HIGH SPEED PHOTOPOLYMER OFFSET PLATE [MUH] FOR PROJECTION AND LASER EXPOSURE

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Abstract: MUH is a high speed photopolymer offset plate especially designed for non-contact exposure systems. By selecting special combination of spectral sensitizer and initiator, the absorption wavelength and exposure energy of photopolymer can be independently controlled and three types of MUH are developed.

Type-1: for projection exposure
absorption maximum (435 nm)
exposure energy (5 mj/cm^2)

Type-2: for visible laser exposure
absorption maximum (488 nm)
exposure energy (1 mj/cm^2)

Type-3: for UV laser exposure
absorption maximum (364 nm)
exposure energy (0.3 mj/cm^2)

By applying maleimide polymer to the binder of photosensitive layer, all three types of MUH can be developed by aqueous alkaline solution. The shelf life of MUH is the same as conventional diazo offset plate due to low-intensity reciprocity-failure mechanism.

Introduction

By the introduction of electronic and computer technology to offset platemaking, microfilm-projection and laser-scanning systems are becoming more widely used in printing industry. New exposure system requires high speed offset plate. For projection platemaking, 50 to 100 time increase in sensitivity compared to conventional diazo offset plate is required. For laser exposure, more than 1,000

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time increase in sensitivity is required.

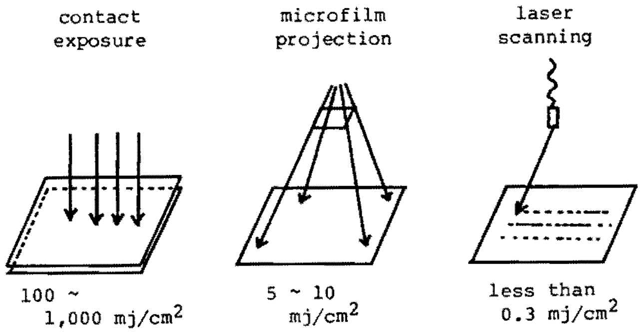


Fig. 1. New Exposure System and Required Sensitivity

As for spectral wavelength, UV sensitive plate can be used for projection and laser exposure, but blue-green sensitive plate is also required for air-cooled argon laser. Small dot gain is very important for projection platemaking because exposure light is spread significantly by the diffraction at optical elements as shown in Fig. 2.

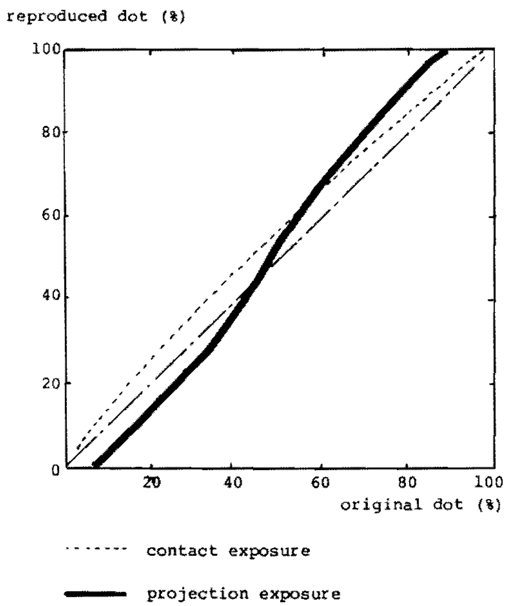


Fig. 2. Comparison of Dot Reproduction between Contact and Projection Exposure

For laser scanning exposure, the plate must not show high-intensity reciprocity-failure, because each small dot is exposed within 1 μ sec by scanning laser beam.

