Diecasting release agent
Efficient diecasting process with the Clean Part & Mold Release concept

Abstract

Die-casted parts made of aluminium, magnesium and zinc alloys are produced in very high quantities. Despite very aggressive cleaning in some cases, release agent residues from the casting process often leads to major quality problems in subsequent processes such as painting, bonding, etc. Residues in the mould additionally cause interruptions in the casting process, as a continuous build-up of residues from the release agent must be regularly removed mechanically in order to guarantee the dimensional accuracy of the manufactured parts.

Keim Additec Surface GmbH has developed the Clean Part & Mold (CPM) Release Concept, where it demonstrates new approaches to the formulation of release agents in order to avoid adhesion on diecasting moulds and the produced parts. This means that mould cleaning during production can be avoided to a large extent and at the same time the problematic impact of residual release agent on the produced parts for bonding and painting can be avoided.

Due to the novelty of the concept, diecasting tests were carried out at the Fraunhofer Institute for Manufacturing Technology and Applied Materials Research IFAM in Bremen and both the diecasting mould and the surface of the casted parts were analysed and evaluated. In addition, the paint adhesion on the casted parts was investigated.

BY PETER PYKA, KIRCHBERG, MARCO HAESCHE, MARTIN WIESING, ANDREAS STAKE and Christoph Pille, BREMEN

Release agent residues on moulds and casted parts are a frequent cause of both rejects and interruptions in the diecasting process. In the following examples, a new formulation is presented that is intended to minimise adhesion and thus increase the economic efficiency of the process.

Aqueous release agents

In aqueous release agents for metal diecasting, a product from the group of modified polysiloxanes (e.g. alkyl-aryl mod. siloxanes) are frequently used as die cast release agent additives. These are modified in such a way that they separate well, are thermally stable and allow subsequent painting/bonding, but have only a low lubricating capacity and can lead to increased wear, especially in the moving parts of the mould (e.g. ejector). Such silicones also tend to form residues. Especially in the warmer areas

of the mould, glass-like deposits can be observed, which are very difficult to remove. Despite the use of special modifications in release agent formulations, problems caused by these additives with good adhesion are observed in downstream processes such as painting or bonding.
Another group of additives frequently used in aqueous release agents are waxes or low-molecular weight polymers. These are mostly long-chain, polyethylene-based molecules that have very good release properties due to their high melt viscosity. They also show very good release properties at the comparatively high temperatures of the Al and Mg diecasting process and burn largely without residue. However, at lower metal temperatures (< 600 °C), such as in the regions of the mould far from the sprue or in areas that do not come in contact with the hot metal, these products tend to progressively build up and from residues (**Photo 1**), so that the mould often has to be cleaned during a casting process. However, such polyethylene additives (waxes) generally have a good lubricating effect, which can reduce wear on moving components of the mould.
Common release agents usually use both additive groups (modified silicones and wax polymers) in combination to enable a trouble-free diecasting process. However, such a formulation is always a compromise and the negative effects of both additive groups are clearly noticeable during casting as well as in the subsequent processes.

Table 1: Comparison of common release agent additives.

	Silicon additives	Wax additives
Release properties	good	good
Residues in the hot part of the mold	yes	no
Residues in the colder part of the mold	Yes but no build up	Tend to build residues (polymeric types)
Lubrication effect (to ejectors)	less	good
Coat ability	negative influence	good
Glue ability	negative influence	good
Alkaline cleaning of parts	Only with high pH cleaners -> influence too the alloy	normal

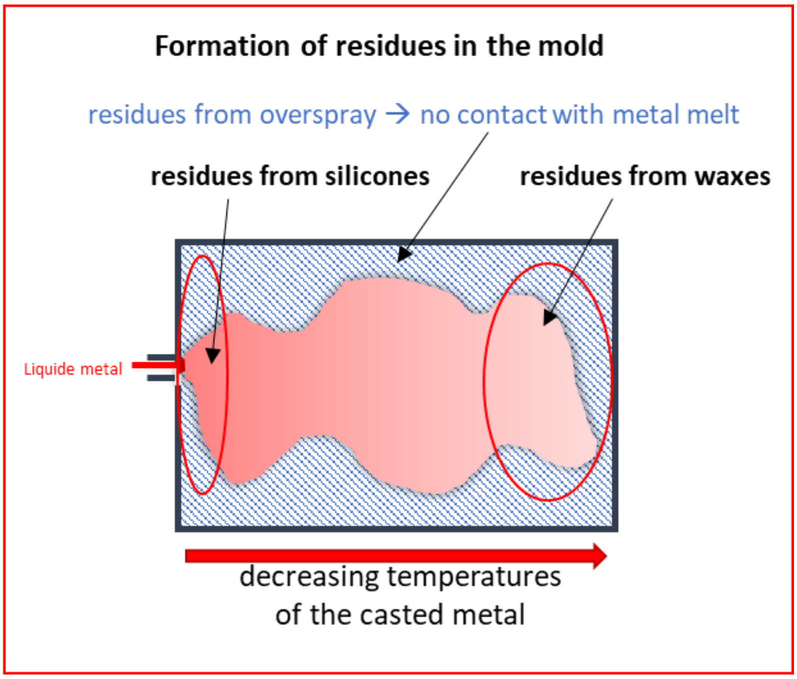


Figure 1: Temperature profile of the cast metal in a mould.

