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(71) Applicant *(for all designated States except US)*: **METSO PAPER, INC.** [FI/FI]; Fabianinkatu 9 A, FI-00130 Helsinki (FI).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: **RUOTSI, Juha** [FI/FI]; Töyhtötiaisenkuja 2, FI-90420 Oulu (FI).

(74) Agent: **TURUN PATENTTITOIMISTO OY**; P.O. Box 99, FI-20521 Turku (FI).

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(54) **Title**: A ROLL FOR A FIBER WEB MACHINE

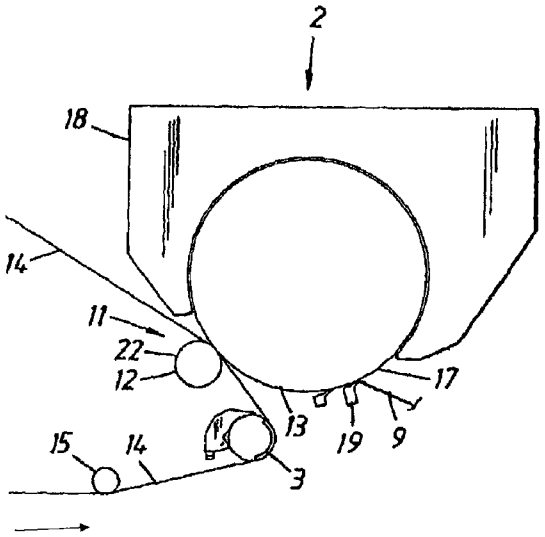


Fig. 1

(57) **Abstract**: The invention relates to a roll cover for a roll of a fiber web machine, comprising at least one rubber compound. A typical roll cover according to the invention further comprises at least one quinone diimine in an amount of 0.05 - 10 parts per hundred parts of rubber.

A ROLL FOR A FIBER WEB MACHINE

FIELD OF THE INVENTION

The present invention relates to a roll cover or a belt for a roll of a fiber web machine, comprising at least one rubber compound. The invention also relates to a roll of a fiber web machine.

BACKGROUND OF THE INVENTION

In paper, board, finishing, pulp and tissue machines several different types of rolls are used, such as press rolls, suction rolls, guide rolls, calender rolls, coater rolls etc. It is known that these rolls, which are typically made of metal, can be covered by elastic covers made of polymers or elastomers or rubber. It is also known that flexible belts made of such materials are used as roll shells in so caller shoe presses.

Rubber covers are traditionally used in press rolls, suction rolls and guide rolls. Rubber covers are subject for the ageing phenomenon especially when used in hot and wet environments. Ageing is noticed on rubber cover as hardness change, surface cracking or colour change. These changes shorten the service life of the rubber roll cover. In rubber cover business, this common ageing effect is typically known as after-hardening. Among the most demanding end applications for rubber compounds are press or suction roll covers in tissue machines in which the rubber covered roll or belt of a shoe press is pressed against a cylinder. These covers are subjected to high external temperatures in wet environments. Dynamical conditions are very severe as loading frequency is high (high machine speed with small pressure roll diameter), combined with remarkable linear load levels. Such covers are also typically softer (hardness typically about 30-50 P&J) than pressure covers used in other paper machine applications.

Covers of press rolls and suction rolls of paper or board machines are also prone to ageing due to wet conditions.

It is know that some rubber polymer types are more inclined to ageing effects than others. Typically, double bond containing polymers (natural rubber, SBR, NBR) are more sensitive than saturated polymers (EPDM, HNBR). There are also several commercial protection agents available. Most of them are also called as antidegradants and common substances are aromatic amines as for example phenylene diamines like IPPD or 5PPD; phenols and phosphates. Also, mostly in static applications, certain waxes are used to improve the effect of the antidegradant. Waxes typically migrate on the compound surface to form a protective film.

A typical problem for conventional antidegradants is their high solubility in aqueous media. This means that when exposed to water and/or steam, conventional antidegradants are extracted out from the rubber compounds. This leads to an undesired change in the properties of the rubber compound. Moreover, conventional antidegradants typically do not form covalent bonds with the rubber polymer or elastomer.

OBJECTS AND SUMMARY OF THE INVENTION

An object of the present invention is to minimise or even totally eliminate the problems existing in the prior art.

An object of the present invention is to create a cover of a roll that has an improved resistance to ageing and hardening during use. Another object of the invention is to provide a roll and a fiber web machine that stand the extreme conditions of for example tissue machine better than the rolls of the prior art.

