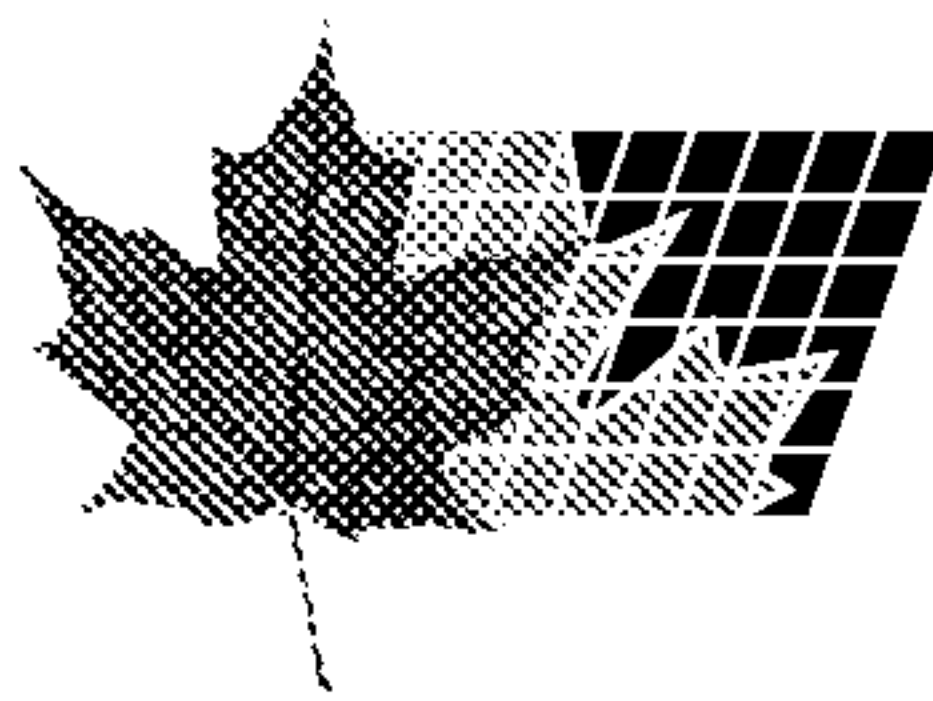




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(54) **PROCEDE PERMETTANT D'AMELIORER LA FIXATION D'UN
MATERIAU POLYMERE ELASTOMERE A UNE COUCHE
INTERNE**

(54) **PROCESS FOR IMPROVING CONNECTION OF AN
ELASTOMERIC, POLYMERIC MATERIAL TO A
SUBSTRATE**

(57) Process for improving the connection of an elastomeric, polymeric material to a substrate during the shaping and vulcanization thereonto, wherein the substrate is wetted in the region of connection with a liquid adhesion promoter composition, the coating so formed is solidified, the elastomeric material subsequently formed thereonto and solidified by vulcanization, whereby an aqueous and/or alcoholic solution of a thiocyanatosilane is used as the adhesion promoter. The specific adhesive strength of the rubber compound on the substrate is significantly increased.

ABSTRACT

Process for improving the connection of an elastomeric, polymeric material to a substrate during the shaping and vulcanization thereonto, wherein the substrate is wetted in the region of connection with a liquid adhesion promoter composition, the coating so formed is solidified, the elastomeric material subsequently formed thereonto and solidified by vulcanization, whereby an aqueous and/or alcoholic solution of a thiocyanatosilane is used as the adhesion promoter. The specific adhesive strength of the rubber compound on the substrate is significantly increased.

**PROCESS FOR IMPROVING CONNECTION OF AN ELASTOMERIC,
POLYMERIC MATERIAL TO A SUBSTRATE**

Field of the Invention

The invention relates to a process for improving the connection of an elastomeric, polymeric material to a substrate during shaping and vulcanization. In particular, the invention relates to a process in which the substrate in the region of connection is wetted by a liquid adhesion promoter composition, the so formed coating is dried, and the elastomeric material subsequently shaped thereonto and solidified by vulcanization.

