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Phase holograms in silver halide emulsion without a bleaching step

A. Beléndez^{*a}, R. F. Madrigal^b, I. Pascual^c and A. Fimia^b

^aDept. de Física, Ingeniería de Sistemas y Teoría de la Señal. Univ. de Alicante, Apdo. 99, E-03080 Alicante, Spain.

^bDept. de Ciencia y Tecnología de Materiales. Univ. Miguel Hernández, Avda del Ferrocarril s/n, E-03202. Elche, Spain.

^cDept. Interuniversitario de Óptica Univ. de Alicante, Apdo 99, E-03080 Alicante, Spain.

ABSTRACT

Phase holograms in holographic emulsions are usually obtained by two bath processes (developing and bleaching). In this work we present a one step method to reach phase holograms with silver-halide emulsions. Which is based on the variation of the conditions of the typical developing processes of amplitude holograms. For this, we have used the well-known chemical developer, AAC, which is composed by ascorbic acid as a developing agent and sodium carbonate anhydrous as accelerator. Agfa 8E75 HD and BB-640 plates were used to obtain these phase gratings, whose colors are between yellow and brown. In function of the parameters of this developing method the resulting diffraction efficiency and optical density of the diffraction gratings were studied. One of these parameters studied is the influence of the grain size. In the case of Agfa plates diffraction efficiency around 18% with density < 1 has been reached, whilst with the BB-640 emulsion, whose grain is smaller than that of the Agfa, diffraction efficiency near 30% has been obtained. The resulting gratings were analyzed through X-ray spectroscopy showing the differences of the structure of the developed silver when amplitude and transmission gratings are obtained. The angular response of both (transmission and amplitude) gratings were studied, where minimal transmission is showed at the Bragg's angle in phase holograms, whilst a maximal value is obtained in amplitude gratings.

Keywords: Holography, Holographic recording materials, silver halide emulsions, phase holograms.

1. INTRODUCTION

Nowadays, thanks to the technological advances made, it is possible to generate high quality holograms with a high diffraction efficiency and low noise level. However, one of the most important factors which affects the quality of the holograms obtained is the material used for recording. Many different holographic recording materials have been developed, with photographic emulsions being the most well-known and most frequently used. Photographic or silver halide emulsions are one of the most commonly used materials in holography, since they have a high energetic and spectral sensitivity together with a high power of resolution, thus enabling high diffraction efficiencies to be obtained¹. There are numerous applications, both scientific and artistic, in which it is possible to use photographic emulsions due to their versatility in that they can be deposited on glass plates or acetate, thereby enabling large holograms to be obtained. Finally, an important factor in the manufacture of certain holograms, such as holographic optical elements, is the repeatability of the results as well as the diversity of chemical processes that may be used. For example, two different chemical processes are used depending on whether phase or amplitude holograms are to be obtained. Phase holograms have the advantage of reaching diffraction efficiencies of almost 100%, while amplitude holograms reach efficiencies of only 3.7% (transmission) and 7.2% (reflection). To obtain a phase hologram in a photographic emulsion, the emulsion must be bleached, either with or without a fixer, after developing. The development process may be chemical, in which case the silver halide on the plate is converted into metallic silver which has a granular structure, or physical or semi-physical when the developer provides the silver. With this type of developer, the structure of the silver becomes colloidal. As we have already mentioned, each development process is different and produces holograms with different characteristics. However, it is possible to produce

* Email: augusto@disc.ua.es.

phase holograms with the type of processing - without the bleaching step - used for amplitude holograms, making use of a developer with a special composition like that of the physical¹ and semi-physical developers^{2,3}. In this study we propose a development process which behaves in some circumstances like a semi-physical process and in others like a chemical process, whereby the resulting hologram has properties of both phase and amplitude holograms. We used a typical chemical developer, AAC, consisting of ascorbic acid as the developer and anhydrous sodium carbonate as the accelerator.

