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(54) Title: METHOD FOR PRODUCING RUBBER FROM RUBBER LATEX

(57) Abstract: A method for producing rubber from a latex by spraying and drying a rubber latex or, in the case of a natural rubber latex, a natural rubber latex, to which a viscosity stabilizing agent has been added when necessary, under an atmosphere of a shock wave generated from pulse combustion.



WO 2005/056611 A1

DESCRIPTION

METHOD FOR PRODUCING RUBBER FROM RUBBER LATEX

5 TECHNICAL FIELD

The present invention relates to a method for producing rubber from a rubber latex. More specifically, it relates to a method for producing rubber, particularly natural rubber, from a rubber latex providing a good productivity and heat efficiency and suppressing degradation of the quality of the rubber.

10 PRIOR ART

At the present time, natural rubber is being produced by manually obtained from rubber trees, followed by filtering, then coagulating and drying the latex, then shipping the natural rubber in the form of a sheet or block from the countries of origin. In this way, even at the present, where the importance of natural rubber is rather continuing to rise, rubber is produced from rubber latex relying on manual labor. Further, the latex coagulation step, rinsing step and drying step, in particular the drying step, have a large influence on the viscosity of the rubber product. The current method for production of rubber from rubber latex cannot be said to be sufficient in view of the variation in rubber quality. From this viewpoint, Japanese Unexamined Patent Publication (Kokai) No. 2003-26704 proposes a method of production of natural rubber enabling improvements in the productivity and quality.

30 Further, synthetic rubber latex obtained from emulsion polymerization is produced by adding brine and acids such as weak sulfuric acid for coagulation, separating the crumbs thus obtained from the serum, followed by washing, then charging the crumbs into a screw extruder type dryer for drying, and weighing and packaging the rubber. Like natural rubber, the step from
35 coagulation to removal of water takes time. Large

facilities are required at the present.

DISCLOSURE OF THE INVENTION

Accordingly, the objects of the present invention
5 are to provide a method for producing rubber having
superior quality and having largely improved work
efficiency and heat efficiency and providing rubber
suppressed in the heat degradation and gelling of rubber
liable to occur in conventional drying by heat when
10 producing the widely used rubber latexes including not
only natural rubber, but also synthetic rubber obtained
from emulsion polymerization.

In accordance with the present invention, there is
provided a method for producing rubber from a rubber
15 latex comprising spraying a rubber latex into an
atmosphere of a shock wave generated from pulse
combustion to thereby dry the rubber.

In accordance with the present invention, there is
also provided a method for producing natural rubber
20 using, as a rubber latex, a natural rubber latex containing
a viscosity stabilizer.

According to the present invention, instead of
conventional processes such as coagulation with an acid,
etc., natural coagulation, pulse combustion is used to
25 instantaneously dry the rubber latex, and therefore, a
major increase in productivity and heat efficiency is
achieved and the heat degradation or gelling of rubber
occurring with conventional drying by heat is suppressed.
As a result, control of the rubber quality becomes
30 extremely easier. Further, there are the advantages that,
due to the gelling being suppressed, the viscosity is
decreased and the mixing process of the rubber can be
streamlined from the past.

BEST MODE FOR CARRYING OUT THE INVENTION

35 It must be noted that, as used herein and in the
appended claims, the singular forms such as "a", "an" and
"the" include plural reference unless the context clearly

indicates otherwise.

According to the present invention, natural rubber latex or synthetic rubber latex synthesized from emulsion polymerization is dried to produce rubber using a pulse combustor generating a shock wave described for example in Japanese Unexamined Patent Publication (Kokai) No. 7-71875. In the present invention, such a pulse combustor is used to spray dry a latex having a solid concentration of 60% by weight or less in a drying chamber under conditions of a frequency of 250 to 1200 Hz, more preferably 300 to 1000 Hz, and a temperature of not more than 140°C, more preferably 40 to 100°C.