Ultimate Sensitivity of Photopolymers

Ultimate sensitivity of photocrosslinkable polymer can be expressed as Eq. 1 using gel point theory,

$$Eg \text{ (number of photons)} = \frac{r \cdot d}{A \cdot Mw \cdot \phi} \qquad (1)$$

where r is the thickness of photopolymer layer, d is specific gravity, Mw is the weight average molecular weight of photopolymer, ϕ is the quantum yield of photoreaction, A is the fraction of light absorbed. If the following values are assumed for system parameter, r = 1 μm, d = A = 1.0, ϕ = 0.5, Mw = 10^5, wavelength = 365 nm, the gel point energy is 6.4 x 10^{-1} mj/cm^2. When this photopolymer is used as photosensitive layer for high speed plate, practical exposure energy of the plate will be more than 10 times of the gel point energy, because exposed photosensitive layer must remain almost 100% after development, while at gel point exposure only small portion of photopolymer remains after development. So, the practical sensitivity of the plate will be about 6 mj/cm^2. This sensitivity is enough for microfilm projection exposure, but too low for laser exposure.

From the similar consideration, ultimate sensitivity of photopolymerization system can be expressed as Eq. 2,

$$Eg \text{ (number of photon)} = \frac{r \cdot d}{A \cdot Mw \cdot \phi \cdot n \cdot Po} \qquad (2)$$

where n is the kinetic chain length and Po is the fraction of bifunctional monomer unit. If following values are assumed, r = 1 μm, d = A = 1.0, ϕ = 0.5, Mw = 10^5, n = 1,000, Po = 0.5, wavelength = 365 nm, gel point energy will be 1.3 x 10^{-3} mj/cm^2. By applying chain reaction, the sensitivity can be increased to a level which is enough for laser exposure.

Description of MUH

MUH is the abbreviation of Mitsubishi Ultra Highspeed offset plate that can be exposed by microfilm projection or laser scanning system. Photopolymer that shows photopolymerization chain reaction is used as the photosensitive layer of MUH. Three types of MUH are developed as shown in Table 1. Type-1 is for microfilm projection exposure and its optimum wavelength is adjusted to 435 nm of mercury lamp. Type-2 is for blue-green argon laser exposure and its optimum wavelength is adjusted to 488 nm. Type-3 is for UV argon laser exposure and its optimum wavelength is adjusted to 364 nm.

Each three types of MUH has different combination of sensitizer and initiator, but other components (binder, monomer, dye etc.) are same, so that each type can be processed with same developer.

Table 1. Description of MUH

	Type - 1	Type - 2	Type - 3
Exposure Energy	5 mj/cm^2	1 mj/cm^2	0.3 mj/cm^2
Spectral Sensitivity	350 ~ 450 nm	400 ~ 500 nm	350 ~ 400 nm
Exposure Machine	SAPP PAGENATOR		Lasexposer LASERITE
Developer	alkaline aqueous solution		
Optical Density of Image	more than 0.8		
Processor	same as conventional diazo plate		
Shelf Life	more than 1 year		
Durability	more than 100,000		
Safe Light	yellow light	red light	yellow light

Technical Discussion

Coating Structure

MUH has two layer coating structure due to photopolymerization mechanism. The upper layer is overcoating layer which reduces the flux of oxygen from atmosphere to photopolymerization layer. The lower layer is photopolymerization layer which is coated on grained and anodized aluminum sheet. Upon exposure, chain reaction occurs in photopolymerization layer and makes the exposed area insoluble to developing solution, so that MUH is a negative working offset plate. The main constituents of overcoat layer are poval and dye. The main constituents of photosensitive layer are binder polymer, vinyl monomer, dye, photosensitizer, initiator and chain transfer agent. The thickness of each layer is 2 μm respectively.