2. EXPERIMENTAL

Unslanted holographic transmission gratings were recorded in Agfa 8E75 HD silver halide emulsion by using two collimated beams from a 15 mW He-Ne laser (633 nm) making an angle of $\sim 45^\circ$ (in air) with each other. With the geometry described, the spatial frequency of the gratings was calculated as ~ 1200 lines/mm. Series of twelve points were done for different values of exposure, each plate being divided into four points. The back of the plates was covered with an adhesive strip of PVC so as to prevent reflections taking place at the glass-air interface at the back of the plate⁴. The gratings were developed with AAC and fixed with F-24. All components of the different processes were used without prior purification and were supplied by Panreac in the PA form (for analysis) which is 99% pure. In our study we determined the effect of the time of development and how the behaviour of a chemical developer differs from that of a semi-physical developer. The density of the plates was calculated using the equation:

$$D = \log \frac{1}{T} \quad (1)$$

where

$$T = \frac{I_{t0}}{I_{i0} - I_{r0}} \quad (2)$$

Where I_{t0} , I_{i0} and I_{r0} are the transmitted, incident and reflected intensities respectively, when the incident light is normal to the surface it falls on. The diffraction and transmission efficiencies, η and τ , respectively, were calculated as:

$$\eta = \frac{I_d}{I_i - I_r} \quad (3)$$

and

$$\tau = \frac{I_t}{I_i - I_r} \quad (4)$$

Where I_d , I_t and I_r represent the diffracted, transmitted and reflected intensities, respectively, when reconstructed at Bragg's angle and I_i is the incident intensity. The angular response was also determined experimentally. The experimental measurements were made using an automatic measuring system. This system consists of two detectors and a rotating micro-positioner, all of which are controlled electronically. Measurements of angular response were taken in a range of -45° to 45° and at intervals of 1° . In order to determine the structure of the silver developed on the plates after processing, a fluorescent X-ray spectroscopy was done.

3. RESULTS AND DISCUSSION

The same chemical composition- 18 g of ascorbic acid and 120 g of sodium carbonate PA in 1 litre of distilled water - was used in all the development processes. In these working conditions, it was seen that when the developing time was varied, the behaviour of this composition changed dramatically from that of a typical chemical process to that of a semi-physical one. At long processing times (5 min) AAC acts as a typical chemical developer, while a transition takes place to a semi-physical process when the time decreases. This is clearly seen in the colour of the grating formed. The colour of the plates varies from dark grey to yellowy brown, and in the latter case the hologram behaves like a phase hologram. With a developing time of 5 minutes, a density of 5 and maximum diffraction efficiency of 2% were obtained for the lowest exposure. When the developing time was 3 minutes a density $D < 1$ and maximum diffraction efficiency of 18% were obtained for an intermediate exposure. Figure 1 shows how the optical density varies as a function of the developing time,

reaching low values when the process is semi-physical. In order to analyze the process in more detail, a grating developed in 5 minutes with the typical dark grey colour and another developed in less time and brown in colour were studied by means of fluorescent X-ray spectroscopy⁵. In the first case (Figure 2), the two peaks characteristic of metallic silver appeared in the X-ray spectrum, while in the second (Figure 3), there was no peak.