The solid (i.e., dried rubber) concentration of the rubber latex dried according to the present invention is preferably 60% by weight or less, more preferably 20 to 50% by weight. If the solid concentration is more than 60% by weight, the viscosity of the latex becomes higher and simultaneously the latex stability is decreased. As a result, when the latex is charged into a shock wave dryer, the latex may coagulate in the transport pipe or, may not be able to be sprayed well into the combustion chamber, or other problems may occur. Further, if the solid concentration is too low, the drying itself will not be a problem, but the amount of latex capable of drying in a unit time is decreased and the productivity will deteriorate, and therefor practical problems will sometimes occur.

The viscosity of natural rubber is known to generally increase along with time. Therefore, a viscosity stabilizing agent is sometimes introduced into the natural rubber to suppress the increase in the viscosity of natural rubber. In the present invention, it is possible to optionally blend a viscosity stabilizing agent into the natural rubber latex to be pulse dried in an atmosphere of a shock wave generated from the present pulse combustion.

It is possible to use any viscosity stabilizing

agent generally used in the past, which is not liable to break down under the above pulse drying conditions used in the present invention. Specifically, for example, one or more of hydroxylamines, semicarbazides and dimedones
5 may be used. These viscosity stabilizing agents are added in an amount of at least 0.001 part by weight, preferably 0.01 to 3 part by weight, based upon 100 parts by weight of solids (i.e., dried rubber) in the starting natural rubber latex. If the amount of the viscosity stabilizing
10 agent is too small, the viscosity stabilizing effect is liable to be not sufficient.

Specific examples of the viscosity stabilizing agents include, for example, hydroxylamine sulfate $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$, semicarbazide $(\text{NH}_2\text{CONHNH}_2)$, dimedone
15 (i.e., 1,1-dimethylcyclohexane-3,5-dione), etc. but the scope of the present invention is not limited to these examples.

The method for drying the latex according to the present invention can produce a rubber, in which rubber
20 compounding ingredients (for example, antioxidants, various types of carbon blacks, various types of silica, other fillers, oils, plasticizers, cross-linking agents, vulcanization accelerators, vulcanization accelerating aids, peptisers, coupling agents, preservatives) are
25 included in an aqueous solution, aqueous dispersion and/or hydrophilic organic solution of the third ingredients in the latex. Further, it is also possible to premix two or more types of latexes in a desired ratio to directly obtain a blend of different types of rubber.

30 EXAMPLES

The present invention will now be explained in detail, but the scope of the present invention is not intended to limit to these Examples.

Example 1 and Comparative Example 1

35 The method for producing natural rubber used in the past (i.e., ribbed smoked sheet (RSS)) is shown as Comparative Example 1.

Natural rubber latex was obtained from rubber tree by tapping, foreign matters were removed therefrom, formic acid was added thereto for coagulation, the water content was removed by rolling the latex (i.e., sheeting), then the resulting product was dried. The unsmoked sheet thus obtained was rinsed, then dried at 70°C, while smoking for 6 to 8 days, graded and ranked, then packed.

On the other hand, 5 liters of natural rubber latex (obtained in Thailand, solid concentration of approximately 35% by weight) stabilized by addition of ammonia in Example 1 was filtered to remove impurities, then spray dried using a pulse combustion dryer (made by Pultech corporation, Hypulcon (Brand Name)) under conditions of a frequency of 1000 Hz and a temperature of 60°C. The times necessary for drying in Example 1 and Comparative Example 1 were compared in Table I. As is clear from the results shown in Table I and, in Example 1 according to the present invention, the drying time for processing 5 liters of latex was decreased to about 3 hours. Note that the drying time was the processing capacity of the pulse combustion dryer. The time actually required for the water content to be removed was less than 1 second. The amount of latex which was able to be dried per unit time was determined by the size of the dryer. The processing capacity of the dryer used in Example 1 according to the present invention was about 2 kg/hour.

