

Die-Plating

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1 Introduction

The industry understands by “die-plating” the occurrence and accumulation of undesirable deposits in the flow channel and at the die orifice of extruders during the extrusion of rubber compounds. With time, such deposits not only can cause fouled extrusion surfaces, but also poor dimensional stability, which means off-quality production and finally expensive non-productive hours because of idle machine time for cleaning or replacement of soiled parts. Similar phenomena are also observed during injection molding.

It seems likely to assume the reasons for die-plating in two areas:

- in process related parameters such as smoothness of machine walls, machine geometry and operating conditions.
- in the formulation of the rubber compound, where the polymers, fillers and various other additives may have an effect.

The objective of the present work was to identify factors of influence in the extrusion process, and thus help to find ways to avoid or at least minimize the occurrence of die-plating under actual factory conditions. Tests were run on EPDM compounds with different fillers, as well as with selected additives and processing aids (but without curing chemicals), by means of working with a special developed proprietary test technique.

2 Experimental

2.1 Base formulation

	phr
EPDM rubber	100
Mineral filler	50
Corax N-550	90
Paraffin oil (plasticizer)	75
Summe	315

Table 1: Base formulation for the extrusion trials

For comparative tests of extrusion parameters and formulation variations with different additives and polymers, the Neuburg Siliceous Earth grade Sillitin Z 86 was used.

2.2 Test design

Individual tests were run with 5 kg of compound each, under the conditions listed in Table 2.

Extruder		Schwabenthan Polytest 30 R
Screw diameter	mm	30
Process length	mm	450
Temperature set point head / zone 1 / zone 2	°C	60 / 60 / 60
Cooling (zone 1 and 2)		¼ turn open
Screw speed	rpm	100
Die-plating measuring device		see drawings
Measuring channel l x w x h	mm	50 x 10 x 3
Metal insert material		Toolsteel CK 45, lengthwise ground
Metal insert roughness R_z (across the flow direction)	µm	5-7
Feed stripes	mm	30 x 6

Table 2: Extrusion test conditions

The extruder used, a Schwabenthan Polytest 30 R, is shown in Figure 1.



Figure 1: Special front-end test device and Schwabenthan extruder Polytest 30 R

The special device for assessment of the die-plating effect, a die insert plate, is represented in Figure 2.

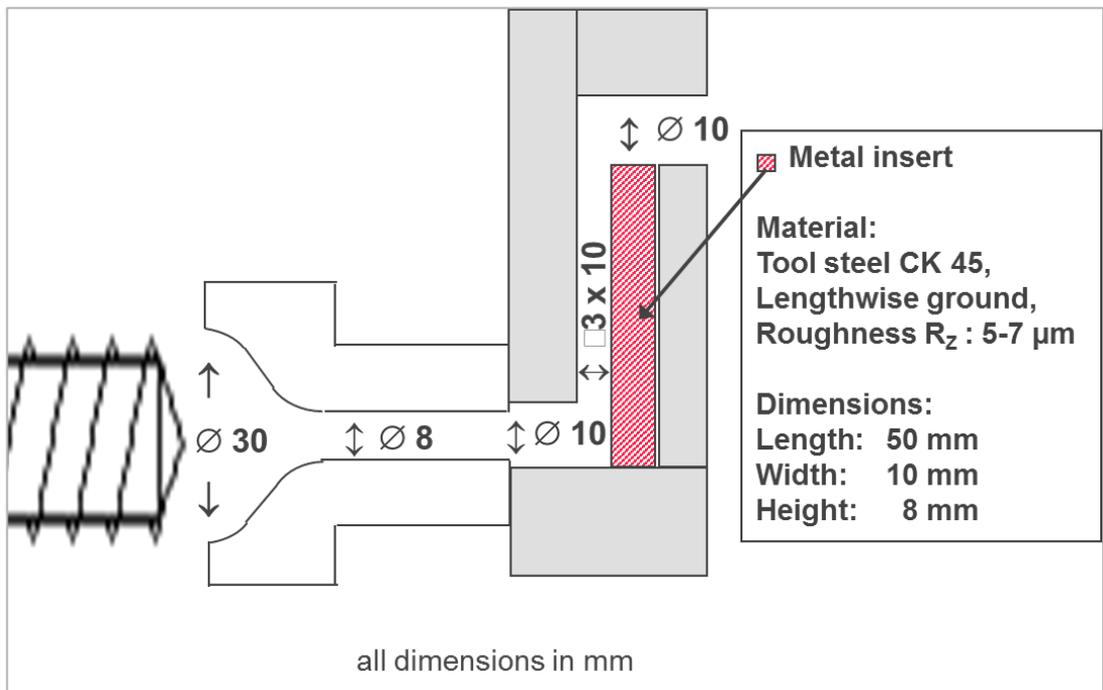


Figure 2: Schematic drawing of the front-end test device with metal insert

The evaluation took place by visual assessment of the metal insert surface.



Figure 3: Examples for different die-plating tendency

3 Results

3.1 Effect of process parameters

For the test, the base formulation with Sillitin Z 86 was used. Figure 4 illustrates in comparison the die-plating effect with normal, polished resp. fluoralkyl silane treated metal surfaces of the die insert plate. Quite obviously, the reduced roughness of a polished surface should be of advantage for minimizing the occurrence of die-plating.