The present invention relates to a roll cover for a roll of a fiber web machine, comprising at least one rubber compound. A roll cover according to the invention further comprises at least one quinone diimine in an amount of 0.05 - 10 parts per hundred parts of rubber.

The invention also relates to a roll of a fiber web machine comprising a roll cover according to the present invention and to the use of quinone diimine, preferably N-

{4-[(1,3-dimethylbutyl)imino]-2,5-cyclohexadien-1-ylidine}-benzeneamine in rubber compositions for roll covers.

BRIEF DESCRIPTION OF THE DRAWING

Figure 1 schematically presents a dryer section of a tissue machines as one example of the environment for the roll of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

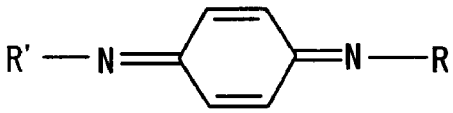
The present invention relates to a roll cover for a roll of a fiber web machine, comprising at least one rubber compound. A typical roll cover according to the invention further comprises at least one quinone diimine in an amount of 0.05 - 10 parts per hundred parts of rubber.

An advantage of the present invention is that when the rubber compound contains this type of antidegradant, it has a better and long lasting protection against changes caused by the environment. When better ageing (or after-hardening) resistance is achieved, the service life of the rubber roll cover can be extended.

Furthermore, as the chemical bonding of quinone diimines occurs during the non-reversible curing process of the rubber compound(s), this leads to durable bonding and problems like water leaching can be thus prevented.

It is to be understood that in this context, although the term roll cover is used it is not meant to limit to such roll covers only that are cast on a metal or fiber reinforced body but flexible roll shell bodies, such as show press belts are also included in the scope of the invention. Moreover, when paper web is mentioned in this text, it is clear that also webs of board, tissue and other webs comprising mainly cellulosic fibers are covered by this expression, which is only used for simplicity of wording.

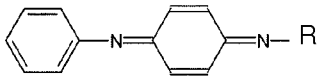
The quinone diimine used in this invention has the general formula (I)



(I)

wherein R and R' represent each independently a chain hydrocarbon group such as a methyl group, an ethyl group, an n-propyl group or an isopropyl group, an alicyclic hydrocarbon group such as a cyclohexyl group, an aromatic hydrocarbon group such as a phenyl group. R and R' may each represent the same substituent, or may be different substituents.

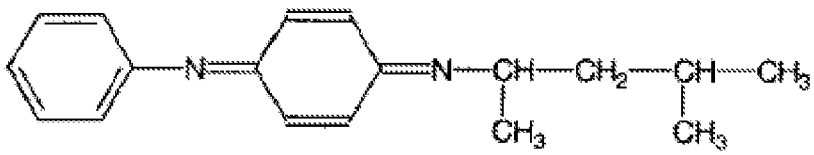
A preferable quinone diimine is N-alkyl-N´-phenyl-p-quinonediimine of the formula (II)



(II)

where R represents an alkyl moiety C_nH_{2n+1} and is selected from the group consisting of methyl, ethyl, propyl, butyl, pentyl, hexyl, either as an n-alkyl or as a branched alkyl in which one or more of the hydrogen atoms is replaced with a methyl group CH_3.

According to an embodiment of the invention, R in the above formula (II) is 1,3-dimethylbutyl group and the quinone diimine is thus N-{4-[(1,3-dimethylbutyl)imino]-2,5-cyclohexadien-1-ylidine}-benzeneamine. This compound has a CAS registration number 52870-46-9 and has the following formula (III).



(III)

It is also sold under the trade name of Q-Flex QDI by Flexsys.

According to another embodiment of the invention, the amount of quinone diimine is 0.1 – 5 parts per hundred parts of rubber, preferably 0.5 – 2 parts per hundred parts of rubber. The amount of quinone diimine can be for example from 0.05, 0.1, 0.15, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.2, 1.5, 1.8, 2.0, 2.25, 2.5, 2.7, 2.9, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0, 8.5, 9.0 or 9.5 parts per hundred parts of rubber up to 0.15, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.2, 1.5, 1.8, 2.0, 2.25, 2.5, 2.7, 2.9, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0, 8.5, 9.0, 9.5 or 10.0 parts per hundred parts of rubber.

Further, the content of the quinone diimine compound is should not be less than 0.05 parts by mass to 100 parts by mass of the rubber component (PHR), and more preferably not less than 0.5 PHR. In case the content of the quinone diimine compound is less than 0.05 part by mass to 100 parts by mass of the rubber component, no improvement in ageing properties of the rubber composition compared with the prior art antidegradants is seen.