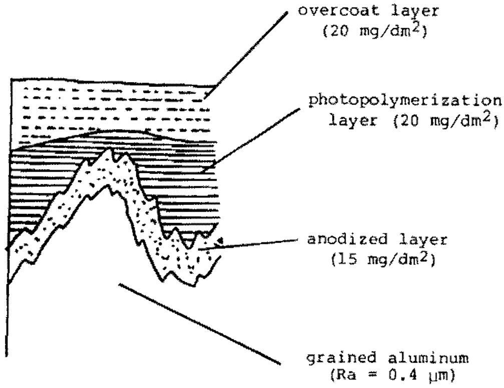


Fig. 3. Coating Structure of MUH

Photoinitiator System

Photoinitiator system is the combination of photosensitizer, initiator and chain transfer agent. Each components cooperates and starts polymerization reaction. By separating photon-absorbing function (photosensitizer), radical generating function (initiator) and chain-reaction controlling function (chain transfer agent), exposure wavelength and energy can be independently controlled.

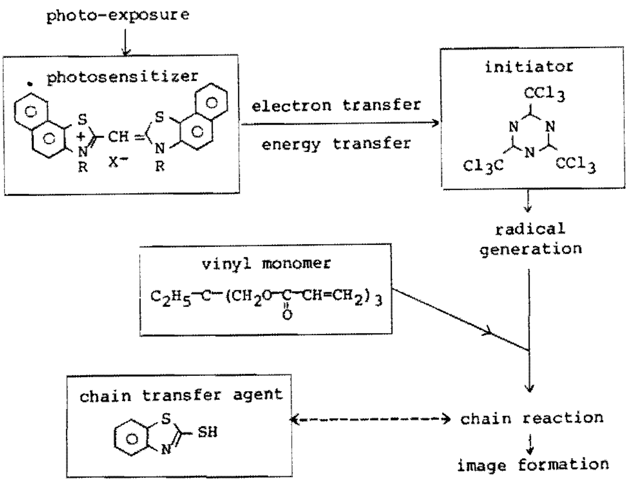


Fig. 4. Mechanism of Photoinitiator System

The longer conjugate structure of photosensitizer molecule brings the spectral sensitivity to longer wavelength, even though the same initiator is used. Typical example of photosensitizer for s-triazine and bi-imidazole initiator are shown in Fig. 5 and Fig. 6.

