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(57) Abstract

The wear surface layer of a plastics floor covering is a thermoset resin such as a thermoset polyester, epoxy or carboxyl-functional acrylic resin, the resin being thermoset by a crosslinking reaction between functional groups on the resin and a crosslinking agent. In a process for forming a floor covering having a wear surface layer of thermoset resin, substantially solvent-free thermosettable resin composition is applied to a release substrate to form a thermosettable film and the film is laminated to a floor covering base. The thermosettable film is thermoset after application to the release substrate and either before, during or after lamination to the floor covering base. Alternatively, the substantially solvent-free thermosettable resin composition may be extrusion coated onto a floor covering base and subsequently thermoset.

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Floor Coverings

Field of the invention

This invention relates to plastics floor coverings and to their manufacture, and it is particularly applicable to floor coverings used in sheet or tile form.

Floor coverings are described in an article entitled "Floor Materials" in Encyclopedia of Polymer Science and Engineering, Volume 7 (Wiley-Interscience, 1987), at page 233ff. They are also described in an article entitled "Floor Coverings" in Ullmann's Encyclopedia of Industrial Chemistry, VCH Publishers, Volume A11 (1988), at page 263 ff.

Vinyl sheet and vinyl tile resilient floor coverings, based on plasticised homopolymers or copolymers of vinyl chloride, commonly referred to as PVC, are well-known and have enjoyed considerable commercial success. For certain uses there is a demand for floor coverings of this type having an increased resistance to marking of the surface, particularly resistance to staining, burn marks and scuffing.

Background Art

According to US-A-4983466, soil- and stain- resistant coatings for flooring products are produced by the steps of:-

1. applying a curable cellulose composition comprising an aminoplast, a polyol, an acid catalyst and a cellulose acetate ester on a polypropylene-coated release paper;
2. drying and curing the composition to produce a crosslinked coating;
3. applying a moisture-curable urethane crosslinking composition to the crosslinked coating;
4. drying and curing the urethane composition;
5. laminating the urethane composition to a flooring substrate; and
6. removing the release paper to expose a sheet vinyl flooring protected by a stain- and scratch-resistant cellulosic wear layer.

US-A-4855165 and US-A-4935286 also describe floor coverings having a wear surface which is the cured product of a polyol, an aminoplast and an acid catalyst.

EP-A-192590 describes a composite plastics cladding for floors comprising a thin top layer of linear polyester associated with a heat-diffusing layer, which is preferably based on PVC. The cladding is claimed to be resistant to burning or crushed cigarettes.

JP-A-2-300390 describes a flooring material prepared by coating a thermoplastic resin sheet with a composition comprising a crosslinkable fluoropolymer and an acrylic polymer which is compatible with the fluoropolymer and which may also be crosslinkable.

US-A-5077112 describes a floor covering having a substrate and a tread layer, which is applied to the substrate by vacuum technology and consists of a 1 to 25 micron thick layer of hard inorganic material such as inorganic oxides, nitrides or oxynitrides. The substrate consists of a polymer, preferably a thermoplastic polyester, polyurethane, polyacrylate, polycarbonate or polyvinyl or a thermosetting polyester, polyurethane, polyacrylate, polyether or epoxide resin.

Disclosure of invention

A plastics floor covering laminate according to one aspect of the invention comprises a wear surface layer and a floor covering base and is characterised in that the wear surface layer is a thermoset resin comprising one or more resins selected from polyester and epoxy resins, the resin being thermoset by a crosslinking reaction between functional groups on the resin and a crosslinking agent having groups reactive with the said functional groups. Most preferably, the wear surface layer is a thermoset saturated polyester resin.

According to another aspect of the invention a plastics floor covering laminate comprising a wear surface layer and a floor covering base is characterised in that the wear surface layer is a thermoset resin comprising one or more carboxylic acid-functional resins selected from polyester and acrylic resins, the resin being thermoset by a crosslinking reaction between carboxylic acid functional groups present on it and a crosslinking agent having epoxide groups or beta-hydroxyalkylamide groups.

The floor coverings having a wear surface layer of thermoset polyester resin, thermoset epoxy resin or thermoset carboxyl-functional acrylic resin

have excellent cigarette burn resistance (both to burning cigarette ends and to cigarettes stubbed out on the floor) and good scuff resistance and stain resistance.

A process according to a further aspect of the invention for forming a floor covering having a wear surface layer of a thermoset resin is characterised in that a substantially solvent-free thermosettable resin composition is applied to a release substrate to form a thermosettable film on the release substrate, and the said film is laminated to a floor covering base, the thermosettable film being thermoset after application to the release substrate and either before, during or after lamination to the floor covering base.

Such a process has the advantage that no solvent is required in the formation of the surface layer, and expensive and potentially hazardous curing equipment such as electron beam or ultraviolet lamps is not required.

The thermoset polyester resins, thermoset acrylic resins and thermoset epoxy resins suitable for use as the wear surface layer of the floor covering are in many cases of the type used in thermosetting powder coatings. For convenient processing by techniques used in the powder coating industry the thermosettable polyester, acrylic or epoxy resin preferably has a glass transition temperature Tg in the range 30 to 90°C, most preferably 40 to 85°C, in its non-crosslinked (uncured) state. The thermosettable resin can, however, have a lower Tg down to 10°C or even 0°C or lower, allowing lower temperature processing of the thermosettable composition using apparatus designed to handle a more sticky mixture.

One preferred type of thermoset saturated polyester is a carboxylic acid-functional polyester which has been thermoset by reaction of carboxylic acid functional groups present in it with a crosslinking agent. Such a carboxylic acid -functional saturated polyester generally has an acid value of up to 150, preferably up to 95, mg KOH/g and at least 10, preferably at least 15, mg KOH/g. The carboxyl-functional polyester is preferably derived from an acid component consisting wholly or mainly of one or more aromatic dicarboxylic acids, for example terephthalic acid, isophthalic acid, phthalic acid or a chloro-substituted phthalic acid, or a polyester-forming derivative thereof such as an anhydride, for example phthalic anhydride, a lower alkyl ester, for example dimethyl terephthalate, or an acid chloride,

and a glycol component consisting wholly or mainly of one or more aliphatic diols, for example ethylene glycol, propylene glycol, propane-1,3-diol, butane-1,4-diol, butylene glycol, neopentyl glycol (2,2-dimethylpropane-1,3- diol), hexane-1,6-diol, 1,4-cyclohexanedimethanol, diethylene glycol, dipropylene glycol and/or 2,2-bis(4-hydroxy-cyclohexyl) propane. The polyester-forming ingredients may comprise an aliphatic or cycloaliphatic dicarboxylic acid such as adipic acid, succinic acid or sebacic acid, or tetrahydrophthalic acid or anhydride. The acid component of the polyester preferably comprises at least 50 mole per cent terephthalic acid and/or isophthalic acid and the hydroxyl component preferably comprises at least 50 mole per cent neopentyl glycol, ethylene glycol and/or propylene glycol. The number average carboxyl functionality of the polyester is preferably from about 2 up to 4, for example 2.2 to 2.6. For this purpose the polyester usually includes a small proportion of an at least trifunctional reagent, which may for example be a trifunctional carboxyl component such as trimellitic acid or anhydride or a triol such as trimethylolpropane, trimethylolethane, tris(2-hydroxyethyl) isocyanurate, glycerol or hexanetriol or a higher polyhydric alcohol such as pentaerythritol. The polyester-forming ingredients may also include a minor amount of an aromatic diol such as 2,2-bis(4-(2-hydroxyethoxy)phenyl) propane, a hydroxy carboxylic acid or a lactone such as epsilon-caprolactone. The polyester is preferably saturated but may include unsaturated units derived for example from maleic anhydride or fumaric acid.

