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Photopolymerization System Thermally Accelerated by a Laser Diode

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Thermal effect on sensitivity of photopolymerization systems containing 2, 4, 6-tris(trichloromethyl)-1,3,5-triazine(TRI) and urethane acrylate (U1) was studied. The photopolymerization system was sensitized by an IR cyanine dye and irradiated with a laser diode (LD), thus, the image can be produced by using a 10 m/s scanning spot of laser beam (spot diameter of 30 µm, 30 mW) at 785 nm. The sensitivity was increased 20× in comparison with a conventional Xe lamp exposure.

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Introduction

In recent years the computerization of photopolymer plate systems has developed rapidly. Mitsubishi Chemical supplies computer-to-photopolymer plate (CTPs) available for air-cooled argon-ion lasers at 488 nm and YAG lasers at 532 nm, as shown in Fig. 1.

Statistical analysis of the color-scanning silver-halide film market is indicated in Fig. 2. The requirement for red-light-sensitive film for HeNe lasers and laser diodes is increasing even though decreasing demand exists for the blue-light-sensitive film for argon-ion lasers. The same trend should appear for computer-to-photopolymer plates for laser diodes. A photoinitiator system (Fig. 3) composed of a cyanine dye sensitizer and a radical generator TRI demonstrated efficient sensitivity in the 450 to 900 nm region, as reported in our previous patents,[1a–c,2] examples of sensitizer dye are depicted in Fig. 4 However the sensitivity was insufficient for IR laser diode imaging systems, as shown in Fig. 3.

In this report we present the improvement in the sensitivity of the IR cyanine dye sensitized photopolymerization under the LD exposure conditions by incorporating urethane acrylate into the photopolymerization system. The remarkable increase of the sensitivity to LD exposure may be owing to the thermal acceleration of the sensitized decomposition process and polymerization with high-power density of the radiation.

Experiments

A photosensitive composition prepared in cyclohexanone was composed of a UV sensitizer. Michler's ketone (5 parts), TRI (5 parts), and an acrylate binder polymer (50 parts). We coated the photosensitive solution on a grained aluminum plate to a thickness of 1 µm, followed by application of polyvinyl alcohol to produce an oxygen barrier layer of 1 µm. For the evaluation of the thermal acceleration effect, the photosensitive sample on a hot plate was used and exposed at various temperatures with conventional exposure using a Xe lamp equipped with a monochromator. The photosensitive sample containing a sensitizer dye, IR cyanine (5 parts), urethane monomer (U1)(50 parts), and an acrylate binder polymer (50 parts) was used for the measurement of the sensitivity under LD exposure with a scanning spot of LD at 785 nm (scanning speed of 0 to 10 m/s, spot diameter of 30 µm). The high-intensity light was employed was employed to compare sensitometry with conventional exposure using low light-intensity at 785 nm.

The incident energy required to make the layer insoluble in aqueous alkai developer was defined as the sensitivity

Result and Discussion

Thermal Acceleration of Sensitivity in Photopolymerization. To improve the sensitivity of the photopolymerization system, the UV sensitizer Michler's ketone was used for realizing experimental conditions conveniently adjusted under a UV cut lamp. The thermal effect on the sensitivity was demonstrated in the Michler's ketone sensitized photopolymerization system that contained TRI, an acrylate monomer, and an acrylate binder. Various kinds of monomer were applied to photopoly-merization, irradiated with a Xe lamp at 366 nm. The influence of temperature on sensitivity for various monomers is described in Fig. 5; the sensitivity was accelerated at high temperature except for Monomers 1 and 4 in Fig. 5.

The viscosity of monomers was strongly dependent on the temperature, as shown in Fig. 6. At the high temperature, the monomers with a large viscosity change demonstrate high increase of sensitivity. However some monomers, such as 1 and 4, which have polyalkyleneoxide structure, only slightly change viscosity and exhibit a decrease of sensitivity.

