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Rapid Conical–Helical Perturbation in Doped Cholesteric Liquid Crystals†

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Abstract—Response times for conical–helical perturbation of ternary mixtures of cholesteric compounds were measured. It was found that by adding 5–30% of MBBA (*p*-methoxybenzylidenebutylaniline) to the mixture, a blue shift and bandwidth broadening in the transmission spectra occur. The response time is reduced by a factor of four and the intensity ratio is increased by a factor of seven, accompanied by a wavelength shift towards the blue. By increasing the percentage of MBBA from 30 to 50% the blue mixture is shifted back to red, while the trend of bandwidth broadening continues. The response time for the first stage is further reduced, but a second response stage with much longer time constants is introduced. Optimum response time and contrast occur at ~30% MBBA

1. Introduction

The internal structure of a cholesteric liquid crystal is determined by intermolecular forces. When one applies an electric field to molecules in such a helical structure, the field acts on the anisotropies of the electric polarizabilities to exert a torque on the system which competes with the intermolecular forces. Expressions have been derived[1,2] for the critical field, applied parallel to the helix axis, needed to cause a cholesteric–nematic transition. Just prior to this field-induced cholesteric–nematic transition, there is an electric field region where one observes a tightening-up of the helical structure. This process is referred to as " conical–helical perturbation ".[3] In previous work, Harper[4] measured the response and relaxation times for this process in some cholesteric mixtures which show vivid reflection colors at room temperature. Recently, Kahn[5] reported on some changes in passive electro-optic properties of cholesterics by doping

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them with MBBA. In this work, it is reported that improved response times and intensity ratios for conical–helical perturbation are observed in doped cholesterics.

2. Experimental

Measurements were performed with the basic ternary cholesteric mixture made of: cholesteryl chloride (CC) 1.1 parts; cholesteryl nonanoate (CN) 0.9 parts; and cholesteryl oleyl carbonate (COC) 2 parts, by weight. This makes a cholesteric liquid crystal which, when illuminated with white light, will scatter (reflect) vivid color in the visible range; color and intensity depend on the angles of illumination and scattering.[6] This liquid crystal is stable in a wide range (16 °C–44 °C) around room temperature.[7]

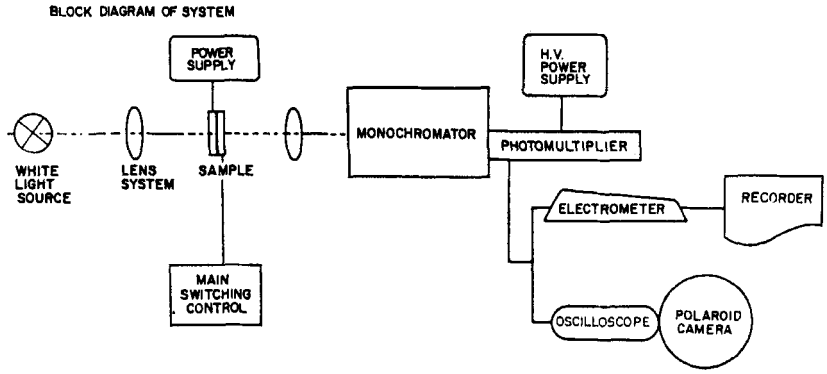

Figure 1. Block diagram of the experimental arrangement.

Eight samples were prepared by adding 5, 10, 15, 20, 25, 30, 40 and 50% MBBA to the cholesteric liquid crystal. A thin layer of each mixture was placed between two transparent conductive glasses (tin oxide coated) and a Mylar spacer (5μ thick) forming a sandwich cell (8–10μ thick). A white tungsten light source and an optical lens system were used to illuminate the sample with a parallel beam.

Figure 1 shows the block diagram of the experimental arrangement. The intensity of scattered or transmitted light for different wavelengths was measured through a Bausch and Lomb grating scanning monochromator with an RCA 1P21 photomultiplier connected to a Keithley 610B electrometer and a recorder. To measure the time

constants, the photomultiplier was connected to a Tektronix 561B dual trace oscilloscope.

Both transmission and reflection measurements were performed. In the former, the sample acts as an optical filter between the light source and the monochromator; in the latter, the sample was illuminated at an angle of 45° and observed from the same side in a direction normal to the surface. Time constants for the same sample for both transmission and reflection measurements were similar.

