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(54) **Title**: METHOD OF PRODUCING AN IMPERMEABLE RUBBER LAYER

(57) **Abstract**: A method of producing impermeable rubber layers, and which includes: a step of preparing an aqueous emulsion containing at least a cross-linkable polymer base, and a surface-active agent of molecular formula (I) { $[R_1R_2R_3NR_5\ (NR_4R_6R_7)\ n]^{(n+1)+}$) y (n+1)$X^{y-}$ where : X is an anionic atom or group; R_1, R_2 and R_3, which may be the same or different, are each C_mH_{2m+1}, where m ranges between 1 and 3, or CH_2CHCH_2 or $CHCHCH_3$; R_4, R_6 and R_7, which may be the same or different, are each CH_2CHCH_2 or $CHCHCH_3$; n is 0 or 1; y is 1 when n is 1; y is 1 or 2 when n is 0; R_5 is an aliphatic group C_{15}-C_{22} when n is 0; and is an aliphatic group C_8-C_{16} when n is 1; when n is 0, at least one of R_1, R_2, R_3 and R_5 has a double bond.

METHOD OF PRODUCING AN IMPERMEABLE RUBBER LAYER

TECHNICAL FIELD

The present invention relates to a method of producing an impermeable rubber layer.

More specifically, the invention relates to an innerliner made from an aqueous emulsion, to which the following description refers purely by way of example.

BACKGROUND ART

As is known, many industrial applications need to produce increasingly thin impermeable layers, but without impairing the impermeability of the layers themselves.

In the tyre industry, a thinner impermeable layer, known as an innerliner, basically amounts to using less material, which has obvious advantages in terms of output, tyre weight reduction, tyre rolling resistance, and overall vehicle fuel consumption.

Mixes for impermeable layers, such as innerliners, are normally produced using internal, so-called Banbury mixers, which involves at least two mixing steps : a longer, high-temperature first mixing step to form the basic mix, and in which ingredients such as carbon black, zinc oxide, stearic acid, wax, antioxiders, etc. are added and mixed with the polymer base; and a cooler second mixing step to complete the basic mix, and in

which curing agents, such as sulphur, and accelerants and/or retarding agents are added to the mix from the first step. The purpose of the cooler second step is to ensure dispersion of the curing agents below temperatures that could prematurely cure the mix. The resulting mix must then be extruded or calendered to the required shape.

Highly impermeable rubber products are normally produced with a butyl rubber matrix.

As is known, the impermeability of rubber can be enhanced using fillers, which, if mixed properly, form a steric obstruction capable of greatly improving impermeability. In other words, when mixed with the polymer base, fillers such as clay, kaolin, mica, etc. form an air barrier in the finished product, preventing airflow through it, and so making it more impermeable.

Any anisotropy of the filler may also improve rubber impermeability.

The impermeability of polymer materials to gas or low-molecular-weight substances is also known to increase with glass transition (Tg). A typical example of this is polyethylene terephthalate (PET), widely used for packaging in the food and drink industry. Using conventional technology, however, mechanically coupling rubber and high-Tg polymers, such as PET, invariably poses serious difficulties.

While enhancing the impermeability and so enabling a reduction in the thickness of rubber products, the above solutions nevertheless pose various processing problems. Using the traditional Banbury mixer method, for example, mixing a clay-containing polymer base is highly energy-intensive, and does not always guarantee effective blending and/or compatibility of all the mix ingredients. Poor blending and/or compatibility of fillers with the rest of the rubber matrix impairs the mechanical characteristics of the end product; and the above problems are further compounded when the polymer base comprises high-Tg polymers.

High energy consumption of the production process not only raises environment issues, but also increases cost.

Current technology is also limited in its ability to produce layers below a given thickness. In fact, the extrusion and/or calendaring step, to which the mix is subjected to form the impermeable layer, demands a minimum thickness of rarely less than 0.5 mm.

The extruded impermeable layer may also vary in thickness, due to the extrusion process itself; and, because it is eventually applied, at the manufacturing stage, to a shape that also varies in thickness, all these varying thickness points may result in small fractures in the impermeable layer, caused by mechanical

and thermal expansion of the tyre at the tyre building stage.