It is presumed that the photoexcited sensitizer transferred an electron to TRI which decomposed yielding radicals. The resultant radicals either induced photopolymerization directly or interacted with urethane monomer or sensitizer to form more active radicals that lead in turn to polymerization.

It may be possible that the increased mobility in the polymer matrix accelerated the sensitized decomposition

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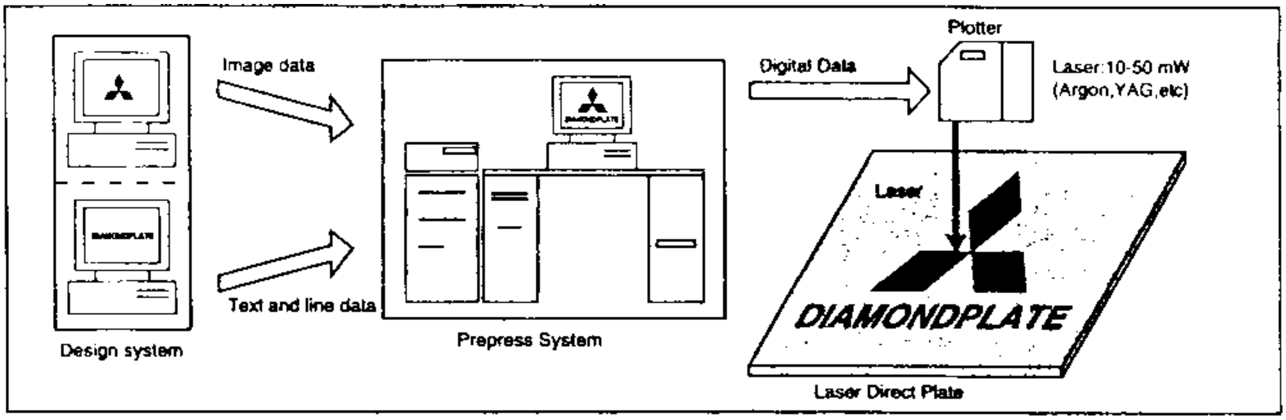

LA-1

- Air-cooled Argon laser (488 nm) exposure
- Sheet-fed and web offset, high quality color printing and business form printing
- Run-length: 100,000 to 200,000 sheets
- UV-ink printing possible without baking
- Plate Thickness: 0.20 mm, 0.24 mm and 0.30 mm

LY-1

- Air-cooled YAG laser (532 nm) exposure
- Sheet-fed and web offset printing, high quality color printing and business form printing
- Plate Thickness: 0.20 mm, 0.24 mm and 0.30 mm

Figure 1. MCC's computer-to-photopolymer plate.

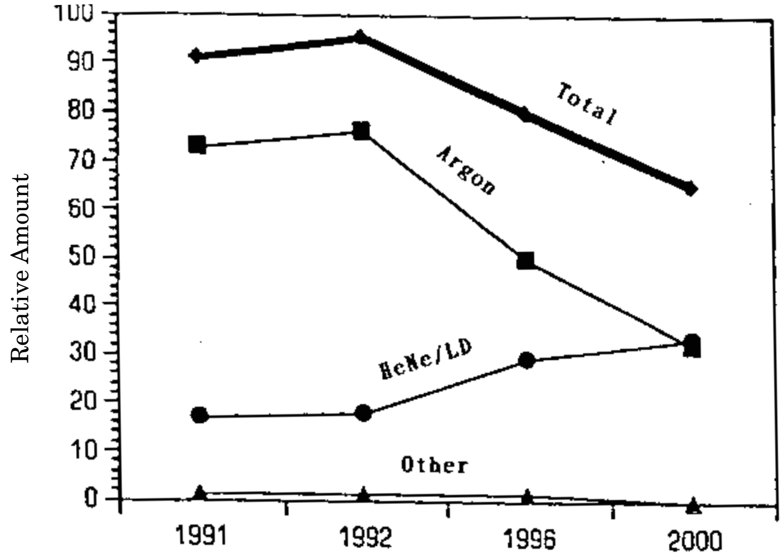

Figure 2. Replacement of color scanner film for gas laser to that for laser diode (LD).

of TRI, the radical transfer, and/or the polymerization at high temperature thereby resulting in an increase in the sensitivity.