3. Results

Doping

The relative transmission spectra of the CC-CN-COC cholesteric liquid crystal mixture is characterized by a peak at 6200 Å and a half-bandwidth of 200 Å. By doping the cholesteric liquid crystal with nematic MBBA, the peak is gradually shifted towards the blue. The shift is accompanied by broadening of the bandwidth. For 30% MBBA doping, the peak is at 5300 Å and the half-bandwidth is 420 Å. When the percentage of MBBA is further increased, the direction of the shift is reversed, while the bandwidth broadening continues: for 40% MBBA doping the peak is at 5550 Å and the half-bandwidth is 490 Å; for 50% MBBA the peak is at 6250 Å and the half-bandwidth is 520 Å. Higher doping moves the peak to the IR range. Figure 2 demonstrates these spectral changes. Curve (a) of Fig. 3 shows the peak-wavelength dependence on percentage of MBBA before any electric field is applied.

Circular dichroism is a characteristic optical property of the helical structure in cholesteric liquid crystals. For an optically thick crystal (thickness $\gg \lambda$) and a range of wavelength centered about $\lambda = pn$, where λ is the optical wavelength in air, p is the helical pitch and n is the average index of refraction, the width $\Delta\lambda$ of the total reflection band is given by:[8]

$$\Delta\lambda = 2[(n_o - n_e)/n]\lambda = 2(\Delta n/n)\lambda$$

where n_o and n_e are the ordinary and extraordinary indices of refraction, respectively.

For molecules which are cholesterol derivatives, the lower limit value for $2\Delta n/n$ is ~ 0.03, and for molecules with a general structure

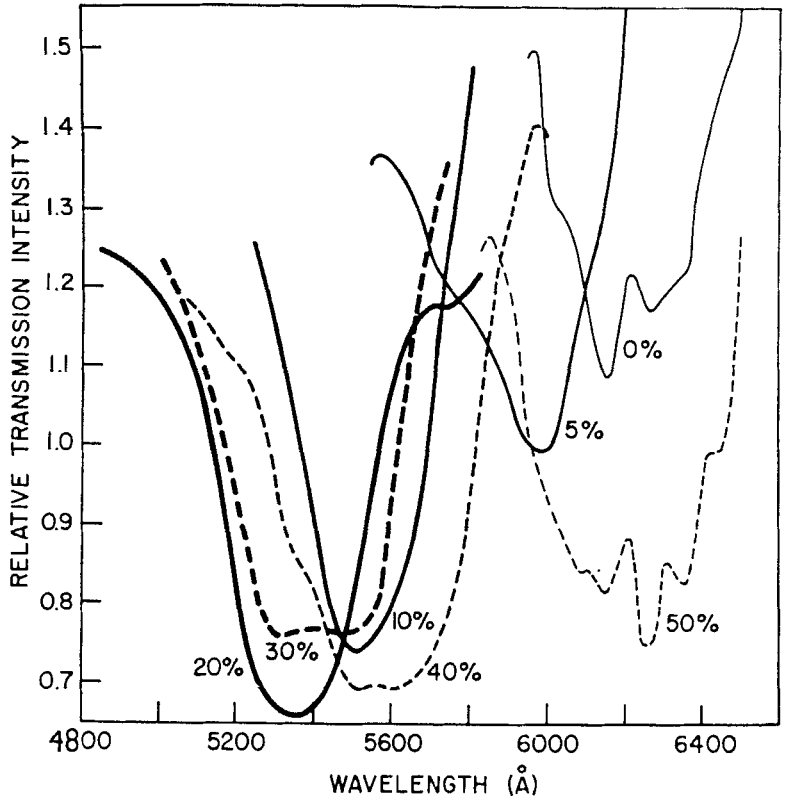

Figure 2. Relative transmission spectra for pure and MBBA doped cholesteric liquid crystals.

similar to MBBA $2\Delta n/n$ is ~ 0.2.[9] As indicated by Kahn,[5] cholesteric liquid crystals which are mixtures of cholesterol derivatives and MBBA may be expected to have values for $\Delta n/n$ intermediate between the values given above. In Fig. 4, the solid line shows the increase of half-bandwidth when the percentage of MBBA is increased and the dotted line shows the dependence of $2(\Delta n/n)$ on percentage of MBBA calculated from experimental values $\Delta\lambda/\lambda$, which actually fit within the range of expected values as indicated above.

