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DECORATIVE CUSHIONING STRIP AND METHOD FOR PRODUCING SAME

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7 Claims

ABSTRACT OF THE DISCLOSURE

Impact or cushioning strips having a decorative or color coating firmly bonded to the surface thereof in which the base material on the surface of the strip contains an EPDM rubber having olefinic unsaturation and which has been prepared for the color coating by exposure to conditions reactive with the unsaturated EPDM, and overcoating with an organo silicon compound having functional groups.

This invention relates to products designed to protect surfaces from destruction or deterioration by impact, abrasion and the like, and it relates to the method for the preparation of same.

In order to cushion the impact and/or to protect the surface from destruction or deterioration, as a result of impact or abrasion, it has become the practice to provide the surfaces exposed to impact or abrasion with a cushioning or guard strip of an elastomeric material. Such cushioning or guard strips have found wide and acceptable use on automotive or other vehicles, as bumper strips, or on other sections of the automobile or vehicle subject to impact or abrasion. They are widely used also on pieces of furniture, home appliances and the like, which are exposed to impact or abrasion.

In order to avoid use of an unattractive cushioning or guard strip, or one that does not fit into the decor or color combination of the object protected, it is desirable to provide the cushioning or guard strip with a surface of elastomeric material having a surface coating embodying tinctorial agents, such as dyes or pigments, or other materials which will make the cushioning or guard strip more attractive or fit into the color scheme or decor of an object being protected.

It has been difficult to achieve a decorative or color coating on the exposed surface of an elastomeric cushion or guard strip by reason of the inability strongly or permanently to bond the coating or primer to the underlying elastomeric material. As a result, the applied coating strips, tears, flakes or otherwise separates from the surface in response to flexure impact or otherwise. As a result, the cushioning or guard strip becomes less attractive than before.

Others have tried to enhance the bonded relationship between the applied surface coating and the underlying surface of the elastomeric material, as by roughening the surface to provide a matte surface onto which a better grip might be obtained by the applied coating, or by irradiation of the surface to effect modification which might be more receptive to the applied decorative coating. The latter technique has offered the greater promise but it requires such additional amounts of expensive equipment, time, labor and space as to be unattractive from the economical standpoint and/or to the mass production industry. Even then, numerous defects in the coating, especially upon aging, continue to exist.

It is an object of this invention to provide an elastomeric based material with a surface treatment which can be carried out in a rapid and efficient manner without an excessive amount of special equipment or labor; which can

be adapted to mass production techniques for the manufacture of parts, materials and assemblies; which provides a base that permits a strong and permanent bond to be established with applied decorative or color coatings, and to which a flexible, decorative and color coating can be adhered without separation in response to flexure or impact thereby to provide a decorative or color coating which does not separate from the base strip during use. It is a related object to provide a method for producing such strips of elastomeric material with a surface to which a decorative or color coating can be strongly bonded, either directly or indirectly via a prime coat.

It has been found, in accordance with the practice of this invention, that a resilient base of elastomeric material for adherence of a decorative or color coating can be obtained by the combination in which use is made of an EPDM elastomeric interpolymer as the elastomeric material, having a sufficient number of unsaturated ethylenic or acetylenic groups to enable modifications of the surface by reaction believed to take place through the unsaturated EPDM elastomer, exposing the surface to such reactive conditions, and then coating the reacted surface with an organo silicon compound in the form of a silane, its hydrolysis product or its polymerization product in which the silane has from 1 to 3 highly hydrolyzable groups attached to the silicon atom and at least one organic group of from 1 to 8 carbon atoms containing a highly functional group, such as an amino group, ester group, epoxy group, unsaturated ethylenic group, or preferably a mercapto group.

EPDM elastomers are now a commodity well known in the market place. The EPDM elastomers preferably employed in the practice of this invention comprise interpolymers of ethylene, at least one monoolefin having from 3 to 16 carbon atoms (preferably 3 to 7 carbon atoms), and a polyene, preferably a non-conjugated polyunsaturated polyene, such as 1,4-cyclohexadiene, dicyclopentadiene, and preferably a non-conjugated bridged ring polyene, such as an alkylidene norbornene, or an alkenyl norbornene in which the alkylidene group or the alkenyl group has from 1 to 8 carbon atoms and which may be represented by such monomers as 5-ethylidene-2-norbornene, 5-propylidene-2-norbornene, 5-butylidene-2-norbornene and 5-isobutylidene-2-norbornene.

