

PVC-FREE METAL VACUUM CLOSURES WITH PROVALIN® FROM ACTEGA

Development and current situation on the market

Introduction

ACTEGA is one of four divisions which belong to specialty chemicals group ALTANA headquartered in Germany. Each division is specialized in developing, producing and distributing products for various markets, like packaging, cosmetics, electronics, consumer goods and medical. The division ACTEGA with its production facilities in Europe, North- and South-America and in China is known for its products for packaging (food and non-food), graphic arts and medical applications.

ACTEGA plant in Bremen (Germany) manufactures polymer compounds that are ideally suited as sealing compounds for food and beverage packaging like crown corks, aluminium caps, metal vacuum closures, and as TPE (thermoplastic elastomer) plastics for injection moulding and extrusion applications in the medical, pharmaceutical and consumer goods industries. ACTEGA's compounds product range covers all available technologies from standard products to specialties. Products manufactured in Bremen can be found in closures for food and beverage all over the world. Depending on the region and its regulatory, technical and sustainability requirements as well as economic situation, various types of sealing compounds are offered to the customers.

For more than 30 years ACTEGA has been developing and delivering PVC-free compounds for different types of closures to the customers from more than 80 countries:



Motivation and development PVC-free sealing compounds

Beginning in 2003, there were reports that foodstuffs packaged in glass jars were contaminated by components of closure sealant gaskets. Particularly, jars with oily food were found to contain huge amounts of plasticizers. Although toxicological relevant limits were frequently exceeded, industry was not able to comply with these limits.

The technology at the time necessitated the use of plasticized PVC as sealant materials, as the only technology available for the manufacture of such vacuum closures had to use a liquid Soft-PVC plastisol. It was not possible to use sealant materials without huge amounts of plasticizers. When such sealant materials come into contact with food, plasticizers tend to migrate into the food, thereby rendering the food unfit for human consumption. In a scientific paper, the situation was described as follows: (cited from A. Fankhauser-Noti, K. Grob / Trends in Food Science & Technology 17 (2006) 105–112)

Glass jars with metal twist closures are used for a wide range of foods, from jam and pickles to spaghetti sauces and fish. Lids seal against the glass rim with gaskets consisting of plasticized PVC. They became an issue as migration of plasticizers from these gaskets into foods with oil in contact with the gasket frequently far exceeded the legal limits in Europe (Fankhauser-Noti et al., 2005; Fankhauser-Noti, Fiselier, Biedermann-Brem, & Grob, 2005).

There are two types of lids for jars. Twist closures have lateral lugs engaging on the glass thread on the jar. They commonly have an indentation in the region forming the seal against the glass rim which is filled with plastisol and cured at around 200°C for some 90 s. Press-on twist-off® (PT) lids are primarily produced for baby food and have no metal lugs; threads are formed in the gasket material present also on the sidewall of the closure.

The plastisols used typically contain 25–45% plasticizer, most frequently epoxidized soy bean oil (ESBO) and [at the time] phthalates (diisodecyl phthalate, DIDP, diisononyl phthalate, DINP, or di-(2-ethylhexyl) phthalate, DEHP), but also sebacates, di-(2-ethylhexyl) adipate (DEHA), epoxidized linseed oil (ELO), acetyl tributyl citrate (ATBC, Citroflex A) and acetylated mono/diglycerides. In addition, they contain slip agents, usually oleamide and erucamide, PVC stabilizers, such as calcium/zinc salts of fatty acids or ESBO, lubricants like silicone or paraffin oil, pigments (titanium oxide) and sometimes blowing agents, such as azodicarbonamide or bicarbonate (Biedermann-Brem, Biedermann, Fiselier, & Grob, 2005).

