
Terms

Kautschuk
Rohkautschuk
Raw rubber

- uncrosslinked, but crosslinkable polymer
- show at high temperature and/or influence of deformed forces increasingly viscous flowing
- basic material for the production of vulcanized rubber

Batch
Batch

- pre-mixture; incomplete raw mixture
- accelerator batches
- filler batches

Rohmischung
Raw stock
Raw mixture
Rubber compound

- uncrosslinked, crosslinkable mixture on the basis of raw rubber which contains all ingredients
- predominantly viscous flowing

Elastomer
Vulkanisat
Gummi
Rubber

- generated by covalent crosslinking of raw rubbers
- below T_G energy elastic (T_G mostly $< 0\text{ °C}$)
- entropy elastic behaviour in the application temperature region
- wide-meshed network, insoluble, but swellable
- under impact of small forces at RT and $T > RT$ stretchability about at least the double



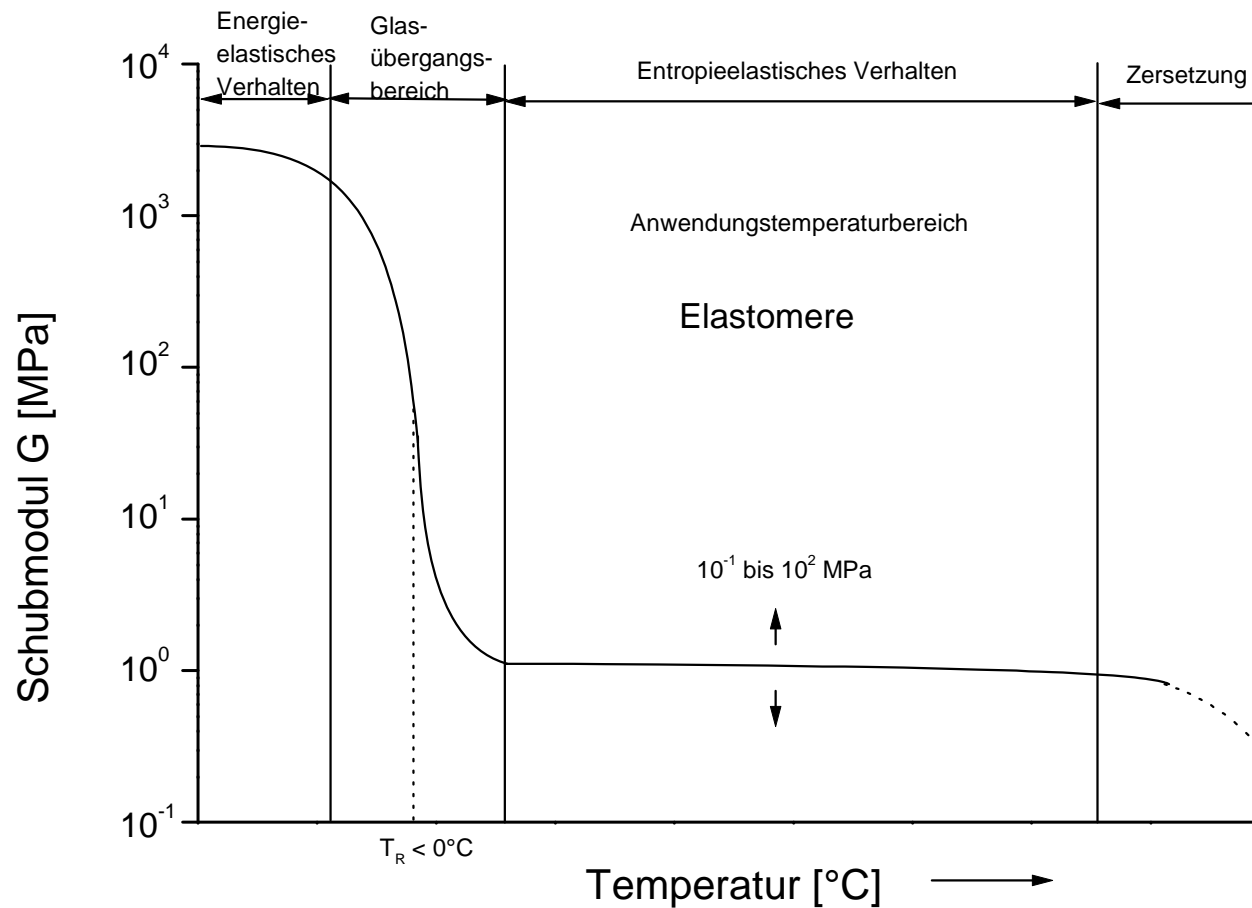
Mechanical behavior versus temperature

Energy elasticity

$$\sigma = E \varepsilon$$

Entropy elasticity

$$E = 3 \rho R T / M_c$$

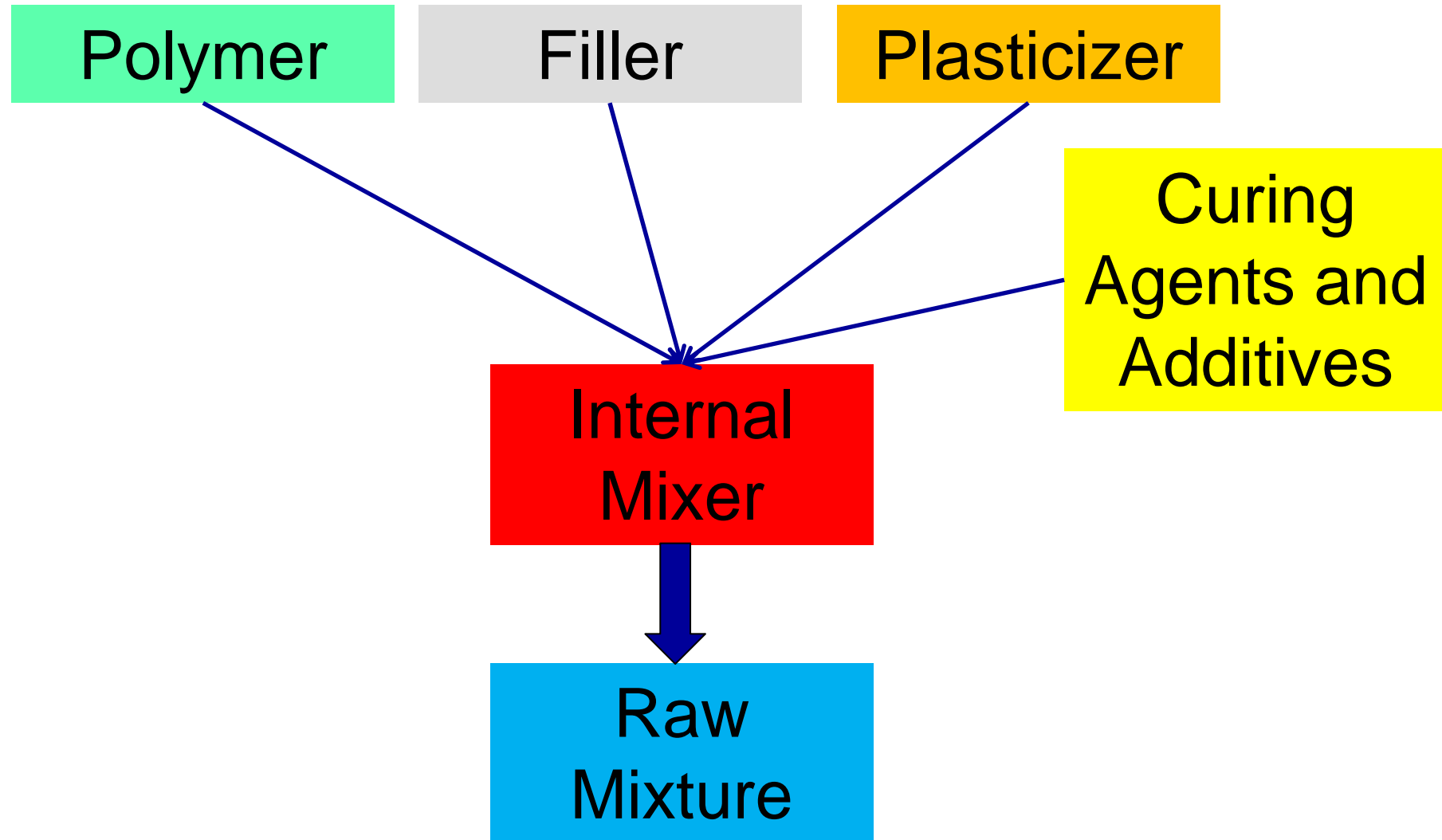


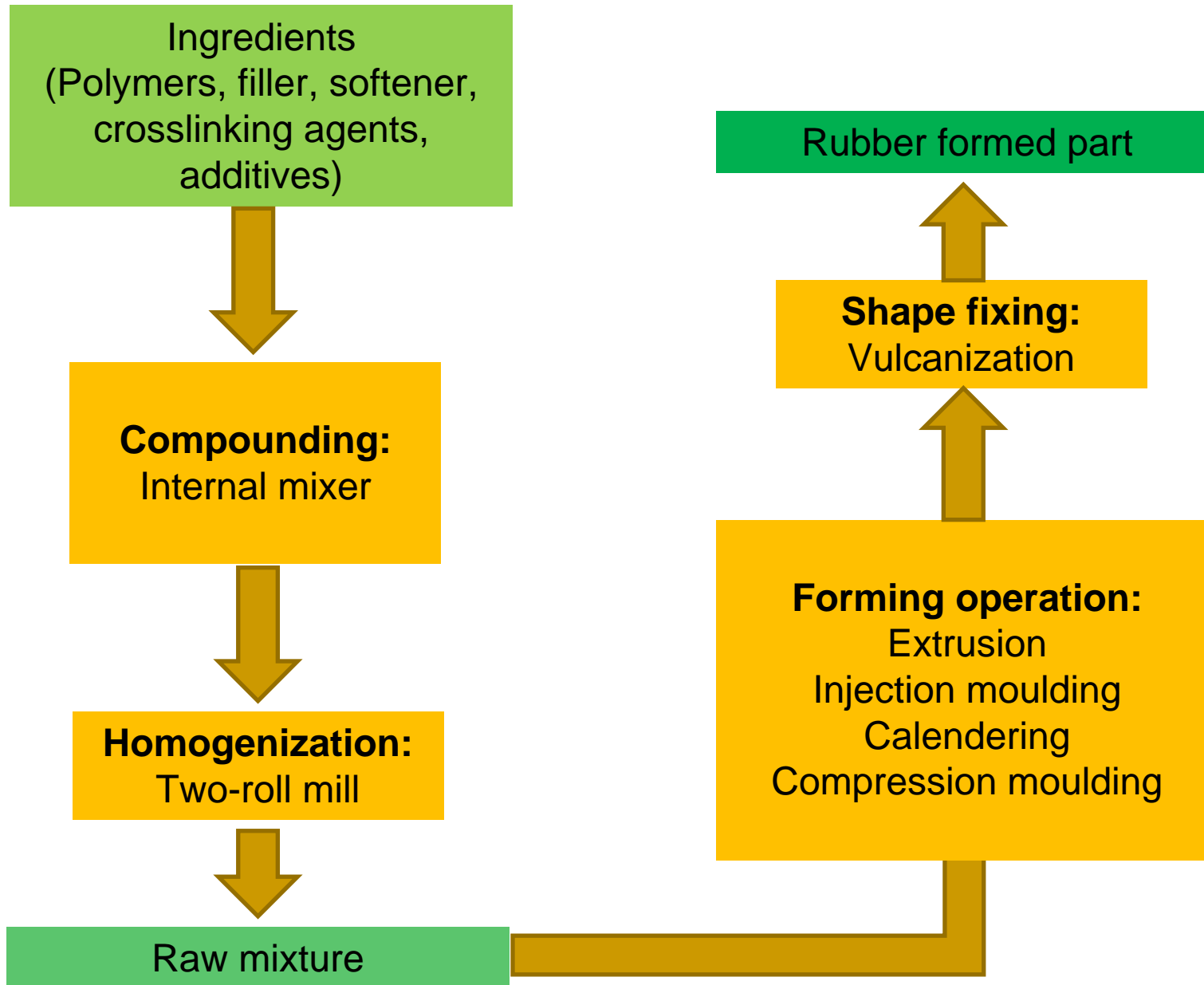
Ingredients of rubber mixtures

Polymer	Natural (NR) or synthetic rubber (SR)	40...60 wt%
Filler	Carbon black, silica, whiting, clay	20...50 wt%
Plasticizer	Aromatic, naphthenic or paraffinic mineral oils, synthetic process oils (ester plasticizer)	1...30 wt%
Curing agents and additives	Curing agents, activators, antioxidants and antiozonants, wax and sunchecking agents, accelerators, retarders, pigments, antitack agents	5...10 wt%