The thermosettable polyester can be a single polymerisation product or can be a mixture of polymers. An amorphous carboxyl-functional saturated polyester is usually preferred, but a polyester containing crystalline phases, for example as described in WO-A-91/14745, can be used as at least part of the carboxyl-functional polyester.

Illustrative examples of carboxyl-functional polyesters that can be used in this invention include commercially available polyesters such as "Uralac P2980", "Uralac P3500", "Crylcoat E2988" and "Grilesta V76-12".

Such a carboxyl-functional polyester preferably has a hydroxyl value of 5 or less. The molecular weight of the polyester is preferably at least 1500, most preferably at least 2000, and may be up to 10000, preferably up to 6000, as calculated according to the method described on page 13 of

"Bulletin 18-65, 1978, Amoco Chemical Corporation, How to process better coating resins with Amoco IPA and TMA". In general, the lower the acid value of the carboxyl-functional polyester, the higher the preferred molecular weight within this range.

The crosslinking agent or agents that may be used with such carboxyl-functional polyesters comprise(s) any organic compound that will react with free carboxyl groups on the polyesters to provide a crosslinked polymer network. The chemical functionality of the crosslinking agent is preferably on average at least two, most preferably greater than two up to and including six.

One preferred type of crosslinking agent for use with a carboxyl-functional polyester resin is a polyepoxide. The polyepoxide can for example be an epoxy resin. A thermosettable polyester composition can for example comprise at least 50% by weight up to 80 or 85% by weight of a carboxyl-functional polyester and up to 50% by weight, generally at least 15 or 20% by weight, of an epoxy resin. The epoxy resin can for example be a polyglycidyl ether of an aromatic polyol such as bis(4-hydroxyphenyl)-2,2-propane (bisphenol A) . The epoxy resin generally has an epoxy functionality greater than 1.0 and more preferably greater than 1.9. The epoxy equivalent weight is generally above 100 and preferably less than 1,000, for example from 150 to 800. Polyepoxides based on aliphatic polyols, for example diglycidyl ethers or condensed glycidyl ethers of aliphatic diols, can alternatively be used. Other epoxide group-containing polymers that can be used as the epoxy resin in such thermosettable polyester compositions include polyglycidyl-functional acrylic polymers or epoxy novolak resins.

The carboxyl-functional polyester for use with an epoxy resin as described above preferably has an acid value of at least 30, for example an acid value in the range 35 to 100.

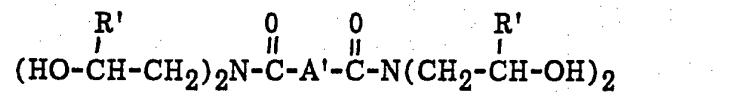
The molar ratio of the functional groups of the crosslinking agent(s), for example epoxide groups, to carboxylic acid groups in the polyester component or components is preferably 0.6:1 to 1.6:1. In general, the weight ratio of thermosettable polyester to crosslinking agent is preferably in the range 70:30 to 96:4.

A polyepoxide crosslinking agent can alternatively be a low molecular weight, solid, non-resinous epoxide compound such as triglycidyl isocyanurate, or triglycidyl 1,2,4-triazolidine-3,5-dione described in US-A-4288569, or the epoxy-functional crosslinker commercially available under the trade mark "Araldite PT810". Such a low molecular weight epoxide curing agent is preferably used in an amount of at least 2% and up to 25% by weight based on the polyester component of the powder composition, most preferably at 4 to 15% by weight.

The carboxyl-functional polyester for use with a low molecular weight solid polyepoxide crosslinking agent preferably has an acid value of up to 50; an acid value of 25 to 45 is most preferred when using the preferred proportions of polyester and polyepoxide.

Mixtures of epoxy resin and low molecular weight polyepoxide crosslinkers can be used if desired.

An alternative type of crosslinking agent for a carboxylic acid-functional polyester is an activated hydroxyl group-containing curing agent, for example a beta-hydroxyalkylamide, a tris(2-hydroxyalkyl)isocyanurate such as tris(2-hydroxyethyl)isocyanurate, or an amino resin such as a urea-formaldehyde or melamine-formaldehyde resin. In the case of an amino resin, some or all of the hydroxyl groups can be etherified, for example hexamethoxymethylmelamine. A beta-hydroxyalkylamide curing agent preferably contains at least one, most preferably two, bis-(beta-hydroxyalkyl)amine groups and can for example be of the formula:



where R' is hydrogen or an alkyl group having 1 to 4 carbon atoms and A' is a divalent organic group, for example an alkylene, arylene or aralkylene group having 2 to 20 carbon atoms. An example of a preferred beta-hydroxyalkylamide curing agent is N,N,N',N'-tetrakis(2-hydroxyethyl)adipamide. An example of a suitable commercially available beta-hydroxyalkylamide is that sold under the trademark "Primid XL552". These activated hydroxyl crosslinking agents are generally used at 3 to 30% by weight, based on the carboxyl-functional polyester, most preferably 4 to 20% by weight. They are generally used with the same type of carboxyl-

functional polyester as disclosed above for use with a solid polyepoxide crosslinking agent.

The thermosettable polyester composition can contain a catalyst for the curing reaction. For example, a strong acid such as p-toluenesulphonic acid can be a catalyst for use with an amino resin curing agent. Catalysts which may be used to accelerate the reaction between the carboxylic acid groups and epoxide groups present in an epoxy resin curing agent or in a polyepoxide curing agent such as triglycidyl isocyanurate include quaternary ammonium salts such as a tetraalkyl ammonium halide, quaternary phosphonium salts, phosphines, amines, imidazoles and metal salts. The catalyst is preferably present in amounts less than 5 per cent by weight, more preferably from about 0.2 to about 2 per cent by weight, based on the total weight of the thermosettable polyester composition.

An alternative type of thermosettable saturated polyester composition is a hydroxy-functional polyester used with a crosslinking agent which is reactive with hydroxyl groups at elevated temperature. The hydroxy-functional polyester generally has a hydroxyl value of at least 25 mg KOH/g and up to 140 mg KOH/g and preferably a hydroxyl value in the range 35 to 95. The hydroxy-functional polyester can in general be prepared from the same dicarboxylic acids and diols as described above for preparing carboxyl-functional polyesters, and the polyester can be prepared under the same reaction conditions, except that a stoichiometric excess of hydroxyl groups over carboxylic acid groups is used and the polycondensation reaction is preferably continued to give an acid value less than 10, for example in the range 2 to 6. The hydroxy-functional polyester is preferably amorphous but can comprise a semi-crystalline polyester as described in WO-A-89/05320.

