Anomalous D-Log E curve with high contrast developer Kodak D8 on ultra fine grain emulsion BB640

M. Ulibarrena, M. J. Méndez, S. Blaya, A. Fimia

Universidad Miguel Hernández de Elche, Departamento de Ciencia y Tecnología de Materiales, Avda. Ferrocarril s/n, 03202 Elche (Alicante), Spain

m.ulibarrena@umh.es

Abstract: D-Log E curves, also known as H-D curves, are used since the XIX century as a tool for describing the characteristics of silver halide emulsions. This curve has a very standard shape, with a linear region, a toe, a shoulder and a solarization region. In this work we present a distortion of the usual curve due to the action of a high contrast developer, Kodak D8, on an ultra fine grain emulsion, BB640.[1] The solarization effect is replaced by a linear zone where developed densities increase with increasing exposures, until all silver halide present in the emulsion is reduced by developer D8 to metallic silver. Densities higher than 11 have been obtained.

OCIS codes: (090.0090) Holography; (090.2900) Holographic recording materials

References and links

1. Plates type BB640 and BB520, formerly manufactured by HRTgmbh of Germany, are currently manufactured by Colourholographics Ltd of England (colourholographics@btinternet.com). Although the results shown in this paper have been obtained with HRT plates, tests with Colourholographics plates have been recently performed and results are very close to those presented, specially regarding the anomalous D-LogE curve and the high density values achieved this paper deals with.
2. F. Hurter and V. C. Driffield, "Photo-chemical investigations and a new method of the sensitiveness of photographic plates," J. Soc. Chem. Ind. 455–469 (1890).
3. C. E. K. Mees and T. H. James, "*The Theory of the Photographic Process*" (The Macmillan Company, New York, 1966).
4. J. C. Dainty and R. Shaw, "*Image Science*" (Academic Press, London, 1974).
5. H. I. Bjelkhagen, "*Silver-Halide Recording Materials*" (Springer-Verlag, New York, 1993).
6. Eastman Kodak Company, "Black-and-White Processing Using KODAK Chemicals," 1985.
7. A. Fimia, M. Pardo, J. A. Quintana, "Improvement of image quality in bleached holograms," Appl. Opt. **21**, 3412–3413 (1982).
8. H.Kasprzak and N. Sultanova and H. Podbielska, "Nonlinear effects of the recording material on the image quality of a Fourier hologram," J. Opt. Soc. Am. A **4**, 843–846 (1987).
9. S. Blaya, L. Carretero, R. F. Madrigal and A. Fimia, H. S. Nalwa editor, "*Handbook of advanced electronic and photonic materials and devices*", vol. 7, "Photosensitive materials for holographic recording," Academic Press, San Diego (2001).
10. R. Birenheide, "BB emulsion series: current standings and future developments," Proc. SPIE, 3358, 28–30, (1997).
11. http://www.Slavich.ru
12. http://perso.wanadoo.fr/holographie/GB/index.html
13. J. M. Kim, B. S. Choi, S. I. Kim, H. I. Bjelkhagen and N. J. Phillips, "Holographic optical elements recorded in silver halide sensitized gelatin emulsions. Part I. Transmission holographic optical elements," Appl. Opt. **40**, 622–632 (2001).
14. R. L. Lamberts and C. N. Kurtz, "Reversal Bleaching for Low Flare Light in Holograms," Appl. Opt. **10**, 1342–1347, (1971).
15. C. Neipp and I. Pascual and A. Beléndez, "Effects of Overmodulation in Fixation-free Rehalogenating Bleached Holograms," Appl. Opt. **40**, 3402–3408, (2001).