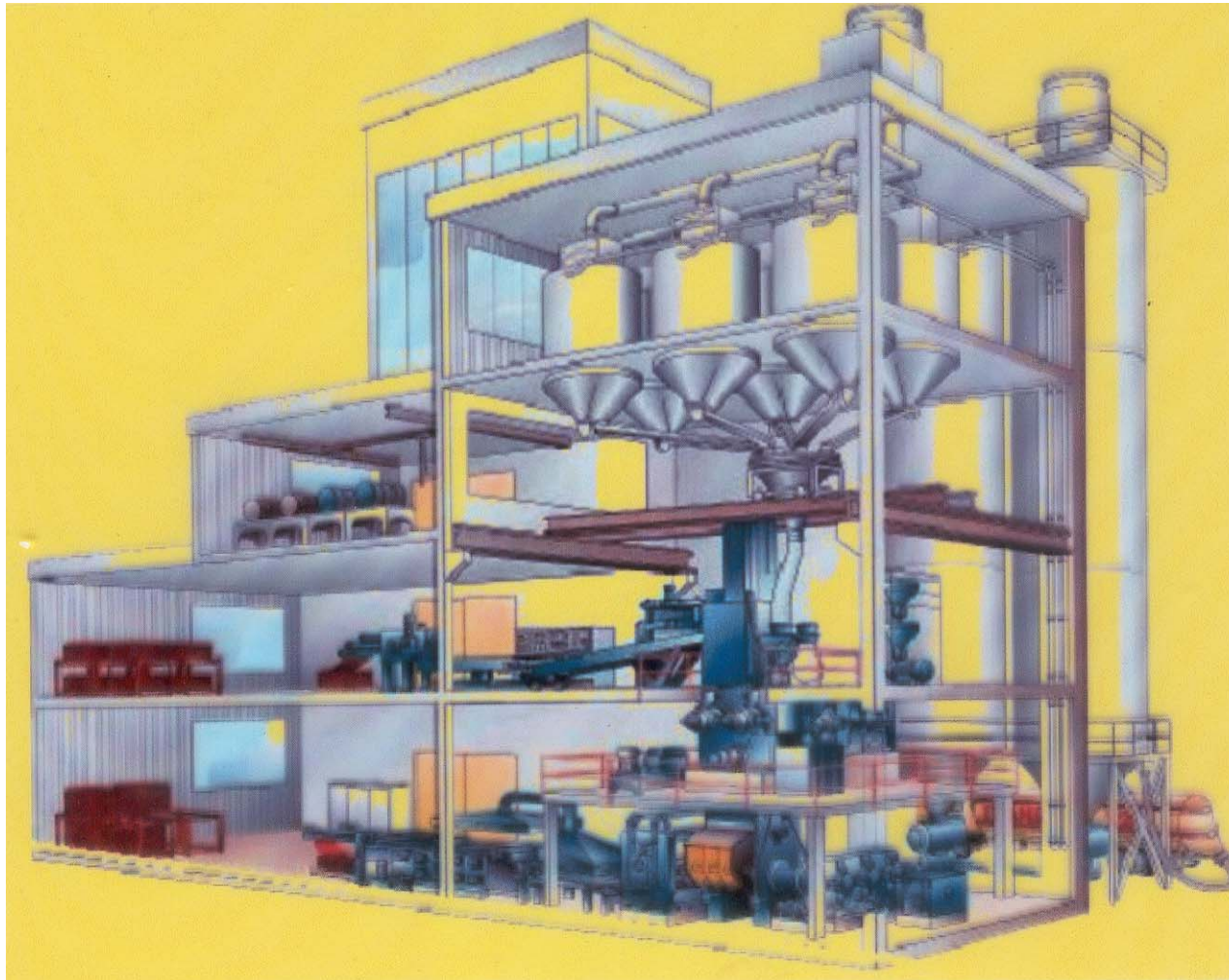


Rubber mixtures





Rubber mixture manufacturing

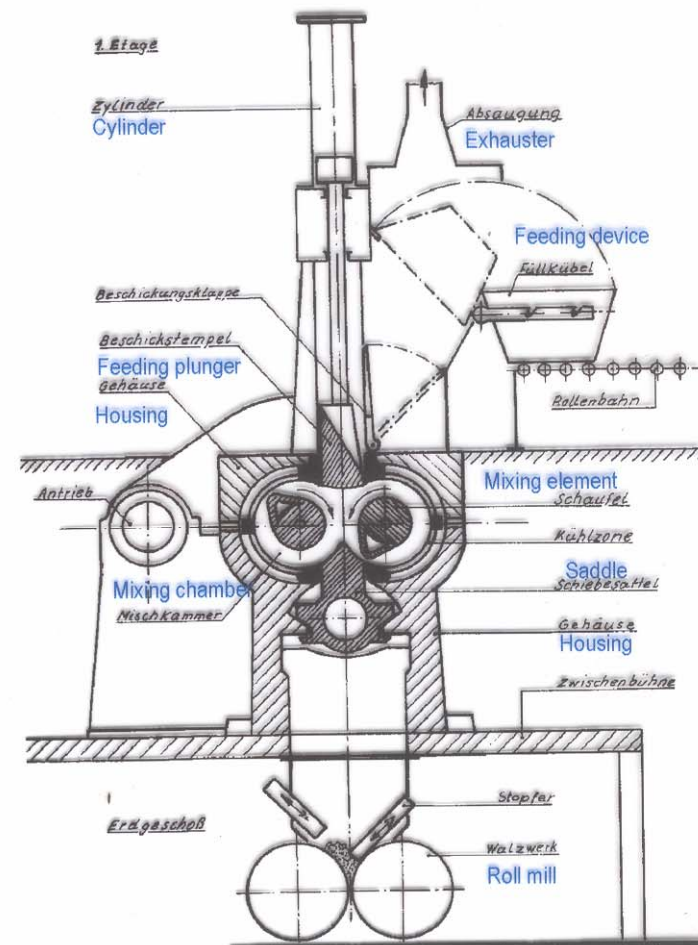


Internal mixer

- Goal of the mixing process: material and thermal homogenization of the raw mixture
- Discontinuous process



Innenmischer
Bauart Krupp-Werner & Pfleiderer GK



Machine sizes

Typ	GK-N50	GK-N100	GK-N200	K5	K7	K10
Blank volume, l	60	110	210	70	165	460
Rotor speed, min ⁻¹	23,6/26	20,9/23	19/21	22-66	22-66	22-66
Power, MW	0,16-0,33	0,3-0,59	0,59-1,2	0,15-0,45	0,375-1,1	1,9-3,0

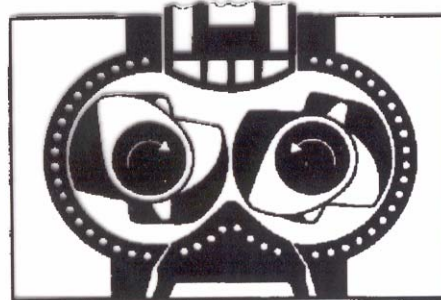
GK-N Krupp-Elastomertechnik, Bauart Werner & Pfeleiderer- Kneeter, tangierend

GK-E Krupp-Elastomertechnik, Bauart Werner & Pfeleiderer- Kneeter, kämmend

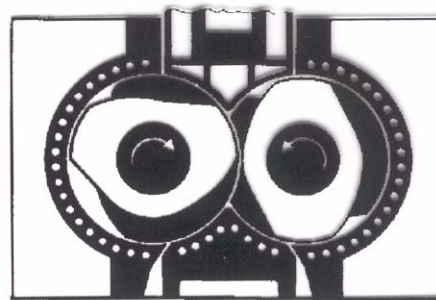
K Farrell, Bauart Shaw Intermix, kämmend



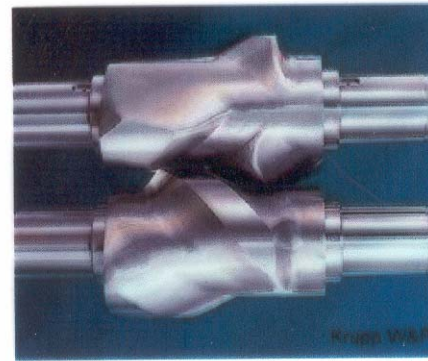
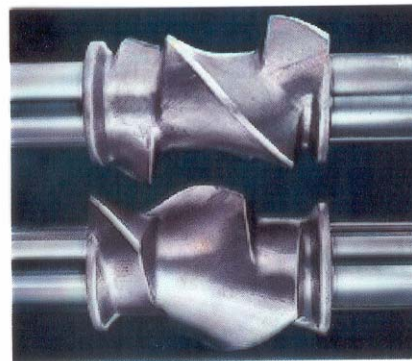
Rotor constructions



Tangierende GK-N-Rotorgeometrien
Tangent rotor geometry



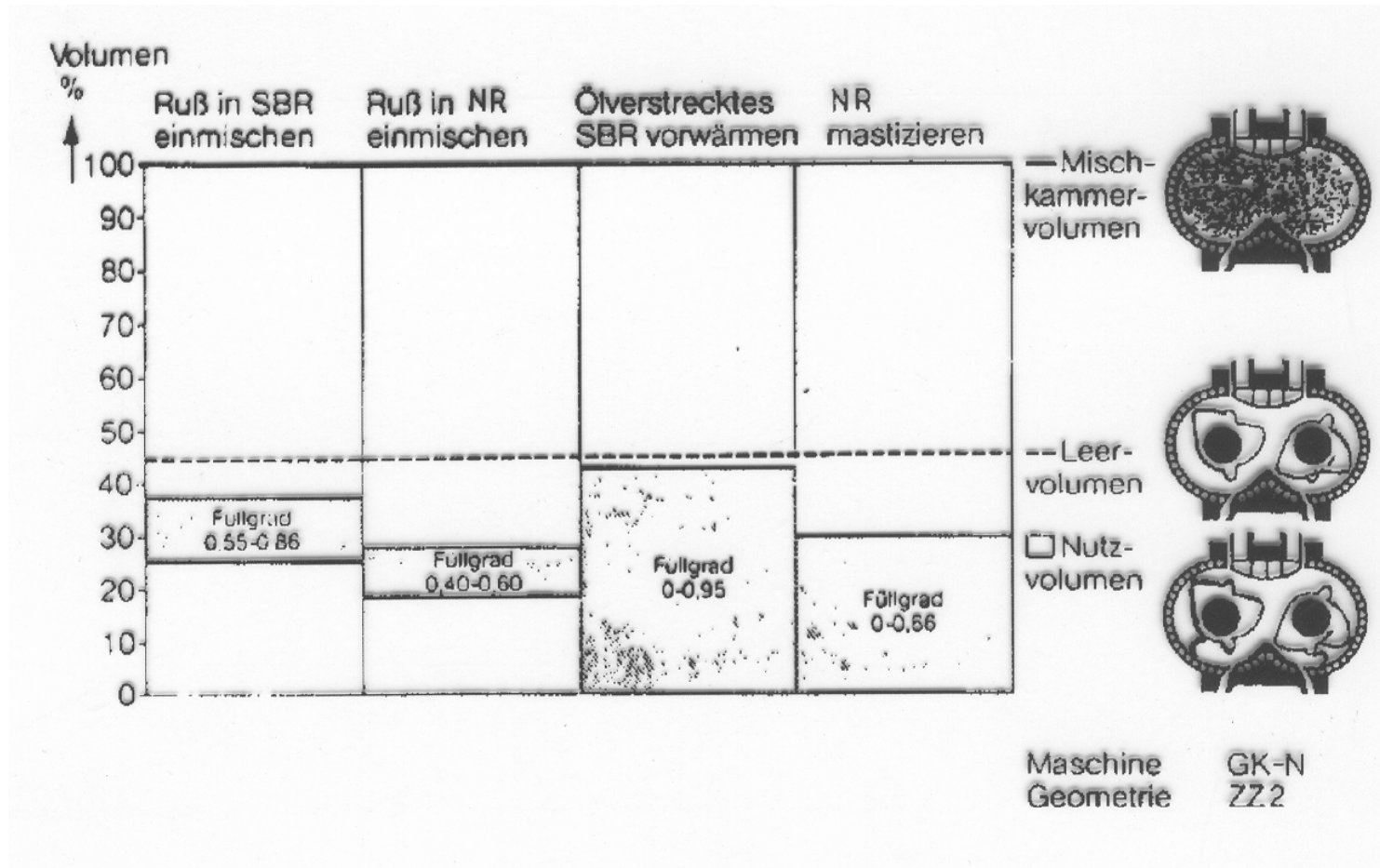
Ineinandergreifende GK-E-Rotorgeometrien
Interlocking rotor geometry



