Methylene-blue-sensitized gelatin holograms

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Like dichromated gelatin (DCG), methylene-blue-sensitized gelatin (MBG) is also a potential holographic recording material[1,2] and can be used in forming a hologram with a high diffraction efficiency (DE) and high signal-to-noise ratio (SNR). The addition of methylene blue (MB) into a gelatin or DCG film renders it effective to record holograms with red light from an inexpensive He–Ne laser, which is the laser most readily available. Two decades of research and development since the first proposal of the use of MB by A. Graube[3] has firmly established its status in holographic recording materials, especially when tetramethylguanidine (TMG), used as an efficient electron donor for its improved photosensitivity, was found by J. Blyth.[4] Solano *et al.*[5] first used a simple postprocessing method in which only MB was added in the fabrication of the gelatin film. In this case, the limited solubility of MB in the presence of the dichromate ion (in DCG) is avoided. Nevertheless, the exposed plate must first be bathed in a dichromate solution and then developed in water and isopropanol so that a permanent phase grating with a high DE can be obtained.

To determine whether the conditions of bathing the plate in a dichromate solution are absolutely necessary, we investigated the effects of different ammonium dichromate concentrations in the film bathing solutions on the DE of the transmission hologram in this Note. The MBG films are fabricated with a method like the one suggested by Solano *et al.*[5] The obtained gelatin film, of a 20 μm thickness, is soaked in a solution of F-5a fixer (the method of fabrication of our fixer is listed in Table 1) for 5 min so as to preharden it. Then the films are soaked in sensitizing solutions with different concentrations of MB dye. Some transmission gratings are recorded on the films by the use of different exposure intensities. The steps of the development method are listed in Table 2.

The spatial frequency is ~1070 lines/mm, the maximum DE of the film appears at a MB concentration of 0.009% and an exposure intensity of ~150 mJ/cm^2, while the relative humidity (RH) is 55% and the concentration of the ammonium dichromate solution is 5%, as shown in Fig. 1. This behavior is quite similar to that obtained by Changkakoti and Pappu,[6] but the MB concentration is somewhat lower.

A moderate temperature of 43 °C, which is lower than the one used by Capolla and Lessard,[7] is adopted for our study. It has been found that the DE of the grating will reach an optimum value of up to 97% at a 5% concentration of dichromate solution but will still retain a moderate value (35%) when no ammonium dichromate is used in the course of postprocessing for the exposed film, as shown in Fig. 2. Here (see Fig. 2), the definition of the DE is the same as the one used in Ref. 8.

Capolla and Lessard[7] discussed the photochemical mechanism of forming a hologram in MBG film. They suggested that the exposing process should be carried out in an inert atmosphere to avoid reoxidation of leuco-MB formed during exposure, which is harmful to the production of a superior grating with a high DE. In fact, the lifetime of leuco-MB depends on the RH of the ambient atmosphere. The speed of reoxidation of leuco-MB in a humid air is high and that in drier air is slower. The maximum absorption of the leuco-form of the dye has been reported to be approximately 256 nm,[9] although the maximum absorption of MB is found to be approximately 640 nm. If the leuco-MB is reoxidated to MB, the transmittance of the plate in response to light of 632.8 nm will decrease. Figure 3 shows that the transmittance decreases more rapidly in humid air (RH > 70%) than it does in drier air. Calixto and Lessard[10] have shown that it is possible to maximize the DE of the film in a normal atmosphere by controlling the RH at the recording time in a real-time holographic configuration, whereas in our experiment it has been found that leuco-MB will effectively play its role in producing a better refractive-index modulation in the exposed film as long as the RH can be kept within a certain range (RH = 45%~65%), which is somewhat different from the one reported in Ref. 10.

After exposure, if the film is immediately dipped in an ammonium dichromate solution, thus causing a change of valence of the chromium ions, the reoxida-

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Table 1. Mixture Method for Fixer F-5a

Fixer Compound and Action	Amount
Water: heat to 50 °C	600 mL
Sodium sulfite Na_2SO_3 (anhydrous A.R.[a]): add	75 gm
Acetic acid CH_3COOH (28%): add	235 gm
Boric acid H_3BO_3: add	37.5 gm
Aluminum potassium sulfate $KAl(SO_4) \cdot 12H_2O$: add	75 gm
Water: add to make final volume of	1000 mL

[a]A.R., analytical reagent.

tion of the leuco-MB with the oxygen in atmosphere can be effectively stopped. It is recognized that the Cr^{3+} ions produced during this step will cross link the gelatin molecules. However, this common mechanism cannot completely explain our experimental results. It should be noted that a moderate DE of 35% is obtained under conditions of nondichromated postprocessing. Something else is found in samples made by the deposition of the gelatin on an IR-transmissive material (such as a Ge plate). The IR spectrum of sensitized and exposed film with dichromated postprocessing is quite similar to that of such films without dichromated postprocessing, but both of them differ from the spectrum of a pure gelatin film, as shown in Fig. 4.

