

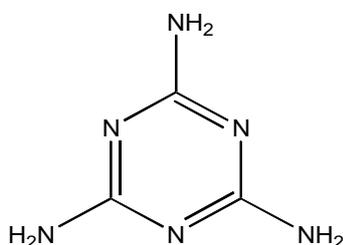
## Freshure® Coatings: Environmentally Friendly Barrier Coatings

Shahab Jahromi  
Knowfort Technologies BV  
Urmonderbaan 20a  
6160MD Geleen  
The Netherlands  
Email: [s.jahromi@knowfort.com](mailto:s.jahromi@knowfort.com)

**Introduction.** Roll-to-roll vacuum deposition of hard materials (inorganic and metallic) has been the method of choice to producing functional coatings in various industries such as semiconductor and flexible packaging. Vacuum deposition of soft organic materials on the other hand is still in its infancy but recently gaining more interest from various industries such as consumer electronics specifically for the production of devices based on Organic Light Emitting Diodes (OLEDs).

Here we present production of functional coatings based on vapor deposition of a class of compounds named triazine. First we will shortly highlight various aspects of the technology including base material and process parameters. Then we will discuss major features of two applications of triazine based coatings, i.e. as a barrier layer in flexible food packaging and as organic layer in multi-stack thin films for encapsulation of OLEDs.

**Basic material.** A large part of our work has been focused on vapor deposition of 1,3,5-triazine-2,4,6-triamine which is a well-known member of triazine family (see figure 1).

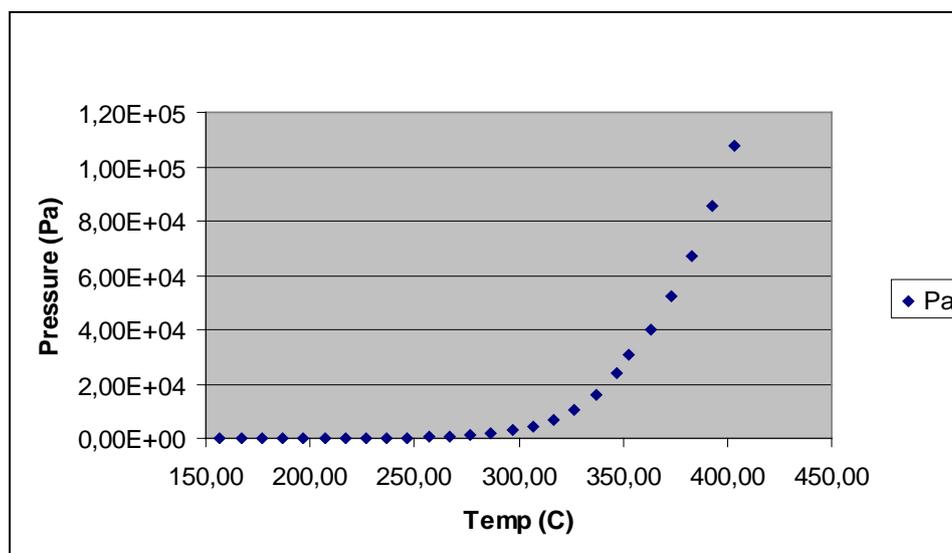


**Figure 1.** Chemical structure of 1,3,5-triazine-2,4,6-triamine.

This is a widely available material produced from natural gas. Gas plus air result in formation of ammonia. From ammonia urea is produced which is commonly used as fertilizer. 6 molecules of urea result in the formation of 1 molecule of 1,3,5-triazine-2,4,6-triamine. In soil environment this material decomposes back to its main ingredients and in fact it is sometimes used as a slow-release fertilizer. 1,3,5-triazine-2,4,6-triamine is a safe chemical and has a LD 50 > 3000 mg/kg which is comparable with table salt.

**Process parameters:** 1,3,5-triazine-2,4,6-triamine sublimes easily above 200°C. Above 350°C it starts a chemical reaction forming its higher homologues such as melam (triazine dimer) which also coincides with melting temperature of this