#37577 - $15.00 US
Received November 07, 2001; Revised November 27, 2001

1 Introduction

The way to characterise a photographic emulsion since the early beginnings of the photographic science is the H-D curve,[2] also known as characteristic or D-Log E curve. It gives information about the photographic speed, the image contrast, density (D) and energy (E) ranges of operation. The curve identifies the processed emulsion, so that any H-D curve is related to both the emulsion and its development process. Density is proportional to the amount of metallic reduced silver, this proportionality depending on the silver halide mean grain size, grain size distribution curve, silver halide concentration, sensitizers, and also on the properties of the developer, such as development agents, their concentrations, pH, and other species present in the developing solution.[3] The shape of the curve has as the primary feature the so called linear region, corresponding to a zone where densities are proportional to the logarithm of exposures, defining the *latitude* of the emulsion as the range of exposure energies corresponding to this linear region, and the γ factor as the slope of this linear zone. At high exposure levels, in the solarization region, developers acting in presence of high concentrations of already developed silver start a reversal process, decreasing the population of metallic silver, i.e. the density, changing the sign of the slope of the curve. The curve is drawn from measurements of the transmittance of exposed and developed emulsions, and these data are converted into optical density values.

D-Log E curve has been extensively reviewed.[3–5] Analytic approaches have been proposed[8] in order to be able to mathematically work with it. In fact, the anomaly shown in this paper was found when trying to fit the obtained D-logE curve in the preliminary studies with BB640 emulsions. We found no good fitting for KODAK D8 developer,[6] while for other developers based on Ascorbic Acid or Pyrogallol good results were obtained.

BB640[1] plates characteristics differ from those of former popular discontinued emulsions in so important features as thickness of the layer (between 7 and 9 μm for BB640 against 6 or less μm for Agfa 8E and Ilford and 12 μm for Kodak 649F), mean grain size (20 nm for BB640 against 40 nm of all mentioned emulsions), sensitivity, and hardness of the supporting gelatin.[9,10] We assume that the mentioned differences between new and discontinued emulsions lead to the results shown in this paper. These results were not found for those popular well studied cited discontinued emulsions in all the years they were used for holographic applications or as high resolution photographic materials. At the moment we have not tested these processes for other currently available holographic materials, as Slavich PFG and VRP emulsions[11] or the newly emergent material Ultimate.[12] A saturation effect has been reported with Slavich VRP emulsions, but reaching a top density of 6, after which the expected solarization region appears.[13]

Although D8 is not a common developer for holographic applications, it has been used in the past with Agfa plates.[7] We have tested it in order to improve the sensitivity of BB640 plates, and in fact this result was achieved, decreasing the typical value of several hundreds of $\mu J/cm^2$ for reference developers AAC and D19, to less than a hundred $\mu J/cm^2$. Further works with this very high contrast and highly concentrated developer resulted in the anomalous D-Log E curve and in the very high density values over 11.3. We have tested BB640 plates developed with D8 in different holographic recording setups and we have post-processed (fixed and/or bleached) the developed plates in order to get information about the photographic process that has taken place. D-Log E curves have been studied with an average of 30 points in the whole range of energies, in order to clearly observe the anomaly.

#37577 - $15.00 US
Received November 07, 2001; Revised November 27, 2001

2 Experimental

Except for the single beam experience, BB640 plates studied in this work were used for recording holographic unslanted gratings with different spatial frequencies with a p polarised He-Ne laser($\lambda = 633nm$). 1200 lp/mm gratings were recorded in a symmetrical layout with two collimated laser beams at an angle of 22.3^o to the plate normal. 4990 lp/mm reflection gratings were recorded with a Denisiuk (or Lippmann Bragg) layout with an incident single laser beam on the plate and with a mirror optically matched with index matching fluid (Xylene) at the back. Beam ratio of holographic exposures was 1:1 and exposure beams power was about 350 $\mu W/cm^2$ each.

