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(71) Applicant: **DSM RESINS BV**
Ceintuurbaan 5
NL-8022 AW Zwolle(NL)

(72) Inventor: **Van der Linde, Robert**
Kuyerhuislaan 10
NL-8024 PD Zwolle(NL)

(74) Representative: **Hoogstraten, Willem Cornelis Roeland et al**
OCTROOIBUREAU DSM Postbus 9
NL-6160 MA Geleen(NL)

(54) Resin composition and process for the preparation of this resin composition.

(57) The invention relates to a resin composition, comprising a mixture of at least two resins A and B, wherein resin A the reaction product of an epoxidized fatty acid ester of a polyvalent alcohol with a carboxylic acid is and resin B a carboxylic acid-modified ester of a polyvalent alcohol is. The resin composition is obtainable by mixing the resins A and B during such a time and at such a temperature that a partial pre-reaction takes place.

The resin composition can be applied in the production of surface-covering layers especially in the production of linoleum.

RESIN COMPOSITION AND PROCESS FOR THE PREPARATION OF THIS RESIN COMPOSITION

The invention relates to a resin composition comprising a mixture of at least two resins A and B, wherein the resin A is the reaction product of an epoxidized fatty acid ester of a polyvalent alcohol with a carboxylic acid and the resin B is a carboxylic acidmodified ester of a polyvalent alcohol, as well as to a process for the preparation of such a resin composition.

Such a resin composition is known from NL-A-8402455. This reference aims at a resin composition suitable as linoleum cement.

In many processes applied for the preparation of a resin composition for linoleum manufacture (the resin composition hereinafter to be referred to as linoleum cement; in the linoleum industry it is also called Bedford cement, after the manner it is formed), use is made of one or more polyunsaturated oils, which can be 'dried' (cured) by air oxidation. Drying oils are understood to mean esters of natural fatty acids with polyvalent alcohols, in particular glycerol or pentaerithrytol. During or after drying, these drying oils are mixed with a resin, in particular with rosin, which yields the Bedford cement. After mixing of this cement with fillers and pigments, the linoleum mix obtained is applied to a, mostly jute, substrate, usually by means of a calander. The product thus formed is then cured at 60-80¤C for a number of weeks (see, e.g., Ullmann, Encyklopädie der technischen Chemie, band 12 (1976), p. 24 ff., and Encycl. of Pol. Sci. and Techn., Vol. 1 (1964), p. 403 ff.). The disadvantage of these processes for the preparation of linoleum is the long time required for curing of the product, which depends on the thickness of the linoleum layer. Furthermore, intensive, manual inspection is required to determine whether the desired hardness has been reached.

NL-A-8402455 describes a resin composition that is suitable as linoleum cement, and wherein the duration of the necessary curing of the linoleum is strongly reduced and the homogeneity of the material obtained is improved. This resin composition comprises a mixture of two resins A and B. The resin A is the reaction product of an epoxidized fatty acid ester of a polyvalent alcohol with a monovalent carboxylic acid, while the resin B is a carboxylic acid-modified ester of a polyvalent alcohol. The term 'carboxylic acid-modified' in this context also embraces the presence of carboxylic anhydride groups instead of, or besides, carboxylic acid groups. This resin composition has however the disadvantage that its viscosity is such as to render it difficult to process the resin composition using the existing production equipment in the linoleum industry.

The object of the invention is to provide a resin composition comprising a mixture of at least two resins A and B, wherein the resin A is the reaction product of an epoxidized fatty acid ester of a polyvalent alcohol with a carboxylic acid, and the resin B is a carboxylic acid-modified ester of a polyvalent alcohol, which can conveniently be processed using the existing equipment in the linoleum industry.

The resin composition according to the invention is characterized in that the resin composition is obtainable by mixing the resins A and B during such a time and at such a temperature that a partial pre-reaction takes place.

This partly pre-reacted condition is hereafter also referred to as B-stage. The dynamic viscosity (η_d) may be between 10^2 and 10^5 Pas, by preference between 10^3 and 10^4 Pas, giving the resin composition the consistency needed to yield an excellent product upon further processing to linoleum. This dynamic viscosity as a function of the frequency of 1 Hz at 100¤C is determined by using a parallel plate viscometer (Rheometric RMS 605).

According to a preferred embodiment of the invention, the resins A and B are partially pre-reacted during 5 minutes -4 hours at a temperature between 60¤C and 250¤C, more preferably during 0.5-2.5 hours at a temperature between 120¤C and 180¤C.

In the preparation of both resin A and resin B, it is convenient to start from modified drying oils. The drying oil in the case of resin A is applied in epoxidized form, use being made in particular of an epoxide of soy-bean oil, linseed oil, sunflower oil and/or a tall oil fatty acid ester. The polyvalent alcohol in the ester is preferably chosen from the group formed by glycerol, pentaerithrytol, trimethylolpropane and/or polyalkene glycol. Mixtures of these or other polyvalent alcohols may also be applied.

