- Vasco Moisés Lopes Almeida
- **Characterization of the factors involved in the tire production process**
- **Caracterização dos factores de produção num processo de manucfactura de um pneu**

Characterization of the factors involved in the tire production process **Characterization of the factors involved in the tire production process** Vasco Moisés Lopes Almeida Vasco Moisés Lopes Almeida

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**Universidade do Minho** Escola de Engenharia



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**Characterization of the factors involved in the tire production process**

**Caracterização dos factores de produção num processo de manucfactura de um pneu**

Tese de Mestrado Ciclo de Estudos Integrados Conducentes ao Grau de Mestre em Engenharia Mecânica

Trabalho efectuado sob a orientação do **Professor Joaquim Barbosa**

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## **Abstract**

 This dissertation has the purpose of describing the tire production methods, production variations, quality issue, specification details and the how the tire will behave.

 It is noted that due to the nature of the internship in the Continental Group several details cannot be described in full detail to avoid publication of trade secret details.

 Tires are one of the most important components in the composition of an automobile, because tires are the only connection between the car and the road. With a bad set of tires it doesn't matter how developed car braking and power systems are unless they can transmit the necessary forces to the ground.

 During this internship the proponent of this dissertation helped and learnt from the industrialization department verifying several tires for specification purposes. Also a database was developed in order to automatically maintain the industrialization process papers.

 Once the proponent noticed the cause of the highest cause of scrap, a solution was developed and presented to the department.

## **Introduction**

 This dissertation has as a background the proponent's internship at a Continental's manufacturing plant situated in Lousado. Here he was integrated within the department of product industrialization at the subsection dedicated to construction.

 The purposes appointed for this dissertation include understanding how PLT (Passenger and Light Truck) tires are produced and try to identify possible issues.

 For this purpose the proponent gathered several materials throughout the internship months.

 The internship was developed at DIP (Department of industrialization) which is responsible for the "in factory" development of the intermediary products in order to achieve the final product as specified by central R&D of Continental tires.

 Unfortunately it wasn't possible to follow an article from compounding to construction due to trademark confidentially issues, therefore the production of tires will be approached as a whole.

#### 1. Theoretical introduction

 To better understand the manufacture process it is important to understand rubber and its processability difficulties and limitations. Tire construction is dependent on millimetric precision of its intermediary components, which in turn means rubber components need to have samples accurately measured with precision before and after the two last stages of construction and vulcanization.

 The most interfering properties of rubber for dimensional stability are viscoelasticity, slow tensions recovery (swelling) and dimensional variations with temperature. Also unvulcanized is very adhesive to other unvulcanized rubber components, this is positive for tire building but can also be a problem if layers aren't well aligned when entering the construction drums.

## 1.1. Linear Viscoelasticity

Viscoelasticity is a polymer property common to a wide range of polymers. Such common phenomena as stress relaxation, creep, compression set (and unrecovered deformations, in general), mechanical irreversibility and energy losses during a deformation cycle ("hysteresis"), limited rebound, heat generation, and temperature rise during flexing are manifestations of the viscous properties of Elastomers. [8]

Ideal linear elastic materials follow Hooke's law in which stress is proportional to strain while ideal viscous liquids obey Newton's law in which stress is proportional to the rate of change of strain with time. Rubber properties lay in between these two physical states.

A Hookean solid may be represented by a spring described by Hooke's law.

$$
F = k \times \text{(eq.1)}
$$

Newton's law of viscosity may be written in the form (eq. 2) where c is the viscous dampening coefficient. Newtonian viscous behavior is usually illustrated by a viscous element called dashpot.

$$
F = c \left(\frac{dx}{dt}\right) \quad \text{(eq. 2)}
$$

These laws may also be written in the following forms (eq. 3 and 4) where  $\sigma$  is the tensile strength,  $\varepsilon$  is the tensile strain, E is the elastic tensile modulus and  $\eta_e$  is the Newtonian viscous coefficient in tension.

$$
\sigma = E \varepsilon \qquad \qquad \text{(eq. 3)}
$$

$$
\sigma = \eta_e \left(\frac{d\varepsilon}{dt}\right) \qquad \qquad \text{(eq. 4)}
$$

Traditionally, viscoelastic behavior has been described by means of phenomenological approaches by employing Maxwell and Voigt elements. Most materials exhibit behavior that is more complex than either of these two simple models. For this reason, it is necessary to use generalized models to describe the viscoelastic behavior of a material quantitatively.



A generalized Maxwell model consists of an infinite number of simple Maxwell elements in parallel and is characterized by the so-called distribution of elastic module E(τ) as a function of the relaxation time  $\tau = \eta_e/E$  of the simple Maxwell elements. The generalized Voigt model consists of an infinite number of simple Voigt elements in series and is described by the distribution of compliances D(τ) as a function of the retardation time  $\tau = \eta_e/E$  of

simple Voigt elements. Both these models (Fig. 1) (and other generalized systems) are completely equivalent and, in theory, any may be used to describe all linear viscoelastic behavior. [9]



**Figure 1 – Maxwell and Voigt Representations [8]**

Linear viscoelastic behavior means Boltzmann superposition principle can be applied. This means strain due to the action of a number of stresses  $\sigma = \sigma_1 + \sigma_2 + \sigma_3 + ... + \sigma_n$  is equal to the sum of strains  $\varepsilon_1, \varepsilon_2, \varepsilon_3, \ldots, \varepsilon_n$  that would result of  $\sum \sigma_n$  acting alone.

Usually for convenience Maxwell model is used to describe stress relaxation and Voigt for creep experiments. Both generalized models can be used for dynamic mechanical experiments with good results although Voigt model is more commonly used.

The following relations show how both models theoretical describe certain aspects



**Figure 2 - Behaviour of Maxwell and Voigt elements: Stress relaxation [8]** 



**Figure 3 - Behaviour of Maxwell and Voigt elements: Creep [8]** 



**Figure 4 - Behaviour of Maxwell and Voigt elements: force required to maintain a constant rate R of deformation[8]** 

#### 1.2. Non-linear Viscoelasticity

Although the previously presented models are good approximations real polymers do not relax with a single relaxation. This is due to different molecular segments lengths, in which the shorter segments relax faster than longer chains. The different segments lengths relaxing at different time periods cause a distribution of several simultaneous relaxations at different speeds thus increasing the complexity.



The superposition of several Maxwell elements will create a nonlinear model with different linear time dependent functions acting together.

$$
\sigma=\sigma_e+\sum_j\sigma_j
$$

 Another well known model is the four element model which is a combination of the Maxwell and Voigt elements assembled in series. Actually any combination that helps creating a mathematical model to approach and explain a certain polymeric chain or viscoelastic material stress/strain and relaxation curves is a workable model. For the study of wood a used model is the four element burger model with a fifth element to account for shrinkage. (Fig. 7) [10]



**Figure 7 - Burger model with a four element model and a fifth shrinkage element [10]** 

### 1.3. Effect of temperature on a Polymer viscosity, Tg (Glass Transition)

Polymeric chains are affected by temperature at a molecular level, this causes these materials to have two different phases depending whether the temperature is above or below Tg. If the temperature drops below the glass transition point molecular chains low energy reduces molecular vibration and the material becomes stiffer and at severely low temperature even brittle. If on the other hand temperature is above Tg the polymeric material becomes relaxed, softens and becomes able to expand without fracturing. At temperatures below Tg rubber is more elastic, but less capable of stretching due to the reduced molecular flow.[4, 11]

Counter intuitively rubber polymers actually contract when heated unlike metal materials which expand. This detail is important when several rubber components with millimetric

 Tg is the point at which the material changes phase and is used as a reference in order to evaluate compounds and their properties. Along with other characteristics obtained through rheological tests, such as speed of vulcanization (for compounds equalization), as well as stress, strain and relax responses. All these parameters must be within certain preset values defined by central R&D for each polymeric raw material and compound. (Fig. 8)





**Figure 9 – Full spectrum of rubber viscoelastic properties: where tan δ represents hysteresis.** 

**Figure 8 - Green tire loading in front of the vulcanization press [1]**

Apart from raw materials and intermediary compounds quality control, ambient temperature variations affect components and green tires causing the last to partially collapse under their weight and partially deformation of the unvulcanized tire walls. This might cause

the tire walls unequal deformation (while the green tire is stored on a flat surface waiting to be vulcanized) not to recover in time for the press and vulcanization (Fig. 9). As demonstrated on previous chapters rubber as a viscoelastic material means both relaxation and deformation are time dependent, which implies that while the green tire (unvulcanized) is stored



**Figure 10 - Irregular bead [1]**

on a flat surface for intermediary storage it will sit on its own weight with enough time to allow tire walls deformation. According to procedure tires are to be hanged by tire wall which was settled on the flat car for the duration of the previous tire vulcanization cycle to relax the tire walls before entering the press.

 This is one of the main reasons why compound formulas are tweaked to adjust the summer and winter ambient temperatures and avoid scrap tires due to "irregular bead / heavy toe". (Figure 10 - Irregular bead)

This is done whether by increasing the stiffness of wall compounds allow the walls to hold the weight of the tire and therefore not deform during storage or by reducing the stiffness of the wall compounds which will enable full equal deformation all around the tire avoiding unequal deformations which cause "Heavy toe" scrap issues. [1]

1.3.1. Glass Transition point variation effect on tire characteristics (Vulcanized Rubber)

100 mn  $10 \text{ mm}$  $1<sub>mm</sub>$  $0,1$  mm length scale Block<br>deformation Contact patch roughness 100% 70%  $~50%$  $~16\%$  $~1%$ contact area

Tire adhesion to the surface consists of three main mechanisms.

