Cross-Linked Naphthalene Bisimide “E-Barrier” Layer Compositions Using Blocked Isocyanate Chemistry

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Abstract

High-quality electrophotographic applications demand a photoreceptor drum that is “perfect” in many aspects, such as being defect-free—almost to the submicrometer level—environmentally insensitive, and possessing a well-defined photosensitivity that matches the electrophotographic rendering process.

Managing hole injection from the conductive substrate is critical to prevent “background and breakdown spots” on the final prints. Typical solutions require a hole-injection barrier layer. These layers need to be environmentally insensitive, resistant to the charge generation layer coating solutions, while allowing transport of photogenerated electrons to the conductive layer to prevent cycling charge buildup.

This work describes the development of naphthalene bisimide hole-injection e-barrier layer compositions that can be both coated thick and uniform, and thermally cross-linked. These coating solutions are very stable at normal coating temperature and suitable for the dip coating process. The blocked isocyanate cross-linkers are activated after coating at a temperature above 120 ºC. We have developed an offline method to study the kinetics of the cross-linking reaction using the GC headspace analysis technique for optimizing the cross-linked network.

Introduction

In a dual-layer photoconductor, managing hole injection from the conductive substrate is critical to prevent “background and breakdown spots” on the final prints. Typical solutions require a hole-injection barrier layer. These layers need to be environmentally insensitive, resistant to the charge generation layer coating solutions, while allowing transport of photogenerated electrons to the conductive layer to prevent cycling charge buildup.

Naphthalene bisimide-based polymers have been shown to provide a high-energy barrier to the injection of positive charges but transport electrons under an applied field [1–4]. Furthermore, these polymers transport charge by electronic rather than ionic mechanisms and therefore are not substantially affected by humidity.

This paper describes the development of naphthalene bisimide hole-injection e-barrier layer compositions that can be both coated thick and uniform, and thermally cross-linked. These coating solutions are very stable at normal coating temperature and suitable for the dip coating process. The blocked isocyanate cross-linkers are activated after coating at a temperature above 120 ºC. We have developed an offline method to study the kinetics of the cross-linking reaction using the GC headspace analysis technique for optimizing the cross-linked network.

Results and Discussions

Malonate Blocked Isocyanates

Blocked isocyanate cross-linking is a very well-established chemistry [5, 6, 7]. The advantages of blocked isocyanates over conventional isocyanate systems include:

a) Stable one-component formulations;
b) Minimal toxic hazard.

However, most blocked isocyanate systems deblock at relatively high deblocking temperatures and often produce byproducts that are nonvolatile; many of these byproducts present the potential to interfere with the charge-transport property of the photoconductive element.

Thus we have chosen diethyl malonate-blocked isocyanates because the reaction byproduct is mainly ethyl alcohol that is easily volatilized from the coating. Furthermore, the diethyl malonate-blocked isocyanates provide relatively low deblocking temperature at 120 ºC.

Naphthalene Bisimide Polyester Polyols

The barrier layer compositions of the work include two main components:

1) A preformed polyol incorporating the electronic-deficient naphthalene moiety;
2) The diethyl malonate-blocked isocyanate.

The synthesis of the naphthalene bisimide polyols is documented elsewhere [8]. A favorite naphthalene-bisimide polyol is shown below where **a** and **b** are mole fraction of a group, **a** represents a value between 0.5 and 0.90, and **b** represents a value between 0.041 and 0.2 (Fig. 1).

Specific examples are shown in Table 1, with the corresponding physical properties in Table 2, and formulations in Formulation 1.