The Applicant has surprisingly discovered a method of producing mixes for impermeable rubber layers, which, compared with those of the known art, are less energy-intensive, thinner, and more impermeable.

DISCLOSURE OF INVENTION

According to the present invention, there is provided A method of producing impermeable rubber layers; said method being characterized by comprising:

- a step of preparing an aqueous emulsion comprising at least a cross-linkable polymer base, and a surface-active agent of molecular formula (I)

$$([R_1R_2R_3NR_5(NR_4R_6R_7)n]^{(n+1)+})y\ (n+1)X^{y-} \qquad (I)$$

where :

X is an anionic atom or group;

R_1, R_2 and R_3, which may be the same or different, are each C_mH_{2m+1}, where m ranges between 1 and 3, or CH_2CHCH_2 or $CHCHCH_3$;

R_4, R_6 and R_7, which may be the same or different, are each CH_2CHCH_2 or $CHCHCH_3$;

n is 0 or 1;

y is 1 when n is 1; y is 1 or 2 when n is 0;

R_5 is an aliphatic group C_{15}-C_{22} when n is 0; and is an aliphatic group C_8-C_{16} when n is 1;

when n is 0, at least one of R_1, R_2, R_3 and R_5

comprises a double bond.

R_1, R_2 and R_3 are preferably CH_2CHCH_2, and, more preferably, n is 1, and R_5 is a saturated aliphatic group.

Preferably, R_5 comprises a double bond, and n is 0.

Preferably, the surface-active agent has a molecular formula in the group comprising :

$[(CH_3)_3N(CH_2)_8CHCH(CH_2)_7CH_3]^+ X^-$;

$[(CH_2CHCH_2)_3N(CH_2)_{15}CH_3]^+ X^-$;

$[(CH_3)(CH_2CHCH_2)_2N(CH_2)_{15}CH_3]^+ X^-$;

$[(CH_2CHCH_2)(CH_3)_2N(CH_2)_{15}CH_3]^+ X^-$;

$[(CH_2CHCH_2)_3N(CH_2)_{12}N(CH_2CHCH_2)_3]_2^+ 2X^-$.

Preferably, X^- is I^- or Br^-.

BEST MODE FOR CARRYING OUT THE INVENTION

The following are non-limiting examples, for a clearer understanding of the invention.

EXAMPLES

The following is a description of five mixes (A-E) in accordance with the present invention, each produced by forming a respective aqueous emulsion by dispersing and mixing the mix components in water.

Part of the aqueous emulsion was subsequently sprayed or brushed onto a substrate, and the water was evaporated.

The five mixes (A-E) according to the invention

differed by comprising a different one of the following five surface-active agents (a, b, c, d, e) of molecular formula (I) :

- surface-active agent (a) of molecular formula $[(CH_3)_3N(CH_2)_8CHCH(CH_2)_7CH_3]^+ I^-$;

- surface-active agent (b) of molecular formula $[(CH_2CHCH_2)_3N(CH_2)_{15}CH_3]^+ Br^-$;

- surface-active agent (c) of molecular formula $[(CH_3)(CH_2CHCH_2)_2N(CH_2)_{15}CH_3]^+ I^-$;

- surface-active agent (d) of molecular formula $[(CH_2CHCH_2)(CH_3)_2N(CH_2)_{15}CH_3]^+ I^-$;

- surface-active agent (e) of molecular formula $[(CH_2CHCH_2)_3N(CH_2)_{12}N(CH_2CHCH_2)_3]_2^+ 2Br^-$.

More specifically, the emulsions were formed by dispersing all the ingredients in the Table below simultaneously in enough water to form a homogeneous emulsion. The resulting aqueous solution was agitated mechanically for 30 minutes and then sonicated for 15 minutes to form an aqueous emulsion.

The above method of producing the aqueous emulsions in no way constitutes a limitation of the present invention.

