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(71) Applicant: **W. R. GRACE & CO.-CONN.** [US/US];  
7500 Grace Drive, Columbia, MD 21044 (US).

(72) Inventors: **SUN, Qi**; Higashihara 4-3-23-A1005, Zama-shi, Kanagawa-ken 252-0004 (JP). **TAKAHASHI, Toru**;  
2958-46 Kokubu, Ebina-shi, Kanagawa Prefecture (JP).  
**IKESHIRO, Yasushi**; 3-39-54 Fuchinobehoncho,  
Sagamihara-shi, Kanagawa Prefecture 252-0202 (JP).

(74) Agents: **WILLIAMS, Stephan, P.** et al; W. R. Grace &  
Co.-Conn., 62 Whittemore Ave., Cambridge, MA 02140  
(US).

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(54) Title: CONTAINER SEALANT COMPOSITION

(57) Abstract: Disclosed is a container sealant composition with improved tensile strength and reduced squeeze-out during seaming. The composition comprises a latex of a carboxylated styrene-butadiene rubber, a colloidal silica filler, wherein the colloidal silica is pretreated with an organosilane, and a tackifier. Also disclosed is a method of sealing a can with the aforementioned container sealant composition.

## Container Sealant Composition

Background of the Invention

[0001] The present invention relates to a container sealant composition with improved tensile strength and reduced squeeze-out during seaming.

[0002] Container sealant compositions based on a rubbery polymer, such as styrene-butadiene rubber (SBR) and carboxylated styrene-butadiene rubber (CSBR) are well known in the art. In order to obtain acceptable water resistance, extrusion resistance and container seam performance, such compositions often include a crosslinking agent, such as a peroxide or zinc compound, to form a crosslinked network within the rubber component. Such sealant compositions also typically include a filler and a tackifier. Examples of such sealant compositions are disclosed in US 4,189,418, WO 82/02721, EP 0182674, US 5,747,579, and WO2008/157217. Although some of the aforementioned disclosures include various silicas among a list of potential fillers, it has been found that the addition of a typical colloidal silica, which is stabilized by double electron layers, will cause the rubber latex to gel, rendering it unusable as a container sealant.

[0003] In US 5,763,388 there is suggested a method of making aqueous compatibilized silica slurry that may be more readily blended with a rubber latex. Fumed silica and precipitated silica are mentioned for the silica dispersion. The aqueous compatibilized silica slurry is made by treating the silica dispersion with an organosilane coupling agent that includes a reactive functional group. It is suggested that this treatment allows the incorporation of greater quantities of compatibilized silica slurry in the rubber polymer. However, this patent does not suggest that the compatibilized silica would be useful with respect to carboxylated rubbers or that it would be useful with respect to container sealant compositions.

### Summary of the Invention

[0004] The present invention embraces a container sealant composition comprising a latex of a carboxylated styrene-butadiene rubber (CSBR) and a filler comprising colloidal silica pretreated with an organosilane.

5 [0005] The present invention also includes a method for sealing a can. The method comprises coating an aqueous dispersion of the container sealant composition according to the present invention onto the curl area of a can cap, drying the composition, placing the coated can cap onto a can body filled with contents, and sealing the can by seaming the flange area of the can body and  
10 the curl area of the cap to obtain a sealed can containing the contents. The method may additionally include subjecting the sealed can to a heat treatment to sterilize the contents.