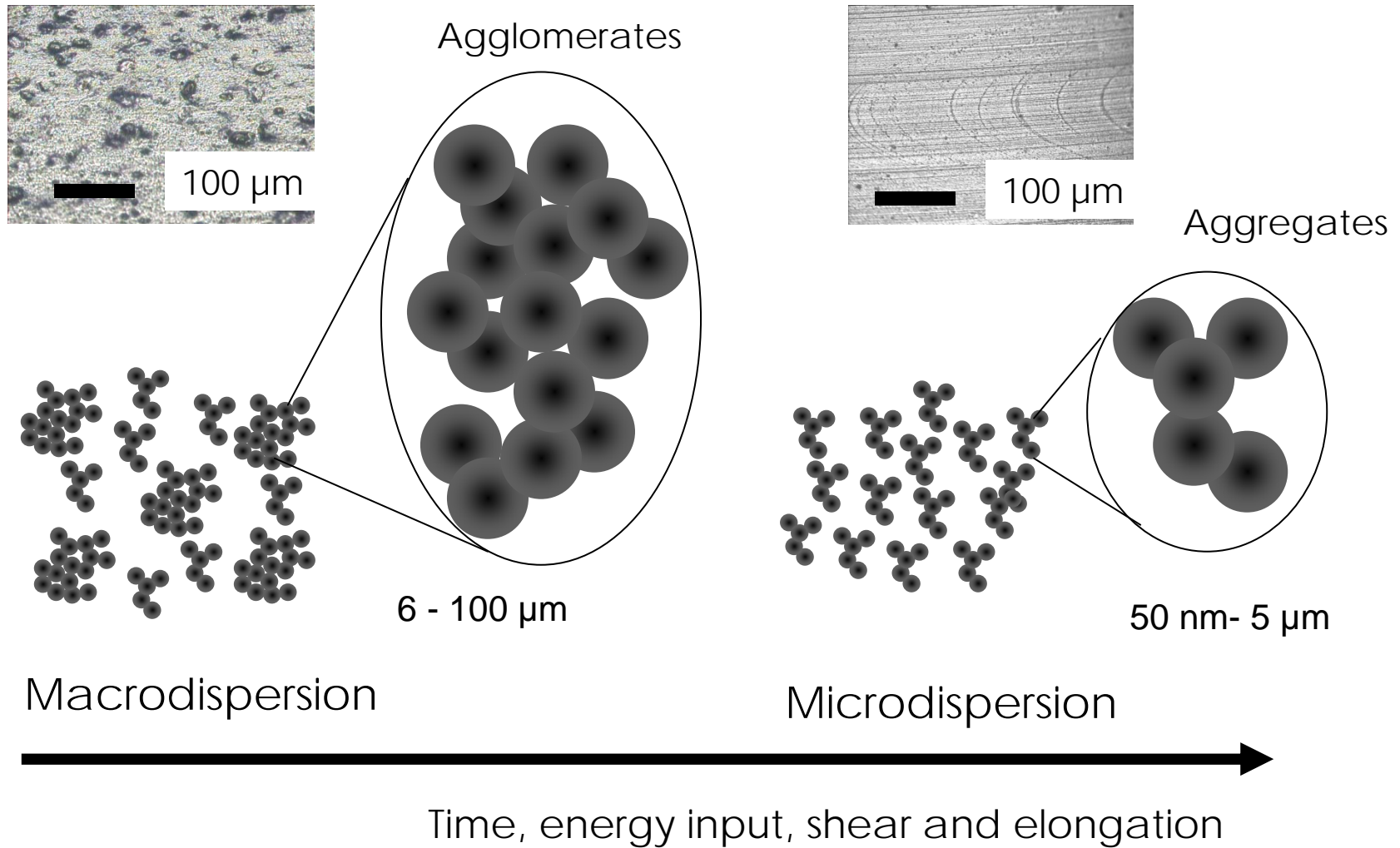
Rotor type	Tangent	Interlocking
Application	Tire industry	Technical rubber
Volumene of the mixer	250 to 650 Liter	40 to 250 Liter
Characteristics	<ul style="list-style-type: none"> • Good feed performance • Larger useful volume • Faster drawdown • Effectiv incorporation of filler (wetting of agglomerates), but disadvantages in dispersion and microdistribution of filler; post-mixing on two-roll mills) • Large throughput • Friction 1: 1,1; mostly constant rotation speed 	<ul style="list-style-type: none"> • Good temperature control) • Larger strain deformationen in spaces either side of the bottom half of the pipe (Zwickelbereich); better Dispersion • Stageless variable rotation speed (for example for 60 kg material: 30 to 90 min⁻¹, for 550 kg Batch 15 to 55 min⁻¹)



Mixing chamber volume / fill factor



Morphology development during the mixing process



Characterization of filler dispersion and distribution

Macroscopic scale

Microscopic scale

Direct

- Optical microscopy
- Thermogravimetry

- Atomic force microscopy
- Transmission electron microscopy

Indirect

- Rheometry
- Tensile test
- Dynamic-mechanical analysis

- Dynamic-mechanical analysis
- Electrical conductivity



Characterization of the filler macrodispersion

Optical Microscopy

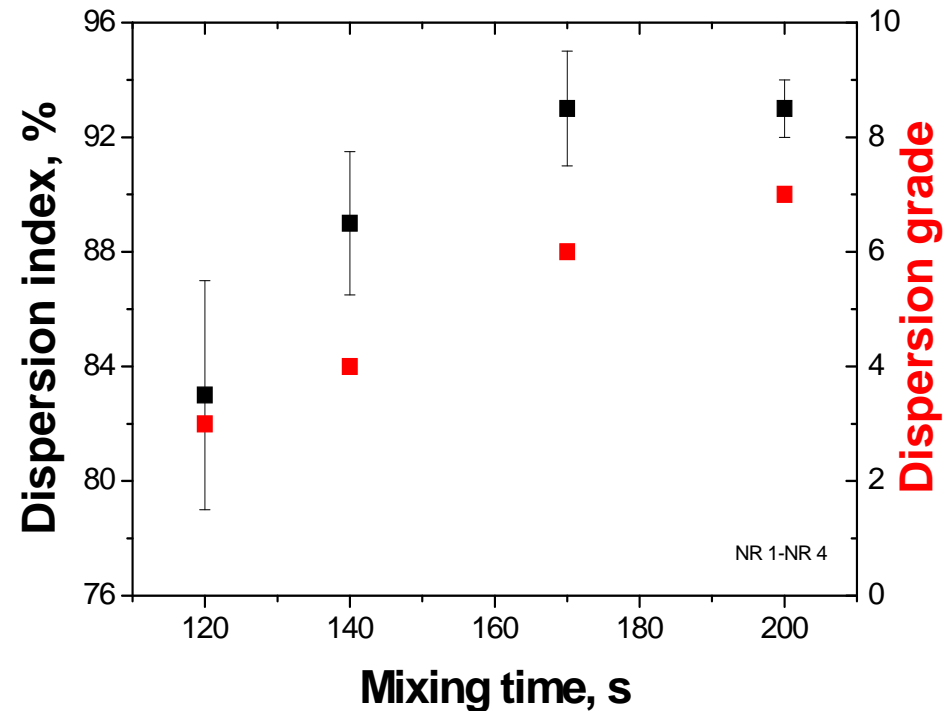
Surface of razor blade cutted samples
Reflected light method
Area of non-dispersed aggregates

Dispersion Index

Dispergrader

Surface of razor blade cutted samples
Reflected light method
Automatic digital comparison to a known standard: 1_worst, 10_best dispersion

Dispersion Grade



75 phr NR
25 phr SBR
50 phr N 330



Dispersion index

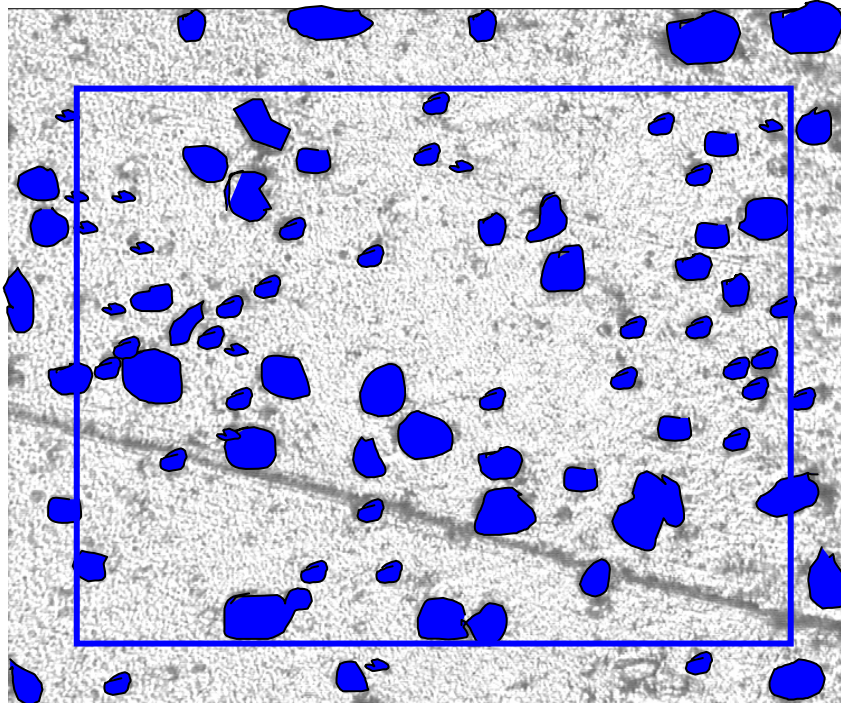
Optical microscopy

Gloss cuts on raw mixtures or vulkanizates

Reflected light method

Area of undispersed aggregates

→ Dispersion index



$$D = \left(1 - \frac{\frac{1}{n} \sum_i^n (A \cdot \varphi_{Med})}{\varphi \cdot A_0}\right) \cdot 100 \%$$

