DESICCANT COMPARISON REPORT

A comparison of humidity reduction of barrier pouches containing calcium oxide as an active barrier with pouches containing sachets of clay, silica gel or molecular sieves

By: Lee Murray, James Sikorsky and Rick Merical (Alcan Packaging - Medical Flexibles Americas)

ABSTRACT

A comparison was conducted between peelable foil pouches containing an active moisture scavenger barrier built into the polyethylene sealant of the flexible package (Alcan Packaging DesiShield™) and standard peelable foil pouch lamination whereby a 1 g sachet of activated clay, silica gel or molecular sieves were inserted, which is typical of the current packaging method to scavenge residual moisture from the headspace of a flexible package.

The humidity in the pouch was ascertained by examining the moisture content of paper placed inside the pouches. The speed of moisture removal and the final moisture levels reflect the capabilities of the desiccants involved. Although the speed of response was faster with one of the sachets; the active moisture barrier pouches where the active moisture scavenger was incorporated into the DesiShield™ polyethylene film sealant layer achieved extremely low package headspace relative humidity (RH) within days and continued to drive package headspace RH to extremely dry conditions of less than 2%, lower than any commercially available inserted desiccant sachet package.

BACKGROUND

Many medical device, pharmaceutical, biochemical, diagnostic, electronic and industrial products may be damaged by atmospheric moisture. For this reason moisture-sensitive products are placed in packaging containing moisture barrier materials such as high density polyethylene (HDPE), Saran® (PVdC-MA copolymer), oriented polypropylene (OPP), metallized OPP, metallized polyester (met-PET) or aluminum foil.

Even using aluminum foil, some moisture will slowly permeate into the package through pinholes and the edges of packages. The details of how this happens and the impact of foil pinholes have been documented in prior technical papers available from Alcan Packaging[i].

One solution to maintaining a particularly low level of moisture within a package is to incorporate desiccant sachets[ii] in the package to remove the moisture from the headspace and absorb any moisture that permeates into the package. Because of the cost of sachets, these are not commonly used for small, low cost products but rather in multiple unit packages. An attractive approach for high value products such as pharmaceuticals, test strips, medical devices or electronics would be to protect each item in a moisture scavenging package[iii]. Each package would capture moisture coming through the edges of the seals, polymeric barrier layers, and aluminum foil pinholes. The desiccant should be positioned inside the barrier layer of the flexible package having intimate contact with headspace of the package. An example of such an active barrier pouch would be the structure: PET/ Print / White LDPE Coex / Al foil/ LDPE Coex/ PE Desiccant Sealant tandem extrusion lamination. This type of package where the moisture scavenger is incorporated into the polyethylene sealant layer of a foil lamination has been commercially marketed for more than 3 years by Alcan Packaging.

This study and paper was initiated to compare commercially available desiccant sachets of various types to the moisture scavenging foil lamination where the scavenger is incorporated into the polyethylene sealant layer. The purpose of the study is to determine comparative performance towards maintaining a steady state humidity within the package headspace, particularly desirable for medical or combination devices and other high value products that are adversely affected by exposure to moisture even at very low levels. Laboratory comparisons were made and reports have been published[iv] to demonstrate the differences between various desiccants which could be employed in sachets or potentially in an active barrier moisture scavenging package.

DISCUSSION

Desiccants types can be classified as:

1. Physical
   a. Molecular sieves (dimensional)
   b. Absorptive surfaces such as alumina, silica gel, and clay
2. Hydrate forming salts
3. Hydroscopic salts
4. Moisture absorbing organic agents
5. Chemically reactive agents

This study is a comparison between very common inserted physical desiccant sachets and Alcan Packaging's chemical desiccant incorporated as part of an active moisture scavenging component of the lamination package sealant

Molecular sieves, or Zeolites, bind water molecules within pore spaces of the material. Surfaces of materials such as silica gel and clay have the ability to adsorb water molecules on their surface. With physical desiccating agents the product is not protected from the reversible release of water back into the package should the temperature increase or the pressure change. This is known as "breathing".

