Smart Cure Technology From Henkel Achieves Cure and Regulatory Compliance in 3 Days

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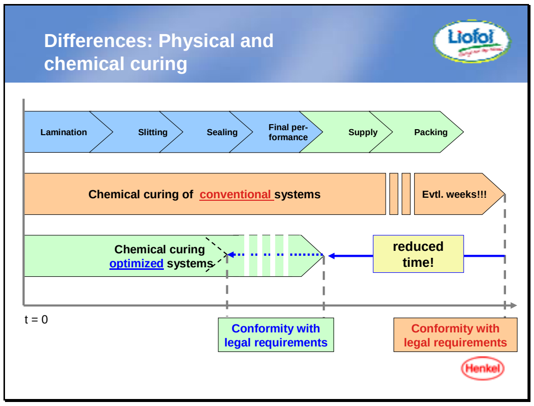
During his tenure at Henkel Corporation, Dr. Guido Kollbach has been responsible for developing new flexible packaging adhesive solutions that provide added value to customers. Most recently, Henkel has led the development of a new curing technology for Henkel's "Smart Cure" solventless polyurethane adhesives, which allow converters to achieve cure and regulatory compliance in three days. Dr. Kollbach was awarded his Ph.D. by Ruhr-University of Bochum, Germany in cooperation with Max-Planck-Institute fuer Kohlenforschung, Muelheim a.d. Ruhr, Germany. He completed his Diploma in Chemistry at Gerhard-Mercator University of Duisburg, Germany.

Abstract

Converters struggle with rising costs and an increasing awareness for food safety. Of all available lamination technologies, solventless polyurethane adhesives are the most cost effective. With adhesive coat weights typically ranging from 1 - 1.15 lbs/ream, these adhesives offer good adhesion to a wide variety of substrates. Printed, metalized, or otherwise coated materials and a myriad of sealant layers are no problem. These systems are convenient to use with near-room-temperature application and long potlifes. Conventional solventless systems, however, require long storage times in order to comply with food safety regulations. With Smart Cure, Henkel's new unique curing technology offered in a new line of solventless polyurethane adhesives, bond development and food safety compliance are both achieved in a very short time. Compliance testing performed using 3% acetic acid is the most stringent, worst case scenario to meet the FDA regulations. Smart Cure adhesives meet the dual needs of physical performance and regulatory compliance for food safety in less than three days for the majority of structures, compared to the many weeks required by conventional systems. A recent study compared the relationship across a range of variables including substrates, coating weight, cure conditions, moisture, etc. Special attention was paid to the filling good used as the food simulant in the migration test. In a time of increased environmental awareness and food safety, Smart Cure adhesives offer fast cure without compromising food safety.

Rapid Compliance

A laminate manufactured with the ideal adhesive would be in compliance with food safety legislation at the same time it reaches its full physical performance. Flexible packaging suppliers have to allow a certain storage time for the polyurethane adhesive to cure prior to further processing, e.g. slitting, pouch making, etc. It is the obligation of the flexible packaging manufacturer to ensure that the packaging material introduced into the market complies with all relevant food safety regulations. With conventional 2-component room temperature adhesive systems, the storage time can eventually take weeks. Due to a special curing mechanism, Smart Cure laminating adhesives are fully cured and reach the legal compliance in only a few days.