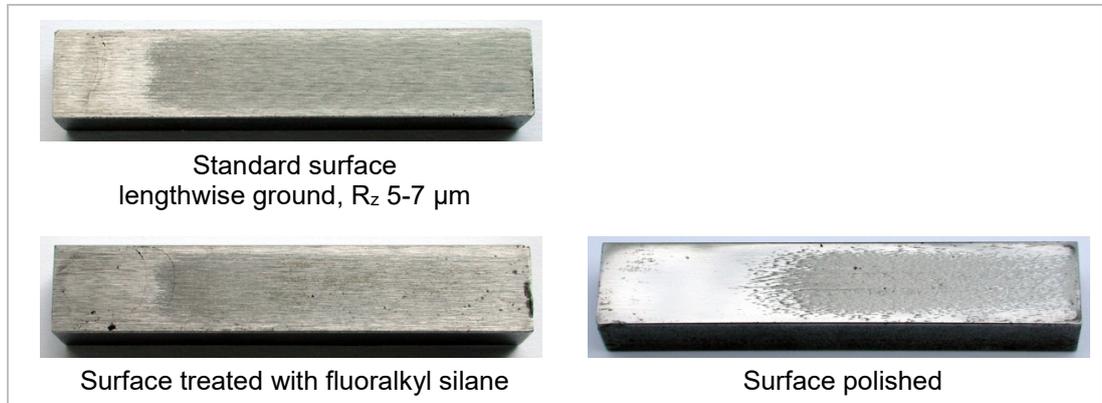


Figure 4: Effect of the die insert surface on the die-plating effect

The favorable effect of reducing the extrusion throughput - although in the tests to an extreme degree - is shown in Figure 5. Higher extruder head temperatures, according to Figure 6, also seem to similarly improve the situation.



Figure 5: Effect of extrusion throughput on the die-plating effect



Figure 6: Effect of extruder head temperature on the die-plating effect

Conclusion: Process parameters

Die-plating can be reduced / avoided by:

- roughness reduction of all surfaces which are in contact with the extrudate, especially in the die and areas of high shear rate.
- decrease of extrusion throughput.
- increase of extruder head temperature.
- based on experience of customers: favorable flow geometry in front of the die orifice.

3.2 Effect of the formulation

3.2.1 Effect of the polymer

Already extrusion tests with straight uncompounded rubbers give evidence of a broad spectrum of deposition tendencies. Figure 7 shows typical results for two EPDM rubbers without respectively with high die-plating tendency.

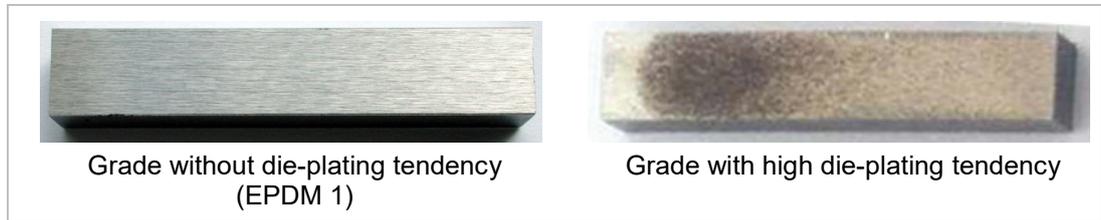


Figure 7: Rubber without resp. with high die-plating tendency

Therefore four different EPDM polymers were compared in the base formulation (with Sillitin Z 86) given in Table 1. Characteristic properties of the EPDM types are listed in Table 3.

	Mooney viscosity 125°C		Molecular weight distribution (MWD)	Ethylene (C2) content (%)	Diene (ENB) content (%)
	ML (1+4)	ML (1+8)			
EPDM 1 (standard)	approx. 90	80	bimodal	52	9
EPDM 2	90	not determined	medium broad	50	9
EPDM 3	60	not determined	broad	52	8
EPDM 4	28	not determined	narrow	50	8

Table 3: Characteristic properties of EPDM types used

After the test runs, the die inserts exhibited distinct differences (Figure 8). The viscosity of the polymers appeared as the decisive parameter: the grades with medium or low viscosity came off favorably. On the other hand, the molecular weight distribution did not seem to exert any substantial effects.