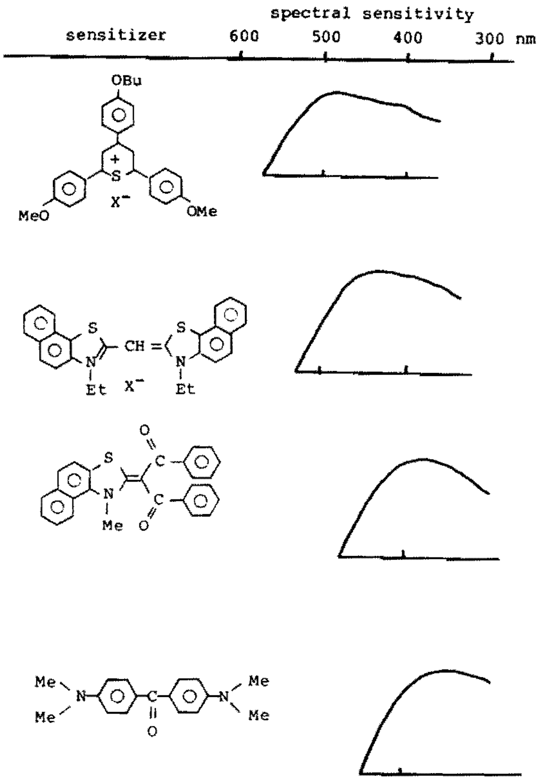


Fig. 5. Spectral Sensitizer for Tris-S-Triazine

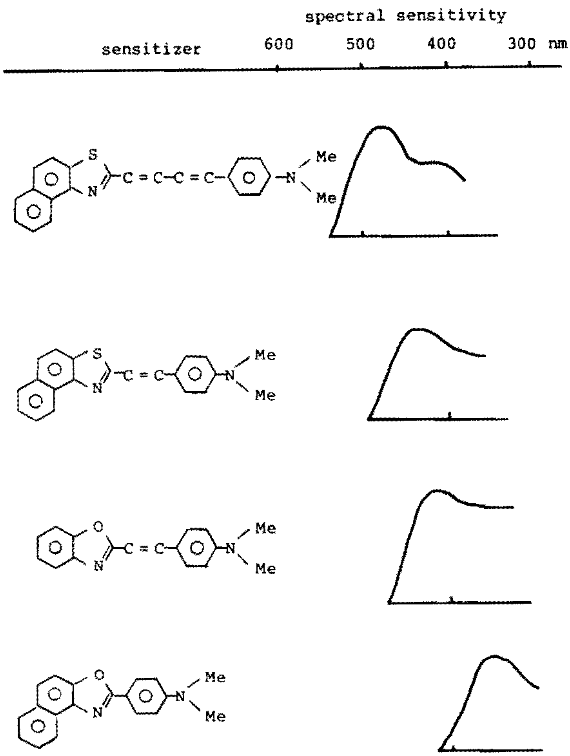


Fig. 6. Spectral Sensitizer for Bi-Imidazole

Overcoating Layer

Poval overcoat layer is colored, which works not only as gas barrier layer but also as spectral filter for photopolymerization layer. By incorporating the dye with proper spectral absorption to overcoat layer, allowable handling time under gold fluorescent lamp is greatly improved without decreasing the UV sensitivity of the plate. Absorption spectra of overcoatlay, emission spectra of gold fluorescent lamp and spectral sensitivity of MUH (Type-1) is shown in Fig. 7.

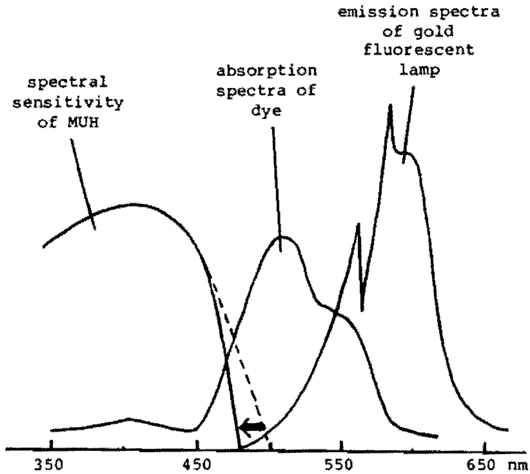


Fig. 7. Filter Effect of Overcoat Layer

Binder Polymer for Alkaline Developer

New binder polymer was searched which can be developed with aqueous alkaline solution. Styrene-maleic anhydride copolymer was reacted with aniline derivatives and new styrene-maleimide copolymer was obtained.

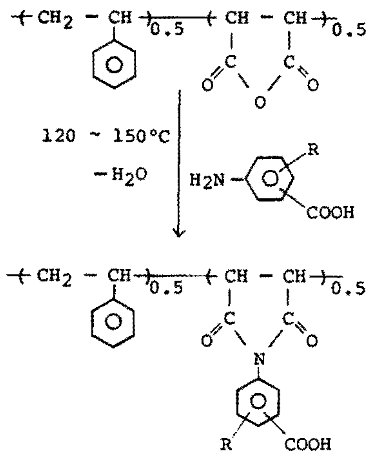
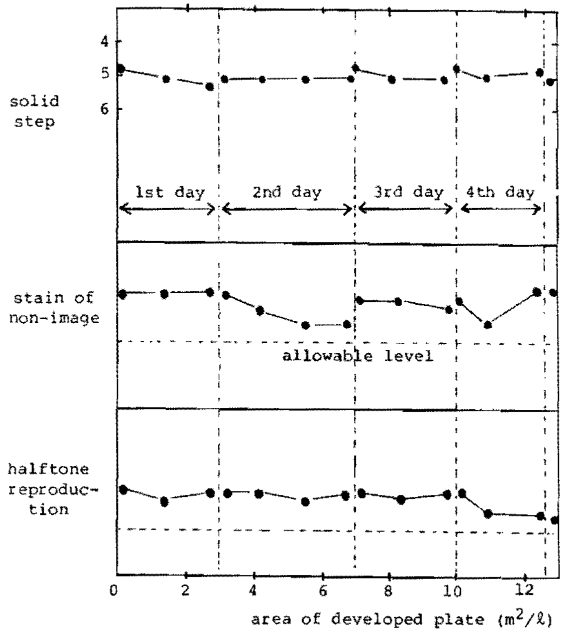