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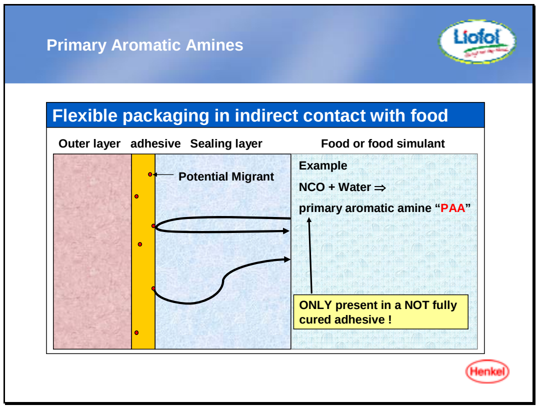
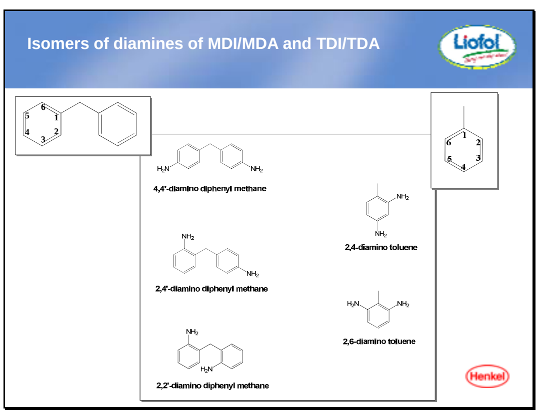
Migration of primary aromatic amines

If the laminating adhesives is not fully cured and still contains unreacted monomeric diisocyanates, these substances may migrate through the sealant film and into the food.



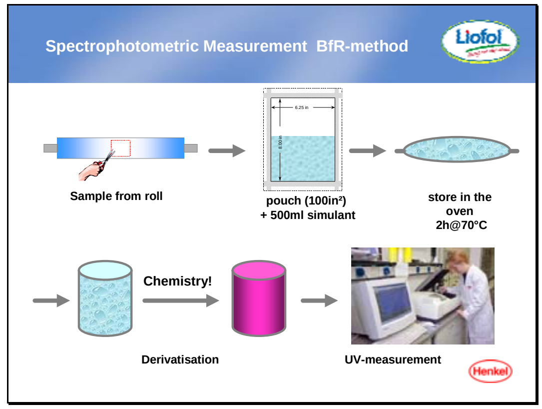
Once migrated, they will react with almost ubiquitous moisture and form the corresponding primary aromatic amines. Primary aromatic amines have been classified as carcinogenic.



Analytics of primary aromatic amines

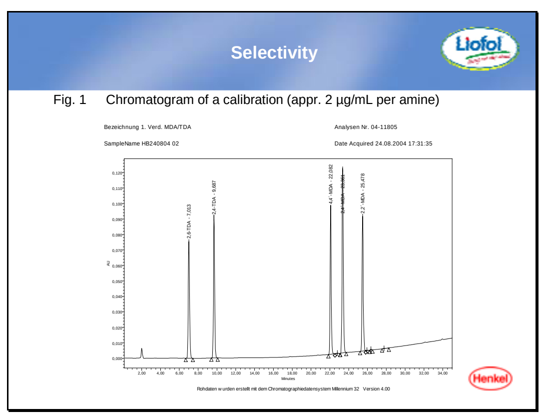
The most practical approach to test a laminate for migratory amines is to make pouches, fill the pouches with a suitable food simulant, and seal and store them for a defined time at an elevated temperature. After storage, the amount of migratory amines present in the food simulant will be measured.

There are many methods available to measure the amount of primary aromatic amines present in test solutions.



One method is the so called photometric test. Here the amines are derivatized with a coupling agent to form a colored dye. The intensity of the test solution is proportional to the concentration of primary aromatic amines (following Beer's law) and can be quantified with a UV/VIS spectrophotometer. The detection limit for this method, which totals all primary aromatic amines, is 2 ppb.

Another method uses HPLC/UV coupling to measure the amines directly. Via high pressure liquid chromatography, the isomers of the primary aromatic amines are separated from each other. Therefore this method is sometimes called the "specific migration method".



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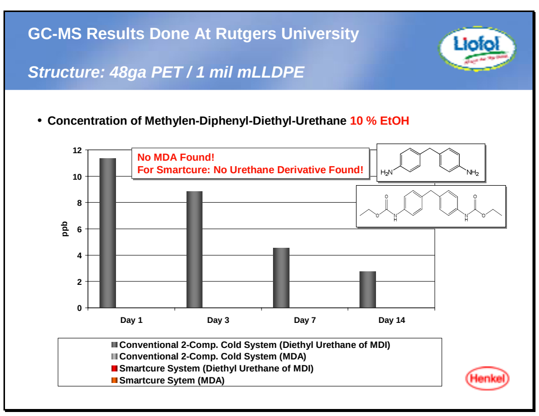
The retention time together with the UV spectrum of the isomers is used to identify the extracted substance. The detection limit for this method is 1.5 ppb per each isomer.

