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Corn syrup holograms

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1. Introduction

Two important properties from the sugar as a means of holographic register have been its natural spectral response, generally found at the ultraviolet zone between 190 nm and 300 nm and the hydrophilic response of this material to the environmental conditions [1]. But the corn syrup is confirmed for different molecular sugars components such as glucose, fructose and sucrose; these sweeteners present more stability to the humid conditions from the environmental room laboratory than any individual molecular sugar structure. We use the corn syrup from Karo[®]; it is made from a blend of sugars from cornstarch and 15–20% glucose. There are two varieties: light, which is almost clear and has vanilla flavoring; and dark, which is brown with a flavor similar to molasses [2].

We added potassium dichromate salt; it is commonly used in holography as materials photosensitizer, due to changes in dichromate oxidation state ion as photoinitiator of chemical reactions produced when this material is exposed to the laser radiation [3].

The corn syrup advantage as holographic material is that do not need damp developing processes and fixing to get the recorded image [1,4].

ABSTRACT

A study of the diffraction efficiency parameter, of holographic gratings recorded with thin emulsion layers of corn syrup (Karo[®]) photosensitized with potassium dichromate salt is presented. This was possible by the interference produced by amplitude division setup using two wavelengths at 473 nm and 530 nm respectively. The maximum diffraction efficiency for corn syrup with potassium dichromate films was on average in the order of 4.0% at first diffraction order. The energy that was applied at blue light was 10 times less than that applied at green light.

Evolution in the behavior profile from the diffraction efficiency parameter is presented as a function of relaxation time necessary to obtain major performance of these gratings made with peculiar sweetener. Holograms with this material do not require developing processes, because these samples develop by

themselves. After of exposition with light laser, is necessary wait to stabilize the material 96 h, to protect the film against the environmental humidity.

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However after the exposure process, the material shows a chemical inertia, which is presented as the evolution from the Cr^{+6} to Cr^{+3} by some time around 96 h, at this point we call that the material takes the photochemical equilibrium and the emulsion can be protected from the environmental conditions. On the transition hours the diffraction efficiency of the gratings shows changes, from minor to high values of this parameter.

The fact is that one application is possible at the industry of the sweeteners, i.e. making attractive products to the consumers, besides openings a door to the bio-optics.

1.1. Corn syrup

Carbohydrates have been important component in the human diet and the most traditional source for obtaining these has been the refinement of sucrose starting from cane sugar and beet sugar [5].

However due to the big advances at the sweeteners industry and to avoid relying on some countries toward the consumption of cane sugar, some processes to get monosaccharides, glucose, fructose and maltose from the starch of some cereals were developed and for economic reasons, the corn starch has been the raw material more used to get the syrups from these sugars. The popularity of these sweeteners has been such, than the use of glucose and fructose; have grown upon the alimentary industry [6].



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Fig. 1. Diffraction pattern generated for diffraction gratings recorded in corn syrup sensitized with K₂Cr₂O₇.

Corn syrup is a liquid sweetener; commercially it is obtained from starch or cornstarch. The process of making the sweetener, high fructose corn syrup (HFCS) was developed in the 1970s by Japanese investigators and its consumption was extended to all over the world [7].

The processes by enzymatic conversion and acid-enzymatic conversion have been one of the advances in the production of corn syrups, before this it was obvious to think that the different enzymes will produce syrups with different compositions from sugars. According to realized studies some bacteria can contribute with such enzymes. However, the process is actually very complicated. One of the great triumphs of the enzymatic technology has been the development of "glucose-*isomerase*" [8,9].

High-fructose corn syrup (HFCS) is produced by processing cornstarch to yield glucose, and then the glucose is processed to produce a high percentage of fructose. White cornstarch is turned into crystal clear syrup.