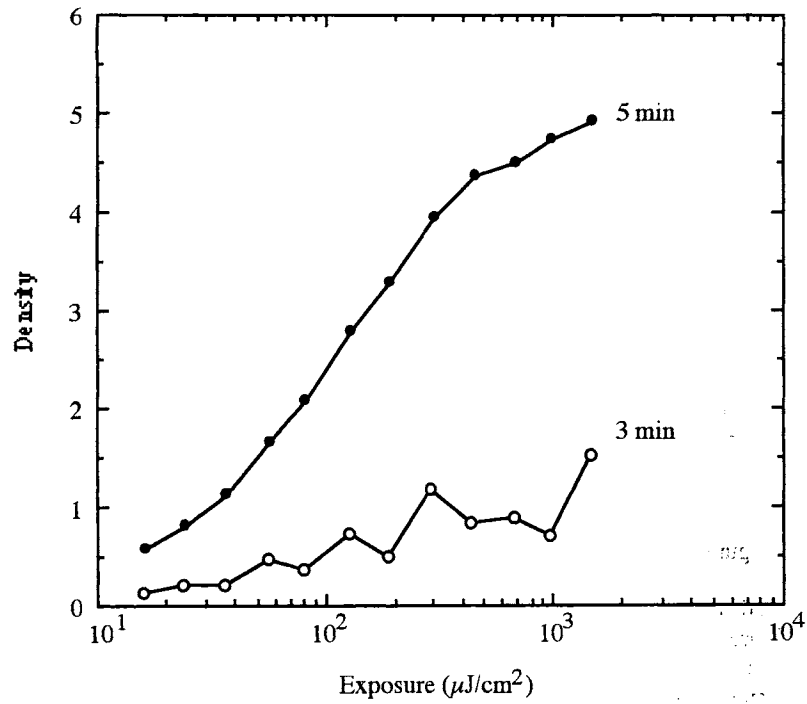


Figure 1.- D - $\log E$ curve for Agfa 8E75 HD emulsion: AAC developer and two developing times.

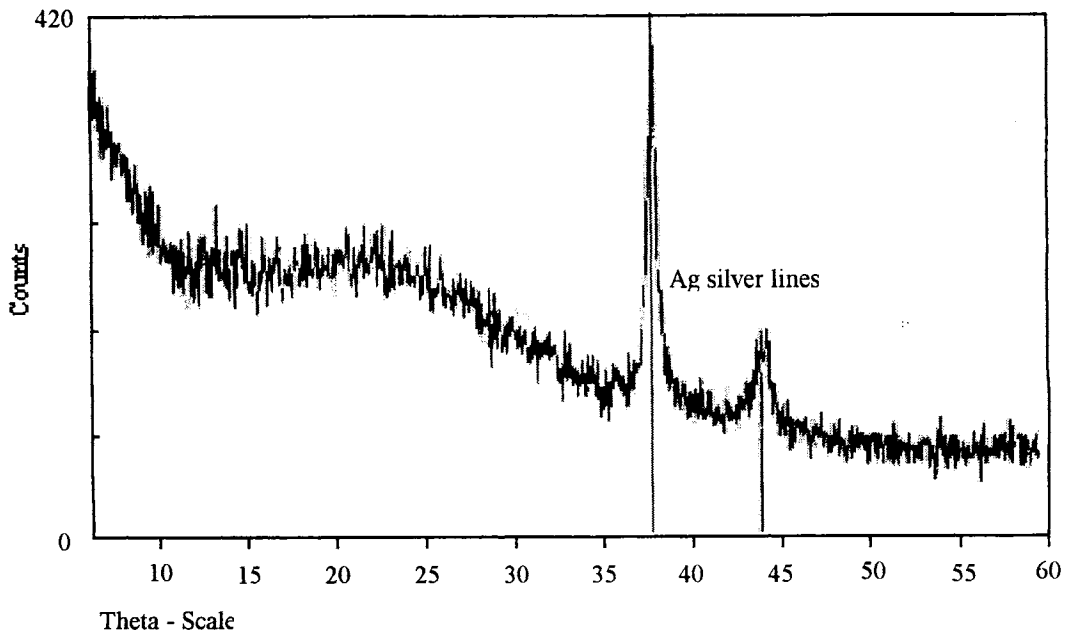


Figure 2.- Fluorescence X-ray spectrum for chemical developer.