### Detailed Description of the Invention

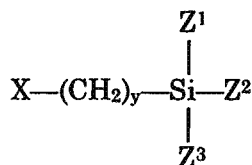
[0006] The container sealant composition of the present invention  
15 comprises a latex of a carboxylated styrene-butadiene rubber (CSBR). The CSBR may be any of those conventionally used to form container sealant compositions. Typical CSBR's are disclosed in US 5,747,579 and include copolymers of styrene and butadiene with a carboxylic acid such as fumaric acid, acrylic acid, methacrylic acid, itaconic acid, aconitic acid, maleic acid or  
20 corotonic acid or with an anhydride such as maleic anhydride or itaconic anhydride. A preferred CSBR is a copolymer of styrene and butadiene with acrylic acid. Generally, the amount of acid (or anhydride) copolymerized with the styrene-butadiene will be about 0.5% to 6% by weight of the elastomer. The proportion of styrene and butadiene will typically range from 30% to 70%  
25 for each component, based on 100 parts of styrene plus butadiene (i.e., 30 to 70 phr (phr = parts per hundred parts rubber)). Typically, the amount of butadiene is about 35% to 55%, while the amount of styrene is about 45% to 65%. Typically, the CSBR has a gel content of 0 to 70 wt.%, a Mooney viscosity of 30 to 150 (MLi<sub>4</sub>, 100°C) and a styrene content of 20 to 60 wt.%.  
30 The CSBR latex will typically comprise about 40% to 70% total rubber solids.

[0007] The container sealant composition additionally includes a filler comprising colloidal silica pretreated with an organosilane. Typically, the composition will include about 5 to 40 parts by weight (solids) of the pretreated, colloidal silica filler per 100 parts by weight (solids) of CSBR (i.e., 5 to 40 phr), preferably about 10 to 30 parts by weight of the pretreated, colloidal silica filler per 100 parts by weight of CSBR (i.e., 10-30 phr). This results in a CSBR (solids) to silica (solids) ratio of 100:5 to 100:40, preferably 100:10 to 100:30.

[0008] The colloidal silica may be selected from any of those known in the art. Colloidal silica (also known as silica sol) is a silica of relatively small particle size that will remain in dispersion over relatively long periods of time. A preferred colloidal silica has a particle size in the range of 1 nm to 150 nm, more preferably about 2 nm to 40 nm. A preferred colloidal silica is LUDOX® HS-40 (W.R. Grace & Co.-Conn.), which is available as a 40% aqueous dispersion of silica particles with an average particle size of about 12 nm.

[0009] The colloidal silica is pretreated with an organosilane to make it compatible with the rubber latex. The organosilane includes a functional group that will react with the carboxyl group in CSBR to build a network structure in the rubber system. It is theorized that formation of such a network structure provides improved tensile strength and reduced squeeze-out during seaming without the need for a crosslinking agent. Thus, in a preferred embodiment, the container sealant composition is substantially free of crosslinking agent.

[0010] Suitable organosilanes useful as pretreatment agents for compatibilizing the colloidal silica include those having the general formula



wherein X is a functional group selected from the group consisting of an amino group, a polyamino alkyl group, a mercapto group, a polysulfide group, an epoxy group, a hydroxy group, a vinyl group, an acryloxy group and a methacryloxy group; y is 0 to 8, preferably 2 to 6; and Z<sup>1</sup>, Z<sup>2</sup> and Z<sup>3</sup> are each independently selected from the group consisting of hydrogen, Ci to Cis alkyl, aryl such as phenyl, benzyl and the like, cycloalkyl such as cyclopentyl, cyclohexyl, etc., or aryl, alkoxy or halo substituted alkyl, and Ci to Cs alkoxy group, with the proviso that at least one of Z<sup>1</sup>, Z<sup>2</sup> or Z<sup>3</sup> must be one of the foregoing alkoxy groups or one of the Z's must be a halogen, hydroxyl, or hydrogen group.

