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# New holographic recording material: bromothymol blue dye with rosin

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**Abstract**

The characterisation of a solution made up of bromothymol blue (BTB) combined with rosin and diluted in isopropyl alcohol, as a holographic recording material was carried out. This process was based on the recording of diffraction grating, under a range of recording parameters such as: BTB concentration, rosin concentration, a range of interference angles for grating generation, as well as a range of illumination wavelengths, and finally a study of the development process using a range of development times. The holographic gratings produced using this material show a high sensitivity to blue and blueish green illumination ($\lambda = 457, 476$ and 488 nm), i.e. using an Argon Ion laser as well as a high-spatial resolution of the order of 1100 l/mm, thus demonstrating that it is feasible to obtain other HOEs using the proposed material.



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*Keywords:* Holographic recording materials; Optical storage media; Holographic optical elements; Holographic grating; Diffraction efficiency; Hologram resolution; Hologram characteristics

## 1. Introduction

Brothymol Blue® (BTB) dye is used as a pH indicator (pH 6.0 yellow and pH 7.6 blue) in some elements as well as measuring the disassociation constant pk, which is equivalent to the acid potential [1]. This dye is amongst the most appropriate for measuring pH in the range found in physiological tissue, for the investigation of lipid-protein interactions and for fluid flow studies [2–4], as well as other biomedical, biological and chemical engineering applications [5]. Some of the characteristics of BTB are discussed below to ease the interpretation of its behaviour: its structure is due to the action of the bromide on the thymol blue in acetic acid crystals, which results in a planar molecular shape, as shown in Fig. 1, while its condensed form formula is $C_{27}H_{28}Br_2O_5S$ [1]. Its molecular weight is equal to 624.39 and its percentage composition is given by C: 51.94%, H: 4.52%, Br: 25.59%, O: 12.81% and S: 5.14%. The molecule is moderately soluble in water, fully soluble in alcohol as well as in watery alkaline solutions, ether, though it is less soluble in benzene toluene and xilene. Moreover, it is almost

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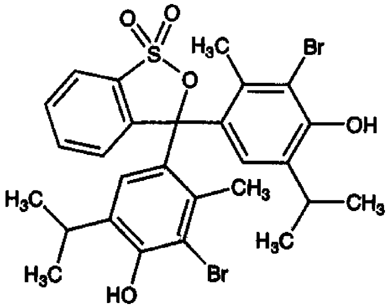


Fig. 1. Molecular structure of bromothymol blue.

insoluble in petroleum ether. To prepare this dye as a pH indicator, its pk = 7.0 and it is dissolved in 0.1 gm of bromothymol blue (BTB) and 8.0 ml of (N/50 equivalent per litre) NaOH and further diluted with 250 ml of water.

A photosensitive material is proposed, based on the mixture of BTB with rosin diluted in isopropyl alcohol, as a photosensitive emulsion to light in the range of $\lambda = 457$–488 nm, where through phase modulation, gratings are recorded in relief. Furthermore, this work describes other characteristics of this emulsion such as: absorbance characteristics, diffraction efficiency curves $\eta$ (%) as a function of energy exposure at a range of rosin and BTB concentrations; a study was done of the angle dependence of spatial resolution; the photosensitivity as a function of wavelength; the behaviour of phase modulation to register gratings with a range of relative beam intensities; and finally the behaviour of diffraction efficiency as a function of development time. The development step is quick and simple, as it only requires rinsing with water with chlorine. Moreover, this emulsion shows a spatial resolution of the order of 1100 l/mm, thus obtaining a material capable of recording other HOEs.

As far as the rosin is concerned, this resin is obtained from pine trees [1,6] and it can be doped with other dyes to make holographic materials, such as: this rosin can be combined with crystal violet (CV) [7], it can be combined with ammonium dichromate (AD) [8], it can be combined with phenol red (PR) [9], and also combined with BPB [10].

