

# UV-activated Reactive Film Adhesives

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## **Introduction:**

For both liquid and solid/film thermally curable adhesives, there typically exists a trade-off between cure temperature and shelf life. Generally, the more chemically active a thermally curable adhesive, the shorter is its shelf life at ambient temperatures as is expected from a basic activation energy perspective. In a practical sense, it is difficult to achieve both rapid low temperature cure and a long, stable shelf-life at ambient temperatures. This trade-off is exemplified by classic approaches to circumvent it, such as 2-part adhesives (separate the chemically reactive species) or frozen one-part systems (freeze the system to slow down molecular mobility and reaction kinetics).

Another approach to improving the shelf life/stability of a thermally curable adhesive is to utilize the concept of “triggered reactivity”. In this approach, some chemical or physical change occurs to the adhesive upon the application of an activation step, or “trigger”. Common examples of such triggers for one part systems include exposure to moisture (e.g. moisture cure one-part polyurethanes or silicones), thermal deblocking of a reactive species or curing agent (e.g. blocked isocyanate curing agents for polyols or salted/adducted amine curing agents for epoxies), exposure to radio frequency radiation (RF cure), internal heating of an adhesive containing ferromagnetic particles upon exposure to a fluctuating magnetic field (induction cure), or simply using UV or visible radiation to photochemically initiate a reaction (radiation curing). The use of triggered cure chemistry potentially allows one to simultaneously achieve both rapid low temperature curing and low reactivity at ambient conditions (i.e. good ambient shelf life). The catalyst or initiator for triggered curing is chemically masked in the unactivated adhesive, and as such long ambient shelf life/work life is practical because no active initiator or catalyst is present. Closer to the time of use, the catalyst or initiator can be activated, creating a system which can be cured rapidly, potentially at low temperatures. A useful “triggered cure” system exhibits some open time between activation and bonding, unlike a “cure-in-place” adhesive which cures rapidly once the trigger impulse is applied (e.g. typical radiation curable adhesives). Specifically, a triggered or activated adhesive allows one to activate the adhesive in one step and bond the adhesive to one or more substrates in a second separate step if desired. A traditional curable/cure-in-place adhesive must be bonded to the desired substrates prior to activation or curing, as it will not wet out and bond to substrates in a second step after it has been activated. A number of approaches to UV-triggered thermal curing are known and some have been exploited commercially. Examples include the retardation/inhibition of cationic cure using nucleophilic counteranions or trace amounts of added weak base<sup>1</sup>, delayed redox initiation systems<sup>2</sup>, “frontal polymerization”<sup>3</sup>, and photogeneration of acid or base catalyst followed by a post-exposure bake as used in chemically amplified photoresists<sup>4</sup>. It is this latter concept which we have extended in the course of our adhesive development.

This work utilizes the living character of a cationic epoxy cure mechanism coupled with the concept of latency derived from molecular immobility of binder film matrix below a certain temperature. This is shown pictorially in Figure 1. Conceptually, an epoxy/binder polymer blend

containing a cationic photoinitiator is formed which is in its glassy state at room temperature. The film can be UV irradiated to generate photoacid catalyst, but because the film is a glass at room temperature molecular mobility is low and the acid catalyst is largely unable to come into chemical contact with the epoxy functionality in the blend. This results in an activated, but mostly uncured state as illustrated in Figure 1a. The low molecular mobility of the film components creates a latency/open time which varies with the true degree of molecular immobility in the adhesive film. At this point, the film can be placed in contact with one or more substrates which are to be bonded. The derived laminated structure including the adhesive is then heated above the glass transition or melting point of the resin blend *vide infra*, and as molecular mobility increases cationic epoxy cure ensues as shown in Figure 1b. If the softening point of the binder resin and epoxy reactivity are chosen judiciously, the adhesive film softens and wets out the substrates prior to extensive epoxy cure resulting in a strong thermoset bond.

