposure at room temperature will do the task. After the relief is gone, the ink remains on the image areas. This ink will start spreading as soon as the gelatin starts drying. Printing the image before the relief is totally diminished can control the ink spreading over the surface of non-image area.

**Recommendations:**

We expect that it is possible to go to much lower resolution of 1µm thick lines. However, we need to expose the plate directly with Laser to avoid diffraction of light through mask. If we reverse calculate from the equation No. (1), we get the wavelength of around 1500 nm for the Laser if the angle between two beams is maintained at 90°. Thus, this is the IR region of light. As we know that DCG does not respond well to wavelengths higher than Green light, we should use a Three Photon Absorption Fluorophore to initiate hardening of DCG due to the exposure to the IR Laser. The cell depths in the gelatin will also be reduced, because of very low spacing.

With the help of the humidification chamber, we should be able to accelerate the moisture loss in the gelatin after the channels and cell in its structure have been
filled with ink. We can also reduce the DCG film thickness to reduce the moisture holding capacity of the whole film.

The ink that will be used for printing should be pigment or particle free and the surface tension should be determined and engineered to avoid unwanted spreading of ink after the cell walls or channel walls are gone due to moisture loss.
BIBLIOGRAPHY

2. Lisa Cross, “Brand security”: Graphic Arts Monthly, January 2006, downloadable from:
5. A D 2000, “Understanding security holograms” (first 2 paragraphs):
7. Christopher Outwater & Van Hamersveld, Practical Holography, ©1995-04 Dimensional Arts Inc.: downloadable from
8. Encyclopedia Britannica Online, “Pulsed Laser holography”:


26. Tomasz Białopiotrowicz and Bronisław Jan´czuk, “Surface Properties of Gelatin Films”, Department of Interfacial Phenomena, Faculty of Chemistry, Maria Curie-Skłodowska University, Maria Curie-Skłodowska Sq. 3, 20-031 Lublin, Poland, July 22, 2002