Table 1
Dye (BTB) with rosin concentration

| Concentration | 10:1 | 30:1 | 60:1 | 80:1 |
|---|---|---|---|---|
| Rosin | 0.1 | 0.3 | 0.6 | 0.8 |
| BTB | 0.01 | 0.01 | 0.01 | 0.01 |
| Alcohol | 5 | 5 | 5 | 5 |

## 2. Photosensitive plate preparation

The procedure for preparing a solution capable of depositing the required emulsion on the plate consists of a number of steps as follows. Firstly, the rosin is diluted in isopropyl alcohol and then the dye is added, mixing until fully integrated. The resulting solution is then filtered to remove impurities that have not fully dissolved into the liquid solution [7], this procedure being repeated for a range of concentrations as shown in Table 1, where the results for four concentrations 10:1, 30:1, 60:1 and 80:1 (rosin to dye ratios) are given. For this case, the dye and isopropyl alcohol quantities were kept constant and only the rosin amount was varied. The objective of this exercise was establishing what the optimum resin concentration was for subsequent use at $\lambda = 457$ nm.

As a second step, this solution was deposited on a glass substrate of size $2 \times 2$ in.$^2$ that had previously been cleaned of grease and silt [10]. Using a gravity technique, approximately 0.17 ml of solution was deposited on each plate, leaving them to rest for at least 12 h so that the solution was fully dried on the substrate.

As a third step, each plate was baked at 100 °C for a total of 3 h so that the isopropyl alcohol totally evaporated and only the BTB dye and resin remained, which was strongly adhered to the substrate with an emulsion layer thickness of approximately 6.5 μm.

## 3. Results

Fig. 2 shows four spectral curves of absorbance of the photosensitive emulsions at the previously mentioned concentrations. These curves show a very similar behaviour but where absorbance increases as rosin concentration is decreased. A

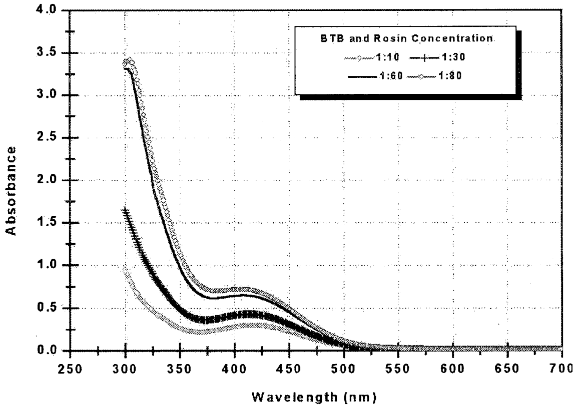


Fig. 2. Shows the absorbance spectrum curves versus wavelength for different concentration of BTB and rosin. In the UV region this material corresponds a higher absorbance.

further important point worthy of mention is that more specifically at $\lambda = 457$ nm, which was the wavelength used to record all the gratings, absorbance only increases from 0.2 to 0.4 as rosin concentration is decreased. However, we also noted that maximum absorbance lies in the UV region, where we believe that this material is most sensitive as a photosensitive medium. The curves also show a relatively high-absorbance band between 300 and 475 nm. To obtain these curves a Perkin Elmer $\lambda 3$ spectrophotometer was used. The emulsion absorbance $A$, for a set illumination wavelength, is given by Beer's law as [10–12]:

$$A = \log\left(\frac{I_r}{I_e}\right) = cl\varepsilon$$

where $I_r$ is equal to the reference beam intensity, $I_e$ is equal to the emulsion beam intensity, $l$ refers to the emulsion thickness expressed in centimetres, $c$ is equal to the molar concentration (mol/l) and $\varepsilon$ is equal to the absorption coefficient, also referred to as molar extinction coefficient. Table 2 shows these parameters as derived from Fig. 1 and Beer's law, thus obtaining molar concentration $c$ as a function of emulsion concentration, so that the absorption coefficient $\varepsilon$ can finally be derived. This parameter allows us to calculate the appropriate rosin concentration to obtain the best characteristics of this photosensitive material, and also using relatively small amounts of BTB to produce said absorbance curves. In this case, when $\varepsilon$ takes high values (of the order of 5000 plus) this material probably has an even better photosensitive characteristics [11,12]. The emulsion layer thickness $l$ achieved was of the order of 6.5 μm, as measured by a FEDERAL® Surfanalizer 400 profilometer, whose measurement of an actual sample plate can be seen in Fig. 3 with a margin of error of approximately ±0.25 μm, which is an adequate measurement accuracy for this application.