Figure 1a. Activated, low temperature/immobile uncured state; acid and epoxy are physically isolated in a glassy resin matrix (glassy binder polymer chains represented as wavy lines):

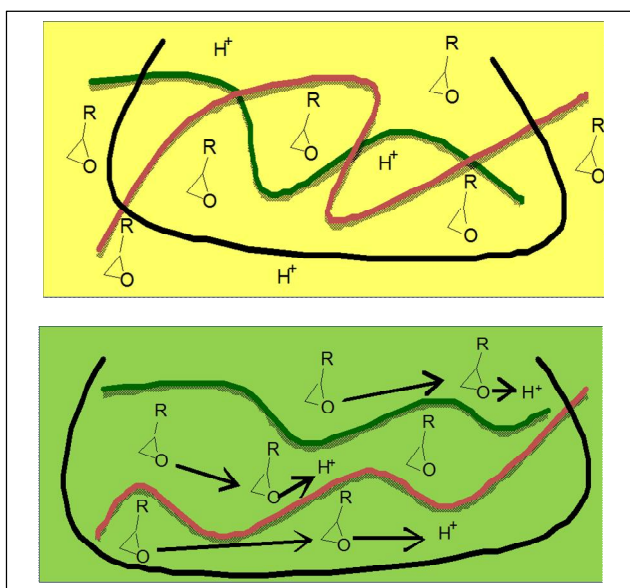


Figure 1b. Heated/mobile state allows for photoacid catalyzed thermal curing as polymer resin mobility increases:

**Figure 1. Cationic Cure Latency *via* Molecular Immobility**

To achieve an immobile polymer resin matrix at room temperature, binder polymers with  $T_g$  and/or  $T_m$  which resulted in non-tacky films at room temperature were blended with solid glycidyl epoxy resins. Glycidyl epoxies were utilized due to their slower cationic reactivity at ambient temperatures *vs.* cycloaliphatic epoxies which are more commonly used for traditional cationic UV curing. It is notable that many glycidyl epoxies are known to cationically cure rapidly at elevated temperatures even if they are sluggish at room temperature. Solid epoxy resins were used for this work to most easily facilitate blends which were solid, molecularly immobile systems at room temperature. Conceptually, any blend which results in a glassy film at room temperature is potentially interesting.

## Results and Discussion:

Several polymeric binders of varying softening points were combined with solid glycidyl epoxies to obtain UV-triggered thermally curable adhesives. Both amorphous and semicrystalline binder polymers have been studied. Although many solid epoxies can be utilized, this work focused on a (nominally) pentafunctional epoxidized cresol novolak resin (Epon 164, Momentive) and a (nominally) octafunctional oligomerized bisphenol A diglycidyl ether resin (SU-8, Momentive). Four representative combinations are summarized in Table 1, and the epoxy structures studied are shown in Figure 2. Based on the premise that the flow temperature/softening point of the binder polymer can control or at least modulate the epoxy cure rate vs. temperature, polymers with a range of flow temperatures were selected as film forming binders. Two different solid epoxies with similar softening points ( $\sim 85^\circ\text{C}$ ) were used. This minimizes variability in the net flow temperature of comparable blended systems while allowing the study of the effect of epoxy functionality on cured properties.

System #	Binder Flow Temperature ( $T_{\text{flow}}$ , $^\circ\text{C}$ )	Solid Epoxy Resin	Comments
1	125	5-functional	firm amorphous binder
2	125	8-functional	firm amorphous binder
3	100	8-functional	firm semicrystalline binder
4	70	5-functional	soft semicrystalline binder