Further, the content of the quinone diimine compound should not be more that 10, more preferably not more than 5, most preferably not more that 2 to 3 parts by mass to 100 parts by mass of the rubber component (PHR). Should the content of the quinone diimine compound be more that 10 PHR, the tendency that the quinone diimine compound is bloomed on the surface of the rubber after vulcanization of the rubber composition of the present inventionwith the consequence that the rubber surface is contaminated, is increased. The maximum benefits of the invention relating to ageing properties in wet and hot conditions are achieved with such levels as less than 5, preferably less that 3, more preferably less than 2 phr, without scarifying other desired properties of the roll cover or belt, such as resistance to tear and wear.

The cover of the present invention may comprise other antidegrading agents in combination with quinone diimine, such as phenylenediamines, in order to achieve preferred properties for the roll cover in its designed position in the machine.

According to the present invention, the at least one rubber compound can be selected from the group consisting of natural rubber (NR), styrene butadiene rubber (SBR), chloroprene rubber (CR), chlorosuphonated polyethylene rubber

(CSM), nitrile butadiene rubber (NBR), hydrated nitrile butadiene rubber (HNBR) and ethylene propylene diene rubber (EPDM). Preferable rubber compounds are here the saturated rubber compounds, i.e. hydrated nitrile butadiene rubber and ethylene propylene diene rubber. It is also possible to use mixtures of these rubber compounds.

The cover of the present invention may contain fillers that are admixed with the rubber material. With the fillers, properties of the cover can be improved or its cost can be cut. Typically, fillers are used to improve wear resistance and to adjust matrix stiffness and hardness. Fillers applicable in the invention are inorganic fillers, such as metal, ceramic and mineral fillers, for example aluminium oxide, silicon oxide, carbides, nitrides, glass, silicates and mica in many different particle forms like powder, balls, pearls, fibers etc., and synthetic organic fillers, such as synthetic polymers, for example ultra high molecular weight polyethylene (UHMWPE), synthetic fibers such as short fibers, chopped fibers, powdered fibers, aliphatic or aromatic polyamide as an example. The particle size of the fillers can vary in the range from 0.01 to 1000 µm.

The cover of the invention may also contain other additives and processing aid agents such as polymerization initiators, activators and accelerators, hardeners, plasticizers, thermal stabilators, antioxidants, antiozonates, pigments etc. for promoting the process and improving physical properties of the cover. These agents are typically mixed with the rubber before it is applied onto the roll shell body. One example of antiozonates is Santoflex 6PPD by Flexsys, and examples of hardeners, i.e. cross-linking agents are sulphurs and peroxides.

The present invention also relates to a roll of a fiber web machine comprising a roll cover according to the present invention. The roll can be for example a nip roll against a yankee cylinder, or another cylinder or roll in a position where a high line pressure is required as well as resistance to high temperatures (such as up to 150 °C). Rubber covers are typically used in press rolls in press section, suction rolls in wire and press section and sizer and film transfer rolls in surface treatment or coating of the web, as well as in guide rolls arranged to move, guide, aling and/or stretch the web or felt or fabric conveying the web.

It is also to be noted that a typical roll for a fiber web machine such as paper, board, finishing or tissue machine comprises a cylindrical roll shell body. The roll shell body is typically made of metal, such as cast iron. The thickness of a finished roll cover is about 5-40 mm, preferably 15-25 mm.

The invention also relates to the use of quinone diimine, most preferably N-{4-[(1,3-dimethylbutyl)imino]-2,5-cyclohexadien-1-ylidine}-benzeneamine in rubber compositions for roll covers.

All the embodiments and characteristics disclosed in this specification apply to all the different aspects of the invention, i.e. the embodiments listed for the cover apply *mutatis mutandis* to the roll, fiber web machine and use according to the present invention.

In this context, the term “comprising” is to be construed as an open term, i.e. that other features may be included in addition to those listed. Moreover, the reference numbers are not to be construed as limiting the scope of protection of the claims.

DETAILED DESCRIPTION OF THE DRAWING

In Figure 1 a press section 11 and a dryer section 2 of a typical tissue machine is shown. The press section 11 comprises a nip roll 12 and a counter roll 13, defining a press nip between them. Running direction of paper web 9 is shown by an arrow. Press felt 14 conveying the paper web 9 is running through the nip in a loop around a plurality of guide rolls 15, of which only one is shown in Figure 1, to move, guide, align and/or stretch the press felt. Suction roll 3 is arranged upstream of the nip. In the nip the web 9 is separated from the felt 14 and adhered to the drying cylinder 13, preferably a Yankee cylinder which has a relatively large diameter and a hard, polished envelope surface 17. Cylinder 13 is covered by a hood 18, in which hot air is blown at high speed against the paper web 9. The paper web is creped off the cylinder 13 with aid of creping doctor 19 and reeled (not shown).