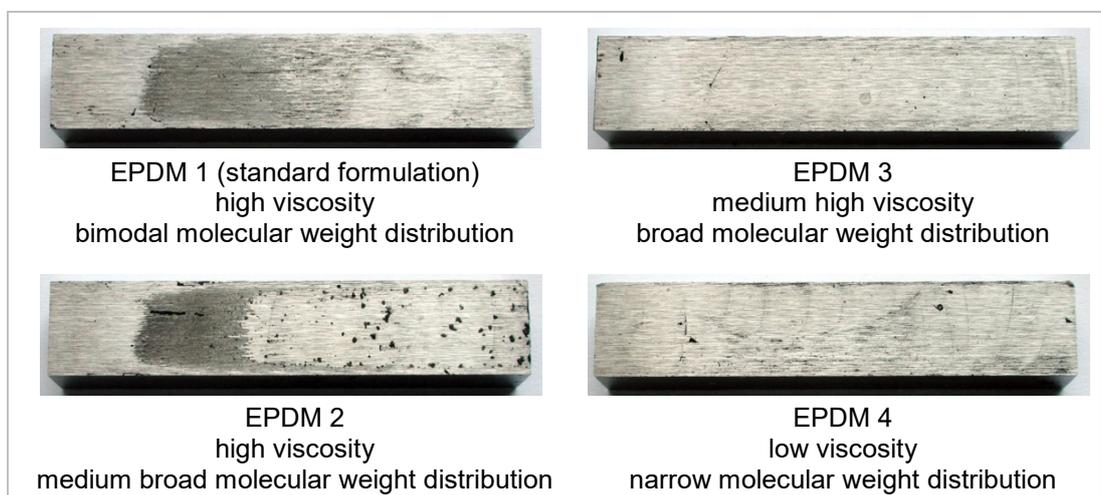


Figure 8: Metal die inserts after trials with compounds based on 4 different EPDM types

Conclusion: Effect of the polymer

Die-plating can be reduced / avoided by:

- use of lower viscosity polymer grades.

3.2.2 Effect of additives besides Neuburg Siliceous Earth

a) Dosage of additives at 2 phr

The additives listed in Table 4 were added at 2 phr to the unchanged base compound (Table 1) with standard EPDM 1 and Sillitin Z 86 as filler.

Product type	Chemical group	Chemical designation	Trade name	Effect
Filler activator / desactivator	Fatty acid	Stearic acid		++
Oligomeric additive	Low molecular polymer	Liquid 1,2-polybutadiene	Lithene AH	+
Oligomeric additive	Low molecular polymer	Liquid 1,2-polybutadiene, silylated	Polyvest 25	+
Oligomeric additive	Low molecular polymer	Liquid EPDM	Trilene 67	+
Coupling agent	Alkoxysilylalkyl-sulfane	TESPT *	Si 69 *	+
Processing aid	Hydrocarbon wax derivate	Perfluoralkyl wax **	Genolub PFF 6/1020 **	o
Processing aid	Fatty acid derivate	Stearyl alcohol	Lorol C 18	o
Processing aid	Fatty acid derivate	Hydroxystearic acid	Edenor OSSG	o
Processing aid	Hydrocarbon wax derivate	Montan acid wax	Luwax S	o
Processing aid	Metal soap	Processing aid based on calcium stearate	Deoflow S	o/-
Filler activator / desactivator	Metal soap	Zinc stearate	Zincum N 37 SL	o/-
Filler activator / desactivator	Quaternary ammonium salt	Dimethyl distearyl ammonium chloride	Varisoft TA 100	--
Filler activator / desactivator	Glycol	Diethylene glycol (DEG)		--
Processing aid	Fatty acid derivate	Stearic(acid)amide	Uniwax 1750	--
		* as Aktisil PF 216		
		** dosage 0.03 and 0.3 phr		
<i>Effect on die-plating</i>		++	<i>strongly reducing</i>	
		+	<i>reducing</i>	
		o	<i>not noticeable</i>	
		-	<i>enhancing</i>	
		--	<i>strongly enhancing</i>	

Table 4: Additives and their effects

The rating of the individual additives here referred to the reduction resp. enhancement of the die-plating effect as observed for the compound containing Sillitin Z 86 without any additives (Figure 9).

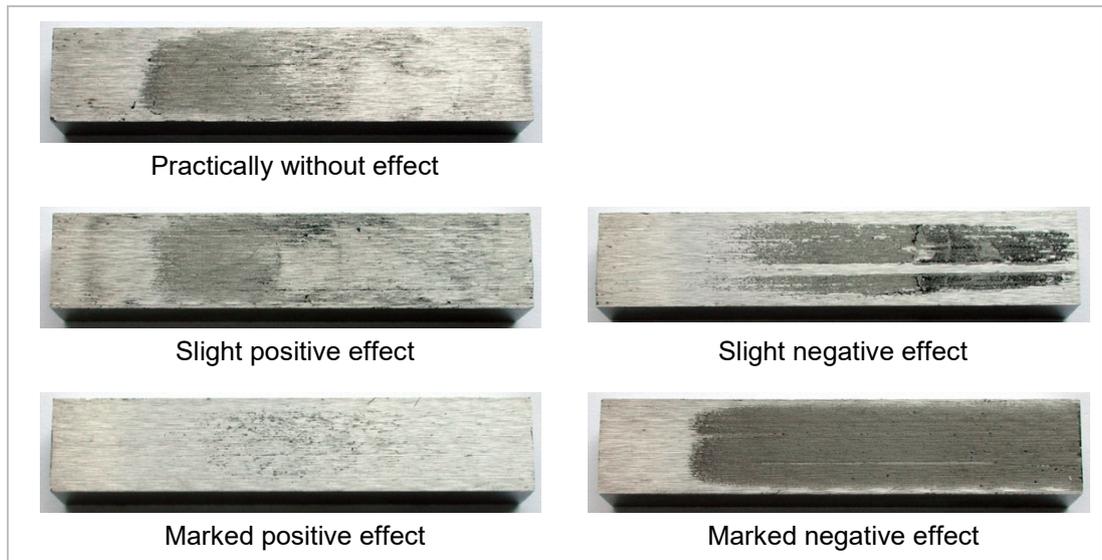


Figure 9: Assessment of the reducing resp. enhancing effect of additives (2 phr)

The results have been included in Table 4: distinct differences were observed between individual groups of additives. A surprisingly big number of additives did not noticeably effect the tendency towards die-plating, others did increase the effect. The compound with the TESPT treated Neuburg Siliceous Earth Aktisil PF 216 without other additive came off rather favorably, and also low molecular polymers as additives showed positive results. The most obvious improvement was obtained with stearic acid.