Electrical Field

When an electric field of 40 Vdc is applied across a 10μ thick sample (4×10^4 Vcm^{-1}), some changes in intensity and spectral

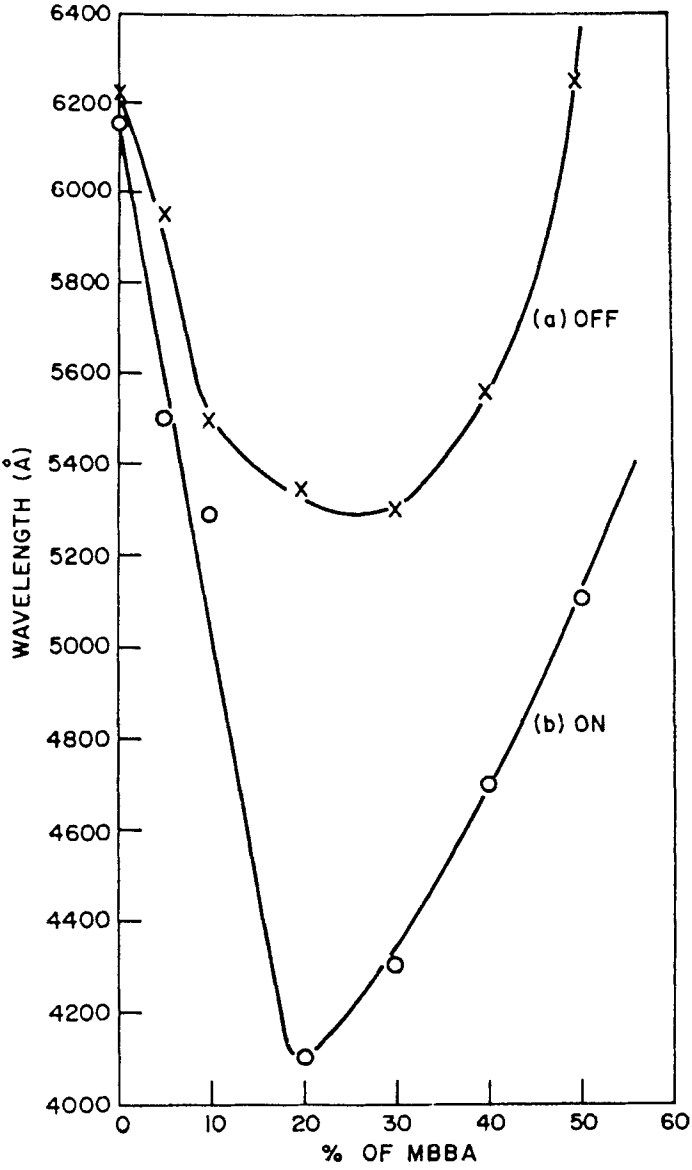

Figure 3. Variation of peak-wavelength with percentage of MBBA: (a) electric field off; (b) electric field on.

