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(54) SEALING COMPOSITION

(71) We, TOYO SEIKAN KAISHA LIMITED, a Japanese Body Corporate of 3-1, 1-chome, Uchisaiwai-cho, Chiyoda-ku, Tokyo, Japan, 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 can end sealing rubber composition comprising a styrene-butadiene rubbery copolymer as a main ingredient.

It is the usual practice to produce closed cans by lining a can end material with a sealing rubber compound, and mounting it onto can bodies by seaming.

The conventional sealing rubber compounds are made of a dry rubber resulting from the separation of solids from a styrene-butadiene rubbery copolymer latex. When the dry rubber is used, it is necessary to masticate it with additives such as a tackifier and a filler in a Banbury mixer, and dispersing it in water using a surface-active agent or dissolving it in a solvent. Disadvantageously, however, the masticating operation causes the cutting of the rubber molecules and consequently deteriorates the properties of the sealing compound.

This invention provides a can end sealing composition which retains the superior properties of a styrene-butadiene rubbery copolymer.

The can end sealing rubber composition of the invention consists essentially of an aqueous emulsion of a styrene-butadiene rubbery copolymer, the emulsion being a latex obtained by emulsion polymerisation at 35° to 70°C, or a diluted or concentrated product thereof, a tackifier and a filler and has (1) a creep resistance coefficient K defined by the following equation of at least 0.1 but not exceeding 0.6,

$$K = \log J^{C}_{90}(10) - \log J^{C}_{90}(1)$$

wherein $J^{C}_{90}(10)$ is the creep compliance measured 10 minutes after exerting a load when a fabricated article of the composition as a specimen is compressed in water at 90°C. by a parallel plate plastometer, and $J^{C}_{90}(1)$ is the creep compliance measured 1 minute after exerting a load when the specimen is compressed in water at 90°C. by a parallel plate plastomer,

and (2) a creep compliance $J^{C}_{25}(1)$ of at least 3×10^{-9} cm^2/dyne but not exceeding 1×10^{-6} cm^2/dyne, the creep compliance being measured 1 minute after exerting a load when the specimen is compressed in water at 25°C. by a parallel plate plastometer.

The composition of this invention characterized by the above-described creep resistance characteristics and creep compliances is obtained by using as a main ingredient a styrene-butadiene copolymer latex (to be referred to as a hot rubber latex) prepared by emulsion polymerization of styrene and butadiene at a temperature of 35 to 70°C. either as such or after diluting or concentrating it to a predetermined solids content without forming it into a dry rubber.

The conventional sealing rubber compound principally uses a styrene-butadiene rubbery copolymer obtained by emulsion polymerization at not more than 10°C. which is called a cold rubber. It is necessary therefore to remove the short stopper used in the polymerization from the rubber component to avoid its inclusion in the sealing compound. This is partly the reason by the copolymer must be used in the form of a dry rubber.

Hot rubber has actually been used in some formulations. But even in such a case, it is incorporated as a dry rubber in accordance with the method using cold rubber.

The present inventors have made investigations in regard to this point, and found that a sealing compound having a creep resistance coefficient of 0.1 to 0.6, preferably 0.15 to 0.45 and a creep compliance of 3×10^{-9} to 1×10^{-6} cm^2/dyne, preferably 1×10^{-8} to 5×10^{-7} cm^2/dyne, can be obtained by incorporating a hot rubber latex or a diluted or concentrated product thereof without separating rubber solids from it; and that the sealing compound having such characteristics possesses superior hot water resistance and exhibits a very good can sealing performance. Sealing compounds having a creep resistance coefficient and a creep compliance outside the above ranges have a poor sealing performance particularly for hot-filled can use.

The conventional sealing compound has deteriorated creep resistance and hot water resistance because the rubber molecules are cut during Banbury mixer mastication. As a result, it has insufficient sealing performance and may cause the leakage of the contents of cans. Furthermore, during masticating by a Banbury mixer, the rubber molecules undergo heat decomposition, and the decomposition product adversely affects the flavor of the contents of cans.

Resistance to hot water is evaluated by a decrease in compression modulus at a constant strain (30%) caused by dipping in boiling water. The decrease should desirably be small. Sealing rubber compounds having a large decrease of the compression modulus have poor sealing performance particularly for hot-filled can use.