Background of the Invention

It is known to use silanes as adhesion promoters during vulcanization of an elastomeric material onto a substrate. However, this known process does not for all elastomeric materials result in a sufficiently strong mechanical connection between the elastomeric material and the substrate. Therefore, resins or latexes are used for the binding of NBR (nitrile butadiene rubber) to achieve a sufficiently strong adhesion. This is associated with large cost when used in large scale production.

Thiocyanatosilanes are known per se for use as additives in the manufacture of homogeneous rubber mixtures. They have the purpose of giving the rubber mixture a higher strength. However, thiocyanatosilanes have so far not been used at all as adhesion promoters or in the manufacture of adhesion promoters.

Summary of the Invention

It is an object of the invention to provide an adhesion promoter which is easy to use and guarantees good adhesion when used with sulfur cross-linked, elastomeric materials.

For the achievement of this object, a process of the above described type is provided wherein the substrate in the region of adhesion is wetted with a liquid adhesion promoter composition containing a thiocyanatosilane, the coating so formed is solidified, and the elastomeric material is subsequently shaped thereonto and solidified by vulcanization.

Thiocyanatosilanes surprisingly allow the achievement of an especially good connection during vulcanization of any sulfur cross-linked, elastomeric material with a solid body, for example, an elastomeric material with a metal.

It is preferred to produce an especially thin and homogeneous film layer on the substrate, which is as much as possible free from irregularities such as bubbles, local variations in layer thickness, or the like. Surprisingly, it is possible by using thiocyanatosilanes to easily fulfill these requirements. It is believed that in particular the excellent adhesion achieved during the subsequent vulcanization of sulfur cross-linked, elastomeric materials can be traced back to this.

The thiocyanatosilane is preferably used in dissolved form, whereby the solid matter content of the solution is preferably a maximum of 10 wgt% of the thiocyanatosilane, most preferably less than 5 wgt%. In a practical example, which is used in the mass production of shaft seals, the content is 0.8 to 1.0 wgt%, preferably 0.9 wgt%. This substantially guarantees an especially thin and even coating of the supporting elements, for example, of the supporting rings of radial shaft seals

made of sheet steel. These can have a diameter which commences in the region of 5 mm.

The solution can include 50 to 80 wgt% of alcohol in order to further provide the homogeneity of the film formed and to prevent irregularities.

Practically all known alcohols can be used as the admixed alcohol, for example, methanol, ethanol, propanol, isopropanol, butanols, pentanols, hexanols and/or mixtures thereof. The use of ethanol is generally preferred. The adhesion promoter should be dried gently in order to ensure formation of an especially even film layer. The use of drying temperatures between 20 and 80° preferably between 40 and 60° have proven especially useful.

An especially good adhesion can be achieved by tempering the adhesion promoter subsequent to drying at a temperature of 50 to 200° and for 5 to 20 min. The tempering is of special importance for safety relevant applications, for example, for applications in the field of support bearings for machines and apparatus, as well as in relation to the adhesion of a rubber sealing lip to a sealing ring, as used in shock absorbers, in wheel bearings or in the hydraulics field.

When an aqueous solution is used for the formation of the adhesion promoting layer, it has proven advantageous when the solution used is slightly acidic. In general, any acid can be used. The use of acetic acid has proven especially advantageous. The adhesive strength of the sulfur cross-linked vulcanizates can be increased when the thiocyanatosilanes include amino silanes. The respective content should be a maximum of 50 wgt%. In practical applications the content lies in general in the region of 0.2 wgt%.

The invention is further discussed in the following by way of examples.