Densities where calculated from transmission measurements taken with a solid state detector ranged from milliwatts to tenths of picowats. The probe beam was a slowly expanded laser beam with an intensity higher than 20 mW/cm^2. With this configuration we cannot measure transmission values corresponding to densities higher than 11.3, so all graphics will show that limit. Transmissions values of 0.0 pW/cm^2 have been measured, pointing towards higher densities out of the detector limits. Diffraction efficiency (DE) measurements of the bleached recordings were made using a collimated He-Ne laser beam at the grating Bragg angle. Detectors were placed 50 cm away from the plate in order to avoid scattering signal on the detector as to obtain indirect information on hologram quality. All experimental values were corrected for reflection losses with both experimental measurements and Fresnel formulae calculations.

A set of tests were done in order to study the effect. For all developers, developing time was 4 minutes at 20^0C, following by non-hardening fixing bath KODAK F-24[6] for 5 minutes. Hydroquinone based developers KODAK D19[6] and D8 were used. A test with a developer with the same composition and pH as D8 but with half concentration of hydroquinone was done. A reference test with AAC (Ascorbic Acid 18 gr/l + Sodium Carbonate 60 gr/l) developed plates (4 minutes at 20^0C) was done to show a good fitting of a standard D-Log E curve.

Holographic gratings developed with D8 and fixed with F24 were bleached at 20^0C with two different bleaches. The first one consists of Potassium Ferricianide rehalogenating bleach (direct bleach[5]) (Potassium Ferricianide 8g/l + Potassium Bromide 7g/l), that reacts with metallic silver resulting in a new silver halide crystal, and the second one was solvent bleach KODAK R9[6] (fixation-free), that acts by dissolving the metallic silver, leaving the unexposed silver halide in the emulsions.[14] The holographic reflection grating was bleached after the fixing bath with the Potassium Ferricianide rehalogenating bleach. Bleaching times depended on the time required for total bleaching of the maximum density spot of the plate, exceeded by 2 minutes to assure completed process. Both bleaching procedures will provide information about the nature of the processes that take place in the development step.

3 Results and discussion

Figure 1 shows clearly the anomaly in the D-Log E curve, both when developing the emulsion with D8 and with D8 with half concentration of hydroquinone. Compared to plates developed with AAC, a typical developer commonly used with fine grain holographic emulsions, it is remarkable the higher slope and sensitivity obtained with D8 in the first linear zone, where it reaches a density higher than 7, similar to the peak density obtained with AAC. After the linear zone the solarization region is expected, and this is true for AAC developer. D8 does not show reversal region, but a continuously increasing density with increasing exposure up to our detection limits, corresponding to a density of 11.3. The shape of this region approaches a linear shape, with an average linear zone slope much lower than the first one. Half-hydroquinone concentrated D8 shows a lower

#37577 - $15.00 US
Received November 07, 2001; Revised November 27, 2001

sensitivity than D8, as expected, but with the same shape and with density reaching the detection limit of 11.3. Except for the case of AAC, where a D-Log E fitting has been calculated, experimental points are connected with straight lines for clarity. D-Log E curve for AAC processing was fitted with a modified version of an approximation based on the Fermi formula for electron energy distribution.[8] The resulting expression is given by:

$$D = 0.15 + \frac{8}{1 + \exp(-13.2 + 3.1 \log E) + \exp(10.8 - 4.3 \log E)} \tag{1}$$

where 0.15 is the experimental fog density and the regression coefficient r^2 is 0.996.

In order to evaluate the influence of the recorded interferometric pattern in the anomaly, the material was exposed to different recording setups and then developed with D8. Figure 2 shows the obtained results. Single beam exposure corresponds to a non holographic setup, the transmission grating with 1200 lp/mm frequency is the same curve shown in Figure 1, and the 4990 lp/mm frequency corresponds to the formerly described holographic reflection recording setup. All recording setups reached the limit density of 11.3. Although the anomaly is most noticeable for the 1200 lp/mm recording curve, the pure (non holographic) D-Log E curve also shows it clearly. The higher spatial frequency recording hardly shows the anomaly at all. All recording setups reached the limit density of 11.3.