Table 2. Steps in the Development Method of a MBG-Film Exposed Plate

Step	Procedure
1	Dip plate in a 0~5% aqueous solution of ammonium dichromate for 5 min.
2	Store plate for 18 h in darkness.
3	Dip plate in water with a temperature of 43 °C until water runs clear to wash out any unexposed MB.
4	Dip plate in a mixture of 70% isopropanol and 30% water for 2 min.
5	Dip plate in a mixture of 90% isopropanol and 10% water for 2 min.
6	Dip plate in 100% isopropanol for 3 min.
7	Dry plate in hot air flow for 1 min.

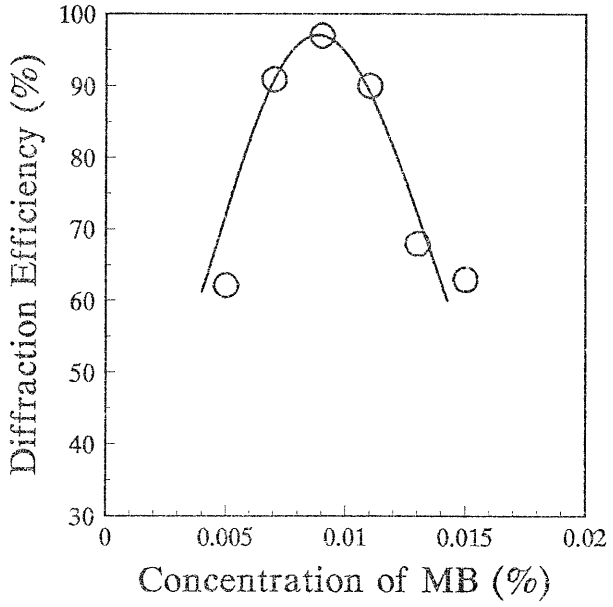

Fig. 1. Plot of the diffraction efficiency (DE) versus the concentration of MB. Experimental conditions: RH of 55%, exposure of 150 mJ/cm^2, and ammonium dichromate concentration of 5%.

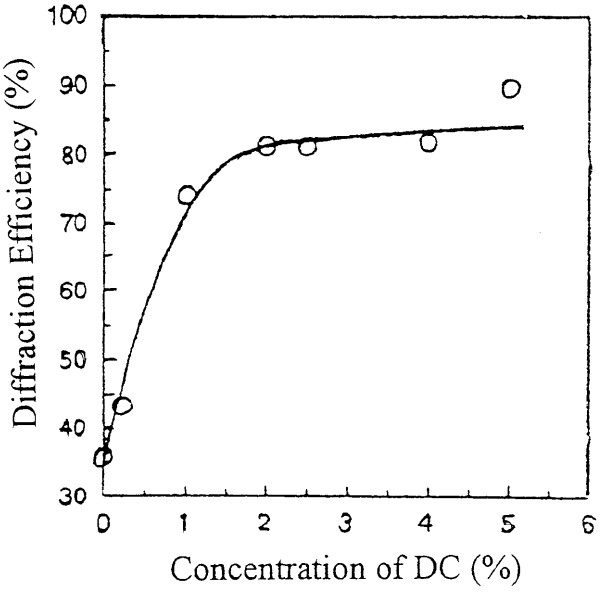

Fig. 2. Diffraction efficiency (DE) plotted versus the concentration of dichromate (DC). Experimental conditions: RH of 50% and MB concentration of 0.009%.