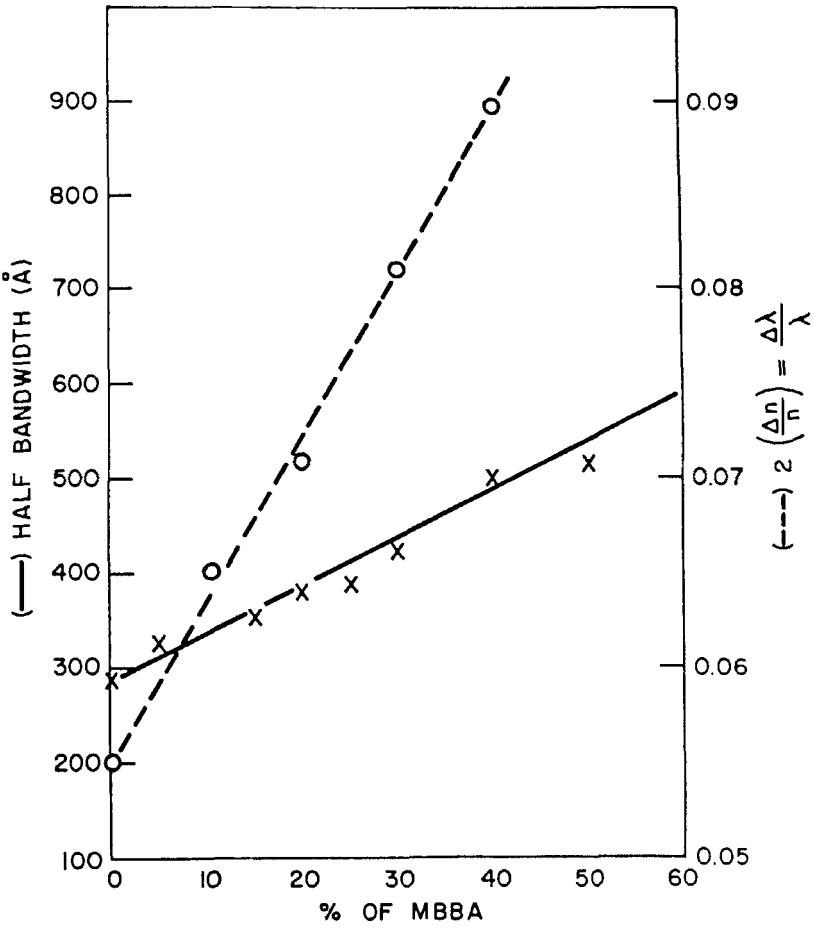

Figure 4. Variation of half-bandwidth and $2(\Delta n/n)$ with percentage of MBBA: ——— half-bandwidth; - - - - $2(\Delta n/n) = \Delta\lambda/\lambda$.

shape of scattered light occur: when this field is applied to the CC-CN-COC mixture, a slight enhancement in the green and quenching in the red is seen. In other words, some shift towards the blue occurs indicating tightening of the helical structure. Higher fields will make this change more pronounced.[4] When this same field is applied to the doped samples, the whole spectra is broadened, accompanied by a further shift towards the blue. The relative transmission intensity is lowered. This trend becomes stronger the higher the percentage

of doping. Figure 5 shows the relative transmission intensity as a function of wavelength for the undoped and the low concentration (5–20%) doped cholesteric, with electric field on (dotted lines) and off (solid lines). Figure 6 gives the same information for the high concentration doping (30–50%).

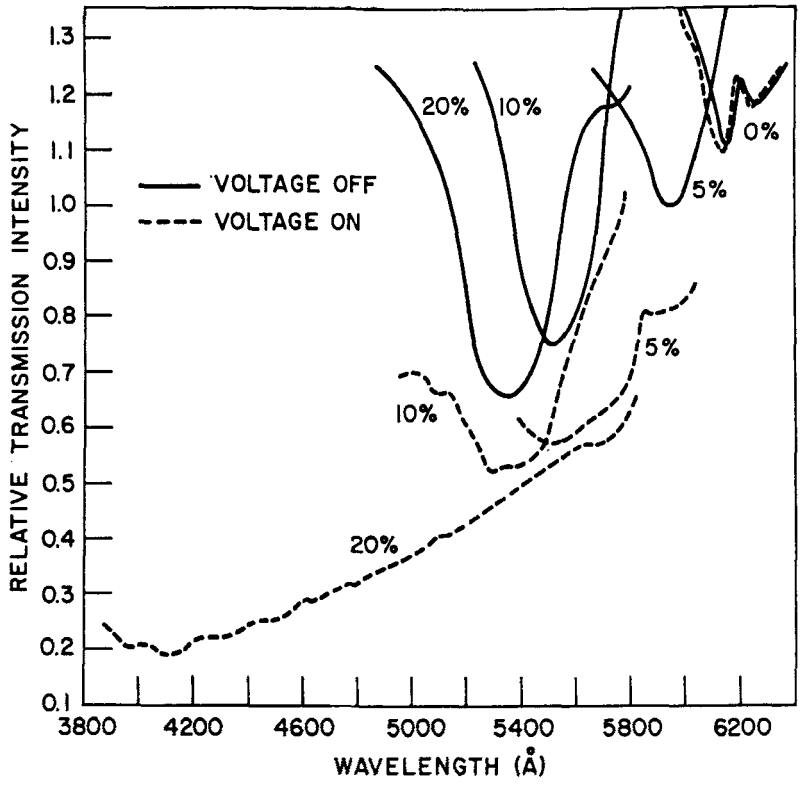

Figure 5. Relative transmission spectra for the low concentration doping—comparing the changes caused by electric field application: ——— electric field off; – – – – electric field on.