Example 1

Subsequent to a previous degreasing, a sheet steel strip was dipped into an aqueous solution of a thiocyanatosilane and subsequently dried. The solution had the following composition:

Water 25 wgt%
Ethanol 74 wgt%
Acetic Acid 0.1 wgt%
Thiocyanatosilanes 0.9 wgt%

After removal from the solution, the sheet steel strip was dried at a temperature of 50°C for 30 minutes and, subsequently, transferred into a temper chamber for a period of 20 minutes. The temperature in the temper chamber was 175°C. Subsequently, a rubber body was shaped onto the sheet steel strip using a vulcanization tool and solidified by subsequent vulcanization for rigid connection with the sheet steel strip. The rubber material used had the following composition:

Nitrile butadiene-Kautschuk	30 wgt%
Soot	30 wgt%
Silicate	30 wgt%
Processing Facilitator Compound	3 wgt%
Anti-aging Compound	2 wgt%
Plasticizer	2 wgt%
Vulcanization Chemicals	3 wgt%

The vulcanization temperature was 190°C, the vulcanization time 4 minutes.

Subsequent to the vulcanization, the resulting compound part was removed from the vulcanization tool, cooled and the strength of the obtained connection between the shaped rubber body and the sheet steel strip measured. The specific strength of adhesion was 11 N/mm^2 . The resulting rip zone was within the rubber body. The surface of the sheet steel strip was therefore still covered by rubber subsequent to ripping off the rubber body.

Example 2

The above experiment was repeated using an aqueous solution for the production of the adhesion promoter coating, which included traces of acidic acid in place of the alcohol. The acidic acid content was about 0.2 wgt%. The specific strength of adhesion of the connection was slightly higher than given above at 12 N/mm^2 .

In the region of rupture, minute defects were visible to the naked eye.

Example 3

The experimentation according to Example 1 was repeated, however, in addition to the thiocyanatosilane, an amount of 0.2 wgt%, relative to the solids content, of an amino silane was added to the mixture. The connection was completely free of defects and had a specific strength of adhesion of 13 N/mm^2 .

Example 4

The experimentation according to Example 1 was repeated with the sole difference that the thiocyanatosilane was replaced with 4,4,15,15-tetraethoxy-3,16-dioxo-8,9,10,11-tetrathio-4,15-di-silaneoctadecane, as available, for example, under the commercial name of SI 69. The specific adhesive strength of the connection was at 1.3 N/mm^2 and, was thereby, completely insufficient for higher quality applications.

Changes and modifications in the specifically described embodiments can be carried out without departing from the scope of the invention which is intended to be limited only by the scope of the appended claims.

CLAIMS

1. Process for improving the connection of an elastomeric, polymeric material to a substrate during the shaping and vulcanization thereof onto the substrate, including the steps of wetting the substrate in the region of adhesion with a liquid adhesion promoter composition, solidifying the coating so formed, shaping the elastomeric material thereonto and solidifying the material by vulcanization, wherein the liquid adhesion promoter composition is selected from the group of aqueous and alcoholic solutions of a thiocyanatosilane.
2. Process according to claim 1, wherein the solution includes a maximum of 10 wgt% of the thiocyanatosilane.
3. Process according to one of claims 1 to 2, wherein the solution contains a maximum of 50 to 96 wgt% of alcohol.
4. Process according to claim 1, wherein the solution is an alcoholic solution and the alcohol is selected from the group of methanol, ethanol, propanol, iso-propanol, butanol, pentanol, hexanol and mixtures thereof.
5. Process according to one of claims 1 to 4, wherein the step of solidifying the adhesion promoter coating includes drying the coating at a drying temperature of 20 to 80°C.
6. Process according to claim 5, wherein the drying temperature is 40 to 60°C.
7. Process according to one of claims 1 to 6, wherein the step of solidifying the adhesion promoter coating includes drying of the coating and subsequent tempering at a temperature of 50 to 200°C for a time period of 5 to 20 minutes.

8. Process according to claim 1, wherein the liquid adhesion promoter composition is an aqueous solution of thiocyanatosilane which is acidified.
9. Process according to claim 8, wherein the solution is acidified with acidic acid.
10. Process according to claims 1 to 9, wherein the solution of thiocyanatosilane further includes an amino silane.
11. Process according to claim 10, wherein the amino silanes are present in the solution in an amount to a maximum of 5 wgt% relative to the solids content of the mixture.