Quasi-Fixable Super Heat Resistant Direct Thermal Paper

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Abstract

This paper presents the development of quasi-fixable thermal paper, where the color forming capability of the non-imaged part (or the white portion) is considerably reduced by simply heating the thermal paper for a few seconds (fixing operation) after the imaging operation.

The use of the word "Quasi-" is because the fixed part can not be made completely unreactive, but still becomes slightly colored when high heat is applied. Nevertheless, the image on this thermal paper can be recognized or read even after heat-ironing the paper at as high as 180°C (360F).

The images can be formed easily as those on the conventional thermal paper, and the images are highly stable because of employing a sulfonyl urea dye-developer.

Introduction

Direct thermal recording paper has been widely used as an easy and convenient recording medium. Successful attempts were made to drastically increase the image-stability of thermal paper by employing the novel dye developer having the sulfonyl urea functional groups.[1]

As a result, the application of thermal paper has been extended from conventional facsimiles to include many other recording devices such as cash registers, cash-dispensers, automatic teller machines and handy terminals.

These new applications have created a new demand: an extreme heat-resistance of the direct thermal paper. When high heat is mistakenly (or intentionally sometimes) applied to the thermal paper, the heated portion becomes deep-colored and obscures the images. Thus, high stability of the images by itself is insufficient for maintaining readability of the images and marks on the thermal paper.

Several attempts have been made so far to produce fixable thermal paper. A successful one was done by Fuji Photo Film,[2] where diazo compounds were used as a color former. A colorless diazo compound forms color when reacted with a colorless coupler by application of heat. Diazo can be made unreactive by decomposing them upon irradiation of UV light after the image formation.

An advantage of this diazo thermal paper is that the photo fixed portion completely loses its coloring capability. However it is disadvantageous that the developed "black" tends not to be deep enough, resulting in a rather insufficient contrast of the image. It is also disadvantageous that an operator should be cautious not to expose the paper to the light before the imaging operations. In addition, the paper requires the recording machines to be equipped with a strong UV light source, making the size of the machine larger and caused the printing speed to slow down, because the photo-fixing practice needs a certain period of time.

Because of these disadvantages, the photo-fixable thermal paper has not been widely used in the market, and its applications have been very limited.

Compared to the photo-fixing, the thermo-fixing, if realized, will have the following advantages:

1. Heat application is a very simple process, requiring only a compact device that needs practically no maintenance effort.
2. Operator can handle the paper with no particular caution, such as avoiding the exposure of paper to the light.

These possible advantages have prompted us to study and develop the thermally quasi-fixable direct thermal paper described in this paper.

Performance of the Quasi-Fixable Thermal Paper

The picture shows the actual performance of the quasi-fixable thermal paper obtained as a result of this study, compared with conventional thermal paper (heat-resistant type).

There are no observable differences between the current fixable type and the conventional (heat resistant) type thermal paper in both stages of the printing operation and the fixing operation (note: the conventional type does not need the fixing operation in actual use, this is done here just for the comparison).

However, once extremely high heat is applied to both papers after the fixing operation, the apparent difference is observed.

The images on the fixable type can be clearly read, because the white portion (or non-imaged portion) colors only slightly. In contrast, the conventional type becomes entirely deep colored, and completely obscures the images.