An example of a commercially available hydroxy-functional polyester that can be used in this invention is that sold under the trademark "Uralac P2115".

The preferred crosslinking agent for use with a hydroxy-functional polyester is a blocked polyisocyanate. Preferred polyisocyanates are aliphatic or cycloaliphatic diisocyanates, for example isophorone diisocyanate (3-isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate) or bis(4-

isocyanatocyclohexyl) methane, although aromatic diisocyanates such as toluene diisocyanate or methylene bis(phenyl isocyanate) can be used. The polyisocyanate can be blocked by lactam groups, for example caprolactam groups. A suitable polyisocyanate blocked by caprolactam is sold under the trademark "Vestagon B1530". Alternatively, the polyisocyanate can be internally blocked by partial condensation to form a biuret or uretdione, for example the material sold under the trademark "Vestagon B1540", or a glycol-uril, for example the material sold under the trademark "Powderlink 1174". The blocked polyisocyanate is preferably used at a level of up to 30% of the total weight of the thermosetting polyester composition; more preferably the ratio of hydroxy-functional polyester to blocked polyisocyanate is from 80:20 to 95:5 by weight. The molar ratio of hydroxyl groups to blocked isocyanate groups is preferably in the range 0.8:1 to 1.6:1.

The thermosettable polyester compositions may contain a catalyst for the reaction between isocyanate and hydroxyl groups, for example a metal carboxylate such as stannous octoate, a tertiary amine or an organometallic compound such as dibutyltin dilaurate. Such a catalyst can for example be used at 0.03 to 1.0 per cent by weight of the thermosettable composition.

Alternative crosslinking agents for hydroxy-functional polyesters include amino resins and anhydride compounds. Examples of amino resins are melamine-formaldehyde resins, urea-formaldehyde resins and benzoguanamine-formaldehyde resins. Solid melamine-formaldehyde resins are preferred, for example hexa-(methoxymethyl)melamine as sold under the trademark "Cymel 300", although "Cymel 301" and "Cymel 303" can be used as alternatives. The amino resin is preferably used at up to 25 per cent of the total weight of the thermosettable composition, most preferably 4 to 10 per cent. With an amino resin an acid catalyst is preferably used, for example 0.1 to 10 per cent p-toluene sulphonic acid based on the weight of amino resin, or a blocked p-toluene sulphonic acid catalyst such as that sold under the trademark "Cycat 4045".

Suitable anhydride compounds for use as crosslinking agents are those containing at least two anhydride groups, for example those solid anhydride adducts sold under the trademarks "Araldite XB 3088", which is an anhydride-functional low molecular weight polyester, or "Epikure H40" or

the anhydride-functional materials disclosed in EP-A-209377. A tertiary amine catalyst can be used with the anhydride adduct.

A preferred type of carboxylic acid-functional thermosettable acrylic resin is an acrylic copolymer having an acid value of up to 120, preferably up to 75, mg KOH/g and at least 10, more preferably at least 15, mg KOH/g.

The carboxylic acid-functional acrylic resin is generally a copolymer of an olefinically unsaturated carboxylic acid such as acrylic, methacrylic, itaconic, maleic or fumaric acid with one or more ethylenically unsaturated comonomers. Examples of ethylenically unsaturated comonomers which can be copolymerised by addition polymerisation with carboxylic acid monomers are acrylic or methacrylic esters such as methyl acrylate, methyl methacrylate, ethyl acrylate, butyl acrylate, ethyl methacrylate, isobutyl methacrylate, n-butyl methacrylate or 2-ethylhexyl acrylate, styrene, acrylonitrile, vinyl esters such as vinyl acetate or vinyl butyrate, vinyl chloride, vinylidene chloride, vinyl fluoride, vinylidene fluoride or vinyl pyridine. Terpolymers may be preferred, for example methyl methacrylate or ethyl methacrylate which tend to raise the Tg of the acrylic resin can be used in conjunction with an acrylate such as ethyl acrylate or particularly an alkyl acrylate of 3 to 6 carbon atoms in the alkyl moiety such as butyl acrylate which tends to lower the Tg. The acrylic resin preferably has a molecular weight of less than 12000 but at least 1500, for example a molecular weight in the range 2000 to 6000. It can for example be prepared by solution polymerisation using a free radical initiator, for example an azo compound such as azobisisobutyronitrile or a peroxide. One example of a suitable commercially available carboxyl-functional acrylic resin is sold under the trade mark "Joncryl 611".

The carboxyl-functional acrylic resin can be thermoset in the process of the invention using a crosslinking agent which will react with carboxylic acid groups to form a crosslinked polymer network, for example a polyepoxide or a crosslinking agent containing activated hydroxyl groups such as beta-hydroxyalkylamide groups. In general, the crosslinking agents described above for use with carboxyl-functional polyesters can be used. The thermosettable acrylic resin composition generally contains 50-96% by weight acrylic resin and 4-50% by weight crosslinking agent.

The thermoset wear surface layer of the floor covering can if desired be based on a mixture of a thermosettable carboxyl-functional acrylic resin and a thermosettable carboxyl-functional polyester used with an appropriate crosslinking agent such as a polyepoxide or a compound containing activated hydroxyl groups. In such a case the acrylic resin and the polyester should preferably be chosen to have broadly similar glass transition temperatures and cure temperatures.

One preferred type of polyepoxide for use with a carboxyl-functional acrylic resin is a low molecular weight, solid, non-resinous epoxide compound as described above, for example triglycidyl isocyanurate. Such a low molecular weight polyepoxide is generally used at up to 25%, preferably up to 15%, by weight of the composition. The carboxyl-functional acrylic resin for use with a low molecular weight polyepoxide preferably has an acid value of up to 50.

The polyepoxide crosslinking agent can alternatively be an epoxy resin. The preferred type of epoxy resin for use with a carboxyl-functional acrylic resin is an epoxide-functional acrylic resin such as a copolymer containing glycidyl ester or ether groups, for example a copolymer of glycidyl acrylate or methacrylate. The glycidyl copolymer can be formed by addition polymerisation in the same manner as the carboxyl-functional acrylic resin, preferably using comonomers of the type described above. The glycidyl copolymer can additionally contain hydroxy-functional comonomers such as hydroxyethyl or hydroxypropyl methacrylate or acrylate, if desired. The thermosettable composition can for example contain at least 50%, preferably 50 to 80 or 90%, by weight of the carboxyl-functional acrylic resin and up to 50%, preferably at least 10% or 20%, by weight of the epoxy resin. The carboxyl-functional acrylic resin for use with an epoxy resin most preferably has an acid value of 30 to 100.

The carboxyl-functional acrylic resin can be used with other epoxy resins, for example with a polyglycidyl ether of a polyol as described above or with an epoxy novolac resin.