The EPDM interpolymer is preferably formulated with ethylene and with propylene as the other monoolefin in the molecular ratio of 45-90 ethylene to 55-10 propylene. The amount of polyene is not critical as long as the interpolymer has unsaturated ethylenic or acetylenic groups which are capable of undergoing chemical modification. In practice, it is preferred to make use of an EPDM interpolymer formed with sufficient polyene to provide 2 to 25 carbon to carbon double bonds per 1000 carbon atoms. For a more detailed description of the preparation of the EPDM interpolymer which may be used in the practice of this invention, reference can be made to the copending application of Boozer et al., Ser. No. 2,367, filed Jan. 12, 1970, now abandoned, or to the issued U.S. Pat. Nos. 3,538,190, 3,538,192 and 3,574,176.

The surface treatment to provide a first activating reaction is performed after the interpolymer has been molded or otherwise formed to the shape of the end product and cured, such as the cushioning guard or strip or other object.

The phenomenon which takes place to make the treated surface more receptive to the organo silicon compound and the subsequent color or decorative coating is not yet known. What is known is that upon brief or extended exposure to activating conditions, reaction takes place, probably through the unsaturated groupings remaining in the cured EPDM elastomer, to provide a modification

of the surface characteristics which operate to enhance the interbonded relation. It is known that such activation can be achieved by brief or extended exposure to ozone, for a length of time depending somewhat upon the ozone concentration and temperature. For example, exposure for a few seconds will be sufficient to an atmosphere in which the ozone is present at a concentration of 100 parts per billion while longer periods of exposure, such as at least 15 seconds, are sufficient at lower concentrations. The foregoing times are minimums since longer times of exposure can be used to achieve the desired effects, as long as the extended exposure is not harmful to the material. While not as immediately effective, modification of the surface can be achieved by exposure to the ozone produced by accelerated aging, or that produced by radiation with direct sun light or preferably ultra violet light, or by extended exposure in air containing a small amount of ozone. The reaction that takes place is believed to be an oxidative reaction occurring across the unsaturated groups in the cured EPDM rubber with oxygen, preferably activated by radiation or as ozone, or made available by chemical oxygenating agents.

The organo silicon component, applied as a coating onto the reacted surface of the EPDM elastomer, is selected of a silane, its hydrolysis product (silanol), or its polymerization product (polysiloxane) in which the silane has the general formula R_nSiX_{4-n} in which X is a highly hydrolyzable group such as chlorine, bromine, or other halogen, a short chained alkoxy group such as methoxy, ethoxy and the like, an acyloxy group such as acetoxy, propionoxy and the like, or an amine, n is an integer of from 1 to 3 and R is hydrogen or an organic group in which at least one of the R groups is an organic group containing a functional group, such as an unsaturated ethylenic group, an amino group, an epoxy group or an ester group, and preferably a mercapto group. Representative are such silanes as vinyl trichloro silane, diallyl dichloro silane, gamma-aminopropyltriethoxy silane, gamma-mercaptopropyltrimethoxy silane and the like.

The organo silicon compound is preferably applied in the form of a silane, such as the gamma-mercaptopropyltrimethoxy silane or gamma-aminopropyltriethoxy silane, which are liquids and can be applied onto the treated surface by brush coating, spray coating, flow coating and the like, at 100% concentration. However, it is preferred, and it is more economical, to coat the treated surface of the EPDM elastomeric material with a solution of the organo silicon compound in a suitable solvent, such as hexane, benzene, chlorinated solvents and the like, in concentrations in which the amount of organo silicon may range from 2.5% to 50% by weight of the composition.

It will be sufficient if only a monomolecular layer of the organo silicon compound is provided as a coating on the pre-treated surface, although more may be applied without loss of bond strength between the composite treated surface and the decorative or color coating. From the economical standpoint, it is undesirable to apply excessive amounts of organo silicon compound because of their relatively high cost. It will be sufficient if an amount is applied to give a dry coating weight of 110 grams per 100 square feet of surface area. The applied coating may be allowed to air dry or drying may be accelerated at elevated temperatures.

It is desirable to make use of a decorative or color coating formed of a binder component which has elastic properties, somewhat similar to that of the base material. Such vehicles, used in the decorative or color coatings have been formulated of a polyurethane type resinous material. Other binders for such color or decorative coatings can be formulated of alkyd type resins, preferably having polar substituents for reaction or coordination with functional groupings of the organo silicon compound.

The following examples are given by way of illustration, but not by way of limitation, of the practice of this invention:

EXAMPLE 1

5 Test strips were molded of the following compound for 30-60 minutes at 320° F. under 500 p.s.i.:

Composition

Material:	Parts by weight
10 EPDM (Epsyn 4506) -----	50
EPDM (Epsyn 5508) -----	50
Carbon black (FEF black) -----	85
Hard clay -----	25
Shellflex 371N -----	25
15 Zinc oxide -----	5
Mots #1 -----	3
Zinc dibutyl dithiocarbamate -----	3
4,4'-dithiomorpholine -----	1
Tellurium diethyldithiocarbamate -----	0.5
20 Sulphur -----	0.5

The above compound formulation is merely representative of the rubber compounds molded into various types of objects for use in the practice of this invention. The Epsyn 4506 is an interpolymer of Copolymer Rubber & Chemical Corporation, Baton Rouge, La., having an ethylene to propylene ratio of 2:1 with about 5 parts per 100 of polyene. The Epsyn 5508 is similar to Epsyn 4506 except for a higher ratio of ethylene to propylene. The Shellflex 371N is an extender oil, and the Mots #1 is a proprietary commercial vulcanization accelerator.