The Clean Part & Mold Release Concept (CPM Concept)

In order to avoid the negative influences described and to increase the economic efficiency of the diecasting process, new short-chain, wax-like polymers were developed which have a completely different structure than the additives used to date. These newly developed polymers are highly polar due to their large number of polar centres in the polymer chain and exhibit very good adhesion to metal surfaces with simultaneously having a very low melt viscosity. As a result, they spread very quickly on hot surfaces and produce very thin, well-adhering release layers. The high adhesion of these polar additives is based on the interaction of the freely moving electrons of the polar centres with the dipoles of the metal oxides on the mould (Van der Waals interaction) [1]. Such ultra-thin and well-

adhering polar films also exhibit high lubricity and contribute to lower wear on the moving parts of the mould (e.g. on the ejectors). In addition, they show a very high release capacity during the casting process. Any release agent residues remaining after the casting process are washed off during the next application, so that no release agent builds up in the cooler zones of the mould. Also, during subsequent cleaning of the casted parts, small amounts of release agent still adhering can be easily removed by a mild alkaline cleaner and usually do not cause any significant disturbances in downstream coating processes.
Additives from the CPM Concept should, however, be combined with a classic high-molecular additive. This is due to the fact that in the areas of highest temperatures and flow velocities of the inflowing metal the historical well-adhering additives (polyethylene or mod. polysiloxanes) are still needed. However, their quantity should be limited to the necessary minimum during formulation, thus effectively avoiding release agent residues and their build-up in the mould. Modified polypropylene dispersions have proven to be a very good alternative to polyethylene additives. Due to its molecular structure, polypropylene is much more thermally degradable and does not tend to form high-polymer residues as can be observed with polyethylenes.

Comparative studies

At the Fraunhofer Institute for Manufacturing Technology and Applied Materials Research in Bremen, aluminium diecasting tests were carried out with three model formulations to test the Clean Part & Mold Release Concept.

Test formulations

Release Agent 1:

This reflects the state of the art in simplified form and serves as a reference. In addition to additives for corrosion protection, hard water stability and the flow of the release agent, an alkyl/aryl-modified polysiloxane and a polyethylene primary dispersion were used as active release additives. Polyethylene primary dispersions are produced by emulsion polymerisation of ethylene in water at very high temperatures and pressures. Polyethylene dispersed in water in this way has very good release properties due to its high melt viscosity, but it has a strong tendency to build up residues in the mould.

Release Agent 2:
Here, 50 % of the primary dispersion was replaced by new CPM additives (HANSA RELEASE R 8198). The solid content of the release agent was taken into account and kept constant. Other recipe components remained unchanged.

Release Agent 3:
Here, the primary wax component was completely replaced by the CPM additive (HANSA RELEASE R 8198). In order to implement the Clean Part & Mold Release Concept (CPM Concept), the alkyl-aryl-polysiloxane was also replaced by a maleic anhydride-grafted polypropylene dispersion (HANSA RELEASE R 8160). This special modified PP wax has a very high melt viscosity and thus a very high release capacity. In contrast to PE waxes, HANSA RELEASE R 8160 has a much lower tendency to leave residues.

Table 2: Release agent formulations, the changes to the comparative formulation (release agent 1) are marked in yellow.

	release agent 1		release agent 2		release agent 3	
	proportion	solids	proportion	solids	proportion	solids
water	72,26%	--	70,46%	--	56,66%	--
emulsifier (Fettalkoholpolyglycolether)	0,24%	0,24%	0,24%	0,24%	0,24%	0,24%
Triethanolamin (90%)	1,50%	1,35%	1,50%	1,35%	1,5%	1,35%
Alkyl-Aryl modified Silicon - emulsion 55% solids	15,00%	7,95%	15,00%	7,95%	--	--
PE-primary dispersion 40% solids	11,00%	4,40%	5,50%	2,30%	--	--
HANSA RELEASE R 8198 (polar mod. Wax-polymer emulsion) 30% solids	--	--	7,30%	2,20%	20,70%	6,21%
HANSA RELEASE R 8160 (mod. PP-emulsion) 35% solids	--	--	--	--	17,90%	6,27%

	100%	13,94%	100%	14,04%	100%	14.07%

Casting tests

The diecasting tests in the foundry laboratory of Fraunhofer IFAM were carried out with a horizontal cold chamber machine of the type Frech-DAK-250. A special tool was selected that allows easy removal of the mould inserts without removing the complete mould from the diecasting machine. The flat geometry of the mould cavities (**Figure2**), or the die-cast component (**Figure 3**), enables the desired surface analyses to be carried out on the mould inserts and cast components. The most important process parameters are listed in **Table 3.**