Table 2
Beer's law parameters

| Concentration BTB–rosin | $\lambda$ of work (nm) | $A$ | $c$ (mol/l) | $\varepsilon$ (l/mol cm) | $l$ (cm) |
|---|---|---|---|---|---|
| 10:1 | 457 | 0.1973 | 0.069325 | 4378.5 | 6.5X$^{-4}$ |
| 30:1 | 457 | 0.2701 | 0.201569 | 2061.5 | 6.5X$^{-4}$ |
| 60:1 | 457 | 0.3937 | 0.399937 | 1514.5 | 6.5X$^{-4}$ |
| 80:1 | 457 | 0.427 | 0.532183 | 1234.4 | 6.5X$^{-4}$ |

Once the photosensitive emulsions were produced, the gratings were recorded using an Argon Ion laser in the blue line, using an experimental set up as shown in Fig. 4.

For each one of the plates containing an emulsion in the concentrations of 1:10, 1:30, 1:60, 1:80 (dye to resin ratio), three sets of nine gratings were recorded in order to allow the derivation of the applicable error margins. The results of these calculations are shown in Figs. 5–8, where they are expressed as diffraction efficiency $\eta$ (%) versus exposure energy. All other parameters were kept equal for the recording of these gratings, such as

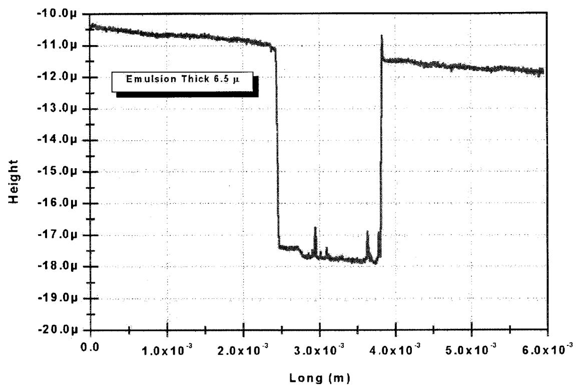


Fig. 3. Thickness of the emulsion, with approximate margin of error 0.25 μm, which to measure oneself with Surfanalizer 4000.

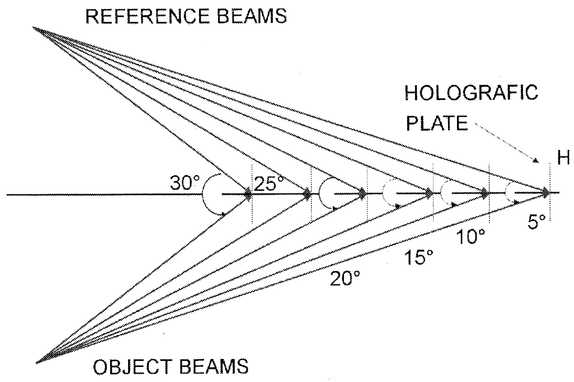


Fig. 4. Experimental configuration employed to make diffraction grating, changing the interference angle between the beams.

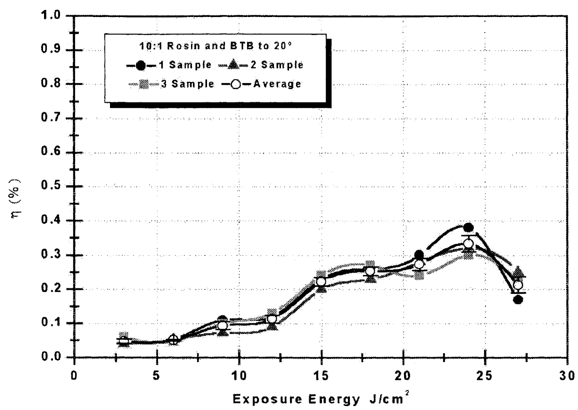


Fig. 5. $\eta$ (%) reproductions of the gratings to obtain margin of error and average for 10:1 concentration where to low $\eta$ the order 0.4% as maximum and 0.33% the average.

