Heat Fastness of Thermal Paper*

Lan-sheng Kuo[1] Ming-horng Duh[2] Yon-tien Chiou[3]

【**Abstract**】A thermal paper is a special paper coated with a heat sensitive coating. It undergoes a color change (to black) when heated. The thermal paper coating is complex both in its composition and method of manufacture. There can be a combination of up to 14 different chemical components to achieve the desired effect. In aging tests (50-70℃), printed images of 6 commercial thermal papers proved less resistant to heat and then faded gradually. In other words, the higher the surrounding temperature was the more color reversion of the printed and non-printed areas occurred. Based on the results observed in this study, we surface treated the coated side of 60 g/m^2 thermal papers with small amounts (5-10 g/m^2) of heat insulating materials such as $MgCO_3$ and $CaSiO_3$ and a low melting point gelatin. It was found that heat fastness of the printed thermal papers could be improved slightly; however, no marked effects were observed. In conclusion, the problem of image stability of thermal papers might be solved by the application of a top (or barrier) coating. We deduced that this should be a transparent, film-forming layer which when coated onto the surface of the thermal coating, acts as a non-penetrable protective layer, but one which will not impair the heat sensitive characteristics of the main coating.

【**Key words**】thermal paper, heat fastness, top coating, barrier coating, permanence.

感熱紙之耐熱性

郭蘭生[1] 杜明宏[2] 邱永添[3]

【**摘要**】感熱紙係於表面塗佈特殊感熱塗料之特種塗佈紙，遇熱部份可呈色。感熱紙塗料之配方及製造均相當複雜。爲符合需要，其塗料配方中可含 14 種以上之化學成份。

本試驗以 50~70℃ 溫度之老化條件，評估比較 6 種市售感熱紙之耐熱性，結果顯示：環境溫度愈高，印刷區及非印刷區之色變情形愈嚴重。市售感熱紙之耐熱性均不佳。此外，本試驗以微量 (5~10 g/m^2)絕緣材料如：$MgCO_3$, $CaSiO_3$ 及低融點明膠 (gelatin)塗佈於感熱紙表面，以改善其耐熱性。試驗結果顯示，列印感熱紙之耐熱性雖有改善，但效果並不顯著。

綜合試驗之結果，可知於感熱紙之表面塗佈微量絕熱材料，可以改善其印刷圖文之熱安定性，便於長期儲存。惟絕熱材料之選擇需十分慎重，除具保護作用外應不影響感熱紙對熱之敏感性爲要。

【**關鍵詞**】感熱紙、耐熱性、頂部塗佈、絕緣塗佈、耐久性。

---

1 國立中興大學森林學系教授
Professor,Dept. of Forestry, NCHU.
2 國立嘉義技術學院林產工業科教授
Dept. of Forest Products Industry, National Chiayi Institute of Technology
3 國立中興大學森林學系研究生
Graduate student, Dept. of Forestry, NCHU.
* 本研究承國科會專題研究計畫(NSC86-2313-B005-088)經費補助，特予致謝。

I. INTRODUCTION

Due to the rapid spread of facsimile-based communication and the ever-increasing use of thermal labels, world demand for thermal paper is increasing year by year. Thermal papers are ideal for bar-coding and for the type of on-site printing of price and weight information commonly found in supermarkets. The non-impact form of printing was developed primarily in Japan, originally for facsimile paper. Thermal paper has a special heat sensitive coating that is applied to a base sheet and undergoes a color change when heated. The most common color change is from white to black. The thermal coating is very complex both in its manufacture and composition. There can be up to 14 different chemical combinations to give the desired effect (Liu, 1986).