High migration of ESBO was observed for foods with a consistency to bring it in contact with the lids and with at least some 4% free oil or fat. Migration may be high even with less fat if the product was strongly heated after filling, as typical for infant food (with fat contents of 1–2%). Less than 3 mg/kg ESBO was found in aqueous products like jam, honey, asparagus and pickles, as well as in foods not in contact with the lid, such as mustard or firm mayonnaise.

The EU Scientific Committee on Food (SCF, 1999a) specified a tolerable daily intake (TDI) for ESBO of 1 mg/kg body weight (bw). Using the conventional assumptions for food packaging materials, a specific migration limit (SML) of 60 mg/kg is derived. ELO has not been toxicologically assessed and is not listed as an authorized additive for plastics by the EU (Directive 2002/72 and its amendments). The TDIs for DEHP and DINP / DIDP are 0.05 and 0.15 mg/kg bw, respectively (SCF, 1999b), from which SMLs of 3 and 9 mg/kg would be derived provided the whole TDI were allotted to food contact materials. For DEHA, Directive 2002/72 specifies an SML of 18 mg/kg.

For tributyl citrate and di(2-ethylhexyl) sebacate, the EU Synoptic Document (European Commission, 2003) lists restrictions of 5 mg/kg food and 0.05 mg/kg bw, respectively.

There were various attempts to reduce the ingress of plasticizers and other undesirable contaminants however there was still the need to continue to use plasticizers. Furthermore, inspection by enforcement authorities in Switzerland, Germany and Austria showed that the official test method at the time tended to underestimate the real level of migration into the food stuffs. This ended in the unpleasant situation that although formal documentation indicated compliance to migration levels, the migration could not be substantiated in real practice. This led to stricter test conditions, e.g. migration later had to

be demonstrated at 60°C for 10 days instead of 40°C.

This made the unsuitability of traditional sealant materials even more apparent. Starting in 2004, ACTEGA GmbH, invented a new technology for the production of vacuum closures, and also invented an innovative kind of sealant materials free of PVC and plasticizers with the brand name PROVALIN[®], which were, for the first time able to meet the technical specification (retort resistance etc.) and the regulatory limits for consumer protection.

The impact of the PVC-free sealing compounds on the migration results was described in 2013 in the report prepared by KLZH and CVUA as follows:

*"In 10 (29 %) of the products with oil in contact with the gasket, migration exceeded the legal limit(s), which is worse than observed in 2011. (...) **An additional jar was closed with a lid sealed against the jar rim by a polyolefin gasket. Pre-liminary tests showed far lower migration (there are no plasticizers)**"*² In another report from 2022 following was stated: *"Larger brands and supermarket chains (at least for the main, high-volume products) have improved the compliance more than the industry average, mainly by switching to non-PVC lids for the highest risk products."*³

PROVALIN[®] compounds are thermoplastic elastomers (TPEs) which consist of a combination of different polymers (polyolefins) that are tailor-made depending on the end use such as pasteurization, sterilization or cold filling.

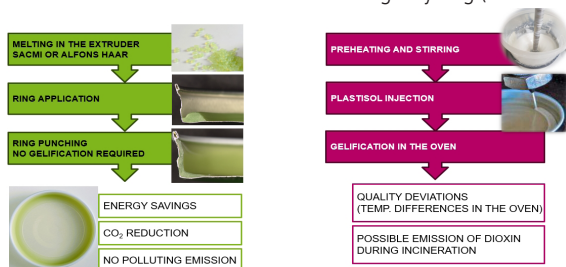
The development work at the ACTEGA Research & Development Department took several years and the products were granted IP rights. To enable the production of the first PVC-free metal vacuum closures, a cooperation with a family-owned company PANO based in Itzehoe (Germany) has started. PANO was producing at that time metal vacuum closures with PVC-plastisol. However, the increasing regulatory requirements regarding food contact materials (migration limits) as well as willingness to take a significant step towards sustainable and innovative solution triggered PANO to invest in the new PVC-free technology and invent first PVC-free closures.