In an additional test series, the replacement of at least 5 phr plasticizer by silicone oil in the standard formulation with Sillitin Z 86 resulted in complete absence of die-plating (Figure 10).

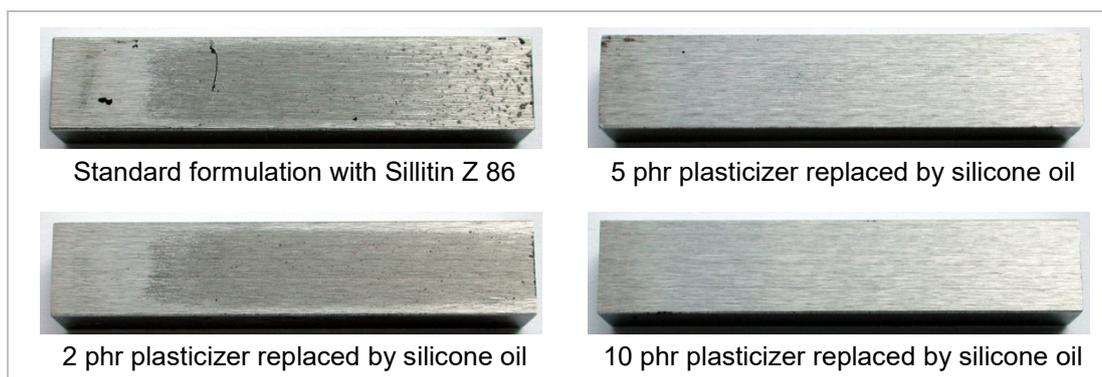


Figure 10: Effect of silicone oil as partial replacement of the paraffinic mineral oil plasticizer on the die-plating tendency

b) Dosage of additives at 5 phr

In view of the results obtained with varying silicone oil concentrations - where 2 phr initially gave a fall-off, but 5 phr caused a marked improvement - the additives listed in Table 5 were now used at 5 phr throughout.

Product type	Chemical group	Chemical designation	Trade name	Effect
	Silicone oil	Polydimethyl siloxane, 1000 mm ² /s	Silikonöl AK 1000	++
Processing aid	Metal soap	Zinc oleate	LIGA Zinkoleat	+
Processing aid	Metal soap	Zinc stearate	Zincum N 37 SL	+
Processing aid	Metal soap	Calcium-/ zinc stearate	Ca/Zn-Stearat SMS	+
Processing aid	Metal soap	Calcium stearate	Ceasit 1	o/-
Processing aid	Metal soap	Processing aid based on calcium stearate	Deoflow S	-
Processing aid	Fatty acid derivate	Stearic(acid)amide	Uniwax 1750	-
Filler activator / desactivator	Glycol	Polyethylene glycol (PEG) 4000 g/mol		--
Filler activator / desactivator	Glycol	Diethylene glycol (DEG)		--
<i>Effect on die-plating</i>		++ <i>strongly reducing</i> + <i>reducing</i> o <i>not noticeable</i> - <i>enhancing</i> -- <i>strongly enhancing</i>		

Table 5: Additives and their effects

Again the rating of the individual additives referred to the reduction resp. enhancement of the die-plating effect as observed for the compound without any additives (Figure 11).