A...Area of filler agglomerates or - aggregates

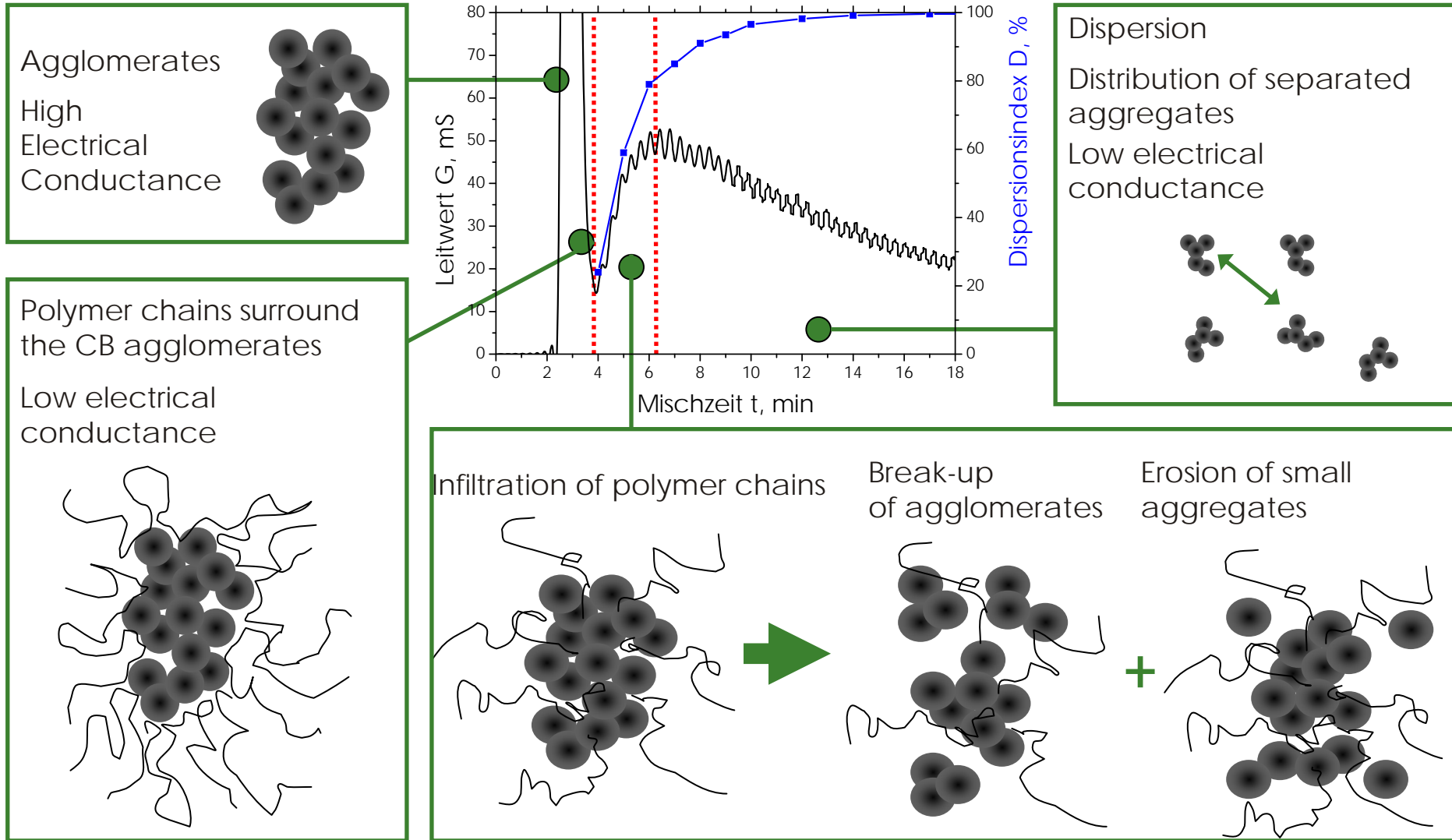
A_0 ...Area of the whole picture

φ ... Filler volume content of the mixture

φ_{Med} ...Factor* (Medalia, 1965), considers the filler volume between the aggregates

$n > 6$

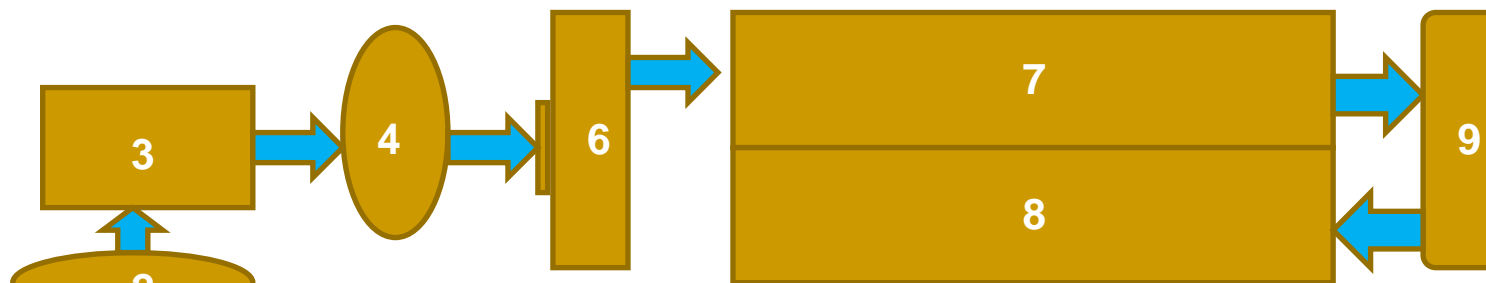
Morphology development during the mixing process



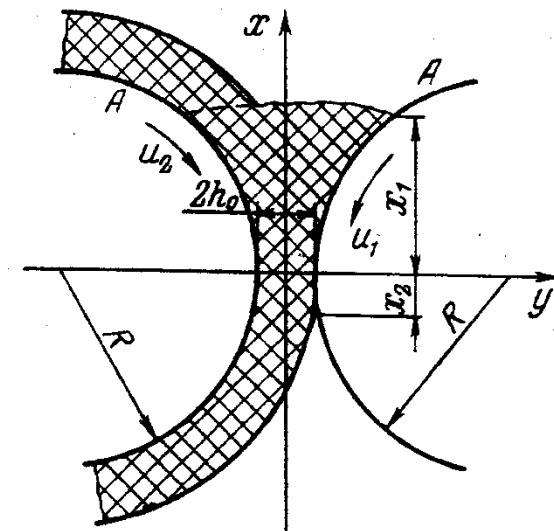
Two-roll mill

Operations: Mastication, mixing, cooling, finishing of rubber compounds and pre-heating of already mixed compounds

Types: Mastication, mixing, washing, fracture, grinding mills, refiner

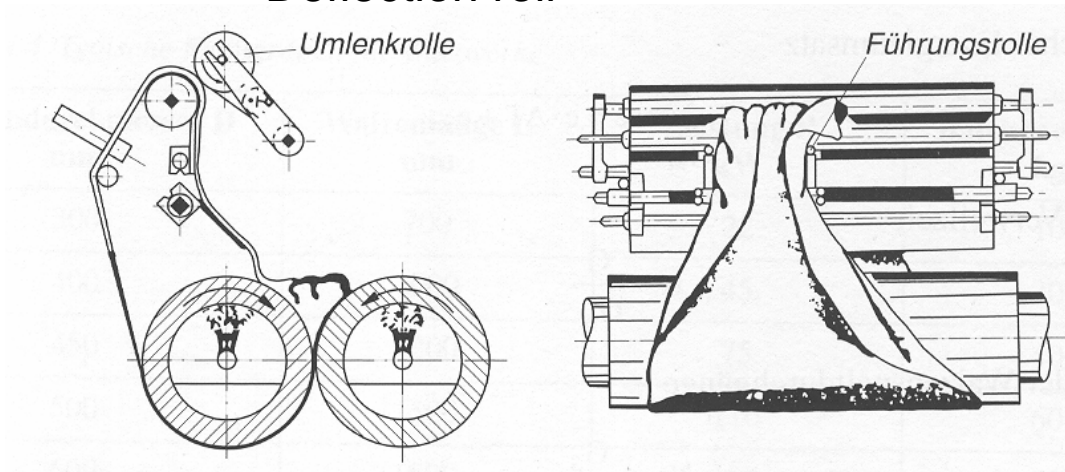


- 1 Electric motor
- 2 Magnetic coupling
- 3 Drive
- 4 Elastic coupling
- 5 Drive pinion gear
- 6 Drive gear
- 7 Front roll
- 8 Back roll
- 9 Drive



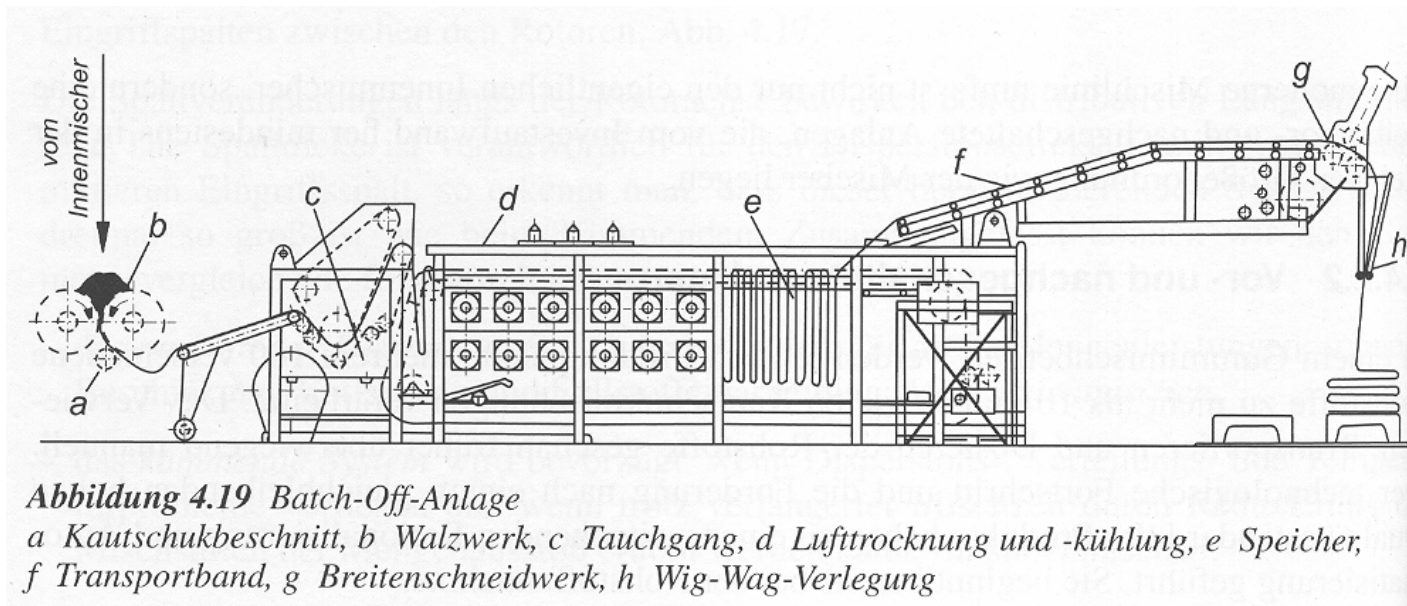
Two-roll mill: stock blender

Deflection roll



Batch-Off-Device

Operations: dip the band coming from the mill into water or non-stick solvent, cool and dry it, cut it in conjunction with cutting equipment into plates or deposit bands it in wig-wag form



Calenders

- Continuous process, two to four rolls
- Processing of sheets or rubberized fabrics
- Only one throughput of the material through the nip

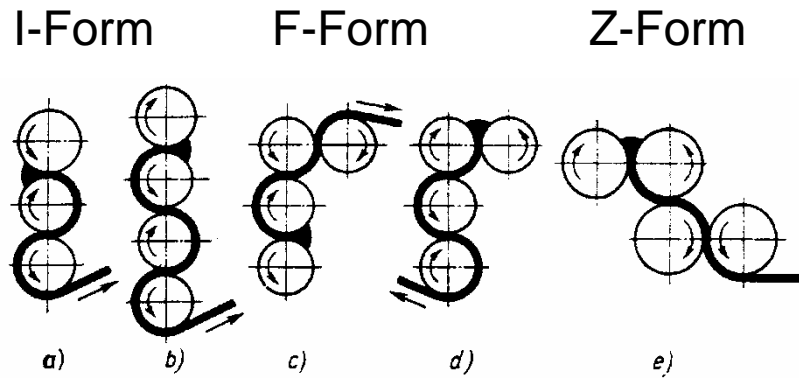


Bild 6.6. Walzenanordnung beim Blattziehen von Elasten
 a) Drei-Walzen-Kalender; b) Vier-Walzen-Kalender; c) Vier-Walzen-Kalender Γ -förmig (Speisung unten); d) Vier-Walzen-Kalender F-förmig (Speisung oben); e) Z-förmiger Kalender