The accompanying drawings are graphs showing a comparison of the properties of one example of the sealing rubber compound of this invention with those of the conventional sealing rubber compound. Figure 1 shows master curves of compression creep compliance-time, and Figure 2 shows boiling water dipping time-compression modulus curves.

In the sealing compound of this invention, the latex is used either as such or after having been diluted or concentrated, and the superior sealing performance especially at elevated temperatures are retained without deterioration. Hence, leakage-free good seals can be obtained, and no adverse effect on the flavors of can contents is caused.

The creep compliance of the sealing rubber composition is measured in the following manner.

A disc-shaped specimen is set between a top plate and a bottom plate of a parallel plate plastometer. The top plate, bottom plate and the specimen are dipped in water by raising a water tank containing water maintained at a predetermined temperature (25°C. or 90°C), and maintained for 30 minutes.

After the dipping for the above-mentioned period, a load is exerted, and a change in thickness is observed after a lapse of a predetermined period (t, minutes). The creep compliance is calculated by the following equation.

$$J_T^C(t) = \frac{3V^2}{8\pi f}\left(\frac{1}{h^4} - \frac{1}{h_o^4}\right)$$

wherein $J_T^C(t)$ is the creep resistance after t minutes from the exertion of a load at T°C.; V is the volume of the specimen, and π is the ratio of the circumference of a circle to its diameter; f is the load exerted; h_o is the initial thickness of the specimen, and h is the thickness of the specimen after a lapse of t minutes from the exertion of a load.

The method of calculating the creep compliance is in accordance with Shoten Oka, Eiichi Fukada and Toshimaro Sone, "Zairyo Shiken" (Material Testing), *10*, 333 (1961).

Preferably, the hot rubber latex used in this invention has a solids content of 30 to 90% by weight and is one wherein the copolymer has a styrene content of 23 to 55% by weight and a Mooney visocisty ($ML_{1+4}^{100°C}$) of 25 to 160.

When the solids content is lower than the afore-said range, the amount of a thickener used for viscosity adjustment in the preparation of sealing compounds must be increased, and this is very likely to deteriorate the physical and/or mechanical properties of the sealing compounds after application. If the solids content is higher than the afore-said range, the stability of a sol of the sealing compound is reduced.

Rubbers having a Mooney viscosity ($ML_{1+4}^{100°C}$) of 30 to 140 and latices having a solids content of 40 to 60% by weight are more preferred.

The above-mentioned hot rubber latices and methods for producing them are known, and they are usually available with a solids content of 30 to 50% by weight. Accordingly, the hot rubber latices produced in a customary manner can be used as such, but if desired, they may be used after having been diluted or concentrated to the desired solids content.

Examples of the filler used as an ingredient of the sealing rubber compound of this invention are silicic fillers such as colloidal silica, silicic anhydride, hydrous silicic acid and synthetic silicates, light and/or heavy calcium carbonates, activated calcium carbonate, kaolin, fired clay, alumina white, talc powder, dolomite, alumina sulfate, barium sulfate, magnesium carbonate, magnesium silicate, magnesium oxide, calcium sulfate, pumice powder, glass powder, asbestos powder, zinc oxide, titanium dioxide and carbon black.

They can be used either alone or in combination of two or more.

The suitable amount of the filler to be incorporated is 30 to 200 parts by weight, preferably 50 to 140 parts by weight, per 100 parts by weight of the rubber solids.

Most preferably, 60 to 100 parts by weight of clay, 10 to 40 parts by weight of titanium white and 0.1 to 1 part by weight of carbon black are used conjointly as the filler.

Examples of the tackifier used in this invention are rosin-type resins such as rosin, hydrogenated rosin, esters of these, or hardened rosin, phenolic resins modified with natural resins such as rosin or terpene, a xylene-formaldehyde resin and its modified products, and petroleum resins ("Piccopale" Registered Trade Mark).

The amount of the tackifier is usually 5 to 200 parts by weight, preferably 80 to 150 parts by weight, per 100 parts by weight of the rubber solids.

As desired, the composition of this invention may incorporate thickeners such as sodium alginate, methyl cellulose, carboxymethyl cellulose, carboxymethyl starch, polyvinyl alcohol, poly(sodium acrylate) and karaya gum, antiseptics, surface-active agents, antioxidants and pH adjusters.

The method of mixing the hot rubber latex with the filler, the tackifier, and the other various additives is not particularly critical, and mixing can be effected by any known mixing machines.