An example of a crosslinking agent containing activated hydroxyl groups which can be used with a carboxyl-functional acrylic resin is a compound containing at least one bis(beta-hydroxyalkyl)amide group as

described above.

Examples of thermosettable epoxy resins which can be used as the basis of a thermoset epoxy resin are epoxide-functional acrylic resins, condensed glycidyl ethers of an aromatic polyol such as bisphenol A and epoxy novolac and epoxy cresol novolac resins, as described above. Epoxy resins which are condensed glycidyl ethers generally have an epoxide functionality of 2 or less, for example 1.2 to 2. Epoxy novolac and epoxy cresol novolac resins generally have a functionality greater than 2. The thermosettable epoxy resin preferably has a molecular weight of at least 600, most preferably at least 1000, and can be up to 12000, preferably up to 4000. The epoxy resin preferably has an equivalent weight (molecular weight per epoxide group, EEW) at least 300, most preferably at least 400. The equivalent weight can for example be up to 4000, preferably up to 2000.

An example of a commercially available condensed glycidyl ether epoxy resin is that sold under the trade mark "Araldite GT7072". "Dow DER 642U" is an example of a suitable epoxy novolac resin, and "Ciba Geigy ECN 1299" an example of a suitable epoxy cresol novolac.

An epoxide-functional acrylic resin (which is both a thermosettable acrylic resin and a thermosettable epoxy resin) can be a copolymer of glycidyl methacrylate or acrylate as described above. The crosslinking agent for such a resin can be a carboxylic acid-functional acrylic resin of high acid value. The molar ratio of epoxide to carboxylic acid groups is preferably in the range 0.6:1 to 1.6:1. An example of a low molecular weight crosslinking agent for epoxide-functional acrylic polymers, which can be used as an alternative or additionally to a carboxylic acid-functional acrylic resin crosslinking agent, is a solid dicarboxylic acid such as dodecanedioic acid.

The crosslinking agent for a thermosettable epoxy resin which is a condensed glycidyl ether of an aromatic polyol or an epoxy novolac or epoxy cresol novolac resin can be a carboxylic acid-functional polymer such as a polyester or acrylic resin of high acid value. Compositions containing both a carboxyl-functional polyester or acrylic resin and an epoxy resin can be regarded as a thermoset polyester or acrylic resin if the weight ratio of polyester or acrylic resin to epoxy resin is 1:1 or higher, and as a thermoset

epoxy resin if the epoxide-functional resin is present in greater weight.

Alternative polymeric crosslinking agents for a thermosettable epoxy resin are hydroxy-functional phenolic resins such as those sold under the trade marks "Varcuum 5416" and "Shell XB3082".

The crosslinking agent for a thermosettable epoxy resin can alternatively be a solid low molecular weight compound. Preferred examples of such low molecular weight crosslinkers are dicyandiamide and substituted dicyandiamides, for example that sold under the trade mark "Dow DEH44". Alternative low molecular weight crosslinkers include polyamines, preferably aromatic polyamines such as that sold under the trade mark "Shell HT2844" and solid acid anhydrides. Such low molecular weight crosslinking agents are generally used at 2-25%, preferably 4-20%, by weight based on the epoxy resin.

The thermoset resin can alternatively comprise a mixture of different resins each with a different curing agent, for example an amine-cured epoxy resin used in conjunction with a blocked isocyanate-cured hydroxy-functional acrylic resin.

The thermoset resin composition can contain a plasticiser, for example up to 65% by weight plasticiser based on the thermoset resin. The thermoset composition forming the wear surface layer of the floor covering preferably has a Shore D hardness of at least 50, more preferably at least 55, up to about 75; the most preferred Shore D hardness is generally in the range 60 to 65. In general, it is possible to vary the hardness of the thermoset composition by varying the functionality and crosslink density of the thermoset resin. For example, increasing the acid value of a carboxyl-functional polyester or acrylic resin tends to lead to a harder thermoset surface, as does use of a highly functional low molecular weight crosslinking agent. For polyesters in particular, it is usually preferred to control the hardness of the thermoset material in this way without using plasticisers. Plasticisers can however be used with any of the thermoset resins, the amount of plasticiser usually being at least 10% by weight based on the thermoset resin, preferably less than 50% by weight. The plasticiser can for example be a simple ester plasticiser such as a phthalic diester, phosphoric triester, a diester of a dibasic aliphatic acid or a trimellitic ester and/or a

polymeric plasticiser such as an aliphatic polyester or polyphthalate.

The floor coverings of the invention are composite materials made by laminating two or more films together. The layer of thermoset resin at the wear surface is generally at least 10 microns (0.01 mm) thick and can be up to 2000 microns (2.0 mm) or more, preferably up to 500 microns, thick. The thickness of the layer of thermoset resin can be chosen for the use which the floor is to receive; for example a relatively thin layer within the above range may be sufficient for domestic use whereas a relatively thick layer may be preferred for commercial premises such as public rooms in hotels. The thermoset polyester resin, thermoset acrylic resin or thermoset epoxy resin preferably contains substantially no filler or pigment (for example less than 5% by weight filler or pigment). It is preferably used in a floor covering having a clear wear layer, either as the whole of the wear layer or as a clear layer at the wear surface of the wear layer.

Known high-quality floor coverings, for example high- quality vinyl tiles, may be a laminate of films having the following construction in sequential order:-

1. Clear wear layer 500-1500 micron thick consisting of one or two clear plastics layers;
2. Patterned printed layer 50-125 micron thick;
3. Face ply layer 250-500 micron thick consisting of a plastics composition containing a pigment, for example a white pigment such as titanium dioxide, to provide visual depth to the pattern; and
4. Backing layer 750-1000 micron thick, embossed on the underside with the pattern of a fabric carrier belt, consisting of a plastics composition containing a pigment, for example a black pigment such as carbon black to ensure opacity.

The thermoset resin can for example be used as one or more clear wear layers laminated to a backing, preferably a patterned layer having a backing sheet. Such a clear wear layer is at least 10, preferably at least 20, more preferably at least 50, microns thick and can for example be 200 or 250 microns to 1000 or 2000 microns thick, for example 500 microns thick, and can be a single layer or formed of two or more layers laminated together. The backing sheet can be a face ply and/or a backing layer as described

above.

The patterned printed layer, face ply and backing layer for use with a clear wear layer of thermoset polyester resin, acrylic resin or epoxy resin can for example be formed of plasticised PVC. A typical plasticised PVC composition, as used in commercially available floor tiles, comprises 10-50 parts by weight per 100 parts PVC resin of a simple ester plasticiser and optionally up to 40 parts by weight per 100 parts PVC resin of a thermoplastic polymer having urethane groups. Alternatively, the layers forming the backing sheet can be of an alternative material such as a thermoplastic urethane polymer or acrylic resin, particularly if it is desired to produce a floor covering of zero halogen content. Alternative materials for the backing layer in the floor coverings of the invention include known materials such as nitrile rubbers and highly-filled ethylene copolymers, for example ethylene/vinyl acetate (EVA) copolymers. The backing layer may be coated in known manner with a plastisol containing a blowing agent which provides a foam structure when heated, so that the floor coverings of the invention may be foam cushion sheets or tiles.