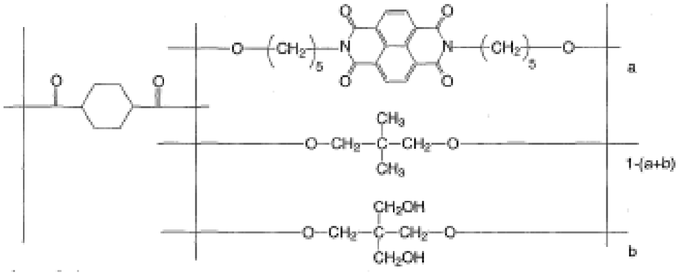

Figure 1

Table 1

Synthesis of Polymers 1-4

Polymer	CHDA	NPG	TMP	Naphthalene Bisimide
1	106.80 g. 0.620 mol	37.11 g. 0.356 mol	----	156.06 g. 0.356 mol
2	106.47 g. 0.618 mol	34.05 g. 0.327 mol	3.81 g. 0.028 mol	155.66 g. 0.355 mol
3	86.96 g. 0.503 mol	12.83 g. 0.123 mol	8.26 g. 0.062 mol	189.04 g. 0.431 mol
4	86.66 g. 0.503 mol	10.57 g. 0.102 mol	6.41 g. 0.048 mol	196.36 g. 0.448 mol

Table 2

Characterization of Polymers 1-4

Polymer	T_g	M_n	M_w	M_w/M_n	Hydroxy Concentration (meq/g polymer)	Acid Number (mg KOH/g polymer)
1	72	8,120	56,500	7	2.25	4.5
2	55	4,860	12,300	2.5	0.65	3.6
3	84	6,140	43,100	7	0.4	6.1
4	75	5,700	40,000	7	0.38	4.7

Table 3

Formulation 1

Components	NCO Equivalent Wt	Hydroxyl Equivalent Wt	Gram	NCO Equivalent Wt	Hydroxyl Equivalent mole	Equivalent Ratio OH/NCO
Polymer 4		2632	218		0.083	0.99
Trixene B9763	681		57	0.084		1.01
VAGH		951	32		0.034	0.4
					TOTAL	1.39

The electrical performance of a typical formulation is shown in Figure 2. The coating conditions and photoconductor architecture are described elsewhere [8].

The degree of curing is important to ensure solvent resistance. We have characterized this property using two different methods. In one method, we take advantage of the UV absorption of the naphthalene bisimide. Cured samples were extracted with 1,1,2 trichloroethane and tested for soluble polymer. This technique was used to optimize the polyol/malonate-blocked isocyanate (Fig. 3). The other method utilizes GC Headspace analysis to assess degree of reaction by monitoring the formation of ethanol from unreacted malonate groups (Fig. 3).

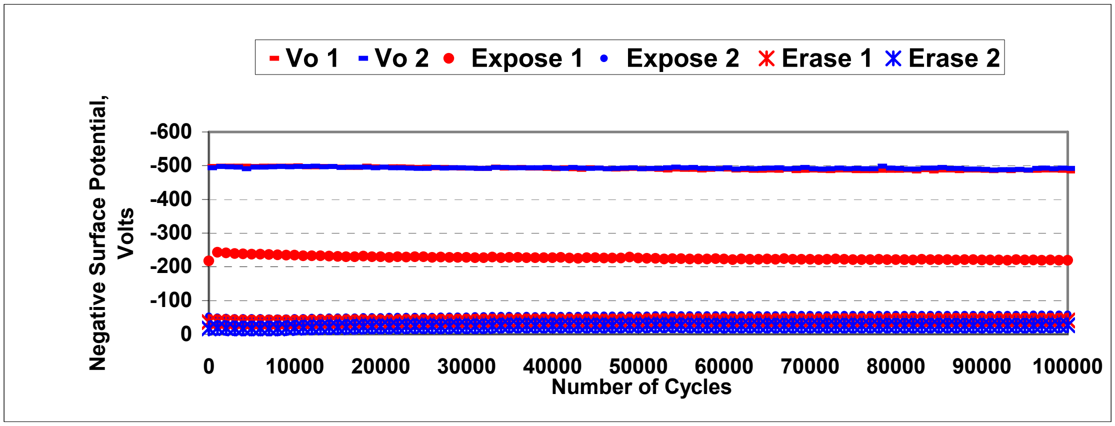

Figure 2.

