Influence of light intensity and hardening agent on the photographic pressure effect

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§ 1 Introduction

It has been observed\(^1\) that surface images were desensitized by exposure after pressure, but deep internal images were sensitized.

In previous paper\(^2\), it was reported that surface images of undigested emulsion layer containing the chemical sensitizer were preferentially sensitized by incubation after the application of pressure, but it of emulsion layer digested to its maximum sensitivity were desensitized under the same condition.

This result could be explained by that, when undigested emulsions added sensitizer were incubated, sensitizing products were also formed at crystal imperfections produced by pressure.

It has been known the reciprocity law failure which the efficiency of latent image formation depends on the light intensity. The surface desensitization and the internal sensitization related to additional imperfection produced by pressure would also depend on light intensity. Therefore, it is necessary to study how the surface desensitization and internal sensitization by pressure are varied with light intensity and how the surface and internal sensitizations by incubation after pressure are varied with it.

The experiment was carried out on two silver-bromo-iodide emulsions which one was undigested but contained the chemical sensitizer, the other was digested to its maximum sensitivity. The dependence of light intensity of pressure sensitization or desensitization was studied.

Further experiment has been concerned with the effect of hardening agent on the photographic pressure effect. Generally, the hardness of gelatin increases with increasing quantities of hardening agent and physical properties of gelatin depend also on relative humidities.

It has been reported\(^3\) that the hardeness of gelatin was concerned with the photographic pressure effect. It has been also shown by Faelens\(^4\) that, when photographic film is incubated before pressure at a higher room temperature, the pressure desensitization increases. In present paper it is reported that the pressure desensitization of undigested films sensitized by incubation is lower than that of undigested films keeping at room temperature in region of small quantities of hardening agent, but with increasing quantities of hardening agent the reverse result is obtained.

§ 2 Experimental procedure

Test emulsions (AgBr–AgI) are prepared by the inactive gelatin\(^6\) treated with hydrogen peroxide and added the known amount of sodium thiosulphate prior to digestion. Emulsions are digested for 10 minutes (undigested emulsion), or to its maximum sensitivity (digested emulsion), then coated and dried.

To study the influence of light intensity on the photographic pressure effect, emulsion layers are exposed from 0.001 to 300 seconds after pressure followed by incubation or not. The bending radius is 3 mm. After exposure, emulsion layers are developed. The surface developer is 10\% sodium carbonate solution containing 10g/l glycine, total and internal developers are D-19 containing 10g/l sodium thiosulphate.

The bleaching of surface image is treated with 0.2\%\(^5\) chromic acid solution and it of internal image, 2\% chromic acid solution.
Another experiment have been concerned with the hardening agent. 0.4, 1.2, 3, and 6 cc of 2% hardening agent solutions are added for 100 cc emulsions prior to coating. After coating, one of emulsion layer is kept at room temperature for a day, the other is incubated at 50°C for three days. Then they are bent before exposure and treated with commercial M-Q developer.

§ 3 Results

(1) Influence of light intensity on pressure effect

Reciprocity failure curves of Fig. 1 were obtained with the surface development of pressed and unpressed parts of test emulsion layers, using surface developer.

curve 1 ; unpressed part of undigested emulsion layer
curve 1' ; pressed part of undigested emulsion layer
curve 2 ; unpressed part of undigested emulsion layer incubated at 50°C
curve 2' ; pressed part of undigested emulsion layer incubated at 50°C
curve 3 ; unpressed part of digested emulsion layer
curve 3' ; pressed part of digested emulsion layer
curve 4 ; unpressed part of digested emulsion layer incubated at 50°C
curve 4' ; pressed part of digested emulsion layer incubated at 50°C

Reciprocity failure curves of Fig. 1 were obtained with the surface development of pressed and unpressed parts of test emulsion layers. Curve 1, 1’ relate to surface images of unpressed and pressed parts of undigested emulsion layers after pressure followed by incubation. Curve 3, 3’ relate to surface images of unpressed and pressed parts of digested emulsion layers. Curve 4, 4’, after pressure followed by incubation.

Reciprocity failure curves of undigested emulsions display a marked variation with incubation, and surface desensitization by pressure shifts to surface sensitization after incubation.

Pressure desensitization of undigested emulsion increases with increasing light intensity and pressure sensitization of undigested emulsion incubated at 50°C increases with increasing light intensity.

However, pressure desensitization of digested emulsion is independent of light intensity and also it of incubated emulsion is the same result.

Reciprocity failure curves of Fig. 2 were obtained with the total development of pressed and unpressed parts of test emulsion layers. Pressure sensitization of total image of undigested emulsion layer incubated at 50°C decreases with increasing light intensity. Pressure desensitization of total image of digested emulsion layer is independent of light intensity.