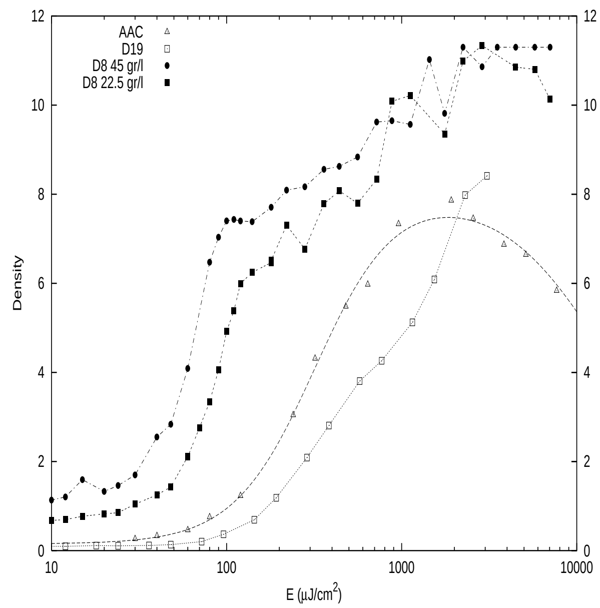

Fig. 1. D-Log E curves of BB640 plates processed with developers AAC (Δ), D19 (□), D8 (●) and D8 with half concentration of hydroquinone (■).

Received November 07, 2001; Revised November 27, 2001

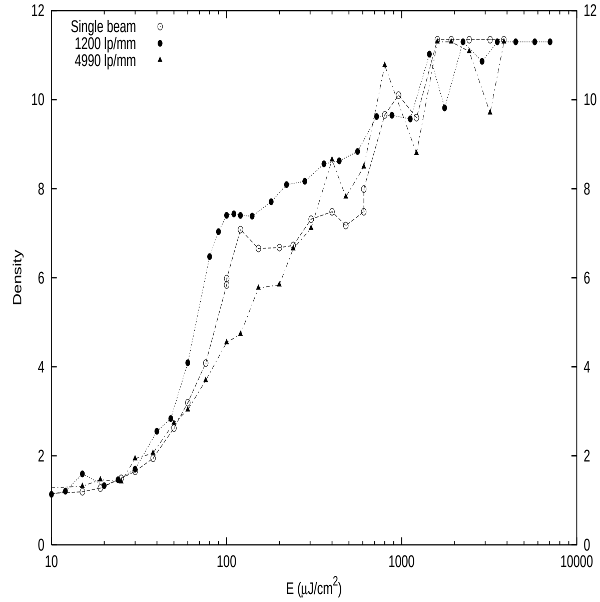

Fig. 2. D-Log E curves of BB640 plates processed with D8 and exposed to single beam (⊙) and holographic setups of spatial frequencies of 1200 lp/mm (●) and 4990 lp/mm (▲).

Figure 3 has the key to the explanation of the anomaly. In this graph, results from different processing techniques of holographic recordings with a spatial frequency of 1200 lp/mm and developed with D8 are shown. The first remarkable point is the apparent holographic overmodulation effect achieved with the fixing + ferricianide rehalogenating bleaching process (direct bleaching). We name it *apparent holographic overmodulation* since we find two maximum DE values separated by a low DE zone. An overmodulation effect has been recently reported with these emulsions but with a totally different processing and analysis scheme.[15] The second, the high DE value obtained with reversal bleach R9. The third, the high DE obtained with a non-fixed ferricianide rehalogenating bleaching process. The fourth, the fact that reversal bleach acts at energy values where rehalogenating shows low DE and very high scattering. All these facts explain the anomaly in the following way.