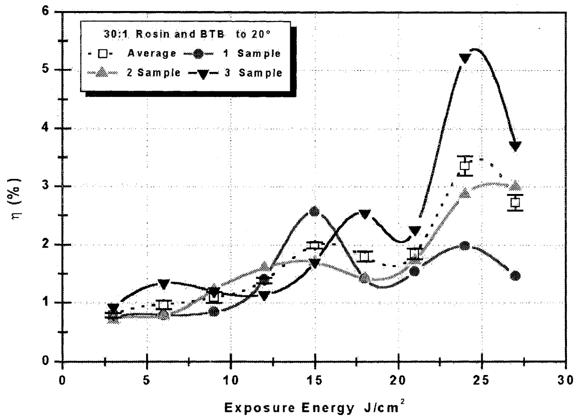


Fig. 6. $\eta$ (%) reproductions of the gratings to obtain margin of error and average for 30:1 concentration. Showing 5.3% of $\eta$ maximum and 5.3% the average.

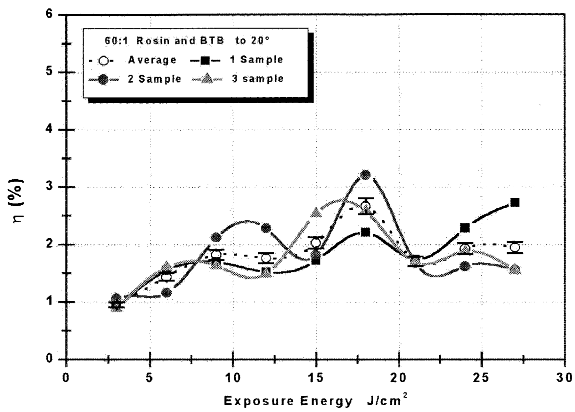


Fig. 7. $\eta$ (%) reproductions of the gratings to obtain margin of error and average, for 60:1 concentration to support a soft increase in your $\eta$ (%). Having 3.25% of $\eta$ maximum and 2.6% the average.

interference angle $\theta = 20°$; the intensity ratio between the two beams was kept constant at 1:1; all grating recording wavelength was kept constant at $\lambda = 457$ nm; and also development time. These diffraction efficiency curves serve to deduce optimum rosin concentration to record said gratings. A development process was then executed, consisting of a development time of 24 s, which is a very fast process indeed. Using a combination of water and chlorine, in a proportion of 1:50 respectively, as a fixing agent serves to increase diffraction efficiency.

Fig. 5, where the resin to BTB ratio is 10:1, shows curves that exhibit the lowest diffraction efficiencies down to approximately 0.5%, compared to the higher concentrations. Fig. 8 where the resin to BTB ratio is 80:1 also shows low diffraction efficiency, slightly higher than 1% for high-energy exposure. For a concentration of 30:1 as shown in Fig. 6, efficiency increases smoothly as exposure energy is increased reaching as high as 5%. Finally, for a concentration of 60:1, efficiency curves increase smoothly at first, and then tend to decrease behaving in a manner more typical of the conventional silver halide holographic materials [13].

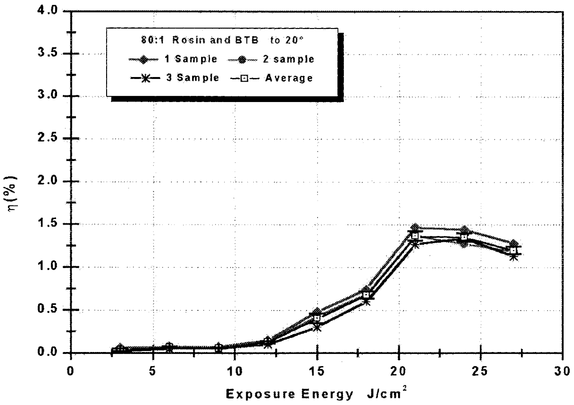


Fig. 8. $\eta$ (%) reproductions of the gratings to obtain margin of error and average for 80:1 concentration to obtain the 1.5% of $\eta$ to exposure energy bigger and 1.35% the average.