Preferably, the filler, the tackifier and other additives are added in the form of an aqueous dispersion. But they may be directly added to the rubber latex.

The following Examples illustrate the present invention more specifically.

Example 1

Two types of a styrene-butadiene copolymer latex were prepared using the polymerization recipes and conditions shown in Tables 1 and 2.

TABLE 1 (Copolymer A)

Polymerization recipe	Butadiene	60 (parts by weight)
	Styrene	40
	Rosin soap	4.5
	Dodecyl mercaptan	0.5
	Potassium persulfate	0.3
	Water	180
pH of the aqueous phase		10
Polymerization temperature		50°C.
Conversion		80%

TABLE 2 (Copolymer B)

Polymerization recipe	Butadiene	60 (parts by weight)
	Styrene	40
	Rosin soap	4.5
	Monohydroperoxide of diisopropylbenzene	0.08
	Sodium ethylenediaminetetraacetate	0.035
	Ferrous sulfate	0.03
	Iron-Trilon complex salt	0.08
	Trisodium phosphate	0.5
	Sodium β-naphthalenesulfonate	0.15
	Dodecyl mercaptan	0.18
	Water	200
pH of the water phase		10
Polymerization temperature		5°C.
Conversion		70%

The characteristics of these styrene/butadiene copolymer latices are shown in Table 3.

TABLE 3

Characteristics	Copolymer latex A (hot rubber latex)	Copolymer latex B (cold rubber latex)
Styrene content (%)	35	31
Mooney viscosity ($ML_{1+4}^{100°C.}$) of rubber solid	40	38
Solids content (%) of the latex	51	50
Viscosity (CPS) of the latex	55	55

The additives shown below are added to each of the Copolymer A latex and the Copolymer B latex to form a sealing rubber compound. Water was added at this time to adjust the solids content of the sealing rubber compound to 40%. The sealing compounds obtained are designated as Compound A and Compound B.

Additives	Amounts (parts per 100 parts by weight of the rubber solid)
Clay (filler)	60
Titanium white (filler)	10
Rosin (tackifier)	75
Karaya gum (thickener)	2
Methyl cellulose (thickener)	1
Di-β-naphthyl phenylenediamine (antioxidant)	1

Each of the Compounds A and B was tested for compression creep compliance (in water at 25°C. and 90°C.) and resistance to hot water.

Figure 1 of the accompanying drawings shows master curves of the compression creep compliance of Compound A and Compound B. It is seen from Figure 1 that Compound A has a less inclination than Compound B in its maste curve of compression creep compliance, and does not easily flow.

The creep compliance [$J^{C}_{25}(1)$] measured in water at 25°C. and the creep resistance coefficient [K] of each of the compounds are shown below.

	$J^{C}_{25}(1)$	K
Compound A	5.6×10^{-8}	0.20
Compound B	7.1×10^{-8}	0.47

The hot water resistance was measured as follows:

A sample was dipped in boiling water for a given period. Then, it was punched into disc-shaped pieces and subjected to a compression test. The hot water resistance was expressed as changes with the dipping time of the modulus of the sample at 30% strain. Figure 2 of the accompanying drawings shows the results of the tests on Compound A and Compound B. It is evident from Figure 2 that Compound A undergoes a less reduction in modulus on dipping in boiling water than Compound B, and therefore has better hot water resistance.

The two sealing Compounds A and B were lined on can ends of 202 Dia, and dried for 10 minutes at 90°C. A 1.5% aqueous solution of citric acid was filled at 0 - 4°C. into side lap seamed open top cans of 202 Dia having a capacity of 250 ml, and sodium bicarbonate was added so as to adjust the volume of carbon dioxide gas to 4.5. The lines can ends were secured to the can bodies by a double seaming process. These cans containing carbon dioxide gas will be referred to as carbonated cans.

On the other hand, 10% orange juice was filled at 95°C. into the same open top cans as described above, and the top end was secured to the can bodies by a double seaming process. The cans filled at 95°C. will be referred to as hot-filled cans. The total number of cans having the aforesaid contents was 3,000 in each case. Out of them, 1500 cans were stored at 50°C., and the remaining 1500 cans, at room temperature, for use in a leakage test.

Sites of leakage were directly observed in the carbonated cans. The hot-filled cans were examined by striking to locate these cans which gave off a bad sound.

