

PATENT SPECIFICATION (11) 1 585 029

1 585 029

- (21) Application No. 20198/78 (22) Filed 17 May 1978 (19)
(31) Convention Application No. 7715277 (32) Filed 18 May 1977 in
(33) France (FR)
(44) Complete Specification Published 18 Feb. 1981
(51) INT.CL.³ E01C 13/00
B32B 5/16 27/40
(52) Index at Acceptance
E1G 60A2 60C1 60E2 60N 60R 60S 61
62
B2E 1744 416S 436T 519U M
(72) Inventors: CLAUDE BOVIS
PIERRE TREBUCHON



(54) COVERINGS

(71) We, NAPHTACHIMIE, a body corporate organised and existing under the laws of France, of Tour Neptune, La Defense 1, 20, place de Seine, 92400 Courbevoie, France, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:-

The invention concerns a process for producing a covering by the successive alternate applications of a polyurethane binder and solid particles of elastic or plastic nature. Such coverings can be used in particular for making tennis courts, sports grounds, gymnasias and games surfaces.

It is known that such coverings may be produced by applying, to a support, a plurality of layers of a paint comprising a binder, generally of vinyl or acrylic nature, and a mineral filler, such as fine sand. Because of their rigidity, coverings produced by this method tend to crack and to cause the users of the surface to suffer from excessive fatigue. They also have a low degree of resistance to wear and poor surface properties, the coverings often being excessively rough in dry weather and excessively slippery in wet weather.

In order to produce coverings of better quality, it has previously been proposed that binders of elastic nature such as two-component polyurethane binders containing granules of rubber in suspension be used. Such rubber granules have the disadvantage of resulting in very viscous mixtures, so that in practice it is necessary to use fairly large granules, of sizes varying generally from 2 to 5 mm, whose thickening effect is less than that of the smaller granules, and also to limit the proportion of such granules in the mixture to 30% by weight. Because of the sizes of the granules used, such coatings can be applied only in relatively thick layers; since such coatings contain a relatively small amount of granules, they have enjoyed only restricted use, as it is difficult and inconvenient to apply them.

It has now been found that it is possible to make thin coverings having good mechanical and use properties that make them suitable for games surfaces, by an economical and convenient method from a polyurethane binder and elastic or plastic particles.

In accordance with the present invention, flexible elastic coverings of a thickness of from 0.5 to 0.5 mm and preferably from 1 to 3 mm, are prepared by applying to a support, successively and alternately, until the desired thickness is achieved: (i) a polyurethane binder having a viscosity of from 1 to 200 poises and preferably from 5 to 30 poises at the temperature of application, viz. from -10 to 40°C, the amount of binder applied being from 200 to 1000 g/m² and (ii) solid particles of elastic or plastic nature in an amount sufficient to cover the layer of binder, the solid particles being simply distributed on the surface of the binder without being compacted, particles that have not been retained by the binder being removed if necessary after any or all application(s) of such particles.

The polyurethane binder may contain, as its essential component, a polyurethane pre-polymer produced by previous reaction between organic polyisocyanates and hydroxyl compounds, such compounds being used in proportions such that the isocyanate index, i.e. the number of isocyanate groups of the polyisocyanates divided by the number of labile

hydrogen atoms of the hydroxyl compounds, is greater than 1 and is preferably from 1.5 to 10. Cross-linking of this polyurethane binder can be achieved by the action of the moisture in the air, after application of the binder, or by more or less complete reaction of the binder with hydroxyl compounds mixed in the binder at the moment of application, the amount of hydroxyl compounds used in then so calculated that the isocyanate index of the mixture does not fall below about 1; it is between 0.9 and 10 in practice.

The polyurethane binder may also be produced by mixing organic polyisocyanates and hydroxy compounds at the moment of application, such compounds being used in proportions such that the isocyanate index is from 0.9 to 10.

The organic polyisocyanates used in the preparation of the binders of the invention are preferably aromatic polyisocyanates such as tolylene-diisocyanate, which is currently called TDI and which is used commercially in the form of mixtures of 2, 4 and 2, 6 isomers, the most frequently encountered mixtures containing 80% or 65% by weight of the 2, 4 isomer; 4,4' diphenylmethane diisocyanate, which is currently called MDI; and polyphenylpolymethylene-polyisocyanates, sometimes denoted by the word PAPI. TDI and MDI can also be used in a crude form: crude TDI is formed by the product of the reaction of phosgene on crude tolylene-diamine containing various isomers and condensed amines, while crude MDI results from the condensation of phosgene on the unpurified product of the reaction between aniline and formaldehyde.