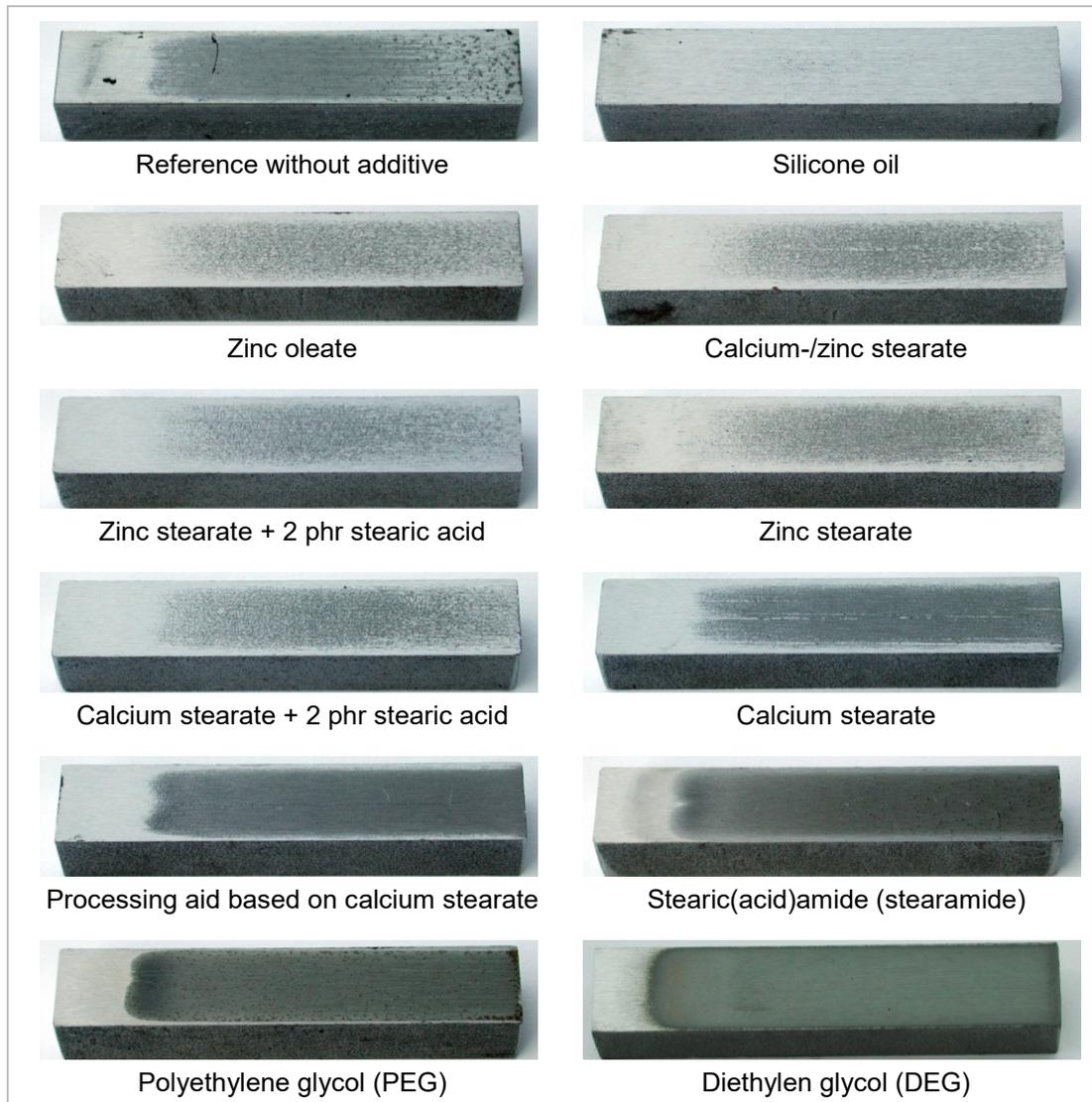


Figure 11: Assessment of the reducing resp. enhancing effect of additives (5 phr)

Figure 11 in addition illustrates combinations with stearic acid. For zinc stearate and calcium stearate, a slight downward trend is evident.

c) Additional trials with selected additives

The additives listed in Table 6 were used in varying concentrations.

Product type	Chemical group	Chemical designation	Trade name	Effect
Processing aid	Metal soap	Zinc oleate	LIGA Zinkoleat	+
	Phosphate ester	Lauric phosphate ester	Lakeland PA 120	+
	Amino alcohol	Triethanol amine (TEA)		++/- *
		* <i>the test plate showed a distinct positive effect, but on the opposite side increased plating was observed</i>		
<i>Effect on die-plating</i>		++ <i>strongly reducing</i> + <i>reducing</i> o <i>not noticeable</i> - <i>enhancing</i> -- <i>strongly enhancing</i>		

Table 6: Additives and their effects

The rating of the individual additives here referred also to the reduction resp. enhancement of the die-plating effect (Figure 12).