Fig. 8. Synthesis of New Binder Polymer

By using this maleimide copolymer as binder, MUH can be developed with the same developer of positive plate. Also this binder shows less swelling tendency during development, which gives small dot gain and good ink receptability.

Replenishment system which is widely used for the development of conventional positive working plate can also be used to MUH. Daily, hourly and processed-volume-proportionate replenishment work perfectly as shown in Fig. 9.



replenishment condition

35 ml/m^2, 250 ml/hr, 2.5 ℓ/day

Fig. 9. Development Test of MUH under Replenishment System

Shelf Life

MUH has excellent shelf life and doesn't show any appreciable decrease in sensitivity and developability when stored in dark and air-controlled (25°C) place more than 1 year. When stored in an accelerated shelf life test oven (55°C), MUH shows less decrease in developability compared to conventional diazo plate.

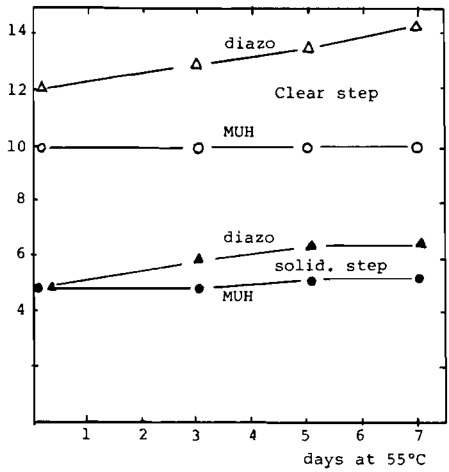


Fig. 10. Comparison of Shelf Life Test

Test Results under New Exposure System

MUH Type-1

Commercial microfilm projection systems were used for the evaluation of MUH Type-1. One is SAPP system of Dainippon Screen and the other is Super 70 Pagenator system of Rachwal. The sensitivity of Type-1 is 5 mj/cm^2 and exposure time for one shot is 2.5 sec for SAPP and 1.0 sec for Pagenator. When 1310 x 1050 mm plate is exposed from 35 mm microfilm using SAPP with the enlargement of 6, total time for 32 shots of image and 12 shots of register mark and step-retrieval motion is about 14 minutes. With Super 70 Pagenator system that uses 70 mm microfilm with the enlargement of 5, total time required for 16 shots of image and 8 shots of register mark on 925 x 1480 mm plate is only 4 minutes. When 100 lines per inch dot chart is exposed with enlargement of 5 using SAPP system, 5 to 80% of halftone range can be reproduced as shown in Fig. 11. MUH Type-1 can also be exposed using contact printer for room-light silver halide film. The exposure time using P-617-GM Printer (Dainippon Screen) is 50% less than silver contact film.