Table 1. Summary of Binder Polymer/Epoxy Blends

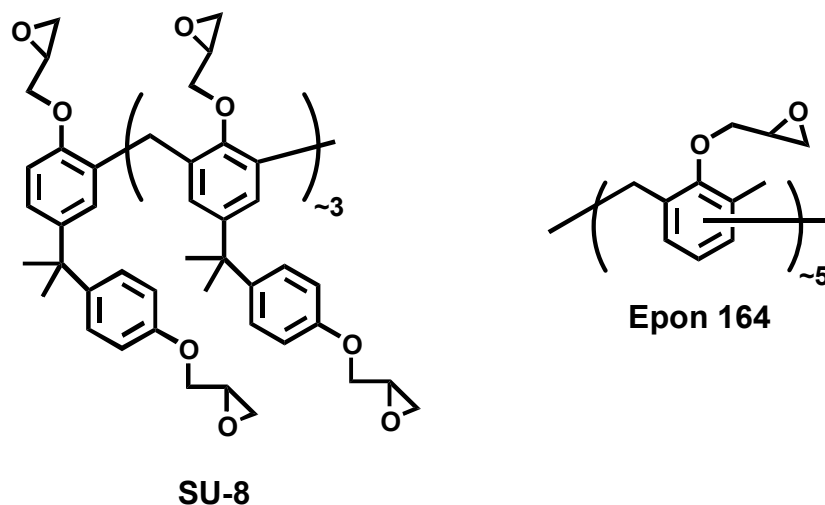
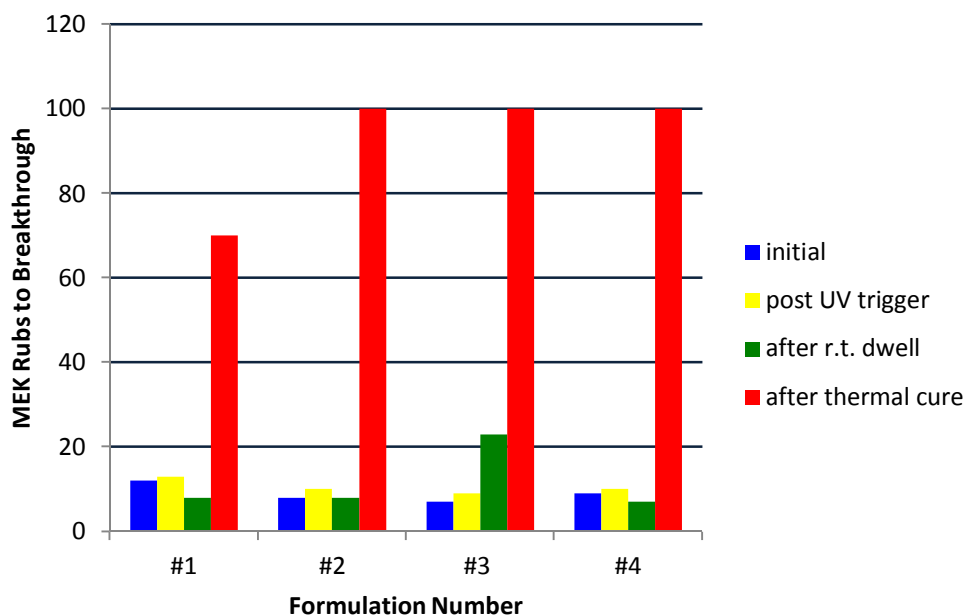


Figure 2. Solid Epoxy Resins

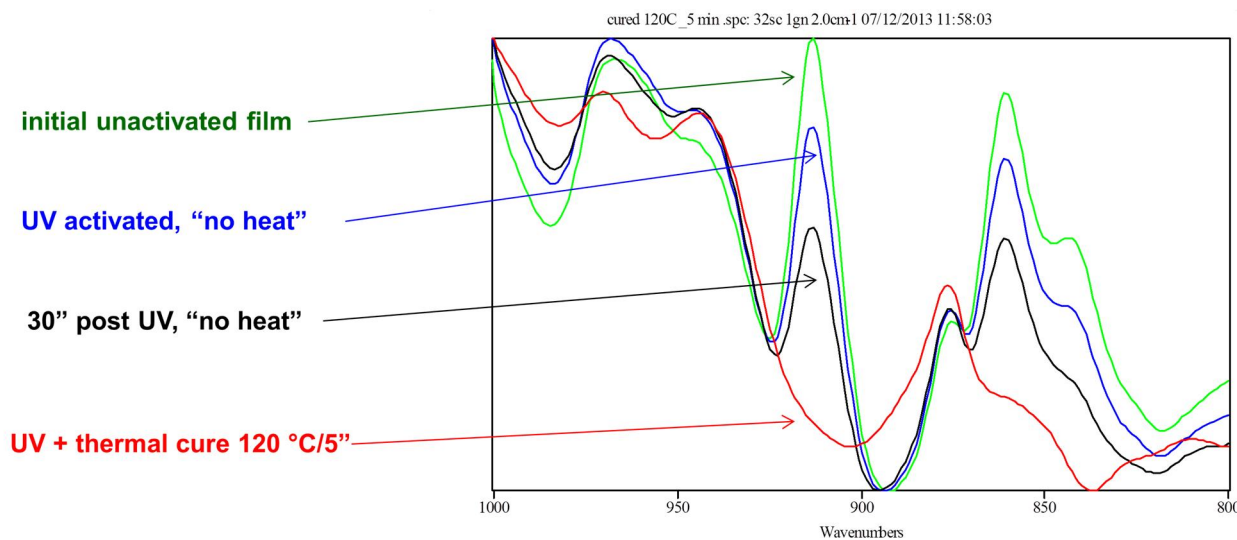
Blends were formulated in either 50:50 (systems 1, 2, and 4) or 60:40 (system 3) Polymer:Epoxy ratios depending on compatibility and solubility. It is noteworthy that this Polymer:Epoxy ratio can affect end properties particularly if the ratio changes drastically, but that for the purposes of this study the slightly lower overall epoxy content of system 3 was acceptable. The polyester and epoxy components were dissolved in a solvent system comprising MEK, THF, and toluene tailored to each specific resin blend. A triarylsulfonium salt photoinitiator (Speedcure 976, Lambson) was added at an experimentally determined level, typically around 1 wt.% on total solids. Details will be discussed below as needed, but in most cases solutions of the blends were solvent cast onto UV-opaque siliconized release liner and dried in a circulating air oven using an appropriate drydown profile for the solvent system used, with maximum oven temperatures not exceeding 120 °C to avoid thermal degradation of the triarylsulfonium salt photoinitiator. Typical dried film thickness was 50-75 microns unless otherwise stated.

