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(54) **NOVEL RHEOLOGY REGULATORS SUCH AS GROUND NATURAL CALCIUM CARBONATES OPTIONALLY TREATED WITH A FATTY ACID OR SALT AND THEIR USE**

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(57) **ABSTRACT**

The invention relates to the selection of a natural calcium carbonate crushed to a high degree of fineness, possibly treated with one or more fatty acids or one or more of their salts or mixtures thereof, and its use as a rheology regulator for polymeric compositions.

The specific surface area is 14 to 30 m²/g measured according to the BET method to ISO 4652, and the oil absorption is greater than 16 measured according to ISO 787-V (Rub-out method).

The conditions of mixing of the constituents and manufacture are improved, as well as the properties of the final product.

Related U.S. Application Data

(60) Continuation of application No. 12/470,501, filed on May 22, 2009, now abandoned, which is a division of application No. 11/733,408, filed on Apr. 10, 2007, now abandoned, which is a continuation of application No. 10/781,686, filed on Feb. 20, 2004, now Pat. No. 7,300,974, which is a continuation of application No.

**NOVEL RHEOLOGY REGULATORS SUCH AS
GROUND NATURAL CALCIUM
CARBONATES OPTIONAL TREATED
WITH A FATTY ACID OR SALT AND THEIR
USE**

[0001] This is a continuation application of U.S. application Ser. No. 12/470,501, filed May 22, 2009, which is a divisional application of U.S. application Ser. No. 11/733,408, filed Apr. 10, 2007, which is a continuation application of U.S. application Ser. No. 10/781,686, filed Feb. 20, 2004, which is a continuation of U.S. application Ser. No. 09/806,473, filed Jul. 3, 2002, which is a 371 of PCT/IB99/01625, filed Oct. 1, 1999.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The present invention relates to the technical sector of sealants, coatings, adhesives, plastiols or rubbers.

[0004] 2. Description of the Related Art

[0005] There are known, in this field, polymeric compositions, with or without fillers, for example polyurethanes with a silane termination which are used as sealants or adhesives setting in moist conditions.

[0006] In the presence of moisture, terminal silane groups undergo, in a known manner, a hydrolysis and condensation reaction. A stable siloxane lattice (Si—O—Si) then foams.

[0007] Such products have many applications in various industrial fields such as the transport and building industries.

[0008] More and more sophisticated formulations have therefore been sought, notably of the "single-component" type, capable of being applied to various substrates posing problems which are more and more difficult to resolve.

[0009] The composition of this type of formulation comprises one or more fillers, which can be one or more calcium carbonates normally referred to as "fine".

[0010] It has been discovered according to the invention that, surprisingly, the selection of a natural calcium carbonate ground to a high degree of fineness, which will be described below, or this calcium carbonate treated also as described below, makes it possible to achieve an unequalled set of satisfactory properties for the final product. These include notably good adaptability to adhesion on many types of substrate, such as certain difficult plastics, including without a prior primer coating called "primer", a reduction in the quantity of polymer required (and therefore a reduction in the cost of materials), or an appreciable reduction in the mixing time (which may reach a factor of $\frac{1}{2}$ for each step, which has an obvious great economic advantage).

[0011] It is even more surprising to find that this remarkable improvement in a set of properties of the final product does not take place, as an expert would logically predict, to the detriment of the final mechanical properties, or properties such as resistance to chemical agents or UV radiation or similar properties conventionally required of such agents.

[0012] Formulations of the plastiol type based on polyvinyl chloride (PVC) are also known.

[0013] It should be stated here that a plastiol designates a suspension of one or more PVC resins in a liquid plasticiser and additives such as mineral fillers, stabilisers, mineral and/or organic pigments, expansion agents, adhesion promoters, fluidifiers and others.

[0014] After thermal gelling, the plastiol takes the appearance of a more or less flexible compact mass.

[0015] One of the mineral fillers normally used consists of a synthetic calcium carbonate obtained chemically (precipitated calcium carbonate: PCC) such as for example the product Winnofil SPT PremiumTM from Zeneca.

[0016] According to the invention, it is proposed to use, as a rheology regulating mineral material, a natural calcium carbonate crushed to a high degree of fineness whether or not with a dispersing agent present. This natural calcium carbonate is chosen from amongst chalk, calcite or marble, alone or in a mixture, or from amongst these same calcium carbonates treated by means of at least one fatty acid or its salt or a mixture thereof and preferentially using stearic acid or its salt, such as notably calcium, magnesium or zinc stearate and highly preferably using stearic acid or its calcium salt, the whole as described in more detail below.