Table I

Comparative Example 1 (Prior Art)		Example 1	
Process	Re-quired time	Process	Re-quired time
1) Tapping (collecting)	-	1) Tapping (collecting)	-
2) Removal of impurities	-	2) Removal of impurities	-
3) Addition of acid and coagulation	0.5 day	3) Pulse combustion drying	3 hours
4) Rinsing	0.5 day		
5) Drying (smoking)	6 days		
Total processing time: about 7 days		Total processing time: 3 hours	

Example 2 and Comparative Example 2

5 The physical properties of the natural rubber
 obtained in Example 1 and commercially available natural
 rubber (i.e., RSS#1) were compared. That is, in each of
 the formulations shown in Table II, the ingredients other
 than the vulcanization accelerator and sulfur were mixed
 in a 1.7 liter Banbury mixer for 5 minutes and dumped,
 10 when reaching 140°C, to obtain a master batch. The
 vulcanization accelerator and sulfur were then mixed into
 this master batch by an 8-inch open roll to obtain a
 rubber composition. The Mooney viscosity (ML₁₊₄, 100°C) of
 the unvulcanized rubber composition thus obtained was
 15 measured according to a method of JIS K-6300-1. The
 results are shown in Table II.

Next, each rubber composition obtained above was
 vulcanized in a 15 x 15 x 0.2 cm mold at 150°C for 30
 minutes to prepare a vulcanized rubber sheet, which was
 20 then measured for physical properties by the test methods
 indicated below. The results are shown in Table II.

300% modulus (MPa): measured according to JIS K-6251
 (JIS No. 3 Dumbbell)

Strength at break: measured according to JIS K-6251
 25 (JIS No. 3 Dumbbell)

Elongation at break: measured according to JIS K-
 6251 (JIS No.3 Dumbbell)

As is clear from the results shown in Table II, in

Example 2 according to the present invention, the properties at break were similar, the Mooney viscosity was decreased and the workability (or processability) was improved.

5

Table II

Name of Material (parts by weight)	Comp. Ex. 2	Ex. 2
Natural rubber (RSS#1)	100	-
Natural rubber*1	-	100
HAF grade carbon (Shoblack N339, Showa Cabot)	50	50
Zinc oxide (Zinc Oxide No. 3, Seido Chemical Industry)	3	3
Stearic acid (Beads Stearic Acid YR, NOF)	2	2
Aromatic oil (Extract No. 4S, Showa Shell Sekiyu)	5	5
Sulfur ("Kinka" sulfur fine powder, Tsurumi Chemical)	2	2
Vulcanization accelerator (Noccelar NS-F, Ouchi Shinko Chemical Industrial)	1	1
<u>Unvulcanized properties</u>		
Mooney viscosity (ML ₁₊₄)	95	91
<u>Vulcanized properties (room temperature)</u>		
300% Modulus (MPa)		
Tensile strength at break (MPa)	17.5	16.6
Elongation at break (%)	30.9	30.4
	495	516

*1: Natural rubber produced in Example 1.

Example 3 and Comparative Example 3

10 The method for producing of emulsion polymerized SBR used in the past is shown as Comparative Example 3.

After the monomer was removed from the polymerized SBR latex, then sodium chloride was added to make a creamy state, then weak sulfuric acid was added to cause
 15 coagulation. The resultant mixture was vigorously stirred by propellers of a coagulation tank, the coagulated crumbs were pulverized, the serum was separated, then the resultant product was washed and passed through a screw extruder type dryer for drying.

20 On the other hand, in Example 3, 5 liters of SBR latex obtained by emulsion polymerization (A9725HT, made by Nippon Zeon, solid content: 50 wt%) was dried using a shock wave dryer (made by Pultech corporation, Hypulcon (Brand Name), processing capacity 2 kg/h) under

conditions of a frequency of 1000 Hz and a temperature of 70°C.