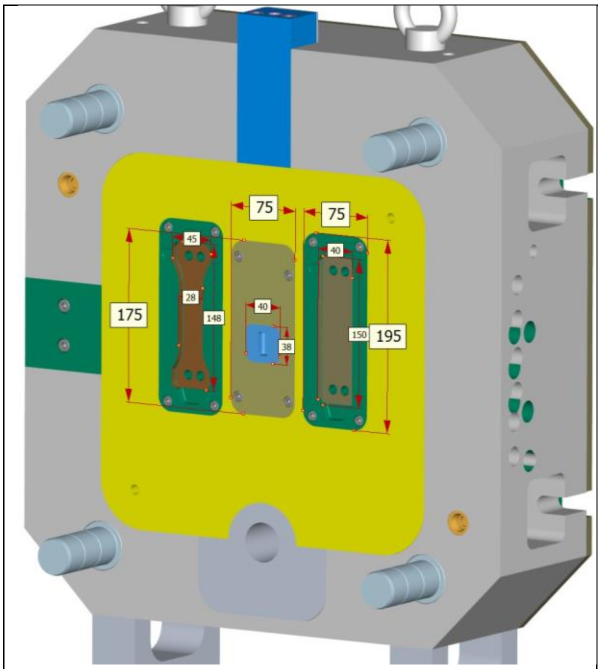


Figure 2: Release agent investigations; fixed mould half with easily exchangeable mould inserts

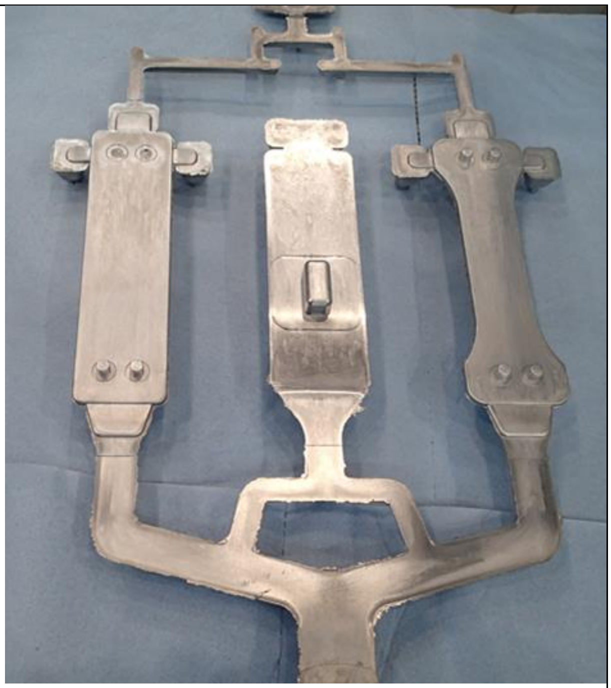


Figure 3: manufactured metal die casting

Before the investigations began, the entire die-casting mould was cleaned using dry ice and this basic condition was documented under a light microscope. Subsequently, the investigation was carried out with the three release agents described, whereby 150 components were produced with each release agent variant. Between the release agent changes, the mould inserts were dismantled, the surface examined, and the entire mould cleaned again with dry ice.

Table 3: Overview of the most important process parameters for the aluminium diecasting tests

Material:	AlSi9Cu3(Fe)
Melt temperature (oven)	680°C
Mold temperature:	190°C - 200°C (measured in the mold cavity)
Number of parts:	150 parts each release agent
Concentration of the release agent:	1:30
Die cast machine:	Typ Fech DAK 250-34 (clamping force 290t)
Cast weight:	approx.. 600g
max. piston speed:	approx. 5m/s

Results

Release properties:

Since only 150 parts per release agent were cast, a very high release agent concentration of 1:30 was chosen to simulate the full potential of release agent build-up. Before the actual casting tests, 10 parts each were cast with a release agent concentration of 1:100 corresponding to the active ingredient proportion. All three release agents showed good release properties at a mixing ratio of 1:100.

Surface of the mould cavities:

The surface images of the mould cavities were taken with a Keyence VHX-7100 light microscope with FI head under confocal illumination. The light falls vertically onto the surface via the imaging lens. Accordingly, flat, reflective areas are illuminated and appear bright. Thin dielectric films usually show iridescent colours. Rough or angled areas reflect the incident light. The mould was not cleaned before the microscopic measurements.
On the photos of the mould insert in the area of the overflow (**Figure 4**), it can be seen that the release agent residues on the surface decrease significantly with increasing HANSA RELEASE R 8198 content. Particularly with release agent 3 (Figure 4d), the surface is bright and the streaking typical of release agents is minimised.