This thermal acceleration effect can be applied to the LD sensitive photopolymer that contains cyanine dye, IR dye, and urethane monomer U1. The structure of cyanine dye is shown in Fig. 7. The sensitivity of 10 mJ • cm^{-2} was obtained at 785 nm for LD exposure with high-power density of light in comparison with the sensitivity of 200 mJ • cm^{-2} at 785 nm for conventional exposure with low-power density. The systems are compared in Fig. 8. It is inferred that the increase of sensitivity is owing to thermal acceleration by heat formed from the LD exposure with high density of radiant energy.

It is difficult to homogeneously bake a large printing plate, hence, postexposure bake systems are disadvantageous for high-quality color printing. Our LD photopolymer system demonstrated good characteristics without the postexposure bake treatment. The LD photopolymerization thus may also be potentially applied

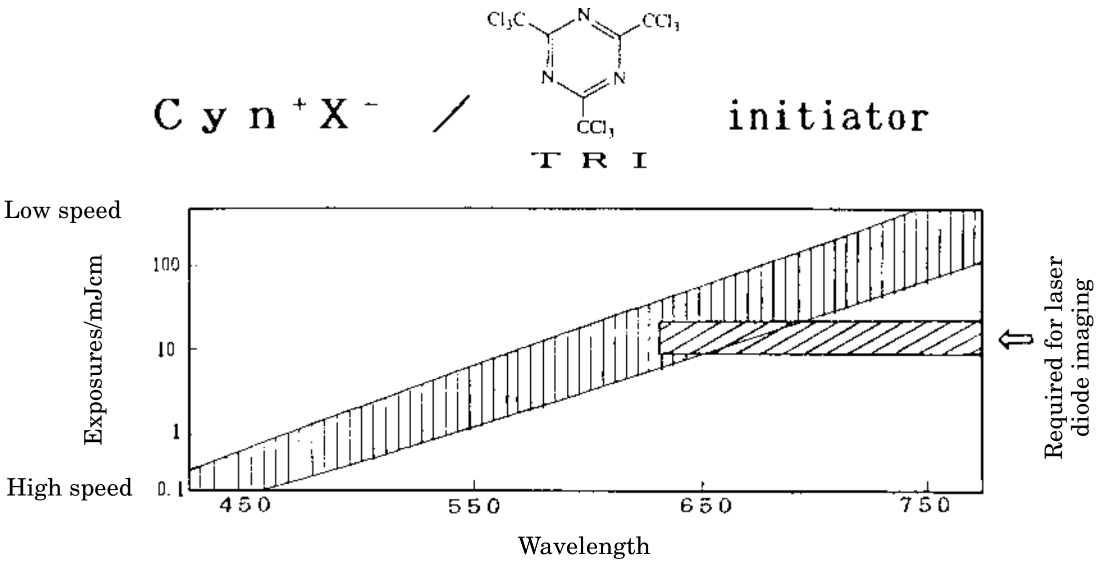

Figure 3. Sensitivity range of photoinitiator systems containing cyanine dye and TRI.[1]