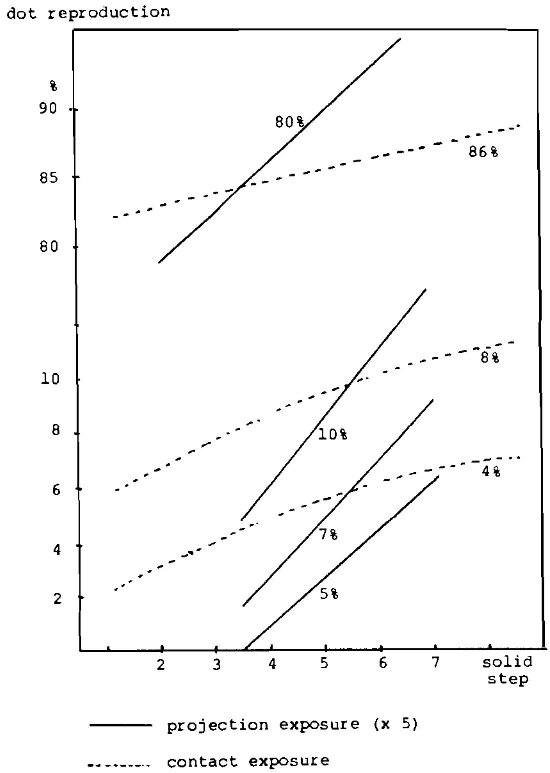


Fig. 11. Dot Reproduction of MUH Type-1

MUH Type-2

MUH Type-2 is designed for visible argon laser exposure but its sensitivity is not enough for air cooled small laser that is used for electrophotographic offset plate. Further research on new photoinitiator system is required to improve the sensitivity.

MUH Type-3

Laserite-V of EOCOM which mounts water cooled UV argon laser is used to test MUH Type-3. When Japanese newspaper size of plate (405 x 560 mm) is exposed within 90 seconds by Laserite-V, the output laser energy is 50 mW. This means that the exposure energy for Type-3 is 0.3 mj/cm^2, which is 1,000 times faster than conventional diazo offset plate. The exposed plate was developed by conventional diazo plate processor and was tested for durability with roll-fed offset printing press used for newspaper. Fig. 12 and Fig. 13 show the example of characters and halftones of laser exposed plate. Appreciable loss of small dot is observed during 130,000 impressions. The advantage of MUH Type-3 is the length of allowable time under gold fluorescent lamp. As its optimum wavelength is around 364 nm and doesn't show appreciable spectral sensitivity near 500 nm, MUH Type-3 is more safe than conventional diazo plate under gold fluorescent lamp.

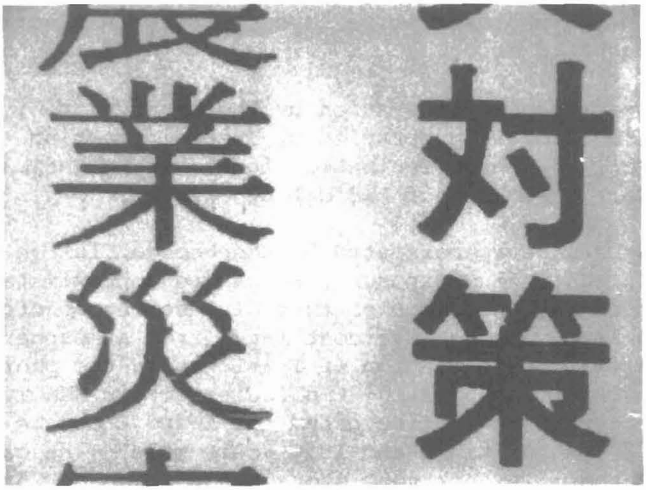


Fig. 12. Chinese Characters of Laser Exposed MUH Type-3 (x 13)

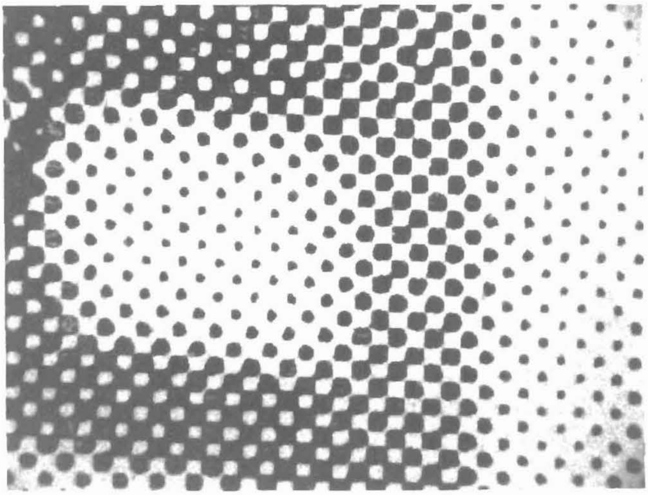


Fig. 13. Halftone Dots of Laser Exposed MUH Type-3 (x 13)