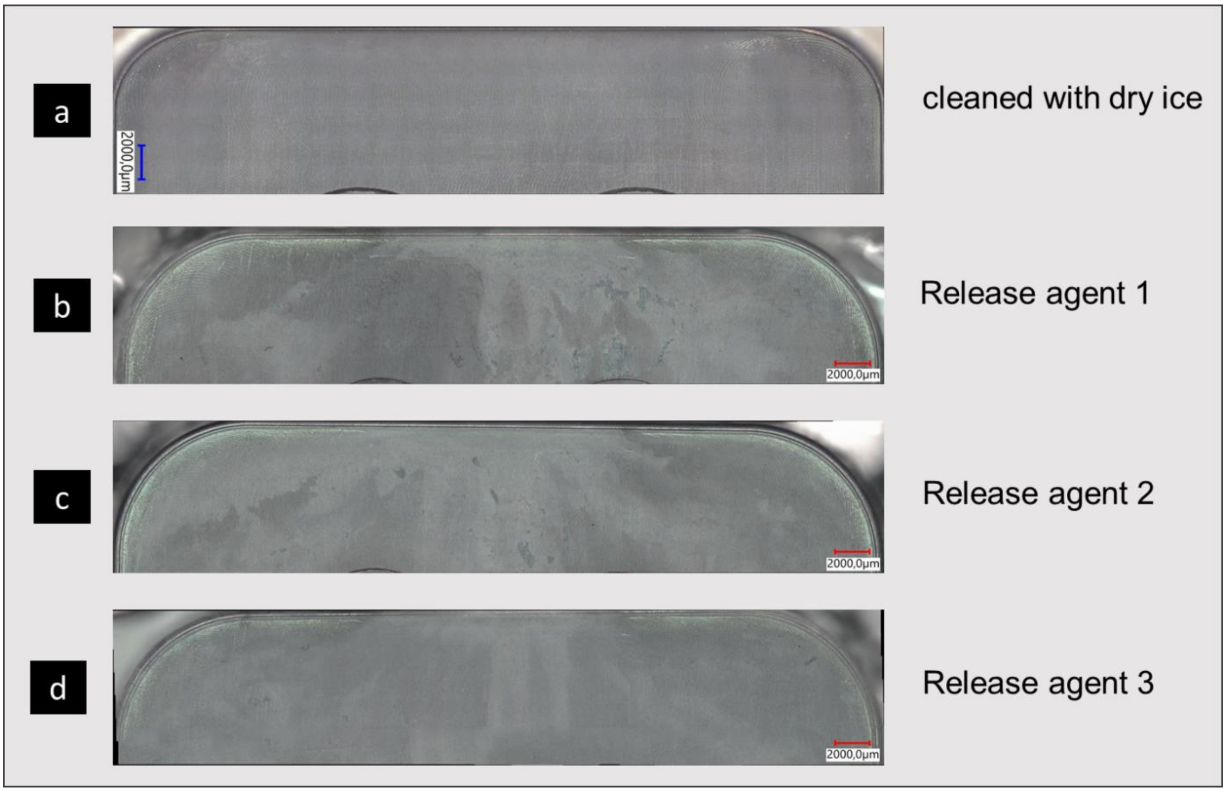
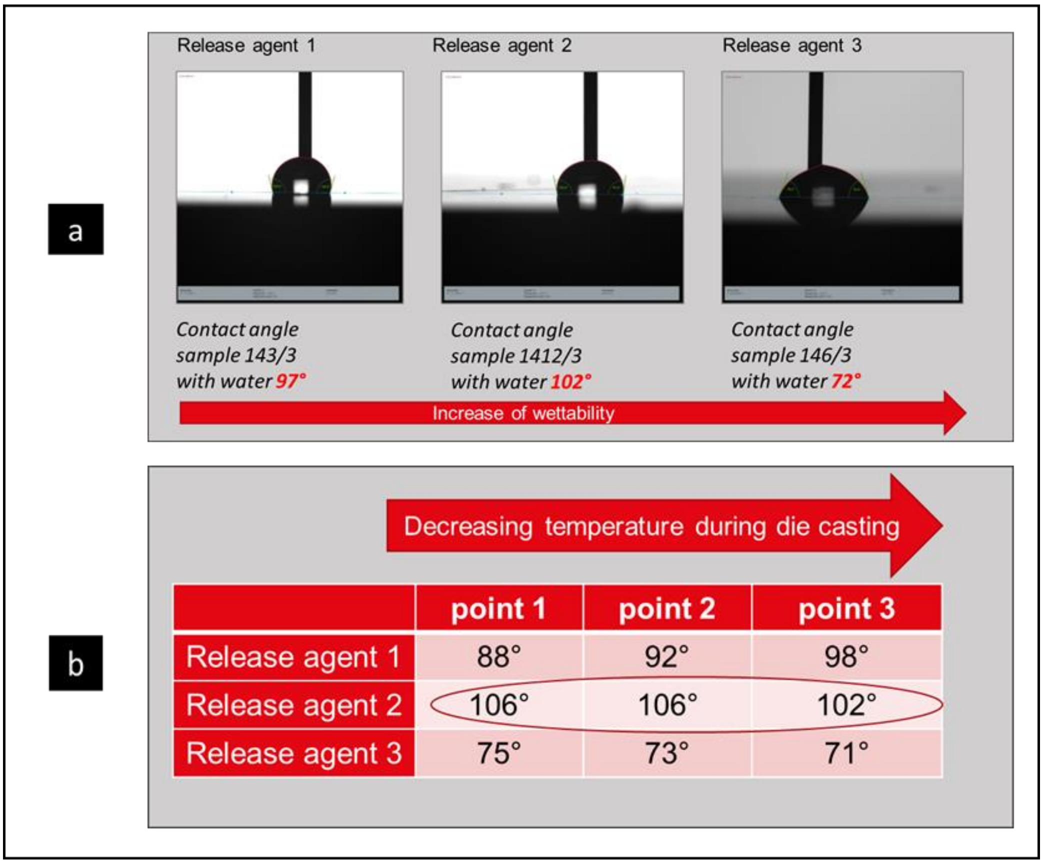