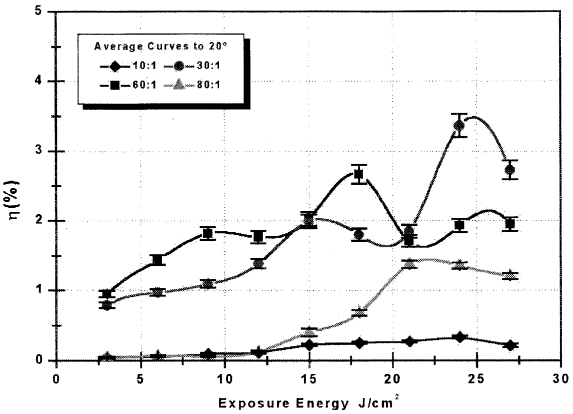


Fig. 9. Average of the $\eta$ (%) versus to exposure energy for BTB and rosin with yours margin of error where the 60:1 concentration have the high $\eta$ (%) a low exposure energy.

In order to observe clearly which concentrations are best for grating recording Fig. 9 shows only average $\eta$ (%), with their respective error margins, resulting in the best concentrations being 30:1 and 60:1. Once again, these results show that an emulsion with a higher absorbance, at least at the wavelength employed for these tests, is not the most photosensitive. We believe that the reason for this is that at higher concentrations the rosin blocks the BTB dye from absorbing the incident light, i.e. it is believed that a saturation obtains at higher concentrations [14]. At a concentration of 10:1 there is less rosin and more BTB in the same amount of solvent, and the emulsion is therefore not saturated [14]. For this reason, we discarded concentrations of 10:1 y 80:1 for the characterisation of BTB under other grating recording parameters for HOE recording purposes.

Table 3 shows average $\eta$ (%) together with the related error margins for a range of emulsion concentrations, taken from the data displayed in Fig. 9.

Another of the parameters that was changed in order to investigate the behaviour of this photosensitive material, was the interference angle between the reference and object beams. An arrangement as shown in Fig. 4 was used, where the angle was varied from $\theta = 5°$, 10°, 15, 20°, 25° to 30°, thus obtaining gratings at a range of frequencies. These results are shown in Fig. 10 where $\eta$ (%) is shown as a function of exposure energy.

For $\theta = 5°$, 15° and 30° the efficiency curves are similar with a tendency to increase slightly as exposure energy is increased, reaching efficiencies from 0.1% to 0.6%. As far as 10° and 25° curves

Table 3
Average $\eta$ (%), together the related error margins for a range of emulsion concentration

| $\eta$ (%) 10:1 | $Y$ (Er±) | $\eta$ (%) 30:1 | $Y$ (Er±) | $\eta$ (%) 60:1 | $Y$ (Er ±) | $\eta$ (%) 80:1 | $Y$ (Er ±) |
|---|---|---|---|---|---|---|---|
| 0.95 | 0.0475 | 0.78 | 0.0393 | 0.04 | 0.0061 | 0.03 | 0.0120 |
| 1.43 | 0.0718 | 0.97 | 0.0485 | 0.05 | 0.002 | 0.06 | 0.0088 |
| 1.81 | 0.0908 | 1.09 | 0.0545 | 0.09 | 0.0113 | 0.05 | 0.0066 |
| 1.76 | 0.0881 | 1.38 | 0.0691 | 0.11 | 0.0120 | 0.12 | 0.0145 |
| 2.02 | 0.1013 | 1.99 | 0.0995 | 0.22 | 0.0120 | 0.40 | 0.0536 |
| 2.66 | 0.1333 | 1.79 | 0.0898 | 0.25 | 0.0120 | 0.67 | 0.0420 |
| 1.70 | 0.0851 | 1.84 | 0.0921 | 0.27 | 0.0176 | 1.37 | 0.0577 |
| 1.92 | 0.0963 | 3.36 | 0.1680 | 0.33 | 0.0240 | 1.35 | 0.0471 |
| 1.94 | 0.0973 | 2.72 | 0.1363 | 0.21 | 0.0233 | 1.2 | 0.0435 |