Table III

Comparative Example 3 (Prior Art)	Example 3
Process	Process
Polymerization ↓ Monomer recovery ↓ Sodium chloride and acid addition and coagulation ↓ Pulverization ↓ Rinsing ↓ Drying ↓ Weighing	Polymerization ↓ Monomer recovery ↓ Pulse combustion drying ↓ Weighing

- 5 *(Note) Required times are omitted, because they differ depending on facility and the process is performed continuously.

Example 4 and Comparative Example 4

10 The rubber physical properties of synthetic rubber obtained by the method of Example 3 (SBR) were compared with those of the commercially available product (Nipol 1502 made by Nippon Zeon). That is, in each of the formulations shown in Table IV, the ingredients other than the vulcanization accelerator and sulfur were mixed
15 in a 1.7 liter Banbury mixer for 5 minutes and dumped, when reaching 140°C to obtain a master batch. The vulcanization accelerator and sulfur were mixed into this master batch by an open roll to obtain a rubber composition.

20 Next, the rubber composition thus obtained was vulcanized in a 15 x 15 x 0.2 cm mold at 150°C for 20 minutes to prepare a vulcanized rubber sheet, which was then measured for physical properties according to the test methods indicated above. The results are shown in
25 Table IV. As is clear from the results shown in Table IV, the physical properties are similar to or better than the

prior art and free of problems, the Mooney viscosity was decreased and an improvement in workability was observed.

Table IV

Name of materials (parts by weight)	Comp. Ex. 4	Example 4
Comparative Example SBR (Nipol 1502, Nippon Zeon)	100	-
Example SBR*1	-	100
HAF grade carbon (Shoblack N339, Showa Cabot)	40	40
Zinc oxide (Zinc Oxide No. 3, Seido Chemical Industry)	3	3
Stearic acid (Beads Stearic Acid YR, NOF)	1	1
Aromatic oil (Extract No. 4S, Showa Shell Sekiyu)	5	5
Sulfur ("Kinka" sulfur fine powder, 150 mesh, Tsurumi Chemical)	2	2
Vulcanization accelerator (Noccelar NS-F, Ouchi Shinko Chemical Industrial)	1	1
<u>Unvulcanized properties</u>		
Mooney viscosity (ML ₁₊₄)	60	57
<u>Vulcanized properties (room temperature)</u>		
300% modulus (MPa)	10.8	11.2
Tensile strength at break (MPa)	20.8	21.6
Elongation at break (%)	470	476

5 *1: SBR produced by the method of Example 3

Example 5 and Comparative Examples 5 to 8

10 The following natural rubbers were used for measurement of the viscosity stabilities and the vulcanized physical properties of the rubber compositions.

15 Natural rubber of Example 5, (Pulse-NRCV): First, 1000 g of "HA LATEX" (made by Golden Hope Plantation BHD (Malaysia), dried rubber constant (DRC) = 60 wt%) was diluted by 2000 g of water to obtain 3000 g of a DRC=20% NR latex. 6 g of a 10% aqueous solution of hydroxylamine sulfate was added to this NR latex to obtain a viscosity stabilizing agent-containing latex. This viscosity stabilizing agent-containing latex was dried using the shock wave dryer used in Example 1 to obtain the sample.

20 Natural Rubber of Comparative Examples 5 to 8: The generally available natural rubber SMR CV60, STR20CV60, RSS#3, and STR20 were used. For the reference, the production methods of the commercially available

viscosity-stabilized natural rubber are shown below.

5 SNR CV60: A type of technically specified rubber (TSR) obtained by adding to natural rubber latex an acid or viscosity stabilizer (i.e., hydroxylamine sulfate) in a natural rubber processing factory to coagulate, then washing, breaking, drying, and otherwise processing it. The viscosity stabilizer was added in an amount of 0.05 to 0.10 part by weight, based upon 100 parts by weight of dried rubber.