The cans with a bad sound were examined for the degree of vacuum by a vacuum meter, and those cans in which the degree of vacuum decreased were classified as leakage cans.

The test results are shown in Table 4. It is clear from Table 4 that the sealing compound of this invention (Compound A) showed superior sealing performance both on the carbonated cans and hot-filled cans to the sealing rubber compound containing a cold rubber latex (Compound B).

TABLE 4

Contents	Compound	Stored at	The number of cans which showed leakage or a decrease in the degree of vacuum				
			After one week	After one month	After 3 months	After 6 months	Total ratio of leakage (%)
Aqueous solution of citric acid plus sodium bi-carbonate	A	50°C.	0	0	0	0	0
		Room temp.	0	0	0	0	0
	B	50°C.	0	0	1	1	0.20
		Room temp.	0	1	1	1	0.13
10% orange juice	A	50°C.	0	0	0	0	0
		Room Temp.	0	0	0	0	0
	B	50°C.	0	0	0	1	0.13
		Room Temp.	0	0	1	1	0.07

Example 2

Three kinds of sealing compound were prepared using rubbers having the characteristics shown in Table 5.

Compound C was prepared by mixing the hot rubber latex polymerized at 50°C. with an aqueous dispersion of 10 parts of titanium white, 85 parts of clay and 1 part of carbon black as fillers, an aqueous dispersion of 60 parts of a rosin-type tackifier, and also 0.5 part of karaya gum, 3.5 parts of methyl cellulose, 1 part of ammonium oleate and 1 part of di-β-naphthyl phenylenediamine with stirring, the amounts of all of the additives being based on 100 parts by weight of rubber solid.

Compound D was prepared by separating rubber from the cold rubber latex polymerized at 5°C., washing and drying it, adding 10 parts of titanium white, 85 parts of clay and 1 part of carbon black, the amounts being based on 100 parts of the rubber, and masticating the mixture in a Banbury mixer, further adding 60 parts of a rosin-type tackifier, 0.5 part of karaya gum, 3.5 parts of methyl cellulose, 1 part of ammonium oleate, and 1 part of di-β-naphthyl phenylenediamine, and dispersing the mixture in water by a high-speed mixer.

Compound E was prepared by adding 60 parts of a rosin-type tackifier and 1 part of di-β-naphthyl phenylene-diamine to 100 parts of rubber obtained by masticating the mixture containing the same fillers as in Compound D, dissolving the soluble ingredients by n-hexane, and dispersing the insoluble ingredients in the mixture.

TABLE 5

Characteristics of rubber

Compound	Polymerization temperature (°C.)	Styrene content (%)	Mooney viscosity $(ML_{1+4}^{100°C.})$
C	50	35	41
D	5	33	39
E	5	36	41

The three kinds of rubber compounds were lined on TFS can ends of 202 Dia and dried, and subjected to a leakage test in the same manner as in Example 1.

The results are shown in Table 6 together with the $J_{25}^{C}(1)$ and K values of the sample compounds. It is seen from the table that Compound C prepared from the hot rubber latex in accordance with this invention exhibits superior sealing performance both on the carbonated cans and hot-filled cans to the Compounds D and E which were prepared by different methods.

TABLE 6

Contents	Compound	$J^C_{25}(1)$ (cm^2/dyne)	K	Stored at	The number of cans which showed leakage or a decrease in the degree of vacuum				
					After one week	After one month	After 3 months	After 6 months	Ratio of leakage (%)
Aqueous solution of citric acid plus sodium bicarbonate	C	5.4×10^{-8}	0.25	50°C.	0	0	0	0	0
				RT*	0	0	0	0	0
	D	5.8×10^{-8}	0.51	50°C.	1	0	0	1	0.13
				RT	0	0	1	1	0.13
	E	2.3×10^{-7}	0.55	50°C.	0	1	3	2	0.40
				RT	0	0	2	2	0.27
10% orange juice	C	5.4×10^{-8}	0.25	50°C.	0	0	0	0	0
				RT	0	0	0	0	0
	D	5.8×10^{-8}	0.51	50°C	0	0	0	1	0.07
				RT	0	0	1	1	0.13
	E	2.3×10^{-7}	0.55	50°C.	1	0	3	3	0.47
				RT	0	1	1	2	0.27