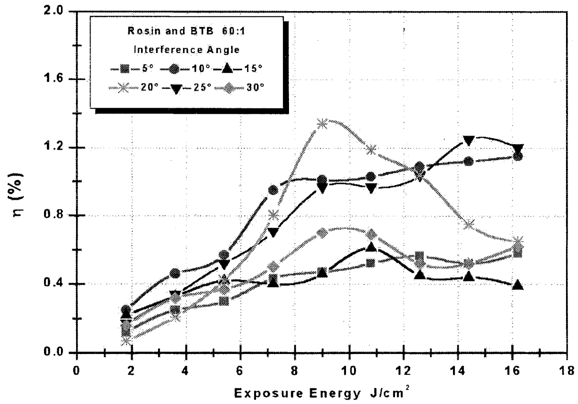


Fig. 10. Diffraction efficiency versus exposure energy changing the interference angle between beams, showing the bigger $\eta$ (%) for the 10° angle.

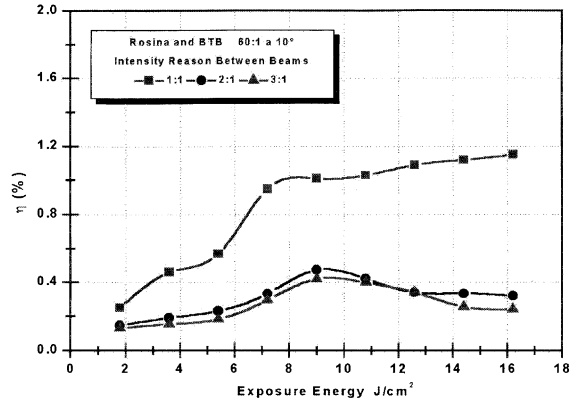


Fig. 11. Diffraction efficiency versus exposure energy in function of the intensity reason between the beams, to obtain the 1:1 reason the better.

are concerned, their $\eta$ (%) grow faster and show a wide range with efficiencies higher than 1%, thus showing these to be the best angles for grating recording on this material, while at 20° the curves show a peak, increasing and then dropping efficiency very rapidly, thus showing this angle not to be ideal for grating recording. So, the range of recording angles yielding high-diffraction efficiencies is in fact quite narrow. All diffraction gratings were recorded using energies in the range 4–36 J/cm$^2$, with exposure times increased in steps of 30 s.

Table 4 shows explicitly data which is implicit in Fig. 10, i.e. that depending on the interference angle, gratings have a set period and frequency.

As the intensity ratio between the beams is changed, when a hologram or diffraction grating is being recorded, a phase distribution is produced, which produces changes in the diffraction efficiency. This effect is illustrated in Fig. 11 where the best intensity ratio between the beams is 1:1 with a $\eta$ (%) almost three times higher than the ratios 2:1 and 3:1. Moreover, the 1:1 ratio also exhibits a wider range at these high $\eta$ (%), higher than 1%.

A further diffraction grating recording parameter was considered of the effect of changing the recording wavelength ($\lambda$) in order to establish the wavelength at which the emulsion is most photosensitive. Fig. 12 contains $\eta$ (%) as a function of exposure energy for a range of.recording wavelengths. The wavelengths used were $\lambda = 458$, 476 and 488 nm, and by inspection it was established

Table 4
Frequency and period of the record grating

| Concentration rosin and BTB | Interference angle | Frequency (l/mm) | Period $\mu$ | Intensity reason between beams |
|---|---|---|---|---|
| 60:1 | 5° | 190 | 5.2 | 1:1 |
| 60:1 | 10° | 380 | 2.6 | 1:1 |
| 60:1 | 15° | 570 | 1.75 | 1:1 |
| 60:1 | 20° | 758 | 1.3 | 1:1 |
| 60:1 | 25° | 945 | 1 | 1:1 |
| 60:1 | 30° | 1130 | 0.8 | 1:1 |