[0017] The rheology regulator product according to the invention is characterised in that it is a case of a natural calcium carbonate, with a specific surface area of around 14 to 30 m²/g, preferably 16 to 24 m²/g and highly preferentially around 20 m²/g, measured according to the BET method to ISO 4652.

[0018] This carbonate is possibly treated with at least one fatty acid or its salt or a mixture thereof, an acid which is an acid containing 10 to 24 atoms of carbon, and more particularly stearic acid or its salt, such as notably calcium, magnesium or zinc stearate and highly preferentially by means of stearic acid or its calcium salt, preferably at the rate of 0.01% to 5% by weight and more preferentially 1% to 4% by weight.

[0019] It should be noted here that stearic acid means stearic acids of industrial quality composed mainly of 50% to 70% octadecanoic acid and 30% to 50% hexadecanoic acid.

[0020] An original advantage of the product according to the invention is that this product is a calcium carbonate which fulfils a rheology regulating function. This function is normally devolved to the polymers and additives contained in the polymeric formulation, such as for example viscosity depressors, and the Applicant was surprised to see it fulfilled by a product of the type consisting of a material with a natural mineral filler with a high degree of fineness.

[0021] The product selected according to the invention consists of a natural calcium carbonate crushed very finely with a dispersant present or not and possibly treated by means of at least one fatty acid or its salt or a mixture thereof.

[0022] Another of its characteristics lies in its oil absorption, which is greater than 16, measured according to ISO 787-V (Rub-out method).

[0023] A calcium carbonate with a specific surface area of 19 to 26 m²/g was described in the patent EP 0 795 588. It is known according to this document as a pigment giving brightness and opacity in the papermaking field. This field of application is totally different. In addition, such a function is completely different from that of a rheology regulating action, and nothing would suggest either the function brought to light by the invention, nor the fact that this novel application could lead to a surprising set of properties having a great economic advantage.

[0024] The invention also relates to the use, as a rheology regulator for the preparation of sealants or coatings, adhesives, plastiols or rubbers, of these natural calcium carbonates crushed to a very high degree of fineness, possibly treated by means of at least one fatty acid or its salt, notably of calcium, magnesium or zinc or a mixture thereof. This acid,

which is an acid containing 10 to 24 atoms of carbon, is more particularly stearic acid or its salt, such as notably calcium, magnesium or zinc stearate and highly preferentially stearic acid or its calcium salt. The processing takes place preferably at the rate of 0.01% to 5% by weight and more preferentially 1% to 4% by weight of at least one fatty acid or its salt or a mixture thereof.

[0025] The invention also relates to the use of dispersions or suspensions, in an organic medium, of these calcium carbonates, treated or non-treated, as a rheology regulator for the preparation of sealants or coatings, adhesives, plastisols or rubbers.

[0026] The invention also relates to polymeric compositions of plastisols, sealant or coating, elastomer or rubber containing, as a rheology regulator, the said natural calcium, carbonates crushed to a high degree of fineness, possibly treated by means of at least one fatty acid or its salt or a mixture thereof.

[0027] Other characteristics and advantages of the invention will be understood more clearly from a reading of the following description and examples. These examples should not be taken to represent any limitative aspect of the invention.

[0028] In the examples, the products have the following characteristics:

[0029] Product A:

[0030] A filler of the prior art, consisting of a natural calcium carbonate of the chalk type, crushed and dried, not treated, with a mean grain diameter of 0.67 micrometres measured by means of the Sedigraph 5100 from Micromeritics, with a specific surface area of 11 m²/g measured according to the BET method to ISO 4652.

[0031] Product B:

[0032] A rheology regulator according to the invention, consisting of a natural calcium carbonate of the chalk type, crushed and dried, not treated, with a mean grain diameter of 0.60 micrometres measured by means of the Sedigraph 5100 from Micromeritics, with a specific surface area of 19.5 m²/g measured according to the BET method to ISO 4652 and with an oil absorption of 18.75 measured according to ISO 787-V (Rub-out method).

