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(71) Applicant(s)
PKU Pulverkautschuk Union GmbH

(72) Inventor(s)
Udo Gorl; Reinhard Stober; Hartmut Lauer; Uwe Ernst

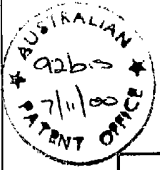
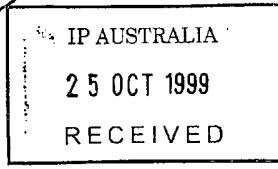
(74) Agent/Attorney
SPRUSON and FERGUSON,GPO Box 3898,SYDNEY NSW 2001

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(71) Anmelder: PKU PULVERKAUTSCHUK UNION GMBH [DE/DE]; Gebäude 32 Postbereich 13, Paul-Baumann-Strasse 1, D-45764 Marl (DE).		Patente* Marken, Standort Marl, Bau 1042-PB 15	
(72) Erfinder: GÖRL, Udo; Herderstrasse 38, D-53332 Bornheim (DE). STÖBER, Reinhard; Bornwiesenweg 22, D-63594 Hasselroth (DE). LAUER, Hartmut; Eckardrother Strasse 2, D-63628 Bad Soden-Salmünster (DE). ERNST, Uwe; Bitterfelder Strasse 7a, D-45772 Marl (DE).			
(74) Anwälte: HERRMANN, Reinhard usw.; Degussa-Hüls AG, Patente und Marken, Postfach 1345, D-63403 Hanau (DE).			
(54) Title: POWDERED RUBBER CONTAINING FILLERS AND METHOD FOR PRODUCING AND USING IT			
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(57) Abstract			
The invention relates to powdered rubbers containing fillers, which remain pourable even after a mechanical strain. The invention also relates to a method for producing these rubbers, according to which powdered rubber is obtained in two precipitation steps. The invention further relates to using such a powder for producing vulcanisable rubber compositions.			
(57) Zusammenfassung			
Die Erfindung betrifft pulverförmige, füllstoffhaltige Kautschuke, die auch nach einer mechanischen Belastung rieselfähig bleiben und ein Verfahren zu deren Herstellung, bei dem man das Kautschukpulver innerhalb von zwei Fällungsschritten gewinnt, und die Verwendung dieser Pulver zur Herstellung vulkanisierbarer Kautschukmischungen.			

Abstract

The invention relates to pulverulent filled rubbers which, even under mechanical load, remain free-flowing, and to a process for their preparation in which the rubber powder is obtained within two precipitation steps, and to the use of these powders for preparing vulcanizable rubber mixtures.



**Pulverulent filled rubber powders, use and process for
their preparation**

5 The invention relates to pulverulent filled rubbers, a
process for their preparation, and their use.

A wide variety of publications have dealt with the
reasoning for the use of rubber powders, and also with
processes which can be used for their preparation.
10

The interest in pulverulent rubbers is likely to stem
from the processing technology used in the rubber
industry, where rubber mixtures are prepared at high
cost in terms of time, energy and personnel. The main
15 reason for this is that the raw rubber material is in
the form of bales.

Comminution of the bale and intimate mixing with
fillers, mineral oil plasticizers and vulcanization
20 auxiliaries takes place on rolls or in internal mixers
in a number of process stages. The mixture is generally
stored between stages. Downstream from the internal
mixers or rolls use is made of extruder-pelletizer
systems or extruder-roller die systems.

25 Completely new processing technology is needed to
escape from this very complicated method of rubber
processing.

For some time, therefore, there have been discussions
on the use of free-flowing rubber powders which allow
30 rubber mixtures to be processed as simply and rapidly
as thermoplastic powders.

DE-C 2822 148 discloses a process for preparing a
pulverulent filled rubber.
35

According to that patent, an aqueous filler emulsion is
added to a rubber latex, rubber solution or the aqueous



emulsion of a rubber, and the desired rubber powder is precipitated.

To avoid the grain-size-dependency of filler content given by this process, the prior art has reported the versions of DE-C 3723 213 and DE-C 3723 214.