Figure 4: Light microscope images of the mould in the area of the overflow; a) cleaned, b) release agent 1, c) release agent 2, d) release agent 3.

Surface tension / contact angle on the casted parts

The contact angle (**Figure 5**) was determined with a measuring device of the type Drop Shape Analyzer - the-100-S on a dust-free surface. The contact angle of a water drop was determined at three points on the test sheet. Five measurements each were taken at the sprue (location 1 = highest temperatures), in the middle of the die-casted part (location 2) and near the overflow (location 3 = coolest temperatures).
The results show that the castings produced according to the CPM Release Concept (release agent 3) have significantly smaller contact angles and are therefore more hydrophilic. This increases the wettability of the surface, e.g. with an aqueous lacquer. In the case of release agents 1 and 2, a strong influence of release agent residues on the surface can be observed. Release agent 2 has a slightly higher contact angle than release agent 1. Both products contain the same amount of the modified polysiloxane additive.



	point 1	point 2	point 3
Release agent 1	88°	92°	98°
Release agent 2	106°	106°	102°
Release agent 3	75°	73°	71°

Figure 5: a) Contact angle measurements and b) Mean values of the contact angles measured in each case at three points

Paintability and paint adhesion

The dust-free parts were coated with an aqueous 2K PU lacquer (surface tension 30 mN / m) by spray application. After curing at 70 °C, for 2 hours, the paintability was first assessed. The coating thickness of the lacquer after drying was 30 µm. Paintability was given for all three release agents tested (**Figure 6**).

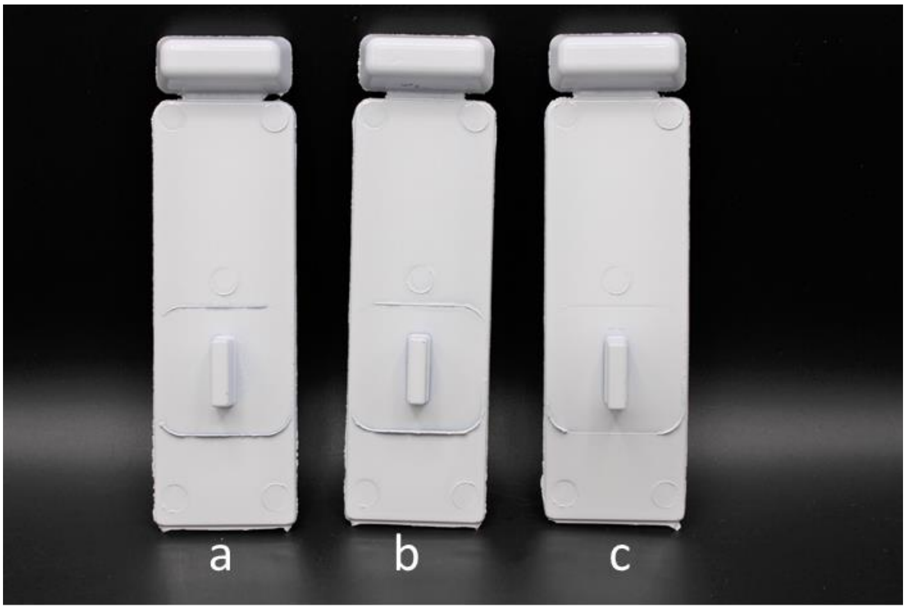


Figure 6: Casted parts after painting

According to DIN EN ISO 2409, the adhesion strength of the coating was determined by a cross-cut test. This simple method is used to determine the adhesive strength and elasticity of single- to multi-layer coatings. A grid is scratched into the coating to be tested and the cuts are then cleaned with a soft brush. Subsequently, an adhesive tape defined in the standard is stuck to the cut grid under slight pressure. The adhesive tape is then removed with an even peeling motion. The evaluation is done visually by comparing the cutting grid image (**Photo 7**). Only release agent 3 (Photo 7c) shows good paint adhesion over the entire area of the casted part. Release agents 1 and 2 (Photos 7a and 7b) show only low paint adhesion in the test, which is probably due to the alkyl-aryl modified polysiloxane.