After cleaning the surface with toluene, one group of the molded test pieces were exposed for 30 seconds and another group for 24 hours in an enclosure heated to 100° F. and containing 100 p.p.h.m. ozone.

After exposure, the test pieces were provided with a coating of gamma-mercaptopropyltrimethoxy silane in 50% solution in hexane and allowed to air dry.

Painting was done by dipping in primer containing a polyurethane binder (DEM-32797—Pittsburgh Plate Glass). The primer was air dried and cured for 10 minutes at 250° F. The paint was air dried and cured for 40 minutes at 250° F.

The pigmented polyurethane coating, with or without a primer, adhered to the treated surface of the rubber under repeated flexure and repeated impact. Control samples which had not been exposed to ozone but coated with the gamma-mercaptopropyltrimethoxy silane flaked and chipped under the same test. Other control samples exposed to ozone but without the organo silicon overcoating also peeled and chipped under the same test.

EXAMPLE 2

The procedure was the same as that of Example 1 except that instead of exposing the strips to ozone, the test strips were exposed to an ultra violet light for from 2-10 minutes. An improved interbonded relationship was obtained by the polyurethane coating on the side of the strip exposed to ultra violet light but not on the unexposed side.

EXAMPLE 3

The same procedure was followed as in Example 1 except that instead of coating the exposed test strips with a 50% solution of gamma-mercaptopropyltrimethoxy silane, one group was provided with a coating of gamma-aminopropyltriethoxy silane and another group with a coating of vinyl trichloro silane, from 5% and 10% solution. Improved bonding was secured between the polyurethane color coating and the treated base rubber.

While the invention has been described with reference to cushioning or impact strips, it will be understood that the inventive concepts have application generally to the combination of a base material having an elastomeric surface containing the described EPDM rubber to which

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it is desired to bond a decorative coating, a color coating or a protective coating, even though the the particular surface is not exposed to impact, wear or abrasion.

It is not essential that the base material be formed entirely of the described EPDM elastomer. It will be sufficient if the base material contains such unsaturated EPDM elastomer alone or in combination with other elastomeric materials. The desired results can be secured when the surface portion to be coated is formulated of GRS rubber, isoprene rubber, polybutadiene rubbers, EPM rubbers, natural rubbers and the like synthetic rubbers, containing an amount of the described unsaturated EPDM elastomer as an essential component of the base material, preferably in an amount greater than 25% by weight up to 100% by weight.

It will be understood that changes may be made in the details of formulation and operation without departing from the spirit of the invention, especially as defined in the following claims.

I claim:

1. In the method of preparing an object having an elastomeric surface for adherence of a coating thereon, the steps of producing the object with a surface containing an EPDM elastomeric material having at least 2 carbon to carbon double bonds per 1000 carbon atoms, exposing the surface to be coated to reactive conditions through the unsaturated groups, to ozone for at least 5 seconds, and coating the exposed surface with an organo silicon compound in the form of a silane, its hydrolysis product or its polymerization product in which the silane has from 1 to 3 highly hydrolyzable groups and at least one organic group attached to the silicon atom containing a mercapto group.

2. The method as claimed in Claim 1 in which the EPDM elastomeric material is formed by copolymerization of ethylene, a monoolefin having from 3 to 16 carbon atoms, and a polyene.

3. The method as claimed in Claim 2 in which the EPDM is formed of ethylene, propylene and a polyene in

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which the ethylene/propylene ratio is within the range of 45-90 ethylene to 55-10 propylene.

4. The method as claimed in Claim 2 in which the polyene is an alkyldiene norbornene having from 2 to 5 carbon atoms.

5. The method as claimed in Claim 1 in which the organo silicon compound is applied from solvent solution.

6. An object having a surface of elastomeric material to which a decorative or color coating is strongly bonded in which the surface portion of the elastomeric material contains an EPDM elastomer formed of ethylene, at least one monoolefin containing from 3 to 16 carbon atoms and a polyene present in an amount to provide unsaturation in the interpolmer of at least 2 carbon to carbon double bonds per 1000 carbon atoms, the surface having a treatment by exposure to ozone for at least 5 seconds, a coating on the ozone treated surface of an organo silicon compound in which an organo group attached to the silicon atom contains a mercapto group and a decorative color coating on the organo silicon coated surface.

7. An object as claimed in Claim 6 in which the decorative color coating is formed with a polyurethane base.

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