[0033] Product C:

[0034] A rheology regulator according to the invention, consisting of a natural calcium carbonate of the Urgonian calcite type, crushed by the wet method and dried, not treated, with a mean grain diameter of 0.44 micrometres measured by means of the Sedigraph 5100 from Micromeritics, with a specific surface area of 16.5 m²/g measured according to the BET method to ISO 4652 and with an oil absorption of 20 measured according to ISO 787-V (Rub-out method).

[0035] Product D:

[0036] A rheology regulator according to the invention, consisting of a natural calcium carbonate of the chalk type, crushed by the wet method and dried, treated by the use of 3% by weight stearic acid, with a mean grain diameter of 0.59 micrometres measured by means of the Sedigraph 5100 from Micromeritics, with a specific surface area, after treatment, of 16 m²/g measured according to the BET method to ISO 4652 and with an oil absorption, after treatment, of 16.3 measured according to ISO 787-V (Rub-out method).

[0037] Product E:

[0038] A rheology regulator according to the invention, consisting of a natural calcium carbonate of the Urgonian calcite type, crushed by the wet method and dried, not treated,

with a mean grain diameter of 0.58 micrometres measured by means of the Sedigraph 5100 from Micromeritics, with a specific surface area of 14.4 m²/g measured according to the BET method to ISO 4652 and with an oil absorption of 17.9 measured according to ISO 787-V (Rub-out method).

[0039] Product F:

[0040] A rheology regulator according to the invention, consisting of a natural calcium carbonate of the chalk type, crushed by the wet method and dried, treated by the use of 1% by weight stearic acid, with a resulting granulometry of 96%<1 micrometre and 39%<0.2 micrometres measured by means of the Sedigraph 5100 from Micromeritics, with a specific surface area, after treatment, of 28 m²/g measured according to the BET method to ISO 4652 and with an oil absorption, after treatment, of 19.5 measured according to ISO 787-V (Rub-out method).

[0041] Product G:

[0042] A rheology regulator according to the invention, consisting of a natural calcium carbonate of the chalk type, crushed by the wet method and dried, not treated, with a specific surface area of 22 m²/g measured according to the BET method to ISO 4652 and an oil absorption of 19.4 measured according to ISO 787-V (Rub-out method).

[0043] Product H:

[0044] A filler of the prior art consisting of a precipitated calcium carbonate sold by Zeneca under the name Winnofil SPTTM.

[0045] Product I:

[0046] A filler of the prior art, consisting of natural calcium carbonate of the chalk type, crushed by the wet method and dried, treated by means of 1% stearic acid, with a mean diameter of 1.4 micrometres measured by means of the Sedigraph 5100 from Micromeritics and with a specific surface area of 6 m²/g measured according to the BET method to ISO 4652.

[0047] Product J:

[0048] A filler of the prior art, consisting of a natural calcium carbonate of the chalk type, crushed by the wet method and dried, treated by the use of 1% by weight stearic acid, with a mean diameter of 1 micrometre measured by means of the Sedigraph 5100 from Micromeritics and a specific surface area of 10 m²/g measured according to the BET method to ISO 4652.

[0049] Product K:

[0050] A filler of the prior art consisting of a treated precipitated calcium carbonate sold by Solvay under the name Socal U1S2.

EXAMPLE 1

[0051] This example relates to the use of calcium carbonate as a rheology regulator for the preparation of plastisols.

[0052] In these tests, tests were carried out on the replacement of the synthetic calcium carbonate obtained by precipitation, of the prior art, or precipitated calcium carbonate (PCC), by the specific natural calcium carbonate according to the invention.

[0053] In a formulation of the plastisol type based on PVC (polyvinyl chloride) containing no calcium carbonate, it was sought to compare the effect of the replacement of 50% to 100% of the mineral filler normally used, namely a precipitated calcium carbonate, by a natural calcium carbonate crushed to a high degree of fineness according to the invention.

[0054] To do this, with 75 g of plastisol without filler, the calcium carbonate to be tested was mixed in a 7 cm diameter receptacle and the mixture was homogenised with a spatula. Then the mixture was put in dispersion for two minutes using a "Pendraulik"™ LD50 laboratory mixing appliance, the diameter of the dispersing disc being 5 cm, the speed of rotation of the disc being 2700 rev/min (manual setting at position 3).

[0055] The dispersing being terminated, the viscosity was measured by means of "Rheomat 120"™ equipment, a measuring appliance according to DIN 125, at 20° C.