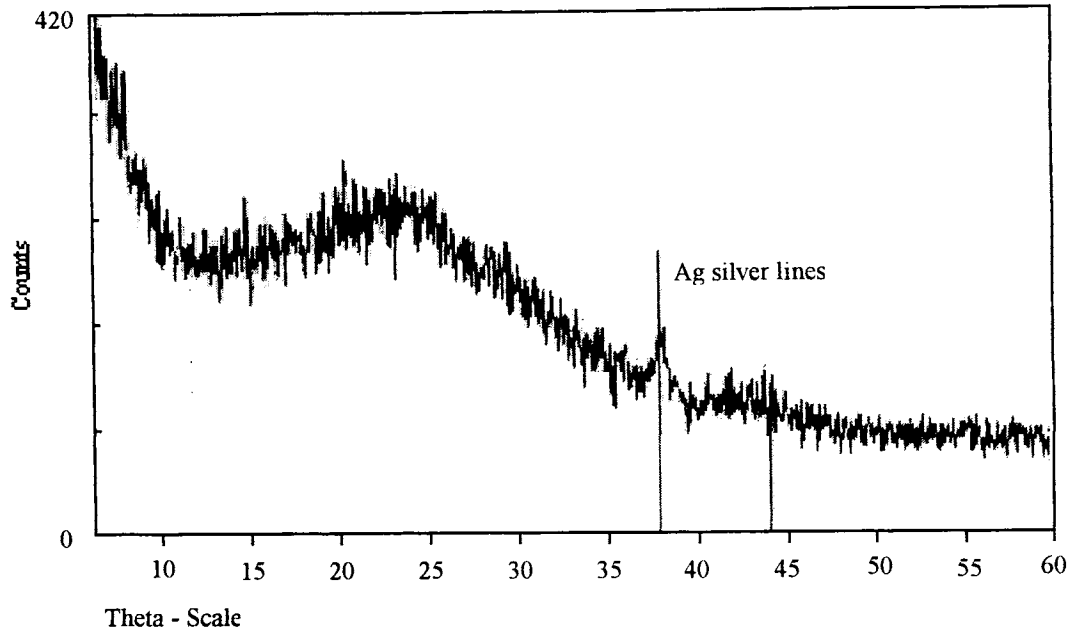


Figure 3.- Fluorescence X-ray spectrum for semi-physical developer.

It may therefore be concluded that with this type of developer, the silver is not in the form of metallic silver when the process is semi-physical. Figure 4 shows the angular response of the diffraction gratings. Minimum values of transmission are reached at Bragg's angle with semi-physical processing (phase gratings, (a)) and maximum values with chemical processing (amplitude holograms, (b))^{6,7}.

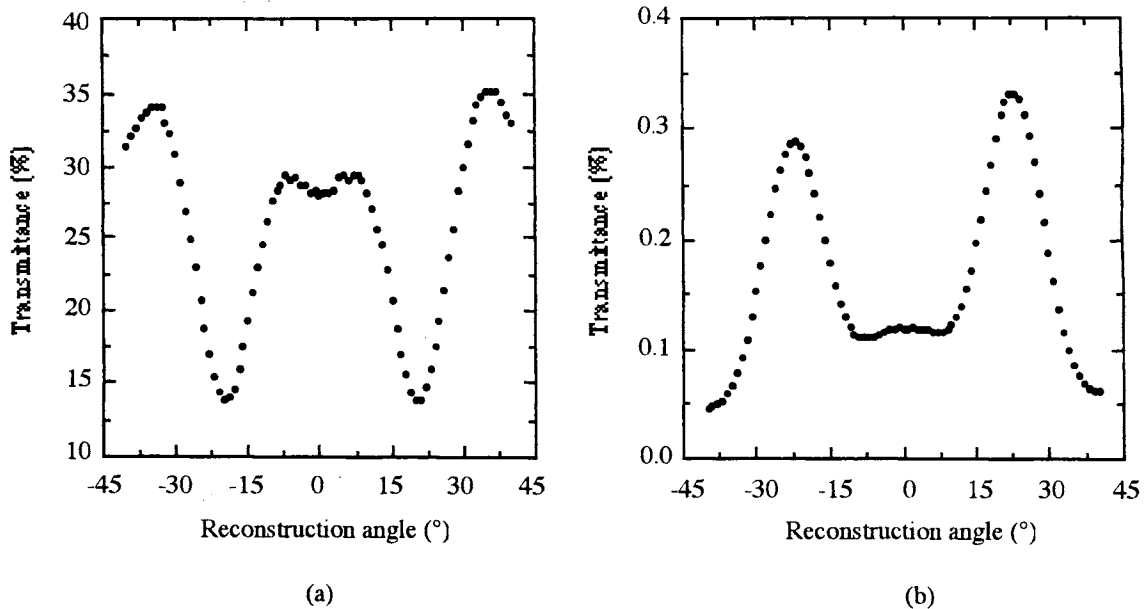


Figure 4.- Experimental measurements of transmittance as a function of the reconstruction angle.