The initial test for triggered UV curing was a simple MEK double rub experiment. In this case, films were solvent cast onto 50 micron PET. An MEK-soaked cloth was rubbed gently back and forth on the film, with one back and forth motion being a “double rub”. Films were tested before UV activation, after UV activation but before thermal cure, and after thermal cure. Results are shown in Figure 3. All four formulations exhibit a UV-triggered response with significant open times from ten minutes to several hours. The films dissolved readily in MEK as demonstrated by low breakthrough numbers before UV activation, just after activation, and after the dwell times at room temperature. This shows the epoxy component of the blends are essentially uncured. All formulations exhibited extensive epoxy conversion after the thermal cure step, as indicated by high MEK rub values (the test was stopped after 100 double rubs). Although the data is not shown, all formulations dissolved readily after thermal exposure if they were *not* UV-activated prior to that exposure. This shows the UV activation process is critical to facilitate effective thermal cure.



**Figure 3. MEK Rubs vs. Cure State**

To further examine and quantify the degree of epoxy cure vs. cure state, film samples were laminated to NaCl FT-IR plates and spectra were acquired at different stages of the activation and cure process. As labeled in Figure 4 below for the lower  $T_{\text{flow}}$  System #4, the epoxy band at  $910\text{ cm}^{-1}$  was observed and semi-quantified (area under peaks using integration to an uncorrected baseline) during the activation and thermal cure process. The softer System #4 shows the least latency, as tangible epoxy conversion occurs during the UV activation step (green vs. blue spectra). The UV irradiation step also heats the sample to some degree, so the lower  $T_{\text{flow}}$  binder resin of System #4 becomes relatively mobile and epoxy groups are able to come into chemical contact. Similarly, during the thirty minute open time examined additional epoxy cure is observed (black spectrum). Finally, as the system is thermally cured above the softening point of the binder system ( $120\text{ }^{\circ}\text{C}/5''$ ), near complete cure and epoxy conversion occurs (red spectrum). A similar study was performed on a System #1 which utilized a higher softening (higher  $T_{\text{flow}}$ ) binder resin (spectra not shown). Approximate epoxy conversion at the various process steps for both systems are summarized in Table 2. From this data it is evident the higher softening point binder resin of System #1 provides better latency during the UV cure process and open time in comparison to the lower softening point binder resin of System #4. It is believed that this is due to the slightly higher molecular mobility present in binder resin #4 across the processing and aging conditions, although additional study is required to confirm this relationship. In a practical sense, both system exhibit adequate latency during UV curing and an open time period on the order of minutes to allow for typical processing steps during the open time, such as sample transfer and/or heated lamination steps to one or more opaque substrates. It is also notable both systems are quite stable prior to UV triggering, as both exhibit little epoxy curing by FT-IR if heated through a cure cycle without first being UV activated.

