

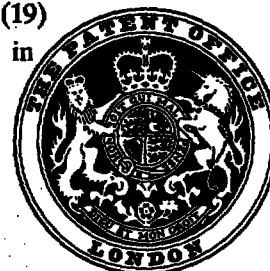
PATENT SPECIFICATION

(11)

1 588 060

1 588 060

- (21) Application No. 53156/77 (22) Filed 21 Dec. 1977 (19)
(31) Convention Application No. 2747277 (32) Filed 21 Oct. 1977 in
(33) Fed. Rep of Germany (DE)
(44) Complete Specification Published 15 Apr. 1981
(51) INT. CL.³ C08K 9/12 5/54
(52) Index at Acceptance
C3L DN
C3W 113 203
(72) Inventors: LOTHAR ROTHBUHR
SIEGFRIED WOLFF



(54) A GRANULAR ORGANO-SILANE PREPARATION

(71) We DEUTSCHE GOLD-UND SILBER-SCHEIDEANSTALT VORMALS ROESSLER a body corporate organised under the laws of Germany of 9 Weissfrauenstrasse, 6 Frankfurt 1, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to a granular organo-silane preparation.

More particularly the invention relates to dustless, flowable, granular preparations composed of organo-silanes which are liquid at room temperature and specific types of carbon black. The silane preparations are distinguished, in particular, by surprisingly good stability in storage, by stability of the silane portion in hydrolysis and by ease of working into rubber mixtures.

A number of organo silicon compounds are known to be recommended and used in rubber technology. Particularly well known are sulphur-containing alkoxy silanes which are eminently suitable as adhesion media and reinforcing agents for vulcanizates composed of rubber mixtures containing silicate fillers. The organo-silanes according to U.S. Patent No. 3,842,111 are particularly suitable for this purpose.

Also known are the reinforcing additives for the said rubber vulcanizates prepared from the liquid organo-silanes according to U.S. Patent No. 3,842,111 and silicate fillers (see German Patent No. 22 55 577 and U.S. Patent No. 3,997,356).

All organo-silanes which have been used hitherto in the art for the said purpose are hydrolyzable liquids which condense to form high molecular weight polysiloxanes upon contact with gaseous or liquid water with elimination of alcohol and which may thus lose, at least in part, their effectiveness as reinforcing additives.

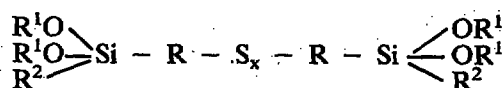
In the rubber-processing industry, all auxiliary chemicals which are liquid at room temperature, thus also the liquid organo-silanes, have serious disadvantages in comparison with solid auxiliary chemicals, for example, they are more difficult to store in silos, give rise to problems in weighing up and, particularly when preparing the mixtures on roller mixers, are difficult to mix in.

A certain amount of progress is made by converting the liquid organo-silanes into pulverulent products, for example by mixing them with highly dispersed precipitated silicas, but this is not the best solution since it is also relatively difficult to introduce pulverulent products into rubber mixtures, prolonged mixing periods are required, dust is raised and the environment and the machinery are consequently damaged and contaminated. In addition, it has been found that the addition of the organo-silanes to the silicate-containing filler particles which is taking place does not eliminate the sensitivity of the silanes to hydrolysis and that the silanes clearly lose their effectiveness during storage of the product. This is expressed, for example, in a drop in the final value of cross-linking during rubber vulcanization. Europa Chemie No. 17/77 page 366 refers to a liquid polysulphide containing organo silane reinforcing additive in the form of 50% mixtures with silica (pulverulent) and with carbon black (beaded-dusters).

Now it has surprisingly been found that when using the silane preparation according to the invention, for example, in rubber mixtures, all the disadvantages mentioned are overcome and, in addition, unexpected advantages are obtained.