[0056] Test No. 1:

[0057] This test illustrates the prior art and uses 20 g of a precipitated calcium carbonate sold by Zeneca under the name Winnofil SPT™ (product H) and 5 g of natural calcium carbonate sold under the name Juraperle™ BS by Jurawieiss.

[0058] Test No. 2:

[0059] This test illustrates the prior art and uses 13 g of a precipitated calcium carbonate sold by Zeneca under the name Winnofil SPT™ (product H) and 12 g of product A according to the prior art.

[0060] Test No. 3:

[0061] This test illustrates the invention and uses 25 g of product B according to the invention.

[0062] Test No. 4:

[0063] This test illustrates the prior art and uses 20 g of a precipitated calcium carbonate sold by Zeneca under the name Winnofil SPT™ (product H).

[0064] Test No. 5:

[0065] This test illustrates the invention and uses 10 g of a precipitated calcium carbonate sold by Zeneca under the name Winnofil SPT™ (product H) and 15 g of product D according to the invention.

[0066] Test No. 6:

[0067] This test illustrates the invention and uses 10 g of a precipitated calcium carbonate sold by Zeneca under the name Winnofil SPT™ (product H) and 15 g of product C according to the invention.

[0068] Test No. 7:

[0069] This test illustrates the invention and uses 13 g of a precipitated calcium carbonate sold by Zeneca under the name Winnofil SPT™ (product H) and 12 g of product E according to the invention.

[0070] Test No. 8:

[0071] This test illustrates the invention and uses 10 g of a precipitated calcium carbonate sold by Zeneca under the name Winnofil SPT™ (product H), 5 g of natural calcium carbonate sold under the name Juraperle™ BS by Jurawieiss and 10 g of product D according to the invention.

[0072] Test No. 9:

[0073] This test illustrates the invention and uses 10 g of a precipitated calcium carbonate sold by Zeneca under the name Winnofil SPT™ (product H), 5 g of natural calcium carbonate sold under the name Juraperle™ BS by Jurawieiss and 10 g of product E according to the invention.

[0074] Test No. 10:

[0075] This test illustrates the invention and uses, for a mixture with 72 g of plastisol, 10 g of a precipitated calcium carbonate sold by Zeneca under the name Winnofil SPT™ (product H), 5 g of natural calcium carbonate sold under the name Juraperle™ BS by Jurawieiss and 13 g of product E according to the invention.

[0076] The results of the viscosity measurements as a function of the speed of flow according to DIN 125 at 20° C. are set out in Tables Ia and Ib below.

TABLE Ia

TEST N°	Prior art 1	Prior art 2	Invention 3	Prior art 4	Invention 5	Viscosity mPa · s					
COMPOSITION	Plastisol without filler (in g)	75.00	75.00	75.00	75.00	75.00	75.00	75.00	75.00	75.00	75.00
	PCC (in g)	20.00	13.00	—	25.00	—	—	—	—	—	10.00
	Juraperle™ BS (in g)	5.00	—	—	—	—	—	—	—	—	—
	Product A (in g)	—	12.00	—	—	—	—	—	—	—	—
	Product B (in g)	—	—	25.00	—	—	—	—	—	—	—
	Product D (in g)	—	—	—	—	—	—	—	—	—	15.00
	Weight of mixture (in g)	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
RHEOLOGY	20	18200	17700	15200	17600	17100					
	40	10040	9650	8430	9900	9650					
	60	7260	7100	6280	7200	7100					
	80	5890	5730	5170	5850	5700					
	100	5100	4880	4390	5000	4800					
	120	4490	4380	3980	4450	4350					
	140	4100	4020	3550	3990	3990					
	160	3780	3650	3310	3650	3650					
	180	3460	3400	3110	3400	3380					
	200	3320	3220	2950	3190	3170					
	220	3140	3030	2780	3110	3000					
	240	3000	2870	2620	2890	2820					
	260	2870	2760	2520	2740	2700					
	280	2760	2680	2420	2610	2600					
	300	2660	2570	2350	2490	2490					