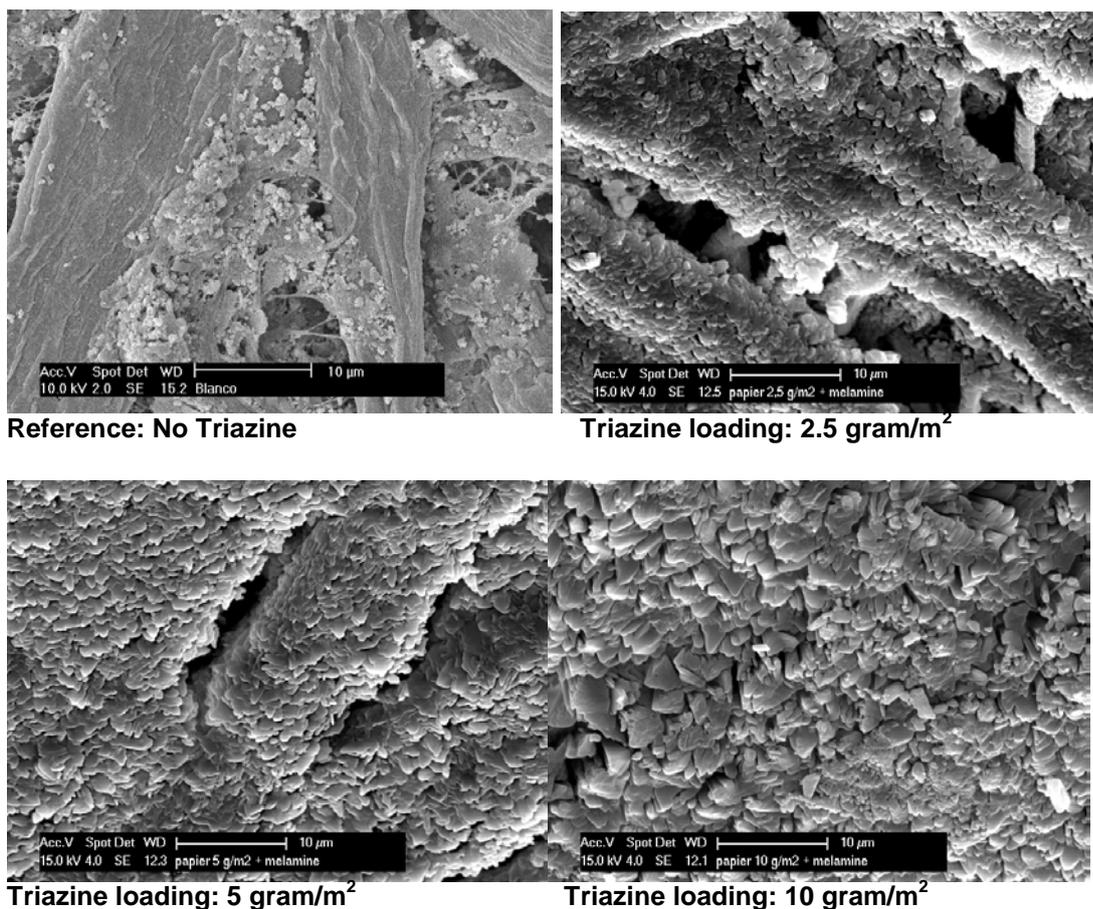
triazine at 354°C. Figure 2 shows the vapor pressure of 1,3,5-triazine-2,4,6-triamine as a function of temperature.



**Figure 2.** Equilibrium solid-Vapor diagram of 1,3,5-triazine-2,4,6-triamine

As can be seen in Figure 2, vapor pressure exponentially increases above 300°C. At such temperatures 1,3,5-triazine-2,4,6-triamine can be deposited under reduced pressure in a roll-to-roll set up on various types of flexible substrates such as plastic foils and paper at speeds exceeding 12 m/s. Typically 1,3,5-triazine-2,4,6-triamine is deposited at  $10^{-2}$  mbar which is mild vacuum especially in comparison with aluminum disposition where pressure levels are used below  $10^{-4}$  mbar. This eliminates the use of expensive and energy consuming diffusion pumps and relatively simple mechanical pumps would suffice. The total energy consumption is in fact much lower than aluminum metallization because of relatively low deposition temperatures and simple water cooling used during evaporation. This in combination with low price and biodegradability of raw material makes this process as a whole very much cost effective and environmentally friendly.

In the past we have demonstrated that triazine layer in a form of columnar structure on plastic foils.<sup>1</sup> Figure 3 shows SEM images of a triazine layer vapor deposited on at different loadings on paper.



**Figure 3.** SEM images of a paper substrate coated with different loadings of triazine.

As can be seen the fibrous structure of the paper is completely jacketed by a triazine layer at loading of 2.5 gram/m<sup>2</sup>. As the loading increases the voids inside the paper is completely filled with triazine material. Currently we are investigating the performance of such triazine coated paper substrates for examples in terms of gas permeability. This potentially opens the way to producing a fully biodegradable high barrier material without the use of plastic (EVOH) or metallic (Aluminum foil) materials for applications such as liquid packaging.