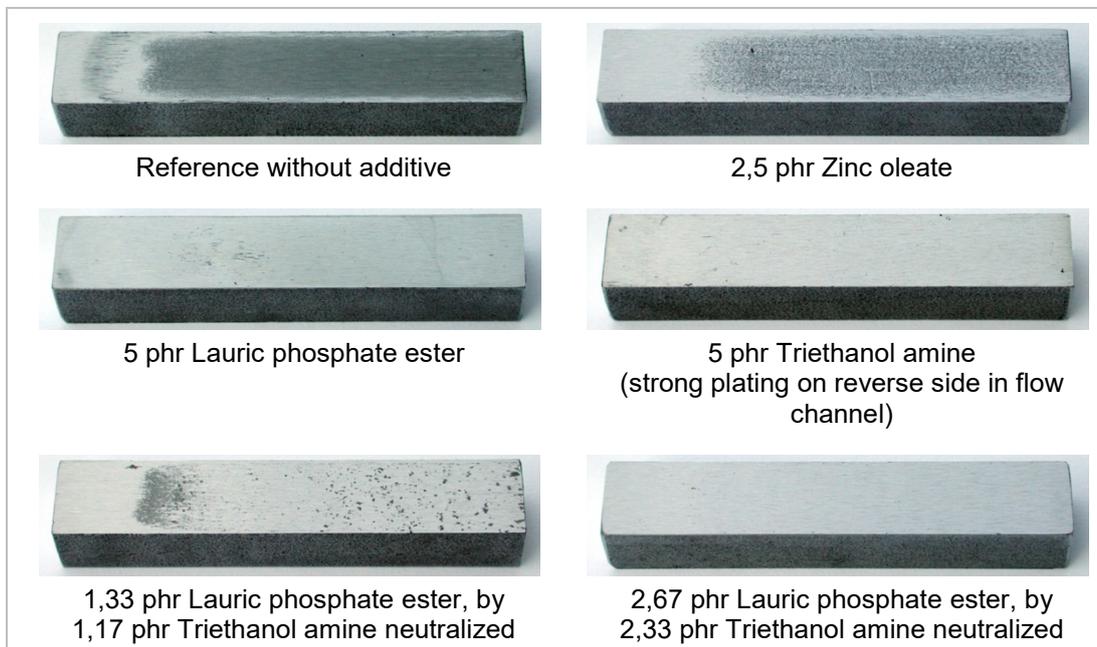


Figure 12: Assessment of the reducing resp. enhancing effect of additives

Conclusion: Effect of additives

Die-plating can be reduced by:

- elimination of diethylene glycol (DEG) or polyethylene glycol (PEG), quaternary ammonium salts or amide waxes (even as part of processing aids).
- addition of triethanol amine (TEA) instead of diethylene glycol (DEG) or polyethylene glycol (PEG).
- addition of stearic acid, if possible at high levels.
- addition of zinc stearate or zinc oleate, preferably in combination with stearic acid.

Die-plating can be avoided by:

- addition of at least 5 phr of silicone oil.
- addition of 2.5 to 5 phr of lauric phosphate ester (also with triethanol amine as neutralizing agent).

3.2.3 Effect of mineral fillers

The fillers listed in Table 7 were compared in the base standard EPDM compound shown in Table 1 (for talc, the loading was increased from 50 to 53 phr).

Filler	Designation
Sillitin Z 86	Neuburg Siliceous Earth natural combination of corpuscular Neuburg silica and lamellar kaolinite
Sillitin V 85	Neuburg Siliceous Earth coarser particle size than Sillitin Z 86
Silfit Z 91	Neuburg Siliceous Earth subjected to a heat treatment (calcined)
Whiting	Natural calcium carbonate Predominantly corpuscular fine particle size (similar to Sillitin Z 86)
Talc 1	Micronized talc lamellar fine particle size (similar to Sillitin Z 86)
Talc 2	Micronized talc lamellar coarser particle size than talc 1

Table 7: Characteristics of the mineral fillers tested

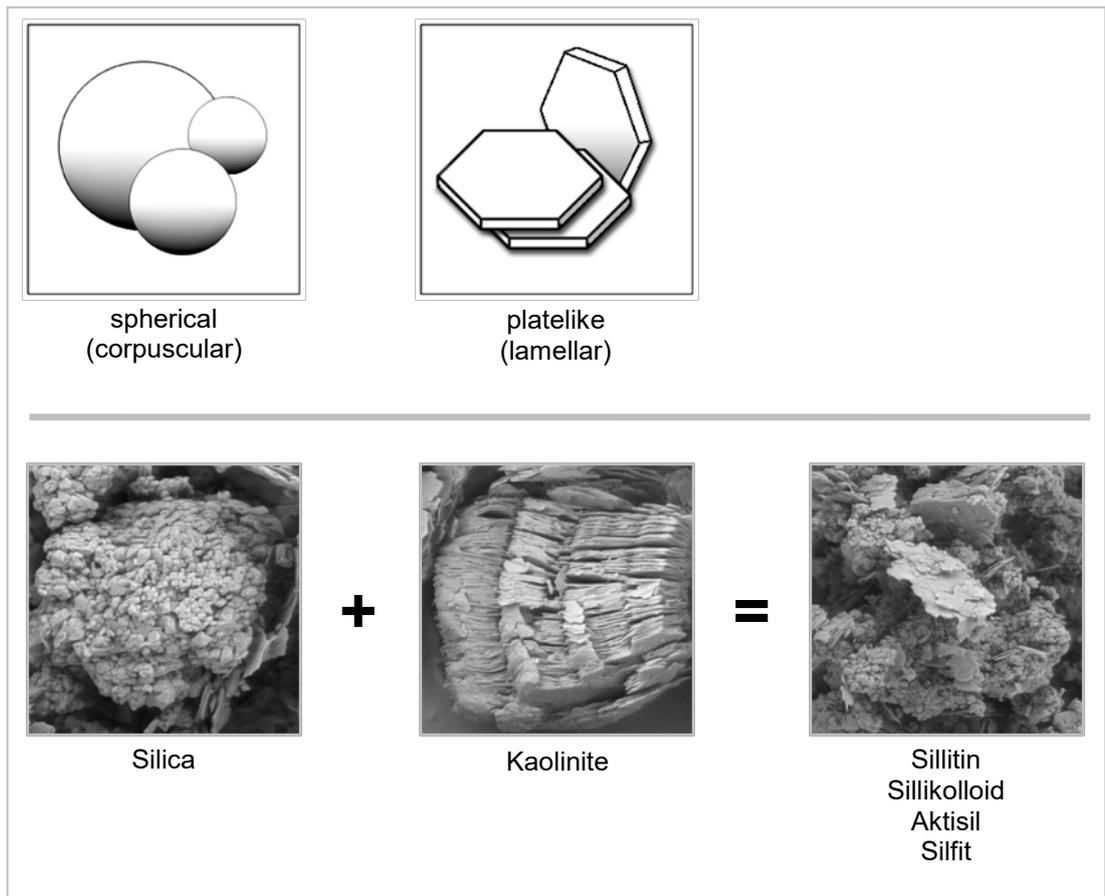


Figure 13: Schematic representation of various tested particle structures and SEM photographs of Neuburg Siliceous Earth

Figure 14 gives evidence of the fact that fillers with lamellar (platelike) structure cause markedly stronger die-plating, compared with fillers of corpuscular particle characteristics.