In DE-C 3723 213, a two-stage process first incorporates $\geq 50\%$ of the filler into the rubber powder particles. In the second step, the remainder of the filler is taken up onto the rubber base particles, as they are called.

This can be regarded as a variant of the powder, since no bonding is produced between filler and rubber. US-A-4-073-755 describes the preparation of pulverulent filled rubbers in an emulsion, the pH being set to between 4 and 9. The remaining carbon black suspension is added only after the neutralisation.

However, as established by E.T. Italiaander (Vortrag 151. Technische Tagung der Rubber Div. der ACS [Paper, 151st ACS rubber division technical conference], California, May 6-9 1997 (GAK 6/1997 (50) 456-464), despite the good prospects predicted in the Delphi report (Delphi Report "Künftige Herstellverfahren in der Gummiindustrie" [Future production processes in the rubber industry] Rubber Journal, Vol. 154, No. 11, 20-34 (1972)) for pulverulent and granulated rubber, and despite numerous experiments carried out by well known polymer producers between the middle of the seventies and the early eighties on the preparation of pulverulent NBR, SBR-carbon black masterbatches and granulated NR, the standard form in which the polymers are supplied is still that of rubber bales.

One disadvantage of known processes is that milling is needed to achieve the $10\text{ }\mu\text{m}$ filler particle diameter regarded as necessary for final product quality.

This not only creates high energy costs, but also damages the filler's structure, which alongside the active surface area is an important parameter for effectiveness in rubber applications.



Secondly, the ease of handling of the products is adversely affected in the prior art by the fact that the particles adhere to one another during storage.

It is therefore an object of the invention to provide a pulverulent, filled rubber which is easy to handle, and a process for its preparation.

5 According to one embodiment of the present invention there is provided a fine-particle pulverulent rubber (rubber powder) with homogeneous distribution of filler and rubber content within the pulverulent products and in the peripheral region bonded thereto, prepared by adding an acid to bring about precipitation from aqueous mixtures which comprise filler in the form of suspensions, 10 comprise water-soluble salts of a metal of groups IIa, IIb, IIIa or VIII of the Periodic Table of the Elements, and comprise a rubber latex or aqueous emulsions of a rubber solution, where $\geq 50\%$ by weight of the fine particle filler are mixed with from 0.1 to 6.5 parts by weight of the water-soluble salts mentioned per 100 parts by weight of rubber and with a rubber latex or with an aqueous emulsion of a rubber solution, the pH of the mixture is lowered to a value within the range from 5.5 to 4.5 (first stage), the remainder of the fine-particle filler is added in the form of a suspension, and 15 the pH is lowered to about 3.2 (second stage), so that the rubber present in the mixture is completely precipitated together with the filler.

According to a second embodiment of the present invention there is provided a process for preparing fine-particle, pulverulent, filled rubbers (rubber powders) by adding an acid to bring about precipitation from aqueous mixtures which comprise filler in the form of suspensions, comprise 20 water-soluble salts of a metal of groups IIa, IIb, IIIa or VIII of the Periodic Table of the Elements, and comprise a rubber latex or comprise aqueous emulsions of a rubber solution, where $\geq 50\%$ by weight of the fine-particle filler are mixed with from 0.1 to 6.5 parts by weight of the water-soluble salts mentioned per 100 parts by weight of rubber and with a rubber latex or with an aqueous emulsion of a rubber solution, preferably in the presence of an emulsifier, the pH of the mixture is lowered to a value within the range from 5.5 to 4.5 (first stage), the remainder of the fine-particle 25 filler is added in the form of a suspension, and the pH is lowered to about 3.2 (second stage), so that the rubber present in the mixture is completely precipitated together with the filler.

Also provided by the present invention is a fine-particled, pulverulent, filled rubber prepared according to the process of the second embodiment of the invention.

30 The present invention relates to a pulverulent rubber (rubber particles) with filler content firmly bonded to the rubber matrix by the precipitation process. There can therefore be no confusion with rubber particles (key word: powdering, precipitation) which merely have a surface covering (adhesively bonded).