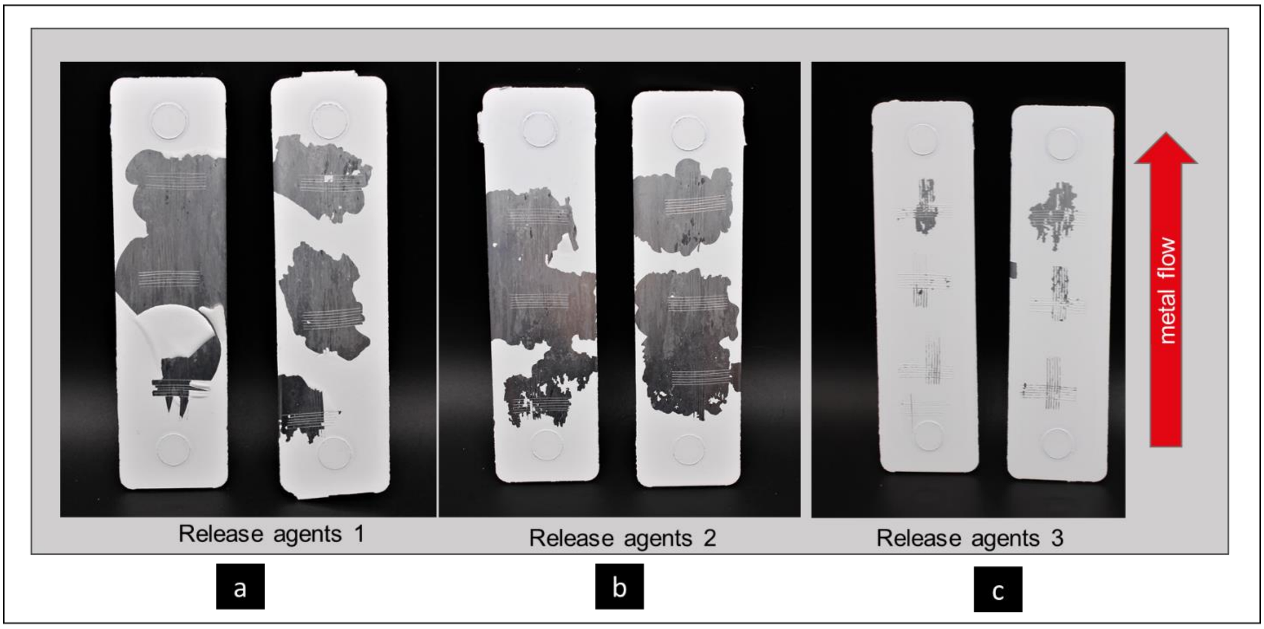


Figure 7: Results of the cross-cut test; a) release agent 1, b) release agent 2, c) release agent 3.

Residues on the surface of the casted parts

X-ray photoelectron spectroscopy (XPS)

This method is established for the non-destructive qualitative and quantitative determination of the elemental composition of solids and their surfaces. The measurement is carried out close to the surface with a penetration depth of the radiation of 5-10 nm. All cast samples were measured dust-free and uncleaned. The results are shown in **Table 4**. For further differentiation of the Si-containing components, the high-resolution Si2p spectra were analysed with a fit model [2]. The resulting spectral proportions of metallic Si were used to determine the respective atomic concentration:

	C	Si *release agent*	O	Si *alloy*	Al	Mg	Atom %∑
Release 1	81,5	5,3	12,6	0	0,46	0,1	99,98%
Release 2	68.7	6,8	18,0	0,6	4,53	0,3	99,7%
Release 3	30,4	0	40,0	2,9	15,4	8.6	94.71%

Residues of the release agent (C, Si release agent, O) — Aluminium alloy (Si alloy, Al, Mg)

Table 4: Results of the XPS measurement (all figures in atomic percent)

- On the sample surfaces, which were cast with release agent 1, the elements C, Si and O dominate (> 99 %), which are typical for the release agent used and indicate corresponding residues.
- On the samples cast with release agent 2, the total proportion of signals typical for the release agent residues (C, Si, O) decreases significantly to approx. 86 %. On these samples, signals of the alloying elements could now also be detected, such as those of the metallically bound silicon and aluminium. The decrease in the observed release agent residues correlates with the use of the CPM additive (HANSA RELEASE R 8198).
- The lowest concentrations of carbonaceous release agent residues were observed when release agent 3 was used. Correspondingly, the observed concentration of alloy-typical elements increased. These include in particular metallically bound Si, Al and Mg in addition to other elements (Na, P, Bi, Pb, Sn, Cu, N). The release agent residues, which can be determined via the carbon content, are only approx. 30 % of the values measured in sample 1, which can be explained by the use of additives from the CPM Release Concept.

TOF-SIMS

TOF-SIMS (secondary ion mass spectrometry (SIMS) with a time-of-flight (TOF) mass analyser) was used with an IONTOF M4 with Bi source (Bi+ 25 keV) to analyse the release agent residues on the casted parts. The method allows the qualitative characterisation of the molecular surface composition at a surface sensitivity of 1-3 nm. For the comparative investigations, the respective release agent components were additionally examined after application to Al foil **(Photo 7a**).