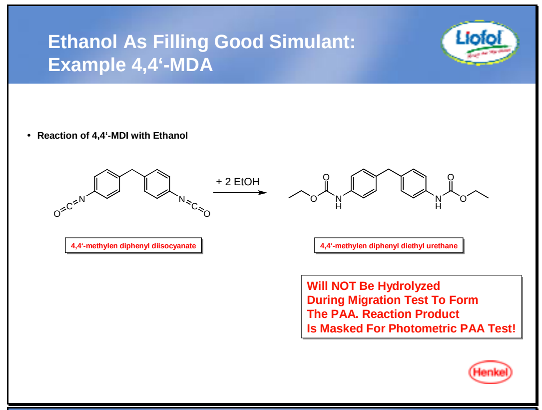
Both the photometric test and the specific migration method focus on determining the amount of migratory amines only. The GC/MS method separates all substances by GC and analyses the separated substances by mass spectrometry. The advantage of this method is that it also finds substances other than primary aromatic amines. The major disadvantage of this method, however, is the very high injection temperature which can induce GC specific chemistry during the measurement.

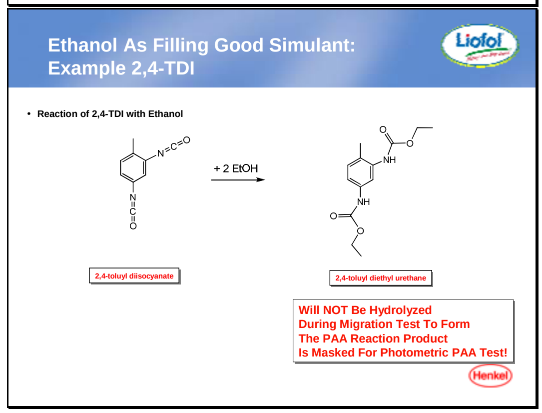
Comparative study of conventional systems and Smartcure adhesives

A 48 ga PET/ 1 mil mLLDPE and a 60 ga Nylon/ 1 mil mLLDPE laminate have been manufactured with a conventional curing system and a Smart Cure system. The laminated samples were shipped overnight to Rutgers University. Pouches were made from them after 1 day, 3 days, 7 days and 14 days cure time. The pouches were filled with different food simulants. The sample solutions have been analyzed by GC/MS. The most interesting result from this study was that in case of 10% ethanol as the food simulant, no MDA was detected even in case of the conventional curing systems. Instead the reaction product of MDI with ethanol was analyzed.



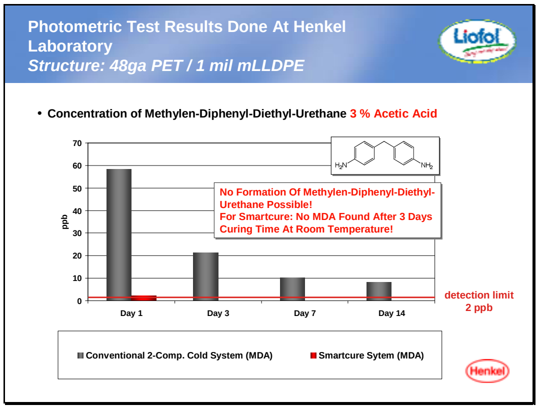
As expected ethanol is the preferred reaction partner rather than water for MDI. The diethyl urethane derivative, however, is stable and will not be hydrolyzed under the storage conditions of the sample preparation.