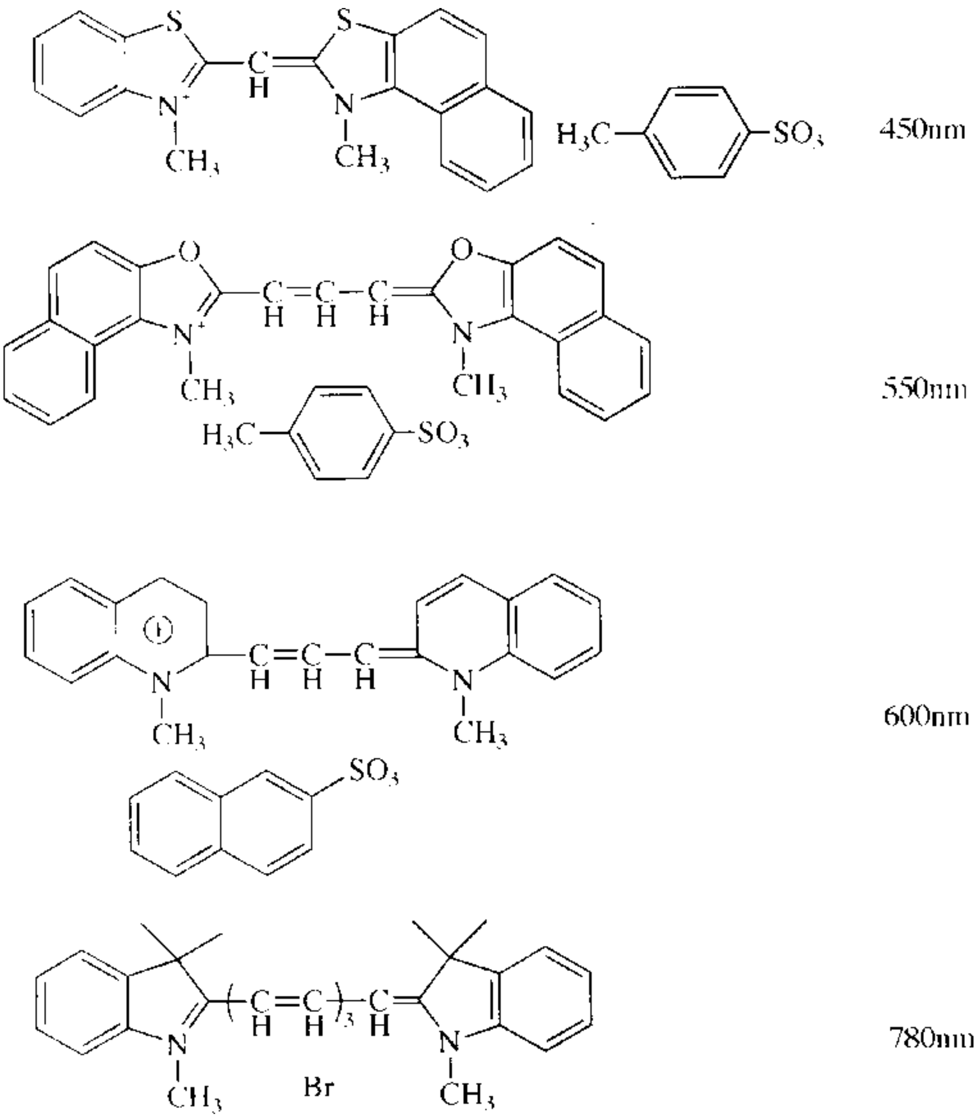

Figure 4. Examples of cyanine sensitizer dyes.