The hydroxyl compounds used in the preparation of the binders of the invention preferably comprise polyols of the polyether-polyol type or the polyester-polyol type having an average from 2 to 6 hydroxyl groups per molecule and an equivalent weight of from 500 to 5000. The equivalent weight is equal to the quotient of the mean molecular weight by the mean number of hydroxyl functions per molecule. Polyether-polyols are generally prepared by the polyaddition of propylene oxide and possibly ethylene oxide on a compound having of from 2 to 6 labile hydrogen atoms such as polyhydric alcohols, polyamines or amino alcohols. Polyester-polyols are generally produced by the esterification of polyacids, e.g. adipic acid or sebacic acid, and/or anhydrides of polyacids, e.g. maleic anhydride or phthalic anhydride, with an excess of polyhydric alcohols such as ethyleneglycol, polyethyleneglycols, propyleneglycol, polypropyleneglycols, glycerol or sorbitol.

In addition to the polyols mentioned above, the hydroxyl compounds may also contain compounds comprising only one labile hydrogen atom per molecule, preferably formed by compounds having a molecular-weight of from 200 to 6000 and comprising a labile hydrogen atom included in a hydroxyl group or in a secondary amino group.

Such compounds may for example be fatty alcohols or fatty secondary amines or may result from the polyaddition of alkylene oxides such as propylene oxide and possibly ethylene oxide on alcohols or secondary amines such as ethanol or diethylamine. In this case, the polyols and the compounds having only one labile hydrogen atom are used in the preparation of the coatings of the invention in proportions such that the ratio between the number of labile hydrogen atoms of the polyols and the number of labile hydrogen atoms of the compounds having only one labile hydrogen atom is from 1:1 to 20:1 and preferably from 2:1 to 12:1.

The binders according to the invention may also contain fillers, in particular chalk in the form of fine powder or crushed kaolin, and pigments such as pigments of red iron oxide. In order to produce binders whose cross-linking period is from 1 hour to 24 hours and preferably from 3 hours to 12 hours, it is possible to introduce into the binders catalysts for cross-linking of the isocyanate groups or formation of the polyurethane groups, in particular organic metal compounds, such as organic compounds of tin, or amines, in particular tertiary amines. The binders may also contain up to 20% by weight of plasticisers or up to 50% by weight of solvents such as aromatic petroleum oils, esters such as dioctyl phthalate or chlorinated paraffins; the addition of plasticisers or solvents make it possible, if necessary, to adjust the viscosity of the binders to the desired value.

According to the properties required for the covering, the solid particles of elastic or plastic nature may comprise various materials such as scrap from manufactured rubbers or plastics material, wood, sawdust or cork; if necessary, these various materials can be used successively or in admixture. The granulometry of these particles is so selected that at least 90% by weight of the particles pass through sieves having a mesh opening of 1.5 mm. The apparent specific gravity of these particles is generally from 0.1 to 0.8, particularly from 0.3 to 0.6.

It has also been discovered that contrary to previous practice, it is advantageous to use particles of irregular shape, which have if possible rugged hollows capable of retaining gas bubbles, which contribute to the elasticity of the covering; such particles of irregular shape can be produced for example by shredding rubber in a crusher with fluted cylinders.

The coatings according to the invention can be applied to supports of various natures such as concrete, asphalt or bituminous coatings. The coatings can be applied directly when

the support is both dry and not very porous. It is preferable to apply a bonding primer to the support beforehand; this primer is preferably a primer of polyurethane type, which can be prepared by diluting a polyurethane binder with a solvent. When the support is porous, it is useful to first apply a pore-closing agent, which may advantageously comprise a binder according to the invention whose viscosity has been increased by means of a thickening agent such as fine silica, kaolin, hydrogenated castor oil or rubber powder.