**Figure 11 - Net contact area tire/road, role of surface roughness [3]** 

- 1) Low frequency macroscopic deformation in which the tire
	- a) Mechanism compression, deformation and shear upon rolling of blocks through the footprint patch.
	- b) Length scale is macroscopic and independent of slip, i.e. > 1mm, corresponding to 10 Hz -  $10^2$  Hz
	- c) Some block deformation mechanisms reduce tire grip by reducing contact area
- 2) High frequency deformation
	- a) Mechanism viscoelastic compression and elongation caused by slip over topology.
	- b) Length scale of road topologies depends on road surface type:
		- i) macro roughness 0,2 mm 10 mm, corresponding to 10<sup>2</sup> Hz 5x10<sup>4</sup> Hz
		- ii) micro roughness 1  $\mu$ m 0,1 mm, corresponding to 5x10 $^4$  Hz 5x10 $^6$  Hz
- 3) Molecular adhesion
	- a) Mechanism bond formation, bond stretching, bond breaking, relaxation
	- b) Length scale for adhesive forces upon slippage:  $1 \text{ Å}$  50 Å, corresponding to $10^6$  Hz - $10^9$ Hz
	- c) Prerequisites for effective adhesion mechanism: clean and dry contact surfaces, i.e. inactive at wet braking.

The glass transition point of a certain compound is of the upmost importance because it will directly determine the hardness of the tire (Fig. 12). This parameter can be affected by a

number of different polymers and additives and depending on which tire component it will be comprise the Tg target may differ. Regarding adhesion the only active component is the thread, while other components will be engineered with rolling resistance and heat build-up issues in mind.



**Figure 12 - Vertically soft compound adherence [3]** 

As a rule of thumb the lower the Tg the softer the tread will be, therefore if the compound is hardened by being exposed to low temperatures it can still maintain enough Viscoelasticity to adhere to the ground by the low and high frequency deformations. On the other hand a regular summer/rain tire will be hardened by the low temperatures and severely unable to act on any adhesion mechanism dangerously increasing the chances of slip.



**Figure 13 – Wet breaking at 100 Km/h speed with summer vs. winter tires [12]** 

As previously stated, generally speaking (because other tire characteristics such as sipes and block edges, pattern, pitch, and void also play a part on breaking) the lower the Tg the better adherence at lower temperatures due to maintaining the rubber at usable stiffness. Below  $7^{\circ}$ C winter tires are on their operational range and summer tires start phasing out due to compound stiffness increase. Conversely winter tires shouldn't be used during the summer because the compound will soften below operating range with an increase in wear and reduction of breaking tension capabilities. (Fig. 13) [12]

 To understand how the Tg acts on snow tires, one must also understand the breaking mechanisms present while breaking on snow.

There are 4 main root-causes that affect snow traction.

a) Milling effect

Depends on the sheer force of snow block edges/sipes



 **Figure 14 - milling effect[3]**

b) Snow-snow interaction

Depends on the dynamical friction coefficient snow-snow



 **Figure 15 - Snow-snow interaction [3]** 

#### c) Snow-rubber interaction

Depends on the friction coefficient between snows and tread rubber at tire surface and at the flanks of the circumferential grooves



#### d) Liquid layer effects

Melted snow produces a liquid layer as lubricant. (snow melts under pressure and to a lower extent also due built up heat due to hysteresis)



 As can be interpreted from [Figure 18 - Patter effects - Snow Grip] the rubber snow friction is the most important factor at low slip conditions, before milling and snow-snow friction effects become more relevant. Over 30-40% slip the tread design gains significance becoming responsible for more than 50% of the grip conditions, although sipes deformation (necessary for snow milling interaction) does depend rubber stiffness and therefore also on Tg.



**Figure 18 - Patter effects - Snow Grip [3]**

 Snow adhesion through molecular adhesion between rubber and snow is under study and its advantages being weighted (Fig. 18). Although there is a potential adhesion

improvement up to  $\mu \approx 0.5$  on soft snow which has a high friction coefficient, if the tire surface covered with snow melts (due to heat buildup or under pressure) the friction goes down to  $\mu \approx$ 0,01. [3]

 Although Tg is most relevant at high temperature variations such as those between



**Figure 19 - Relationship between glass transition point to loss tangent and to friction on a wet cement surface [4]** 

summer and winter, it is also very important for other characteristics. As previously stated molecular adhesion isn't significant during wet breaking, therefore low and high frequency deformation gain responsibility.

 Due to this a tire with a target Tg prepared for winter temperatures will be too soft for regular summer temperatures suffering from excessive block deformation which reduces grip and increases wear.



1.4. Compression recovery after extrusion (Swelling)

As referred on chapter 1.1 rubber compounds are viscoelastic. This means the reaction is time dependent, this means after extrusion there will be a fast recovery which relates to the elastic response with a secondary expansion over time (as previously described) and also while the extruded components cools down it suffers further expansion (Fig. 21).

 Extrude products need a reliable dimensional stability especially if these are sub-products which must further interlink with other rubber components (Fig. 22). Due to this need extrusion of treads and side walls is somewhat critical and severely controlled through laser profile scans. [13, 14]

 Another issue relating to rubber swelling after extrusion is that expansion isn't equal all over the sample, but instead it differs with the die geometry.[15]

 Controlling die swell during extrusion is very dependent on the applied shear rate. Usually the higher the shear rate to a rubber compound during extrusion, the higher the die swell will be. The amount of shear rate applied to the rubber is determined by the geometry of the die and the screw speed. This means that if the speed of the screw is reduced die



**Figure 21 - rubber reaction to heat [4]**



**Figure 22 - Viscoelastic extrusion expansion [4]**



**Figure 23 - The SLS5000 noncontact industrial gauging sensor is shown in a scanning frame system as it profiles extruded rubber tread.** 

swell should also decrease. [14]

 The die land length is also another parameter that will interfere with the extruding shear rate. It should be 5 to 6 times longer than the die opening with a 30 $^{\circ}$  to 60 $^{\circ}$  degrees inclination and if feasible coated with anti adherent materials such as Teflon. The state of the mixture might also affect the degree of die swelling. Also compounds with higher amounts of carbon black or with higher structured carbon black tend to display less swell during extrusion.

## 1.5. Effect of pressure on a Polymer viscosity

The effect of pressure on the polymer is the opposite the effect of temperature because it reduces the free volume and molecular mobility. This effect is particularly important on injection molding due to the high pressures applied, but it is also significant in extruding processes. [15]

 Some studies [16-18] were done to determine the variation of viscosity in relation to the temperature at constant pressure as well as the variation of viscosity in relation to the pressure with constant temperature. It was concluded that these variations are linear when represented on a semi-logarithmic scale. Therefore it was suggested that the effect of pressure should be represented as an equivalent to a variation of temperature but with an opposite effect.

 As result equivalence coefficients of temperature-pressure were generated at constant viscosity for several polymers. This means the increment of pressure equates a drop in temperate in the context of viscosity, on the other hand the increment of pressure also increases the polymer temperature due to viscous dissipation.

 This counter effect which reduces the impact of pressure and the inherent experimental study complexity of these two opposing variable properties leads to the frequent omission of the effect of pressure on viscosity.[15]

 The prediction of this effect is important for dimensional precision during extrusion, at least for the original die as these are often corrected after the first profile laser measurements or due to die wear.

#### 1.6. Curing systems

These are the components responsible for the vulcanization in the curing process.

The purpose of vulcanization is to create bonds between the long polymeric chains of NB, SBR, BR and IIR. This way the soft and almost inelastic, which is easily deformed with small

tensions becomes hardened, with a higher tensile strength and elastic.

By creating these bonds these chains become stranded in place and loose the liberty to deform with breaking either the bonds or the polymeric chain (Fig. 24).



#### **Figure 24 – Polymeric chains cross linked with sulphur chains. [4]**

By far the most common vulcanizing methods depend on sulphur. Sulphur, by itself, is a slow vulcanizing agent. Sulphur alone is not enough for a satisfactory vulcanization of rubber, because the process will require large amounts of sulphur, high temperatures along with long periods of curing time. Even then the final product will not have created enough bonds between the polymeric chains, while being vulnerable to the aging process (which will result in surface cracks).

A proper vulcanization can only be achieved through the use of reaction accelerators (catalysts), these will enhance the vulcanization speed and increase the reactions obtained, therefore increasing the linkage between polymeric chains.

#### 1.6.1. Compounding.

Compound formulation is dependent on each factory conditions, such as suppliers, year round temperature average, machinery and factory floor conditions and targets. Due to this compounding mix formulas seldom can be exported between plants and often need to be locally developed and fine tuned to achieve lower raw material costs, increased processability and achievement of target finished product properties. This means all materials received are sampled and tests to assure contracted properties which must be met by the suppliers and also to fine-tune the mixing formulas in which these raw materials will be used. [19]

Since rubber elastomers have no usable application unless their properties are tweaked in order to achieve certain target properties these are added during the mixing stages. Compounding adds sulphur as a cross linking agent (after the initial mixing stages to avoid premature vulcanization), addictive fillers which act to either to enhance rubber's mechanical properties (reinforcing fillers) or to extend the rubber to reduce cost (nonreinforcing fillers). Compounding will affect properties, cost and processability.