Thermal paper consists of a special form of dye in the coating that will cause a color-forming chemical reaction that is brought about by heat action (Fig. 1). Usually thermal paper is coated with a leuco form of a dye, such as crystal violet lactone, and a co-reactant, typically a phenol capable of oxidizing the leuco dye to the colored form (Clack, 1964; Adhikary, 1966). Heat from a stylus of thermal printing head causes the color-forming reactants to combine and produce contrasting colored marks in the area heated by the stylus. The thermal printing head is capable of reaching a surface temperature of about 150-260℃ in milliseconds (Park, 1989). Thermal paper is available with a range of initiation temperature that must be matched to the characteristics of the printing head employed. The base paper for preparing thermal papers is a white bond paper that must have solvent resistance for the coating employed and good formation for uniform thermal energy transfer to take place.

As of now, there is no high-quality thermal paper being made in Taiwan. The main obstacle to local-made thermal paper is its weak resistance to the temperature of the immediate surroundings. High temperatures in storage facilities induce rapid fading to the thermal paper housed in them.

The purpose of this study was to investigate the effects of heat on the stability (heat-fastness) of the printed and non-printed areas of certain commercial thermal papers commonly found in the market. We also have attempted to determine a new approach to solve the stability problems encountered.

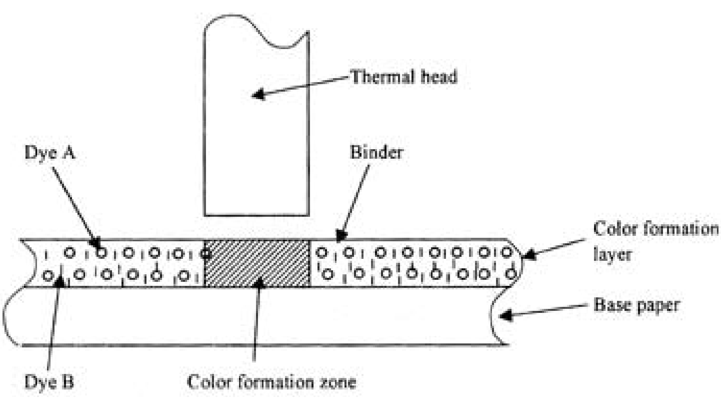

Fig. 1. Color formation mechanism of thermal paper.
(Kadoya, Takashi, 1988, Speciality paper, Japan, P. 70)

II. MATERIALS AND METHODS

(I)Raw materials

Six imported commercial thermal papers were obtained from the local market. They were chosen based on the following considerations related to the nature of image generating: basis weight; caliper; strengths; smoothness; brightness; opacity and pH values. These properties were measured in conformity with relevant TAPPI standards.

Preparing heat insulated coatings which consist of $MgCO_3$ (50 parts), $CaSiO_3$ (50 parts), starch (5%, parts by weight of pigment) and latex (15%) and then apply this coating color (25-30% solids) on the surface of commercial thermal papers. This is expected to improve the heat fastness of thermal papers.

(II)Determination of heat fastness of non-printed thermal papers

In this study, to help understand the permanence of these thermal paper samples when subjected to heat, examinations of varying temperature range (-5℃ to 70℃) and color changes (expressed as ΔL^*, Δa^*, Δb^*) were conducted on samples A and B. Data from 3 to 9 days heating time, where discernible color change and brightness difference ($\Delta E > 1.0$) resulted is available. Optical properties of CIE $L^*a^*b^*$ and brightness were measured on the coated side of the thermal papers.

(III)Determination of heat fastness of printed thermal papers

Since the shade of the original print may affect the color forming effect of thermal paper, we selected 3 kinds of black paper (Fig. 2, the blackness of these samples are expressed as BL* value (Kuo et.al. 1998), i.e. light black, medium black, and dark black paper (dimension: 4 × 4 cm^2) as the original print. In other words, a lower BL* value implies a darker black paper. According to the extent of color change (reversion) of thermal papers under varying temperatures in our preliminary experiment, it was found that considerable color change $\Delta E > 1.0$) may occur at temperatures over 50℃ (Kuo and Shiau, 1994). These black papers were pasted onto white bond paper (Fig. 2). We then used a fax machine to make printed thermal papers.