The binder can be applied to the support at a temperature in the range from -10 to 40°C and by any suitable means such as gun spraying or by application with a roller or a brush. The solid particles of elastic or plastic nature are spread over the layer of binder, before it hardens, in a layer that is sufficiently thick to totally cover the surface to be coated. This operation can be performed by any known means, in particular by throwing or scattering the particles on the surface and levelling the layer by means of a rake or broom. When the layer of binder is sufficiently cross-linked to fix the solid particles that have been at least partly immersed therein, any excess of solid particles is removed, e.g. by sweeping or by suction. A fresh layer of binder is then applied to the resulting surface, followed by further solid particles, and these operations are repeated until a covering of the desired thickness has been produced. The total thickness of the covering is generally from 0.5 to 5 mm and, in most cases, from 1 to 3 mm.

In order to increase the roughness of the covering, it is advantageous to finish its production by an application of solid particles. It is also possible to apply a paint to the coverings of the invention; this paint is preferably of the polyurethane type and may be prepared like the binders described above.

Because of the properties in respect of flexibility and elasticity of the coverings produced, the process of the invention is particularly suitable for making sports or games areas. The coverings obtained by the process of the invention as set forth in the illustrative Examples below also have a high degree of resistance to wear and have good non-slip properties in dry and wet conditions. These characteristics are maintained over a wide temperature range, ranging from -20 to 80°C, and they are also maintained over a prolonged period of time. The coverings have the additional advantage of being very conveniently produced.

In the Examples, all parts and percentages are by weight unless otherwise indicated.

Example 1

A pre-polymer containing 3.5% of free NCO groups is prepared by the reaction of 75°C for a period of 3 hours of 15 parts of 80/20 tolylene diisocyanate and 85 parts of a triol having an equivalent weight equal to 1000 and produced by the polyaddition of propylene oxide on glycerol.

A binder is then prepared by mixing, at a temperature of 20°C, 80 parts of the above pre-polymer, 10 parts of red iron oxide, 10 parts of ethylglycol acetate and 0.3 part of dibutyl tin dilaurate. This binder has a viscosity of 16 poises at 20°C.

The covering is produced on a smooth dry bituminous support. A first layer of binder is applied to the support by roller, at a rate of 500 g/m². A layer of polyurethane rubber granules is then spread over the layer of binder, by means of a brush, the amount being 1000 g/m². The granules have a specific gravity of 0.4 and were produced by shredding slugs of polyurethane rubber in a crusher with fluted cylinders, and then sifting; their grain size is such that all the grains pass through a sieve having a mesh opening of 1 mm. After 12 hours, the granules that have not been fixed by the binder are brushed away; about 500 g of granules is recovered in this way.

The same sequence of operations is repeated twice successively.

The covering produced is 3 mm in thickness, and its characteristics are as follows:

	Density:	1 g/cm ³	
	Appearance:	even, without surface cracking	
5	Rupture strength (standard NF T 46 002):	28 daN/dm ²	5
	Elongation to rupture (standard NF T 46 002):	300%	
10	Reduction in rupture strength after 3 weeks irradiation under U.V. at 60°C (standard NF T 30 049 type E2):	<10%	10
15	Bounce of tennis balls from a height of 2.54 m:	1.34 to 1.47 m	15
	Resistance to wear, measured with a Lhormargy wear meter, with C 180 abrasive paper, under a load of 1 kg and over a surface area of 10cm ² :	loss of 0.2 g after 1500 hours	
20			20
	Slipperiness, measured with a RRL pendulum, on a scale from 0 to 150		
25	dry covering:	90	25
	wet covering:	72	

Example 2

30 A bonding primer is prepared by dissolving 50 parts of the prepolymer of Example 1 in 50 parts of ethyl acetate. A polyurethane binder, comprising two components A and B, of the following composition is also prepared: 30

Component A

35		<i>Parts</i>	35
	Polyoxypropyleneglycerol having an equivalent weight of 1000	30	
40	Crushed fine chalk	54.8	40
	Crushed kaolin	10	
45	4 Å molecular sieve in powder form	2	45
	Red iron oxide pigment	3	
	Dibutyl tin dilaurate	0.2	

50 Component B 50

Pre-polymer of Example 1.