A control mix (ctrl) was also produced using the traditional Banbury mixing method, and with the same composition as the mixes according to the invention, but obviously without the surface-active agent, and

comprising stearic acid necessary for conventional curing.

The Table below shows the compositions in phr of the control mix, and the mixes produced from respective emulsions in accordance with the present invention.

For each mix, the Table also shows mixing power consumption; the impermeability index, for the same thickness, with respect to that of the control mix; and thickness for the same impermeability.

More specifically, the impermeability indices refer to impermeability to oxygen, and were determined from respective 0.3 mm thick mix layers, which, in the case of mixes A-E, were formed by spraying or brushing the respective emulsions onto a 1 mm substrate. The measurements were made using conventional equipment, such as a MOCON OX-TRA (2/20 module) at 0% relative humidity and 30°C temperature.

TABLE

	Ctrl	A	B	C	D	E
BUTYL RUBBER	100	100	100	100	100	100
CARBON BLACK	30	30	30	30	30	30
CLAY	50	50	50	50	50	50
PROCESS OIL O	15	15	15	15	15	15
RESIN	5	5	5	5	5	5
STEARIC ACID	2	--	--	--	--	--

ZnO	3	3	3	3	3	3
ACCELERANTS	1,5	1,5	1,5	1,5	1,5	1,5
SULPHUR	0,5	0,5	0,5	0,5	0,5	0,5
SURFACE-ACTIVE AGENT (a)	--	2	--	--	--	--
SURFACE-ACTIVE AGENT (b)	--	--	2	--	--	--
SURFACE-ACTIVE AGENT (c)	--	--	--	2	--	--
SURFACE-ACTIVE AGENT (d)	--	--	--	--	2	--
SURFACE-ACTIVE AGENT (e)	--	--	--	--	--	2
MIXING POWER (KWh)	35	20	20	20	20	20
PERMEABILITY INDEX	100	105	107	105	105	108
THICKNESS FOR A GIVEN IMPERMEABILIY (mm)	0,90	0,86	0,84	0,86	0,86	0,83

As shown clearly in the Table, compared with conventional Banbury mixing methods, the method according to the present invention provides for producing more impermeable, less energy-intensive rubber layers.

To improve the impermeability of the rubber layer using the method according to the present invention, high-Tg polymers and large amounts of filler can be

employed, while still ensuring homogeneous blending of the ingredients, and lower energy consumption.

The fillers used in the impermeable layer according to the present invention are preferably defined by mineral particles with a diameter of 0.2 to 2 μm, and an aspect ratio of 5 to 30 and preferably 8 to 20, and are preferably in the group comprising kaolin, clay, mica, feldspar, silica, graphite, bentonite, and alumina.

In short, compared with the known art, the impermeable layers produced according to the present invention have the major advantage of being producible thinner, and of being more impermeable and less energy-intensive.

In fact, using an aqueous emulsion comprising surface-active agents of molecular formula (I), the various ingredients - especially those that are difficult to mix using conventional methods - are dispersed effectively and cheaply; and very thin layers can be formed, by virtue of being formed directly on the application surface, once the water in the applied emulsion evaporates.

Reducing the thickness of the impermeable layer amounts, in the examples described, to a roughly 5% reduction in tyre weight as a whole, with obvious advantages in terms of rolling resistance.

The impermeable layers according to the present

invention also have the advantage of being formed directly upon application, i.e. with no short- or long-term storage, which could degrade the rubber.

The impermeable layers may even be applied to the built tyre, after all the expansion work is completed, thus safeguarding against cracks and surface defects frequently encountered in impermeable layers produced using conventional methods.

Finally, the water-mixed impermeable layers may also be used to repair impermeable layers produced using conventional methods.