[0011] Representative of such compatibilizing pretreatment agents which are commercially available include 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 3-aminopropyldimethylmethoxysilane, 3-aminopropyldihydroxymethoxysilane, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, N-(2-aminoethyl)-3-aminopropyltriethoxysilane, N-methyl-aminopropyltrimethoxysilane, 3-hydroxypropyltripropoxysilane, 3-mercaptopropyltriethoxysilane, glycidylpropyltrimethoxysilane, 3-methacryloxypropyltriethoxysilane, 3-methacryloxypropyltrimethoxysilane, 2-mercaptoethyltriethoxysilane, 3-thiocyanatopropyltriethoxysilane, bis-(3-triethoxythiopropyl) tetrasulfide, vinyltriethoxysilane, vinylphenylmethylsilane, vinyl dimethylmethoxysilane, divinyl dimethoxysilane, divinylethyldimethoxysilane, dimethylvinylchlorosilane, and the like. Preferred pretreatment agents are the amino-organosilanes, particularly 3-aminopropyltriethoxysilane and N-(2-aminoethyl)-3-aminopropyltrimethoxysilane.

[0012] In carrying out the reaction between the organosilane treatment agent and the silica, the agent can be dissolved in a lower alkanol such as propanol or ethanol at a pH below 9 and preferably within the range of 3 to 9 to which water is slowly added, either continuously or incrementally, to commence hydrolysis of the hydrolyzable groups contained in the coupling agent to form the corresponding silanol. To assist in the hydrolysis of an

alkoxy group, a pH in the range of 4-4.5 is desirable to minimize side reactions such as oligomerization of the organosilane, and can be maintained by use of dilute mineral acid such as hydrochloric or weak organic acids such as acetic acid. To assist in the hydrolysis of a hydride group, more alkaline  
5 conditions are preferred and bases such as KOH, NaOH, NH<sub>4</sub>OH, triethylamine, or pyridine can be employed to maintain a pH of 8-9. The choice of base will be dependent on the chemical nature of the specific latex to which the silica slurry is added. When the hydrolyzable group is halogen, it is preferred to mix the organohalo-silane directly with the colloidal silica.

10 The hydrolyzed treatment agent is then blended with a colloidal silica, whereby the silanol groups present in the treatment agent chemically react with the surface of the silica to form a siloxane bond (Si—O—Si) between the agent and the silica surface.

[0013] The concentration of the silica in colloidal silica can be varied  
15 within relatively wide limits, e.g. 1% to 50%, preferably 20% to 40% by weight silica based on the weight of the slurry. Temperature and reaction time also can be varied within wide limits, but is advantageously performed at elevated temperature (e.g., 80°C) for several hours. The amount of the organosilane treatment agent can likewise be varied within relatively wide limits, e.g., 1 to  
20 15 parts of agent per 100 parts by weight (dry solid) of colloidal silica, preferably 2 to 5 parts by weight of agent per 100 parts by weight of colloidal silica.

[0014] After the colloidal silica has been treated with the organosilane compatibilizing agent, the treated colloidal silica may be blended with the  
25 rubber latex with sufficient agitation to uniformly distribute the treated colloidal silica throughout the latex. This silica treated latex is stable and can be stored for later use.

[0015] The container sealant composition preferably additionally includes a tackifier. The tackifier may be selected from any those commonly used in  
30 container sealant compositions. Generally, the tackifier may include at least one material selected from the group consisting of rosin-based resins (e.g.,

rosin, hydrogenated rosin, rosin ester, hydrogenated rosin ester), terpene-based resins (e.g.,  $\alpha$ -pinene,  $\beta$ -pinene, dipentene), phenol-formaldehyde-based resins and petroleum hydrocarbon-based resins. The amount of the tackifier included in the composition may be varied, but will typically be included in an amount of about 10 to 150 parts, preferably 15 to 100 parts, by weight per 100 parts by weight (solids) of the rubber component (i.e., 10 to 150 phr, preferably 15 to 100 phr).

[0016] The container sealant composition may also comprise an additional filler. Such additional filler may be at least one material selected from the group consisting of clay, titanium dioxide, calcium carbonate, kaolin, alumina white, calcium sulfate, aluminum hydroxide and talc. The amount of the additional filler may be varied, but will typically be included in an amount of about 5-150 parts by weight per 100 parts by weight (solids) of the rubber component (i.e., 5 to 150 phr).