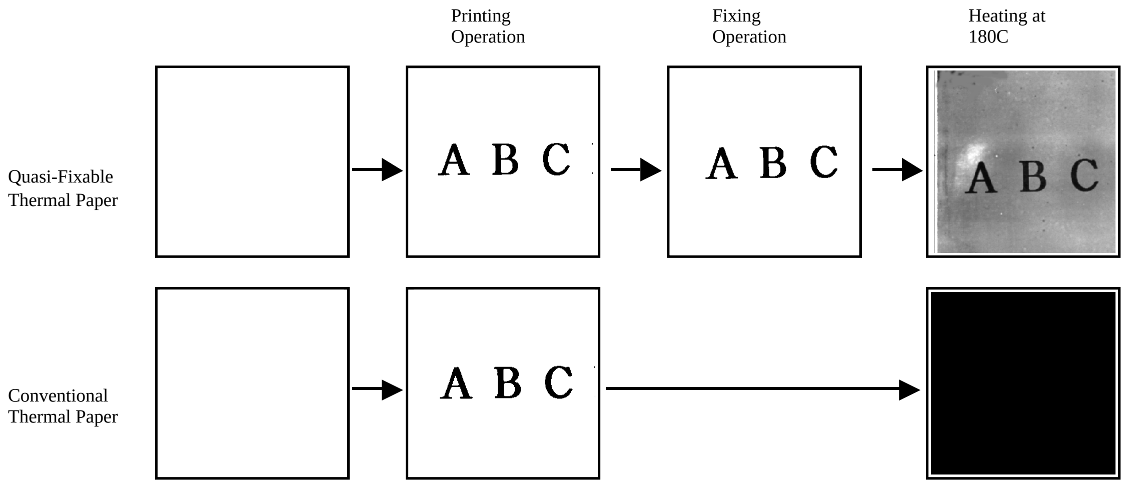
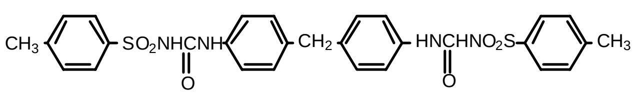


Figure 1. Performance of Quasi-Fixable Thermal Paper Compared with Conventional Thermal Paper

Technological Clue

A clue of the technological developments, which eventually lead to the present "Quasi-fixable Super Heat Resistant Paper", came from the interesting behavior of the sulfonylurea developers.

A specific sulfonylurea dye developer, the chemical structure shown below, was designed, synthesized and applied to the thermal paper that showed an unprecedented stable image formation on the paper.[1]



The images formed on the above paper strongly resist the various chemicals that would cause the fade of images if a conventional phenol type dye developer was used. This is schematically shown in the process I in figure 2.

It was also found, quite interestingly, that if certain chemicals were in contact with the thermal paper made of the sulfonyl urea prior to the image formation, only the pale images could form as shown in the process II in figure 2.

Image forming capability and its stability apparently depend on whether the sulfonyl urea compound interacts with the dye first or certain chemicals first.

We thought we could take advantage of this phenomenon to manufacture fixable thermal paper.

Basics of the Current System

The chemicals that are capable of reducing the dye-developing activity of the sulfonyl urea compound were found to include oil and fat, plastisizers and amine compounds.

In practice, these chemicals must be in the liquid phase to interact well with the sulfonyl ureas of the solid phase. Thus, the chemicals should be either liquid, solution, or melts to effectively reduce the dye-developing capability of the unreacted sulfonylureas.

To satisfy this requirement, we designed several possible systems including a mechanical coating of oil and plastisizers on the surface of the thermal paper after the imaging operation, and finally have reached to the current system that takes advantage of thermal energy to melt solid amine compounds.

The basic idea and how it works are presented in Fig. 3.

1) Thermal paper has at least two coated layers, one being a color forming layer mainly composed of a dye and the sulfonyl urea dye developer, and the other being a (quasi-) fixing layer having solid fixing agents.
2) Application of image-wise thermal energy as a form of pulsed heat produces deep colored (black) images on the paper.
3) Heating the thermal paper to 85 - 100°C for 3 - 5 sec, by using, for instance, a heat stamp to melt the amine compounds in the fixing layer.
4) The melted fixing agents penetrates into the adjacent color-forming layer, contacts with the unreacted dye-developer and considerably reduces its color developing capability.

Once the paper goes through the above processes, an non-imaged portion (namely the white portion) will lose a considerable part of its image developing capability, and will produce only weak color even if it is heated as high as 180°C (360 F).

Because of this weak color formation after the fixing operation, this paper may be called "Quasi"-fixable thermal paper" with super heat resistance.