TABLE Ib

Test N°		Invention 6	Invention 7	Invention 8	Invention 9	Invention 10
COMPOSITION	Plastisol without filler (in g)	75.00	75.00	75.00	75.00	72.00
	PCC (in g)	10.00	13.00	10.00	10.00	10.00
	Juraperle™ BS (in g)	—	—	5.00	5.00	5.00
	Product C (in g)	15.00	—	—	—	—
	Product D (in g)	—	—	10.00	—	—
	Product E (in g)	—	12.00	—	10.00	13.00
	Weight of mixture (in g)	100.00	100.00	100.00	100.00	100.00
Viscosity mPa · s						
	Speed of flow s ⁻¹	Test N° 6	Test N° 7	Test N° 8	Test N° 9	Test N° 10
RHEOLOGY	20	12700	17300	13100	12500	17000
	40	7280	9450	7600	7160	9500
	60	5360	6950	5630	5250	7030
	80	4430	5600	4850	4330	5580
	100	3820	4830	4040	3780	4800
	120	3400	4230	3600	3300	4320
	140	3110	3950	2290	3000	3790
	160	2860	3550	3040	2770	3550
	180	2680	3260	2850	2590	3280
	200	2520	3110	2680	2480	3080
	220	2400	2910	2550	2320	2950
	240	2290	2790	2430	2200	2800
	260	2190	2670	2340	2130	2710
	280	2120	2580	2250	2050	2610
	300	2040	2490	2180	1970	2490

[0077] A reading of the table shows that the use of the calcium carbonate according to the invention makes it possible to regulate the rheological behaviour of the plastisol composition, even when 100% of the precipitated calcium carbonate has been replaced by the calcium carbonate according to the invention.

EXAMPLE 2

[0078] This example relates to the study of the conventional mechanical properties conferred by product F according to the invention, that is to say a natural chalk crushed so as to obtain a specific surface area of 28 m²/g, on mixtures based on plasticised PVC, in comparison with mixtures filled by means of natural calcium carbonates well known in the prior art.

[0079] For each of these tests, the following mixture was produced:

“SOLVIC 239 D” PVC sold by Solvay	100
Dioctyl phthalate (Jayflex™ DOP from Exxon)	50
Dibasic lead sulphate	1
Tribasic lead sulphate	2
Filler to be tested	80

[0080] Preparation of the Composition:

[0081] The dry mixtures or “dry blends” were prepared in a “GUEDU”™ adiabatic mixer at 100° C. for a period of 15 minutes. The mixtures were then gelled on cylinders at 150° C. in a mixing mill. For all the mixtures, this operation was performed in 12 minutes.

[0082] Sheets of 90×90×2 mm were then moulded at 160° C. after preheating of the blank for 3 minutes and pressurising for 2 minutes before cooling, using a compression press.

[0083] The test pieces necessary for determining the mechanical properties were cut from these sheets.

[0084] The different calcium carbonates tested were:

[0085] Test No. 11:

[0086] This test illustrates the prior art and uses a natural chalk, treated with 1% stearic acid, with a specific surface area of 6 m²/g measured according to the BET method to ISO 4652 (product 1).

[0087] Test N° 12:

[0088] This test illustrates the prior art and uses a natural chalk, treated with 1% stearic acid, with a specific surface area of 10 m²/g measured according to the BET method to ISO 4652 (product J).

[0089] Test No. 13:

[0090] This test illustrates the invention and uses product F according to the invention.

[0091] The mechanical properties were assessed by means of dynamometric tests (tensile strength, breaking elongation, modulus 100%) carried out using the Instron™ equipment according to ISO 37, at a temperature 23° C. and with a traction speed of 10 cm/min.

[0092] The ASTM-C tear strength was for its part determined according to the method of ISO R-34 and Shore C hardness according to the method of ISO 868.

[0093] The results of these measurements of mechanical properties are set out in Table II below.

TABLE II

Test No.	Prior art 11	Prior art 12	Invention 13
Tensile strength (daN/cm ²)	128	130	136
Breaking elongation (%)	300	260	172

TABLE II-continued

Test No.	Prior art 11	Prior art 12	Invention 13
Modulus 100% (daN/cm ²)	83	106	127
ASTM-C tear strength (daN/cm)	47	56	58
Shore C hardness at 15 s (in daN/cm)	60	64	74

[0094] It can be seen that the mechanical properties obtained are excellent and are superior to those obtained with natural calcium carbonates which are crushed but which have a specific surface area outside the scope of the invention.

[0095] The invention therefore makes it possible to optimise the formulations according to the mechanical property to be favoured.

EXAMPLE 3

[0096] This example relates to the use of calcium carbonates as a rheology regulator for the preparation of elastomer based on natural or synthetic rubber.