One or more wear layers of the thermoset resin can alternatively be used as the wear surface layer which is laminated to a clear wear layer which is a substantially unpigmented layer of a different plastics material, the latter layer being laminated to a patterned layer having a backing sheet. Such a wear surface layer of thermoset resin can for example be at least 10 microns, preferably at least 20 microns, thick and may for example be up to 200 or 300 microns thick. Preferably, it is 50 to 150 microns thick. The different plastics material forming the underlying clear wear layer can for example be plasticised PVC. Alternatively, the underlying clear wear layer can be formed of any of the plastics materials which have been suggested as alternatives to PVC in floor tiles, for example a thermoplastic halogen-free polymer such as a urethane polymer or an acrylic resin. Similarly, the backing sheet (patterned printed layer, face ply and/or backing layer) can be of plasticised PVC or can be of an alternative material such as a thermoplastic urethane polymer or acrylic resin if it is desired to produce a floor covering containing no chlorine or bromine.

It is a feature of the process of the present invention that the wear surface layer of the floor covering is formed from a thermosettable

composition comprising components which are thermally reactive but which are nevertheless formed into a layer and applied to the floor covering with substantially no use of solvents, for example less than 10% by weight and preferably less than 5% by weight of any solvent based on the thermosettable composition. The thermoset wear surface produced generally has better cigarette burn resistance and scuff and stain resistance than thermoplastic surfaces.

In a preferred process for forming a floor covering according to the invention the thermosettable composition is applied to the release substrate to form a thermosettable film by extrusion in melt form (which term includes plastified melt form) through an extrusion coating die onto the release substrate, there being relative movement between the die and the substrate so that successive areas on the substrate are coated with the thermosettable composition.

In this process the thermosettable composition is supplied to the extrusion coating die in melt (eg plastified) form. Melting (eg plastification) of the composition may be carried out in any suitable melt-mixing apparatus, which may be a static or dynamic mixer, for example a Banbury mixer or a Z-blade mixer. The melt-mixed composition may be supplied to the extrusion coating die by means of a suitable pump, such as a gear pump or other positive-displacement pump. An extruder may be used as a melt-mixer and a pump, or may it be used only as a pump for a composition which has been melt-mixed by some other means, for example a Z-blade mixer or a separate compounding extruder.

The film-forming polymer and the curing agent can each be independently metered to a mixer located immediately upstream of the extrusion coating die. Examples of mixers which may be used in such a process include high-efficiency mixers such as static or cavity-transfer mixers. Thus, for example, the film-forming polymer and the curing agent can each be fed through a separate melt hopper into a respective gear pump or other positive-displacement pump, which in turn feeds the corresponding component to a mixer located immediately upstream of the extrusion coating die. Such a process has the advantage of preventing or reducing unnecessary premature contact between co-reactive components of the composition.

A catalyst for the curing reaction, if used, may be premixed with one or other of the co-reactive components of the composition, or it may be injected directly into the composition immediately upstream of the extrusion coating die.

The temperature of the molten composition immediately before application to the substrate is preferably in the range of 20 to 200°C, most preferably 40 to 180°C. The preferred temperature of the composition immediately before application to the substrate is generally related to the glass transition temperature (Tg) of the uncured thermosettable composition and is preferably in the range of from Tg + 10°C to Tg + 200°C, more especially Tg + 25°C to Tg + 150°C. The temperature of the extrusion coating die is thus also preferably in the range 20 to 200°C, especially 40 to 180°C, and in the range Tg + 10°C to Tg + 200°C, especially Tg + 25°C to Tg + 150°C.

The residence time of the thermosettable composition at the application temperature should be kept as low as possible, so as to minimise premature curing of the composition, and it should in particular be well below the gel time of the composition at that temperature. By way of illustration, the residence time of the composition at the application temperature is advantageously less than 60 seconds and preferably less than 30 seconds, for example less than 20 seconds, more especially less than 10 seconds. To assist in minimising any premature curing of the composition, the extrusion coating die should not contain any zones in which the melt flow may become stagnant.

The viscosity of the coating composition at the point of application to the substrate advantageously does not exceed 50 Pas (500 poise), preferably does not exceed 10 Pas (100 poise) and is most preferably less than 5 Pas (50 poise) (as measured at the application temperature by a cone and plate viscometer such as that supplied by Imperial Chemical Industries).

The outlet orifice of the extrusion coating die is generally in the form of a slot of normally rectangular cross-section. The outlet gap width of the extrusion coating die may be in the range of from 50 or 100 to 1500 microns, typically in the range of from 400 to 1000 microns.

The release substrate to which the thermosettable composition is applied

can for example be a release-coated paper such as a siliconised paper or a release-coated film such as a polyethylene terephthalate or nylon film coated with a low-surface-energy silicone material, or it may comprise another low-surface-energy substrate, for example a fluoropolymer-impregnated support such as that sold under the Trade Mark "Tygaflor", or it may comprise a metal support, for example a stainless steel belt, having a low-surface-energy coating. A metal support or an impregnated support such as "Tygaflor" may be in the form of an endless belt, carrying the layer of thermosettable material through a curing area before being separated from the resulting thermoset or partly thermoset material.

The distance between the release substrate surface (at the point at which it is closest to the extrusion coating die) and the outlet of the extrusion coating die is generally up to 2000 microns, advantageously from 10 to 500 microns and preferably from 20 to 200 or 250 microns. If the die is positioned too close to the substrate, there is a risk that the composition will flow around the side of the die and deposit at the edge of the die. Usually, it is preferred that the closest distance between the release substrate surface and the die outlet is at least equal to the thickness of the layer of thermosettable material being formed on the release substrate. If, on the other hand, the die is too far from the substrate, there is a risk that the substrate will not be completely coated, and a "herringbone" pattern may be produced.

The release substrate may be heated before application of the thermosettable composition, for example to a temperature of up to 200°C, to facilitate the production of smooth and even coatings.

The rate of relative movement between the die and the substrate may be in the range of from 1 to 300 metres/minute, advantageously from 5 to 200 metres/minute, for example from 10 to 150 metres/minute. In general, relative movement is achieved by moving the release substrate past a fixed extrusion coating die of length equal to the width of the release substrate, although the extrusion coating die can move across the release substrate if desired.

In a preferred form of process according to the invention, the release substrate is arranged to pass closely adjacent to the extrusion die outlet and

is passing across or around a backing roller (coated, for example, with rubber) at the point of application of the extruded thermosettable composition. For example, when the substrate is passing around a backing roller from below during application of the coating, the site of application may be at any point around the circumference of the backing roller with which the moving substrate is in contact. Preferably, the arrangement is such that the axis of the extrusion die extends along a radius of the backing roller. More particularly, control of application of the thermosettable composition, in terms of uniform thickness and appearance of the wear surface material after curing, is facilitated if the backing roller is disposed horizontally and the site of application of the thermosettable composition is in a plane perpendicular to the axis of rotation of the roller. In such a process, the extrusion coating pressure is controlled by the position of the die in relation to the substrate. In the case in which the substrate is passing over or across a backing roller at the point of application, good control of coating thickness and appearance can in general be achieved without it being necessary to pass the coated release substrate through any subsequent calender rollers.