Rubber compounding is made up of the following constituents.

- 1) Base polymer or blend of polymers
- 2) Cross linking agents
- 3) Accelerators of the cross linking reaction
- 4) Accelerators modifiers (activators and retarders); zinc oxide and stearic acid form a common activator system for sulphur-vulcanized systems.
- 5) Antidegradants (antioxidants, antiozonants, inhibitors of metal catalyzed oxidation, protective waxes).
- 6) Reinforcing fillers (black, mineral and organic)
- 7) Processing aids (chemicals peptisers for polymers, softeners, plasticizers, dispersing aids, tackifiers, factice and lubricants)
- 8) Diluents (inert mineral fillers, organic materials and extending oils)

When different types of rubber need to be vulcanized together at the same conditions of pressure, temperature and time, each individual rubber compound needs to be either accelerated in order to align their vulcanization timings to a single frame.

Also these compounds need to be inhibited to avoid vulcanization and oxidation (aging) at previous stages that might generate high pressures and/or temperatures, such as mixing or extrusion or being stored as unvulcanized components vulnerable to oxidation. Because even with oxidation inhibitors unvulcanized rubber is still vulnerable these components have a short storage life to avoid compromising the quality of the finished products.

To avoid pre-vulcanization in the compound mixing stages in which high temperatures are often obtained (aprox. 150 °C) pre-vulcanization inhibitors (PVI) are used.

### 1.6.2. Cross linking agents

These cross linking agents are the main players in the vulcanization reaction by regenerating new chains that will anchor the rubber compound polymeric chains increasing its tensile strength and reducing plasticity. As presented on chapter 1.6 the cross link agent used in tire manufacture is sulphur.

In order to sulphur act effectively as a cross linking agent elastomers must have double bonds with *allylic* hydrogen. All rubber elastomers used in tire build, such as BR, SBR, NR and IIBR meet this requirement.

Rubber grade sulphur has a purity of 99.5%, with less than 0.5% of ash. Also it is acid free, which is important since acidity retards curing. To be effective sulphur must be well dispersed in the compound rubber, otherwise it will lead to lack of homogeneity on the final product with over vulcanized or incomplete vulcanized areas. As it would be expected such flaws increase the probability of failure initiation during serviced life.

An elastomer with high solubility will facilitate dispersion. NR and SBR have a greater solubility than BR, therefore it is easier to disperse sulphur in the former two elastomers, particularly at high levels of sulphur. [20]

Sulphur is presented either as a soluble (rhombic crystal form) or insoluble (amorphous) form in rubber. Although soluble sulphur is easier to disperse than insoluble sulphur, the latter is sometimes used to prevent sulphur blooming. At temperatures below 120°C insoluble sulphur does not dissolve, instead it is presented in discrete particles which cannot readily diffuse through rubber. At high temperatures elastomer solubility increases absorbing high amounts of sulphur, but as temperature decreases solubility decreases and the excessive sulphur migrates to the surface and crystallizes. This effect results on surface precipitation which causes tack reduction, a needed property during tire construction to pile up several layers of rubber components during construction.

In order to prevent bloom soluble sulphur needs to be complemented with insoluble sulphur, this way after the compound cools down soluble sulphur has little bloom with insoluble sulphur dispersed throughout the compound and unable to migrate due to its particle size. Insoluble sulphur becomes soluble at temperatures above 120  $^{\circ}$ C achieved during curing procedures, for this reason mixing stages are refrigerated to control the process temperature. [20]

## 1.6.3. Activators

Activators are both inorganic and organic chemicals used to activate or extract the full potential of accelerators. Actually in the absence of accelerators zinc oxide and stearic acid are unable to effectively increase the number of cross links generated during curing. [21]

The most common accelerators used in the curing process are zinc oxide and Stearic acid, although lead and magnesium oxides can also be used. Activators (along with accelerators) allow the reduction of activation energy necessary for the vulcanization process from 210 kJ/mole to the of range 80 - 125 kJ/mole. [22]

Activators and accelerators facilitate the breaking of sulphur chain and the "accelerated sulphur" vulcanization system requires only 5 to 15 sulphur atoms per crosslink as compared to 40 - 55 sulphur atoms per crosslink for un-accelerated sulphur vulcanization.

2 RH +  $S_{x+1}$  + ZnO  $\frac{curve}{1}$  RS<sub>x</sub>R + H<sub>2</sub>O + ZnS

**Figure 25 - Zinc oxide interaction [4]** 

 In order to for the zinc oxide to be fully effective it must be in a form that is able to react with the accelerator system, which means ZnO particle sized must be very fine or the zinc must be in soluble form (Fig. 25).

 Most natural rubbers and some synthetics contain enough fatty acids to form soluble zinc salts which are able to react with the accelerators.

 To ensure there are enough fatty acids it is common to add 1 to 4 parts per hundred of stearic acid. The fatty acid acts as a plasticizer or lubricant to reduce the viscosity of the compound, besides being a solute to zinc oxide.[21]

#### 1.6.4. Accelerators

Accelerators are typically classified as primary or secondary. Generally primary accelerators provide considerable scorch delay, medium to fast cure and good modulus development, while secondary accelerators produce scorchy, very fast curing stocks

Nowadays the most used primary accelerators are thiazoles and sulfonamides, being the latter a reaction product from MBT or MBTS and amines. Examples of these amines are CBS (cyclohexyl), TBBS (tertiary butyl), MBS (morpholine) and DCBS (dicyclohexylamine), the effects of these amines are reflected in differences in scorch safety and cure rates.

Typically secondary accelerators are DPG, DOTG, TMTD, ZMDC and ZBPD. These are seldom used alone, generally being applied in combination with primary accelerators to gain faster cures. [21] This practice usually results in shorter scorch safety and smaller vulcanization plateaus, this means shorter opportunity windows on the vulcanization curve and a need for greater process stability and control.

There are major differences in scorch safety, cure rates and state of cure. MBS provides a greater scorch safety, while TBBS provides a faster cure rate and higher state of

cure (modulus). Similar comparative results are seen when secondary accelerators are used to speed up cure times. Regarding the secondary accelerators TMTD and TMTM develop higher modulus and longer scorch safety than DPG or ZDMC, but are still scorchy than TBBS alone. (Fig. 26)

Primary and secondary accelerators may be combined to achieve greater flexibility in processing and curing properties.



Although being applied at different **Figure 26 - Comparison of accelerator classes in natural rubber [8]**phr (parts per hundred) modulus vs time

curves are similar both in natural rubber and SBR, which allows easy accelerators applications for simultaneous curing constructions such as tires.[21]

The higher the torque achieved during the curing process, the higher is the amount of cross links created.

Since the curing curve declines due to over vulcanization after it peaks, it is important to avoid small plateaus when curing thick sections. The reason for these details is the time necessary for heat to be transferred into the thick of the cured part as well as to be removed from the same.



 When compounding a certain rubber product the engineer needs to, select a curing system [22] which must account for:

- Process temperature available
- Required target modulus achieved during curing (state of cure)
- No reversion on over cure
- Fast curing rate for economical production
- Adequate processing safety for scorch free procedures
- Accelerators solubility in rubber (high solubility to avoid bloom and improve dispersion)
- No adverse effects on other required properties, such as bonding, ageing adhesion.
- Stability of accelerator as chemical
- No known health hazardous for production personnel



#### **Table 2 - Accelerators classifications [22]**

#### 1.6.5. Retarders and inhibitors

Retarders are materials which provide longer scorch safety with little change to other properties. Acidic materials such as salicylic acid, benzoic acid and phthalic anhydride are used as retards, mostly with thiazole-based cure systems. This option is good to increase scorch

delay although it reduces rate of cure. On the other hand when combined with sulfonamide accelerators they may act as accelerators instead.

Pre-vulcanization inhibitors (PVI), N-cyclohexylthiophthalimide (CTP) are greatly effective on the control of scorch with little effect to other properties. This is of the utmost importance to avoid the rubber nightmare of unintentional vulcanization and allow better, shorter or with higher mixing temperatures mixing cycles. From figure 27 it is easy to judge CTP effect on compounds. One limitation of this PVI is that at levels of 0.5 phr or above it may cause some bloom, although such high levels are rarely used.





### 1.7. Addictives

Generally there are 3 different types of addictives, antioxidants (to provide oxygen protection), antiozonants (for ozone protection) and softeners (for processing purposes).

#### 1.7.1. Antioxidants

Oxygen reaction with elastomers can cause both chain scission and cross linking, which means the compound stiffness will be affected on either way. This effect may also facilitate the initiation of cracks and fractures that under stress may grow to become failures. For this reason tires are controlled by their DOT (as mandated by the United States Departement of Transportation) with a print of week and year of production on the sidewall.

Although most elastomers embrittle due to oxidation due to a dominance of cross linking, natural rubber actually softens. Oxidation is accelerated by heat, ultraviolet light and some metals such as copper, cobalt and manganese. Stress also hastens oxidation by providing polymeric chain movement, as well as the sulphur content due to the allylic cross link. [20]

The mechanism of oxygen attack on elastomers involves autocatalytic free radical chain propagation. These macro radicals are created with the abstraction of hydrogen from rubber chains by a proton acceptor. Oxidation then continues with the reaction of these macro radicals with oxygen and the subsequent generation of hydroperoxides and peroxy radicals.