A chemically reactive desiccant can be used for maintaining a moisture level at an extremely low level. Chemical desiccant materials chemically react with water molecules to form a new product. For example, calcium oxide binds water in the following reaction:

$$CaO + H_2O \leftrightarrow Ca(OH)_2$$

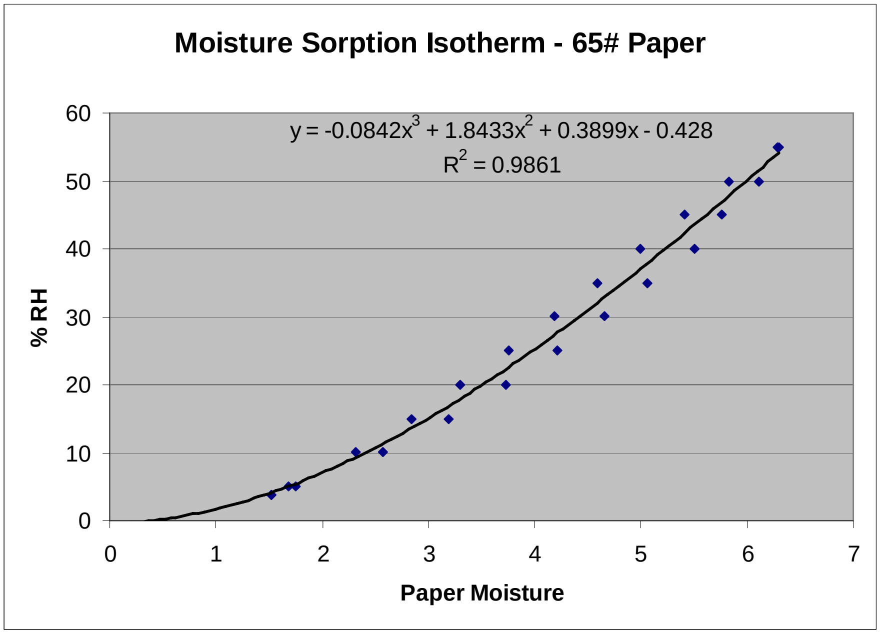
Because the reaction requires very high temperature levels to reverse, it is, for all practical purposes, irreversible. Chemical desiccant materials typically absorb water at all humidity levels, and will continue to take up water until the desiccant reactant is consumed. These chemical desiccant materials, therefore, may reduce levels of moisture within the package headspace to zero or near zero with no danger of reversing the reaction. In addition, the insensitivity to heat allows CaO to go through compounding and extrusion with olefin polymers without "breathing" or liberating moisture that can take place when dealing with other types of desiccants.

The capacity of the sealant film is related to the filling level and the thickness of the filled layer in the structure. The reaction rate of the CaO with moisture is slower than the rate at which other scavenger types pick up moisture. While perhaps not as beneficial for the moisture sensitive product, this is an advantage for the Outside Equipment Manufacturer (OEM), converter or packager who may expose the film to moisture on his equipment as the packages are filled and sealed.

Alcan Packaging has designed, developed and marketed a moisture scavenger using CaO as the active desiccant where the desiccant containing layer is buried in the core of a coextruded blown film laminated as part of a high barrier foil package where the moisture scavenger is on the inside of the package, i.e. the sealant layer. Conversely, desiccant sachets are typically produced using a vertical form process using a breathable Dupont Tyvek® that will permit residual headspace moisture to pass through the Tyvek® to the scavenger. The desiccant sachet is typically inserted into the package containing the device using auxiliary equipment for inserting resulting in a loose component inside the package that provides the moisture scavenging capability.

Direct measurement of internal pouch RH over a long period of time presents experimental problems. Miniature RH sensors with data loggers have been used in other studies, where data is accumulated over months rather than years with accurate and reliable results. This study here however aims to challenge the scavengers over real time aging for more than 1 year with ongoing real time aging evaluations to 5 years. Electronic data loggers are expensive and the batteries have limited life and were not practical for this extended study. Interrogating the data loggers also requires opening the pouch. If one can associate the moisture level of paper, which is related to relative humidity, the RH can be indirectly determined. Samples of a paper were tested at an independent contract laboratory to determine the moisture sorption isotherm of the paper[v]. The measurements were done with increasing humidity and with decreasing humidity. Due to the time lag in reaching equilibrium, the average between the increasing and decreasing humidity was used for the algorithm for relating humidity to paper moisture. That isotherm is shown in Figure 1.