Reciprocity failure curves of Fig. 3, 4 were obtained with internal development after bleaching with 0.2 and 2% chromic acid solution. Internal desensitization of undigested emulsion by pressure increases with increasing light intensity and it of digested emulsion by pressure is also the same result. After pressure
Fig. 3. Reciprocity failure curves of pressed and unpressed parts of test emulsion layers, using internal developer after bleaching the surface image with 0.2\% chromic acid solution.

Fig. 4. Reciprocity failure curves of pressed and unpressed parts of test emulsion layers, using internal developer after bleaching the internal image with 2\% chromic acid solution.

followed by incubation, internal image of pressed part of undigested emulsion layer is sensitized at low intensity and is desensitized at high intensity.

Internal image of digested emulsion is the same result. The dependence of light intensity of surface image of undigested emulsion layer after pressure followed by incubation obeys the effect of chemical sensitization on light intensity, but it of internal image does not obey. Probably, the internal imperfection produced by pressure would be subjected to polygonization by incubation and act as a condensation center.

Surface and internal images of pressed parts of emulsion layers without incubation are desensitized at high intensity. This may be explained by that the crystal imperfection produced by pressure acts also as traps of electron and hole, and the efficiency of latent image formation decreases.

(2) Influence of hardening agent.

Table 1 shows the relation between melting points of emulsion layer and quantities of hardening agent. Hardening of emulsion layer increases with increasing quantities of hardening agent and melting points of emulsion layer incubated for three days at 50°C is higher than that of emulsion layer kept for a day at room temperature.

Table 1.

<table>
<thead>
<tr>
<th>sample No.</th>
<th>quantities of hardening agent (%)</th>
<th>m.p.(°C) keeping for a day at room temp. after coating</th>
<th>m.p.(°C) after incubation at 50°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>32.0</td>
<td>32.8</td>
</tr>
<tr>
<td>2</td>
<td>0.4</td>
<td>33.5</td>
<td>35.1</td>
</tr>
<tr>
<td>3</td>
<td>1.2</td>
<td>59.5</td>
<td>80.5</td>
</tr>
<tr>
<td>4</td>
<td>3.0</td>
<td>above 95.0</td>
<td>above 95.0</td>
</tr>
<tr>
<td>5</td>
<td>6.0</td>
<td>above 95.0</td>
<td>above 95.0</td>
</tr>
</tbody>
</table>

It is shown that hardening is not complete in emulsion layers kept for a day at room temperature after coating.

Physical property of emulsion layer relates to hardening and to relative humidity. Because the moisture absorbed by emulsion layer is a function of relative humidity of the environment, the moisture desorbed from emulsion layer by incubation may be progressively absorbed by placing it in an atmosphere and it may be in equilibrium with its relative humidity.

Fig. 5 exhibits the relation between the ratio of pressure desensitization and the time of keeping the emulsion layer in an atmosphere after incubation. Pressure desensitization decreases with increasing the keeping time after incubation, and then it closes to constant values. Pressure desensitization also increases with increasing quantities of hardening agent added in emulsion layer.
All bending test were carried out after incubation followed by keeping for 24 hours in an atmosphere. In digested emulsions, pressure desensitization is only a function of hardening. Pressure desensitization increases with increasing hardening.

As shown in Table 1, hardening of emulsion layer kept for a day at room temperature is not complete, therefore pressure desensitization of emulsion layer kept for a day at room temperature is lower than that of incubation.

However, in undigested emulsion, pressure desensitization does not only relate to hardening but also to proceeding of digestion by incubation. In emulsion layer added very small quantities of hardening agent, pressure desensitization is reverse result compared with other, and in non hardened emulsion layer, also the same result; pressure desensitization of emulsion layer after incubation is lower than that of keeping for a day at room temperature. Pressure desensitization of digested emulsion which is not added hardening agent is not varied with incubation.

These results do not consist with the Faelen's result[4] that, when emulsion layer is incubated before pressure at a higher than room temperature, the pressure desensitization increases.

§ 4 Conclusion

The pressure effect of photographic emulsion should be considered from the view-point of the crystal imperfection of silver halide crystals produced by pressure. The unstable imperfection produced by pressure would be subjected to light annealing by incubation and shift to stable state. Therefore, efficiency of latent image formation of pressed part on light intensity would vary with it of unpressed part. However, it is important that physical properties of gelatin or polymer as a binder of silver halides act as a factor of photographic pressure effect.

Acknowledgements

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References

1) P. Faelens & P. De Smet; Colloque sur la sensibilité des cristaux et des émulsion photographiques 1951, Sci. Industr. photogr. 23 A, 77, (1952)

2) Y. Kobayashi; Bull. Soc. Phot. Japan, No. 9, 6, (1959)


6) W. D. Kelly; J. Phot. Sci., 6, 16, (1958)