**A selection of applications:** The vapor deposited triazine layer display a series of unique properties as listed in table 1:

**Table 1.** Basic properties of layers based on vacuum deposition of 1,3,5-triazine-2,4,6-triamine

Property	Performance
Optical	Transparent layer with absorption in UV range (Refractive index= 1.87)
Permeability	High barrier to gases such as oxygen.
Dielectric	Dielectric constant of 4.25 in the frequency range 10 Hz to 10 kHz
Thermal	Stable up to 350°C.
Surface	Scratch resistance with a high surface tension (> 50 dyn/cm)

The collection of properties as listed in table 1 opens a number of applications for example as gate dielectric in organic field-effect transistors<sup>2</sup> and nanostructure surface in anti-reflective layers<sup>3</sup>. Here we highlight the applications of triazine based coatings in flexible packaging and thin film OLED encapsulation.

**Flexible food packaging:** Unique performance characteristics of triazine based vacuum coatings translate in certain key features which are important in various applications in flexible packaging (see Table 2).

**Table 2.** Performance characteristics of triazine based vacuum coatings resulting in certain key features important in flexible food packaging.

Performance	Key feature
High gas barrier	Attractive alternative for existing barrier materials such as PVdC and EVOH.
High surface tension	Printable with various types of inks used in flexible packaging (for both Flexo and Rotogravure) eliminating the use of primer.
UV-barrier	The only material that combines the optical transparency with UV- and gas barrier.
Scratch resistance	As an in-line Top Coat on other metalized films protecting the metal or metal oxide layer against mechanical damages.

Naturally gas barrier is the most prominent feature of triazine coatings. In this regard Triazine Single Coat, i.e. coating directly on the films, offers barrier performance which is superior to PVdC and sometimes even better than EVOH based materials.<sup>4</sup> Table 3 shows typical barrier values for PET-Triazine Single Coat and OPA-Triazine Single Coat laminated against PE.

**Table 3.** Barrier values of laminates based on Triazine Single Coat. The laminates are prepared with solvent less glue.

Substrate	WVTR (g/m <sup>2</sup> .24h) 23°C at 85% RH	OTR (cm <sup>3</sup> /m <sup>2</sup> .24h) 23°C at 0% RH
PET12μ-Triazine-PE50μ	0,71	1,0
OPA15μ-Triazine-PE50μ	0,63	0,3

In combination with other metalized films, Triazine Top Coat, which is an in-line process improves significantly the barrier of metalized films (Table 4).

**Table 4.** Barrier values of a series of metalized films with and without Triazine Top Coat applied as an inline-process.

Substrate	OTR [cc/m <sup>2</sup> /day @23°C; 0% RH]	
	Without Triazine Top Coat	With Triazine Top Coat
metCPP (20μ)	>300	<20
metBOPP (20μ)	>50	<10
metPET (12μ)	1-2	<0.5

Triazine Top Coat raises the bar and improves the performance of standard metalized films with metalized CPP entering the market for metalized OPP (e.g. confectionary, sacks etc), metalized OPP entering the high barrier markets (e.g. gas flushed products) and metalized PET replacing some of the applications which is now dominated by aluminum foil.

In using triazine based vacuum coated films in flexible packaging it is important to study the migration of this material under different conditions into packaged food. We have carried out a series of migration tests with different types of simulants on various types of film structures. Table 5 shows the migration results for a typical

laminate structure used for Modified Atmosphere Packaging (MAP) applications (PET12µm-Triazine-PE50µm).

**Table 5.** Migration tests results carried out according EN 13130-1 on a PET12µm-Triazine-PE50µm laminate. Test conditions: 10 days at 40°C (triplicates).

Component	Simulant	Specific migration individual results (mg/kg)	Specific migration mean results (mg/kg)
1,3,5-triazine-2,4,6-triamine	Water	<0.1 <0.1 <0.1	<0.1
	3% acetic acid	<0.1 <0.1 <0.1	<0.1
	10% ethanol	<0.1 <0.1 <0.1	<0.1
	50% ethanol	<0.1 <0.1 <0.1	<0.1
	Olive Oil	<1 <1 <1	<1
	MPPO	<0.1 <0.1 <0.1	<0.1

\*) Detection limit in olive oil is 1 mg/kg which is higher than in other simulants (0.1 mg/kg)

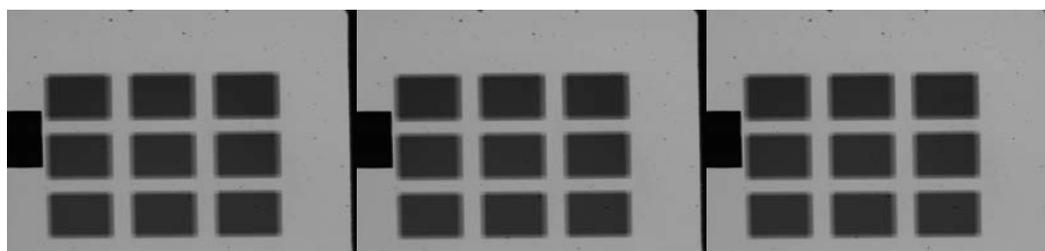
The results in Table 5 indicate that in all cases there is no measureable migration of triazine compound. Similar experiments have been conducted on various different laminate structures with similar outcomes. Based on these results DSM Safety and Regulatory affairs has issued Non-Migration Declarations stating that the use of triazine coatings for food packaging applications is compliant with both US and European regulations.