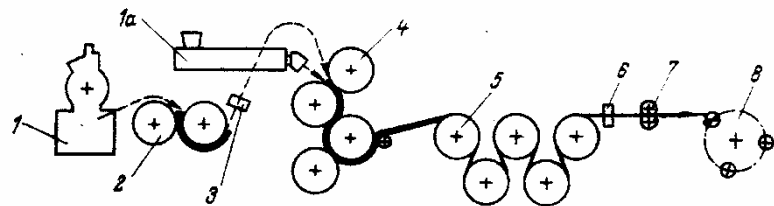


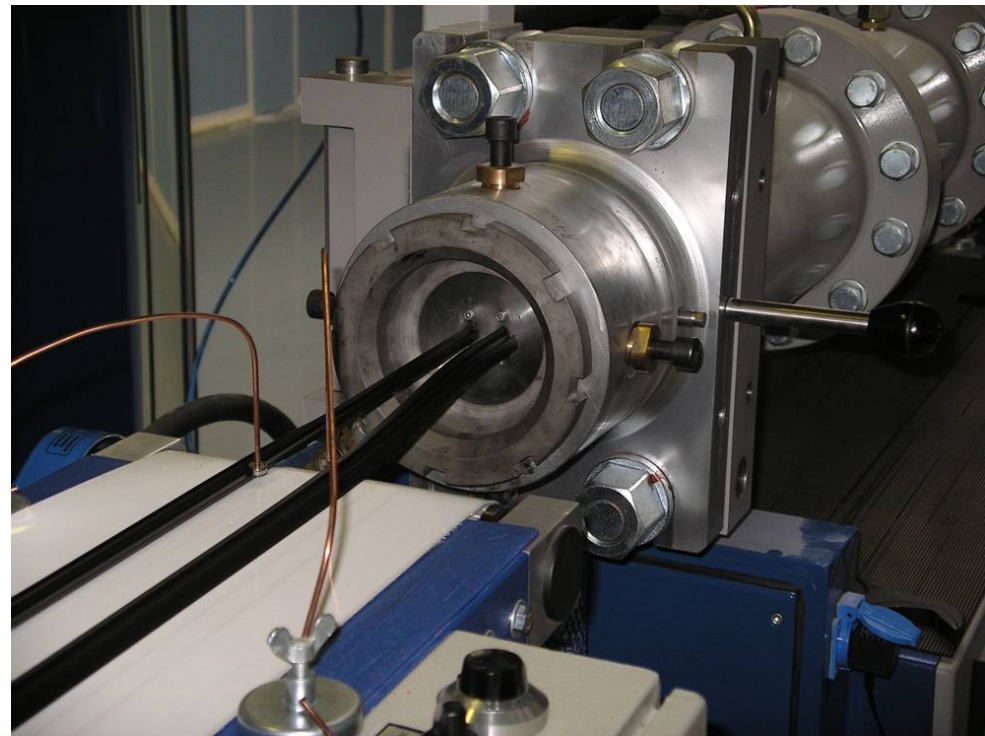
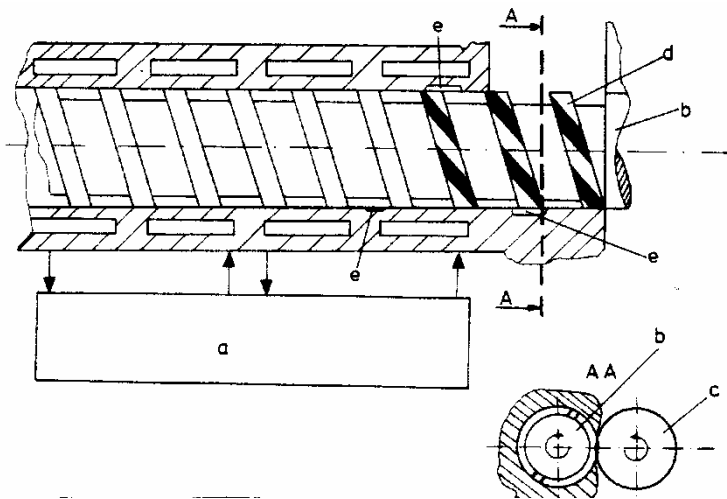
Bild 6.1. Schema einer Kalandrieranlage

- | | |
|-----------------------------------|-------------------------------|
| 1 - Innenmischer | 5 - Kühltrommeln |
| 1a - kontinuierlicher Mischer | 6 - Dickenmesser |
| 2 - Speisewalzwerk | 7 - Randbeschneidevorrichtung |
| 3 - Metallabscheider | 8 - Aufwicklung |
| 4 - Z-förmiger Kalender (geneigt) | |



Extruder

- Continuous process
- Manufacture of rods, hoses, profiles, treads for tires and sheets, coat cables and wires
- Heatable or coolable screw rotates in a heatable or coolable cylinder



Vulcanization

- Continuous process
- Manufacture of profiles, hoses etc.
- F.i. liquid bath vulcanization

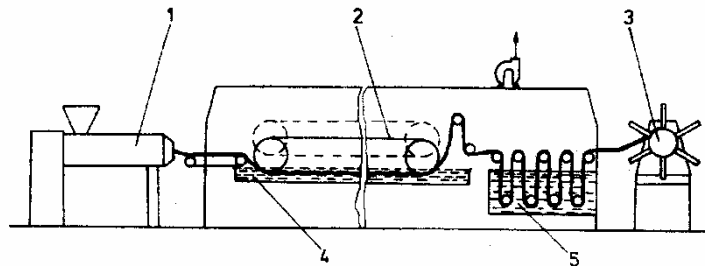


Bild 4.14 Salzbadanlage
1 Extruder, 2 Stahlband, 3 Wickler, 4 Salzschnmelze, 5 Kühlbad



- Discontinuous process
- Manufacture of tires, .
- Compression moulding

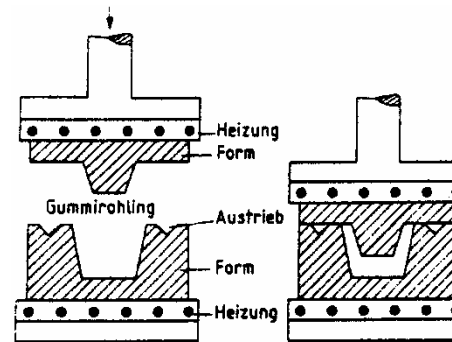
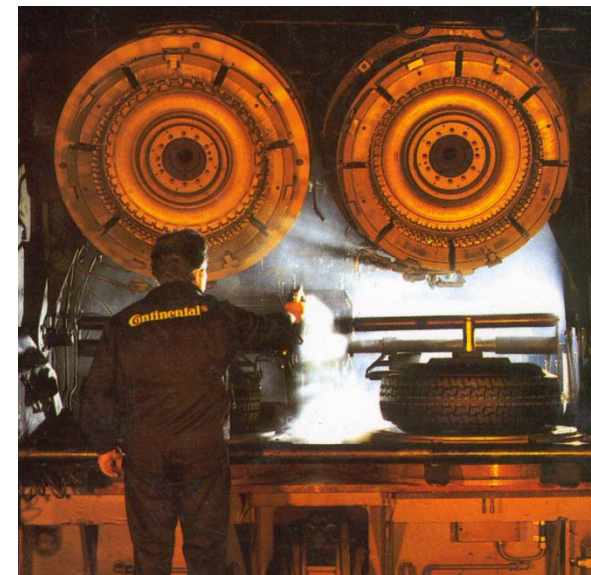


Bild 6.2 Das Preßverfahren/Compression Moulding [1]
links: Form offen,
rechts: Form geschlossen



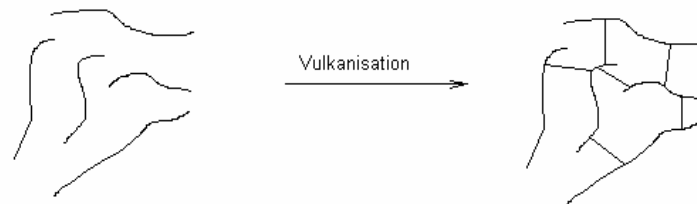
Vulcanization: Terms

- **Vulkan** (grecian god of blacksmiths) or **Vulcanus** (grecian god of fire and sulphur containing volcanos)
- Procedure to transfer the raw mixture by changing the chemical structure (i.e. by cross linking) to a more elastic behavior (over a wide temperature range)

Vulcanisation is

- The **chemical process** with different reaction partners (rubber, cross linking system, accelerator, activator a.o.),
- The **technological process** for the realization of the cross linking.

VAN ROSSEM: Cross linking theory



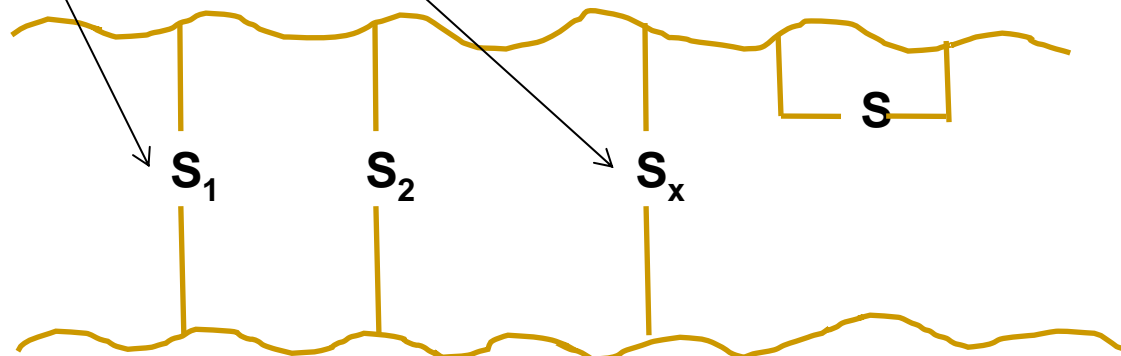
Vulcanization

- During the vulcanisation process **covalent crosslinks** are generated
- **Crosslinking agents:**
 - Sulphur,
 - Peroxides,
 - Resins,
 - High-energy irradiation,
 - Metal oxides,
 - polyfunctional amines
- **Crosslinks:**
 - chains of sulphur atoms (polysulfidic crosslinks)
 - single sulphur atoms (mono- or disulfidic crosslinks)
 - carbon-carbon-bonds