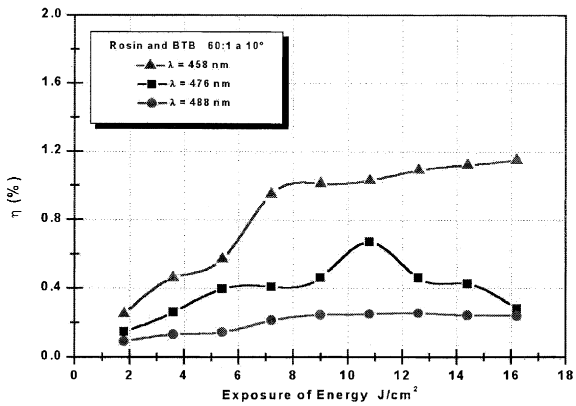


Fig. 12. Diffraction efficiency versus exposure energy, influence of color ($\lambda$). Diffraction grating record with the next wavelength $\lambda = 457$, 476 and 488 nm where the material in the blue color $\lambda = 457$ nm is more photosensitive.

that the most photosensitive wavelength was $\lambda = 458$ by a ratio of $\eta$ (%) almost four times higher than the efficiency obtained at $\lambda = 476$ and 488 nm. Furthermore, the range was much wider for a diffraction efficiency $\eta$ (%) higher than 1% and therefore the lower wavelength of $\lambda = 458$ nm was chosen as the most suitable.

Next, a curve of $\eta$ (%) as a function development time is shown, where eight diffraction gratings were recorded for the same length of time, using the same interference angle and at the same emulsion concentration, varying only development time, increasing said development time in steps of 4 s. This curve is shown in Fig. 13, which shows an interesting peak at a development time of 24 s, at which point there is a sharp increase in diffraction efficiency reaching almost 0.25%, while at all other development times the efficiency is comparable and rather low at under 0.05%. Therefore, the optimum development time is 24 s [10].

Fig. 14 shows a photograph of the diffraction pattern due to a sinusoidal grating, produced using the proposed material, where the three diffraction orders, that in the centre is the zero diffraction order, while either side of it the +1 and −1 diffraction orders can be clearly seen. This grating was recorded with a $\theta = 20°$ and a frequency of 760 l/mm, where the $\eta$ (%) corresponds to one of the higher efficiencies obtained at 2.76%, for a concentration of resin to BTB of 60:1.

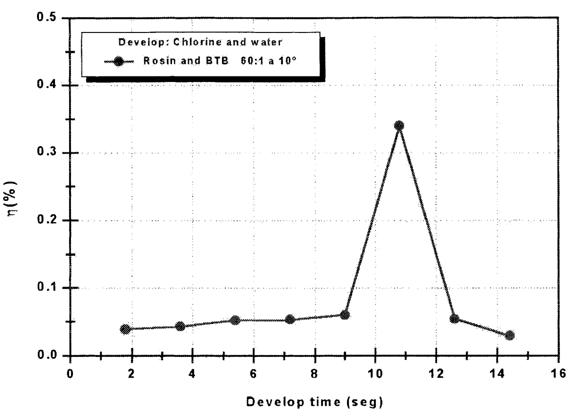


Fig. 13. Diffraction efficiency versus develop time, which one have peak significant, where your $\eta$ (%) increase very high, that correspond develop time at 24 s.

Fig. 14. Diffraction efficiency pattern of the grating of BTB and rosin, with 60:1 concentration and with 2.76% of $\eta$ showing the 0, +1 and −1 orders.

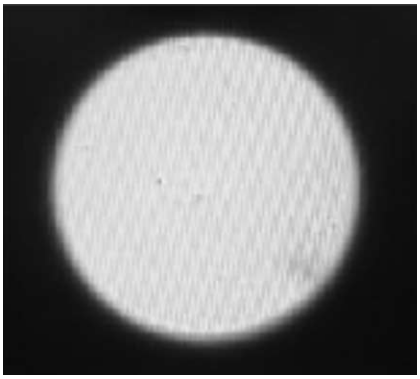

Fig. 15. Diffraction efficiency 400 times amplification showing in the emulsion uniformity grid.