In another form of process according to the invention, there is no backing roller behind the substrate at the point of application of the thermosettable composition. The extrusion coating pressure in such a process is controlled by the tension under which the release substrate is maintained during transport past the extrusion die outlet.

The curing temperature of the thermosettable composition may be in the range of from 130 to 300°C, depending upon the nature of the composition, and it may typically be in the range of from 150 to 250°C. The curing time depends upon the thickness of the thermoset layer and the temperature of curing. The curing time is typically at least 10 seconds and may be up to 20 or 30 minutes, for example from 2 to 15 minutes, particularly from 5 to 12 minutes.

In an alternative process, the thermosettable resin composition can be supplied to the release substrate as a powder coating. Techniques known for powder coating, for example electrostatic spray gun or fluidised bed coating, can be used. The thermosettable composition is then heat- fused on the release substrate to form a continuous film. The heat treatment used

to fuse the thermosettable composition preferably also serves to at least partially crosslink the composition. The temperature used to fuse the thermosettable composition is generally at least 15°C above the Tg of the uncured composition, for example 25 to 150°C above the Tg.

The thermosettable material, however it is applied to the release substrate, is preferably at least partially crosslinked while supported on the release substrate. The release substrate carrying the thermosettable composition can for example be passed through a curing area such as an oven where full or partial crosslinking of the thermosettable composition takes place. Full crosslinking of the thermosettable composition while supported on the release substrate is usually preferred, so that the thermoset layer does not need to undergo further crosslinking during or after lamination to the backing sheet of the floor covering. We have found that thermoset polyester resins, thermoset acrylic resins and thermoset epoxy resins as described above all adhere well to plasticised PVC layers during the normal lamination process involved in making floor coverings. If enhanced adhesion is required, the thermosettable composition may be only partially crosslinked while supported on the release substrate, and it may be further crosslinked during or after lamination to the backing of the floor covering. Partial crosslinking can be achieved by maintaining the thermosettable composition at a curing temperature for at least 25%, preferably at least 50%, of the time required for full curing. For example, a thermosettable saturated polyester requiring 10 minutes cure at 200°C may be held at 200°C for 8 minutes to give partial crosslinking, with further heat curing taking place during and optionally after crosslinking.

After the thermoset layer has been fully or partially crosslinked on the release substrate it can optionally be separated from the release substrate. If the thermoset layer is to pass directly to the lamination apparatus, it may be separated from the release substrate before lamination or the release substrate can pass through the lamination apparatus and be separated subsequently from the wear surface layer of the laminated floor covering. Usually, it is preferred for manufacturing convenience to store the layer of thermoset material, for example on a reel. A fully crosslinked thermoset material can be reeled on the release substrate or stripped from the release substrate and reeled separately. A partially crosslinked layer is preferably reeled on the release substrate. If the release substrate is an endless belt,

the wear surface material is preferably fully crosslinked on the belt so that it can be stripped and stored.

Alternatively, the process of the invention can be carried out without any crosslinking step between application of the thermosettable composition to the release substrate and lamination to the backing of the floor covering. In this case, the thermosettable composition is preferably carried through the laminating apparatus on the release substrate and crosslinking is effected during and/or after lamination. Any crosslinking carried out after lamination can be carried out by a form of heating which preferentially heats the wear surface layer of the floor covering, for example radiant heating of that face of the laminate.

The release substrate is intended to be separated from the thermoset resin layer at some time. This may be before lamination as described above, immediately after lamination, or after any subsequent processing such as tile cutting. The floor covering of the invention can alternatively be supplied with the release substrate attached, for removal during or after laying of the floor covering on a floor.

In a typical lamination procedure for the manufacture of floor coverings, two or more films are fed between heated nip rollers, preferably maintained at a temperature in the range 150 to 200°C, for example around 175°C, in order to fuse the films together. One or more sets of nip rollers may be used. The films may all be fed between the first set of nip rollers or one or more of the films may be introduced between later sets of nip rollers. The resulting film laminate may then be bonded to a backing fabric by passage of the laminate and the fabric between a further set of heated nip rollers. The backing fabric may be coated with a plastisol containing a blowing agent to provide a foam layer. Alternatively, the lower face of the film laminate may be embossed to provide a roughened surface, for example by contact with a fabric carrier or a drum. The wear layer may be patterned by passage over a heated drum whose surface is the negative of the desired pattern to provide a wear layer with an embossed surface. The resulting floor covering is then cooled and is typically cut into strips or squares ready for use. Any waste material flooring product resulting from the production process incorporating a thermoset wear layer can be ground and incorporated into the backing layer of a floor tile laminate.

The thermosettable resin composition for use in the process of the invention preferably comprises one or more resins selected from polyester resins having functional groups, epoxy resins and carboxyl-functional acrylic resins as described above, together with a crosslinking agent having groups reactive with functional groups on the said resin, but the process can be applied with other thermosettable resins which on heating exhibit plastic flow before setting, for example hydroxyl-functional acrylic resins used with blocked polyisocyanate or amino resin crosslinkers.

In an alternative process according to the invention for forming a floor covering having a wear surface layer of a thermoset resin, a layer of a substantially solvent-free thermosettable resin composition is extrusion-coated onto a floor covering base and is subsequently thermoset. The thermosettable resin composition can for example be extrusion-coated onto a backing sheet comprising an opaque backing layer, a white pigmented face ply layer, a patterned printed layer and optionally a clear wear layer as described above, or onto a less complex backing sheet. The thermosettable resin composition can alternatively be extrusion-coated onto the layer which it is to contact in the final floor covering, for example onto the patterned printed layer or the clear wear layer, and the extrusion-coated layer can be laminated to the backing layers in a lamination process as described above.

The thermosettable resin composition for use in such an extrusion coating process preferably has a relatively low softening temperature so that it can be extrusion coated at a temperature lower than the softening temperature of the floor covering onto which it is extruded, and it preferably has a relatively low Tg, for example less than 70°C, most preferably 0 to 50°C. The thermosettable resin composition can be thermoset by the heat of the lamination process and/or in a subsequent heating step as described above. The cure temperature of the thermosettable resin composition should preferably be no higher than the softening temperature of the other material used in the floor covering, for example no higher than 200°C and preferably no higher than 175°C in the case of a floor covering having a PVC base.