The carboxylic acid with which the epoxidized drying oil is reacted is for instance, a monovalent carboxylic acid such as benzoic acid, para-tertiary-butyl-benzoic acid, tall oil fatty acid, bi-or polyvalent carboxylic acids, rosin, acid hydrocarbon resins, and/or mixtures thereof. For linoleum preparation, preference is given in particular to rosin as acid, so as to retain the properties characteristic of linoleum, which originate from the rosin. Suitable polyvalent carboxylic acids are carboxylic acids with 4-54 C atoms in the molecule. In particular a di-or trimer fatty acid, or a mixture thereof, may be applied as polyvalent carboxylic acid.

The carboxylic acid-modified ester in resin B may consist of the reaction product of an unsaturated fatty acid ester of a polyvalent alcohol with one or more ethylenically unsaturated mono-or polyvalent carboxylic acids or the anhydrides thereof. An unsaturated fatty acid ester, a vegetable oil or a tall oil fatty acid ester may be started from, esterification taking place in particular with a polyvalent alcohol taken from the group formed by glycerol, pentaerithrytol, trimethylolpropane and/or polyalkene glycol, while mixtures of these or other polyvalent alcohols may also be applied. As vegetable oil to be applied, in the context of the invention particularly soy-bean oil, linseed oil, sunflower oil, olive oil, safflower oil and/or rape seed oil are suitable.

The ethylenically unsaturated carboxylic acid or the anhydride thereof, which is applied for the preparation of resin B, may contain one or more ethylenically unsaturated groups in the molecule. As monovalent carboxylic acid, use can preferably be made of acrylic acid, methacrylic acid, sorbic acid and/or crotonic acid. As polyvalent carboxylic acid, use can preferably be made of maleic acid and/or fumaric acid and/or the anhydride thereof. Maleic anhydride is particularly suitable for the purpose, for the so-called maleinized oils can easily be prepared and are commercially available.

The carboxylic acid-modified ester in resin B may also consist of the reaction product of a hydroxy-functional fatty acid ester of a polyvalent alcohol with a polyvalent carboxylic acid. For this, use can be made in particular of the esters derived from castor oil, hydroxystearic acid and/or hydroxypalmitic acid. The polyvalent alcohol used for esterification is then preferably chosen from the group formed by glycerol, pentaerithrytol, trimethylolpropane and/or polyalkene glycol. Mixtures of these or other polyvalent alcohols may also be applied. The polyvalent carboxylic acid that is reacted with the said hydroxy-functional fatty acid ester can preferably be taken from the group formed by phthalic acid, tetra-or hexahydrophthalic acid and trimellitic acid.

Resin B may also consist of one or more acid-functional alkyd resins and/or acid-functional hydrocarbon resins and/or mixtures thereof.

In the preparation, first of all resin A can be prepared by reaction of the epoxidized ester with the carboxylic acid. This preparation takes place at a temperature between 100 to 250¤C, and preferably at a temperature between 150 to 200¤C, optionally in the presence of a catalyst. As catalyst, use is preferably made of a customary catalyst for the acid-epoxy reaction, such as, for instance, triethylamine.

When resin A is combined with resin B, a catalyst of the same type as used in the preparation of resin A may be added.

The resin composition according to the invention can also be applied in combination with resin compositions on the basis of one or more polyunsaturated oils that are 'dried' by air oxidation.

Though the preceding mainly discussed the application of the resin composition according to the invention in the preparation of surface covering layers, in particular in the linoleum preparation, the application of the resin composition according to the invention is not limited thereto. Other systems using resin compositions, customarily in the form of so-called two-components resins, with a view to obtaining a surface covering layer, are suitable for application of this resin composition. Among the applications that may be considered are roof coverings and the so-called "Unterbodenschutz" in the automotive industry.

The invention will be elucidated with reference to the following non-restrictive examples.

Examples

1) Preparation of resin A

A 3-l reaction vessel, provided with a mechanical stirrer, thermometer and a vertical cooler, is charged with 60 parts by weight epoxidized linseed oil (Edenol B 316 of Henkel, oxirane content higher than 8.5 %), 40 parts by weight rosin and 1 part by weight triisobutylamine. While nitrogen is being passed over, the reaction mixture is heated to 180 ¤C. The contents of the reaction vessel are kept at this temperature until the acid number has decreased to 3 mg KOH/g. The product is subsequently cooled. The epoxy equivalent weight is 600.

2) Preparation of resin B

In equipment similar to that used for resin A, 878 parts by weight linseed oil are heated to 200¤C under nitrogen. Subsequently 294 parts by weight maleic anhydride are cautiously added, divided into portions over 2 hours. Care is taken that the temperature does not exceed 200¤C. After everything has been added, the temperature is gradually raised to 225¤C and maintained for 4 hours.

3) Preparation of the B stage

The resins A and resin B obtained above are mixed in a weight ratio of 1 : 1 at 100¤C and heated to 125¤C. The resins are subsequently kept at this temperature for two hours, after which the composition is cooled. Immediately after this the resin composition can be processed into linoleum in the customary manner.