Finally, a photograph is shown in Fig. 15 of a diffraction grating recorded using this emulsion with a magnification of ×600, taken using a Carolina BM-200 microscope, where the dark and bright fringes can be clearly seen with a resolution of approximately 760 lines/mm.

## 4. Conclusions

An analysis of the behaviours of a new photosensitive emulsion was carried out, where the following parameters were investigated such as concentration of rosin and BTB, where the optimum ratio was established to be 60:1. This behaviour shows that as the amount of BTB is increased the photosensitivity does not increase correspondingly, as a molecular equilibrium must exist between BTB and the resin to be able to achieve the optimum concentration. The variation of interference angle between the beams yielded a characteristic behaviour and the resolution of this material, with the maximum resolution being 1100 lines/mm.

Changing the intensity ratio between the recording beams shows a phase modulation of the grating, which alters the diffraction efficiency $\eta$ (%). Using recording wavelengths of $\lambda = 458$, 476 and 488 nm to record diffraction gratings, it was found that the material was most sensitive towards the UV region of the spectrum, so the 458 nm line of the laser was employed, which had a low absorbance factor, and so high energies were used to record the diffraction holographic gratings. The emulsion composed of BTB and rosin was therefore shown to be available photosensitive material. These emulsions show rather low diffraction efficiencies of 3.5% on average at most. However, this material is of the order of only a quarter of the price of conventional materials, it needs only chlorinated water for 24 s as a developing stage, and needs no fixing stage in the development process.

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## References

[1] The Merck Index, 12th ed., Whitehouse Station USA, NJ, 1996, p. 236.
[2] J.B. Puschett, B.S. Rao, Indicator characteristics of bromothymol blue derivatives, Talanta 38 (3) (1991) 335.
[3] G.P. Gorbenko, Bromothymol blue as a probe for structural changes of model membranes induced by hemoglobin, Biochim. Biophys. Acta 1370 (1998) 107.
[4] P.T. Sotomayor, I.M. Raimundo Jr., G. de Oliveira Neto, W.A. de Oliveira, Evaluation of fibre optical chemical sensor for flow analysis systems, Sensor Actuators B 51 (1998) 382.
[5] A.M. Scheggi, F. Baldini, pH sensing by fibre optics, Opt. Acta 33 (12) (1986) 1587.
[6] J. Louis-Marignier, M. Miñana, Decuverte de L'invention par niepce et daguerre, procédé photographique a base de colophane, Le Photographe 1524 (1995) 36.
[7] D. Luna-Moreno, A. Olivares-Pérez, L.R. Berriel-Valdos, F. Osorio-Moreno, Rosin resin with crystal violet tint, Opt. Mater. 11 (1998) 95.
[8] J.C. Ibarra-Torres, A. Olivares-Pérez, M. Ortiz-Gutierrez, M. Pérez-Cortes, D. Iturbe-castillo, Holographic materials composed by rosin with ammonium dichromate, Proc. SPIE 3956 (2000) 397.
[9] J. Ibarra-Torres, A. Olivares-Pérez, Holographic material film composed by rosin with phenol red, Proc. SPIE 4296 (2001) 347.
[10] J. Ibarra-Torres, A. Olivares-Pérez, T.J. Ibarra, D. Luna-Moreno;, Rosin with bromophenol blue dye as holographic material, Opt. Mater. 16 (2001) 389.
[11] L.G. Wade Jr., Química Orgánica, second ed., Prentice-Hall, Hispanoamericana, SA, 1993, p. 708.
[12] K.J. Leidler, J.H. Meiser, Fisicoquímica, second ed., Compañía Edit, Continental, SA de CV, 1997, p. 586.
[13] J. Collier, B. Burckhardt, H. Lin, Optical Holography, Academic Press, Inc LTD, 1971, p. 280.
[14] H. Maron, F. Prutton, Fundamentos de Fisicoquímica, Edit. Limusa, 1972, p. 269, 626.