In the practical application of processless CTP plates that have high printing durability and adaptability to UV ink printing, one of the most important issues is the balance between high-definition suitability and high reactivity in the photopolymerization system. By formulating a mathematical model for the initiation system, we found that it is possible to maintain this balance through a combination of controlling the amount of radicals and delaying their generation.

Abstract

In the practical application of processless CTP plates that have high printing durability and adaptability to UV ink printing, one of the most important issues is the balance between high-definition suitability and high reactivity in the photopolymerization system. By formulating a mathematical model for the initiation system, we found that it is possible to maintain this balance through a combination of controlling the amount of radicals and delaying their generation.
The UV printer market is expected to grow constantly. The conventional processless CTP SUPERIA ZP did not have high printing durability to UV ink printing and we needed to develop a processless CTP plate with high printing durability and adaptability to UV ink printing.

### 2.2 Necessity of high reactivity of photosensitive layer

The reason why UV ink reduces printing durability is that the photosensitive layer of processless CTP and UV ink are similar in composition (Table 1). As both processless CTP and UV ink cure by radical polymerization, similar materials are used and they are compatible with each other. When processless CTP and UV ink are compatible with each other, an image area may swell and that leads to reduction in printing durability (Fig. 2 top drawing). To make CTP adaptive to UV ink printing, we need a design to reduce damage to image areas, like swelling, by UV ink by increasing reactivity of the photosensitive layer (Fig. 2 bottom drawing).

![Diagram](image)

**Fig. 2** Influence of UV ink on exposed image area

Oil based ink cures by oxidative polymerization. The ink is not very compatible with processless CTP and it is unlikely to reduce the printing durability.

### 2.3 Negative effects of high reactivity

Simply increasing the reactivity does not solve the problem. Fig. 3 (a) shows an example of a result of enhancing the reactivity of the photosensitive layer in relation to laser intensity. (The vertical axis represents relative monomer conversion (Fig. 3 (a)) with the saturated polymerization rate assumed to be 100.) If the reactivity is increased, polymerization increases in both low and high exposure areas. When the laser profile of an exposure machine has an intensity distribution like Gaussian distribution (Fig. 3 (b)), the reactivity of a low exposure area is increased and the range of an image formed by laser irradiation is broadened. Therefore, each halftone dot is enlarged and the suitability for high-definition printing is reduced (Fig. 3 (c)).

To balance high reactivity and high-definition suitability,
reactivity has to be suppressed in low exposure areas and enhanced in high exposure areas. That means a design to achieve high reactivity represented by the dotted line in Fig. 4. It is the ideal "high reactivity."

3. Design based on chemical kinetics

To suppress the reactivity of a low exposure area, it is effective to remove radicals, for instance, by adding a reaction inhibitor and stop reaction, but it also reduces radicals in a high exposure area as a drawback. It is important to develop a new mechanism that removes radicals in a low exposure area and polymerizes radicals efficiently in a high exposure area. For this purpose, we have developed a design based on chemical kinetics.

We have thought of a simple system with a photosensitive layer consisting of an initiator and a monomer only. The initiator is represented by I, initiator radical by $R_\bullet$, monomer by $M$, monomer radical by $M_\bullet$ and polymer by $P$. The following formulas are used for the reaction scheme.

\[ I \xrightarrow{v} R_\bullet \]
\[ R_\bullet + M \xrightarrow{k_i} M_\bullet \]
\[ M_\bullet + M \xrightarrow{k_p} M_\bullet \]
\[ M_\bullet + M_\bullet \xrightarrow{k_t} P \]

$v$ represents the radical generation rate constant, $k_i$ the reaction rate constant for initiation of polymerization, $k_p$ the reaction rate constant for propagation and $k_t$ the reaction rate constant for termination.