The first maximum of the direct bleach DE-E curve is in the energy range of the first linear zone of the D-Log E curve, as expected. In the following region, corresponding to the beginning of the lower slope region, high scattering and low DE appears, while reversal bleach gets its higher DE results. In this second region we have a relatively high concentration of well localised silver halide grains, that render a clean and efficient reversal diffraction grating, while metallic silver is randomly dispersed around the exposed areas with a deformation of the recorded sinusoidal profile, resulting in noisy gratings when processed with a direct bleaching process. This behaviour is similar to what has been reported in the literature as adjacency or edge effect[4] that takes place with high pH developers, as is the case of D8. In this study we are working with ultra fine grain emulsions whose mean grain size is 20 nm, so that we assume that at higher exposure energies adjacency effect occurs simultaneously with some silver diffusion from unexposed to exposed areas inside the emulsion.

#37577 - $15.00 US
Received November 07, 2001; Revised November 27, 2001

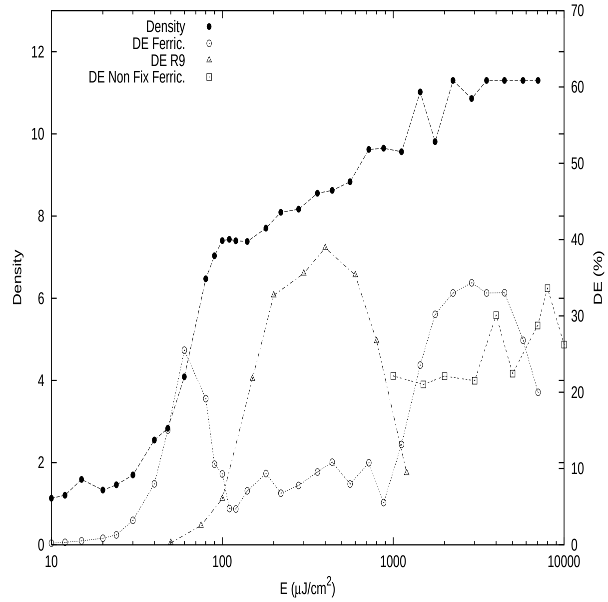

Fig. 3. BB640 plates exposed holographically with a spatial frequency of 1200 lp/mm and processed with D8. D-Log E curve (•) is related with DE of direct bleached plate (⊙), DE of reversal bleached plate (Δ) and DE of non fix direct bleached plate (□).

With this mechanism we arrive at the zone with exposure levels higher than 1 mJ/cm^2, where solvent bleaching grating DE decreases to zero (there is no more unexposed silver halide crystals left in the emulsion) and there is a new maximum of DE for the direct bleaching process, so some reordering of the profiles occurs. The relatively low DE peak obtained with the direct process results from the high tanning of the gelatin with oxidation products from the development process. Another experimental result is that a spectral study of direct bleached reflection gratings showed no shrinkage in the layer, although this is expected when a fixing step, that removes undeveloped silver halide crystals, is performed. Furthermore, the corresponding curve shown in Figure 3, with DE data measured from a plate processed with a fixation free ferricianide bleach, results in DE values quite close to those of the fixed plate. In this point we can conclude that we are using the whole silver population present in the emulsion, a fact that is backed with the low scattering value obtained. So that plates developed with D8 at this high exposure levels work as if the developer converts all exposed silver halide to metallic silver but also acts as a kind of fixer, removing all silver halide from the unexposed regions of the recording by diffusing these crystals towards exposed regions, where they are later developed, resulting in the very high densities observed.

4 Conclusions

We have studied a D-Log E curve whose shape differs substantially from the standard one. The most remarkable performance is that there is no solarization region, and that density grows continuously with exposure energy, reaching density values higher than 11.3. This result may be of use for photolithographic applications of BB640 plates. Studies of the holographic performance of the material have shown an apparent overmodulation effect with a high second DE maximum. An approach to the mechanism that explains these effects based on holographic results has been stated.

#37577 - $15.00 US Received November 07, 2001; Revised November 27, 2001

Acknowledgements

This work received financial support from CICYT project MAT-99-0622.