The polyurethane binder is prepared at the moment of application by mixing 100 parts of components A and 40 parts of component B (the isocyanate index is equal to 1.10). Its viscosity at 20°C is equal to 120 poises. A layer of bonding primer is applied to a support of smooth, clean and dry concrete. After drying, 800 g/m² of binder is applied with a roller, then a layer of 1000 g/m² of granules of styrene-butadiene rubbery polymer is spread over the layer of binder, by means of a brush. 55

These granules, which have a specific gravity of 0.45, are produced by shredding rubber scrap in a crusher with fluted cylinders, then sifting; their grain size is such that all the granules pass through a sieve with a mesh opening of 1.5 mm. 60

After 12 hours, the granules that have not been fixed by the binder are swept away; about 400 g/m² of granules is recovered. The coating and the granules are applied a second time, in the manner described above.

The covering produced is 2.5 mm in thickness, and its characteristics are as follows:

	Density:	1.1 g/cm ³	
	Appearance:	Even, without surface cracking	
5	Rupture strength (standard NF T 46002):	16 daN/dm ²	5
	Elongation to rupture (standard NF T 46002):	150%	
10	Reduction in rupture strength after 3 weeks of irradiation under U.V. at 60°C inside (standard NF T 30049 type E2):	≤10%	10
	Bounce of tennis balls from a height of 2.54 m:	1.43 to 1.47 m	
15	Bounce of basketballs from a height of 1.80 m:	1.50 to 1.55m, i.e. 100 to 105% relative to concrete	15
	Resistance to splitting of the covering applied to concrete, measured by means of an EDF apparatus:	>1.8 mm	
20			20
	Wear resistance, measured with a Lhomargy wear meter, with C 180 abrasive paper, under a load of 1 kg and over a surface area of 10 cm:	loss of 0.6 g after 1500 hours	
25			25
	Slipperiness, measured with a RRL pendulum, on a scale from 0 to 150.		
30	dry covering	90	30
	wet covering	70	

WHAT WE CLAIM IS:-

- 35 1. A method of producing coverings suitable for games surfaces, the coverings being flexible and elastic and of a thickness of from 0.5 to 5 mm, that comprises applying to a support, successively and alternately until the desired thickness is achieved: (i) a polyurethane binder having a viscosity of from 1 to 200 poises at the temperature of application, viz. from -10 to 40°C, the amount of binder applied being from 200 to 1000 g/m², and (ii) solid particles of elastic or plastic nature in an amount sufficient to cover the layer of binder, the solid particles being simply distributed on the surface of the binder without being compacted, particles that have not been retained by the binder being removed if necessary after any or all application(s) of such particles.
- 40 2. A method as claimed in Claim 1 in which the viscosity is from 5 to 30 poises at from 40 -10 to 40°C.
- 45 3. A method as claimed in Claim 1 or 2 in which the thickness of the covering is 1 to 3 mm.
4. A method as claimed in any preceding claim in which the binder has been produced by previous reaction of one or more organic polyisocyanates and one or more hydroxyl compounds, used in proportions such that the isocyanate index is greater than 1.
- 50 5. A method as claimed in Claim 4 in which the isocyanate index is from 1.5 to 10.
6. A method as claimed in any preceding claim in which the binder is cross-linked by air humidity.
7. A method as claimed in any one of Claims 1 to 4 in which the binder is at least partially cross-linked by means of hydroxyl compounds mixed with the binder at the moment of application and is used in proportions such that the isocyanate index of the mixture is from 0.9 to 10.
- 55 8. A method as claimed in any one of Claims 1 to 4 in which the binder is prepared at the moment of application by mixing organic polyisocyanates and hydroxyl compounds used in proportions such that the isocyanate index is from 0.9 to 10.
- 60 9. A method as claimed in any preceding claim in which the hydroxyl compounds are formed by polyols of polyether-polyol or polyester-polyol type having an average from 2 to 6 hydroxyl groups per molecule and an equivalent weight of from 500 to 5000.
- 65 10. A method as claimed in any preceding claim in which the solid particles have a grain size such that at least 90% by weight of the particles passes through a sieve with a mesh 65

opening of 1.5 mm.

11. A method as claimed in any preceding claim in which the particles are of irregular shape and are provided with rugged hollows.

5 12. A method as claimed in Claim 1 substantially as hereinbefore described in any one of the Examples. 5

13. Coverings produced in accordance with a method as claimed in any one of Claims 1 to 12.

10

For the Applicants,
D. Young & Co.,
Chartered Patent Agents,
9 & 10 Staple Inn,
London WC1V 7RD.

10