Comparison of the " on " and " off " intensities for the peak wavelength gives a scale of the better contrast achieved by doping the cholesteric liquid crystal with MBBA. For the undoped cholesteric, the off intensity (Yf) is slightly higher than the on intensity (Yn) and the ratio $Yf/Yn = 1.02$. A saturation value for the intensity ratio is achieved at about 30% doping where $Yf/Yn = 7.6$ Thus,

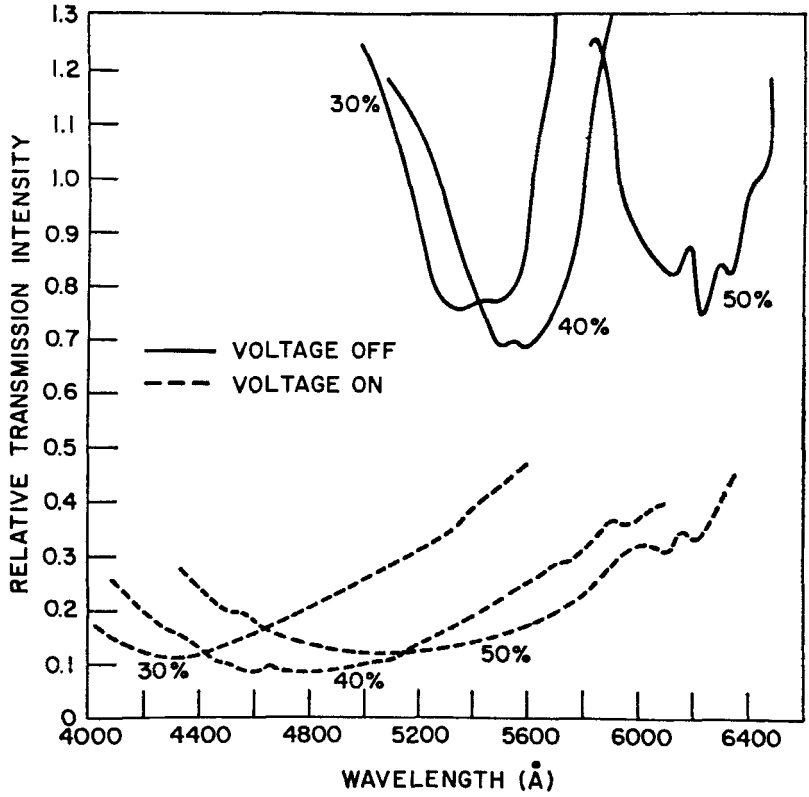

Figure 6. Relative transmission spectra for the high concentration doping—comparing the changes caused by electric field application: ——— electric field off; – – – – electric field on.

using the same voltage, the contrast can be improved by a factor of seven. Curve (b) of Fig. 3 shows the peak-wavelength dependence on the percentage of MBBA after an electric field is applied.

Time Constants

Time constants were measured by applying square waves of 0.4–5 sec. wide and 40 Vdc high. Both applied voltage and the light intensity signal were displayed and photographed using Type 47, 3000 Speed Polaroid film. A 1 sec/div and 5 sec/div time-base and longer square wave pulses (40 sec) were used to determine the saturation intensity value reached after application of the voltage. A 200 msec/div scale was used to determine the time constant.

Response time is defined as the time interval from application of the electric field until 63% of the maximum intensity is reached. For each sample the response time was measured at two points corresponding to the wavelengths where either the maximum or minimum intensity ratios were measured.