The spectra of the casted parts that were cast with release agent 1 and 2 are essentially identical and show very good agreement with the alkyl-aryl polysiloxane used from the release agent (Photo 7b). The polysiloxane signals dominate the spectra, so that the presence of at least one monomolecular layer of the polysiloxane can be assumed. The spectra of the casted parts, which were cast with release agent 3, show no agreement with those of the reference materials. In comparison, mainly inorganic signals of the (oxidised) alloy components can be observed. Longer-chain organic fragments with masses above 400 m / z are negligible. The contamination layer on the parts is therefore most likely not completely covering. In addition, the remaining organic contaminants are probably low molecular weight (thermal degradation products) or very strongly adsorbed, so that extensive fragmentation occurs during the measurement.

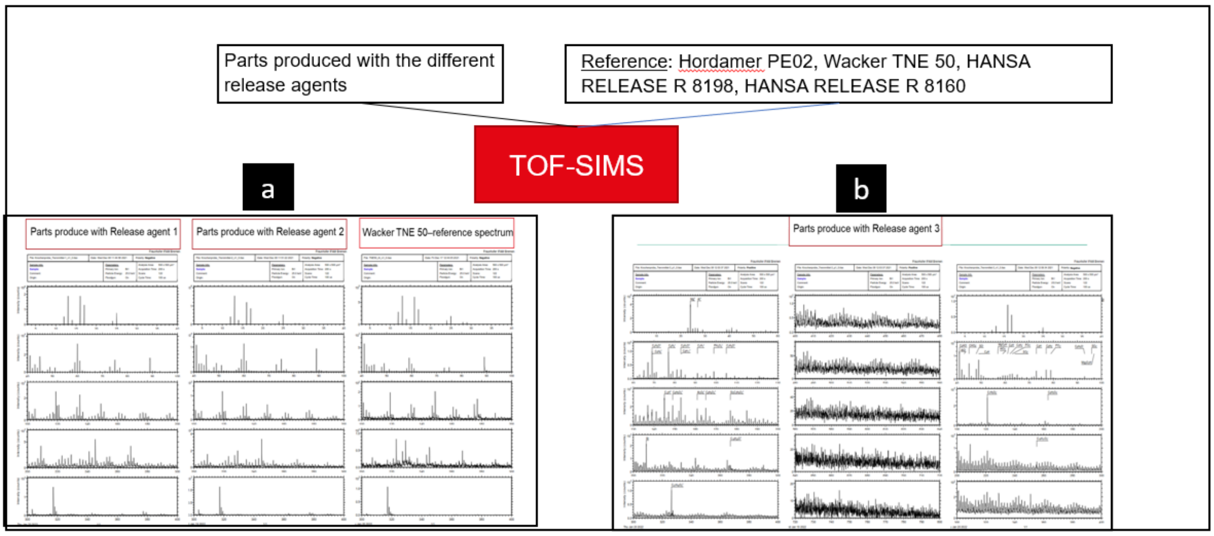


Figure 7: a) TOF-SIMS spectra of the release agent residues on the components, b) TOF-SIMS spectra of the components manufactured with release agents 1 and 2 in comparison to the alkyl-aryl-polysiloxane.

Summary and conclusions

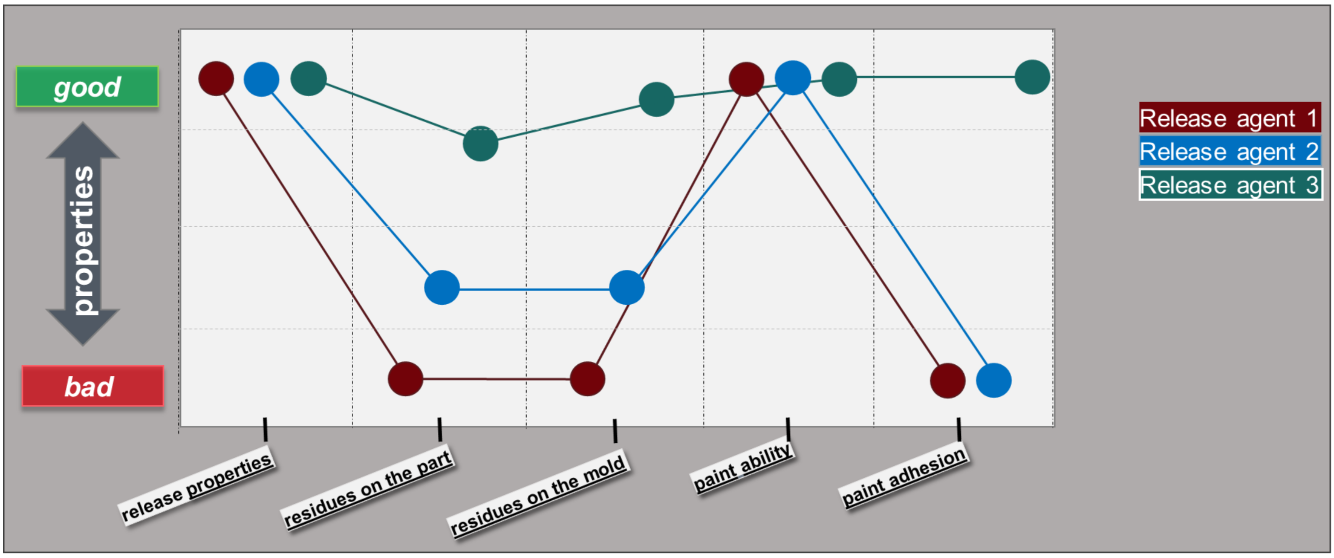


Figure 8: Graphical summary of the test results.