Figure 1



RESULTS

Our study focuses on a comparison between common physical desiccants and calcium oxide desiccant incorporated into the sealant of an active package. Commercially available desiccant sachets were obtained in moisture protected packaging and placed into the pouches with about 5.5 sq in samples of 65# paper which had equilibrated to the moderately moist 50% RH at the time. The pouches had an internal surface area of about 60 sq in and were produced on a Multivac machine. The pouches were taken to an environmentally conditioned room where 73deg F/ 50% RH is continually maintained. The next morning, paper moistures were determined on paper samples removed from pouches representing the various sachets and active packaging. The testing continued on a frequent schedule for over a month. Testing was again taken up at six month intervals until 1 year worth of aging data had been accumulated. Testing will continue on 6 month intervals for 4 more years with results to be published accordingly. The remaining moisture scavenging capacity was also measured on the desiccant in the active barrier pouch. Ingress into the package through the edge is expected to be slow enough that the small capacity of the desiccant will guarantee the package for many years. The moisture sorption capacity of the Alcan Packaging DesiShield™ was measured at 77 mg/sq dm during the first weeks, at 67 mg/sq dm at 195 days and at 65 mg/sq dm at 370 days.

Figure 2 shows the plot of pouch RH as determined by paper moisture vs. time in the pouch, starting ½ day after the packages were closed. A log scale is used to show more detail at the beginning and less detail as changes became slower. The sachets of physical desiccant removed moisture more rapidly than the CaO incorporated sealant lamination in the active package. Humidity levels under 20% RH were achieved in less than 2 days for the pouches with CaO incorporated sealant lamination desiccant and the sachets using clay or silica gel with the molecular sieves very quickly in a matter of hours drawing headspace moisture from 50% to less than 20%. The activated clay 1g sachet achieved and continued to hold a package headspace RH around 10% while silica gel never dropped below 12% RH. Both the Alcan Packaging lamination achieved and continued to hold below 2% as did the 1g sachet molecular sieve desiccant. Package testing continues with significant capacity remaining in all the desiccants that will allow the study to progress and likely confirm package headspace moisture control for 5 years based upon remaining capacity and rate of scavenger consumption.

Details of the data appear in Table I below.

Table I

Alcan Packaging DesiShield™ CaO in Sealant		Commercial Sachet Inserted Activated Clay		Commercial Sachet Inserted Silica Gel		Commercial Sachet Inserted Molecular Sieve	
d(days)	Pouch RH	d(days)	Pouch RH	d(days)	Pouch RH	d(days)	Pouch RH
0.5	38.3	0.5	25.7	0.5	20.2	0.5	10.1
0.5	31.3	0.5	20.0	0.5	20.0	0.5	16.0
0.5	30.9	1.5	15.2	1.5	16.4	1.5	10.0
1.5	20.5	1.5	16.2	1.5	16.6	1.5	9.0
1.5	19.0	2.5	17.0	2.5	17.5	2.5	6.9
1.5	17.9	2.5	17.0	2.5	17.6	2.5	8.6
2.5	11.9	2.5	17.1	5.5	18.2	5.5	4.1
2.5	13.9	5.5	13.6	5.5	19.3	5.5	5.0
2.5	14.7	5.5	15.2	5.5	16.5	5.5	4.7
5.5	11.6	5.5	17.0	6.5	17.9	6.5	5.4
5.5	8.3	6.5	15.1	6.5	16.9	6.5	5.7
5.5	8.6	6.5	15.3	6.5	16.5	6.5	4.5
6.5	9.8	6.5	15.2	7.5	17.6	7.5	4.0
6.5	8.3	7.5	14.2	7.5	19.2	7.5	4.0
6.5	8.2	7.5	14.0	7.5	16.7	8.5	4.6
7.5	11.0	8.5	14.3	8.5	16.3	8.5	4.8
7.5	8.9	8.5	13.1	8.5	16.3	8.5	3.3
7.5	8.4	8.5	13.7	8.5	15.8	15.5	4.0
8.5	6.1	15.5	14.4	15.5	15.1	15.5	3.5
8.5	4.8	15.5	11.1	15.5	16.4	15.5	3.2
15.5	4.2	15.5	13.4	15.5	14.7	22.5	2.8
15.5	4.3	22.5	12.0	22.5	15.3	22.5	2.5
15.5	4.5	22.5	11.9	22.5	16.1	22.5	2.8
22.5	6.3	30.5	14.2	22.5	15.7	195.5	0.7
22.5	4.6	30.5	12.4	33.5	17.5	195.5	1.0
22.5	5.4	195.5	7.1	33.5	16.0	195.5	1.1
33.5	2.6	195.5	8.3	33.5	15.0	370.5	1.2
33.5	2.8	195.5	8.2	195.5	12.0	370.5	1.8
195.5	0.2	370.5	7.7	195.5	13.0	370.5	1.8
195.5	0.4	370.5	10.4	195.5	12.0		
370.5	0.7	370.5	9.9	370.5	13.1		
370.5	1.5			370.5	14.6		
370.5	1.5			370.5	13.9		