The invention is illustrated by the following Examples, in which parts and percentages are by weight:-

Example 1

A thermosettable polyester-epoxy hybrid composition was prepared from the following formulation:

			%
Uralac P2980	carboxyl-functional polyester Tg=54°C, acid value (AV) 70-85 mg KOH/g	49.8
Epikote 3003	epoxy resin Tg 51°C, epoxyequivalent weight (EEW) 770-880	9.0
Acronyl 4F	acrylic resin flow aid	1.0
Araldite GT 7072	epoxy resin, EEW 570-595 softening point 82-90°C	39.6
Crylcoat E2564	5% of active catalyst in 95% carboxyl-functional polyester Tg 70°C, AV 30 mg KOH/g	0.4
Benzoin	flow control additive	0.2

The ingredients were mixed at a temperature above the Tg of the polyester, extruded as a layer, chilled and broken into chips. The formulation was fed in chip form into an extruder, the output of which was coupled to a gear pump. The extrudate in molten form was pumped via a heated hose to a slot die of width 300 mm on a laboratory coating machine. The temperature of the molten thermosettable composition at the die was 140°C. A siliconised polyethylene terephthalate (PET) release film of thickness 120 microns was continuously coated with 360 g/min of the formulation at web speed 10 m/min. The closest distance between the film and the die outlet was 100 microns. The coated film was passed through a long horizontal oven such that the coating experienced 10 minutes at 200°C, whereby crosslinking was achieved. After passage through the oven, the thermoset layer was separated from its PET support and both the thermoset film and the support were wound on separate reels. The PET support can either be recycled or reused in the process; the thermoset film, which was 100 microns thick, was stored on reel and used for the production of a floor covering.

The floor covering was formed by laminating successively a black pigmented plasticised PVC backing layer 800 microns thick, a white

pigmented layer 400 microns thick, a patterned printed plasticised PVC layer 80 microns thick, a clear wear layer of plasticised PVC 500 microns thick and the 100 micron thermoset polyester film. The temperature of lamination was 175°C. The thermoset polyester film was not substantially softened at this temperature but became securely adhered to the underlying PVC layer.

The properties and performance of the laminated flooring incorporating the thermoset wear layer are described in Table 1 below.

Examples 2 to 11

Following the procedure of Example 1, thermoset film layers were prepared from the compositions described and a laminated flooring material was produced incorporating the thermoset film at the wear surface. The properties and performance of the flooring material are described in Table 1 below.

Example 2

A thermosettable polyester urethane composition:

			%
	Uralac P2115	hydroxy-functional polyester Tg 48°C, hydroxyl value (OHV) 35-45 mg KOH/g, AV 10 mg KOH/g	78.66
	Vestagon B1540	uretdione (internally blocked adduct) of isophorone diisocyanate, crosslinker, NCO content 15%, Tg 60-85°C	19.64
	Troykd EX486	proprietary flow aid	1.5
	Benzoin		0.2

Example 3

A thermosettable polyester urethane composition:

			%
	Uralac P2115	(See Example 2)	78.66
	Vestagon B1530	caprolactam-blocked adduct of isophorone diisocyanate, crosslinker, NCO content 15%, Tg 60-85°C	19.64
	Troykd Ex 486	(See Example 2)	1.5
	Benzoin		0.2

Example 4

A thermosettable polyester composition:		%
Grilesta V76-12	carboxyl-functional polyester, Tg 62°C, AV 34 mg KOH/g	93.1
Primid XL 552	tetrakis hydroxyalkyladipamide crosslinker, hydroxyl equivalent weight 82-86	4.9
Irganox 245	hindered phenolic antioxidant	0.3
Troykd EX486	(See Example 2)	1.5
Benzoin		0.2

Example 5

A thermosettable polyester composition:		%
Uralac P2115	(See Example 2)	89.4
Powderlink 1174	glycoluril crosslinker MPt 90-110°C, equivalent weight 90-125	8.1
MTSI (Cyanamid)	proprietary catalyst	0.8
Troykd EX486	(See Example 2)	1.5
Benzoin		0.2

Example 6

A thermosettable polyester composition:

		%
Uralac P3470	carboxyl-functional polyester Tg 66°C AV 25-30 mg KOH/g	89.1
XB 990 (Ciba-Geigy)	proprietary epoxy-functional cross linker. MPt 95-105°C EEW 141-154	6.7
DT 3126 (Ciba-Geigy)	proprietary accelerator	2.5
Benzoin		0.2
Troykd EX 486	(See Example 2)	1.5

Example 7

A thermosettable polyester-epoxy hybrid composition:

			%
	Uralac P2450	carboxyl-functional polyester Tg 63°C AV 30-38 mg KOH/g	69.2
	Epikote 3003	(See Example 1)	9.0
	Acronyl 4F	(See Example 1)	1.0
	Araldite GT7072	(See Example 1)	20.2
	Crylcoat E2564	(See Example 1)	0.4
	Benzoin		0.2

Example 8

A thermosettable epoxy composition:		%
Araldite GT 7072	(See Example 1)	86.1
Epikote 3003	(See Example 1)	9.0
Acronyl 4F	(See Example 1)	1.0
Epikure 108 FF	catalyst epoxy dicyandiamide blend	3.7
Benzoin		0.2

Example 9

A thermosettable polyester urethane composition:

			%
	Crylcoat E3089	hydroxy-functional polyester Tg 50- 60°C, OHV 21-22 mg KOH/g	88.9
	Vestagon B1530	(See Example 3)	9.4
	Benzoin		0.2
	Troykd EX486	(See Example 2)	1.5

Example 10

A thermosettable acrylic composition:

			%
	SCX815B (S C Johnson)	a carboxyl-functional acrylic resin Tg 60°C AV 38 mg KOH/g	93.2
	Primid XL552	(See Example 4)	5.1
	Benzoin		0.2
	Troykd EX486	(See Example 2)	1.5

Example 11

A thermosettable acrylic composition:		%
Joncryl 611	carboxyl-functional acrylic resin, Tg 60°C, AV 53 mg KOH/g	91.5
Primid XL552	(See Example 4)	7.3
BYK 360	Flow aid	1.0
Benzoin		0.2

Examples 12 and 13

Thermoset film layers were prepared from the compositions described below, following generally the procedure of Example 1 but using a heated hopper (80-100°C) to feed the slot die which was at a temperature of 100°C. Laminated flooring material incorporating the thermoset film at the wear surface was produced according to the invention. The properties and performance of the flooring material are described in Table 1 below.

Example 12

A thermosettable polyester composition:	%
Carboxyl-functional polyester Tg 10°C, AV 41 mg KOH/g	88.5
Triglycidyl isocyanurate crosslinker EEW 100-108	9.8
Benzoin	0.2
Troykd EX486 (See Example 2)	1.5

Example 13

A thermosettable polyester urethane composition:

	%
Hydroxy-functional polyester Tg 10°C OHV 140 mg KOH/g	37.0
Hydroxy-functional polyester Tg -20°C OHV 75mg KOH/g	51.0
Desmodur N75 aliphatic polyisocyanate crosslinker	12.0

Comparative Example A

100 parts of PVC plasticised with 30 parts of phthalate ester plasticiser.