[0017] The container sealant composition may also include minor amounts of other additives such as colorants (e.g., carbon black), antioxidants, thickeners (e.g., bentonite, karaya gum, methyl cellulose), bactericides, surfactants, and pH adjusters.

[0018] The above-described container sealant composition is advantageously used to seal a can. Generally, the method comprises coating an aqueous dispersion of the container sealant composition onto the curl area of a can cap, drying the composition, placing the coated can cap onto a can body filled with contents, and sealing the can by seaming the flange area of the can body and the curl area of the cap to obtain a sealed can containing the contents. The method may additionally include subjecting the sealed can to a heat treatment to sterilize the contents. The sealant composition of the present invention provides reduced squeeze-out during the seaming process, thus forming a better seal.

### Example 1

[0019] This example demonstrates the improvements resulting from the combination of pretreated colloidal silica with CSBR latex in comparison to the use of untreated colloidal silica and in comparison to SBR latex. The colloidal silica or the pretreated colloidal silica are added slowly, while stirring, into SBR latex or CSBR latex in the amounts and ratios shown in Table 1, then these mixtures are stirred for 15 to 20 minutes at 200 to 300 rpm. The results are shown in Table 1.

Table 1

Ingredient	Amount (parts by weight)							
	A1/A2	B	C	D	E1/E2	F	G	H
SBR (70%) <sup>1</sup>	143	143	143	143				
CSBR (50%) <sup>2</sup>					200	200	200	200
Colloidal Silica (40% dispersion) <sup>3</sup>	25 & 75				25 & 75			
Pretreated Colloidal Silica (40% dispersion) <sup>4</sup>		0	25	75		0	25	75
Rubber/Silica Ratio	100/10 100/30	100/0	100/10	100/30	100/10 100/30	100/0	100/10	100/30
Tensile strength <sup>5</sup> (MPa)	Both gelled	4.61	4.69	7.22	Both gelled	7.42	12.69	13.61
Increase in Tensile Strength		---	2%	57%		---	71%	83%

10 <sup>1</sup> Butonal 2230 (70% SBR solids; BASF)

<sup>2</sup> Lacstar 3290N (50% CSBR solids; Dainippon)

<sup>3</sup> Ludox HS-40 (40% Si solids; W.R. Grace)

<sup>4</sup> Ludox HS-40 treated with N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (KBM603; ShinEtsu) in amount of 3% by weight Si solids.

15 <sup>5</sup> Tensile strength is measured by Autograph tester (model no AG-1S) (Shimadzu)

[0020] From the above data, it can be seen that neither SBR nor CSBR could be successfully combined with untreated colloidal silica. (See A1, A2, E1 and E2.) In each case, the latex solution gelled in several hours. By comparison, both SBR and CSBR could be successfully combined with colloidal silica pretreated with organosilane. (See C, D, G and H.) In the case



of SBR, the addition of pretreated colloidal silica had essentially no effect on tensile strength at the 100:10 ratio (SBR:Si), and increased tensile strength by 57% at the 100:30 ratio, compared to the tensile strength of the rubber with no silica filler. As a result, the tensile strength of the hybrid SBR:Si sample is too low to adequately meet the needs of a container sealant. (Compare C and D to B.) In the case of CSBR, the addition of pretreated colloidal silica increased the tensile strength by 71% and 83% respectively at the 100:10 and 100:30 ratio (CSBR:Si). (Compare G and H to F.) More importantly, the tensile strength of the CSBR/pretreated colloidal silica compositions was substantially higher than the tensile strength of the SBR/pretreated colloidal silica compositions. (Compare G and H to C and D.)

Example 2

[0021] A container sealant composition is prepared having the ingredients listed below.