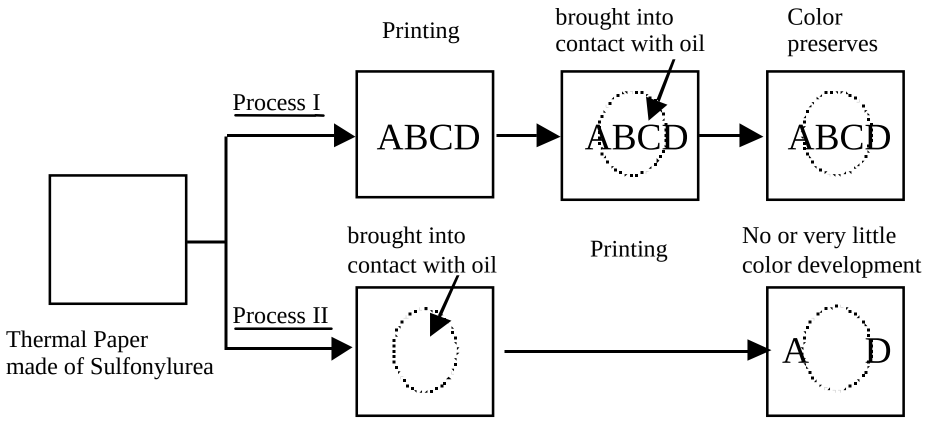


Figure 2 : Unique Character of Thermal Paper made of a Sulfonylurea Developer

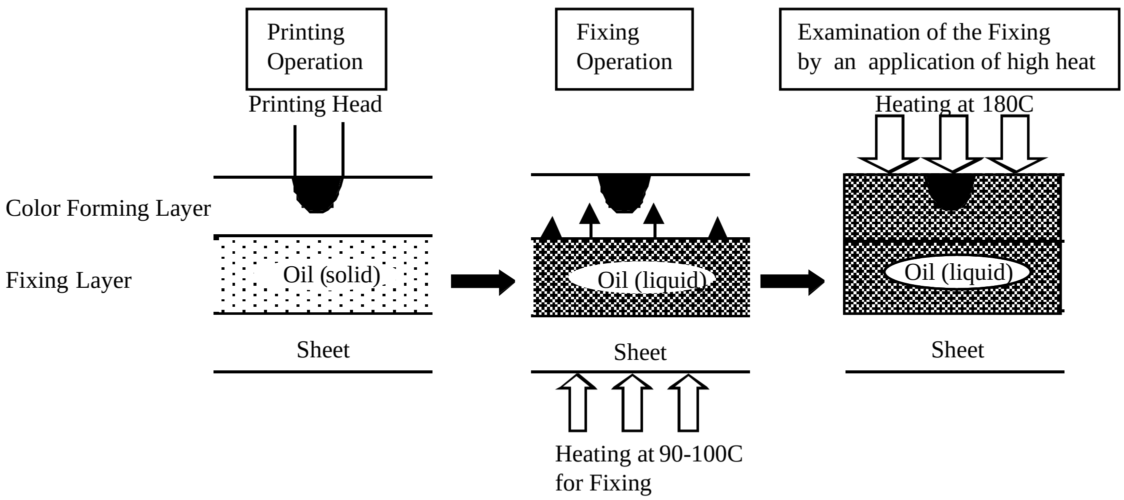


Figure 3. Basic Idea and How it works of the Quasi-Fixable Direct Thermal Paper

Actual Constitution and Performance of the Quasi-Fixable Thermal Paper

Based on the paper constitution shown in figure 4, an appropriate choice of chemicals and further improvements to refine the functions were made.

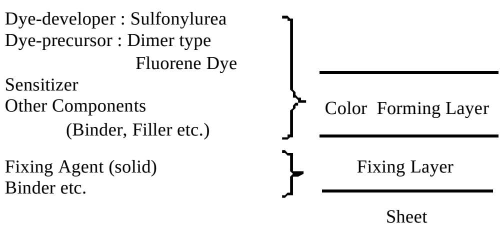


Figure 4. Constitution of Quasi-Fixable Thermal Paper

One of the crucial choices was to decide which chemicals are to be used as a fixing agent. Table 1 presents the data obtained by using solid vegetable oil (triglycelide, mp 54°C), and by using hindered amine compounds (type A, mp 80°C and type B, mp 130°C) as a fixing agent in the fixing layer.

The fixing operation was done by heating the surface of the pre-imaged thermal paper by using a heat stamp with temperature adjusted to be 90 - 100°C with pressing pressure of 1 Kg/m2 for 3 - 5 sec. The color densities of the image and white portion were measured by using Macbeth 914 color densitometer.