After heating at 50℃ for 10, 20, 60, and 120 minutes respectively, color reversion, expressed as ΔE(color difference)and the p.c. (post color number) (Rydholm, 1965) of all samples were measured with Macbeth Color-Eye 3000 spectrophotometer according to TAPPI standards. The p.c. number of the thermal papers can be calculated as per the following formula:

$$\text{p.c. number} = [(1-R)^2/2R]-[(1-R')^2/2R'] \times 100$$

Where R, R' is the brightness of aged and untreated thermal paper respectively.

Fig. 2. Systematic black samples used for testing image stability of thermal papers.
(BL* = L* + | a* | + | b* |)

(Ⅳ)Improvement of the permanence of thermal paper

In order to solve the problem of image stability of thermal paper, we attempted to apply $CaSiO_3$ and $MgCO_3$ (insulating materials) onto the surface of the thermal paper by a semi-automatic bar coater. Coat weights were adjusted to 5-10 g/m^2 to avoid the elimination of heat energy transfer when heated. We also applied a small amount of 5% low-melting-point gelatin, which acts as a non-penetrable protective coat, onto the surface of the thermal papers. The permanence of each of the insulating materials could be evaluated by the color change under accelerated aging tests.

Ⅲ. RESULTS AND DISCUSSION

(Ⅰ)Properties of commercial thermal papers

Basis weights of various commercial thermal papers are in the range of 60-66 g/m^2 as shown in Table 1. Interestingly though, the thickness of all papers is the same (0.06 mm). Machine-made paper shows different mechanical properties in MD (machine direction) and CD (cross direction). Therefore, in addition to the tear of samples A & E, there are different tensile, tear and fold properties in 2 directions. As for burst strength, it can be observed that sample B has the greatest value of 1.33 kg/cm_2 followed by sample C at1.30 kg/cm^2 and then sample A at1.2 kg/cm^2.

In order to improve heat sensitivity and image stability, all the commercial thermal papers used in this study are one-side coated papers. The prime purpose of coating the thermal paper is to improve the smoothness beyond that possible by calendering. Table 1 shows smoothness values for a series of commercial thermal papers. Aside from the little smoothness difference between two sides (felt side and wire side) of the test paper, it will be noted that there is generally high smoothness for these commercial thermal papers. It seems that small amount of coating color might be applied to

Table 1. Fundamental properties of commercial thermal papers.

Specimen / Items	A	B	C	D	E	F
Basis weight , g/m^2	60.0	61.0	60.2	65.2	59.3	66.0
Caliper, mm 0.06	0.06	0.06	0.06	0.06	0.06	
Tensile, KN/m						
MD	3.07	3.09	3.92	2.55	3.15	2.59
CD	1.4	1.66	1.50	----^{2}	1.50	-----^{2}
Tear, mN						
MD	329.5	382.5	362.9	248.1	304.0	323.6
CD	345.2	500.2	441.3	395.2	333.4	519.8
Burst, KPa	117.7	130.4	127.5	103.0	112.8	95.1
Fold (MIT, 0.5 kg), double fold						
MD	2070	4922	1959	1201	1865	1843
CD	1840	3053	1191	1042	1299	1231
Smoothness(Bekk), sec						
Felt side	396	399	399	401	396	401
Wire side	393	396	395	398	391	400
Brightness, % G.E.	89.3	109.6^{*1}	86.4	113.7^{*1}	85	112.8^{*1}
Opacity, %	91.57	90.6	91.7	94.79	91.9	94.9
pH	8.2	8.5	8.4	8.6	8.2	8.5

*1Fluorescent whitening agent was added.
*2 -------- undersize sample.

either side of base paper since the smoothness on both sides is quite the same.

Practically speaking, there is only one-side printing on thermal paper, so there doesn't seem to have a concern with the "show through" problem. Obviously, a thermal paper with its opacity over 90 % as shown in Table 1 must meet its practical use.

Table 1 also shows that high brightness over samples B, D and F can be realized by the fluoresent whitening agents present in the paper stock.