The present invention provides a granular organo-silane preparation composed of

a) from 30 to 60 % by weight of one or more organo silanes corresponding to the formula



5 in which

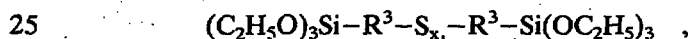
R^1 represents an alkyl radical containing from 1 to 3 carbon atoms,
 R^2 represents an alkyl radical or an alkoxy radical containing from 1 to 3 carbon atoms,
 R represents an alkylene radical containing from 1 to 5 carbon atoms and
 x has a value from 2.0 to 6.0, and,

10 b) from 70 to 40% by weight of one or more carbon blacks with BET specific surface areas between 30 and 140 m^2/g and average primary particle sizes between 20 and 60 nm, the percentages being based on the weight of the organo-silane preparation.

The sum of the organo-silane and carbon black fractions amounts to 100 percent by weight in each case in the context of the invention.

15 The organo-silanes which are preferably used are those in which R^2 represents an alkoxy radical according to formula I. These are, therefore, organo-silanes each having three alkoxy groups on the silicon atom which, in addition, have an alkylene radical (R) containing from 2 to 4 carbon atoms and from 2 to 4 sulphur atoms (x). In particular, the industrial product bis-(3-triethoxy-silylpropyl)-tetrasulphide is very suitable for the purpose of the present invention. Mixtures of several organo-silanes may also be used for producing the preparation. In this context "several" means, in particular, 2, 3 or 4.

Particularly advantageous organo-silane preparations according to the invention are composed of from 45 to 57% by weight of an organo-silane, corresponding to the formula



in which

R^3 represents an alkylene radical containing from 2 to 4 carbon atoms and
 x_1 has a value from 2.0 to 4.0

30 and from 55 to 43% by weight of HAF carbon black having the following test data:

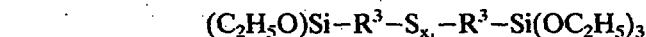
BET specific surface area 78 m^2/g (± 3)

35 Average primary particle size (arithmetic average) 27 nm (± 2)

pH value 9 (± 1)

40 Dibutylphthalate absorption 100 ml/100 g (± 5)

A further advantageous organo-silane preparation according to the invention is composed of 30% by weight of one or more organo-silanes corresponding to the formula



in which

R^3 represents an alkylene radical containing from 2 to 4 carbon atoms and
 x_1 has a value from 2.0 to 4.0, and

70% of a furnace carbon black having the following test data:

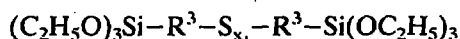
50 BET specific surface area 45 m^2/g (± 3)

55 Average primary particle size (arithmetic average) 56 nm (± 4)

pH value 9 (± 1)

Dibutylphthalate absorption 44 ml/100 g (± 5).

60 A still further advantageous organo-silane preparation according to the invention is composed of 60% by weight of one or more silanes corresponding to the formula



in which,

R^3 represents an alkylene radical containing from 2 to 4 carbon atoms and x_1 has a value from 2.0 to 4.0, and 40 % by weight of a carbon black having the following test data:

BET specific surface area 78 m²/g (± 3)

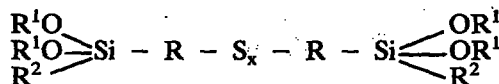
Average primary particle size (arithmetic average) 27 nm (± 2)

pH value 9 (± 1)

Dibutylphthalate absorption 155 ml/100 g (± 5).

The present invention also provides a process for the preparation of a granular organo-silane preparation composed of

a) from 30 to 60% by weight of one or more organo-silanes corresponding to the formula



in which

R^1 represents an alkyl radical containing from 1 to 3 carbon atoms, R^2 represents an alkyl radical or an alkoxy radical containing from 1 to 3 carbon atoms, R represents an alkylene radical containing from 1 to 5 carbon atoms and x has a value from 2.0 to 6.0, and

b) from 70 to 40% by weight of one or more carbon blacks,

which comprises adding the organo-silane or mixture of organo-silanes to the carbon black with thorough mixing, for example using conventional fast-acting mixers such as powder mixers, propeller mixers or bead machines, until the granulate formed is dust-free.