[0097] It was sought in this example to assess the effect of the specific surface area of a crushed natural chalk according to the invention on the properties of mixtures based on natural and synthetic rubbers, in comparison with a precipitated calcium carbonate of the prior art.

[0098] To do this, for each of Tests 14 and 15, the following mixture was produced;

Natural rubber (smoked sheet quality RSS 1)	100
SBR rubber (styrene-butadiene, Cariflex™ 1502 from Shell)	40
Zinc oxide (snow quality) from Vieille Montagne	5
Stearic acid	2
Sulphur	1.5
N-cyclohexyl 2 benzothiazyl sulphenamide (Vulcafor™ CBS from Vulnax)	1
Tetramethylthiuram disulphide (Vulkacit™ DTMT from Bayer)	0.5
Calcium carbonate to be tested	100

[0099] Test No. 14:

[0100] This test illustrates the prior art and uses a precipitated calcium carbonate sold by Solvay under the name Socal U1S2 (product K).

[0101] Test No. 15:

[0102] This test illustrates the invention and uses product F according to the invention.

[0103] These two tests were carried out as follows:

[0104] A pure gum master-batch was prepared, by the successive incorporation of the various ingredients, except for calcium carbonate, according to the normal technique of experts, on a mixing mill regulated for temperature, by mixing for 10 minutes (friction I/I,4) at 60° C.

[0105] From this master-batch two samples were taken in which the calcium carbonates to be tested had been incorporated, by mixing at 60° C. for 12 minutes.

[0106] After determination of the vulcanisation optima at 155° C. using a Monsanto flow meter, sheets were moulded and vulcanised to this optimum in order to effect the measurement of the mechanical properties according to the same operating method as in the previous tests.

[0107] The results of the mechanical properties are set out in Table III below.

TABLE III

Test No.	Prior art 14	Invention 15
Vulcanisation optimum at 155° C.	5 min. 15 s	5 min.
Tensile strength daN/cm ²	119	109
Modulus 300% daN/cm ²	41	39
Elongation %	500	485
Tear strength ASTM-C daN/cm	23	26
Shore A hardness (15 s)	61	61

[0108] It can be seen that the product according to the invention reduces the implementation time (the vulcanisation optimum) as well as the tear strength properties.

[0109] Likewise Tests 16, 17 and 18 were carried out using the following formulation:

SBR rubber (styrene-butadiene, Cariflex™ 1502 from Shell)	40
Natural rubber (smoked sheet quality RSS 1)	60
Zinc oxide (snow quality) from Vieille Montagne	5
Stearic acid	2
Sulphur	2
N-cyclohexyl 2 benzothiazyl sulphenamide (Vulcafor™ CBS from Vulnax)	0.9
Diorthotolylguanidine accelerator (Vulkafor™ DOTG from Vulnax)	0.3
Calcium carbonate to be tested	100

[0110] Test No. 16:

[0111] This test illustrates the prior art and uses a precipitated calcium carbonate sold by Solvay under the name Socal U1S2 (product K).

[0112] Test No. 17:

[0113] This test illustrates the prior art and uses a calcium carbonate of the chalk type, crushed by the wet method and dried, treated, with a mean diameter of 1.4 micrometres measured by means of the Sedigraph 5100 from Micromeritics and with a specific surface area of 10 m²/g measured according to the BET method to ISO 4652 (product J).

[0114] Test No. 18:

[0115] This test illustrates the invention and uses product G according to the invention.

[0116] From this master batch manufactured with the same operating method as in the previous test, three samples were taken in which the calcium carbonates to be tested had been incorporated, by mixing at 60° C. for 12 minutes.

[0117] After determination of the vulcanisation optima, sheets were moulded and vulcanised to this optimum in order to effect a measurement of the mechanical properties according to the same operating method as for the previous tests.

[0118] The results of the mechanical properties are set out in Table IV below.

TABLE IV

Test No.	Prior art 16	Prior art 17	Invention 18
Vulcanisation optimum at 150° C.	23 min. 30 s	16 min. 45 s	11 min.
Tensile strength (daN/cm ²)	1.22	132	132
Modulus 300% (daN/cm ²)	16.5	20	20
Elongation %	695	715	695
ASTM-C tear strength (daN/cm)	23	28	28
Shore A hardness (15 s) in (daN/cm)	51	50	50

[0119] It can be seen that the product according to the invention improves the implementation time (the vulcanisation optimum) and the majority of the mechanical properties.