(Ⅱ)Heat fastness of commercial thermal papers

Because thermal paper is used for all sorts of documents and records, its permanence over a period of years is of great importance. Due to the heat-sensitivity of thermal paper, heat resistance is essential during the storage of printed thermal paper. A test to account for the deterioration of thermal paper qualities, such as the permanence of image with age at 50℃ was carried out in our laboratory. Fig. 3 shows that color difference (ΔE^*) and lightness difference (ΔL^*) of various printed areas with varying tints of black increases with increasing heating time. The ΔE^* and ΔL^* values show less influence on the tinting color (higher lightness). Because color difference (ΔE^*) is calculated from lightness difference (ΔL^*) in formula of $\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}$, we are not surprised by the similar tendency for both of ΔE^* and ΔL^* as Fig. 3 shows.

As a result, due to the marked color difference in the aging test ($\Delta E > 2.0$ is discernible by eye, Kuo and Shiau, 1994), we have undesirable thermal

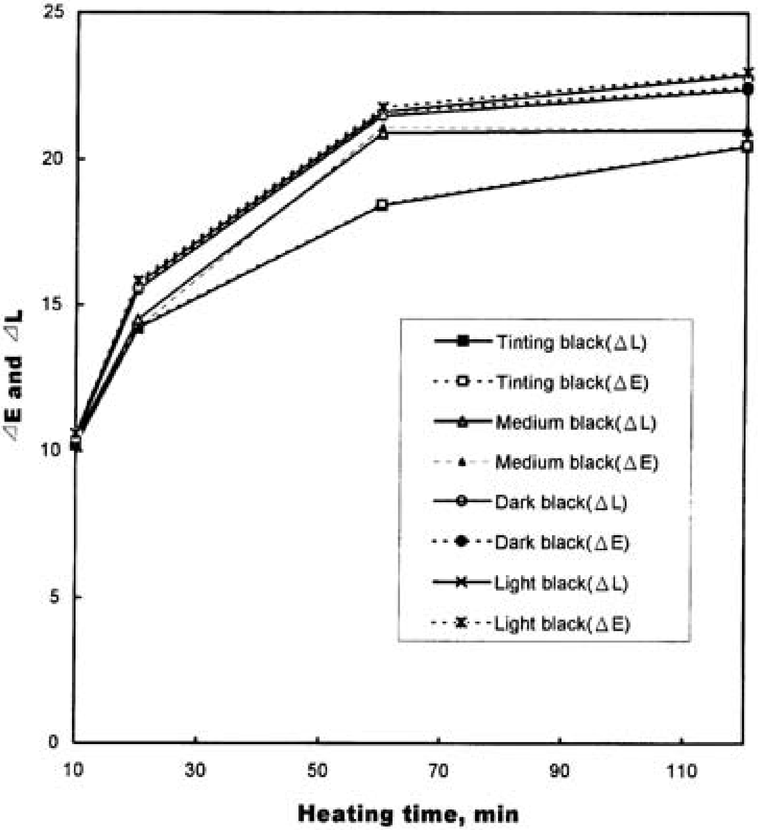

Fig. 3. Heating time vs.color difference (Δ E) and lightness difference (Δ L) of thermal paper sample D in accelerated aging test(50℃).

Table2. Heat fastness of commercial thermal papers without printing.