10 STR20CV60: A type of technically specified rubber (TSR) obtained by field coagulum (cup lump) to the steps of washing, breaking, and drying in a natural rubber processing factory, then mixing in a viscosity stabilizing agent (i.e., hydroxylamine sulfate) by a
15 prebreaker. The viscosity stabilizing agent was added in an amount of 0.05 to 0.10 part by weight, based upon 100 parts by weight of dried rubber.

20 In each of the formulations shown in Table V, the ingredients other than the vulcanization accelerator and sulfur were mixed in a 1.7 liter Banbury mixer for 5 minutes and discharged, when reaching 140°C to obtain a master batch. The vulcanization accelerator and sulfur were mixed into this master batch by an 8-inch open roll to obtain a rubber composition.

25 Next, the rubber composition obtained above was vulcanized in a 15 x 15 x 0.2 cm mold at 150°C for 30 minutes to prepare a vulcanized rubber sheet which was then measured for physical properties according to the test methods indicated above. The results are shown in
30 Table V.

Table V

		Ex. 5	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7	Comp. Ex. 8
Properties of starting material (impurities content)*1		0.01	0.01	0.10	0.05	0.09
Viscosity of starting material (Viscosity stability)*2	Viscosity after 1 week (index)	101	100	102	113	109
	Viscosity after 1 month (index)	101	102	107	120	113
	Viscosity after 3 months (index)	102	103	108	133	120
Formulation (parts by weight)	Pulse-NRCV	100	-	-	-	-
	SMR CV60	-	100	-	-	-
	STR20CV60	-	-	100	-	-
	RSS#3	-	-	-	100	-
	STR20	-	-	-	-	100
	Carbon (HAF grade) (Shoblack N339, Showa Cabot)	45	45	45	45	45
	Zinc oxide (Zinc Oxide No. 3, Seido Chemical Industry)	5	5	5	5	5
	Stearic acid (Beads Stearic Acid YR, NOF)	3	3	3	3	3
	Aromatic oil (Extract No. 4S, Showa Shell Sekiyu)	6	6	6	6	6
	Sulfur ("Kinka" sulfur powder, Tsurumi Chemical)	2	2	2	2	2
	Vulcanization accelerator (Noccelar NS-F, Ouchi Shinko Chemical Industrial)	0.7	0.7	0.7	0.7	0.7
	300% Modulus (index)	104	101	96	103	100
Physical properties after vulcanization*3	Tensile strength at break (index)	108	104	96	101	100
	Elongation at break (index)	98	100	93	100	100

*1: Measured according to ISO 249: 1987

*2: Measured according to ISO 289-2: 1994. The viscosity stability is indexed to the Mooney viscosity right after production and indicates the Mooney viscosity after storage a predetermined time at room temperature. The larger the value, the larger the change in viscosity indicated.

*3: Tensile test conducted according to JIS K 6251-1993 using a dumbbell shaped No. 3 test piece at room temperature with a tensile rate of 500 mm/min. The value is indicated indexed to the value of Comparative Example 8 (STR20). The larger the value, the better the physical properties shown.

INDUSTRIAL APPLICABILITY

In the rubber production method from a latex according to the present invention, in the case of natural rubber, the latex is obtained by tapping and the
5 impurities etc. filtered from the latex, then the latex is sprayed in an atmosphere of a shock wave generated by pulse combustion, without coagulation by an acid, etc. and the moisture is removed to instantaneously dry the rubber latex, and therefore the processing efficiency and
10 heat efficiency of production of rubber from latex can be improved. Further, the quality of the rubber obtained is not liable to degrade under heat or to gel as in the past and is excellent. Further, even in the case of synthetic rubber obtained by emulsion polymerization, there are no
15 steps of coagulation by an acid, separation of crumbs and serum, washing, and drying, i.e., the water content in the latex can be directly removed by the pulse combustion, and therefore, not only is the production efficiency largely increased, but also the heat history
20 is greatly reduced and the physical properties of the rubber can be improved. Further, adjustment and management of the pH of the crumbs and serum and the salt concentration become unnecessary as well, and therefore the quality of the rubber becomes stable and facilities
25 for the recovery and reuse of acid and measures against corrosion of the same also become unnecessary. The present invention is therefore useful as a rubber production method from natural rubber or other rubber latex.