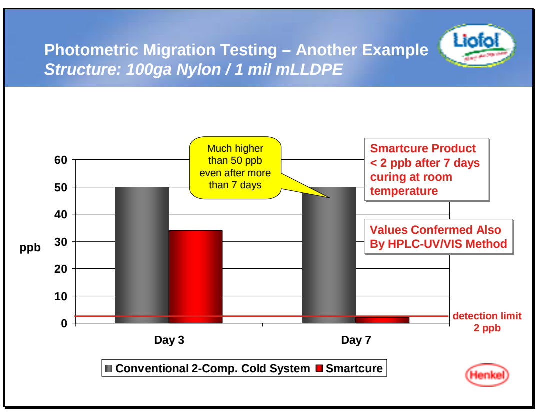


This means that through the reaction with ethanol, diisocyanates are partly masked and cannot be converted to the corresponding primary aromatic amine.

So far we have not been able to calibrate the photometric test for the measurement of ethanol solutions. The much more severe test with 3% acetic acid clearly demonstrates that conventional systems cannot be considered safe for food packaging applications. Even after 14 days, primary aromatic amines are detected.



In case of Nylon as a substrate, the cure rate of polyurethane adhesives is reduced. As a consequence, the cure time to comply with food safety regulations takes longer. In both cases, Henkel Smart Cure adhesives comply with regulations in only a few days; while the adhesives cured according to the conventional curing mechanism do not comply even after 14 days cure time.



The “specific migration method” confirms that conventional solventless adhesive systems were not migration free after 14 days cure. Henkel’s Smart Cure system, however, is free of migratory amines after 1 day cure at room temperature under the same circumstances.

	4,4'-MDA	2,4'-MDA	2,2'-MDA
Day 1			
3% acetic acid			
conventional 2 comp. cold system	< 1.5	6.8	36
smartcure adhesive	< 1.5	< 1.5	< 1.5
10% ethanol			
conventional 2 comp. cold system	< 1.5	3.7	2.2
smartcure adhesive	< 1.5	< 1.5	< 1.5
95% ethanol			
conventional 2 comp. cold system	< 1.5	< 1.5	< 1.5
smartcure adhesive	< 1.5	< 1.5	< 1.5
Day 3	**4,4'-MDA**	**2,4'-MDA**	**2,2'-MDA**
3% acetic acid			
conventional 2 comp. cold system	< 1.5	< 1.5	11.5
smartcure adhesive	< 1.5	< 1.5	< 1.5
10% ethanol			
conventional 2 comp. cold system	< 1.5	< 1.5	< 1.5
smartcure adhesive	< 1.5	< 1.5	< 1.5
95% ethanol			
conventional 2 comp. cold system	< 1.5	< 1.5	< 1.5
smartcure adhesive	< 1.5	< 1.5	< 1.5
Day 14	**4,4'-MDA**	**2,4'-MDA**	**2,2'-MDA**
3% acetic acid			
conventional 2 comp. cold system	< 1.5	< 1.5	8.8
smartcure adhesive	< 1.5	< 1.5	< 1.5
10% ethanol			
conventional 2 comp. cold system	< 1.5	< 1.5	< 1.5
smartcure adhesive	< 1.5	< 1.5	< 1.5
95% ethanol			
conventional 2 comp. cold system	< 1.5	< 1.5	< 1.5
smartcure adhesive	< 1.5	< 1.5	< 1.5

If 10 % ethanol is used as a food simulant, suddenly the conventional curing systems comply with food regulations after the 3rd day of cure time. No primary aromatic amine was detected in any case if 95 % ethanol was used as the food simulant.

Most food on store shelves contains water or moisture, not 10% ethanol.

If laminates are tested on migratory amines and 10% ethanol is used as a food simulant, the ethyl urethane derivatives of MDI and/or TDI must be considered and reported. Otherwise the values could be compromised by the reaction of ethanol and the isocyanate, resulting in under-reported PAA concentration.

The FDA accepts the use of 3% acetic acid as the food simulant that best mimics a worst case scenario, and it is easier to evaluate.

Conclusion

The use of 3% acetic acid as the food simulant best mimics a worst case scenario, and it is easier to evaluate. Laminates manufactured with Henkel's Smart Cure technology are in compliance with food regulations in only a few days even under worst case circumstances.

If you have any questions about our technology please do not hesitate to contact us.

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