Cross linking results from the coupling of macro radicals or by macro radical addition to a double bond with an H abstraction. Chain scission on the other hand is somewhat more complex, in which after several transformations the polymeric chain is broken at βposition.[20]

During the ageing process carbonyl, hydroperoxides and peroxides are formed and can be detected by an infrared spectroscopy.

Since it isn't feasible to run real times aging tests, these are conducted in laboratory conditions with accelerated aging tests. However since aging depends both on temperature and stress it is complicated to infer how it will evolve. For example natural rubber will stiffen on tests run at 50  $^{\circ}$ C, but soften at tests of 110  $^{\circ}$ C.

Antioxidants act in two ways, the first called preventive, by reacting with hydroperoxides to form harmless non-radical products, during this reaction the antioxidant is oxidized. And the second called chain breaking anti-oxidant which destroy the peroxy chains radicals which would otherwise propagate

Organic phosphites are preventive oxidants and are nonstaining, but they lose much of their activity during curing and are mostly used as emulsion rubber stabilizers. Common chain breaking antioxidants include bisphenols, thiobisphenols, hydroquinone derivates and hindered amines.

To maximize the anti-oxidation effect the best option is to combine both preventive and chain breaking options since these act in synergy much more effectively than they would solo. Since during service some fluids may leach out the antioxidants, polymer-bound variations are now in use to avoid this issue. [20]

## 1.7.2. Antiozonants

Ozone even at a few parts per hundred million readily breaks carbon-carbon double bonds in elastomers. If an unsaturated vulcanized elastomer suffers strain in the presence of ozone it will quickly develop cracks, with the severity of the same increasing with the strain.

Paraphenylenediamines (PPD) are effective in reduction of ozone cracking, oxygen, as well as fatigue, heat and metal ions. These are relatively expensive but due to the large spectrum of protection against degenerative forces, they are widely used in several variations.[21] there is good evidence that PPDs react directly with the ozone, thereby providing competition for the ozone-rubber reaction.

## Standard formulations are 6PPD, IPPD, DTPD and TMQ

 Since PPDs are expensive and react directly when exposed other more affordable solutions are used to the extent of their capabilities. These are the petroleum waxes, which do not offer any protection against oxygen and due to their inextensibility can't protect the tire during cyclic stress-relaxation. In the case of cycle loadings the way surface film ruptures exposing the polymer to the atmosphere, on this occasion protection is secured by PPDs.

 Petroleum waxes are supplied as two major types: paraffin and microcrystalline. Each of these two is characterized by an optimum migration temperature where the mobility and solubility of the wax in the rubber are balanced so sufficient bloom can form at the surface to provide optimum protection. Microcrystalline waxes have higher molecular weights compared to paraffin waxes and exhibit optimum bloom levels at higher ambient temperatures. To provide the best protection both of these two waxes are applied usually at different particle sizes to provide blooming at different temperatures.[21]

1.7.3. Softeners (process aids)

The purpose of softeners is to aid the processing stages of the compound by reducing its viscosity and therefore reducing the energy necessary and reducing the temperatures.

These are presented in two general kinds, chemical peptizers and physical plasticizers. The former are used with 1 to 3 phr and act by reducing molecular weight by increasing the rate of oxidative chain scission. Sulfonic acids and pentachlorothiophenol are part of this group and particularly effect on natural rubber, although in excess it may reduce the vulcanized strength by breaking its chains.

Physical plasticizers soften the compound by reducing entanglement and decreasing internal friction. The entanglement plateau modulus depends on the concentration of rubber in a rubber-plasticizer mixture to the power of 2.0 to 2.3. An additional benefit of physical

Softener	Paraffinic	Naphthenic	Aromatic
Tensile Strength			
Wear			
Toughness			
Hardness			
Tearing Resistance			
Elasticity			

**Figure 29 - Softeners interaction with rubber compounds [4]** 

plasticization may be the improvement in low temperature flexibility.[20] Plasticizers must be carefully selected to have good compatibility, otherwise they may "bleed" from the compound at low temperatures when the solubility is reduced.

Common plasticizers include oils, fatty acids and esters.

Softeners reduce mixing torques and extrusion defects, such as shark skin, by reducing the elastic effect of the compound and improving its plasticity. They are also responsible for the reduction of green compound viscosity, improved filler dispersion and adjustment of cured rubber modulus. [4]

## 1.7.4. Tackifiers

Tack is necessary for tire construction because during tire assembly several different layers of rubber are overlapped to create a green tire.

Generally there are several types available: [20]

- Rosin derivates, which are chemical mixtures of abietic and related acids.
- Coumarone indene resins consisting of indene, coumarone, styrene, methyl styrene, methyl indene, and other hydrocarbons which are obtained from coal coke oven light oils.
- Aliphatic petroleum resins made from unsaturates obtained while cracking crude oil
- Terpene oligomers obtained from pine tree stumps
- Alkyl modified phenol formaldehyde resins

Tackifiers are used to prevent the loss of tack a compound suffers after being processed and also to improve it, as well as to improve adhesion of different rubber compounds (NR/SBR) which might otherwise not be so easily bonded. Tackifiers usually have molecular weights spread across 500-2000 and have limited compatibility to the elastomer they are added.[20]

## 2. Tire components

 Most PLT tires are all built with the same base components. What differs tires from each other is the construction and the composition of the rubber, this is what segregates a budget from a brand tire.

 Construction wise there are some significant variations, although the most significant aspects of a tire performance are the rubber behavior while in contact with surface, tread pattern and the stiffness of the walls.

 This will be explained further on along with the compromises that each of these aspects has.

 Different components have different purposes. Both the tread and the sidewalls have a mix of several components which results in several different compounds, with the exceptions of the textile and steel components.

## 2.1. Compounds

Although passenger car tires and truck tires are similar in construction there is a huge difference in the weight of materials used. (Fig. 30)



 These four elastomers present excellent qualities in some areas but need the combination or overlapping of other compounds to complement each other (Fig. 31). This is why tire construction combined several layers of these elastomers.



**Figure 31 - comparison between elastomers properties. The lowest the number the better the polymer in the referred properties [2]** 

### 2.2. Elastomers

Elastomers are polymers with viscoelastic properties. This means that these materials behave both as viscous and as elastic materials.

There are 4 main types of Elastomers used in the car tire industry:

-Natural Rubber (NR)

- Styrene-Butadiene or Styrene-Butadiene-

Rubber (SBR)

- Polybutadiene (BR)
- Isobutylene Isoprene Rubber (IIR)



**Figure 32 - raw rubber materials [4]**

2.2.1. Hysteresis

A pure elastic element (a) will deform, within the elastic phase, and when the applied tension is removed it returns to its original dimension.

On the other hand, the viscoelastic component (b) will demand more energy to achieve a certain deformation than it gives back when returning to the original deformation (Fig. 33). This means that the energy difference is dissipated as heat, through a process known as hysteresis.

This effect is responsible for the heat generation on the tire during service as well as loss of energy. The reduction of this effect will save the tire from unnecessary exposure to heat and increase the car millage, being a central point in the development of new car tires.

It also increases the air temperature inside the



**Figure 33 – Hysteresis [4]**

tire, causing raise of internal pressure inside the tire because the air is unable to expand. This effect is countered by the tire and the textile ply contraction due to the heat buildup.

2.2.2. Natural rubber (NR)

**Natural Rubber** (NR) is obtained through the farming of **Pará rubber tree** (*Hevea brasiliensis*) which is most frequently referred simply as rubber tree.

NR Derives from the milk like liquid of the Heavea Brasiliensis tree, this natural rubber latex contains many organic and inorganic impurities. [21]

The Monomer chain if the natural rubber is Isoprene CH2=C(CH3)–CH=CH2

Natural rubber is mostly used in the tread due to its vitrification (glass transition) properties which are important for wet grip.

Also Natural rubber has a high resistance to cut resistance, elasticity (when vulcanized) and high tensile strength. Due to this property it is used on the upper half of the external side of the sidewall to protect the tire from lateral contact.

Its Tg is about -70 °C and due to its stereo regularity NR crystallizes a low temperatures and upon straining. Straining crystallization imparts outstanding green strength and tack and provides vulcanization with high cut growth resistance at severe deformations. [20]

This allows for a good green strength and tack which enable the uncured component to hold its shape during building and green tire storage. As rule of thumb, compounds with a durometer between 30 and 95 can be produced by using NR [21]

 NR holds its strength during deformation it is highly resilient and experiences little heat buildup, being a material of choice when shock and dynamic load requirements are important.

 Its shortcomings are poor resistance to ozone, high temperatures, weathering, oxidation, oils and concentrated bases and acids. When compounded with other chemicals such as Antidegradants (antiozonants and antioxidants) a usable finished product is achieved.[21]

## 2.2.3. Styrene-Butadiene Rubber

**Styrene-Butadiene** or **Styrene-Butadiene-Rubber** (SBR) is a combination of two different polymers **Styrene** and **1,3-Butadiene.** This polymer has similar properties to natural rubber and is used to cover natural rubber shortages and also in combination with the same due to its properties.

SBR has a high resistance to abrasion and traction, chipping, aging along with a low vitrification temperature which allow good wet grip (better traction).

SBR is a copolymer of styrene and butadiene. It is synthesized via free radical emulsion polymerization or anionically in solution, most common using butyllithium initiator. A typical SBR contains 23% styrene and has a Tg of -55  $^{\circ}$ C. The molecular weight of the emulsion SBR is controlled (to prevent gelation) by mercaptan chain transfer.