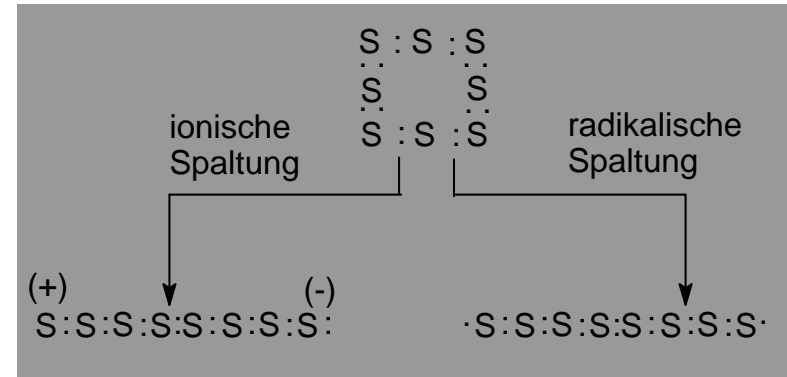
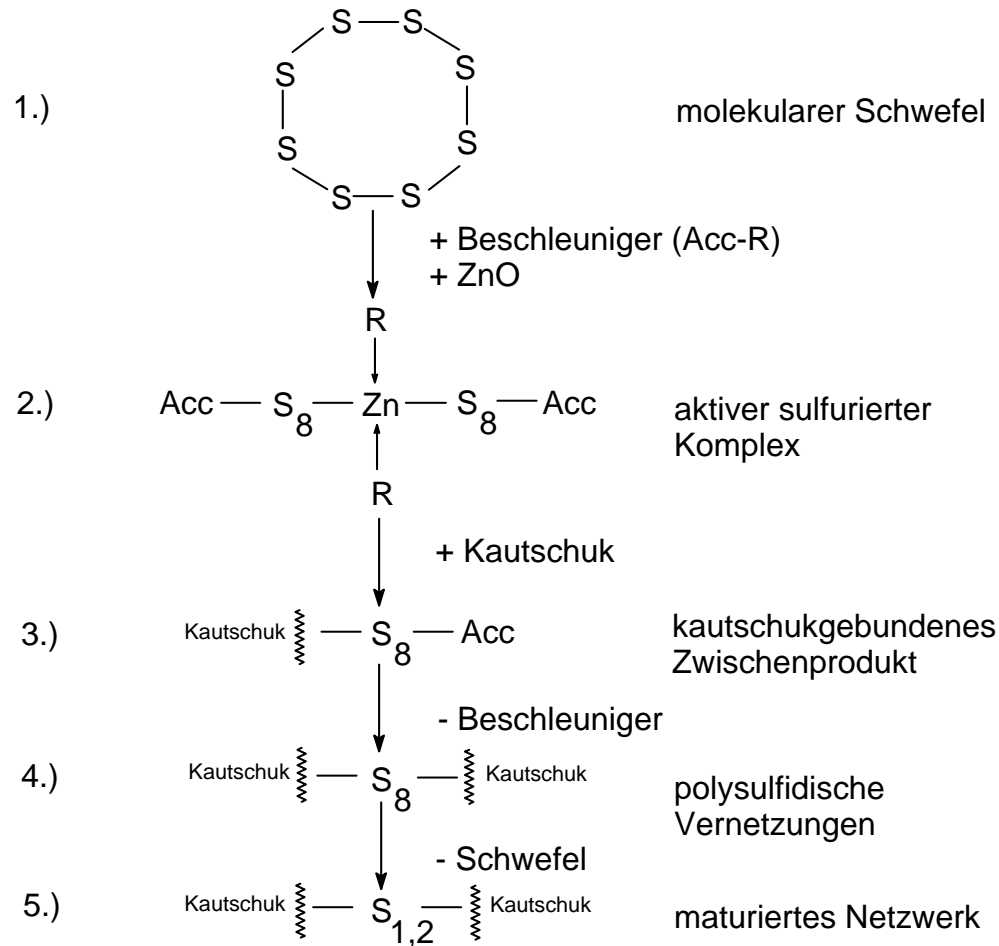


Vulcanization

Classification	Accelerator concentration (phr)	Sulphur concentration (phr)
CV	0,5-1,5	1,5-2,5 (and higher)
SEV	1,5-2,5	0,5-1,5
EV	2,5-3,5 (and higher)	0,0-0,5



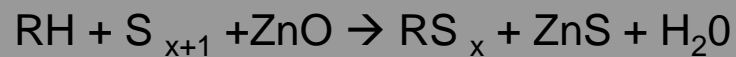
Mechanism of accelerated sulphur vulcanization



Aktivierung des Schwefels nach dem ionischen und radikalischen Mechanismus

Ringspaltungsenergie 268 kJ/mol

Mechanismus	System
Gemischt radikalisch/ionisch	SBR/S/CBS/ZnO/Stearinsäure
Ionisch	NR/TMTD/S/ZnO/Stearinsäure



Stages of vulcanization

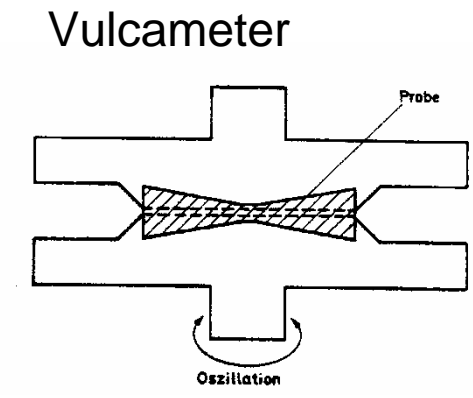
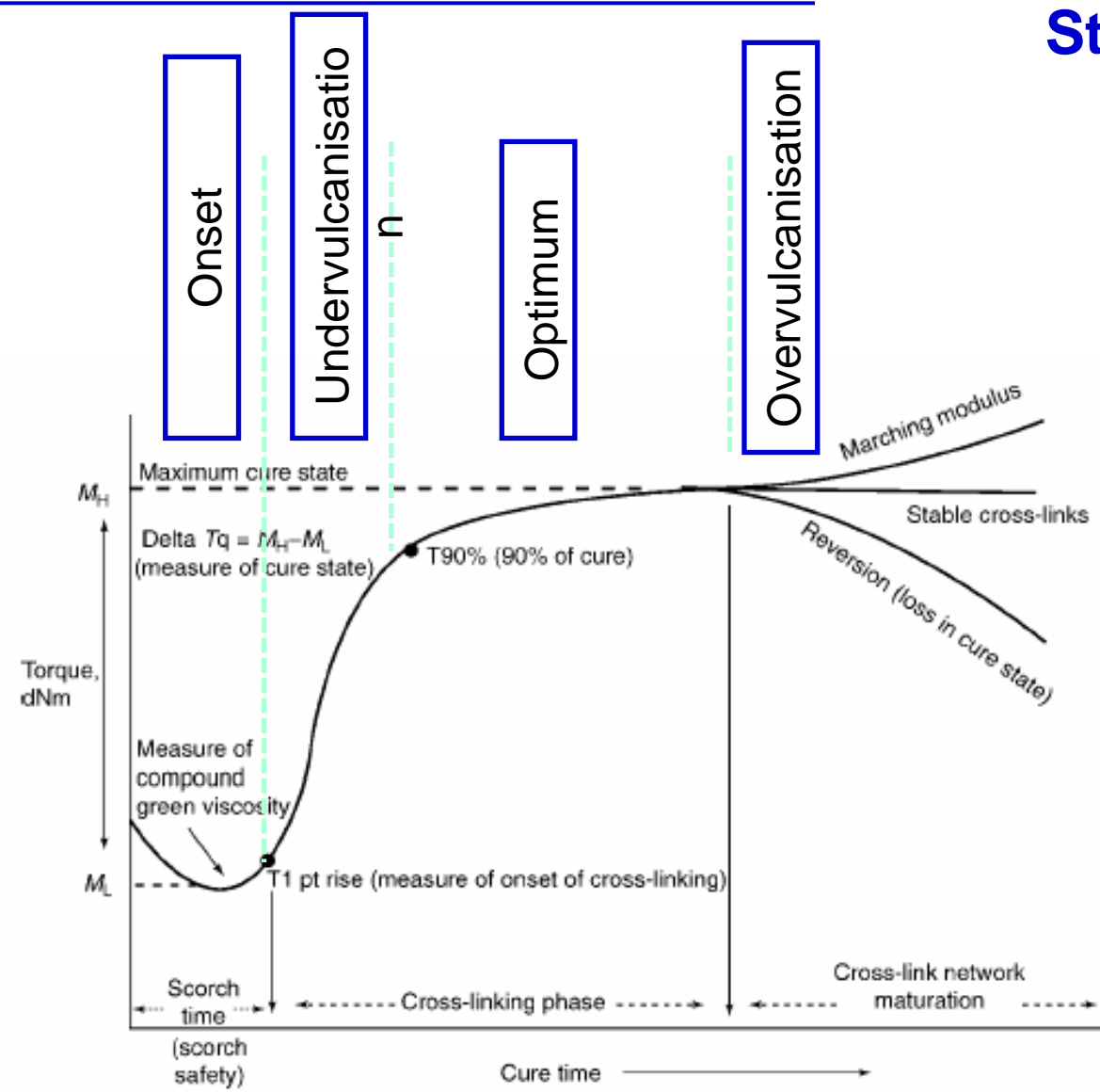
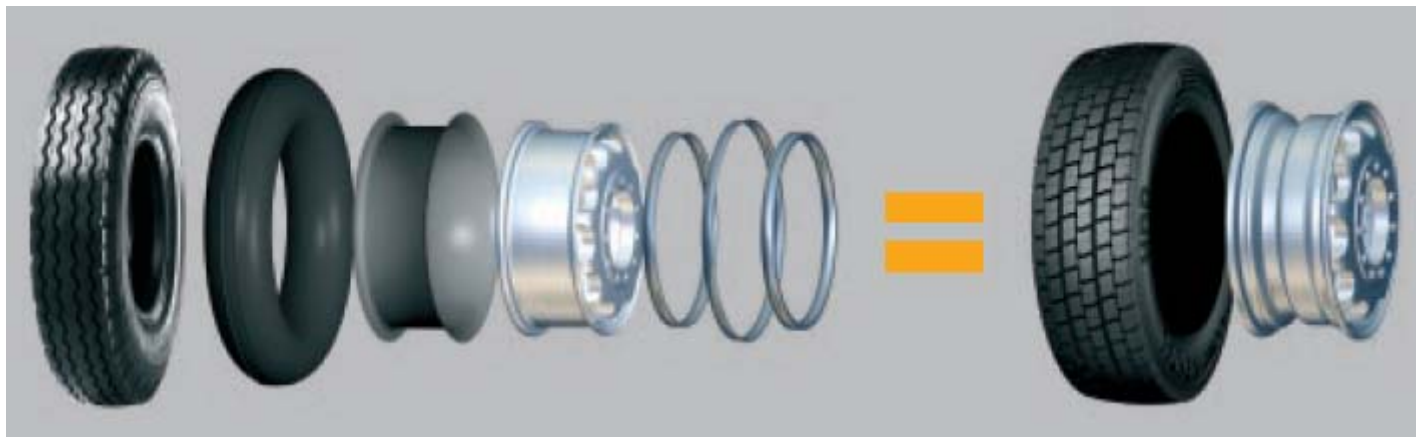
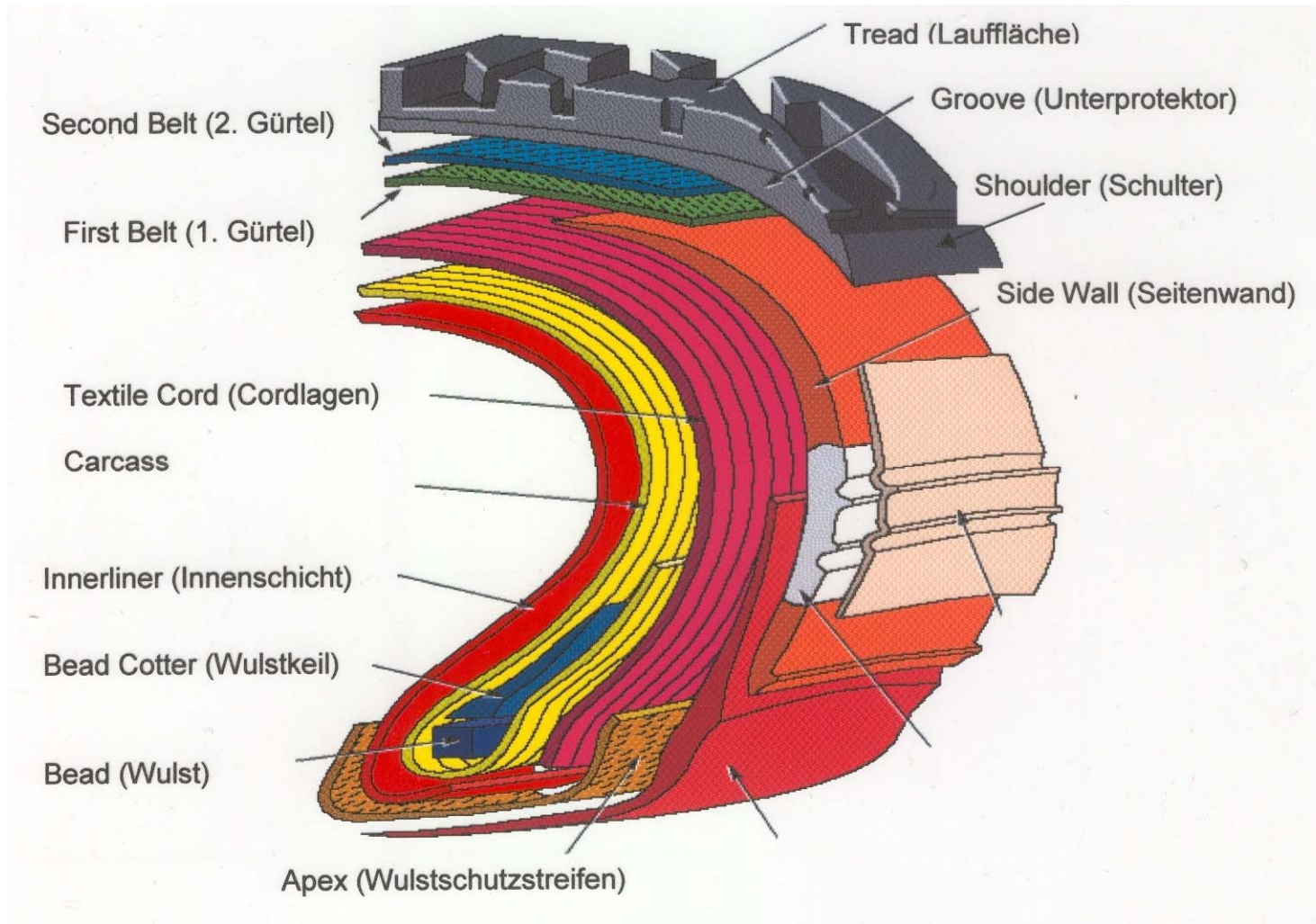