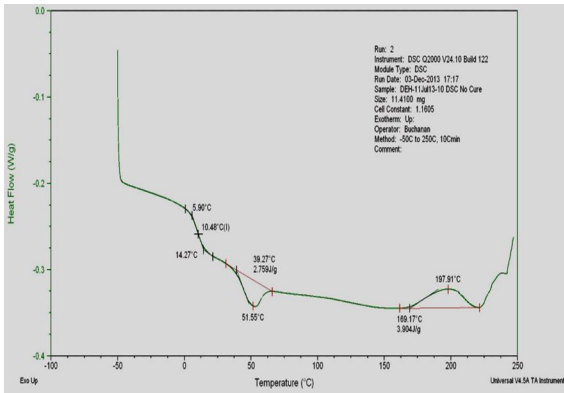


**Figure 4. FT-IR  $910\text{ cm}^{-1}$  Epoxy Band vs. Cure State (System #4  $T_s \sim 70\text{ }^{\circ}\text{C}$ )**

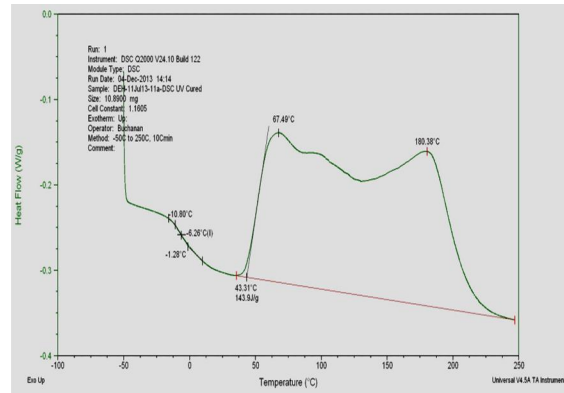
System	Initial (% conversion)	Immediately After UV Activation (% conversion)	After Open Time at r.t. (% conversion)	After Thermal Cure (% conversion)	<i>Unactivated</i> Film After Thermal Cure Cycle (% conversion)
#1	0	10	19	91	12
#4	0	26	44	100	7

**Table 2. Approximate % Epoxy Conversion from FT-IR 910  $\text{cm}^{-1}$  Band**

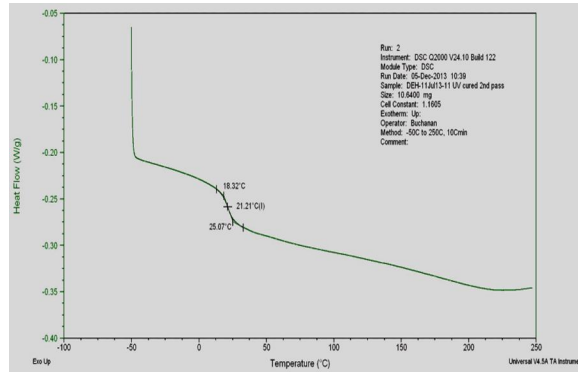
The UV-triggered cure process can also be studied using differential scanning calorimetry (DSC). A sample of System #1 was analyzed by ramping from room temperature to 250 °C at a rate of 20 °C/minute under nitrogen after various stages of cure activation. Results are summarized in Figure 5a-5c. The unactivated sample scan is shown in Figure 5a, and it can be seen that no cure occurs up to temperatures on the order of 170 °C, where it is known typical triarylsulfonium salts will begin to thermally decompose to generate acidic species. The  $T_g$  and  $T_m$  of the resin blend components are seen at 10 °C and 52 °C respectively. This scan demonstrates there is essentially no low temperature cure response in the unactivated state. This stability allows one to store typical products at room temperature for extended periods of time. The DSC scan shown in 5b is that of the UV-activated system. An extensive cure exotherm is now observed, with an onset of ca. 43 °C. This exotherm is absent in the unactivated material, and its presence clearly demonstrates the UV-triggered thermal cure concept. The cure enthalpy was 143J/g, which indicated an epoxy conversion of ca. 70% based on the literature enthalpy for glycidyl epoxies of 94 kJ/mol.<sup>5</sup> It is also notable that when a two day dwell was placed between UV-activation and DSC analysis the cure enthalpy was still 86% of that obtained if DSC was run a few minutes after UV activation. This again indicates good latency of the UV triggered system which relates to open time in a typical lamination or bonding process. Finally, a DSC samples which was UV activated and cured in the DSC was cooled back to room temperature and then run through a second DSC scan. This second DSC scan is shown in Figure 5c. Clearly, the sample was fully cured during the first DSC cycle, as no exotherm was observed in the second scan. Also, the  $T_g$  of the amorphous region is still observed, but at a slightly higher temperature (21 °C) vs. the uncured resin system (10 °C). The authors suspect this indicates a biphasic cured morphology for this epoxy/polyester blend, with some reaction of the polyester terminal hydroxyl groups into the epoxy matrix. Additional studies are underway to clarify this theory.