Roll 12 can be a press roll, a suction press roll, a deflection compensated roll or a shoe roll. It has a jacket 22 which can be solid, i.e. metal body covered with

rubber, or a flexible belt jacket. The jacket 22 can be smooth or patterned on its periphery with grooves and/or blind-drillings and/or through-drillings, the latter only in case of suction roll. Combinations of the said patterns is also possible. Suction roll 3 may also have a rubber cover which has drillings and optionally also grooves and/or blind-drillings. Guide roll 15 may also be rubber covered and may have surface pattern as above.

The felt 14 running through the nip between roll 12 and cylinder 13 has a remarkable water content which exposes rolls 15, 3 and 12 to wet conditions. Conditions for roll 12 and its cover are even more demanding because of the high temperature of the cylinder surface 17 and vicinity of the hot hood.

Rolls used in tissue machine press/dryer section are only one example of the applicability of the present invention. Other applications could be for example rolls in coaters or sizers and naturally, press rolls and suction rolls and guide rolls in other positions than tissue machines.

EXPERIMENTAL PART

A rubber composition for roll cover sample was made according to the formulation

	PHR
NBR elastomer (medium ACN, medium Mooney viscosity)	100
N550 carbon black	30
Calcined clay	20
Plasticizer	5
TMPTMA (trimethylolpropane triacrylate)	15
Q-Flex QDI	0.5
6PPD	0.5
Peroxy (DBPH-50)	6

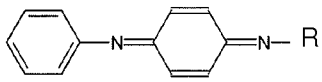
Steam ageing test was performed for the sample as follows. The composition was cast on a thickness of 6 mm on a metal disc with a diameter of about 3 cm and cured. P&J Hardness of the weighted sample was measured. The sample was put in a bowl and exposed to vapor of boiling water for a period of time, from several

days up to several weeks. The sample tempered to room temperature was tested for P&J hardness and weight at certain intervals. After being saturated with vapour the sample was dried in hot air for several hours and the final hardness together with the final weight were measured. A comparative test was performed with the same composition as above except that instead of Q-Flex QDI, 1 phr of 6PPD was used in the rubber composition. Initial hardness for both samples was 41 P&J. After 7 days, the hardness of the sample according to the invention remained the same as initially, while the hardness of the comparative sample had increased by 2 units of P&J. After 14 and even 21 days the hardness of the sample according to the invention still remained unchanged, while the comparative sample showed further increase in hardness.

CLAIMS

1 A roll cover for a roll of a fiber web machine, comprising at least one rubber compound, **characterised** in that it further comprises at least one quinone diimine in an amount of 0.05 - 10 parts per hundred parts of rubber.

2. A roll cover according to claim 1, **characterised** in that the quinone diimine has the general formula (II)



(II)

3. A roll cover according to any of the preceding claims, **characterised** in that the quinone diimine is N-{4-[(1,3-dimethylbutyl)imino]-2,5-cyclohexadien-1-ylidine}-benzeneamine.

4. A roll cover according to any of the preceding claims, **characterised** in that the amount of quinone diimine is 0.1 – 5 parts per hundred parts of rubber.

5. A roll cover according to claim 1, 2 or 3, **characterised** in that the amount of quinone diimine is 1 – 2 parts per hundred parts of rubber.

6. A roll cover according to any of the preceding claims, **characterised** in that the at least one rubber compound is selected from the group consisting of natural rubber, styrene butadiene rubber, chloroprene rubber, chlorosuphonated polyethylene rubber, nitrile butadiene rubber, hydrated nitrile butadiene rubber and ethylene propylene diene rubber.

7. A roll cover according to any of the preceding claims, **characterised** in that it further comprises at least one component selected from the group consisting of fillers, polymerization initiators, polymerization activators, polymerization accelerators, hardeners, plasticizers, thermal stabilators, antioxidants, antiozonates and pigments.

8. A roll of a fiber web machine comprising a roll cover according to any of the claims 1-7.

9. A roll of a fiber web machine according to claim 8, **characterised** in that it is apress roll, a suction roll, a guide roll or a sizer roll.

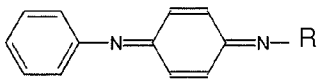
10. A roll of a fiber web machine according to claim 9, **characterised** in that it has a smooth surface or a patterned surface.

11. A roll of a fiber web machine according to claim 10, **characterised** in the patterned surface is selected from the group consisting of grooved, blid-drilled and a combination thereof.