Sample	Temp(℃)	Heating time(days)	L* / a* / b*	Δ E*	Tappi brightness(%)
A	-5	0	92.17/-1.36/3.30	0.00	89.3
		3	92.11/-1.54/3.46	0.29	89.2
		6	92.21/-1.55/3.12	0.26	89.4
		9	92.16/-1.45/3.32	0.10	88.7
	Room	3	92.36/-1.33/3.68	0.43	89.2
		6	92.32/-1.30/3.73	0.46	89.1
		9	92.25/-1.31/3.85	0.57	89.0
	50	3	91.61/-1.88/2.66	0.99	89.4
		6	91.68/-1.85/3.22	0.70	89.1
		9	91.69/-1.86/2.78	0.86	89.2
	60	3	90.43/-1.44/1.92	2.22	88.6
	70	1	89.23/-2.00/0.97	3.81	87.4
B	-5	3	90.71/-0.63/2.05	0.05	86.4
		6	90.88/-0.63/2.12	0.15	86.5
		9	90.82/-0.64/2.11	0.10	86.6
	Room	0	90.73/-0.61/2.09	0.00	86.4
		3	90.87/-0.60/2.15	0.16	86.7
		6	90.87/-0.57/2.12	0.15	86.9
		9	90.78/-0.52/2.06	0.11	86.7
	50	3	90.23/-0.61/1.85	0.73	85.3
		6	89.68/-0.67/1.93	1.06	84.4
		9	89.27/-0.64/1.95	1.46	83.5
	60	3	89.31/-0.57/1.68	1.48	83.9
	70	1	84.85/-0.40/0.65	6.05	75.7

Optical properties were measured on coated side.

paper in that the printed images are not lasting. This means that we must strive to improve the heat stability of some chromophores in the coating color of the thermal paper.

Do varying temperatures affect the heat fastness of thermal paper A and B? Table 2 shows that no discernible color changes (Δ E<2.0) were observed, if temperatures are not greater than 50℃. It is evident from these observations that low temperatures have hardly any effect on the colorants present in the coating layers. However, the unknown colorants may rapidly decompose (ΔE>2.0) in higher temperature (>60℃) environments. Although the real reason for the deterioration of the thermal paper with aging is not known here, a marked decrease in lightness was also found in samples A and B in accelerated test at 70℃.

Table 2 also shows the general quantitative relationship between the color change and aging temperature. It is interesting to note that even a high grade thermal paper like sample A still showed a considerable loss in shade and brightness, i.e., higher ΔE^* and ΔL^*, Δa^*, Δb^* values under heating test. Table 3 shows that the printed areas of commercial thermal papers are greatly affected by the temperature of the surroundings. In other words, the higher the temperature is, the more color reversion (paper becomes lighter or poor heat fastness results) there will be. It seems that good heat fastness of both thermal papers (Table 2) will result if the temperature is within -5℃ to 50℃. In this situation, color differences are less than 1.5, where color change is not discernible by the human eye.

Even though we have put much effort in preparing heat fastness coatings and test their image stability, due to the complex composition of coating color we were still unable to make the kind of heat resistant thermal paper we had envisioned. Improving the heat fastness of thermal paper by top coating with some heat-insulating materials such as $CaSiO_3$ and $MgCO_3$ or applying low-melting-point gelatine to act as a non-penetrable protective coating was also tested in our laboratory. However, it was found that there were no marked effects to the stability of image and non-printed areas of the thermal papers when subjected to long term heating.

Table 3. Color reversion of printed thermal papers.