Table 1

Example No	Type of Thermoset	Taber Abrasion (g/1000 cycles)	Cigarette Burn Resistance	Scratch Resistance	Colour & Clarity
1	Polyester-Epoxy Hybrid	0.15 - 0.20	4	3	PASS
2	Polyester - Urethane	-	-	-	-
3	Polyester - Urethane	0.15 - 0.20	3	4	PASS
4	Polyester	0.15 - 0.20	2	3	PASS
5	Polyester	0.15 - 0.20	2	3	PASS
6	Polyester	0.15 - 0.20	2	3	PASS
7	Polyester-Epoxy Hybrid	0.15 - 0.20	3	3	PASS
8	Epoxy	0.1 - 0.15	1	2	FAIL
9	Polyester - Urethane	0.15 - 0.20	3	4	PASS
10	Acrylic	-	-	-	-
11	Acrylic	-	-	-	-
12	Polyester TGIC	0.05 - 0.10	1	3	PASS
13	Polyester - Urethane	0.30 - 0.40	4	2	PASS
A	Typical PVC	0.10 - 0.20	6	2-3	PASS

Explanation of Tests:-

Taber Abrasion :		Frick Taber Abrasion test (SIS 92-3509)
Cigarette Burn Resistance:	1 =	Very Good, No Char, only very slight marking
	2 =	Good, Slight Charring and Marking
	3 =	Fairly Good, Some Charring and Marking
	4 =	Mediocre, Significant Charring and Some Pitting
	5 =	Poor, Severe Charring and Pitting
	6 =	Very Poor, Severe Burns
Colour and Clarity		Pass indicates colour and clarity similar to that of the plasticised PVC wear layers used commercially
Scratch Resistance		This test is carried out by scratching the wear surface with the milled edge of a coin
	1 =	No visible mark
	2 =	Slight marking of surface
	3 =	Slight removal of material from surface
	4 =	Deep scratch with brittle removal of material
	5 =	Deep scoring with extensive removal of material

Example 14

The thermosettable polyester-epoxy composition described in Example 12 was formed into chips and extruded onto a release film as described in Example 1 except that the web speed was 2 m/min and the distance between the film and the die outlet was 500 microns . A 500 micron thick thermoset film was formed.

A floor covering was produced by laminating this thermoset film to a backing sheet comprising the plasticised PVC backing layer, the white pigmented layer and the printed plasticised PVC layer used in Example 1.

CLAIMS

1. A plastics floor covering laminate comprising a surface wear layer and a floor covering base, characterised in that the wear surface layer is a thermoset resin comprising one or more resins selected from polyester and epoxy resins, the resin being thermoset by a crosslinking reaction between functional groups on the resin and a crosslinking agent having groups reactive with the said functional groups.

2. A floor covering according to claim 1, characterised in that the wear surface layer is a thermoset saturated polyester resin.

3. A floor covering according to claim 2, characterised in that the thermoset saturated polyester is a carboxylic acid-functional polyester which has been thermoset by reaction of carboxylic acid functional groups present in it with a crosslinking agent.

4. A floor covering according to claim 3, characterised in that the thermoset saturated polyester has been obtained from a carboxylic acid-functional polyester and a crosslinking agent at a ratio in the range 70:30 to 96:4 by weight.

5. A floor covering according to claim 3 or claim 4, characterised in that the crosslinking agent is a polyepoxide.

6. A plastics floor covering laminate comprising a surface wear layer and a floor covering base, characterised in that the wear surface layer is a thermoset resin comprising one or more carboxylic acid-functional resins selected from polyester and acrylic resins, the resin being thermoset by a crosslinking reaction between carboxylic acid functional groups on the resin and a crosslinking agent having epoxide groups or beta-hydroxyalkylamide groups.

7. A floor covering according to any of claims 1 to 6, characterised in that the thermoset resin forming the wear surface layer contains essentially no filler or pigment.

8. A floor covering according to claim 7, characterised in that at least

one wear surface layer of said thermoset resin is laminated to a patterned layer having a backing sheet.

9. A floor covering according to claim 7, characterised in that at least one wear surface layer of said thermoset resin is laminated to a substantially unpigmented wear layer of a different plastics material which is laminated to a patterned layer having a backing sheet.

10. A floor covering according to claim 9, characterised in that the said different plastics material is plasticised polyvinyl chloride, a thermoplastic urethane polymer or an acrylic resin.

11. A floor covering according to any of claims 1 to 7, characterised in that the thickness of the thermoset resin layer is 0.01 to 2.0 mm.

12. A process for forming a floor covering having a wear surface layer of a thermoset resin, characterised in that a substantially solvent-free thermosettable resin composition is applied to a release substrate to form a thermosettable film on the release substrate, and the said film is laminated to a floor covering base, the thermosettable film being thermoset after application to the release substrate and either before, during or after lamination to the floor covering base.

13. A process according to claim 12, characterised in that the thermosettable composition is applied to the release substrate to form a thermosettable film by extrusion in melt form through an extrusion coating die onto the release substrate, there being relative movement between the die and the substrate so that successive areas on the substrate are coated with the thermosettable composition.

14. A process according to claim 13, characterised in that the molten thermosettable composition immediately prior to application to the substrate is at a temperature in the range of from Tg + 10°C to Tg + 200°C, where Tg is the glass transition temperature of the uncured thermosettable composition.

15. A process according to claim 14, characterised in that the said range is from Tg + 25°C to Tg + 150°C.

16. A process according to any of claims 13 to 15, characterised in that the distance between the substrate surface (at the point at which it is closest to the extrusion die) and the outlet of the extrusion die is from 10 to 2000 microns.

17. A process according to any of claims 13 to 16, characterised in that the release substrate is passing across or around a backing roller at the point of application of the extruded thermosettable composition.

18. A process according to claim 12, characterised in that the thermosettable resin composition is applied to the release substrate as a powder coating and is heat-fused on the release substrate to form a continuous film.

19. A process for forming a floor covering having a wear surface layer of a thermoset resin, characterised in that a layer of a substantially solvent-free thermosettable resin composition is extrusion-coated onto a floor covering base and is subsequently thermoset.

20. A process according to any of claims 12 to 19, characterised in that the thermosettable resin composition comprises one or more resins selected from polyester, acrylic and epoxy resins and a crosslinking agent having groups reactive with functional groups on the said one or more resins.

INTERNATIONAL SEARCH REPORT

Internati· ·l Application No
PCT/GB 94/02788

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 E04F15/16 E04F15/02 C09D167/00 B32B27/06

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)
IPC 6 E04F C09D B32B

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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB,A,2 075 995 (ARMSTRONG CORK CO.) 25 November 1981 see page 1, line 1 - line 18 see example 36	6,7,10
A	---	19,20
A	WO,A,91 14745 (COURTAULDS COATINGS) 3 October 1991 cited in the application see claims 1,10,12	1-6

A	DE,A,17 20 502 (DEUTSCHE BAUAKADEMIE) 1 July 1971 see page 1, line 1 - line 12 see page 2, line 21 - line 27	1

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in 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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Date of the actual completion of the international search	Date of mailing of the international search report
25 April 1995	09. 05. 95

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

Internat[illegible]l Application No
PCT/GB 94/02788

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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Internat[illegible]l Application No
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