*RT = room temperature

Example 3

Each of the six kinds of hot rubber latices having.the characteristics shown in Table 7 was mixed with stirring with an aqueous dispersion of 15 parts of titanium white, 40 parts of clay and 1 part of carbon black, an aqueous dispersion of 35 parts of a rosin-type resin, and also with 5 parts of karaya gum, 5 parts of methyl cellulose, 1 part of sodium oleate and 1 part of di-β-naphthyl phenylene-diamine, the amounts of the additives being based on 100 parts of the rubber solids. Thus, six kinds of sealing compounds were obtained. These sealing compounds were each coated on TFS can ends of 202 Dia and dried, and subjected to the same leakage test as in Example 1. Table 8 shows the results of observation of leakage or the decrease in the degree of vacuum and the $J_{25}^{C}(1)$ and K values of the sealing compounds.

It is seen from Table 8 that sealing compounds having very good sealing performance can be obtained by using hot rubber latices in which the rubber solid had a Mooney viscosity ($ML_{1+4}^{100^\circ C}$) of 25 to 140 (G - K).

TABLE 7

Compound	Polymerization temperature of latex (°C.)	Mooney viscosity ($ML_{1+4}^{100°C.}$) of the rubber solid	pH of the latex	Solids content (%) of latex	Viscosity (cps) of latex	Styrene content (%)
G	50	25	10.0	50	55	40
H	50	31	9.9	50	53	42
I	50	52	10.0	51	58	41
J	50	98	9.8	48	60	42
K	50	140	9.9	49	56	39
L	50	159	10.1	51	55	39

TABLE 8

Contents	Compound	$J^{C}_{25}(1)$ (cm^2/dyne)	K	Stored at	The number of cans which showed leakage or a decrease in the degree of vacuum: After one week	After one month	After 3 months	After 6 months	Total Leakage ratio (%)
Aqueous solution of citric acid plus sodium bi-Carbonate	G	1.4×10^{-8}	0.44	50°C.	0	0	0	1	0.07
				RT*	0	0	0	1	0.07
	H	6.5×10^{-8}	1.39	50°C.	0	0	0	0	0
				RT	0	0	0	0	0
	I	4.0×10^{-8}	0.22	50°C.	0	0	0	0	0
				RT	0	0	0	0	0
	J	1.8×10^{-8}	0.16	50°C.	0	0	0	0	0
				RT	0	0	0	0	0
	K	1.1×10^{-8}	0.13	50°C.	0	0	0	1	0.07
				RT	0	0	0	0	0
	L	5.0×10^{-9}	0.19	50°C.	0	1	1	2	0.27
				RT	0	0	0	1	0.07
10% orange juice	G	1.4×10^{-8}	0.44	50°C.	0	0	0	1	0.07
				RT	0	0	0	1	0.07
	H	6.5×10^{-8}	1.39	50°C.	0	0	0	0	0
				RT	0	0	0	0	0
	I	4.0×10^{-8}	0.22	50°C.	0	0	0	0	0
				RT	0	0	0	0	0
	J	1.8×10^{-8}	0.16	50°C.	0	0	0	0	0
				RT	0	0	0	0	0
	K	1.1×10^{-8}	0.13	50°C.	0	1	0	1	0.13
				RT	0	0	0	1	0.07
	L	5.0×10^{-9}	0.19	50°C.	0	0	1	3	0.27
				RT	0	0	1	2	0.20

*RT = room temperature

Example 4

Five kinds of sealing compounds were prepared using the same recipes as in the compounds of Example 2 except that hot rubber latices having the characteristics shown in Table 9 were used.

These sealing compounds were lined on TFS can ends of 202 Dia and dried. In the same way as in Example 1, the two kinds of contents as used in Example 1 were filled in open top cans and the top end was secured to them by a double-seaming process. Three thousand cans in total were filled. Out of them, 1500 cans were stored at 50°C., and the remainder, at room temperature. Leakage or the decrease of the degree of vacuum with time were observed. The results are given in Table 10 together with the $J_{25}^{C}(1)$ and K values of the sealing compounds.

The results show that the preferred styrene content of rubber is 23 to 55% (M - P).