35 Compared with the prior art, the profile of the powders according to the invention is narrower and shifted toward smaller particle sizes (Kautschuk + Gummi + Kunststoffe 7, 28 (1975) 397-402). This circumstance makes the powders easier to process. The preparation process also causes no grain-size-dependency of filler content in the individual particles.



The pulverulent rubbers comprise from 20 to 250 phr, in particular from 50 to 100 phr, of filler (phr: parts per hundred parts of rubber).

Rubber types which have proven suitable are the following varieties, individually or in a mixture with one another:

5 natural rubber, emulsion SBR with styrene content of from 10 to 50%, butyl-acrylonitrile rubber; butyl rubbers, terpolymers made using ethylene, propylene (EPM) and unconjugated dienes (EPDM), butadiene rubbers, SBR, prepared by solution polymerisation, with styrene content of from 10 to 25%, and also 1,2-vinyl-constituent content of from 20 to 55%, and isoprene rubbers, in particular 3,4-polyisoprene.

10 Besides the rubbers mentioned, the following elastomers may be used, individually or in a mixture:

carboxyl rubbers, epoxy rubbers, trans-polypentenamers, halogenated butyl rubbers, 2-chlorobutadiene-based rubbers, ethylene-vinyl acetate copolymers, epichlorohydrins, and, if desired, also chemically modified natural rubber, e.g. epoxidised grades.

15 Fillers which should be mentioned are the white synthetic fillers and carbon blacks known from rubber processing, e.g. precipitated silicas, or naturally occurring fillers, e.g. silicious chalk, clays, etc.

Particularly suitable materials are carbon blacks, as generally used in rubber processing.

20 These include furnace blacks, gas blacks and flame blacks with an iodine adsorption value of from 5 to 1000 m²/g, a CTAB value of from 15 to 600 m²/g, a DBP adsorption of from 30 to 400 ml/100g and a 24 M4 DBP value of from 50 to 370 ml/100g, in amounts of from 5 to 250 parts, such as from 20 to 250 parts, in particular from 20 to 150 parts of carbon black, for each 100 parts of rubber, in particular from 40 to 100 parts.

Other suitable materials are the precipitated silicas known from the rubber sector.

25 These generally have an N₂ surface area, determined by the known BET method, of from 35 to 700 m²/g, a CTAB surface area of from 30 to 500 m²/g and a DPP value of from 150 to 400 ml/100g.

The product of the invention comprises from 5 to 250 parts, such as from 5 to 200 parts, in particular from 20 to 100 parts, of these silicas, based on 100 parts of rubber.

30 If white naturally occurring fillers are used, such as clays or silicious chalks with an N₂ surface area of from 2 to 35 m²/g, these are used in amounts of from 5 to 350 parts, based on 100 parts of rubber.

Filler rubber powders which comprise a mixture of silicas and carbon black are also suitable. The total amount of filler in this case is from 20 to 250 parts of filler per 100 parts of rubber.

35 Suitably, fillers present in a fine particle rubber powder of the invention comprise in total from 5 to 250 parts silica and carbon black per 100 parts rubber.

If desired, and besides the fillers mentioned above, the rubber powders of the invention comprise known processing or vulcanisation auxiliaries, such as zinc oxide, zinc stearate, stearic



5

acid, polyalcohols, polyamines, plasticisers, aging inhibitors to protect against the action of heat, light, oxygen or ozone, reinforcing resins, flame retardants, e.g. $\text{Al}(\text{OH})_3$ or $\text{Mg}(\text{OH})_2$, pigments, various crosslinking chemicals and, if desired, sulfur, in the concentrations usual in rubber technology.

5 The rubber powders of the invention have a cross-section which differs distinctly from that of the products known from the prior art. While in the ideal case these have a homogeneous distribution of the filler in the rubber composition, or vice versa, and a shell of filler particles, the invention has a homogeneous distribution of filler and rubber content in the interior of the pulverulent products and in the peripheral region bonded thereto.