15	<u>Ingredient</u>	<u>Dry Weight (PHR)</u>
	CSBR (50%) <sup>1</sup>	100
	Pretreated Colloidal Silica <sup>2</sup>	20
	Aluminum Silicate (Kaolin clay)	30
	Titanium Dioxide	8
20	Tackifier <sup>3</sup>	33.6
	Thickener <sup>4</sup>	0.48
	Carbon black	0.34
	Surfactant <sup>5</sup>	1.13
	Antioxidant <sup>6</sup>	1.07
25	Bentonite	0.01

<sup>1</sup> Lacstar 3290N (50% CSBR solids; Dainippon)

<sup>2</sup> Ludox HS-40 treated with N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (KBM603; ShinEtsu) in amount of 3% by weight Si solids.

30 <sup>3</sup> Blend of Aqueous Dispersion of Polymerized Rosin Ester (8.6 phr Foralaxe from Eastman Chemical), Hydrogenated Ester Rosin (15 phr Forelyn 5020-F from Eastman Chemical) and Hydrogenated Rosin (10 phr Superester E-787 from Arakawa Chemical Industries Ltd.)

<sup>4</sup> Methyl cellulose (0.225) and Karaya gum (0.251)

<sup>5</sup> Naphthalene sulfonic acid, formaldehyde, Na (1.074) and Naphthalene sulfonic acid, Na (0.057)

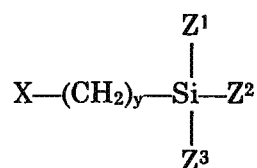
35 <sup>6</sup> Tetrakis methylene ditertbutylhydroxycinnamate methyl

[0022] The pretreated colloidal silica is mixed with the CSBR latex and stirred at 30 to 70 rpm for 30 to 90 minutes. The remaining ingredients are added to this dispersion, which is stirred for one hour then defoamed under vacuum. The above-described composition has a tensile strength of 13.15  
5 MPa.

[0023] The above-described composition is used to seal a can in the conventional manner. The aqueous dispersion of sealant composition is coated onto the curl area of a can end (or can cap) using a reciprocal liner and heat-dried in an air circulating oven at 90°C for ten minutes. A 190 ml can is  
10 filled with hot liquid (e.g., boiled water to simulate food contents), then the can end is placed on the filled can and seamed using a reciprocal double seamer. The seamed can is then subjected to heat sterilization (e.g., 125°C for 30 min.), then allowed to cool to room temperature. The can exhibits  
15 substantially reduced squeeze-out of the sealant composition upon seaming and maintains excellent sealed conditions.

### Claims

1. A container sealant composition comprising a latex of a carboxylated styrene-butadiene rubber (CSBR), a filler comprising colloidal silica pretreated with an organosilane, and a tackifier, wherein the weight ratio of CSBR solids to silica solids ranges from 100:5 to 100:40.
2. The container sealant composition according to claim 1, wherein the organosilane has the general formula



wherein X is a functional group selected from the group consisting of an amino group, a polyamino alkyl group, a mercapto group, a polysulfide group, an epoxy group, a hydroxy group, a vinyl group, an acryloxy group and a methacryloxy group; y is 0 to 8, preferably 2 to 6; and Z<sup>1</sup>, Z<sup>2</sup> and Z<sup>3</sup> are each independently selected from the group consisting of hydrogen, Ci to Cis alkyl, aryl such as phenyl, benzyl and the like, cycloalkyl such as cyclopentyl, cyclohexyl, etc., or aryl, alkoxy or halo substituted alkyl, and Ci to Cs alkoxy group, with the proviso that at least one of Z<sup>1</sup>, Z<sup>2</sup> or Z<sup>3</sup> must be one of the foregoing alkoxy groups or one of the Z's must be a halogen, hydroxyl, or hydrogen group.

3. The container sealant composition according to any of claims 1 to 2, wherein the colloidal silica has a particle size of 2 nm to 40 nm.
4. The container sealant composition according to any of claims 1 to 3, wherein the organosilane is selected from the group consisting of 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 3-aminopropyldimethylethoxysilane, 3-aminopropyldihydroxymethoxysilane, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, N-(2-aminoethyl)-3-aminopropyltriethoxysilane, and N-methyl-aminopropyltrimethoxysilane.