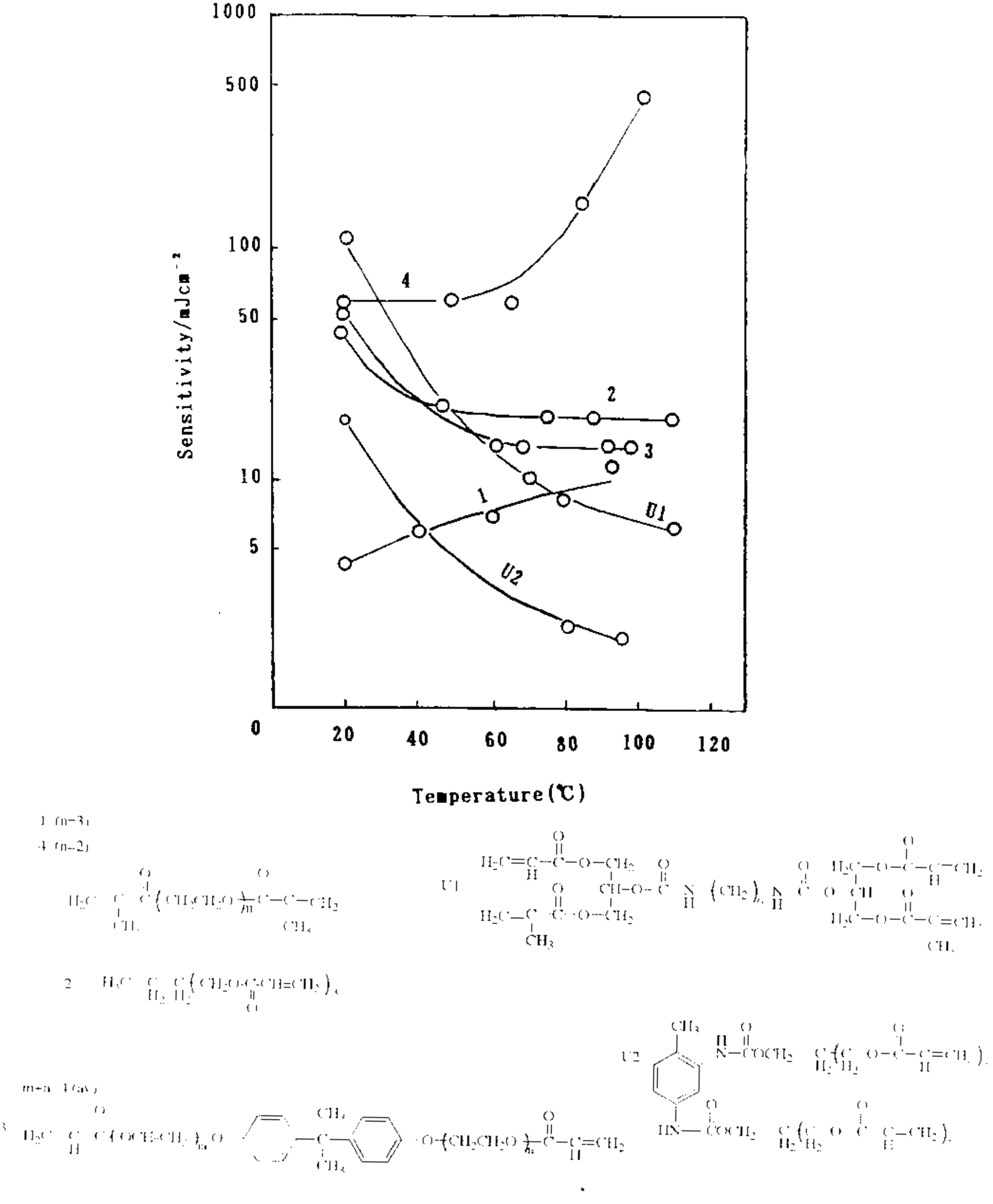

Figure 5. Thermal effect of the sensitivity in Michler's ketone sensitized photopolymerization system.