The first PVC-free Twist Off[®] closures produced with annular lining technology were introduced to the market in 2008 and the changeover from PVC to PVC-free Twist Off[®] closures took place in 2011, together with PANO and Feinkost Dittmann.

Production of the PVC-free closures

In contrast to the PVC-containing closures, where liquified PVC plastisols are injected into metal shells that are subsequently cured by means of high temperature, TPE granules PROVALIN[®] are melted by extrusion and applied into the metal shells by molding rather than a curing process. This makes it possible to do away with gasfired drying ovens thus saving energy and significantly reducing carbon footprint.

The picture below illustrates differences between the production of the PVC-free (left) and PVC-containing closures (right) as well as their possible impact on the environment after their service life – during recycling (incineration):



Incineration of the PVC-containing closures is connected with the risk of emissions of hazardous substances, like dioxins, which is not the case when incinerating the PVC-free closures.

There are currently two suppliers of lining machines for production of the PVC-free closures: SACMI and ALFONS HAAR with the production speed up to 1000 caps/min resp. 500 caps/min.

SACMI is also manufacturer of most of the lining machines for other closure types like crown corks, aluminum and plastic closures.

In the first few years after starting the production of PVC-free Twist Off[®] closures, the commissioning of lining machines at closures producers was mostly accompanied by technicians from all involved parties. To find the optimum settings for production of closures of a required quality, different trials with various temperature and induction heating settings were carried out. As result, Processing Recommendation Sheets for all commercial as well as new developed PROVALIN[®] compounds are available. The experience collected in the past few years allows closures producers smooth running's of the PVC-free compounds PROVALIN[®] on their existing as well as new lining machines.

Functionality of the PVC-free closures lined with PROVALIN[®]

The aim of the project metal vacuum closures lined with PVC-free compounds PROVALIN[®], besides the migration aspect, was to design closures with sealing compounds that can be applied for all kind of foodstuffs that are cold filled as well as thermally treated under pasteurization or sterilization conditions and which can be used on the standard steam vacuum capping machines. Therefore, PVC-free closures had to undergo intensive testing before being released, in the first step under laboratory conditions and thereafter at the fillers with real filling goods.

Although, there are differences in the composition and physical properties of PROVALIN[®] and PVC compounds, usually there are just small adjustments on the capping machines required. To see whether the settings on the cappers have been set correctly and thus the glass jars can be properly closed, some indicators for a proper capping process with PROVALIN[®] lined closures, like pull-up distance, security, compound- and residual thickness were defined by ACTEGA and recommended to be checked before starting the regular production.

All qualification trials (pack tests) with the PVC-free closures were carried out and directly compared with reference glass jars closed with PVC closures.

The properties to be checked over the whole shelf life of the filling goods and requirements to be fulfilled were defined by the filler.

After years of intensive testing, there are now closures with well-developed and fully operational PROVALIN[®] compounds for different type of applications available (Tab.1 and Tab. 2). The good functionality of PROVALIN[®] lined closures has been proven.

However, the same as with PVC closures, when introducing to a new customer/ filler or when changing from one to another product grade, the suitability must be confirmed for each application by filling tests under real conditions and subsequent pack tests.

Application Twist Off[®] for the steam vacuum cappers

HOT FILL / PASTEURIZATION	STERILIZATION / PASTEURIZATION	COLD FILL / COLD STORAGE
up to 98°C, 60 min. For all kind of foodstuffs e.g., pesto, jams, pasta sauces	up to 131°C, 60 min. (for non fatty-, oily- products) up to 125°C, 60 min. (for fatty-, oily- products) For all kind of foodstuffs e.g., Bolognese, black olives	~20°C / 4°C For all kind of foodstuffs e.g., yoghurt, mayonnaise, mustard
PROVALIN [®] 1242	PROVALIN [®] 1288	PROVALIN [®] 1269