Figure 5 shows the diffraction efficiency as a function of exposure for two different developing times. After 3 minutes phase gratings are obtained (semi-physical developing), while after 5 minutes amplitude gratings are formed (chemical developing). In Figure 5 it can be seen that for short developing times, the diffraction efficiency is greater than the theoretical limit for amplitude holograms⁸. This demonstrates that an index modulation has taken place, creating a phase hologram with a development process which is typical of amplitude holograms.

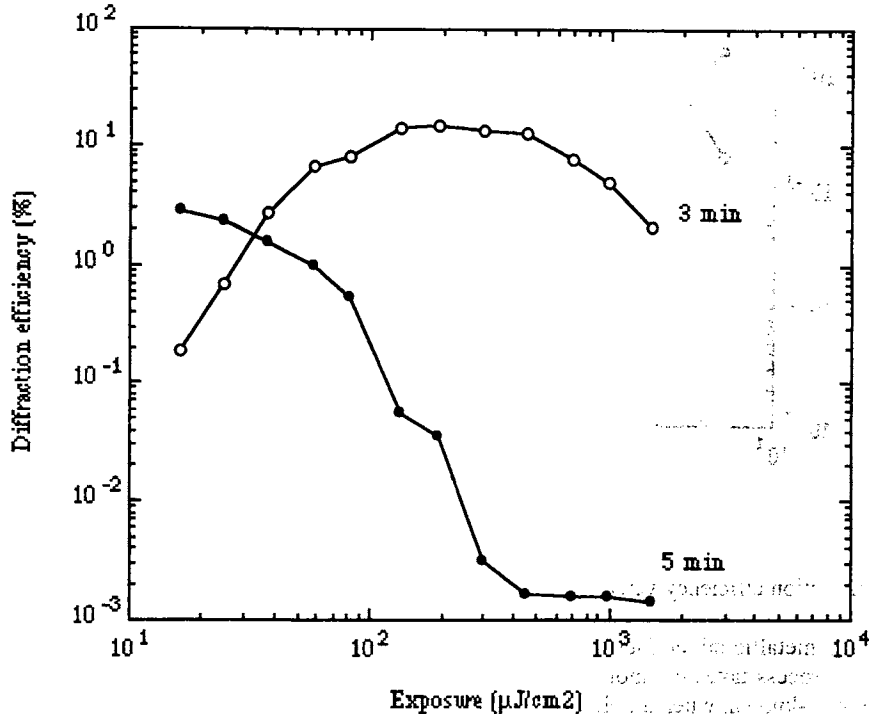


Figure 5.- Diffraction efficiency versus exposure, under Bragg condition, for two developing times.

Experiments were performed varying the temperature used to develop and determining how the behaviour of the developer changed. In Figure 6 it can be seen that at higher temperatures, the developer behaves like a chemical developer. In experiments done using BB-640 emulsion, the grains of which are smaller than those of Agfa 8E75 HD emulsion, diffraction efficiencies greater than 30% -without bleaching- were obtained when the appropriate development conditions were used.

4. CONCLUSIONS

In this study we show how under certain conditions it is possible to obtain phase holograms by developing and fixing with a known developer, AAC, usually used for amplitude holograms. This developer consists of ascorbic acid as the developing agent and anhydrous sodium carbonate (the type used for analysis - PA) as accelerator. This type of amplitude hologram obtained by developing and fixing produces a structure of very small, compact silver halide grains in the emulsion, while chemical developers produce a fibrous structure. Moreover, with chemical developing, the colour of the holograms developed and fixed varies between grey and black depending on exposure. Both physical and semi-physical developing give rise to a colour somewhere between yellow and brown. When a chemical developer is used, an amplitude hologram is formed with a low diffraction efficiency, which is insufficient for many applications. However, this type of hologram has the advantage of having a low noise level which makes it ideal for other applications such as copying holograms. When a semi-physical development process is used, the hologram formed is in part a phase hologram, which means the diffraction efficiency is greater. However, it also has many properties of amplitude holograms, and so the advantages of both types of holograms are obtained.