TABLE 9

Compound	Polymerization temperature of latex (°C.)	Mooney viscosity ($ML_{1+4}^{100°C.}$) of the rubber solid	pH of the latex	Solids content (%) of latex	Viscosity (cps) of latex	Styrene content (%)
M	50	40	10.0	50	55	23
N	50	43	10.0	48	56	35
O	50	41	10.0	50	55	40
P	50	40	10.0	50	54	50
Q	50	41	10.0	49.5	56	60

TABLE 10

Contents	Compound	$J^{C}_{25}(1)$ (cm²/dyne)	K	Stored at	The number of cans which showed leakage or a decrease in the degree of vacuum				Total leakage ratio (%)
					After one week	After one month	After 3 months	After 6 months	
Aqueous solution of citric acid plus sodium bi-carbonate	M	6.1×10^{-7}	0.30	50°C.	0	0	0	2	0.13
				RT*	0	0	0	1	0.07
	N	2.2×10^{-7}	0.25	50°C.	0	0	0	0	0
				RT	0	0	0	0	0
	O	6.3×10^{-8}	0.21	50°C.	0	0	0	0	0
				RT	0	0	0	0	0
	P	3.1×10^{-8}	0.36	50°C.	0	0	0	1	0.07
				RT	0	0	0	0	0
	Q	1.0×10^{-8}	0.47	50°C.	0	1	1	1	0.20
				RT	0	0	1	1	0.13
10% orange juice	M	6.1×10^{-7}	0.30	50°C.	0	0	0	1	0.07
				RT	0	0	0	0	0
	N	2.2×10^{-7}	0.25	50°C.	0	0	0	0	0
				RT	0	0	0	0	0
	O	6.3×10^{-8}	0.21	50°C.	0	0	0	0	0
				RT	0	0	0	0	0
	P	3.1×10^{-8}	0.36	50°C.	0	0	0	1	0.07
				RT	0	0	0	0	0
	Q	1.0×10^{-8}	0.47	50°C.	1	0	1	2	0.27
				RT	0	0	1	1	0.13

* RT = room temperature

Example 5

Compound a of this invention prepared in Example 1 was coated on each of aluminum can ends, tin-plated steel can ends and TFS can ends, and dried. In the same way as in Example 1, two kinds of contents were filled in open top cans and the top end was secured by a double seaming process. In this experiment, 12 kinds of combinations of can body-can end were used as follows:

Three-piece can of tin-plated steel - aluminum end,
three-piece can of tin-plated steel - tin plated steel end,
two-piece can of tin-plated steel - aluminum end,
two-piece can of tin-plated steel - tin-plated steel end,
two-piece can of tin-plated steel - TFS end,
two piece can of aluminum - aluminum end,
two-piece can of aluminum - tin-plated steel end,
two-piece can of aluminum - TFS end,
TFS cement bonded can - aluminum end,
TFS cement bonded can - tin-plated steel end, and
TFS cement bonded can - TFS can end.

The same compound was lined on can ends for a No. 1 oval can and a No. 8 rectangular can and dried. The two kinds of contents were filled in the same way, and the top end was secured by a double seaming process.

These filled cans were stored either at 50°C. or at room temperature in the same way as in Example 1, and leakage or a decrease in the degree of vacuum was observed. None of the cans showed leakage or gave off a bad sound during a six-month period.

Example 6

Using the recipes shown in Table 11, eleven kinds of sealing compounds were prepared.

Compound I was prepared by adding 100 parts of kaolin clay to 100 parts of a rubber solid of styrene-butadiene copolymer (SBR) polymerized at 50°C., masticating the mixture by a Banbury mixer, adding 100 parts of a rosin-type resin (tackifier) and 1 part of di-β-naphthyl phenylene-diamine per 100 parts of the rubber, dissolving the soluble ingredients by n-hexane, and dispersing the insoluble ingredients in it.

Compound II was obtained by adding benzoyl peroxide to Compound I in an amount of 0.5 part per 100 parts of rubber solid.

Compounds III to XI were obtained by mixing the styrene-butadiene copolymer latex with stirring with a resin, a filler, a thickener, an antioxidant, a surfactant and other additives. The characteristics of the rubber, and the types and amounts of the resin and fillers are shown in Table 11. The thickner was a mixture of 3 parts of methyl cellulose and 1 part of kayara gum per 100 parts of the rubber solid, and the surface-active agent was 1 part of ammonium oleate per 100 parts of the rubber solid. the antioxidant was 1 part of di-β-naphthyl phenylenediamine per 100 parts of the rubber solid.

The eleven kinds of sealing compounds were lined on can ends of 202 Dia, and dried at 90°C. for 10 minutes. When compound B was used, the ends were further heated at 120°C. for 1 minute to cure the compound.