**Thin film encapsulation of OLEDs:** Life time of OLEDs is in large degree controlled by the quality of encapsulation material which should protect the various components against the action of oxygen and moisture. Current solutions involve encapsulation using metal and glass lids containing water scavengers (getters). Such encapsulation methods are expensive and not suitable for use in large surface areas and flexible substrates. Multi-layer barrier systems (organic/inorganic stacks) are being developed by various groups as alternatives to current encapsulation method. As the organic layers different materials are being evaluated such as acrylics, organic polymers, and nano-particles. We have explored vacuum deposition of triazine based compounds as an alternative to current solutions because of following advantages:

- Vacuum deposition of triazine coatings is a PVD process and completely compatible with vacuum deposition of Small Molecule OLEDs (no atomization or spin coating is required).
- As opposed to acrylics, no in-line curing step is required.
- Base materials are safe and widely available.

The above advantages result in a very competitive Cost of Ownership for triazine coatings as compared with other organic layers.

To demonstrate the basic feasibility of the use of triazine coatings in thin film encapsulation of OLEDs, Calcium (Ca) tests were carried out on multi-layer films consisting of Oxide/Triazine/Oxide. Oxidation of Ca coated on glass and covered by such thin film multi-layer films was monitored as a function of time (see figure 4).



A: 0 days storage

B: 6 days storage

C: 13 days storage

**Figure 4.** Ca tests carried out with multi-layer thin films consisting of Oxide/Triazine/Oxide layer. Ca coated glass substrates were vacuum deposited with such thin barrier films. The oxidation was followed by monitoring increase in light transmission (indicating oxidation of Ca) as function of time at 50°C and 50% relative humidity.

Ca can react easily with water and oxygen resulting in increase of the optical transmission of test cells. As can be seen in figure 4 there is no increase in optical transmission of the test cells coated with Oxide/Triazine/Oxide layers after almost 2x weeks of storage at ambient conditions indicating basic feasibility of our concept for thin film encapsulation of OLEDs. Currently we are in the process of conducting such Ca tests at elevated temperatures and humidity's.

**Conclusions.** Here we have discussed physical vacuum deposition of organic compounds to producing functional coatings as an alternative to the traditional way, i.e. vacuum deposition of inorganic materials. From functionality point of view, vacuum deposition of organic compounds offers more possibilities since the base material can be much more easily chemically modified rendering different functionalities. In comparison with vacuum deposition of inorganic compounds, coating of organic compounds occurs at much softer conditions, i.e. lower temperatures and higher pressures. This has been demonstrated for vacuum deposition of 1,3,5-triazine-2,4,6-triamine which is a prominent member of triazine family. It is shown that vacuum deposition of such compounds provide a very effective gas barrier opening applications in flexible food packaging. Migration studies have shown that the use of such compounds is fully compliant with both US and European regulations. Next to applications in flexible food packaging the basic feasibility of the use of such coatings for thin film encapsulation of OLEDs has been demonstrated.

<sup>1</sup> S. Jahromi, U. Moosheimer, "Oxygen barrier coatings based on supramolecular assembly of melamine" *Macromolecules*, 33, 7582, 2000

<sup>2</sup> M. Irimia-Vladu, N. Marjanovic, M. Bodea, G. Hernandez-Sosa, A. Ramil, " Small molecule vacuum processed melamine-C60, organic field effect transistors" *Organic Electronics*, 10, 408, 2009

<sup>3</sup> U. Schulz, C. Prafke, P. Munzert, C. Godeker, N. Kaiser, "Formation of antireflective nano-structures on melamine and N,N'-di (1-naphthyl)-N,N'-diphenyl benzidine (NPB)" *Optical Materials Express*, 1, 101, 2011

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<sup>4</sup> A typical OTR value for PET-PVdC based laminates is around 9 cm<sup>3</sup>/m<sup>2</sup>.24h and for OPA-CoexEVOH is around 1 cm<sup>3</sup>/m<sup>2</sup>.24h.