EXAMPLE 4

[0120] A second series of tests (Tests 19 and 20) were carried out in a natural rubber 40 per filled with a mineral filler with the basic formula:

Natural rubber (smoked sheet quality RSS 1)	100
Coumarone resin 60/70	5.6
Rosin	3
Zinc oxide (snow quality) from Vieille Montagne	40
Stearic acid	0.5
Oil	4.3
Benzothiazyl disulphide accelerator (Vulcafor™ MBTS from Vulnax)	1
Diphenylguanidine accelerator (Vulcafor™ DPG from Vulnax)	0.36

[0121] The calcium carbonates to be tested were:

[0122] Test No. 19:

[0123] A precipitated calcium carbonate (product K) for this test, which illustrates the prior art.

[0124] Test No. 20:

[0125] A natural calcium carbonate according to the invention (product G) for this test, which illustrates the invention.

[0126] The results of the mechanical properties, measured with the same operating method as for the following tests, are set out in Table V below.

TABLE V

Test No.	Prior art	Invention
	19	20
Vulcanisation optimum at 150° C.	7 min. 15 s	8 min. 15 s
Tensile strength (daN/cm ²)	246	246
Modulus 300% (daN/cm ²)	32	31
Elongation %	710	710
Shore A hardness (15 s) in (daN/cm)	45	46.5

[0127] It can be seen that the product according to the invention makes it possible to obtain equivalent mechanical property results, even by completely replacing the precipitated calcium carbonate with a natural calcium carbonate.

1. A method of regulating the viscosity as a function of speed of flow during the application of a plastisol to a substrate, comprising adding natural calcium carbonate, crushed to a high degree of fineness, with a specific surface area of around 14 to 30 m²/g measured according to the BET method to ISO 4652, to a plastisol, and adjusting the amount of added

natural calcium carbonate in order to achieve a desired relationship between speed of flow and viscosity of the plastisol.

2. The method of claim 1, wherein the calcium carbonate has a specific surface area of around 16 to 24 m²/g.

3. The method of claim 1, wherein the calcium carbonate has a specific surface area of around 20 m²/g.

4. The method of claim 1, wherein the natural calcium carbonate has a specific surface area of at least 14.4 m²/g and up to around 30 m²/g.

5. The method of claim 1, wherein the natural calcium carbonate has a specific surface area of at least 16 m²/g and up to around 30 m²/g.

6. The method of claim 1, wherein the natural calcium carbonate has a specific surface area of at least 16.5 m²/g and up to around 30 m²/g.

7. The method of claim 1, wherein the natural calcium carbonate has a specific surface area of no higher than 22 m²/g and at least around 14 m²/g.

8. The method of claim 1, wherein the natural calcium carbonate has a specific surface area of no higher than 28 m²/g and at least around 14 m²/g.

9. The method of claim 1, wherein the natural calcium carbonate is treated with at least one fatty acid containing 10 to 24 carbon atoms or a salt thereof selected from the group consisting of calcium salt, magnesium salt, zinc salt, and mixtures thereof.

10. The method of claim 1, wherein the natural calcium carbonate is treated with stearic acid or a calcium salt thereof in a proportion of around 0.01% to 5% by weight.

11. The method of claim 1, wherein the natural calcium carbonate is treated with stearic acid or a calcium salt thereof in a proportion of around 1% to 4% by weight.

12. The method of claim 1, wherein the natural calcium carbonate has an oil absorption which is greater than 16 g/100 g measured according to ISO 787-V (Rub-out method).

13. The method of claim 1, wherein the plastisol is PVC-based.

14. A method of regulating the rheology during the application of a plastisol to a substrate, comprising adding natural calcium carbonate, crushed to a high degree of fineness, with a specific surface area of around 14 to 19.5 m²/g measured according to the BET method to ISO 4652, to a plastisol, in an amount to regulate the rheology of the plastisol.

15. The method of claim 14, wherein the natural calcium carbonate has a specific surface area no higher than 16.5 m²/g and at least around 14 m²/g.

16. The method of claim 14, wherein the natural calcium carbonate has an oil absorption which is greater than 16 g/100 g measured according to ISO 787-V (Rub-out method).

17. The method of claim 14, wherein the plastisol is PVC-based.

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