10 As a function of the filler level in the particles, there are filler particles bonded within the surface, and therefore no adhesion of the particles takes place, even under pressure, e.g. if a number of sacks lie on top of one another.

This "inertisation" of the surface should not be confused with the known powdering of tacky powders with fillers. These fillers merely adhere to the surface and

15



- are rapidly released under mechanical load, e.g. in conveying systems or on storage in silos. The powdering does not then prevent blocking and caking of the fine-particle powder, as would be desirable. The invention
- 5 provides incorporation of filler particles into the surface during the precipitation process for preparing the pulverulent rubber, unlike when, as is known from the prior art, the surfaces of tacky particles have a covering of fillers serving as flow promoters. A useful
- 10 distribution between particle interior and an outer region bonded thereto is established, and depends on the level of filling with one or more of the abovementioned fillers.
- 15 In the case of a product with a high filler level (≥ 80 parts of filler per 100 parts of rubber) there are only from 1 to 10 parts of this amount of filler bonded within the outer region of the grain.
- However, if the pulverulent rubber comprises in total
- 20 < 80 parts of filler per 100 parts of rubber, there are from 10 to 20 parts thereof bonded within the outer region of the grain (peripheral region), i.e. not merely adhering by way of adhesive forces, which are less effective.
- 25 The distributions of the filler in the interior of the particles and in what is known as the peripheral region generally vary between these proportions.
- 30 As the total content of filler increases, there is less need for the tackiness of the powder to be suppressed by increased concentration of the fillers in the peripheral region.
- 35 The invention also provides a process for preparing fine-particle, pulverulent filled rubbers (rubber powders) by adding an acid to bring about precipitation from aqueous mixtures which comprise filler in the form



of suspensions, comprise water-soluble salts of a metal of groups IIa, IIb, IIIa or VIII of the Periodic Table of the Elements, and comprise a rubber latex or comprise aqueous emulsions of a rubber solution, where
5 $\geq 50\%$ by weight of the fine-particle filler are mixed with from 0.1 to 6.5 parts by weight of the water-soluble salts mentioned per 100 parts by weight of rubber and with a rubber latex or with an aqueous emulsion of a rubber solution, the pH of the mixture is
10 lowered to a value within the range from 5.5 to 4.5 (first stage), the remainder of the fine-particle filler is added in the form of a suspension, and the pH is lowered to about 3.2 (second stage), so that the rubber present in the mixture is completely
15 precipitated together with the filler.

The extent of the precipitation procedure, and its duration, which is pH- and filler-content-dependent, may readily be established by making a series of
20 measurements.

In the case of a rubber powder with a high filler level (≥ 80 phr filler), from 1 to 10 parts from this amount will generally be used as the remainder in the second
25 stage when precipitating the rubber powder.

If the rubber powder comprises less than 80 phr of filler, e.g. a total of only 50 phr, from > 10 to 20 parts of this amount are then introduced in the form of
30 a suspension into the mixture prior to completion of the precipitation procedure.

In this way the fillers are bonded into the outer region of the grain (peripheral region) in the rubber
35 powders.

There is therefore integration of these amounts of filler into the rubber surface rather than superficial



absorption onto the individual rubber particles (see DE-C 37 23213).

5 This distribution of filler, and the nature of the
bonding of the fillers within the rubber composition,
give rise to the high flowability of the powders of the
invention and prevent blocking during storage of the
powders, these properties being retained under
mechanical load during conveying, transferring to
10 silos, etc.

The fillers used comprise the abovementioned carbon
blacks in fine-particle (fluffy) form, and these
generally have an average grain diameter of from 1 to
15 9 μm , preferably from 1 to 8 μm , prior to entering into
suspension.

This makes dispersion easier, and aqueous suspensions
with filler particles of average diameter well below
20 10 μm are therefore obtained without high energy costs.
Precipitated silica may advantageously be used in the
form of a filter cake washed until free from salts.