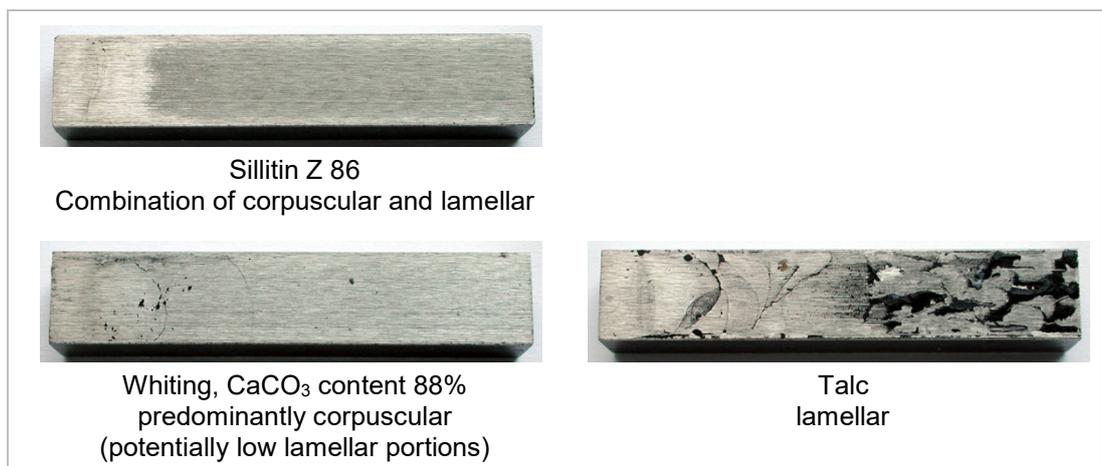


Figure 14: Comparison of fillers of different particle structure

As shown in Figure 15 for Neuburg Siliceous Earth and talc, coarser particle size of a filler has a favorable effect in the direction of reducing the tendency towards die-plating.

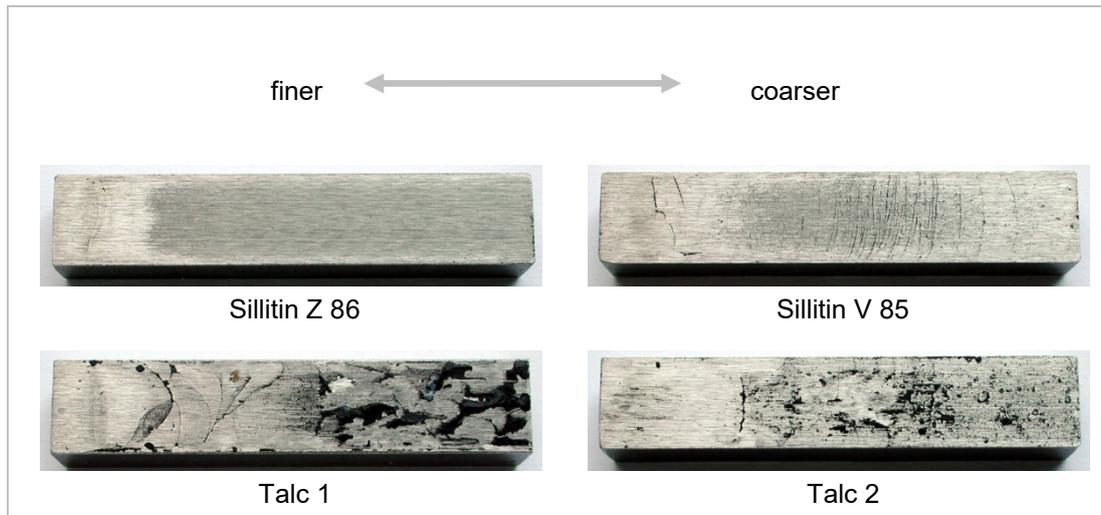


Figure 15: Effect of particle size

Figure 16 shows the effect when Neuburg Siliceous Earth is subjected to a heat treatment: the lamellar portions are aggregated by calcination – this avoids die-plating caused by the mineral filler.