12. A roll of a fiber web machine according to claim 9, 10 or 11, **characterised** in that it is a nip roll forming a press nip against a Yankee cylinder.

13. Use of quinone diimine in rubber compositions for roll covers.

14. Use according to claim 13, **characterised** in that the quinone diimine has the formula (II)



(II)

15. Use according to claim 14, **characterised** in that the quinone diimine is N-{4-[(1,3-dimethylbutyl)imino]-2,5-cyclohexadien-1-ylidine}-benzeneamine.

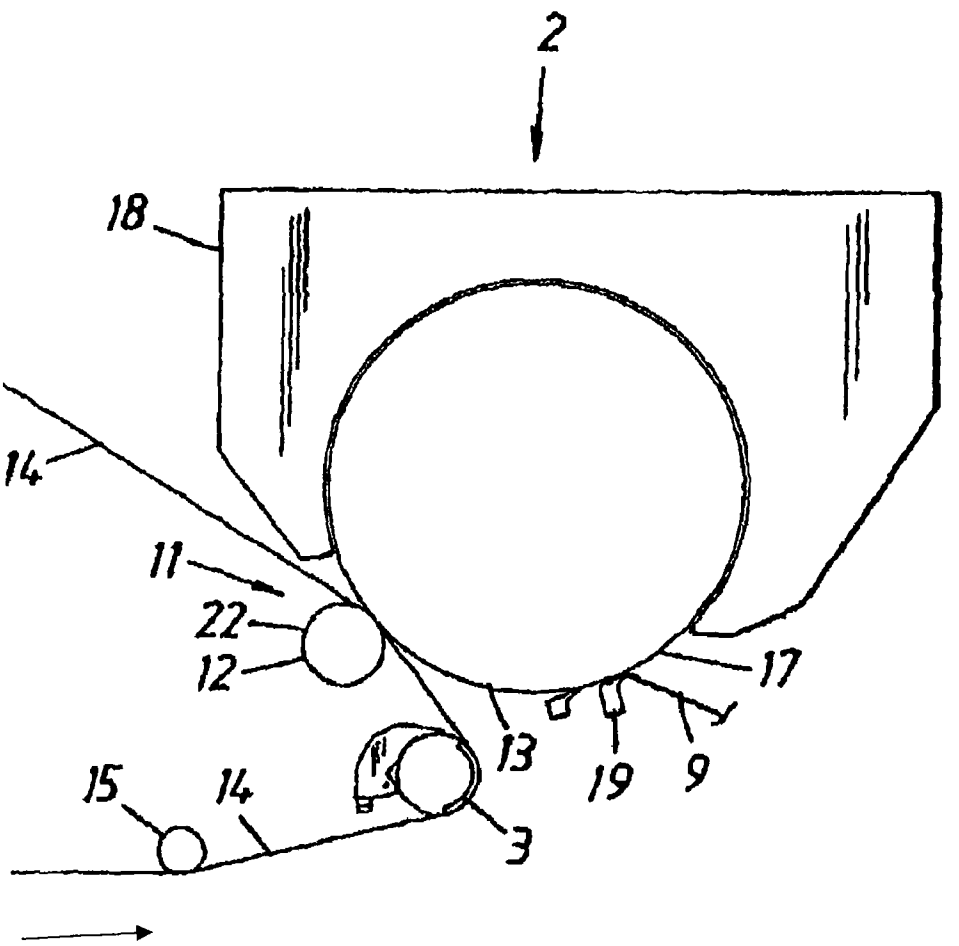


Fig. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/FI2010/050374

A. CLASSIFICATION OF SUBJECT MATTER
INV. D21F3/08 D21G1/02
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)
D21F D21G C08K B60C

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2010/003460 A1 (METSO PAPER INC [FI]; SERAIN HUGUES [FR]) 14 January 2010 (2010-01-14) the whole document	1-15
A	EP 2 138 536 A1 (SUMITOMO RUBBER IND [JP]) 30 December 2009 (2009-12-30) the whole document	1-15
A	US 6 184 276 B1 (IGNATZ-HOOVER FREDERICK [US]) 6 February 2001 (2001-02-06) the whole document	1-15

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

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
6 October 2010	13/10/2010

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Lux, Rudolf

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/FI2010/050374

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2010003460 A1	14-01-2010	NONE	
EP 2138536 A1	30-12-2009	CN 101679684 A	24-03-2010
		JP 2008285548 A	27-11-2008
		WO 2008142906 A1	27-11-2008
		US 2010132867 A1	03-06-2010
US 6184276 B1	06-02-2001	NONE	