EXPERIMENTAL

Moisture determinations were conducted on a Mitsubishi CA-100 coulometric Karl Fisher moisture analyzer equipped with a VA-100 evaporator unit. The paper used is a 65# Boise Cascade MP Cover Paper. Samples were removed from the pouch in less than 30 seconds and placed in a tared 4 ml test tube closed with a rubber stopper. From the small test tubes the paper samples were rapidly transferred to the VA-100. The method used for the Mitsubishi analyzer is shown in Table II.

Table II

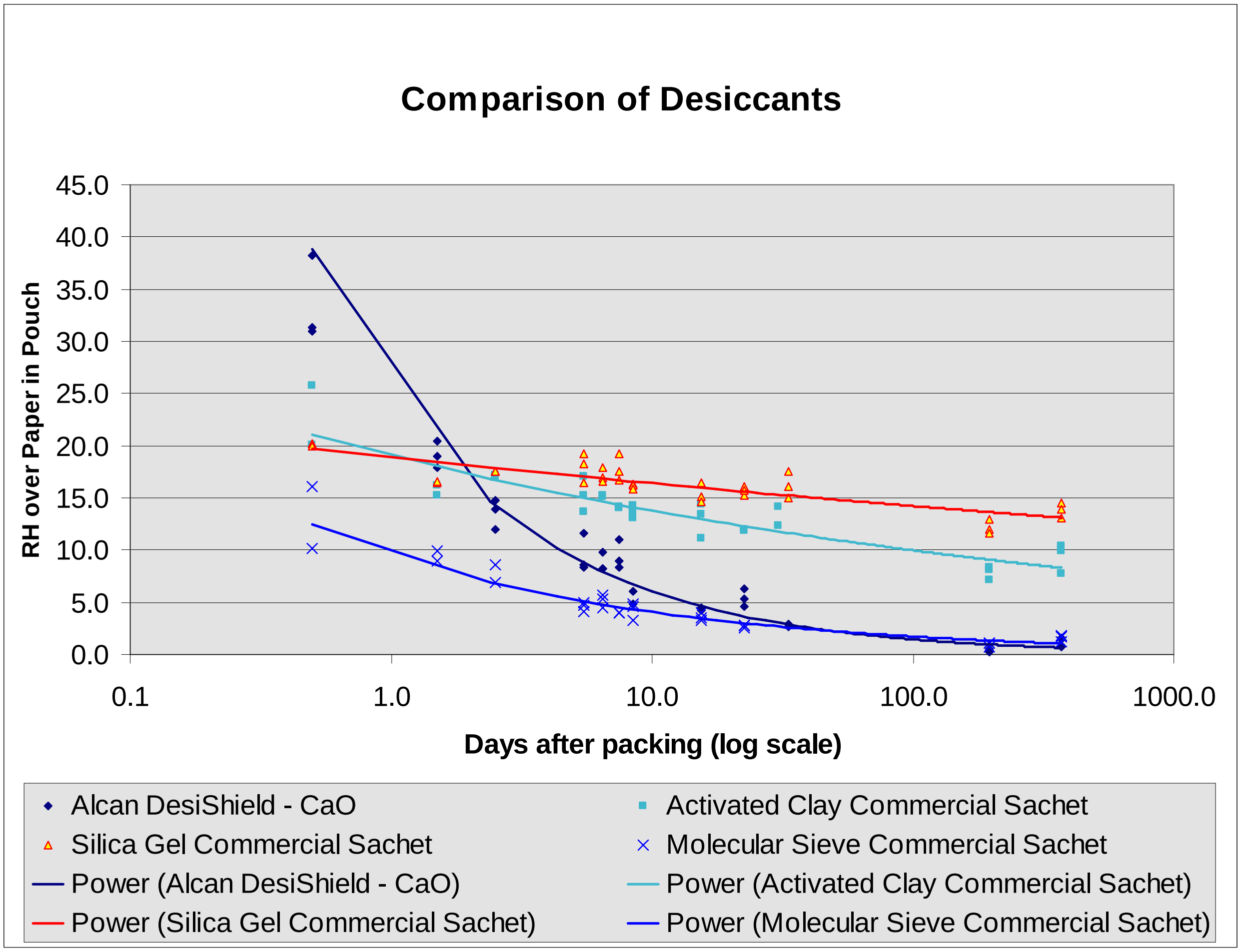
KF Method Parameters	
Delay	1 min
Min. Titration Time	3 min
Titration Stop	0
End Sense	0.1 (0.1 above background value before start)
VA Select	1
VA Temp.	150 deg C
Nitrogen Flow Rate	150 ml/min
Purge	1 min
Pre Heat	2 min
Cooling	2 min