From this scheme, $[I]$, $[R_\bullet]$, $[M]$ and $[M_\bullet]$ respectively, are represented by the differential equation below.

\[ \frac{d}{dt}[I] = -v[I] \]
\[ \frac{d}{dt}[R_\bullet] = v[I] - k_i[R_\bullet][M] \]
\[ \frac{d}{dt}[M] = -k_i[R_\bullet][M] - k_p[M_\bullet][M] \]
\[ \frac{d}{dt}[M_\bullet] = k_i[R][M] - 2k_i[M_\bullet]^2 \]

When the differential equation is solved, the equation below is obtained to show the relationship between remaining monomer $[M]$ and remaining initiator $[I]$.

\[ [M] = [M]_0 \exp \left[ -k_p \frac{2}{\sqrt{v k_i}} \left( \sqrt{[I]_0} - \sqrt{[I]} \right) \right] \]

$[M]_0$ and $[I]_0$ represent the initial concentrations of monomer and initiator, respectively. When the number of generated radicals is constant, in other words, when the constant is $\sqrt{[I]}$, from the relational equation of monomer and initiator above, the polymerization rate has dependence on the radical generation rate $v$ as shown in Fig. 5.

Fig. 5 shows that the polymerization rate increases as the value of $v$ decreases. We have found that even if the total number of generated radicals is constant, the polymerization rate can be improved if radical generation is delayed.

With the reaction scheme of the conventional formula (SUPERIA ZP), the reaction rate constant $v$ depends on the excitation life of dye and therefore it is difficult to delay radical generation. To delay radical generation, we have considered introducing a new reaction scheme to the conventional formula (Fig. 6). The point of this new scheme is to
Deactivated

(A) Conventional reaction scheme

\[
\text{Dye} \xrightarrow{hv} \text{Dye}^* \xrightleftharpoons{v} M^* \xrightarrow{\text{Deactivated}} \]

(B) New reaction scheme

\[
\text{Dye} \xrightarrow{hv} \text{Dye}^* \xrightleftharpoons{v_1} \text{M}^* \xrightarrow{v_2} \text{R}_2^* \]  
\text{Delayed radical}

Fig. 6 Reaction scheme for delaying the generation of radicals

Further accelerate radical reaction using the product \((\text{Dye}^*)\) of reaction by the conventional formula as a trigger.

To verify whether the new reaction scheme above improves the reactivity, we have applied a mathematical model to SUPERIA ZP and determined the values of the reaction rate constants so that the dependence of the polymerization rate of the material on laser intensity and formula would be reproduced. We have then added radicals \([\text{R}_2^*]\) that can be generated after exposure as shown in the reaction scheme in Fig. 6 to the mathematical model. Assuming the \([\text{R}_2^*]\) generation rate constant \(v_2\) to be 1/100 of the initiator radical generation rate \((v_2/v_1 = 1/100)\), we have obtained changes of the polymerization rate with time (Fig. 7). The polymerization rate is enhanced with the new reaction scheme (B) compared with the conventional formula (A). That confirms that delaying radical generation by the new reaction scheme helps increase the reactivity.

4. Balancing high reactivity and high-definition suitability

Based on the result of the studies above, we have started to work on a design to delay generation of two or more types of initiator radicals. We have checked whether there were delayed radicals by nanosecond transient absorption measurement (Fig. 8). In the conventional formula, radical generation reaches the peak immediately after laser exposure and it is the only peak. In the formula with a scheme designed to delay radicals, there is a peak of radical generation besides the peak immediately after exposure. That shows that there are delayed radicals and that the design is as it is intended.

We have also confirmed that generation of the delayed radicals is drastically increased when an oxygen-blocking layer is used (to control the amount of oxygen to pass) even if the material composition of the photosensitive layer is the same (Fig. 9 (a) vs. (b)). In addition to incorporating the mechanism of generating delayed radicals, controlling the permeation of oxygen makes a photosensitive layer design that maximizes the polymerization efficiency.

We have developed a required system by reducing the amount of the initiator to suppress the reactivity of low exposure areas and adding a reaction scheme that delays radical generation and controlling the permeation of oxygen of the photosensitive layer to increase the reactivity of high exposure areas. Fig. 10 shows the reactivity of SUPERIA ZD in relation to laser intensity. SUPERIA ZD has high-definition suitability while having drastically improved printing durability and adaptability to UV ink printing.
5. Conclusion

To put the processless CTP plate with high printing durability and adaptability to UV ink printing into practical use, one of the important issues was how to balance high reactivity in a photo polymerization system and high-definition suitability. We have studied an initiation system that could both limit the number of radicals to be generated and improve the reactivity using a mathematical model. As a result, we have found that delaying radical generation is effective. We have added a reaction scheme that delays radical generation, reduced the total number of initiator radicals and controlled the permeation of oxygen to achieve a contrast in reaction. This way, we have succeeded in developing SUPERIA ZD.

References


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