The known types of carbon black with BET specific surface areas (see J.A.L.S. 60 p. 309 (1938) between 30 and 140 m²/g and average primary particle sizes between 20 and 60 nm (nanometers) may be used for the production of the organosilane preparation. So-called furnace carbon blacks and from these, in turn, carbon blacks of the HAF class, are preferably used. The term "HAF" is an abbreviation known in rubber technology for "high abrasion furnace". Particularly suitable carbon blacks are the commercially available pulverulent Printex types of carbon black made by Degussa having BET specific surface areas of between about 30 and 140 m²/g and average primary particle sizes (arithmetic average) of between about 20 and 60 nm (nanometer). Mixtures of various types of carbon black may also be used for the production of the silane preparations according to the invention, for example mixtures composed of Printex 60 and Printex 300 or mixtures of Printex 30 and Printex 300. Printex is a Trade Mark.

In order to produce the new preparations, the starting materials are placed in suitable apparatus and mixed. Production is generally completed in a few seconds. If the given proportions by weight are used, powder and paste are not formed, but rather a gritty or bead-shaped granulate. Apparatus advantageously used for production are the trough-shaped powder mixers known *per se* with a rotating propeller element. Such mixers have been used hitherto for mixing pulverulent plastics and for preparing PVC dry blends. At conventional speeds of between about 300 and 3000 revolutions per minute, the granulated preparation is ready in a few seconds, for example within about 10 to 30 seconds.

The new organo-silane preparations have many and surprising advantages. They are suitable for storage in silos, are easy to measure out and may be worked into the rubber mixtures particularly well and in reduced mixing periods. The organo-silane active material is insensitive to hydrolysis in the preparation. The preparation itself is extremely stable in storage. The fact that the preparations are readily dispersible in rubber mixtures is striking. The organo-silane preparations according to the invention are more effective in conventional vulcanization of rubber mixtures using elementary sulphur than compositions corresponding to the known mixtures of silica and silane and, surprisingly, it is also more effective to use the organo-silane preparations than a corresponding quantity of the pure organo-silane. If so-called elementary sulphur-free cross-linking is carried out in accordance with Germany Offenlegungsschrift No. 25 36 674, then the organo-silane preparation according to the invention is optimally effective.

25

4

1 588 060

4

The new organo-silane preparations thus achieve the object according to the invention of producing a silane preparation which is very stable in storage owing to its composition, that is to say fully guarantees its effectiveness as a reinforcing additive in rubber mixtures even after a prolonged period of storage irrespective of climatic conditions. It has surprisingly been found that the use of carbon black as a support component for the organo-silane preparation gave the decisive technical progress.

The invention is illustrated by the following Examples.

Example 1

Printex 30 was used as carbon black, this carbon black having the following test data:

BET specific surface area	78 m ² /g	
Average primary particle size (arithmetic average)	27 nm	
pH value	9	
Dibutylphthalate adsorption (abbreviated as DBP-Abs.) (ASTM D 2414)	100 ml/100 g	

10 kg of the furnace carbon black Printex 30 was weighed in a trough-shaped powder mixer having a propeller-like mixer element and a capacity of 150 litres, 10 kg of bis-(3-triethoxysilylpropyl)-tetrasulphide (abbreviation: Si 69) was then added and the two components were worked up for 25 seconds at 360 r.p.m. The apparatus used is described in German Offenlegungsschrift No. 1,592,861. After raising the discharge flap, 20 kg of a granulate having a particle size of about 0.8 mm was ejected. The granulate was dust-free, non-adherent and readily flowable.

Example 2

The following organo-silane preparation was produced not in a discontinuous process but in a continuous mode of operation. The bead machine shown in Figure 2 in German Patent No. 2,147,503 was used for this purpose. 160 kg per hour of practically dust-free granulate was accordingly produced in bead form from 80 kg of Printex 30 per hour and 80 kg of the silane Si 69 per hour.

Example 3

The following quantities and types of carbon black, as well as the silane Si 69, were used in the specified quantities for the production of silane preparations according to the invention:

Type of Carbon Black and quantity in percent by weight	BET specific surface area in m ² /g	DBP-Abs. according to ASTM D 2414 in ml/100g	Silane Si 69 in % by weight
Printex 200 : 70	45	44	30
Printex 400 : 65	100	48	35
Printex 3 : 45	80	135	55
Printex 3H : 40	78	155	60

Production was carried out as in Example 1. The silane preparations produced had optimum granulate properties: Bead form of from 0.8 to 1.0 mm average particle size and bead dust of from 0.5 to 2.0% (see DIN 53 583)