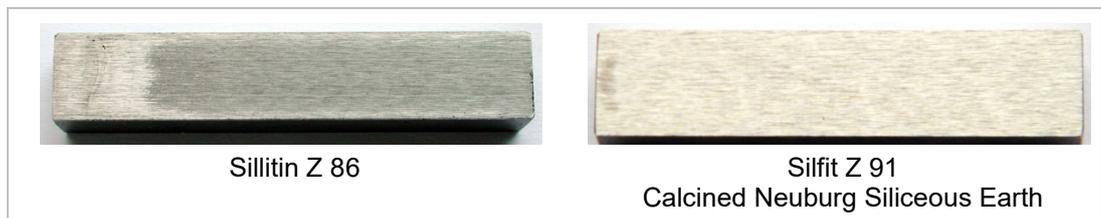


Figure 16: Effect of calcined Neuburg Siliceous Earth

Conclusion: Effect of mineral fillers

Die-plating can be reduced by:

- elimination of lamellar fillers, e.g. talc (even as powdering agent or in dip baths of batch-off units).
- preferred incorporation of Sillitin V or Sillitin N grades as fillers (less favorable: Sillitin Z or Sillikolloid).

Die-plating can be avoided by:

- use of Silfit Z 91.

4 Summary

For minimizing or avoiding the occurrence of die-plating during the extrusion of EPDM compounds, according to the results presented the following measures should act favorably:

Process parameters:

- Roughness reduction of all surfaces which are in contact with the extrudate, especially in the die.
- Decrease of extrusion throughput.
- Increase of extruder head temperature.
- Based on experience of customers: favorable flow geometry in front of the die orifice.

Formulation:

- addition of at least 5 phr silicone oil
- addition of 2.5 to 5 phr of lauric phosphate ester (also with tri ethanol amine as neutralizing agent)
- addition of zinc stearate or zinc oleate, preferably in combination with stearic acid
- addition of stearic acid, if possible at high levels
- addition of tri ethanol amine (TEA) instead of diethylene glycol (DEG) or polyethylene glycol (PEG)
- elimination of diethylene glycol (DEG) or polyethylene glycol (PEG), quaternary ammonium salts or amide waxes (even as part of processing aids)
- use of lower viscosity polymer grades
- elimination of lamellar fillers, e.g. talc (even as powdering agent or in dip baths of batch-off units)
- preferred incorporation of Sillitin V or Sillitin N grades as fillers (less favorable: Sillitin Z or Sillikolloid P)
- use of Silfit Z 91

Recommended fillers of the Neuburg Siliceous Earth product range:

- Sillitin N or Sillitin V: economic way to reduce die-plating.
- Silfit Z 91: eliminates die-plating caused by mineral fillers.

5 Interpretation

Based on the results obtained, a hypothesis can be formulated as follows:

Lamellar fillers become oriented under shear/elongational flow conditions, accumulate near the walls in the area of highest shear rate, and thus are separated out of the compound without being further moved on by the shear stresses of the flowing compound. In the case of wall or film slippage, this phenomenon will not occur at all or only to a marginal degree.

This hypothesis is supported by the following facts:

In his discussion of the rheology of highly loaded EPDM compounds, Geiger [1] arrived at the conclusion that wall slippage will prevail below a critical wall shear stress, but shear flow with wall adhesion will occur above this threshold. The parameters of influence for this critical wall shear stress are:

- the surface quality (roughness) of the walls of the die
- the plastic-viscoelastic properties of the compound

By way of a model, the rubber compound can be visualized to slip on a very thin film over the irregularities of the wall below the critical wall shear stress level. Under these conditions, it is subjected only to minimum shear. The normal stress differences developing in the shear plastic-viscoelastic compound tend to cause a widening of the slipping compound which fills out the cavities in the wall surface. As long as the shear stress in the direction of flow exceeds the effect of the normal stress differences acting towards the wall, slippage will occur.

This situation may also be considered as a case of “lubricated” solid state friction. The shear stress corresponds to the friction force F_R , and the components of the normal stress differences to the normal force F_N . The ratio F_R / F_N would make up the friction coefficient μ , which - apart from the viscosity of the lubricating film - depends upon the roughness of the surface. If the roughness and thus the friction coefficient with unchanged other conditions are continuously increased, a critical point will be reached at which no movement at the wall is any longer possible. In the inverse case, beyond a critical point of overcoming the adhesion friction, movement will start.

This model when applied to the die insert test plate, would mean that reducing the roughness of the insert surface will result in increasing the level of the critical wall shear stress (prevailing wall shear stress < critical wall shear stress), and as a result wall slippage phenomena would be encouraged. The real test results as well as comments from rubber manufacturers are in qualitative agreement with these assumptions.

The reduced die-plating tendency with higher extruder head temperatures could also be explained by this model. With the shear/elongational flow situation as assumed for the die-plating effect, increased temperature will result in reduced viscosity of the compound. The resulting shear stresses at a given extrusion rate (= shear rate) will decrease and approach, or even end up below the critical wall shear stress. Decreasing the extrusion rate at a constant temperature leads to the same result of reduced shear stresses.

The observed positive effects of compound formulation modifications can similarly be explained by postulating that, under constant other conditions, different rubber grades or selected additives are able to shift the range of wall slippage to higher wall shear stresses, i.e. the compounds remain at levels below the critical wall shear stress.

Literature:

- [1] K. Geiger IKT Stuttgart, „Rheologische Charakterisierung von EPDM-Kautschukmischungen mittels Kapillarrheometer-Systemen.“
Kautschuk Gummi Kunststoffe **42** (1989), 273 (reprint).

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