Two kinds of contents were filled in the same way as in Example 1.

The total number of filled cans was 3000 in each case. Our of them, 1500 cans were stored at 50°C., and the remainder, at room temperature. They were subjected to the leakage test in the same way as in Example 1.

The compression creep compliance of the eleven sealing compounds in water were measured.

The samples used for measuring compression creep compliance were obtained by superimposing several dry films of a given sealing compound to a thickness of about 5 mm, and punching the laminate into a disc-shaped piece with a diameter of about 5 mm.

The creep resistance coefficient (K) and $J^{C}_{25}(1)$ values of the eleven compounds used in the leakage test are shown in Table 12, and the results of the leakage test are shown in Table 13. A comparison of Table 12 with Table 13 shows that compounds having a creep resistance coefficient of at least 0.1 but not exceeding 0.6 and a $J^{C}_{25}(1)$ value of at least 3×10^{-9} but not exceeding 1×10^{-6} have superior sealability, and those having a creep resistance coefficient of at least 0.15 but not exceeding 0.45 and a $J^{C}_{25}(1)$ value of at least 1×10^{-8} but not exceeding 5×10^{-7} show a figure improvement in sealing performance.

TABLE 11

Compound	Method of preparation	Characteristics of rubber solid Polymerization temperature (°C.)	Styrene content (%)	Mooney viscosity ($ML_{1+4}^{100°C.}$)	Resin Type and softening point (°C.)	Content (PHR)	Filler Type	Content (PHR)	Content of other ingredient (PHR)
I	Solvent	50	23	30	Rosin-type (83)	100	Kaolin clay	100	1
II	Solvent	50	23	30	Rosin-type (83)	100	Kaolin clay	100	1.5
III	Latex	50	23	30	Rosin-type (83)	50	Kaolin clay	120	6
IV	Latex	50	23	40	Xylene-type (95)	70	Kaolin clay	100	6
V	Latex	50	30	50	Petroleum (90) resin	100	Kaolin clay	90	6
VI	Latex	50	40	70	Rosin-type (83)	120	Kaolin clay + white carbon	80	6
VII	Latex	50	50	120	Rosin-type (104)	70	Calcium carbonate	100	6
VIII	Latex	50	50	120	Rosin-type (83)	100	Kaolin clay	100	6
IX	Latex	50	60	140	Rosin-type (83)	100	Kaolin clay	120	6
X	Latex	5	23	30	Rosin-type (83)	80	Kaolin clay	100	6
XI	Latex	5	35	50	Rosin-type (83)	90	Kaolin clay	100	6

TABLE 12

Compound	K	$J^{C}_{25}1(1)$ (cm^2/dyne)
I	0.96	2.1×10^{-6}
II	0.05	7.0×10^{-7}
III	0.41	6.1×10^{-7}
IV	0.15	1.3×10^{-8}
V	0.21	3.2×10^{-9}
VI	0.28	3.5×10^{-8}
VII	0.34	2.9×10^{-7}
VIII	0.59	2.2×10^{-8}
IX	0.45	1.5×10^{-9}
X	0.66	6.2×10^{-9}
XI	0.52	1.1×10^{-9}

TABLE 13-1

Content: Aqueous solution of citric acid plus sodium bicarbonate

		The number of cans which showed leakage or a decrease in the degree of vacuum				
Compound	Stored at	After one week	After one month	After 3 months	After 3 months	Total leakage ratio (%)
I	RT*	0	1	0	1	0.13
	50°C.	1	1	1	1	0.27
II	RT	2	0	1	0	0.20
	50°C.	3	0	0	1	0.27
III	RT	0	0	0	0	0
	50°C.	0	0	1	0	0.07
IV	RT	0	0	0	0	0
	50°C.	0	1	0	0	0.07
V	RT	1	0	0	0	0.07
	50°C.	0	0	0	0	0
VI	RT	0	0	0	0	0
	50°C.	0	0	0	0	0
VII	RT	0	0	0	0	0
	50°C.	0	0	0	0	0
VIII	RT	0	0	0	0	0
	50°C.	0	0	0	1	0.07
IX	RT	2	0	0	1	0.20
	50°C.	2	0	1	1	0.27
X	RT	0	0	1	1	0.13
	50°C.	0	1	0	3	0.27
XI	RT	3	1	0	0	0.27
	50°C.	2	0	1	2	0.33