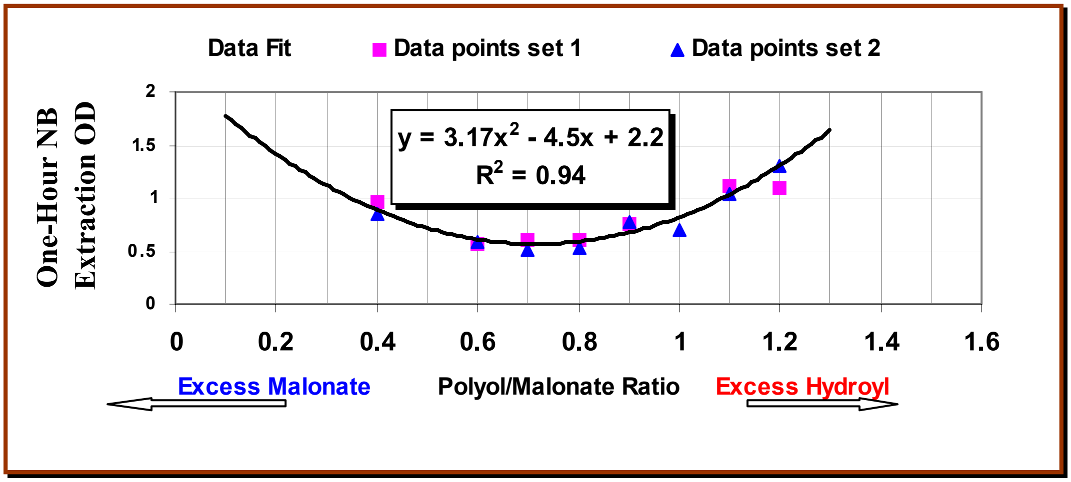

Figure 3.

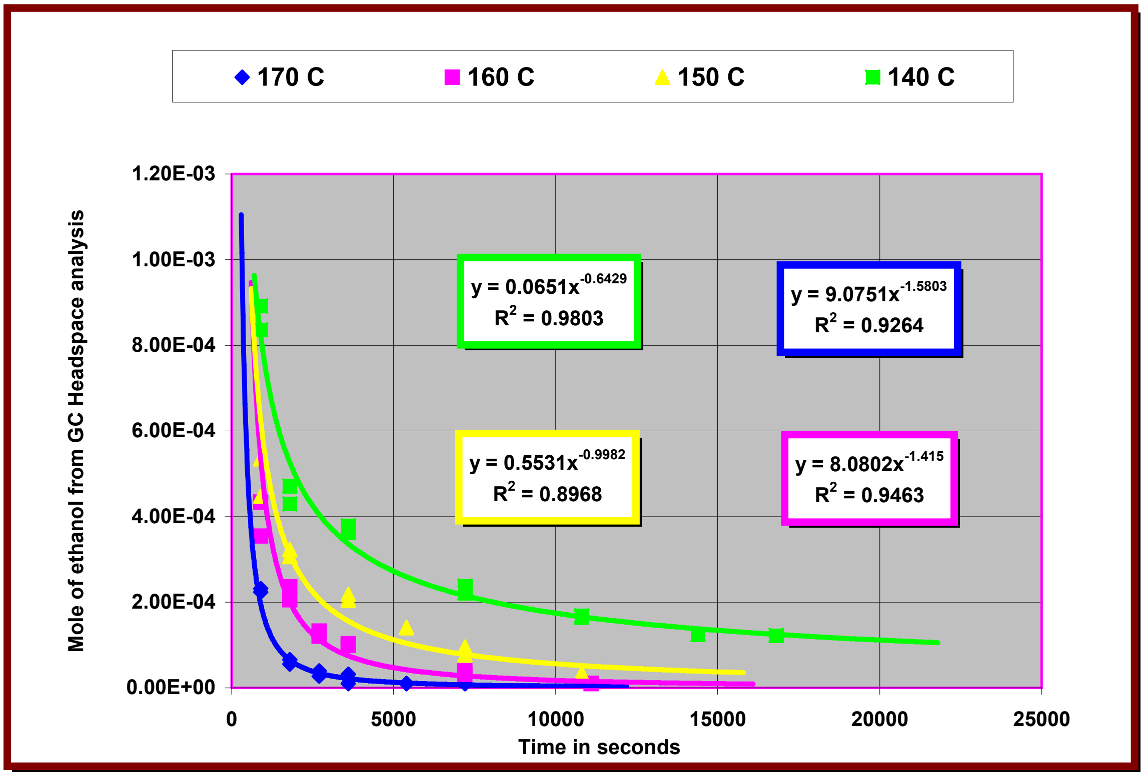

Figure 4.

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