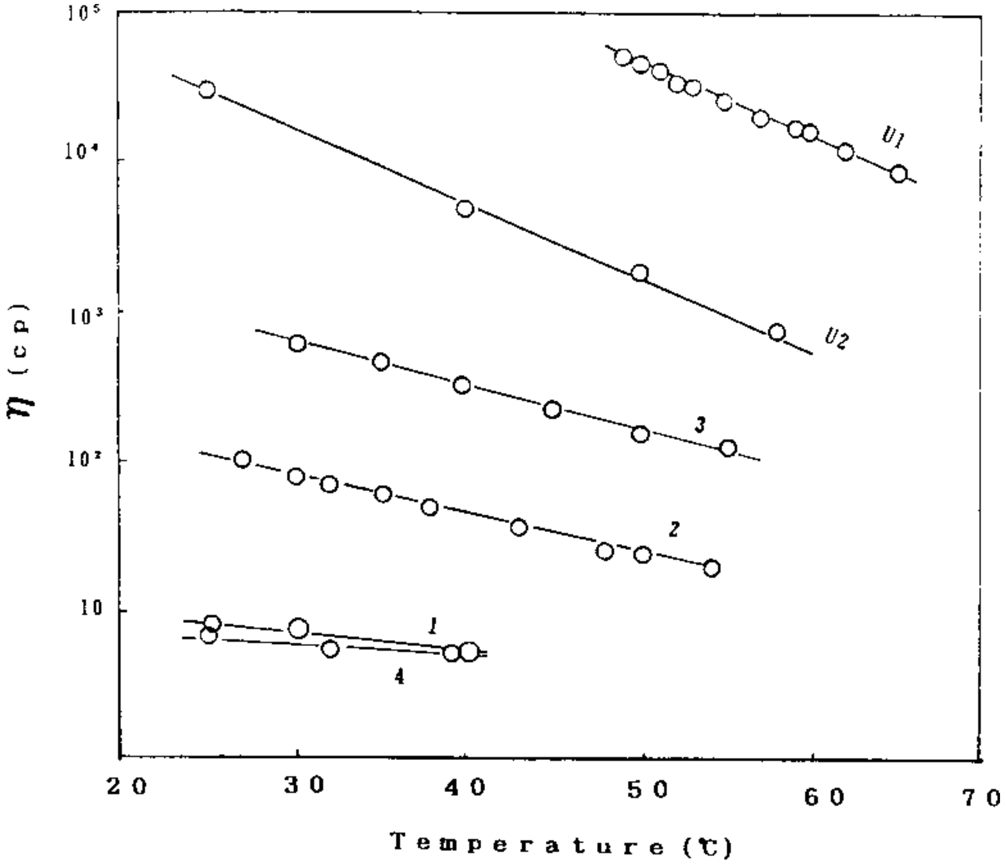

Figure 6. Thermal effect of viscosity of acrylate monomer.

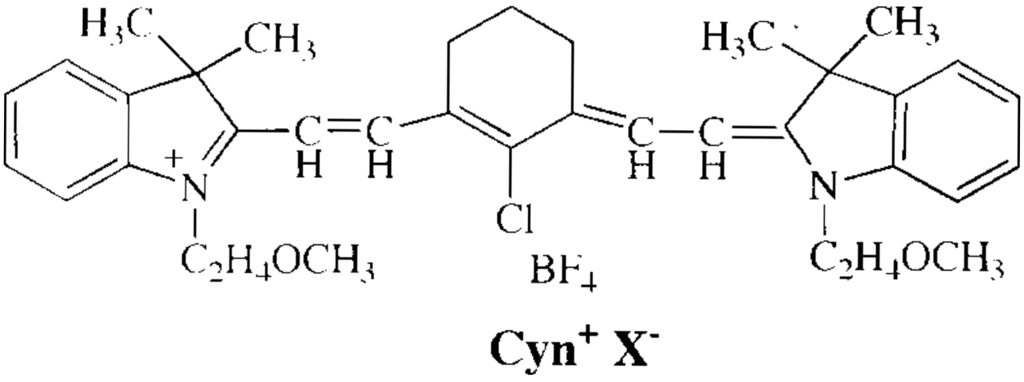

Figure 7. IR sensitizer dye.