Hot lattices are produced when the emulsion polymerization temperature is elevated to approximately 50 °C. The rate of radical generation and chain transfer is high which causes the polymeric chains to be much branched. These hot SBR have low vulcanized strength. Due to this another process with a polymerization temperature around 5  $^{\circ}$ C (called cold SBRs) allow the production of a polymer with less branching which adds up to a vulcanized final product with higher strength than hot SBRs

Anionically prepared SBR molecular weight is readily controlled by initiator concentration and molecular weight distribution is narrow. The resulting solution rubber is purer than emulsion SBR, because of the absence of emulsion residues.[20]

2.2.3.1. Styrene/vinyl

In order to improve Styrene properties small percentages of vinyl may be added to tweak the glass transition point and the compound service characteristics. (Fig. 34)

High vinyl content will have negative effects on wet grip and tear resistance of SBR, while increasing its rolling resistance and tear resistance. [2]



2.2.4. Polybutadiene Rubber

**Polybutadiene** (BR) is a synthetic rubber compound formed through the polymerization of the monomer of **1,3-Butadiene**.

Historically it was first synthesized in 1910 and became industrial since 1950.

Polybutadiene is capable of absorbing more energy during the elastic phase of deformation than NR and SBR, and release it again as force and not so much as heat. BR is more resilient and therefore more elastic, which means the hysteresis loop, has lower energy dissipation. BR also has a high resistance to abrasion.

Due to more elastic behavior BR is used on tires sidewalls to provide a lower rolling resistance. It has positive wear, rolling resistance and winter characteristics but is bad for wet grip.

Free-radical polymerization of butadiene gives polymers of low stereoregularity of little interest ot the rubber manufacturer. Commercial polymers are prepared in solution using either alkyllithium or Ziegler-Natta catalysts. [8]

Polybutadiene is produced by emulsion process or by a solution process. The material offers the best low-temperature resistance of any organic elastomer (with the expction of silicone). Due to this property it suffers extensive cold flow at room temperature which causes bales to deform if not properly stored in specially reinforced containers. It is often blended with NR and SBR to improve low temperature flexibility of those compounds. Internal mixing is the process of choicce when compounds contain high proportions of BR.

The choice of a high-vinyl BR results in a slower cure rate for the compound compared to conventional BRs. Therefore the use of primary and secondary accelerators is suggested and recommendations include sulfenamides and possibly thiuram type accelerators to acchieve good curing times and properties.

BRs have a fair resistance to oxidation despite their low saturation, although most compounders prefer to add Antidegradants to improve ozone resistance.[21]

## 2.2.5. Butyl Rubber (IIR)

**Butyl rubber** (Isobutylene Isoprene Rubber or IIR) is used to replace tire tubes, which have become absolutely obsolete in the last decades.

Historically it was firstly synthesized in 1939 and became since industrial 1941

IIR has a low gas permeability, very low elasticity and excellent high heat aging properties. Due to this it is used in the inside of the tire in a layer called Inner liner to keep the air trapped and under pressure.

Nevertheless this is not an impermeable layer to air, which means air pressure needs to be regularly verified.

IIR usually has low resilience at room temperatures for an elastomer with such a low Tg (approximately -70  $^{\circ}$ C). Since IIR is largely saturated the rubber has excellent aging properties.[20]

Butyl rubber is a copolymer of isobutylene with a small percentage of isoprene, which provides sites for curing.[20]

This elastomer is made via low temperature cationic polymerization. The halogenated forms which are produced in hexane solution by using chlorine or bromine, provide the compounder with greater flexibility in cross linking and enhanced cured compatibility along with general use elastomers. [21]

Because of its chemical inertness butyl polymers tend to not experience molecularweight breakdown during processing. This allows operations such as heat transfer treatment or high temperature mixing to affect the vulcanizate characteristics of a compound. Because of its properties it is the choice polymer for curing bladders.

In addition, flexibility is increased by the addition of some mineral fillers in the clay talc, and silica families along with promoters. Such promoters improve resilience and processing and can also increase compound modulus. [21]

## 2.3. Fillers

Fillers are used to reduce the cost of Elastomers, while at the same time increasing processability, increasing the resistance to abrasion, tensile strength and Young modulus.

There are 2 types of fillers, active and inactive.

In the inactive branch we have clay, argyle and chalk. These are simply used reduce costs while maintaining the necessary properties.

Within the active fillers we have 2, Carbon black and Silica.

## 2.3.1. Carbon Black

 **Carbon Black** is produced through the incomplete combustion of heavy oils in the presence of ammonia (NH3). (Fig. 36)



**Figure 36 - Carbon black production [4]** 

**TEM of Carbon Black** 

high structure

 When combining carbon black with rubber, through the mixing process, it is important that the structure of the carbon black to be high. This will provide a better absorption by the rubber polymers, due to the higher active surface. Carbon black absorption is noticeable on the tire's black color. [4, 23]

 The higher the structure, the higher the tread durability, the better the wet-grip and rolling resistance (Fig. 35).

The dispersion of Carbon black in the compound is mechanical.

**Figure 35 - Carbon black grain size [4]**

The presence of carbon black increases the tensile resistance of the rubber compound.



Due to the low electrical conductivity of the silica compounds and rubber, carbon black is used to discharge static electricity into the ground and avoid its discharge through the cars passengers while boarding or unboarding the vehicle.

For this purpose the base of the tread is a carbon rich compound connected to the surface of the tread by one (or more) center carbon beam. Cars using tires with this carbon link to the ground will be immune to static electricity discharges.



**Figure 38 - close up of the carbon center** 

Reinforcement is achieved by interlocking of the very rough carbon black surface with the polymer chains.



**Figure 39 - Carbon black effects on wet skid, RR and wear [2]** 

Target conflict: Wet-Skid vs RR , Wear

The use of carbon black improves wet-skid tire properties, but reduces rolling resistance and wear. Due to this target conflict when a tire is developed it is thought out for a specific range of application. (Fig. 39)

#### 2.3.2. Silica

**Silica** addition increases the elasticity of the compounds (better rolling resistance, less hysteresis), increases breaking distances and winter compounds performance and also increased resistance to cuts.

Silica is produced through the precipitation of silica from dissolution SiO2.

 Silanes form covalent bonds to the silica surface during mixing, facilitating filler dispersion. When curing the rubber composite, highly stable silica-sulphur-polymer cross links are formed. (Fig. 40)



**Figure 40 - Silica and silane interaction with rubber elastomers [4]** 

 The dispersion of Silica fillers is dependent on presence of silane which acts as an activator for the primary reaction. The primary reaction is extremely fast and occurs with temperatures around 155°C if a good dispersion is obtained during the first mixing process.

The second reaction is slower and only occurs in the presence of water.

During the curing process silica will attach itself to several polymer chains, increasing polymer linkage which increases the elasticity of the whole by creating anchoring points.

Silica has no target conflicts, it slightly increase wet-breaking and significantly increases rolling resistance.

### 3. Reinforcements

## 3.1. Metal reinforcements

Steel reinforcements are used in the bead core and tread in PLT tires and most CVT tires, although some CVT and high performance PLT tires also use steel reinforcements on the sidewall or as a mesh from bead to bead. (Fig. 41)



**Figure 41 - Metal reinforcements [5]** 

#### **Steelcord Components**



**Figure 42 - steel cord components and wrap [5]** 

## Steelcord Construction Types

## **Regular Cord**

Direction of Strands in opposite to direction of Cord

## **Lang's Lay Cord**

Direction of Strands and Cord is the same

## **Open Cord**

Filaments are loosely associated to enable a high compound penetration.

## **Compact Cord**

Same direction of Strand and Cord



#### **Figure 43 - steelcord construction types [5]**

## **High Elongation Cord**

Preformed Filaments (picture) or short lay length (~3mm) for ensuring high structural elongation

3.1.1.Filament pre-formation

A common method for achieving the requirements of an Open Cord (high compound penetration) and a High Elongation Cord (high total elongation) is the filament pre-formation as shown below. A 2-dimensional, with 2 teeth wheels, or a 3-dimensional, with 4 teeth wheels, pre-formation is possible. The distance of the teeth wheels as well as the teeth shape allows several grades of pre-formation. With regard to fatigue a round teeth shape should be preferred.

## 3.1.2.Production Steps





### **Wire Rod Æ 5.5 mm**

-Basis material for all steel cord constructions.

-Different quality depending on required tensile strength (NT, HT, ST).

-Depending on the supplier the surface is phosphated.

### **Cleaning/Coating/Drying**

-Cleaning by mech. descaling and brushing for removing oxide films and scales. -Coating with a product based on borax secures a well adhesion of dry lubricant. Not needed if wire is phosphated. -Drying by air pressure.

#### **1st Drawing**

-In 8 steps the diameter is reduced from 5.5 to 2-3mm. Thereby the wire passes 8 drawing dies with a more and more reduced diameter.

- Soap powder is used as lubricant for reduced friction.

- During the drawing the dies and the cabestans are cooled with water.

- The drawing speed depends on the wire quality: High C-ratio results into decreased speed.



**Figure 45 - Second Drawing and Patenting [5]** 

#### **2nd Drawing**

-Same process as in 1st drawing.

- Reduction of diameter from 2-3mm down to 1-2mm in around 8 drawing steps.

- Drawing speed is also here depending on the C-ratio (around 9m/s).