Conclusion and Future Prospect

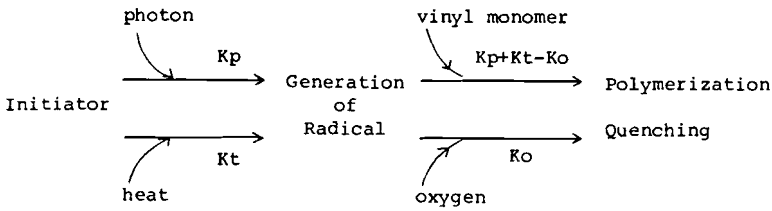
By the combination of photopolymerization reaction and oxygen quenching reaction, MUH attained 1,000 times increase while maintaining the same shelf life as diazo plate. Now it is time to think "What is the ultimate sensitivity of MUH". Though MUH makes the best use of the quenching effect of oxygen for its excellent shelf life, this oxygen may also lower the ultimate sensitivity of MUH.

In MUH photosensitive layer, four main reactions can be thought to occur.

Kp: Radical generation by Photo reaction
Kt: Radical generation by Thermal reaction
Kc: Chain-polymerization initiated by Radical
Ko: Quenching of Radical by Oxygen

Kp can be approximated by the photon flux on the surface of MUH during exposure, Ko can be approximated by the number of oxygen molecules that diffuse into photopolymerization layer through overcoat layer from atmosphere. As the initial concentration of initiator in the photopolymerization layer is 7.5×10^{15} molecules/cm^2 in MUH Type-3, and its Arrhenius activation parameter A and E can be approximated 2.7×10^8 min^{-1} and 15.8 Kcal $\cdot$ $mole^{-1}$, Kt can be calculated. In dark room storage condition at 25°C, Kt is 8.2×10^{10} molecules/$cm^2 \cdot$ sec. Whereas Ko can be calculated as 1.8×10^{13} molecules/$cm^2 \cdot$ sec. Ko is far larger than Kt, so that thermally generated radical is trapped by diffusing oxygen completely. Under photon exposure, for example, 0.3 mj/cm^2 exposure on MUH by laser beam, Kp can be calculated as 5.4×10^{14} photons/$cm^2 \cdot \mu$ sec. This photon flux is large enough compared to oxygen flux through overcoat layer, so that photosensitivity is not damaged by oxygen.

When photon flux reaches to the level of oxygen flux through overcoat layer, photoreaction will be seriously damaged by the quenching reaction of oxygen. This energy level can be thought as ultimate sensitivity that MUH can be reached. In other words, the sensitivity of present MUH Type-3 can further be increased to 30 times, whose required energy is 0.01 mj/cm^2. When this sensitivity is attained, small air-cooled laser can work perfectly as the light source for MUH.



under storage (25°C, dark)

$Kt = 8.2 \times 10^{10}$ molecules/cm$^2 \cdot$ sec

$Ko = 1.8 \times 10^{13}$ molecules/cm$^2 \cdot$ sec

$Kp = 0$

$Kp + Kt < Ko$

under exposure (0.3 mj/cm$^2 \cdot \mu$ sec)

$Kp = 5.4 \times 10^{14}$ photons/cm$^2 \cdot \mu$ sec

$Kp + Kt > Ko$

Fig. 14. Photo and Thermal Reaction of MUH

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