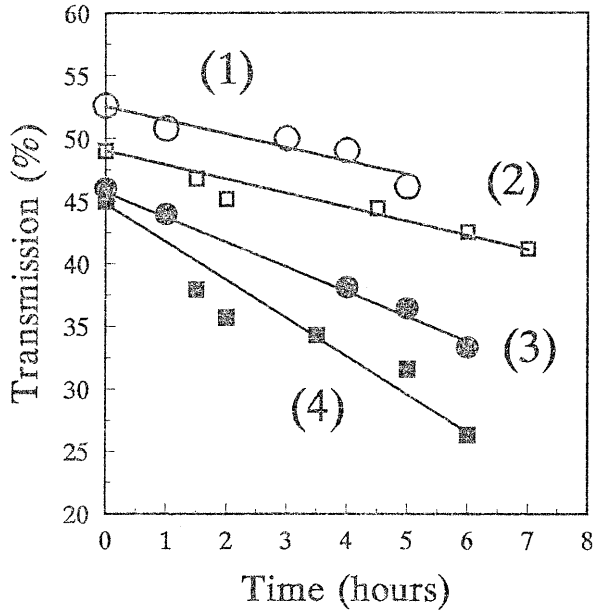

Fig. 3. Transmittance of an exposed MBG plate versus time with differing RH levels: the open circles represent a RH of 40% (curve 1); the open squares, a RH of 50% (curve 2); the filled circles, a RH of 60% (curve 3); and the filled squares, a RH of 70% (curve 4). Exposure intensity: 170 mJ/cm^2; MB concentration: 0.01%. The numbers in parentheses represent the RH: (1) RH: 40%; (2) RH: 50%; (3) RH: 60%; (4) RH: 70%.

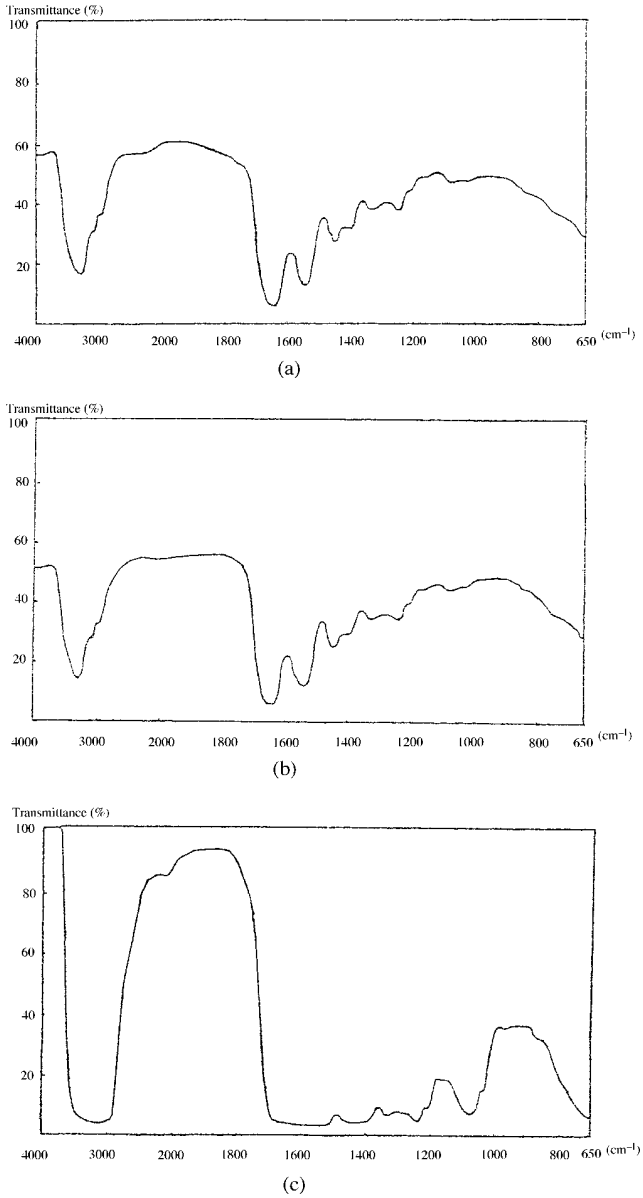

Fig. 4. The IR spectra of exposed gelatin films: (a) a MB-sensitized gelatin film with dichromated processing, (b) a MB-sensitized gelatin film without dichromated processing, and (c) a pure gelatin film.

It is clear that the characteristics of the Cr^{3+} ligands do not appear. This means that the quantity of Cr^{3+} ligands is too small to measure, even if it exists in the processed films. Nevertheless, the IR spectra of exposed films both with and without dichromate processing are different from those of the pure gelatin film. The increased relative absorption of ν_{NH} and δ_{NH}, where the subscript NH represents a functional group, around 3300, 1650, and 1550 cm^{-1} implies that some big molecules may form, and the increased relative absorption around 1450 cm^{-1} implies that some functional groups containing S may appear.