(5a)



(5b)



(5c)

**Figure 5. DSC Analysis of UV-triggered Curing**

The improvement in material strength which occurs with UV-activated cure was readily demonstrated by measuring lap shear strength. Samples were constructed by bonding 1"x 4" substrates of FR4 laminate or stainless steel together using a 1"x 1" piece of ca. 75 micron thick UV-triggerable adhesive. The adhesive square was first heat tacked to the first substrate, followed by activation with an appropriate UV dose (200-1000 mJ/cm<sup>2</sup> UVA, 300 W/in. Fusion H bulb). The second substrate was then placed on top of the activated adhesive in a typical lap shear geometry. The lap shear specimen was then thermally cured in a Sencorp bar heat sealer using 25 psi pressure. System #1 was heated to 140 °C/5" and System #3 was heated to 120 °C/1.5". Samples were allowed to sit for 24 h at room temperature prior to lap shear testing using a pull rate of 0.05 (#3) or 0.1 (#1) in./minute. Lap shear strength results are shown in Table 3.

Sample	25C, unactivated (psi)	25C, UV activated (psi)	65C, unactivated (psi)	65C, UV activated (psi)	80C, unactivated (psi)	80C, UV activated (psi)
System #1 , FR4/FR4	488	636	0.8	8.5	0.4	3.4
System #2 , FR4/FR4	346	417	9.7	22.0	1.8	10.1
System #3, FR4/FR4	230	540	4.6	55	1.6	18
System #1, SS/SS	37	444				

**Table 3. Lap Shear Strength vs. UV Activated Cure**

The lap shear specimens all showed significant increases in room temperature lap shear strength when comparing samples bonded with UV activation to those bonded without UV activation. Semi-structural bond strengths are obtained. For stainless steel samples, the increase was more than a factor of ten. The increase was also clear for FR4 to FR4 lap shear specimens. When elevated temperature lap shear testing was performed on FR4 based samples, UV-activated specimens again exhibited an order of magnitude improvement when compared to unactivated bonds. Systems #2 and #3, which utilize the higher octafunctional epoxy resin, exhibit better cohesive strength at elevated temperatures as would be expected from a more highly crosslinked material. The strength increase resulting from UV triggered cure of the epoxy component in the systems was significant, and has been commercially applied to improve the holding power of thermosetting film adhesives at elevated temperatures.

### Conclusions:

Several blends of solid glycidyl epoxies and polyester binder resins have been shown to exhibit UV-triggered cationic cure when the softening points of the components are selected such that molecular mobility is hindered in the solid state at room temperature. This limited molecular mobility creates chemical latency after the materials are UV activated to photogenerate acid catalyst. Only when the materials are subsequently heated above the flow temperature of the resin blend does rapid epoxy curing occur. This chemistry allows for the production of thermosetting film adhesives that cure to semi-structural strength values while allowing for the storage of product at room temperature in the unactivated state. Once UV activated, the latency of the cure system at room temperature allows for long open times (minutes to hours) and thus the assembly of opaque bonded parts. The activated, bonded parts can then be fully cured at relatively low temperatures (70-140 °C) and short cure times (second to minutes) depending on the softening temperatures and flow properties of the binder and epoxy resins selected. The UV activation, open time, and thermal cure process were studied using FT-IR, DSC, and physical testing such as MEK rubs and lap shear strength testing. The design principles for the systems are relatively simple, and a wide range of cured properties and specific adhesion performance can be obtained through proper selection of the polymeric binder resin, epoxy structure, and epoxy loading level.

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<sup>2</sup> Konarski, M.; Levandoski, S. *U.S. Pat. Appl. 2007/0267134*, **2007**.

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