Three different enzymes are needed to break down cornstarch, which is composed of chains of too lengthy glucose molecules, into the simple sugar glucose and fructose. First, cornstarch is treated with alpha-amylase to produce shorter chains of sugars called polysaccharides. Alpha-amylase is industrially produced by a bacterium, usually Bacillus sp., which becomes purified before. Next, an enzyme called glucoamylase modifies the sugar chains down to yield the simple sugar glucose. Unlike alpha-amylase, glucoamylase is produced by Aspergillus, a fungus, in a fermentation vat. The third enzyme, glucose-isomerase, is very expensive. It converts glucose to a mixture of about 42% fructose and 50-52% glucose with some other sugars mixed in. While alpha-amylase and glucoamylase are added directly to the cornstarch conversion, glucose-isomerase is packed into columns and the sugar mixture is then passed over it. Alpha-amylase and glucoamylase are used only once, glucoseisomerase is reused until it loses most of its activity. There are two more steps involved. First is a liquid chromatography step that takes the mixture to 90% fructose. Finally, this is blended with the original mixture to yield a final concentration of about 55% fructose; called industrially high fructose corn syrup [7].

2. Recording hologram experimental

The coating mixture consists of corn syrup (Karo[®]) and a photosensitizer as potassium dichromate (Meyer Chemical Co., A.C.S. Reagent [2025-100], Purity 99.7%, FW = 294.18, crystal K₂Cr₂O₇). Samples were prepared by mixing 10 ml of corn syrup in 1.0 ml of water distiller and 3% (wt/wt) K₂Cr₂O₇. The solutions were coated onto clean glass substrates (5 cm × 5 cm) with relative stable environmental conditions with average temperature of 25 °C and 42% relative humidity environment. The thickness of the layers corn syrup sensitized with K₂Cr₂O₇ and blue dye film was 122 µm, the layers of emulsion were obtained applying gravity technique, pouring drops on the substratum, this is evened initially for a circular level of central bubble.



Fig. 2. Evolution in time of the diffraction efficiency parameter at first order, recorded with diode laser (473 nm) of thin films made with corn syrup and $K_2Cr_2O_7$.

The films were exposed with two coherent beams; blue recording beams came in the form of diode laser (473 nm) and green recording beams came in the form of diode laser (530 nm). The reading beam came from coherent He–Ne laser (632.8 nm). The basic experimental setup is an array; it consists of a symmetrical arrangement of two arms, where the photosensitive emulsion is centered in the vertex between the two arms, where this is displaced in order to change the spatial frequencies of the gratings.

To get a photosensitive material with a very low toxicity, was necessary to use very low concentration of potassium dichromate. However is known that potassium dichromate is a potent pollutant for human and animal health [10]. In the future, could work with a photosensitive salt less toxic, such as Fe (III) for this material [11].

3. Experimental results

Our diffraction gratings made with corn syrup and sensitized with potassium dichromate do not require developing processes. Fig. 1 shows an example of one diffraction pattern reconstructed with He–Ne laser, it was recorded with a wavelength 530 nm. The pattern shows two diffraction orders, all the measurements of the diffraction efficiency parameter were made at first order only, the zero order presents low spatial scattering and it is not superimposed to the first order, assuring that the material with which it is built the grating is appropriate. Commonly the materials that are not very appropriate produce much space dispersion, for effects of crystallization of the salts that are contained in the emulsion.

The dependence of the diffraction efficiency parameter, with the exposure energy from the corn syrup films with $K_2Cr_2O_7$, they were measured continuing a temporary chronology, the first measures were made immediately after the registration of the diffraction gratings, the following measure was taken every 24 h, until conclude to 96 h.

Fig. 2 presents a family of curves that show the historical evolution of the parameter of diffraction efficiency as a function of the time lapsed after the registration of the gratings using this material, the exposition energy was from 0.12 J/cm^2 to 1.2 J/cm^2 .

The gratings were recorded with a diode laser at 473 nm. We can see that maximum diffraction efficiency was 4.0% obtained at 96 h after recording the grating in the films, which is centered to the energy of 0.5 J/cm². All the family of curves is centered on this point, where the value of diffraction efficiency parameter begins to increase with the course of time, until it begins to decay the value of this parameter, this happens after 96 h. At this point this could be



Fig. 3. Evolution in time of the diffraction efficiency parameter at first order, recorded with diode laser (530 nm) of thin films made with corn syrup and $K_2Cr_2O_7$.

understood that emulsion is stable and one could proceed to protect it with a layer of hydrophobic polymer on emulsion surface, or with a plate of glass on emulsion.