A comparison of the UV spectra of a pure gelatin film processed with and without a dichromate solution shows that the absorption in the UV and visible spectra of the exposed plates appears as a gradually ascended broad

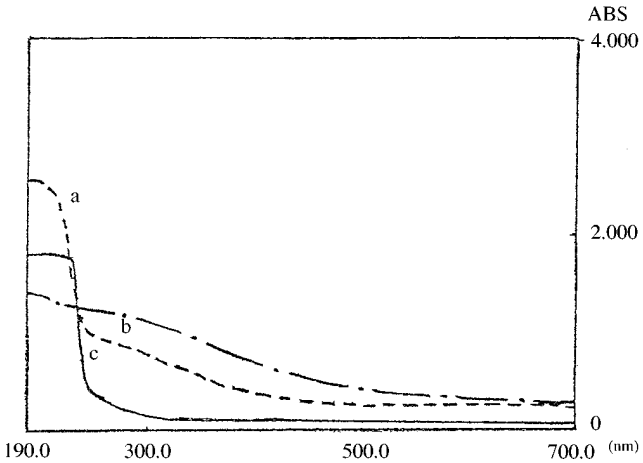

Fig. 5. UV and visible spectra of exposed gelatin films: curve a shows a MB-sensitized gelatin film with dichromated processing, curve b shows a MB-sensitized gelatin film without dichromated processing, and curve c shows a pure gelatin film.

band below 400 nm (Fig. 5), which indicates that the molecular structure of the processed gelatin film has truly changed. This behavior is also different from that obtained by Sjölinder,[11] in which the 372-nm absorption in the UV spectrum is an obvious mark of the Cr^{3+} ligand formed in the exposed DCG film.

The similarity in the spectra of the MB-sensitized plates after exposure with and without dichromated postprocessing might mean that the final molecular structures of the films are quite similar, although their intermediate chemical steps are somewhat different. As for plates sensitized with MB only after nondichromated processing has taken place, it is possible to bond the MB molecules, especially in place of S^+ and N^+, with the gelatin molecules, as the gelatin itself is an electron donor.

Judging from the results described above, to explain completely the mechanism of formation of the interference pattern in MBG film, we see that more research needs to be done to determine exactly what happens during the fabrication of the hologram within it.

References

1. T. Kubota, T. Ose, M. Sasaki, and K. Honda, "Hologram formation with red light in methylene blue sensitized dichromated gelatin," Appl. Opt. **15,** 556–558 (1976).
2. B. J. Chang and D. C. Leonard, "Dichromated gelatin for the fabrication of holographic optical elements," Appl. Opt. **18,** 2407–2417 (1979).
3. A. Graube, "Holograms recorded with red light in dye-sensitized dichromated gelatin," Opt. Commun. **8,** 251–253 (1973).
4. J. Blyth, "Methylene blue sensitized dichromated gelatin holograms: a new electron donor for their improved photosensitivity," Appl. Opt. **30,** 1598–1602 (1991).
5. C. Solano, R. A. Lessard, and P. C. Roberge, "Methylene-blue-sensitized gelatin as a photosensitive medium for conventional and polarizing holography," Appl. Opt. **26,** 1989–1996 (1987).
6. R. Changkakoti and S. V. Pappu, "Towards optimum diffraction efficiency for methylene-blue-sensitized dichromated gelatin holograms," Opt. Laser Technol. **21,** 259–263 (1989).

7. N. Capolla and R. A. Lessard, "Processing of holograms recorded in methylene-blue-sensitized gelatin," Appl. Opt. **27,** 3008–3012 (1988).
8. N. J. Phillips, A. A. Ward, R. Cullen, and D. Porter, "Advance in holographic bleaches," Photogr. Sci. Eng. **24,** 120–124 (1980).
9. H. Obata, "Photoreduction of methylene blue by visible light in the aqueous solutions containing certain kinds of inorganic salts: two photobleached products," Bull. Chem. Soc. Jpn. **34,** 1057–1063 (1961).
10. S. Calixto and R. A. Lessard, "Diffraction efficiency improvement of undeveloped dichromated gelatin gratings," Appl. Opt. **24,** 317–318 (1985).
11. S. Sjölinder, "DCG and the mechanism of hologram formation," Photogr. Sci. Eng. **25,** 112–118 (1981).