Fig. 1. Example of rheometer cure curve illustrating major cure attributes. To convert dNm to in lb, multiply by 0.885. ²

Tire development

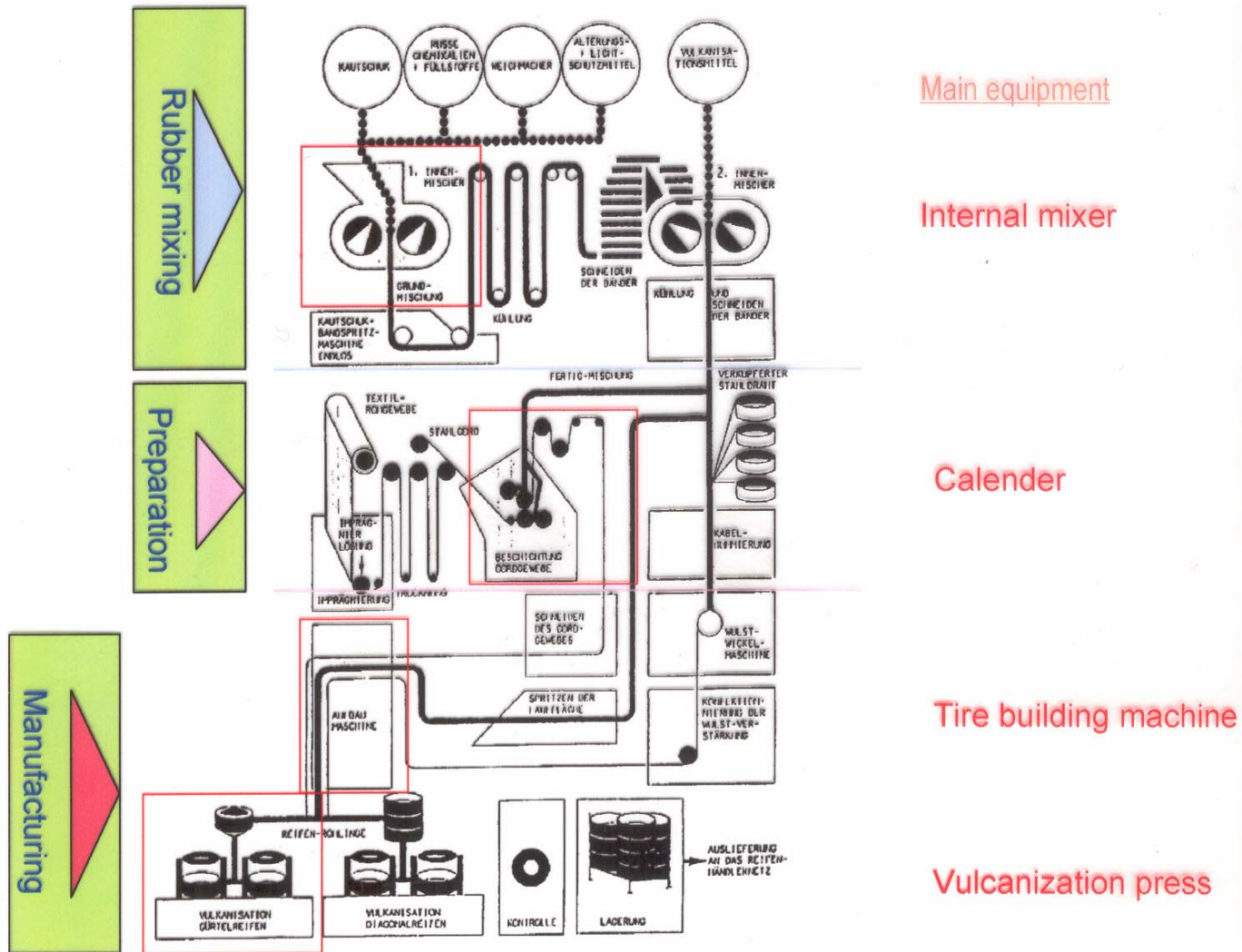


Devices of passenger car tires



Reifenherstellung

The Tire Production



Tire built-up: Material

Content	Material	Properties/Application
50-60 wt% polymer	NR	Low heat build-up → truck tires Very good flexibility → side wall Good abrasion resistance → tread Carcass (Blend with SBR)
	SBR	E-SBR: high dynamic heat built-up in comparison with NR, IR, BR → no use in truck- or high speed applications, styrene content is an advantage for wet skid resistance → tread mixtures Carcass (Blend with NR) S-SBR: broad variation of the vinyl content
	BR	Carcass, side wall, improved ice skid resistance → winter tires
	IR	Like NR
	IIR	Reduced gas permeability → innerliner
	EPDM	Side wall

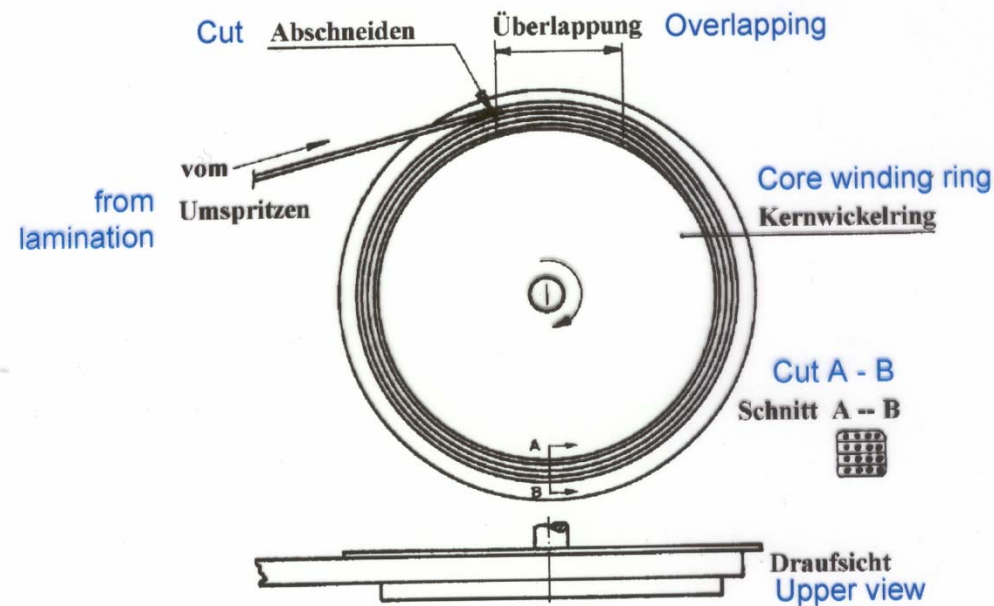


Content	Material	Properties/Application
20-25 wt% filler	Carbon black	High structured active CB → tread Semi active CB (N 660) → carcass
	Silica	In tread for optimization of RR, WSR and abrasion
5-15 wt% additives	Softener	In dependence on compatibility, in Europa from 1.1.2010 no aromatic process oil
	Processing aid	
	Vulcan. system	Sulphur/accelerator
	Aging protectors	Anti-aging, UV- and ozone
Approx. 20 wt% strength improver	Textile	Nylon/Perlon (polyamide silk), polyester, cellulose fibres
	Steel cord	Steel with brass coating, brass (approx. 62-74 wt% copper, 38-26 wt% zinc) adhesion dependent on reaction of copper and zinc with sulphur → ZnO, copper sulfid



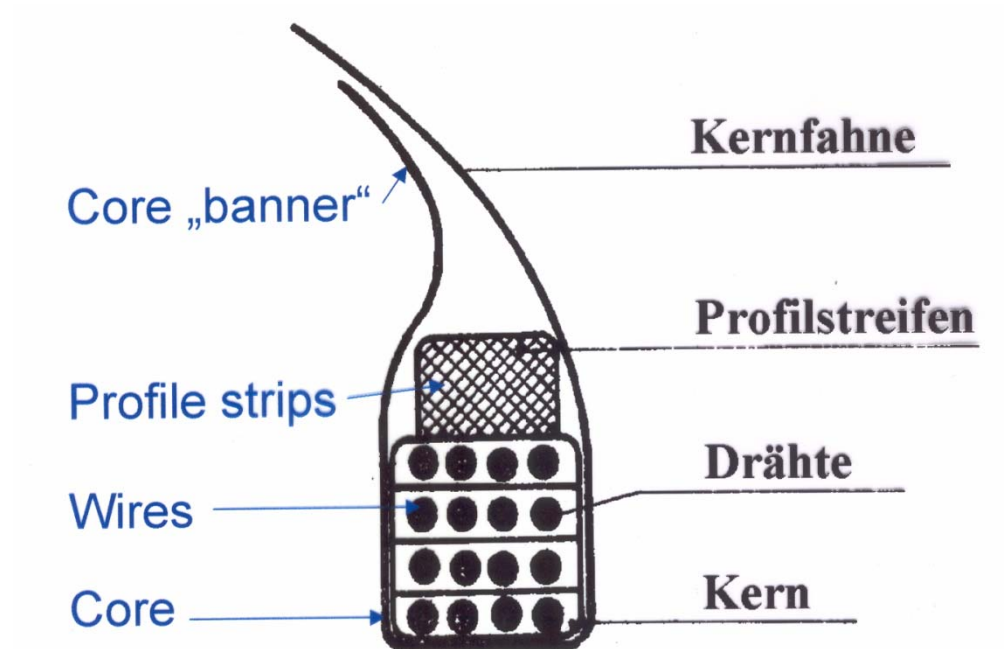
Tire built-up: Technology

Part	Attribute
Bead (Kerne, auch Drahring oder Wulstring)	Rubberized wire hoops with open or closed build-up Rubber injection moulded around inserted wires, cutting to required length, stick together Kerne, die im inneren Abschluss der Reifenflanken liegen (umspritzen der Drähte, Schneiden auf erforderliche Länge, Verkleben) Are responsible for the close seat on the rim Sind für festen Sitz der Reifen auf der Felge verantwortlich