Metal salts which may be used are those which derive
25 from elements of groups IIa, IIb, IIIa or VIII of the
Periodic Table of the Elements. This Group
classification corresponds to the earlier IUPAC
recommendation (see Periodisches System der Elemente
[Periodic Table of the Elements], Verlag Chemie,
30 Weinheim, 1985). Typical examples are magnesium
chloride, zinc sulfate, aluminum chloride, aluminum
sulfate, iron chloride, iron sulfate, cobalt nitrate
and nickel sulfate, and the salts of aluminum are
preferred. Aluminum sulfate is particularly preferred.
35 From 0.1 to 6.5 parts by weight of the salts are used
per 100 parts by weight of rubber. Acids suitable for,
and used where appropriate for, establishing the
specified pH are primarily mineral acids, e.g. sulfuric



acid, phosphoric acid and hydrochloric acid, particularly preferably sulfuric acid. However, use may also be made of carboxylic acids, e.g. formic or acetic acid.

5

The amount of acid depends on the nature and amount of the water-soluble metal salt, of the filler, of the rubber and of any alkali metal silicate present. It may readily be determined by a few exploratory experiments.

10

In one preferred embodiment of the process of the invention, up to 5 parts by weight of silica (SiO_2) in the form of an alkali metal silicate solution, preferably as waterglass with a molar $\text{Na}_2\text{O}:\text{SiO}_2$ ratio of from 2:1 to 1:4, are used per 100 parts by weight of rubber. The alkali metal silicate solution may be added to the rubber component and/or to the filler suspension. Addition to the rubber component is preferable, especially when using the continuous method.

20

The process of the invention is generally carried out as follows:

first, a filler suspension is prepared by dispersing a portion, preferably $\geq 50\%$, of the filler present in the final product in water, together with the metal salt and, where appropriate, with the alkali metal silicate solution. The total amount of water used depends on the nature of the filler and on the degree of disaggregation. The water-insoluble constituents in the filler generally amount to about 6% by weight. This value does not represent a binding restriction, and larger or smaller amounts may be used. The maximum content is limited by the pumpability of the suspension.

30

The resultant filler suspension is then mixed intimately with the rubber latex, where appropriate



comprising alkali metal silicate solution, or with the aqueous emulsion of a rubber solution, the emulsion where appropriate comprising alkali metal silicate solution, preferably in the presence of an emulsifier.

5 Known stirrer systems, e.g. propeller stirrers, are suitable for this purpose.

After the mixing, and while maintaining stirring, a pH in the range from 5.5 to 4.5 is first established,

10 whereupon core grains of rubber precipitate with constant filler content. The size of these core grains is controlled via the amount of metal salt selected within the range 0.1 to 6.5 phr. The nature of this control is such that the smallest amount of metal salt

15 gives the largest grain size.

The solids content of the latices used is generally from 20 to 25% by weight. The solids content of the rubber solutions is generally from 3 to 35% by weight,

20 and that of the rubber emulsions is generally from 5 to 30% by weight.

These mixtures and their preparation are known from the prior art.

25

For the work-up of rubber powders with filler contents ≥ 100 phr it is advantageous to lower the pH to 2.5 prior to phase separation. This is advantageously done using an acid from the abovementioned group of acids.

30

The process of the invention may be carried out either discontinuously or continuously.

The precipitated rubber powder is advantageously

35 separated off with the aid of a centrifuge and then dried, in particular in a fluidized-bed dryer, to a residual water content generally $\geq 1\%$.



During the preparation process, other processing and/or vulcanization auxiliaries may be added to the rubber powder of the invention in amounts which are generally present in vulcanizable rubber mixtures, or smaller amounts.

The rubber powders of the invention are used to prepare vulcanizable rubber mixtures. The rubber powders here may comprise all of the constituents needed to prepare the mixture. However, these preferably comprise rubber of the types listed above and fillers, but they may also be mixed with other rubbers and fillers in a conventional manner if this is a requirement for the desired rubber mixture.

The invention can prepare fine-particle rubber powder which is free-flowing and remains free-flowing even after it has been subjected to mechanical loading (e.g. conveying, packaging).