### **Patenting (Normalizing)**

- Chemical cleaning for reducing remaining soap.
- Steam drying.

- Normalizing of the crystal structure by passing an oven with 1000°C for getting an austenitic structure. The speed is depending on the wire diameter. It increases with lower diameters. The process is possible for diameter from 0.94 to 2.40mm.

- The next step is passing a quench of lead at around 590°C.



**Figure 46 – Patenting [5]** 







### **Cleaning**

-The wire passes 4 cleaning bathes with Water+NaOH - Water - Hydrochloric Acid - Water. In the last step the wire is dried by air pressure.

### **Plating**

Method 1:

-Cleaning quench with NaOH.

 -In an electrolytic Na cyanide quench the brass layer is generated. 16 electrolytic cells are in series connected. The thickness of the layer is controlled by the amount of quenches. For generating a lower thickness some of the quenches will be omitted.

 -For removing rests of the cyanide, a water quench and a drying by air pressure follows.

 -Plating speed is depending on the wire diameter (around 60m/min.). Method 2:

 -After cleaning the wire in the first step only the copper layer will be generated electrolytic. In the same way the zinc layer will be generated afterwards.

 -Finally the brass layer will be generated by thermal diffusion with conductive or inductive warming at 400-500°C.

-Remaining oxide films are removed by a pickling bath afterwards.

#### **Fine Drawing**



**Figure 49 - Fine Drawing [5]**

**Cabling** 



### **Stranding/Cabling/Wrapping**

-Depending on the required product up to 3 steps are necessary for processing a cord.

- Stranding generates simple constructions like 2x0.30.

 $\sim$ 

- During cabling two or more strands are combined together to a cord like 3x0.20+6x0.35

- With spiral wrapping finally a spiral is wound around the cord.

- The twisting speed is 3300 turns/min. The cabling speed depends on the cable construction (around 1200-1500 turns/min.).
- The lay length is controlled by the extraction (let off) speed.



Figure 51 – Cabling [5]

**Crystal Structure** 



**Original Structure** 

**Textured Structure** 

**Figure 52 - Crystal structure before and after drawing [5]** 

Original structure at Æ 5.5mm

Slight textured structure after pre-drawing to Æ 1.0mm

Normalizing (Patenting) back to austenite structure at 900- 1000°C

Final textured structure after fine drawing to e.g. Æ 0.30mm



After Pre-Drawing from 5.5mm to  $\sim$  1mm a further diameter reduction would destroy the material due to too high brittleness related to the textured structure.

 Therefore a **Normalization** of the crystal structure is necessary. By increasing the temperature up to 1000° the textured orientation will be lost. Further drawing to lower diameter is possible.

### **Adhesion Mechanism**

To improve adhesion between the rubber compound and the steel cords, these are covered with a layer of brass which capable of bonding with the sulphur present during the curing process. (Fig. 53)

> *Bonding System of Copper from Brass Layer together with Sulphur from Compound to CUxS Layer.*



**Figure 53 - Adhesion Mechanism [5]** 

#### 3.2. Textile reinforcements

In tires industry textiles are used to increase the resistance to expansion. This is the only component which is held between both beads and provides a counter force to expansion during the pressurized phase of curing process. This effect is due to this elastomer contraction when heated, this way it will counter act the internal increase in air pressure due to the same increase in heat.

Another purpose of this textile reinforcement is to hold the assembly in place during construction.



**Figure 54 - Tire section with textile reinforcements visible between the bead metal cores and all around the tires** 

Textile cords are responsible for holding the air pressure inside the tire. For this purpose the innerliner (rubber layer which with a high impermeability to air) is

placed on the inwards side of the layered construction next to the textile cords.

The fact that textile cords suffer no or little compression makes this component relevant to vibration, as well as to maintaining the shape limits. (Fig. 55)



**Figure 55 - textile reinforcement's contribution to shape [2]** 

These are the four of the most used textiles and their details used in tire construction:

**Table 3 - Textile strengths and constructions [2]** 

Nylon (Polyamide) dtex $1400\times1 - 110$ epdm - 140 epdm dtex $1400\times2$ - 90 epdm dtex $940\times1$ - 120 epdm dtex $940\times2 - 101$ epdm	Polyester dtex $1100\times2 -110$ epdm dtex $1100\times2 - 100$ epdm dtex $1440\times2 - 95$ epdm - 105 epdm $-121$ epdm dtex $2200\times2 - 94$ epdm
Rayon dtex $1840\times2 - 118$ epdm - 125 epdm - 110 epdm dtex $2440\times2 - 104$ epdm	Aramid dtex $1670\times2-90$ epdm dtex $1670\times2-75$ epdm $D$ tau lines densitu of the thread $(n_1/10000m, af$ thread

Dtex - Liner density of the thread (gr/10000m of thread) Xn – cord composed of n threads.

epdm – nº of cords by decimeter**.** 

Depending on the application different textile materials are used as nylon and polyester are the textiles with less tensile strength, while rayon and aramid are on the high end of the scale in textile tensile strength.

Aramid is used in high performance and critical situations for heavy aircraft tires. To better understand the scope of its usage the same textile used to produce Kevlar.

## 4. Tire construction

 To understand how a tire is built it is first necessary to know how the components come together. For this purpose here are the main components involved in the tire construction.

 Some details, such as bead core may change from brand to brand since different solutions are in use in different tires.



**Figure 56 - Tire components [6]** 

The innerliner (Fig. 57) is a relatively new introduction to tire industry and has replaced the inner tube. The rubber compound in use is IIR due to its impermeability to air.



**Figure 57 – Innerlinner [6]**

#### 1. Innerlinner

- Material: Halobutyl.
- Function: Hold compressed air<br>within the tire. Functions as an air<br>tube, hence the tubeless definition

It also protects the cords from possible

degradation due to atmospheric moisture absorption. It is usually calendared as a two layered laminate having stepped edges. The overall gauge may be as high as 2 to 5 mm and the with must ensure that edges are over lapped by the inner edges of the chaffer.[19]

 As previously described the textile ply (Fig. 58) has the function of holding the construct together during construction, providing a counter action to air expansion.

 Also the textile ply helps on the transfers breaking and sideways forces to the rim.



**Figure 58 - textile ply [6]**

#### 2. Textile ply

- Material: Nylon, Polyester e Rayon (wrapped in rubber).
- Function: Support the air pressure held by the interlinear also provides resistance to the tire and vibration reduction.

 The purpose of the bead core (Fig. 59) is to make sure the tire is well settled on the rim.



**Figure 59 - Bead core [6]**

#### 3. Beade Core

- Material<sup>-</sup>
- Steel wire covered in a layer<br>of brass
- Function: Make sure the tire is firmly secured to the rims. Increases the strength of the<br>tire in this area.

 The apex (Fig. 60) is a compound with high elasticity which provides good rolling resistance properties, which maintaining the tire shape during steering maneuvers.

This is textile reinforcement (Fig. 61) for the apex area applied on high performance tires. Its contributions are the same as that of the apex.

Note: Apex reinforcement is not always present.

 This is a hard and elastic compound wrapped around the bead core to allow the tire to sit on the rim and transfer all forces between the rim and the tire.



**Figure 61 - apex reinforcement [6]**



## 6. Bead wrap/Flange

- protection. Material: Synthetic Rubber
- Function: Reinforce the area of contact between tire<br>and rim with the purpose of providing enough resistance to the connection

**Figure 62 - Bead wrap / flange rib protection [6]**

 Along with the tire tread the side is one of the most critical components of a tire because it will impact rolling resistance, steering and must protect the tire of small impacts and shearing forces that may occur due to sidewall impact during parking maneuvers.

**Figure 64 – Sidewall [6]**

#### 7. Sidewall

- Material: Natura rubber.
- Function: Protect the construction from lateral impacts and atmospheric aging/degradation.

 Steel breakers are responsible for shape at high speeds, transferring breaking forces to the rest of the tire and providing directional stability and increased durability

Note: Not present in temporary tires, which are supposed to be used under 80 Km per hour and for no more than 100km.

 Cap ply is responsible for high adaptability and to protect the rubber from the sharp edges of the metal reinforcements.

 It will also maintain the breakers in place during construction

allowing better production characteristics.

 Tread is composed of three areas.

 The top layer is in contact with the ground and has the prime rubber components for a target tire purposes.

 The base layer which aims to reduce rolling resistance and is often

composed of work-off components. This is a purely structural component as it shouldn't be in contact with the ground.

 Shoulder area is composed of the same rubber as the side wall and has the purpose of improving the adherence between the tread and the sidewall during curing.



**Figure 63 - Steel belt (breakers) [6]**



**Figure 65 - Cap ply [6]**

## 8. Steel Belt (Breaks)

- Material: Steel cross angled wires wrapped in rubber.
- Function: Provides shape and directional stability. Reduces rolling resistance and increases durability.

#### 9. Cap Ply

- Material: Nylon wrapped in rubber
- Function: Provides adaptability to high speeds and high performance characteristics, uniformity and production precision.



- Material: Natural and synthetic rubber
- Function:

Top Layer-Promotes adherence in any road condition; gives resistance to wear<br>and directional stability.

Base - Reduces rolling resistance and<br>protects the carcass from road irregularities.

Shoulder - Transition between the tread and the sidewall. This is the most critical area of the tier because it has to endure<br>the highest tensions and temperatures.

**Figure 66 – Tread [6]**

## 4.1. Production stages

There are 5 stages in a tire manufacturing plant.