Example 4

Following the mode of operation described in Example 1,

- | | | | |
|----|-----|--|----|
| 5 | 4.1 | 200 g Printex 30 with 200 g of the silane
(CH ₃ O) ₃ Si(CH ₂) ₃ -S-S-(CH ₂) ₃ -Si(OCH ₃) ₃ | 5 |
| | 4.2 | 200 g Printex 30 with 200 g of the silane
(CH ₃ O) ₃ Si(CH ₂) ₃ -S-S-S-(CH ₂) ₃ -Si(OCH ₃) ₃ | |
| 10 | 4.3 | 200 g Printex 30 with 200 g of the silane
(CH ₃ O) ₃ Si(CH ₂) ₃ -S-S-S-S-(CH ₂) ₃ -Si(OCH ₃) ₃ | 10 |

were homogenized with each other in a 7 litre pan mixer. The mixing period was ten seconds at 1400 r.p.m. Dust-free, flowable, readily processible granulates were also obtained in this case.

Example 5

In order to examine the stability in storage and the proof of effectiveness in relation to the duration of storage, a known pulverulent mixture composed of 50% by weight of silica Ultrasil VN₃ and 50% by weight of bis-(triethoxysilylpropyl)-tetrasulphide on the one hand and a granulated dust-free preparation according to the invention composed of 50% by weight of carbon black Printex 30 and 50% by weight of bis-(triethoxysilylpropyl)-tetrasulphide on the other hand were introduced into a synthetic rubber test mixture based on a styrene-butadiene rubber (SBR 1500). The rubber mixtures had the following composition:

- | | | |
|----|--|----|
| | 100 parts by weight of styrene-butadiene rubber (SBR 1500) | |
| | 35 parts by weight of silica filler (Ultrasil VN ₃) | |
| 30 | 10 parts by weight of organo-silane preparation or organo-silane mixture (see above) | 30 |
| | 3 parts by weight of zinc oxide | |
| | 2 parts by weight of stearic acid | |
| | 2 parts by weight of sulphur | |
| 35 | 1 part by weight of sulfenamide accelerator (N-cyclohexyl-2-benzothiazal-sulfenamide). | 35 |

These mixtures were examined at 155°C in a Monsanto-Rheometer at an amplitude of 3° and 3 cycles.

The following unknown quantities were evaluated:

- | | | | |
|----|----------------------|---|----|
| 40 | D_{α} = | maximum torque | 40 |
| | D_a = | minimum torque | |
| 45 | $D_{\alpha} - D_a$ = | torque caused by cross-linking
(end value of cross-linking) | 45 |
| | t_i = | incubation period | |
| 50 | K_v = | rate constant of the crosslinking
reaction according to a first order
reaction law. | 50 |
| | $t_{5\%}$ = | period for the cross-linking
reaction of 5% of the total of
cross-linking | |
| 55 | $t_{95\%}$ = | period for the cross-linking reaction
of 95% of the total of cross-linking | 55 |

27

Test Results

a) When using the granulated dust-free preparation composed of 50% by weight of Printex 30 carbon black and 50% by weight of bis-(triethoxysilylpropyl)-tetrasulphide.

			Results when mixing in the preparation directly after production	Results when mixing in after storing the preparation for one year	
5					5
10	D_α	mkp	1.186	1.193	10
	D_A	mkp	0.071	0.078	
	$D_\alpha - D_A$	mkp	1.115	1.115	
15	t_1	sec	699	679	15
	$K_1 \times 10^3$	min^{-1}	131	140	
20	$t_{5\%}$	min	10.4	10.2	20
	$t_{95\%}$	min	33.3	32.6	

b) When using the pulverulent mixture composed of 50% by weight of silica filler and 50% by weight of bis-(triethoxy-silylpropyl)-tetrasulphide, for comparison.