Since the material has fine particles, no milling or other comminution measures are needed to obtain fine-particle dispersions.

These then give the fine-particle rubber powders which are easy to process, giving vulcanizates with improved properties.

Examples

A. The examples describe the processing behavior of rubber powders prepared using the prior art (DE-C 3723213) and that of the rubber powders of the invention. The vulcanizate properties of these powders are also compared.

In Example 1, mixtures 1 to 4 are prepared using an N 375 carbon black in the only form generally available, namely in wet-beaded form. It first had to be milled to achieve the 10 μ (average grain



diameter) fineness needed according to DE-C 3723213. This corresponds to the position when the patent mentioned was filed. Mixtures 5 to 8 are prepared using N 375 in "fluffy" form.

5 Vulcanizates prepared using the rubber powders of the invention are found to give superior vulcanizate properties, for identical compositions of the mixtures, with shorter mixing times for the rubber mixtures.

10

B. Test standards used in the examples:

	Unit	Standard
Tensile strength	MPa	DIN 53504
300% modulus	MPa	DIN 53504
Tear propagation resistance	N/mm	DIN 53507
Shore A hardness	-	DIN 53507
DIN abrasion	nm ³	DIN 53516
Elongation at break	%	DIN 53504

C. Chemicals used in the examples:

15 TESPT bis(triethoxysilylpropyl)tetrasulfane
(Si69 Degussa AG)

Naftolen ZD plasticizer, aromatic hydrocarbons

20 6PPD N-1,3-dimethylbutyl-N'-phenyl-p-phenylenediamine

CBS N-cyclohexyl-2-benzothiazolesulfenamide



Example 1

Comparison of E-SBR mixtures filled with (82 parts) of
N 375 with varying mixing times. (Standard process
5 against process of the invention)

<u>a) Mixture specifications</u>	1-4	5-8
PB 1 (standard)	180	---
EPB I (inventive)	---	180
ZnO RS	3	3
Stearic acid	2	2
Naftolen ZD	30	30
6PPD	2	2
Wax	1	1
CBS	1.35	1.35
Sulfur	1.35	1.35

b) Mixing process

10 1st stage

Internal mixer: GK 1,5 N, volume: 1.6 L, friction: 1:1.11, ram pressure: 5.5 bar	
Mixture	1 - 8
PRM [sic] [1/min]	60
Temperature [°C]	50
Filler level	0.85
Mixing time:	
0 - 0.5'	PB I and, respectively, EPB I
	Naftolen ZD, ZnO RS, stearic acid,
	6PPD, wax
0.5'	Clean and aerate
0.5' - x'	Mix and discharge
x' = 1,2,3,4	
Batch temperature: - 150 °C	



2nd Stage

Internal mixer: GK 1,5 N, volume: 1.6 L, friction: 1:1.11, ram pressure: 5.5 bar, rpm: 40, temperature: 50°C, fill level: 0.68	
Mixing time: 0 - 0.5'	Batch stage 1 Accelerator, sulfur
0.5 - 1.5	Mix, discharge and form roll-milled sheet
Batch temperature: ~ 110 °C	

c) Tests on vulcanizate

5 1. Filler dispersion, particle size, polydispersity

	Standard				Process of the invention			
Mixing time [min]	4	3	2	1	4	3	2	1
Dispersion coefficient [%]	96.5	95.7	95.4	93.5	95.4	95.6	95.2	93.4
1st moment (um) [sic]	13.0	17.6	16.3	16.5	11.4	10.8	12.3	12.1
2nd moment (um)	21.7	28.9	28.9	27.7	15.8	13.5	17.9	16.8
3rd moment (um)	36.4	40.5	40.7	41.5	27.6	19.6	30.2	26.4
Polydispersity	0.67	0.64	0.65	0.68	0.38	0.25	0.46	0.39

The comparison shows that products from the process of the invention have particle sizes (1-3 moment) markedly smaller than in the standard, and also that the particles are less polydisperse (smaller polydispersity value)