5. The container sealant composition according to any of claims 1 to 4, wherein the organosilane is N-(2-aminoethyl)-3-aminopropyl-trimethoxysilane .
6. The container sealant composition according to any of claims 1 to 5, wherein the weight ratio of CSBR solids to silica solids ranges from **100:10** to **100:30**.
7. The container sealant composition according to any of claims 1 to 6, wherein the tackifier is at least one member selected from the group consisting of rosin-based resins, terpene-based resins, phenol-formaldehyde-based resins, and petroleum hydrocarbon-based resins and the amount of the tackifier is **10-150** parts by weight per **100** parts by weight of the rubber component.
8. The container sealant composition according to any of claims 1 to 7, comprising an additional filler, wherein the additional filler comprises at least one material selected from the group consisting of clay, titanium dioxide, calcium carbonate, kaolin, alumina white, calcium sulfate, aluminum hydroxide and talc, and wherein the amount of the filler is **5-150** parts by weight per **100** parts by weight of the rubber component.
9. The container sealant composition according to any of claims 1 to 8, wherein the carboxylated styrene-butadiene rubber has a gel content of **0** to **70** wt.%, a Mooney viscosity of **30** to **150** (ML1+4, 100°C) and a styrene content of **20** to **60** wt.%.
10. The container sealant composition according to any of claims 1 to 9, wherein the composition is substantially free of crosslinking agent.
11. A method for sealing a can which comprises coating an aqueous dispersion of the container sealant composition according to any of claims 1 to **10** onto the curl area of a can cap, drying the composition, placing the coated can cap onto a can body filled with contents, and sealing the can by seaming

the flange area of the can body and the curl area of the cap to obtain a sealed can containing the contents.

12. The method according to claim 11 additionally comprising subjecting the sealed can to a heat treatment to sterilize the contents.

**INTERNATIONAL SEARCH REPORT**

International application No PCT/US2012/070451
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A. CLASSIFICATION OF SUBJECT MATTER  
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 ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
**C09K C08K C08L**

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**EPO-Internal , WPI Data**

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 350 204 A1 (GRACE W R & CO [US]) 10 January 1990 (1990-01-10) page 3, line 33-37; page 4, lines 51-58; example 1	1-12
A	----- US 5 763 388 A (LIGHTSEY JOHN W [US] ET AL) 9 June 1998 (1998-06-09) cited in the application column 8, line 31 - line 37; example 1 ----- -/- .	1-10

Further documents are listed in the continuation of Box C.

See patent family annex.

\* Special categories of cited documents :

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- "E" earlier application or patent but published on or after the international filing date
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Date of the actual completion of the international search

**26 March 2013**

Date of mailing of the international search report

**04/04/2013**

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 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040,  
 Fax: (+31-70) 340-3016

Authorized officer  
**Kappen , Sascha**

## INTERNATIONAL SEARCH REPORT

International application No  
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>GOERL U ET AL: "RUBBER/FILLER COMPOUND SYSTEMS IN POWDER FORM A NEW RAW MATERIAL GENERATION FOR SIMPLIFICATION OF THE PRODUCTION PROCESSES IN THE RUBBER INDUSTRY PART 2: POWDER RUBBER BASED ON E-SBR/SI LICA/SI LANE//KAUSCHUK/FUELLVERBUNDSYSTEME IN PULVERFORM - NEUE ROHST", KAUSCHUK UND GUMMI - KUNSTSTOFFE, HUTHIG VERLAG, HEIDELBERG, DE, vol . 55, no. 10, 1 October 2002 (2002-10-01), pages 502-506,508, XP001132688, ISSN: 0948-3276 the whole document</p> <p style="text-align: center;">-----</p>	1-10

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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