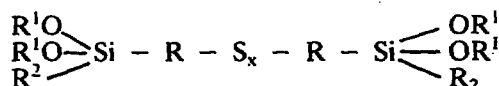
			When incorporating the mixture directly after production	When incorporating the mixture after storage for 1 year	
30					30
	D_α	mkp	1.190	1.141	
	D_A	mkp	0.089	0.141	
35	$D_\alpha - D_A$	mkp	1.101	1.000	35
	t_1	sec	685	698	
	$K_1 \times 10^3$	min^{-1}	117	69	
40	$t_{5\%}$	min	10.0	10.5	40
	$t_{95\%}$	min	30.0	55.0	

After storing the granulated dust-free preparation composed of 50% by weight of Printex 30 carbon black and 50% by weight of bis-(triethoxysilylpropyl)-tetrasulphide for 1 year, no change is noted in the properties of the test mixture. On the other hand, the pulverulent mixture composed of silica filler and silane demonstrates a clear drop in the final value of cross-linking ($D_\alpha - D_A$) and a characteristic drop in the rate constant of the cross-linking reaction K_1 , which denotes a rise in the vulcanization period to practically double ($t_{95\%}$).

The new granular organo-silane preparations are used predominantly in rubber mixtures and rubber compositions of any type, both in so-called master batches and in mixtures to be used immediately, owing to their good stability in storage, their resistance to hydrolysis and their surprising readiness of working in. The term "of any type" relates in particular to the known types of rubber of natural and synthetic origin and to the fillers which are conventional in rubber technology such as preferably carbon blacks, but also the known white fillers such as silica fillers, silicate fillers, kaolin, clays, carbonates, quartz and kieselguhr as well as mixtures of the said fillers including and preferably carbon black.

WHAT WE CLAIM IS:

1. A granular organo-silane preparation composed of
a) from 30 to 60 % by weight of one or more organo-silanes corresponding to the formula



Test Results

a) When using the granulated dust-free preparation composed of 50% by weight of Printex 30 carbon black and 50% by weight of bis-(triethoxysilylpropyl)-tetrasulphide.

			Results when mixing in the preparation directly after production	Results when mixing in after storing the preparation for one year	
5					5
10	D_α	mkp	1.186	1.193	10
	DA	mkp	0.071	0.078	
15	$D_\alpha - Da$	mkp	1.115	1.115	15
	t_I	sec	699	679	
	$K_I \times 10^3$	min^{-1}	131	140	
20	$t_{5\%}$	min	10.4	10.2	20
	$t_{95\%}$	min	33.3	32.6	

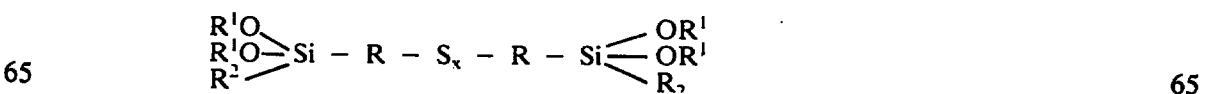
b) When using the pulverulent mixture composed of 50% by weight of silica filler and 50% by weight of bis-(triethoxy-silylpropyl)-tetrasulphide, for comparison.

			When incorporating the mixture directly after production	When incorporating the mixture after storage for 1 year	
30					30
	D_α	mkp	1.190	1.141	
	Da	mkp	0.089	0.141	
35	$D_\alpha - Da$	mkp	1.101	1.000	35
	t_I	sec	685	698	
40	$K_I \times 10^3$	min^{-1}	117	69	40
	$t_{5\%}$	min	10.0	10.5	
	$t_{95\%}$	min	30.0	55.0	

45 After storing the granulated dust-free preparation composed of 50% by weight of Printex 30 carbon black and 50% by weight of bis-(triethoxysilylpropyl)-tetrasulphide for 1 year, no change is noted in the properties of the test mixture. On the other hand, the pulverulent mixture composed of silica filler and silane demonstrates a clear drop in the final value of cross-linking ($D_\alpha - Da$) and a characteristic drop in the rate constant of the cross-linking reaction K_I , which denotes a rise in the vulcanization period to practically double ($t_{95\%}$). 45

50 The new granular organo-silane preparations are used predominantly in rubber mixtures and rubber compositions of any type, both in so-called master batches and in mixtures to be used immediately, owing to their good stability in storage, their resistance to hydrolysis and their surprising readiness of working in. The term "of any type" relates in particular to the known types of rubber of natural and synthetic origin and to the fillers which are conventional in rubber technology such as preferably carbon blacks, but also the known white fillers such as silica fillers, silicate fillers, kaolin, clays, carbonates, quartz and kieselguhr as well as mixtures of the said fillers including and preferably carbon black. 50