CLAIMS

1) A method of producing impermeable rubber layers; said method being characterized by comprising:

- a step of preparing an aqueous emulsion comprising at least a cross-linkable polymer base, and a surface-active agent of molecular formula (I)

$$([R_1R_2R_3NR_5(NR_4R_6R_7)n]^{(n+1)+})y\ (n+1)X^{y-} \qquad (I)$$

where :

X is an anionic atom or group;

R_1, R_2 and R_3, which may be the same or different, are each C_mH_{2m+1}, where m ranges between 1 and 3, or CH_2CHCH_2 or $CHCHCH_3$;

R_4, R_6 and R_7, which may be the same or different, are each CH_2CHCH_2 or $CHCHCH_3$;

n is 0 or 1;

y is 1 when n is 1; y is 1 or 2 when n is 0;

R_5 is an aliphatic group C_{15}-C_{22} when n is 0; and is an aliphatic group C_8-C_{16} when n is 1;

when n is 0, at least one of R_1, R_2, R_3 and R_5 comprises a double bond.

2) A method of producing impermeable rubber layers, as claimed in Claim 1, characterized in that R_1, R_2 and R_3 are CH_2CHCH_2.

3) A method of producing impermeable rubber layers, as claimed in Claim 2, characterized in that n is 1, and

R_5 is a saturated aliphatic group.

4) A method of producing impermeable rubber layers, as claimed in Claim 1, characterized in that R_5 comprises a double bond, and n is 0.

5) A method of producing impermeable rubber layers, as claimed in Claim 1, characterized in that said surface-active agent of molecular formula (I) has a molecular formula in the group comprising :

$[(CH_3)_3N(CH_2)_8CHCH(CH_2)_7CH_3]^+ X^-$;

$[(CH_2CHCH_2)_3N(CH_2)_{15}CH_3]^+ X^-$;

$[(CH_3)(CH_2CHCH_2)_2N(CH_2)_{15}CH_3]^+ X^-$;

$[(CH_2CHCH_2)(CH_3)_2N(CH_2)_{15}CH_3]^+ X^-$;

$[(CH_2CHCH_2)_3N(CH_2)_{12}N(CH_2CHCH_2)_3]_2^+ 2X^-$.

6) A method of producing impermeable rubber layers, as claimed in one of the foregoing Claims, characterized in that X^- is I^- or Br^-.

7) A method of producing impermeable rubber layers, as claimed in one of the foregoing Claims, characterized in that said aqueous emulsion comprises a mineral filler comprising particles with a diameter of 0.2 to 2 µm and an aspect ratio of 5 to 30.

8) A method of producing impermeable rubber layers, as claimed in Claim 7, characterized in that said mineral filler comprises particles with an aspect ratio of 8 to 20.

9) A method of producing impermeable rubber layers,

as claimed in Claim 7 or 8, characterized in that said mineral filler is in the group comprising kaolin, clay, mica, feldspar, silica, graphite, bentonite, and alumina.

10) A method of producing impermeable rubber layers, as claimed in one of the foregoing Claims, characterized in that said cross-linkable polymer base comprises polymers with a Tg of over 0°C.

11) An impermeable rubber layer, characterized by being made using the method as claimed in one of the foregoing Claims.

12) An innerliner, characterized by being made from an impermeable rubber layer as claimed in Claim 11.

13) An innerliner repair layer, characterized by being made from an impermeable rubber layer as claimed in Claim 11.

14) A tyre, characterized by comprising an innerliner as claimed in Claim 12, or a repair layer as claimed in Claim 13.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2011/055828

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08J3/03 C08K5/19
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)
C08J C08K

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2 181 861 A1 (BRIDGESTONE CORP [JP]) 5 May 2010 (2010-05-05) claims 1,4, 6, 7; examples A-F	1-14
X	US 3 840 382 A (BURKE O) 8 October 1974 (1974-10-08) example 41	1,4,7-11
A	US 2007/161734 A1 (FUDEMOTO HIROYUKI [JP] ET AL) 12 July 2007 (2007-07-12) paragraph [0061]; table 8	1-14

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 2181861 A1	05-05-2010	EP 2181861 A1	05-05-2010
		ES 2371371 T3	30-12-2011
		US 2011275741 A1	10-11-2011
		WO 2010049470 A1	06-05-2010
US 3840382 A	08-10-1974	NONE	
US 2007161734 A1	12-07-2007	NONE	