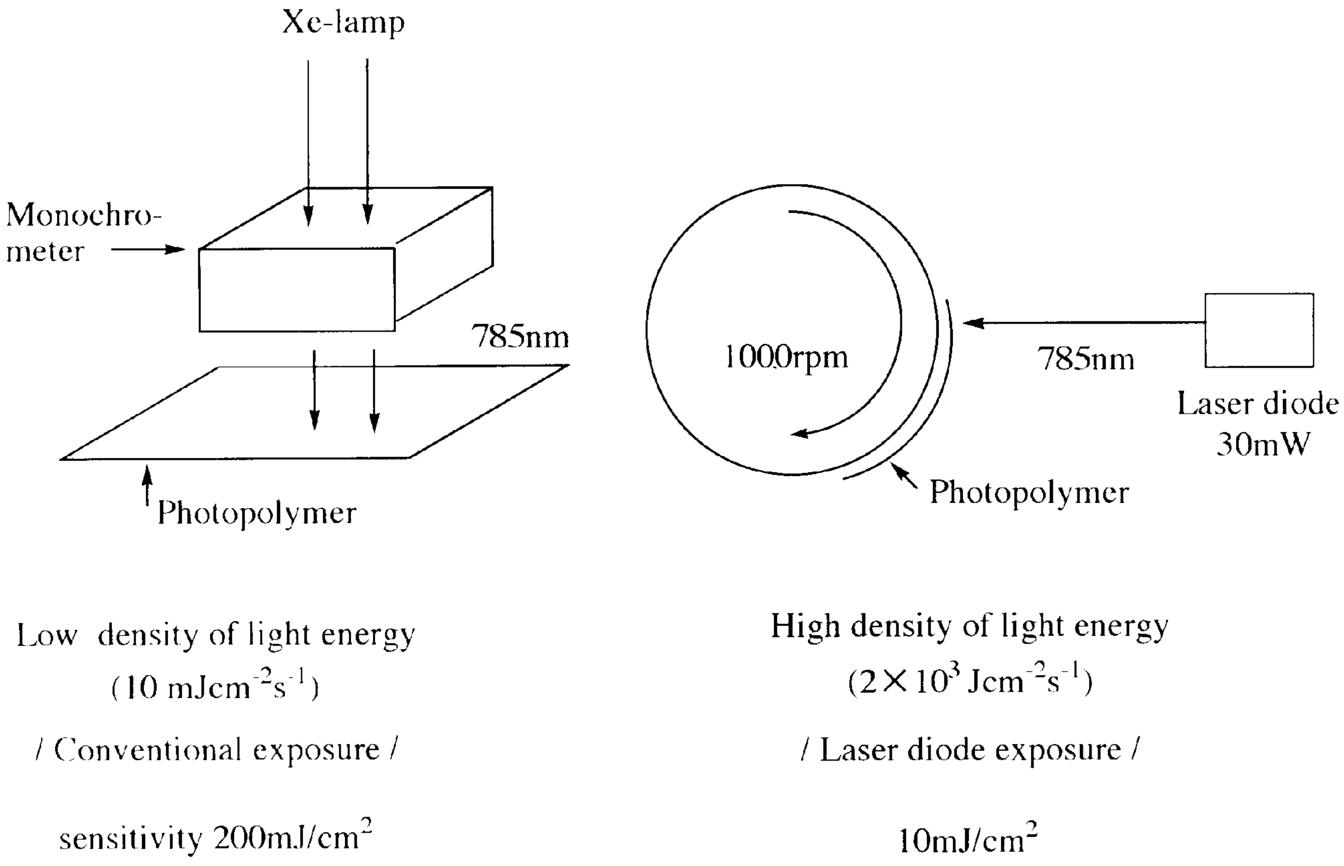

Figure 8. Exposure system and density of light energy.

to copper etching photoresists as well as presensitized printing plates.

Conclusion

Sensitivity was enhanced 20× by using LD exposure with high energy, to reach the sensitivity for LD imaging, compared to conventional exposure conditions. Photopolymerization could thus form images without a postexposure bake treatment.

References

1. (a) H. Nagasaka, Japan Patent 81-128406; (b) H. Nagasaka and K. Ota, Japan Patent 90-189548; (c) H. Nagasaka and T. Ota, Japan Patent 92-31863.
2. T. Urano and H. Nagasaka, Japan Patent 96-114915.