55 WHAT WE CLAIM IS:
1. A granular organo-silane preparation composed of 55
60 a) from 30 to 60 % by weight of one or more organo-silanes corresponding to the formula 60





1 588 060

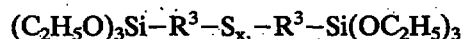
28

in which

R¹ represents an alkyl radical containing from 1 to 3 carbon atoms,
R² represents an alkyl radical or an alkoxy radical containing from 1 to 3 carbon atoms,
R represents an alkylene radical containing from 1 to 5 carbon atoms and
x has a value from 2.0 to 6.0, and

b) from 70 to 40% by weight of one or more carbon blacks with BET specific surface areas between 30 and 140 m²/g and average primary particle sizes between 20 and 60 nm, the percentages being based on the weight of the organo-silane preparation.

2. An organo-silane preparation as claimed in claim 1, composed of from 45 to 57% by weight of an organo-silane corresponding to the formula

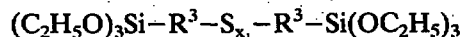


in which

R³ represents an alkylene radical containing from 2 to 4 carbon atoms and
x₁ has a value from 2.0 to 4.0, and
from 55 to 43% by weight of a HAF-carbon black having the following test data:

BET-specific surface area	78 m ² /g (± 3)
Average primary particle size (arithmetic average)	27 nm (± 2)
pH value	9 (± 1)
Dibutylphthalate absorption	100 ml/100 g (± 5).

3. An organo-silane preparation as claimed in Claim 1, composed of 30% by weight of one or more organo-silanes corresponding to the formula

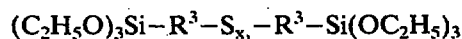


in which

R³ represents an alkylene radical containing from 2 to 4 carbon atoms and
x₁ has a value from 2.0 to 4.0, and
70% of a furnace carbon black having the following test data:

BET specific surface area	45 m ² /g (± 3)
Average primary particle size (arithmetic average)	56 nm (± 4)
pH value	9 (± 1)
Dibutylphthalate absorption	44 ml/100 g (± 5).

4. An organo-silane preparation as claimed in Claim 1, composed of 60% by weight of one or more silanes corresponding to the formula



in which,

R³ represents an alkylene radical containing from 2 to 4 carbon atoms and
x₁ has a value from 2.0 to 4.0, and
40% by weight of a carbon black having the following test data:

BET specific surface area	78 m ² /g (± 3)
Average primary particle size (arithmetic average)	27 nm (± 2)
pH value	9 (± 1)
Dibutylphthalate absorption	155 ml/100 g (± 5).

29
8

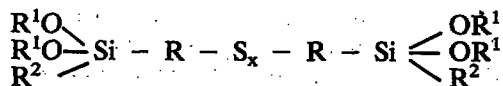


1 588 060

8

5. A granular organo-silane preparation substantially as described with particular reference to any of Examples 1 to 4.

6. A process for the preparation of a granular organo-silane preparation composed of (a) from 30 to 60% by weight of one or more silanes corresponding to the formula



10 in which

R^1 represents an alkyl radical containing from 1 to 3 carbon atoms,
 R^2 represents an alkyl radical or an alkoxy radical containing from 1 to 3 carbon atoms,
 R represents an alkylene radical containing from 1 to 5 carbon atoms and
 x has a value from 2.0 to 6.0, and

15 b) from 70 to 40% by weight of one or more carbon blacks,
which comprises adding the organo-silane or mixture of organo-silanes to the carbon black with thorough mixing until the granulate formed is dust-free.

7. A process for the preparation of a granular organo-silane preparation substantially as described with particular reference to any of Examples 1 to 4.

20 8. An organo-silane preparation when prepared by a process as claimed in claim 6 or 7.

ELKINGTON & FIFE,
Chartered Patent Agents,
High Holborn House,
52/54 High Holborn,
London WC1V 6SH.
Agents for the Applicants.