*RT = room temperature

TABLE 13-2

Content: 10% orange juice

		the number of cans which showed leakage or a decrease in the degree of vacuum				
Compound	Stored at	After one week	After one month	After 3 months	After 6 months	Total leakage ratio (%)
I	RT*	2	0	1	0	0.20
	50°C.	0	1	2	1	0.27
II	RT	2	0	1	0	0.20
	50°C.	2	1	0	1	0.27
III	RT	0	0	0	1	0.07
	50°C.	0	0	0	0	0
IV	RT	0	0	0	0	0
	50°C.	0	1	0	0	0.07
V	RT	1	0	0	0	0.07
	50°C.	0	0	0	0	0
VI	RT	0	0	0	0	0
	50°C.	0	0	0	0	0
VII	RT	0	0	0	0	0
	50°C.	0	0	0	0	0
VIII	RT	0	0	0	0	0
	5048C.	0	0	0	1	0.07
IX	RT	3	0	0	0	0.20
	50°C.	2	1	0	1	0.27
X	RRT	0	1	1	1	0.20
	50°C.	0	1	1	2	0.27
XI	RT	2	0	1	1	0.27
	50°C.	3	0	0	0	0.20

*RT = room temperature

WHAT WE CLAIM IS:

1. A can end sealing rubber composition (A) consisting essentially of an aqueous emulsion of a styrene-butadiene rubbery copolymer, the emulsion being a latex obtained by emulsion polymerization at 35 to 70°C., or a diluted or concentrated product thereof, a tackifier and a filler, and (B) having (1) a creep resistance coefficient K defined by the following equation of at least 0.1, but not exceeding 0.6, $K = \log J^C_{90}(10) - \log J^C_{90}(1)$ wherein $J^C_{90}(10)$ is the creep compliance measured 10 minutes after exerting a load when a fabricated article of the composition as a specimen is compressed in water at 90°C. by a parallel plate plastometer, and $J^C_{90}(1)$ is the creep compliance measured 1 minutes after exerting a load when the specimen is compressed in water at 90°C. by a parallel plate plastometer, and (2) a creep compliance $J^C_{25}(1)$ of at least 3×10^{-9} cm^2/dyne but not exceeding 1×10^{-6} cm^2/dyne, the creep compliance being measred 1 minute after exerting a load when the specimen is compressed in water at 25°C. by a parallel plate plastometer.

2. A composition according to claim 1 where the styrene-butadiene copolymer latex has a solids content of 30 to 90% by weight.

3. A composition according to claim 1 or 2 wherein the styrene-butadiene copolymer

has a Mooney viscosity ($ML_{1+4}^{100°C}$) of 25 to 160.

4. A composition according to claim 1, 2 or 3 wherein the styrene-butadiene copolymer has a styrene content of 23 to 55% by weight.

5. A composition according to any one of the preceding claims which further comprises a surface active agent, an antioxidant and a thickener.

6. A composition according to claim 1 substantially as described in any one of the Examples.

7. A closed can comprising a can body sealed to a can end by means of a composition as claimed in any one of the preceding claims.

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1566924 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*

Fig. 1

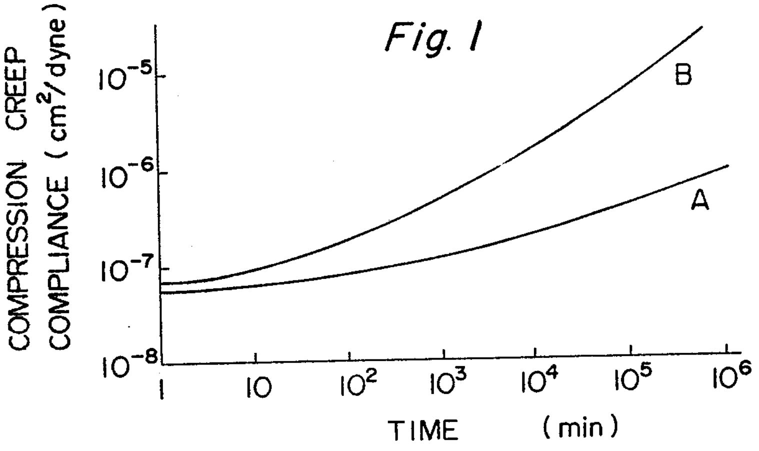

Fig. 2