Tab. 1

Application Press-On Twist Off® on the steam vacuum cappers

STERILIZATION / PASTEURIZATION IN AUTOCLAVE	PASTEURIZATION IN TUNNEL AND IN AUTOCLAVE
Sterilization up to 126°C up to 60 min. Pasteurization up to 100°C up to 60 min.	Pasteurization in tunnel up to 95°C up to 60 min. Pasteurization in autoclave up to 95°C up to 60 min.
For all kind of foodstuffs e.g., baby food, drinks, functional food	For all kind of foodstuffs e.g., baby food, drinks, functional food
ACTGreen® PROVALIN® 1771 U	ACTGreen® PROVALIN® 1741

Tab. 2

Current market situation PVC-free metal vacuum closures

Current trends in packaging which are driven by rise of regulation and sustainability claims like wish to use environmentally friendly packaging or reducing the carbon footprint can be clearly observed in the constantly increasing demand for the PVC-free compounds PROVALIN®.

The total market closures Twist Off® in Europe is estimated to be around 20 billions¹ and, considering the amounts of PROVALIN® compounds sold to the European closures' producers, ~18% of all are PVC-free. On top of that, significant amounts of PROVALIN® are delivered to the customers in Asia. There are currently more than 50 lining machines on the market available giving impressive production capacities for PVC-free closures Twist Off® as well as Press-On Twist Off® (mainly baby food). For Twist Off® closures, there are tools for all sizes in the range of 38 – 82 mm available.

Recently, ACTEGA has carried out market studies with food in glass jars randomly bought at some supermarkets, discounters and drugstores in Bremen (Germany). The aim was to check whether the closures are PVC or PVC-free. In addition, opening torques, which express the force needed to open the glass jars, have been checked and evaluated as there is a specific range that is considered to be convenient for the consumers. The results of the ACTEGA internal studies reflect the situation described above:

315 (50%) out of the 626 glass jars closed with Twist Off® closures (different closures diameters, various filling goods) were closed with PROVALIN® lined closures, 311 were with PVC-plastisol.

Opening torques with most of the tested samples were within a good range with both PVC-free and PVC closures. However, especially with bigger closures diameters, e.g. 82 mm, the opening torques were lower with PROVALIN® compared to PVC. The study included also glass jars with baby food closed with Press-On Twist Off® (PT) closures. The results were similar to those obtained with Twist Off® closures:

66 (55%) out of the 119 glass jars with baby food were closed with PROVALIN® lined PT closures and 53 were with PVC-plastisol. Opening torques with all tested samples were within a good range.

To sum up, PVC-free closures are well established on the market and fulfill consumers' expectations regarding food safety and convenience.

Summary

PVC-free closures lined with PROVALIN®, introduced for the first time in 2008, have been successfully established on the market and cover all application fields and requirements for metal vacuum closures for food.

Elimination of PVC and thus plasticizers from the sealing compounds covers both:

protection of humans' health by elimination of potentially harmful substances as well as demand for environmentally friendly packaging.

Development observed in the past few years shows clear direction on the closures market, which is striving for safe and sustainable solutions, even though, high investments are usually needed.

The availability of the PVC-free closures at all European closures manufacturers and constantly increasing production capacities confirm on the one hand the need for change from PVC to PVC-free and on the other hand a high acceptance of the PVC-free solution PROVALIN®.

Sources

¹ Source: Statistics – Euromonitor: Passport

² "Coordinated European Enforcement 2.0 on the migration of plasticizers from the gaskets of lids with focus on compliance work" Kantones Labor Zürich und Chemisches und Veterinäruntersuchungsamt Stuttgart, December 2013

³ Food Packaging and Shelf Life 33 (2022) 100922 "Migration of plasticisers from the gaskets of lids into oily food in glass jars: An update of the situation on the Swiss market a decade after large European campaigns" Maurus Biedermann, Tanja Altherr, Sandra Biedermann-Brem, Angela Eicher, Celine Muñoz, Gregor McCombie

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