After the fixing operation, the thermal paper was again heated by an electric iron with 180°C for 5 sec. to examine the heat resistance of the images and the (fixed) white portion. The paper using solid vegetable oil as a fixing agent was disadvantageous in that the color intensity of the images was low, and the white portion after the fixing operation was slightly colored.

On the contrary, the paper using either hindered amine A or B showed a deep color formation of the image and no coloring by the fixing operation with temperature of 90°C.

In addition, the white portion developed only weak color (D=0.4), and the images retained the strong color intensities (D>1.1), even after heating the paper as high as 180°C, thus the images on the paper were found to be easily recognizable or readable. In case of the commercially available thermal paper of so-called "high temperature resistance", the entire paper became completely deep colored when the paper was heated at 180°C.

The other improvements include the usage of a dimer type fluorene dye instead of the conventional (monomer type) dyes, and the formation of an intermediate layer between the coloring and the fixing layers. These have contributed to the refinement of the performance of the quasi-fixable, super heat resistant direct thermal paper.

Conclusion

By combining a sulfonyl urea dye developer, which enables the highly stable images on thermal paper, and hindered amine fixing agent, we have developed a thermally fixable direct thermal paper. Although the thermal paper could not achieve full fixing character, namely the white portion of the paper slightly develops color, the image on the paper can be recognized or read even heating the paper as high as 180°C. The fixing operation requires only a few seconds.

In addition to the fixable character, the current paper satisfies the good thermal sensitivity(figure 5) as well as the high stability of the images (table 2).

References

1. Y. Takahashi, T. Segawa, A. Shirai and K. Toyofuku, *Proceedings of IS&T's 10th International Congress on Advance in Non-Impact Printing Technologies*, 349-351 (1994).
2. K. Nakamura, *Japan TAPPI Journal* (Kamipa Gikyo-Shi), **42**(5), 425-432(1998).

Biography

Takako Segawa obtained her B.Sc.in Chemistry from Aoyama Gakuin University in Japan in 1991. She joined Oji Paper Company Ltd., and has been involved in the development of direct thermal recording paper for the last 8 years.

Table 1 : The Choice of the Fixing Agents and its Effect on Thermal Paper

Fixing Agents	Color Density Of the Developed Part	Color Density of after Fixing Operation		Color Density of after heated at 180C		Contrast between Printed and White Part after heated at 180C*
		Printed Image	White Part	printed image	White part	
Oils:Triglycelide	0.91	0.91	0.16	0.91	0.35	good
Hindered Amine A	1.37	1.37	0.10	1.15	0.38	very good
Hindered Amine B	1.39	1.38	0.09	1.10	0.40	very good
ref.Conventional Thermal Paper	1.34	-	-	1.48	1.41	poor

*impression

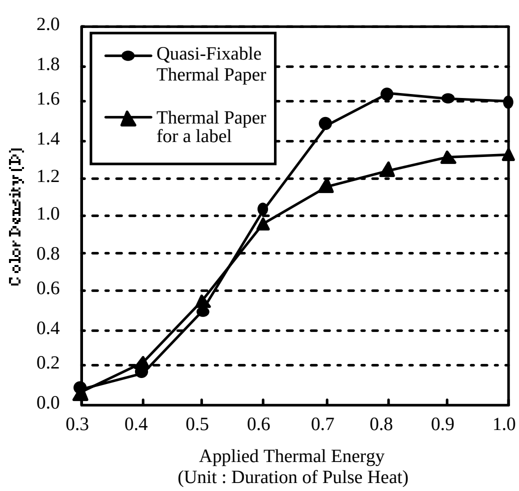


Figure5 : Sensitivity Curve of Thermal Paper

Table 2 : Image Stability Test

Sample Treatment	Quasi-fixable paper retainment of image density(%)	Thermal paper for a label retainment of image density(%)
Heating (60C for 24hrs)	100	100
Heating and Moistening (40C 90%, 24hrs)	100	100
Application of Oil (30min later)	100	97
Application of a Plastisizer (30min later)	98	35