Heating time[*1] Min		Color reversion after aging								
		Sample A			Sample B			Sample C		
		lb	mb	db	lb	mb	db	lb	mb	db
0[*2]	L*	48.45	30.75	26.06	48.45	30.75	26.06	48.45	30.75	26.06
	a*	1.26	0.94	0.66	1.26	0.94	0.66	1.26	0.94	0.66
	b*	-5.96	-2.22	-0.95	-5.96	-2.22	-0.95	-5.96	-2.22	-0.95
10[*3]	L*	6.99	7.13	7.53	9.32	9.52	15.99	4.77	6.08	6.28
	a*	-2.29	-2.32	-2.52	-2.50	-2.64	-3.02	-2.22	-2.31	-2.37
	b*	-0.57	-0.63	-0.71	-1.15	-1.22	-1.31	-1.41	-1.52	-1.61
	E	7.38	7.54	7.96	9.76	9.95	16.32	5.53	6.72	6.86
	p.c. no	-10.09	-10.39	-13.09	-14.62	-15.56	-16.94	-3.14	-3.40	-3.80
20	L*	9.50	10.40	10.68	10.25	11.01	12.21	6.25	7.55	7.96
	a*	-2.74	-2.83	-2.84	-2.77	-2.84	-3.26	-2.42	-2.50	-2.56
	b*	-0.83	-0.85	-0.87	-1.22	-1.27	-1.37	-1.51	-1.60	-1.61
	E	9.92	10.82	11.08	10.71	11.42	17.60	6.93	8.15	8.48
	p.c. no[*4]	-10.34	-10.59	-13.84	-14.68	-15.76	-16.97	-3.59	-3.85	-4.22
60	L*	14.24	14.47	17.55	17.78	19.36	20.60	8.66	10.19	10.33
	a*	-3.29	-3.31	-3.60	-1.28	-1.52	-1.52	-2.62	-2.91	-2.91
	b*	-1.00	-1.02	-1.05	-1.28	-1.52	-1.52	-1.51	-1.67	-1.68
	E	14.63	14.88	16.18	18.15	20.95	22.60	9.20	10.71	10.87
	p.c. no	-10.73	-10.76	-14.21	-15.11	-16.22	-16.99	-4.20	-4.21	-4.53
120	L*	17.91	17.98	18.33	18.84	18.57	20.96	10.17	11.06	13.69
	a*	-3.47	-3.72	-3.76	-3.54	-3.56	-3.77	-2.85	-2.98	-3.20
	b*	-1.01	-1.06	-1.11	-1.36	-1.42	-1.43	-1.63	-1.67	-1.68
	E	18.31	18.34	18.76	18.96	19.35	23.81	10.69	11.56	14.14
	p.c. no	-10.98	-11.10	-14.30	-15.25	-16.31	-17.11	-4.25	-4.40	-4.80

*1 Heating at 50℃ .

*2 lb, mb and db represent the color of light black, medium black and dark black papers (dimension: 4 x 4 cm^2) printed on white paper as the indication of printed image.

3;L;a* and b* indicated the color changes of the printed areas on thermal papers after varying heating times.

*4 Negative p.c. number means lighter shade appeared on the printed areas of thermal paper after aging.

IV. CONCLUSIONS

From the experimental results, the conclusions were summarized as follows:

1. Based on the considerations of heat resistance of 6 commercial thermal papers in aging tests (50℃- 0℃), printed images of all test samples proved less resistant to heat and then fade gradually.
2. When coated the coated side of commercial thermal paper with small amount (5-10 g/m^2) of heat insulating materials such as $MgCO_3$ and $CaSiO_3$ and a low-melting-point gelatin, the heat fastness of the printed thermal paper can be improved slightly; however, no marked effects were observed.
3. In conclusion, the higher surrounding temperature is, the more color reversion of both the printed and non-printed areas of thermal papers there will be.

V. REFERENCES

Adhikary, P. (1966)U.S. Patent 3236717.

Casey, J. P.(1983)Pulp and paper chemistry and chemical technology, 3rd edition, Vol. IV, Interscience, New York, p. 2305-2306.

Clack, B. L.(1964)U.S. Patent 3147134.

Kadoya, Takashi(1988)Speciality paper, Japan, p.70

Kuo, L. S., C. M. Shu, and M. H. Duh(1998) Expressing the color of black paper, Forest Products Industry 17(1): 185-196, Taiwan.

Kuo, L. S., and W. J. Shiau(1994)A relationship between lightness variations and color difference while performing visual matching for various color papers, Bull. Expt. Forest of NCHU 16 (1):92-102.

Liu, C. Y.(1986)Personal communication, William Non-Carbon Reproduction Paper Company, Taichung, Taiwan.

Park, E.(1989)What is thermal paper?, Paper Technology, August, p. 14-16.

Rydholm, S.(1965)Pulping processes, Interscience Publishers, New York, p. 852.

ACKNOWLEDGEMENTS

The authors wish to thank National Science Council, Taiwan, Republic of China for the financial support (NSC-86-2313-B-005-088) of this study.