## 4.1.1. Mixing

 This is the area in which the different compounds are weighted and mixed according to meticulous recipes which are constantly under control to compensate ambient temperature changes, new developments, raw materials variations and process variations.

 Since the specific characteristics of the rubber compounds are critical this is one of the most important stages.



**Figure 67 – Mixer [12]** 

There are 3 types of mixing, dispersive and distributive mixing.



**Figure 68 - Distributive mixing [4]** 

Distributive mixing creates a homogeneous material which provides the necessary interaction between the different materials. In this mixing shape and size of particles remains the same.



**Figure 69 - Dispersive mixing [4]** 

Dispersive mixing on the other hand is the effect by which particles shape and size are changed due to shear forces.



**Figure 70 - laminar mixing [4]** 

 Laminar mixing elongates and shears materials which increase contact surfaces between materials.

In reality all of these effects have to occur simultaneous to enable a good compound homogeneity.



To achieve all these mixing effects different mixers are used during the mixing stages.

**Figure 71 - mixing types and screws [4]** 

 Following the mill the compounds is cooled down and packed into transportable batches.



**Figure 72 - Mixing sequence [4]** 

Mixing is done in 3 stages and with different settings.

## *1st stage*

 Polymers and fillers are loaded and the mixing process reduces viscosity and increases the dispersion of fillers.

This stage is characterized by high shear forces and high temperatures.

## *2nd stage*

 Chemicals and softeners are loaded and dispersion and distribution of all materials increases.

This stage is characterized by medium shear forces and high temperatures.

## *3rd stage*

Vulcanizations are loaded and further distribution of all materials.

This stage is characterized by low shear forces and low temperatures.

This stage is carried out separately from the previous stages because it has to be done at low temperatures, because with the addition of vulcanization agents (i.e. sulphur) the polymers are in danger of unwanted curing.



Below is an example of the mixing process in stage 2 and the silanisation reaction in which silica bonds with the rubber polymer.



## 4.1.2. Preparation

 This is the stage in which all intermediary components are created to be conjugated on the III stage.

## *Textile ply*

 The production of this component starts with the extrusion of a final mix directly followed by slicing to prepare the compound for the mill. This extrusion and milling may seem excessive but is necessary to provide a fine rubber compound.



**Figure 74 - Compound preparation. [7]** 



**Figure 75 - Compound Calendaring [7]** 

 Once compound is ready and ply rolls are feed into the Calendaring machines both textile and rubber are compressed together to form a single pane.

 At this stage (depending on the production setting) the textile ply is stored or follows through the preparation of cap ply (cap strips).

#### *Cap strip*

Cap strip is cut on a dedicated machine called slitter and then rolled on cassettes by the mini-slitter. These cassettes are then feed to several singular P.U. machines to be applied over the Steel Breakers.



**Figure 76 – Slitter [7]**

Steel breaker wire is imported from external sources and mounted in parallel supports to allow simultaneous feeding to a continuous calendaring process in which the steel wires are assembled into a continuous thread.



Nowadays steel breakers are used as pairs of over posed layers with opposite angles.

For this purpose the continuous thread built by calendaring is cut at specific angles and stored to be used at P.U. construction machine.

**Figure 77 - Steel breaker calendar feed [7]**



**Figure 78 - Steel breaker angle cutter [7]**

#### *Apex*

Apex reinforcements are constructed in two stages, first the bead and then the apex.

This type of reinforcement is composed by wire wrapped with rubber compound.

Due to the many different configurations of wire matrix and wedge size these are built at separate stages.

 Firstly the bead is extruded with a matrix of steel wires.



**Figure 79 - Bead core [7]**

 These rectangular extruded beads are then rolled into the size of the rims to which they will be mounted in the future. Once rolled the extra is cut and the bead is ready to receive the wrap which will be the apex



The second stage of the apex building is the extrusion and wrapping of the previously prepared wire bead.

**Figure 80 - Bead core to rim size production [7]**



**Figure 81 - extruded rubber and its wrapping around the bead core to form the apex [7]** 

Once the process is complete apex is ready to be transported to K.M.

## *Tread preparation*

Treads are extruded from several different extruders, once for each rubber compound, and shaped into a single dye.

Treads have at least 3 feeder to a single die, in order to produce the tread, base and wing tips.



### **Figure 82 - Piggy back extruder with compounds [7]**

This is a very critical process due to dimensional tolerances and porosity which can appear in the compound. For identification color lines are added to the extruded tread for identification.



**Figure 83 - Tread markings with painted lines for later identification [7]** 

During extrusion compounds are heated due to the shearing forces and rubber-rubber friction. This may generate pre-vulcanization reactions if the temperature goes above 150°C. To avoid this problem pre-vulcanization inhibitors (PVI) are

added to compound while at the same time the entire process is cooled down through the use of water after the extrusion.

 Porosity may appear in the extruded compound due to insufficient cooling after the extrusion. Which maintains the compound high solubility while exposed to the atmosphere, this will cause the compound to absorb air and when cooled to release it due to the fall of solubility. The released air will be trapped and cause porosity.



Porosity is a real issue to avoid because it may force the compound out of specified dimensions and generate air bulges due to trapped air expansion during vulcanization.

**Figure 84 - Tread with a high level of porosity** 

## *Sidewall preparation*

 Sidewall preparation is very similar to the tread extrusion with the difference that only two compounds enter the sidewall composition. The rim compound composed of synthetic rubber and the lower sidewall composed of natural rubber. The lower sidewall and the tread wingtips are composed of the same compound mixture to improve components bonding.



**Figure 85 - Sidewall extruder with 2 feeders [7]**

After extrusion sidewalls are cooled and stored into cassettes for transport.

## 4.1.3. Construction

The first stage of construction is the carcass which will be the base in which the tread is applied. When combined both tread and carcass form a green tire, which is the common name for un-vulcanized tires.



**Figure 86 - Construction drums [7]** 

1) Firstly the drum separates itself from the left support so that the operator can introduce both apex reinforcements on each side of the working area.



**Figure 87 - open construction drum for apex placement [7]** 

2) Innerliner - The drum then starts to rotate and the innerliner is stretched throughout the drum diameter.





**Figure 88 – Innerlinner [7]**



**Figure 89 - textile ply over innerlinner [7]**

4) Bead Setting - In this stage the drum expands and stretches the combination of innerliner and ply slightly increasing its diameter. This is done to provide the correct position for the apex reinforcement. After the drum expansion the apex, which were previously placed on each side of the drum are moved into position with the use of compressed air.



**Figure 90 - Bead setting [7]**



**Figure 91 - Bead setting during Ply turn up [7]** 

5) Turn up – After the apex placement the machine collapses from both sides.

After the ply turn up the innerlinner covers both apex reinforcements and the center of tire and with enough turn up it provides resistance to the combination. On this stage the bead is trapped



**Figure 93 - Carcass after ply turn up. [7]**



**Figure 92 - Ply interaction during ply turn up [7]** 

between the ply and set in place. The ply tackiness allows it to adhere together and maintain this construction.

6) Sidewall setting - This is one of the most critical stages in the production of tires.

The position is guided by the PU machine feeder with the operator being responsible to confirm its placement with the help of guiding lasers.

 Once the sidewall is set all around the drum and its position confirmed the next stage is to roll the sidewall around the apex. This is done automatically and it depends only on the machine settings for this operation. Therefore it is very important to control all the procedures to correct any issues that may occur.



 Once the sidewall is turned around the apex the drum collapses and releases the construct. This construct is called Carcass.

**Figure 94 - sidewall setting and roll over apex [7]** 

## 7) Belt/Tread assembly

In this stage a separate set of drums is used to combine 2 belts of steel breakers which are laid on top of each other then covered with cap ply and finally with the tread.

 These steel breakers are composed of an extrusion of steel wires and rubber, which are then trimmed to length and an angle. On some constructs the first breaker (the breaker on bottom) has its edges wrapped in rubber to encapsulate the steel wires edges.

This angle is used to provide extra resistance to deformation.

On top of the steel breakers a layer of cap ply, composed of a stronger textile, is positioned with the double purpose of holding the construction together and protecting the surrounding rubber layers from the steel wires.

This protection is important because the radius of the steel breakers changes in the flat spot due to the weight which acts upon it. This radius variation creates a width variation on the steel wires.

The process in this stage uses two drums mounted on a vertically rotating support, a carcass support which emulates the rim supports and a transfer ring which slides between both previously described components.

Construction sequence:

Firstly the belt is feed to the drum which has access to the transfer ring side, and then the drums vertical support rotates for the cap ply servicer.

This step increases productivity because the application of cap ply is the operation with the longer period of time in this stage. Cap ply is applied in cap strips, this means the cap ply (or cap strips due to the application method) is feed unto a rotating drum while the cap ply feeder moves in a perpendicular motion, in relation to the rotation of the drum.

There can be either one or two cap ply feeders, depending on the tire construct.

Once both the steel breakers and cap ply are applied the drum vertical support rotates once more, back to the original position and the tread is now applied.

Once this assembly is complete the drum collapses while magnets on the transfer ring carry the assembly to the carcass. Here the tread assembly and the carcass are compressed and combined through

knurling from the center to the edges.

The tread is placed on top of the two belts covered with cap ply.



**Figure 95 - on the right the tread construction drums and on the left the assembly of the carcass and the tread [7]** 



**Figure 96 - Tread assembly with two breakers, cap ply and on top of it the tread. [7]** 



8) Carcass and Belts/tread combination.