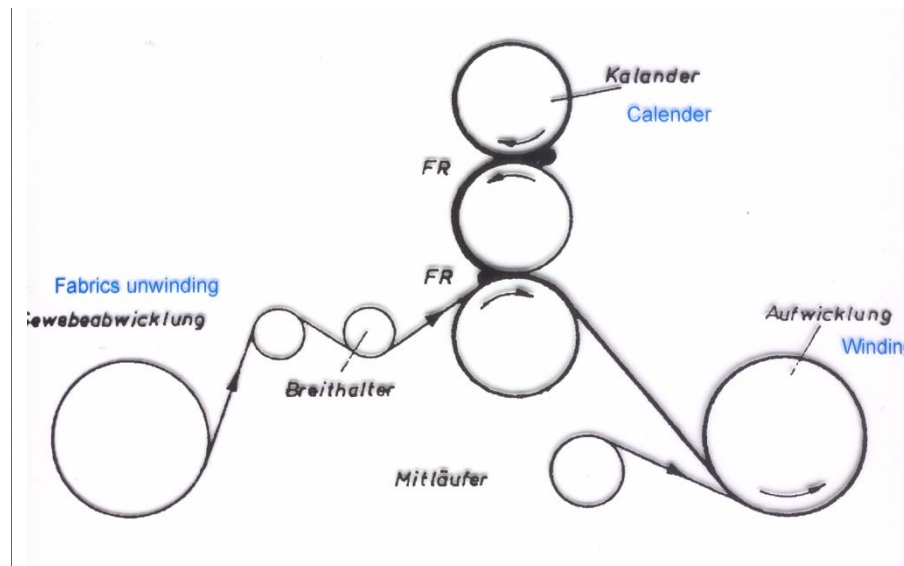
Tire built-up: Technology

Part	Attribute
Bead cotter (Wulstkeil oder Kernprofil)	Extruded mixture strip



Tire built-up: Technology

Part	Attribute
Carcass	Skeleton of the tire, all other units are fixed on it
Innerliner	Fine two-roll milled raw mixture, fixed on the inner side of the carcass, prevents the leakage of air
Steel belt	Strength improver, in the calander rubberized steel cord, angle approx. 20°
Textile belt	In the calander rubberized textile cord below the tread, cor cutted in angle of 90° cross to the fibre direction

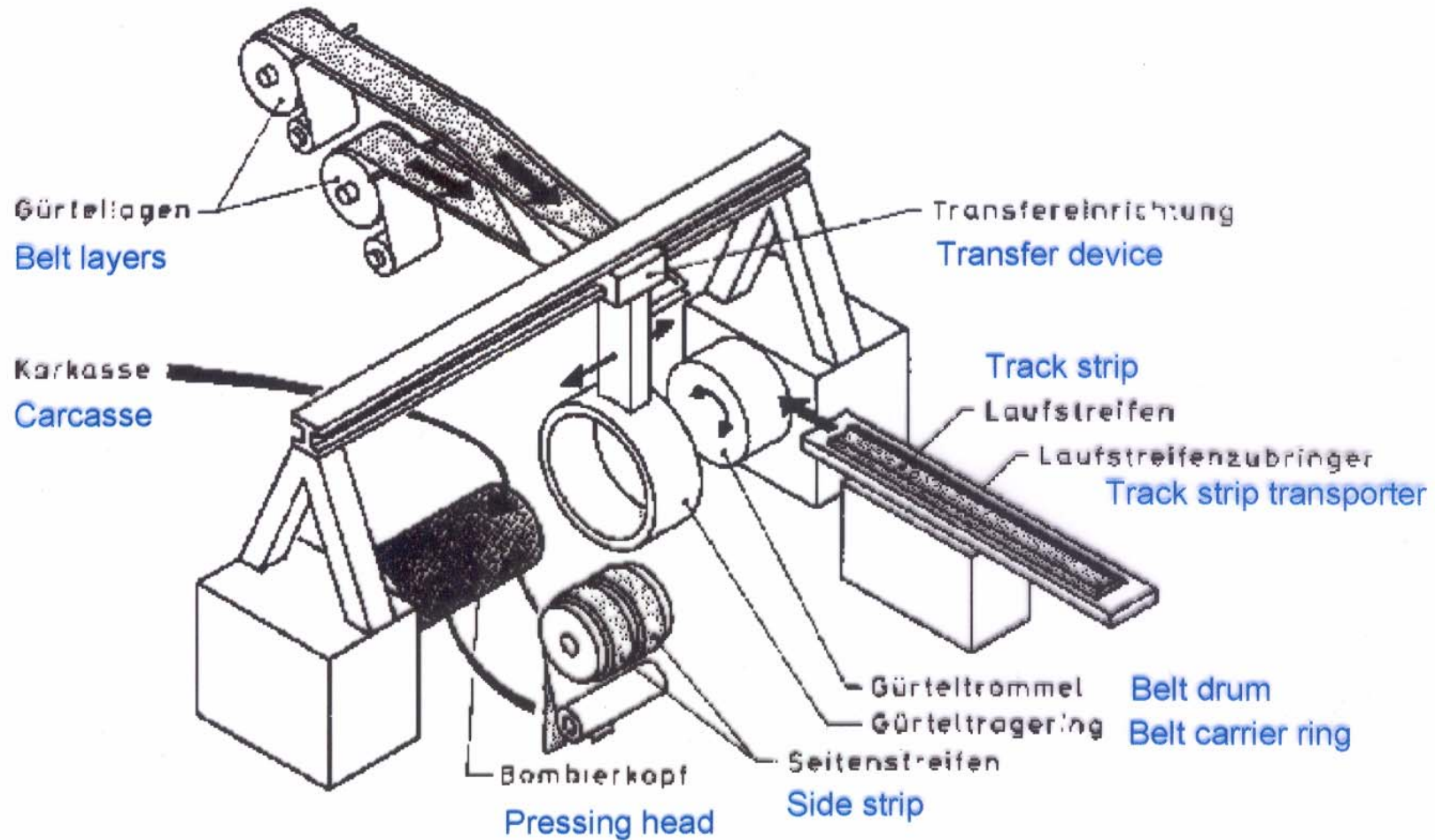


Tire built-up: Technology

Part	Attribute
Side wall	Extruded mixture strip with defined contour (injection head)
Apex (Wulststreifen)	Extruded mixture strip
Tread	Mostly two layers: Cap (upper layer), where the profile is compression moulded in; responsible for road grip, surface discharge of water (Wasserablenkung) and cornering grip (Seitenführung) Base (Lower layer), special mixture for reduction of the rolling resistance and improvement of straight ahead stability (Verbesserung der Geradeausstabilität) Both layers are produced via coextrusion



Tire finishing: Packaging (Konfektionierung)



Tire finishing: Packaging (Konfektionierung)

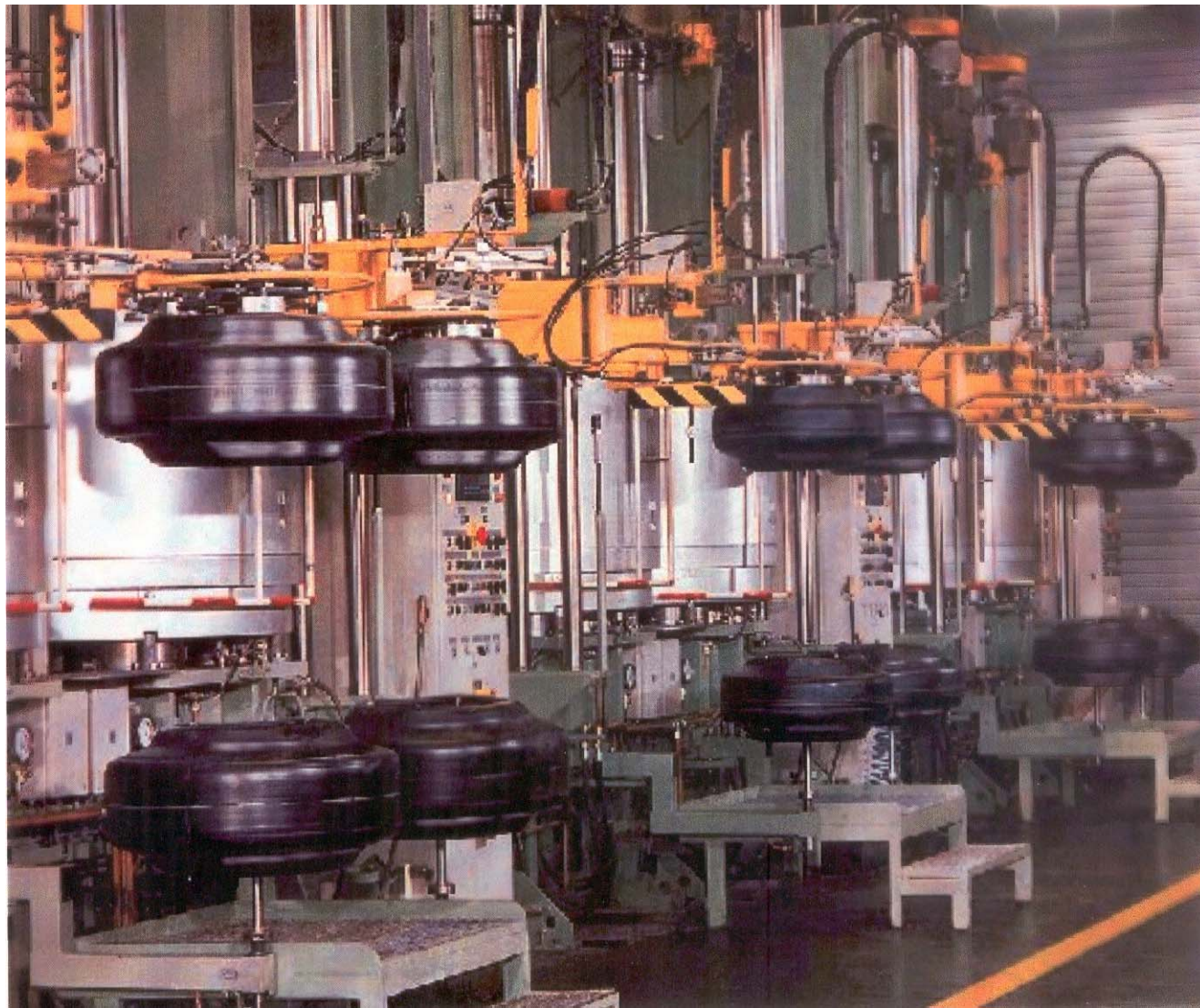
Part	Attribute
Carcass Winder (Karkasswickelmaschine)	<p>Main tool: winder (Wickeltrommel)</p> <p>Right and left: bead Umbukanroller</p> <ol style="list-style-type: none">1. Applying the inner liner: winder turns one time around the axis, a knife cuts the required part from the band2. First textile cord3. Prepare bead cotters4. Umbuken: überstehende Enden der ersten Lage werden von unten über die Kerne umgelegt und angepresst5. Je nach Reifentyp 2. Gewebelage6. Apex, Anlegen und Andrücken zweier Wulfstreifen



Tire finishing: Packaging (Konfektionierung)

Part	Attribute
Belt machine (Gürtelmaschine)	Magnet barrell (Magnettrommel) 1. Two layers rubberized steel cord (Basislage und schmalere Oberlage, Stahldrähte in beiden Schichten verlaufen über Kreuz in einem spitzen Winkel von 18 bis 25° zueinander) 2. Two layer textile cord
Emboss machine (Bombiermaschine)	1. Insert the carcass (Aufstecken der Karkasse) 2. Insert of the tread (Aufsetzen des Laufstreifens mittig über der Karkasse) 3. Druckluftunterstütztes Aufblähen eines Gummibalges, der von innen Karkasse gegen Laufband drückt 4. Durch umlaufende Walze Aneinanderpressen von Karkasse und Laufband 5. Flanken der Karkasse werden mit Seitenstreifen abgedeckt: Tire blank (Reifenrohling)





Vulcanization and testing

Part	Attribute
Vulcanization	Tire moulding press (Reifenpresse, im Zentrum des Reifenrohlings wird Heizbalg (Butylkautschuk) aufgebläht, presst Rohling an die Form)
Testing	<ol style="list-style-type: none">1. Untersuchung auf Fertigungsfehler (defects), Luftblasen (bubbles), Falten (crinkles)2. Concentricity, true running (Rundlaufprüfung) obligatorisch3. X-ray control , Random sampling (Stichproben)