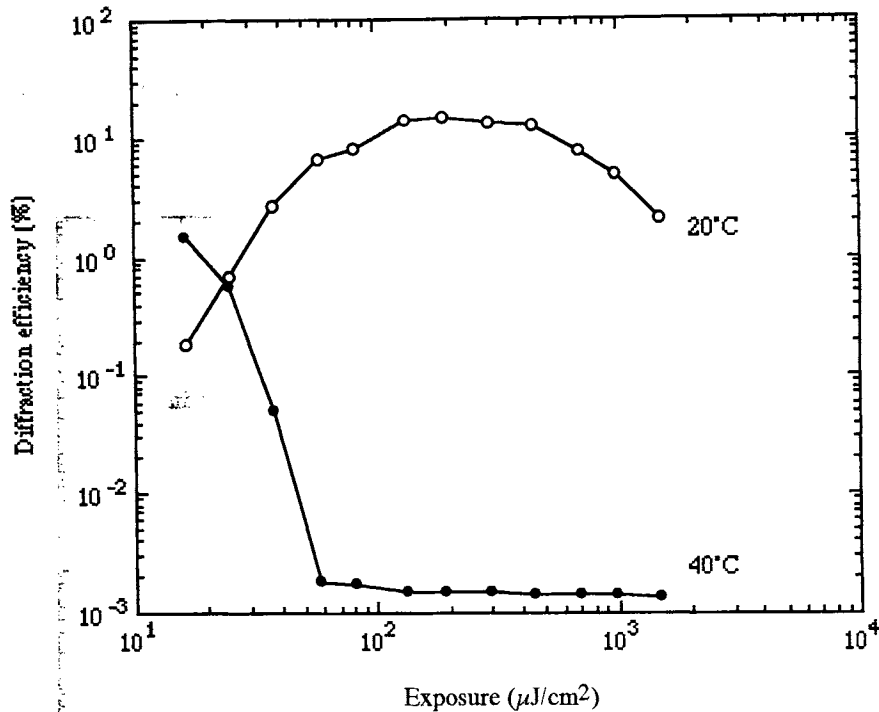


Figure 6.- Diffraction efficiency versus exposure, under Bragg condition, for two developing temperatures.

The different quantity of metallic silver found in both types of processing is related to the reactivity of the process. The longer the development process takes the more metallic silver is formed as a result of the reduction process undergone by the silver grains. As is well-known, when a holographic emulsion is illuminated non-uniformly, the grains in the bright zone are activated and they react more rapidly with a chemical developer giving rise to variations in the concentration of metallic silver, and this results in a difference in the absorption coefficient. When the development process lasts for only 3 minutes, this reaction hardly takes place, since there is no metallic silver present at the end of the process. With short developing times, very little metallic silver is produced and so instead of metallic silver grains being formed, the structure of the silver changes to that of colloidal silver. This has a different electronic structure from that of the original silver, thus producing a difference in the refraction index.

Therefore, the fact that AAC behaves like a semi-physical developer is due to the development conditions which result in the amount of metallic silver present being small. The rate of this process in the material is given by the following rate equation⁹:

$$\frac{d[Ag^0]}{dt} = K[R]S e^{-\frac{F\Delta E n \alpha}{RT}} \quad (5)$$

where S is the surface of the grain to be developed, $[R]$ the concentration of ascorbic acid, α a symmetry factor and n the number of electrons transferred during the reduction process. R , T and F have their usual electro-chemical meaning. ΔE is the potential at the solution/silver surface interface, which limits the process of transfer of electrons between the developer and the silver. The influence of some of these parameters such as the developing temperature, and the surface have been studied. According to the above equation, at higher developing temperatures the reactivity increases and so a chemical process would take place. The size of the grain also has a significant effect, since the rate of reaction is proportional to the grain size. Therefore, the bigger the grain the greater the reactivity and the process will be a chemical one.

Due to the fact that Agfa plates have been taken off the market, studies are being carried out with BB-640 plates and better results are being obtained since the grains are smaller and this favours semi-physical development. The effects observed are the same as those obtained with Agfa plates. However, BB-640 plates have a harder gelatine than Agfa plates and so it has been necessary to include a hypersensitization process using a mixture of sodium sulphite and urea.

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