The curve fitting method of Figure 2 below follows the form of

DesiShield / CaO $Y = 25.2293 X^{-0.6200}$ $R^2 = 0.89$
Activated Clay Sachet $Y = 19.047 X^{-0.1404}$ $R^2 = 0.85$
Silica Gel Sachet $Y = 18.927 X^{-0.0620}$ $R^2 = 0.70$
Molecular Sieve Sachet $Y = 9.6259 X^{-0.3745}$ $R^2 = 0.90$

Pouch moisture was converted to pouch RH through the equation:
RH = -0.0842*(W)^3 + 1.8433*(W)^2 + 0.3899*W -0.428
where W = the weight % of water in the paper.

Figure 2



CONCLUSION

The active moisture barrier pouches where the active moisture scavenger was incorporated into the DesiShield™ polyethylene film sealant layer achieved extremely low package headspace relative humidity (RH) within days, and continued to drive package headspace RH to extremely dry conditions of less than 2%, lower than any commercially available moisture scavenging flexible package using inserted desiccant sachets. Further, moisture scavenging desiccant integrated heat seal films and laminations such as the DesiShield™ pouch may be an ideal alternative to traditional physical absorbers because DesiShield™ ensures no potential for moisture release, provides increased consumer safety by eliminating use of inserted sachets, offers extended shelf life related to incremental protection and can lend to process improvements.

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[i] Murray, Lee, *The Impact of Pinholes and Flex-Cracks on the Moisture and Oxygen Permeation of Foil Containing Packaging*, 2005 Tappi PLACE Conference.
[ii] Desiccant sachets such as those produced by Süd-Chemie and MultiSorb are used to provide moisture protection for a wide range of products. MIL-D-3464E and MIL-P-116 describe characteristics of the desiccants and desiccant-sachet combination.
[iii] Merical, et.al., *Films Having a Desiccant Material Incorporated Therein and Methods of Use and Manufacture*, EU Patent ….
[iv] Murray, Lee et.al., *Moisture Scavenging Packaging for Diagnostic Test Strips, Pharmaceuticals and Other Moisture Sensitive Products*, 2003 Tappi PLACE Conference and Global Hot Melt Symposium
[v] Hiden Isochema was contracted for the moisture sorption isotherm.

Special acknowledgement to Daniel Rynearson for support with data gathering and pouching.