4) Determination of the viscosity

Using a parallel plate viscometer (Rheometrics RMS 605 spectrometer), the dynamic viscosity (η_d) of the resin composition is determined as a function of the frequency at 100¤C. This viscosity (at 1 Hz) is 6 × 10^3 Pas.

5) Determination of the curing rate of linoleum final product

Using a Schwabenthan twin roller mill (diameter 80 mm, speed 27/35 rpm), test sheets are produced. From these test sheets, subsequently plates (250 × 250 × 4 mm) are moulded at 100¤C during 4 minutes. From these, test bars are punched, of which, after curing, the E-modulus, tensile strength and elongation at break are determined.

Curing of the test bars at 80¤C takes place during 1, 5, 11 or 50 days.

	E-modulus (N/mm^2)	Tensile strength (N/mm^2)	Elongation (%)
2 days in refrigerator	23 ± 1	1.6 ± 0.1	6.7 ± 0.4
1 day	105 ± 4	7.8 ± 0.8	4.9 ± 0.7
5 days	150 ± 5	12.6 ± 0.7	5.8 ± 0.1
11 days	307 ± 3	11.7 ± 0.1	4.7 ± 0.3
50 days	450 ± 0.1	15.4 ± 0.3	4.1 ± 0.1

This shows that the resin composition results in fast curing and in a product having excellent properties.

Claims

1. Resin composition, comprising a mixture of at least two resins A and B, wherein the resin A is the reaction product of an epoxidized fatty acid ester of a polyvalent alcohol with a carboxylic acid and the resin B is a carboxylic acid-modified ester of a polyvalent alcohol, characterized in that the resin composition is obtainable by mixing the resins A and B during such a time and at such a temperature that a partial pre-reaction takes place.

2. Resin composition according to claim 1, characterized in that the resins A and B have been partially pre-reacted during 5 minutes-4 hours at a temperature of between 60¤C and 250¤C.

3. Resin composition according to any of claims 1-2, characterized in that the resins A and B have been partially pre-reacted during 0.5-2.5 hours at a temperature of between 120¤C and 180¤C.

4. Resin composition according to any of claims 1-3, which is adapted for processing to linoleum using the existing production equipment in the linoleum industry.

5. Process for the preparation of a resin composition, comprising a mixture of at least two resins A and B, wherein the resin A is the reaction product of an epoxidized fatty acid ester of a polyvalent alcohol with a carboxylic acid and the resin B is a carboxylic acid-modified ester of a polyvalent alcohol, characterized in that the resin composition is obtained by mixing the resins A and B during such a time and at such a temperature that a partial pre-reaction takes place.

6. Process for the preparation of a resin composition according to claim 5, characterized in that the resins A and B are partially pre-reacted during 5 minutes-4 hours at a temperature between 60¤C and 250¤C.

7. Process for the preparation of resins according to any of claims 5-6, characterized in that the resins A and B are partially pre-reacted during 0.5-2.5 hours at a temperature between 120¤C and 180¤C.

8. Surface-covering layer, prepared using a resin composition according to any of claims 1-4 or obtained by the process according to any of claims 5-7.

9. Linoleum, prepared using a resin composition according to any of claims 1-4 or obtained by the process according to any of claims 5-7.

10. Object, made whole or partly using a resin composition according to any of claims 1-4 or obtained by the process according to any of claims 5-7.

Claims for the following Contracting State : AT

1. Process for the preparation of a resin composition, comprising a mixture of at least two resins A and B, wherein resin A the reaction product of an epoxidized fatty acid ester of a polyvalent alcohol with a carboxylic acid is and resin B a carboxylic acidmodified ester of a polyvalent alcohol is, characterized in that the resin composition is obtainable by mixing the resins A and B during such a time and at such a temperature that a partial pre-reaction takes place.

2. Process for the preparation of a resin composition according to claim 1, characterized in that the resins A and B have been partially pre-reacted during 5 minutes-4 hours at a temperature of between 60¤C and 250¤C.

3. Process for the preparation of a resin composition according to either of claims 1-2, characterized in that the resins A and B have been partially pre-reacted during 0.5-2.5 hours at a temperature of between 120¤C and 180¤C.

4. Process for the preparation of a resin composition according to any of claims 1-3, which is adapted for processing to linoleum using the existing production equipment in the linoleum industry.

5. Surface-covering layer, prepared using a resin composition obtained by the process according to any of claims 1-4.

6. Linoleum, prepared using a resin composition obtained by the process according to any of claims 1-4.

7. Object, made whole or partly using a resin composition obtained by the process according to any of claims 1-4.

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EUROPEAN SEARCH REPORT

Application number

EP 86 20 2139

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y	US-A-3 308 077 (J.P. PATTISSON et al.) * Claims; example 10 * ---	1-10	D 06 N 1/00 C 08 G 59/16 C 08 L 63/00 C 09 F 7/00
Y	US-A-2 909 496 (H.G. COOKE et al.) * Claims; column 2, lines 54-57 * ---	1-10	
D,P X	EP-A-0 174 042 (DSM RESINS BV) * Claims * -----	1-10	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

D 06 N
C 08 G
C 08 L

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	02-04-1987	DERAEDT G.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
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