2. Vulcanizate properties

	Standard				Process of the invention			
Mixing time [min]	4	3	2	1	4	3	2	1
<u>Test method:</u>								
Tensile strength [MPa]	15.9	15.8	15.1	15.0	16.4	16.7	16.4	16.4
300% Modulus [MPa]	6.8	7.1	6.8	7.0	7.3	7.5	7.3	7.4
Elongation at break [%]	600	570	560	550	590	590	590	600
Fracture energy [J]	145	135	127	124	147	149	148	155
Shore A hardness	64	63	65	65	64	63	64	65
<u>Ball rebound:</u>		%						
0°C	18.7	18.1	17.9	18.1	18.4	18.3	18.2	18.4
60°C	35.1	34.8	34.3	33.9	37.5	36.8	37.1	36.3
<u>Loss angle:</u>								
tan δ (0°C)	0.374	0.373	0.368	0.368	0.381	0.374	0.359	0.365
tan δ (0°C)	0.311	0.304	0.318	0.311	0.298	0.299	0.302	0.300

The comparison shows that even at the shortest mixing time (1') the products of the process claimed give an excellent property profile. The advantages are particularly marked in the strength values, fracture energy and greater elongations at break. Advantages are also found in rebound and the tan δ at 60°C.



Example 2 Comparison using an E-SBR-based car tread mixture filled with silica/TESPT (standard process against process of the invention)

5

<u>a) Mixing specifications</u>	1	2
PB II (standard)	175	---
EPB II (inventive)	---	175
ZnO RS	3	3
Stearic acid	2	2
Naftolen ZD	10	10
6PPD	2	2
Wax	1	1
CBS	1.5	1.5
DPG	2	2
Sulfur	1.5	1.5

b) Mixing process

1st stage

Internal mixer: GK 1,5 N, volume: 1.6 L, friction: 1:1.11, ram pressure: 5.5 bar	
Mixture	1 + 2
rpm [1/min]	60
Temperature [°C]	50
Filler level	0.8
Mixing time:	
0 - 3'	PB II and, respectively, EPB II Naftolen ZD, ZnO RS, stearic acid, 6PPD, wax
3'	Clean and aerate
3' - 4'	Mix and discharge
Batch temperature: - 155 °C	



2nd Stage

Internal mixer: GK 1,5 N, volume: 1.6 L, friction: 1:1.11, ram pressure: 5.5 bar, rpm: 40, temperature: 50°C, fill level: 0.68	
Mixing time: 0 - 0.5'	Batch stage 1 Accelerator, sulfur
0.5 - 1.5	Mix, discharge and form roll-milled sheet
Batch temperature: ~ 110 °C	

c) Vulcanizate properties

Test method:	Unit	1	2
Dispersion	Roughness factor	3025	960
Tensile strength	MPa	20.2	22.7
300% modulus	MPa	12.9	13.7
Elongation at break	%	410	440
Fracture energy	J	126	143
Shore A hardness	-----	78	77
DIN abrasion	mm ³	90	80

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The products from the process of the invention have better dispersion, greater strength, better reinforcement performance and better DIN abrasion.



The claims defining the invention are as follows:

1. A fine-particle pulverulent rubber (rubber powder) with homogeneous distribution of filler and rubber content within the pulverulent products and in the peripheral region bonded thereto, prepared by adding an acid to bring about precipitation from aqueous mixtures which comprise filler in the form of suspensions, comprise water-soluble salts of a metal of groups IIa, IIb, IIIa or VIII of the Periodic Table of the Elements, and comprise a rubber latex or aqueous emulsions of a rubber solution, where $\geq 50\%$ by weight of the fine particle filler are mixed with from 0.1 to 6.5 parts by weight of the water-soluble salts mentioned per 100 parts by weight of rubber and with a rubber latex or with an aqueous emulsion of a rubber solution, the pH of the mixture is lowered to a value within the range from 5.5 to 4.5 (first stage), the remainder of the fine-particle filler is added in the form of a suspension, and the pH is lowered to about 3.2 (second stage), so that the rubber present in the mixture is completely precipitated together with the filler.
2. A fine-particle rubber powder as claimed in claim 1, wherein $\geq 50\%$ by weight of the fine-grain filler material is mixed with 0.1 to 6.5 parts by weight per 100 parts by weight of caoutchouc of said water-soluble salts and a caoutchouc latex or an aqueous emulsion of a caoutchouc solution in the presence of an emulsifier.
3. A fine-particle rubber powder as claimed in claim 1 or 2 with from 20 to 250 phr content of fillers.
4. A fine-particle rubber powder as claimed in any one of claims 1 to 3, in which the filler comprises from 5 to 200 phr of a precipitated silica.
5. A fine-particle rubber powder as claimed in any one of claims 1 to 3, in which the filler comprises from 20 to 250 phr of a carbon black.
6. A fine-particle rubber powder as claimed in any one of claims 1 to 5, in which the fillers present comprise from 5 to 250 phr in total of silica and carbon black.
7. A fine-particle rubber powder as claimed in any one of claims 1 to 6 which additionally comprises customary processing and vulcanization auxiliaries.
8. A fine-particle rubber powder, being substantially as hereinbefore described with reference to any one of the examples.
9. A process for preparing fine-particle, pulverulent, filled rubbers (rubber powders) by adding an acid to bring about precipitation from aqueous mixtures which comprise filler in the form of suspensions, comprise water-soluble salts of a metal of groups IIa, IIb, IIIa or VIII of the Periodic Table of the Elements, and comprise a rubber latex or comprise aqueous emulsions of a rubber solution, wherein $\geq 50\%$ by weight of the fine-particle filler is mixed with from 0.1 to 6.5 parts by weight of the water-soluble salts cited per 100 parts by weight of rubber and with a rubber latex or with an aqueous emulsion of a rubber solution, the pH of the mixture is lowered to a value within the range from 5.5 to 4.5 (first stage), the remainder of the fine-particle filler is added in the form of a suspension, and the pH is lowered to about 3.2 (second stage), so that the rubber present in the mixture is completely precipitated together with the filler.



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10. The process as claimed in claim 9, wherein $\geq 50\%$ by weight of the fine-particle filler is mixed with from 0.1 to 6.5 parts by weight of the water-soluble salts cited per 100 parts by weight of rubber and with a rubber latex or with an aqueous emulsion of a rubber solution in the presence of an emulsifier.

11. The process as claimed in claim 9 or 10, wherein the total proportion of filler used is ≥ 80 parts phr, and from 1 to 10 parts from this amount are added as the remainder in the second stage.

12. The process as claimed in claim 9 or 10, wherein the total proportion of filler used is < 80 parts phr, and from > 10 to 20 parts from this amount are added as the remainder in the second stage.

13. The process as claimed in any one of claims 9 to 12, wherein use is made of a carbon black with an average particle size of from 1 to 9 μm .

14. The process as claimed in any one of claims 9 to 13, wherein use is made of silica in the form of a filter cake washed until free from salts.

15. The process as claimed in any one of claims 9 to 14, wherein during the precipitation of the rubber powders other customary processing or vulcanization auxiliaries are added.

16. The process as claimed in any one of claims 9 to 15, wherein the water-soluble metal salt used comprises aluminium sulfate.

17. The process as claimed in any one of claims 9 to 16, wherein operations are carried out in the presence of alkali metal silicate.

18. The process as claimed in claim 17, wherein up to 5 phr of SiO_2 are added in the form of alkali metal silicate solution.

19. The process as claimed in any one of claims 9 to 18, wherein during preparation of rubber powders with filler levels ≥ 100 phr, the pH is lowered to 2.5 prior to phase separation.

20. A process for preparing fine-particle, pulverulent, filled rubbers (rubber powders), substantially as hereinbefore described with reference to any one of the examples.

21. Fine-particled, pulverulent, filled rubbers, prepared according to the process of any one of claims 9 to 20.

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PKU Pulverkautschuk Union GmbH

Patent Attorneys for the Applicant/Nominated Person
SPRUSON & FERGUSON