CLAIMS

1. A method for producing rubber from a rubber latex comprising spraying a rubber latex into an atmosphere of a shock wave generated from pulse
5 combustion to thereby dry the rubber.

2. A method for producing rubber as claimed in claim 1, wherein a solid concentration of the rubber latex is 60% by weight or less, in terms of dry rubber.

3. A method for producing rubber as claimed in
10 claim 1 or 2, wherein a frequency of the pulse combustion is 250 to 1200 Hz and a temperature of a drying chamber for spraying the latex is 140°C or less.

4. A method for producing rubber as claimed in any one of claims 1 to 3, wherein the rubber latex is a
15 natural rubber latex.

5. A method for producing rubber as claimed in claim 4, further comprising spray drying under an atmosphere of a shock wave generated from the pulse combustion in the presence of a viscosity stabilizing
20 agent added to the natural rubber latex.

6. A method for producing rubber as claimed in claim 5, wherein the amount of the viscosity stabilizing agent is at least 0.001 part by weight based upon 100 parts by weight of solid content in the latex.

7. A method for producing rubber as claimed in
25 claim 5 or 6, wherein the viscosity stabilizing agent is at least one compound selected from the group consisting of hydroxyl amines, semicarbazides and dimedones.

8. A rubber composition obtainable from a method
30 according to claim 1 to 7.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP2004/018690

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08C1/12 C08L7/00 C08L7/02

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)

IPC 7 C08C 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 practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 708 159 A (LOCKWOOD, JR. ET AL) 24 November 1987 (1987-11-24) the whole document	1-8
A	US 5 252 061 A (OZER ET AL) 12 October 1993 (1993-10-12) column 7, line 42; claim 1	1-8
A	US 4 859 248 A (THALER ET AL) 22 August 1989 (1989-08-22) the whole document	1-8
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

° Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
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Date of the actual completion of the international search

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Name and mailing address of the ISA

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP2004/018690

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>LIU X D ET AL MUJUMDAR A S (ED): "PULSE COMBUSTION DRYING" DRYING '98. PROCEEDINGS OF THE 11TH INTERNATIONAL DRYING SYMPOSIUM. IDS '98. HALKIDIKI, AUG. 19 - 22, 1998, DRYING. INTERNATIONAL DRYING SYMPOSIA, THESSALONIKI : ZITI EDITIONS, GR, vol. VOL. A, 1998, pages 496-503, XP000788172 ISBN: 960-431-468-8 the whole document -----</p>	1-8

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4708159	A	24-11-1987	AT 129325 T	15-11-1995
			AU 7392987 A	09-11-1987
			CA 1297761 C	24-03-1992
			CA 1313124 C2	26-01-1993
			CA 1309651 C2	03-11-1992
			CA 1313042 C2	26-01-1993
			CN 87102874 A ,C	30-03-1988
			CN 1071500 A	28-04-1993
			DE 3751565 D1	23-11-1995
			DE 3751565 T2	30-05-1996
			EP 0265490 A1	04-05-1988
			JP 1500048 T	12-01-1989
			US 4838784 A	13-06-1989
			US 4819873 A	11-04-1989
			US 4767313 A	30-08-1988
			WO 8706321 A1	22-10-1987
			US 4992043 A	12-02-1991
			US 4941820 A	17-07-1990
			US 4992039 A	12-02-1991
			ZA 8702620 A	25-11-1987
<hr/>				
US 5252061	A	12-10-1993	NONE	
<hr/>				
US 4859248	A	22-08-1989	US 4667654 A	26-05-1987
<hr/>				