Fig. 3 shows a family of curves that describes the evolution of the parameter of diffraction efficiency through the times; this history is similar to the previous graphic, all these data were obtained with a diode laser at 530 nm. It shows maximum diffraction efficiency in the order of 1.0% obtained 72 h after of its register, applying energy at 4.5 J/cm². In this case the photosensitive emulsion needs more energy in order to register this case of good form. We applied energy from 1.2 J/cm² to 7.8 J/cm² in order to obtain gratings with an acceptable diffraction efficiency.

Both figures show a symmetrical family of curves each one represents the diffraction efficiency of the gratings through the time after their register. All the plots show a central important point of symmetry located at 0.5 J/cm² for 473 nm and 4.5 J/cm² for 530 nm respectively. At this point it is possible to see that in order to obtain the central maximum of these curves, there is a factor of 10 times of energy required between them lines 457 nm and 530 nm used for this purpose.



Fig. 4. Behavior of the MTF of gratings made with corn syrup sensitized with $K_2Cr_2O_7$ recorded with diode laser (473 nm).



Fig. 5. Behavior of the MTF of gratings made with corn syrup sensitized with $K_2Cr_2O_7$ recorded with diode laser (530 nm).

The plots can be interpreted as the stabilization from corn syrup altered by the photosensitive salt $K_2Cr_2O_7$. The plots show the relaxation of dichromate and fructose or glucose molecules, they were altered when we applied light at this emulsion and this emulsion needs time to amplify the information in our case, a holographic image. After these threshold times, we recommended to protect the emulsion of the environmental humidity, for longevity of the gratings made with these materials.

Fig. 4 shows Module of Transfer Function (MTF) behavior of gratings made with corn syrup used like emulsion, with photosensitive $K_2Cr_2O_7$ salts. The registration was made with a diode laser at 473 nm.

The MTF is the material signature in space resolution; this parameter determines the emulsion capacity of solving several space frequencies like function of diffraction efficiency.

With 12 positions in the holographic arrangement that we used, 12 families of gratings to several frequencies were obtained, plotting only the average of 9 gratings for each point, we observed that in space frequency of 1100 l/mm, it correspond to maximum value diffraction efficiency parameter with 5%.

The behavior of the MTF in this material is not lineal; the points were adjusted with splines technique. We obtained only 12 positions due to the experimental limitations of our holographic setup used for building the gratings.

The band width of space frequencies obtained with holographic arrangement was from 900 l/mm to 1600 l/mm, observing two maxima zones between the frequencies 1100 l/mm and 1600 l/mm respectively.

Fig. 5 presents the MTF behavior of gratings recorded with diode laser at 530 nm, this graph is more lineal than the previous graph. But more energy is needed from the order of 10 times to obtain acceptable results. We worked with 12 experimental setup positions to build gratings with different spatial frequencies. The maximum average value from the parameter diffraction efficiency was in the order of 1.2%, for all the band width in frequencies from 790 l/mm to 1375 l/mm. Although it was the same arrangement that in previous graph the frequencies are obviously different because we used a wavelength different in the grating registration.

4. Conclusions

Holographic gratings recorded in corn syrup films sensitized with potassium dichromate salt presented adequate behavior to make diffraction devices (gratings), this material shows easy handling. However, according to the diffraction efficiency curves the holographic gratings made with this matrix requires a stabilization process from which the parameter of diffraction efficiency (taking the maximum value of this parameter) is determined. After of this stabilization process is recommended to protect the hologram of the environmental humidity, with glass or plastic polymeric mask on the surface of this emulsion.

The fact is that one application is possible at the industry of the sweeteners, making attractive products to the consumers, provided a photosensitive salt with low toxicity with very low concentration. It is known that potassium dichromate is a potent pollutant for human and animal health. In the future we could use photosensitive not so toxic salts, such as Fe (III) for building with these matrix holographic elements for human consumption besides openings a door to the holography in the bio-optics field.

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