An appropriate definition for relaxation time is: the time-interval from the instant the voltage was switched off until relaxation occurred to the extent of 63% of its original state. However, it seems that when a dc field is applied, the relaxation process consists of two stages: the first one has relaxation times of the order of magnitude of 10^2 msec, while the second stage is much longer, with relaxation times of several 10 sec. Additional evidence for the existence of the long relaxation transient has recently been given.[10] The mechanism for the relaxation process and a procedure for shortening it using ac voltages is discussed elsewhere.[11]

Figure 7 shows an additional important feature achieved by doping the cholesteric liquid crystal with MBBA. For low concentration doping (0–30%) the response time is steeply decreased reaching a saturation value at about 30% MBBA. However, at about 25% doping, a second stage in the response process is introduced, which delays the stabilization of the intensity after the electric field is switched on. The time constants related to this stage are about one order of magnitude longer that those of the first stage. It seems likely that this second stage response process is connected with the optical storage mode of dynamic scattering which is characteristic of these mixtures. When the concentration of MBBA is increased, the time constants for the second stage decrease, as shown by the dotted line in Fig. 7. Some decrease in relaxation time is seen for the first stage of the relaxation process. For high concentration doping the relaxation becomes very slow. It should be noted that, unless the sample is completely relaxed, some hysteresis phenomena must be taken into account which might change the response time and intensity level. The restoration depends on the voltage and the time since the voltage was removed. However, by applying the same conditions, high reproducibility was achieved in the time constant measurements in all performed experiments.

The general conclusion from the experimental work is that two different processes control the optical behavior of the doped chol-

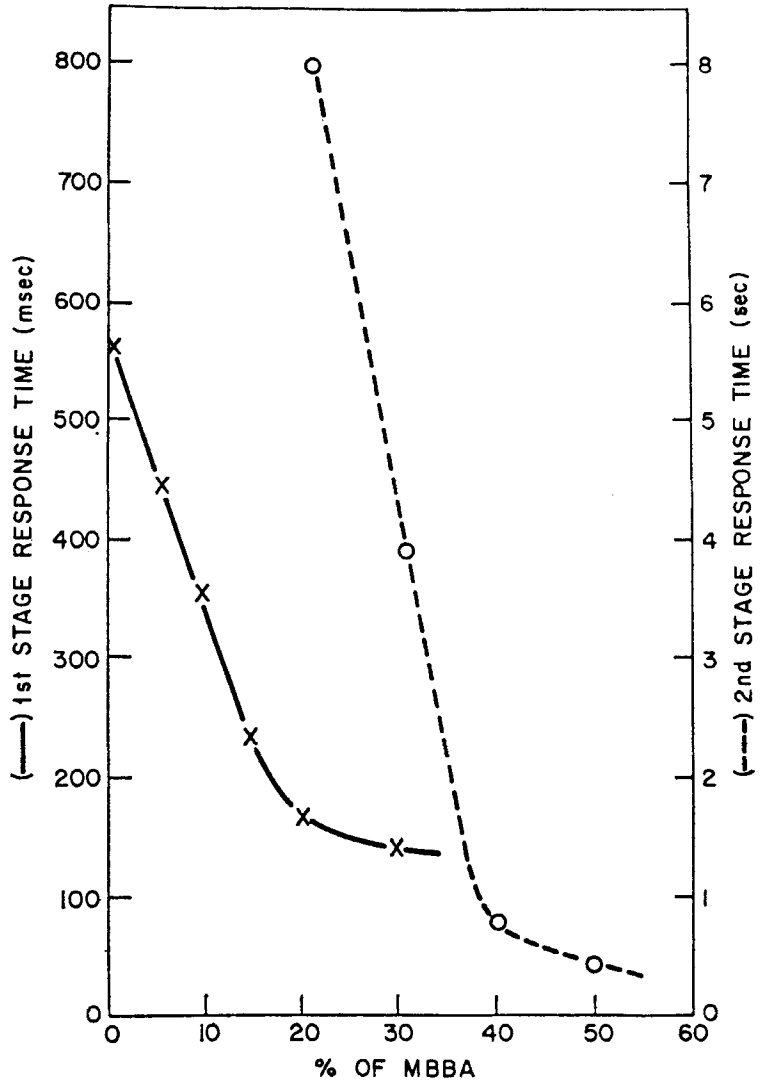

Figure 7. Variation or response time with percentage of MBBA: ——— 1st stage; – – – – 2nd stage.

esteric mixtures. The concentration regions in which these processes exert an influence can be determined by the turning point from a blue shift to a red shift as measured in the transmission spectra. The best combination of rapid response-time and high contrast can be achieved at this turning point. For the cholesteric system used, doping with 25–30% of MBBA will give the highest contrast and the lowest response-time almost without interference of the second stage response process.

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