**Figure 97 - tread and carcass assembly [7]** 

In this stage the operator places the carcass (which placed in a chute feed by the operator on stage 7) on the right support of the KM machine. Here the carcass is fixed on two rings similar to rims and once held together in place it is inflated.

During inflation the carcass beads are held in place and become air tight due to the pressure of inflation itself. This will shape the carcass into a recognizable tire shape while the tread assembly is placed on the outside of the carcass.

 Once the assembly of the green tire is complete the tread assembly is compressed to hold the construct in place and shape the tread into position.

This a very important stage and the compression start from the center of the tread with two rolls moving sideways to the outer edges. The purpose of this procedure is to squeeze any trapped air between the layers, because when trapped air is heated during the curing process it expands and creates bulges.





**Figure 98 - tread rollers [7]** 

9) Green tire

Green tires are prepared for transport to the curing area.



**Figure 99 - green tire storage and transfer [7]** 

The main issue during this stage is green tire storage, because green tires are still vulnerable to plastic deformations.

 In a perfect situation green tires should be stored in holed trailers to avoid sidewall collapsing. In reality holed cars occupy too much space and are rim size specific and aren't interchangeable, because if the holes aren't correct for the stored tire it will be damaged.

 Flat bed trailers can be used and reassigned to different tire sizes without creating extra complexity, which is the main reason for the continued use of these transport cars.

## 4.1.4. Curing

 The procedure of the tire production in this stage is quite simple in terms of procedure.

- 1- Green tires are carried in flat bed trailers (or trailers with holes) to the presses
- 2- The operator hangs the tire in front of the curing press
- 3- The press robotic arm extracts the hot tire into a conveyer belt and loads the next green tire hanging in front of the press for the next curing cycle.
- 4- Periodically after a certain amount of curing cycles the rubber Bladders are stretched without tires to improve the uniformity elasticity.



**Figure 100 -Curing press with inflating curing bladder and robotic arm to extract the tire [7]** 

 When a new mold is mounted or when production is restarted molds need to heat up to operating temperatures which depend on the curing cycles defined for each article.

 Articles curing cycle with similar time periods and of which only a mold is in production are frequently assigned to the same press. This is relevant because presses are designed in pairs, having two cavities for tire curing. Also this stage has the longer time per tire ratio, therefore optimization is essential.

 There are several types of molds, nowadays the most used are segmented molds. These consist of 2 solid sidewall plates (top and bottom) and 8 segments which close under pressure against the green tire. This enables the mold segments to move in direction to the center of the circumference.



**Figure 101 -Curing reaction overtime [24]** 

 Once the tire is set on the press and the curing bladder inflated the curing process begins. For a passenger tire the curing time is approximately 15 mins.

 It is important to notice that if the press cycle is too short the tire will be under cured or if the opposite happens the tire will be over cured and suffer a reversion of the achieved properties during the curing.

 Since rubber isn't a very good heat conductor, tires come out of the about 2/3 of the curing cycle and finish the curing cycle outside of the press while cooling down. This effect as to be taken into account since rubber stores large amounts of heat and releases it quite slowly.

4.1.5.Curing maintenance and accessories

4.1.5.1. Mold cleaning

 After several cycles moulds are cleaned with dry ice (while heated) to remove oils, lubricants and rubber which stain the cured tire. Dry ice (CO2) method is the solution used while the molds are mounted,

 There are several solutions using laser to clean molds, but they aren't very used because air vents cavities aren't easily cleaned with lasers. This is due to lasers only acting upon surfaces with direct line of sight. **Figure 102 - open mould [7]**





## 4.1.5.2. Air vents.

 Air vents are necessary to expel trapped air while the bladder expands and during air expansion due to the increase of temperature.

 The modern air vents do not create flash of rubber, instead they are barely noticeable. These air vents are similar to counter pressure valves used in

 Using air vents reduces the force necessary to pull the tire from the curing press, because there are less grabbing points. Also the finished product (see below) is of greater quality and ready to be used at

full performance, while the flash from the old air vents increases pass by noise and reduces certain performance qualities.



**Figure 105 - On the left a tire moulded with micro vents and on the right a tire moulded with airvents.** 



**Figure 104 – Airvents [2]**

## 4.2. Final inspection

 This is the last stage in the tire assembly line and is composed of two different operations.

 Tires need to be visually inspected by a qualified inspector which has the responsibility of detecting bulges, blisters blemish, cords penetration (visible cords) trapped air between the mold and the green tire, residues of lubricants and oil used during the curing process, visible dimensional deformations and overall imperfections.



**Figure 106 - Manual inspection [7]** 

 The second stage is called uniformity consists of automatically verifying each tire for conicity, roundness, inflated dimensions, strength of the bead in relation to the rim and in general how the tire will behave during operation.



**Figure 107 - Automatic uniformity robot [7]** 

 In order to be able to inspect the uniformity of thousands of tires per day all this process is automatic. Tires are feed into conveyer belts and separated accordingly; in the informatics system the information is stored in relation to each tire bar code.

 To verify how the tire behaves once inflated; the tire is automatically mounted into a rim and inflated to 4 bars (which is about the double of the inflation while mounted) and several laser measure the most critical points while the tire rotates.

## 4.3. Conclusion

Due to its properties rubber components have increased complications when assembled on a multi-layered construction. Since rubber dimensions alter with temperature a constant certification of extruded components is necessary after said parts have cooled down to room temperature. Since the average room temperature varies between winter and summer adjustments are necessary on the mixing ratios.

Also, due to rubber tackiness there is usually only one attempt to join two components together at the correct dimensions.

A large part of unvulcanized discarded rubber components are reutilized for new batches where an exact mixture isn't crucial for performance or safety.

As a consequence of a large amount of articles being produced at the same time an impeccable organization on the factory floor is paramount. Failure to do so could result in articles with switched over components or construction settings from other articles.

Everyday tire engineering is based on mixture of base knowledge and experience which inform a trial and error approach until all specifications comply with the original design. Because of its nature it's very difficult to predict how all components will behave until the first test tire is cured.

Overall it is an efficient system with low waste and with the added advantage of most being recyclable.

The interconnection between university departments and enterprises is to be encouraged because it provides a better integration between these two realities. This opportunity was of an enormous value providing a great change for practical learning and curriculum valorization.

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## **Annex 1**

PATENTING OF STEEL WIRE

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Patenting of steel wire, a technique invented back in the Eighteen Seventies in Britain, was kept a strict secret for decades. Keeping this technique "under wraps" enabled British firms to produce steel wire and fabricate steel-wire rope for a variety of applications.

The technology of patenting steel wire was first mastered in the USSR by S. S. Shteinberg [1] in 1922, following protracted experiments, at the Beloretsk steel wire factory, in joint work with engineers N. F. Andrianov and P. F. Zabaluev; the secret of the method was discovered, and since that time steel wire production has undergone rapid development in our country.

The essentials of patenting involve an isothermic transformation of supercooled austenite in the first step, i.e., at 450-550°C. In order to ensure uniformity of the austenite and marked isothermal decay of the supercooled austenite at the temperature of the supercooling bath (fused salt or molten lead), the wire is heated to 150-200°C above the critical point (at  $870^{\circ}$ C to  $920^{\circ}$ C). In the supercooling bath the austenite decays rapidly to a quasieutectoid ferritic carbide mixture of thin lamellar structure\* known as patenting sorbite. Investigators of steel wire attach great importance to the grain size of the steel in thin lamellar patenting sorbite, on the assumption that a coarse grain must aid in the production of long wires in drawing processes, when total area reductions are considerable. It has turned out, in effect, that a highly disperse, thin lamellar structure must form as a result of the high isothermicity of the austenitic decay process in response to severe overheating and to the formation of coarse grains.

The shape and size of the carbides is of great importance in cold drawing. The most highly favored form of cementite is the thin lamellar and uniform structure, and the least favored form is that of a network around pearlite grains. Reticular cementite (we prefer the term shell-type cementite) reveals cracks (fragments) leading to ruptures of the wire at the very outset of the drawing process. Carbides of pearlite in coarse lamellar form occupy an intermediary position in terms of their effect on the ductility of the wire.

The presence of carbides of granular shape makes it possible to carry out various forms of cold plastic deformation (drawing, rolling, stamping, etc.). Grainy carbides deform plastically to an extended shape in the wire-drawing process, when area reductions are



Fig. 1. Dependence of interlamellar distance in pearlite (sorbite) on the temperature of isothermal decay of supercooled austenite.

considerable.

The most striking ductility properties in drawing, given excellent strength characteristics, are exhibited by steel containing carbides in thin lamellar form (patenting sorbite). The degree of disperseness of the patenting sorbite (throughout the thickness of the carbide particles) depends on the temperature of the supercooling bath: the disperseness of the sorbite increases as the temperature of the bath (molten lead or fused salts) drops. Carbon steel with 0.45 to 0.85% C is usually subjected to patenting, and the temperature of the lead or salt bath is brought to 450-550°C.

\* Given the limitations of microscopy techniques of the early Twenties, S. S. Shteinberg was of the opinion that cementite had a globular shape in patented wire [1].

Urals Polytechnical Institute. Translated from Metallovedenie i Termicheskaya Obrabotka Metallov, No. 9, pp. 49-56, September, 1972.

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**Annex 2** 

*Tread dimensions profile for the extrusion product and die settings*