In order to investigate different release agents with regard to their release suitability, and the formation of residues as well as the paintability of components manufactured with these release agents, diecasting tests were carried out. The model release agents used in these tests were formulated in such a way that effects from the release agent additives were recognisable (**Figure 8**). Initially, comparably good release properties were observed for all three release agents. Microscopic examinations of the mould inserts showed that different residue behaviour could be observed after only 150 parts:

- Release agent 1 (reference) already showed clear release agent residues in the area of the overflow of the mould.
- Release agent 2 already showed less residue in the mould due to the partial use of HANSA RELEASE R 8198.
- Release agent 3 with a completely new additive combination caused only very low release agent residues on the mould.

In the investigations of the three release agents, large differences were observed in the surface coatability of the casted parts in downstream process steps. The less release agent residue there is on the casted part after the casting process, the less the paint adhesion is impacted. Casted parts cast with release agents 1 and 2 showed good paintability with the aqueous paint system used due to the specially modified polysiloxane, but paint adhesion was significantly negatively influenced by these release agents. In contrast, casted parts made with polysiloxane-free release agent 3, consisting of additives from the CPM Concept, showed no problems either in painting or in paint adhesion.

Replacing 50% of the original PE primary dispersion in release agent 2 with the HANSA RELEASE R 8198 significantly reduces the percentage of carbonaceous residues, as evidenced by the XPS measurements (see Table 4). As a result, the percentage of polysiloxane increases in the samples cast with release agent 2. This can also be observed in the increase of the edge angles (see Photo 4b). This result should be taken into account in a possible formulation of polysiloxane in combination with the additives of the CPM Concept in an adjusted amount of polysiloxane.

The XPS measurement results of the casted parts made with release agent 3 show a significant decrease in carbonaceous residues. Significantly less release agent residues are found (approx. 30 % compared to > 99 % for the standard). The modified polypropylene used in release agent 3 as a substitute for the PE primary dispersion shows significantly better thermal residue behaviour compared to PE additives due to its molecular structure, combined with good release properties as well. The combination of additives from the CPM Concept (HANSA RELEASE R 8198) together with modified PP waxes (HANSA RELEASE R 8160) then leads to this drastic reduction of surface residues on the casted parts. It can be assumed that this has improved paint adhesion. It is very likely that other surface-dependent treatments such as bonding, electroplating, etc. are also positively influenced by the use of the CPM Concept additives.

The results of the TOF-SIMS measurements show that modified polysiloxanes are very temperature-stable on the casted parts and can be found structurally almost unchanged on the parts after the diecasting process. On the other hand, it could be shown that both the highly polar, low viscosity wax-like polymers from the CPM Concept and those of the PE primary dispersion are degraded to such an extent under the temperature load of the diecasting that it was no longer possible to identify the structure of the original molecules.
By changing the formulation of the release agents with the new additives from the CPM Concept, the residue behaviour of the release agents on the casted parts and in the mould can be drastically reduced. Lower residues have positive effects on the entire process chain and should lead to a more efficient diecasting process in the future.

Outlook

Diecasting release agents have a decisive influence on the process, the die-casted parts produced and their machining as well as the finished components. A release agent should only be a necessary aid in the diecasting process without influencing the process in any way. This goal has been achieved by developing the new additives from the CPM Concept.
The CPM Concept has the potential to positively influence the economic efficiency of the diecasting process over the entire process chain up to the end product. By reducing release agent residues on the mould and ensuring good lubrication of the ejectors, it should be possible to minimise process interruptions for cleaning and maintenance. In addition, surface-dependent treatments such as painting, bonding, electroplating, etc. should be less affected by this new technology due to the low residues. This should significantly reduce reject rates and increase the efficiency of die-casted parts. Also, due to the low release agent residues, mild alkaline cleaning of the casted parts should be sufficient to meet the increased surface requirements, for example for electronic components.

Therefore, the HANSA RELEASE R 8198 from the CPM Concept for release agents is likely to become an important component in the production of casted components for electromobility in the future.
www.cht.com; www.keim-additec.de

Peter Pyka, Keim Additec Surface GmbH, Kirchberg
Dr.-Ing. Marco Haesche, Dr. Martin Wiesing and Andreas Stake, Christoph Pille, Fraunhofer IFAM, Bremen

Literature:

[1] J. Schulz and W. Holweger, Interaction of additives with metal surfaces, Expert Verlag, 2010.
[2] Surface and Interface Analysis 26 (2004); [No. 10], pp. 1427-1434.

PHOTOS AND GRAPHICS: KEIM ADDITEC SURFACE GMBH