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(71) Applicant *(for all designated States except US)*: TIDIS B.V. [NL/NL]; Gaarstraat 66, NL–6121 HG Born (NL).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: STANSSENS, Dirk, Armand, Wim [BE/BE]; De Huttestraat 93, B–3530 Houthalen (BE).

(74) Agent: LAND, Addick, Adrianus, Gosling; Arnold & Siedsma, Sweelinckplein 1, NL–2517 GK The Hague (NL).

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(54) Title: USE OF A WATER SOLUBLE BINDER SYSTEM FOR THE PRODUCTION OF GLASS OR STONE WOOL

(57) Abstract

Use of a water soluble binder composition for the production of glass or stone wool, characterized in that the binder composition contains one or more compounds with carboxylic acid groups and β–hydroxyalkyl amide groups.

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USE OF A WATER SOLUBLE BINDER SYSTEM FOR THE PRODUCTION OF GLASS OR STONE WOOL

The invention relates to the use of a water soluble binder composition for the production of glass or stone wool, i.e. mineral wool.

Generally, phenol formaldehyde resins are used as binder for glass or stone wool.

During the curing of the binder, phenol, formaldehyde, and ammonia which are toxic, are released. From an environmental point of view this is undesirable. Furthermore, during the spraying of the binder on the spun glass or stone fibers a relative large amount of binder is lost, which cannot be recovered.

The binder composition according to the present-invention is characterized in that it contains one or more compounds with carboxylic acid groups and/or ß-hydroxy alkylamide groups.

By using this binder composition a more efficient use of the binder is achieved due to easy recovery of the binder, which, although having been sprayed, failed to reach the target of the fibers and therefore remained unused. Furthermore, during the curing of the binder no toxic materials are released in the environment.

The cured compounds have very good properties with regard to hardness, scratch resistance, chemical resistance, mechanical properties and adhesion to glass.

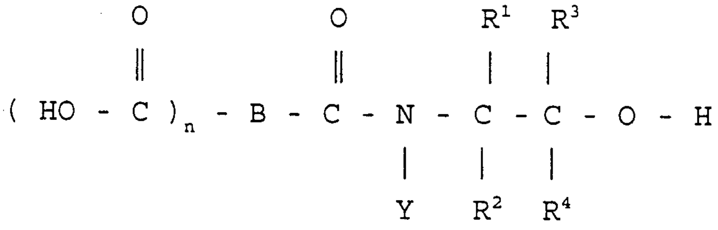
Preferably, the equivalent ratio of the carboxylic acid groups and the ß-hydroxy alkylamide groups lies between 1,0 : 5,0 and 5,0 : 1,0.

According to a preferred form of the invention the equivalent ratio of the carboxylic acids and the ß-hydroxy alkylamide groups lies between 1,0 : 3,0 and 2,0 : 1,0.

Generally, the functionality of the ß-hydroxy alkylamide groups lies between 1 and 250, for example and mostly between 2 and 50.

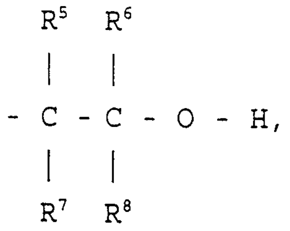
The functionality of the carboxylic acids lies generally between 1 and 250 and preferably between 1 and 50.

According to a preferred form of the invention the applied binder contains a compound represented by formula (I), or (X) as shown in claim 5:



$$\left(HO-\overset{\overset{\displaystyle O}{\|}}{C}\right)_n-B-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle Y}{|}}{N}-\overset{\overset{\displaystyle R^1}{|}}{\underset{\underset{\displaystyle R^2}{|}}{C}}-\overset{\overset{\displaystyle R^3}{|}}{\underset{\underset{\displaystyle R^4}{|}}{C}}-O-H \qquad (I)$$

In which:



$$Y = -\overset{\overset{\displaystyle R^5}{|}}{\underset{\underset{\displaystyle R^7}{|}}{C}}-\overset{\overset{\displaystyle R^6}{|}}{\underset{\underset{\displaystyle R^8}{|}}{C}}-O-H, \quad H \text{ or } (C_1\text{-}C_8)\text{(cyclo)alkyl,}$$

n = 1,2 or 3,

R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 = H, (C_1-C_8) aryl- or (cyclo)alkyl radical or CH_2-OR, of which R = H, aryl or (cyclo) alkyl radical is B = (C_2-C_{20}) eventually substituted, aryl or (cyclo) alkyl aliphatic radical, or a part of a polymer.

The binder can contain more than 10 weight % for example more than 25 weight % and preferably more than 50 weight % of a compound according to formula (I).

In formula (I) the R-groups with the exception of R9 as shown in claim 4 can form together or with the adjacent carbon atoms or with the carbon atoms on B or Y a cyclo aliphatic group.

Preferably, B is a 1,2-ethylene, 1,2-ethylidene, 1,3-propylene, 1,2-cyclohexyl, 1,2-phenylene, 4-carboxyl-1,2-phenylene, 1,3-phenylene, 1,4-phenylene and/or 1,2 cyclohex-4-enyl radical.

B can be saturated or unsaturated.

B can be substituted with for instance a (C_1-C_{12}) alkyl group which is saturated or unsaturated.

B is in a preferred form a part of a polymer. Such polymers can be obtained by reaction of anhydride function polymers with a ß-hydroxy alkylamine or a derivative thereof.

Anhydride functional polymers can for instance be obtained by a radical polymerisation of maleic anhydride with styrene and with (meth)acrylate monomers.

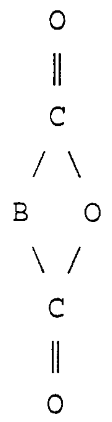
Maleïec anhydride can also be grafted on unsaturated compounds. A reaction between maleïc anhydride and oils, such as for instance linseed oil, results into products, which are called maleïnised oils.

If B does not form a part of a polymer, the molecular weight of the compounds, applied according to the invention is less than 1000, preferably less than 600.

Depending on the chosen starting monomers the variables B, R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 can be chosen differently in the molecule or the mixture of the molecules per variable.

The applied compound according to formula (I) can, for instance, be obtained by reacting a cyclic anhydride with an alkanolamine to a ß-hydroxy alkylamide at temperatures between, for instance 20°C and 100°C, preferably at a temperature, above 50°C and most preferably at about 70°C, see figure 1, for example, which illustrates the reaction between tetrahydro phthalic anhydride and diethanolamine.

The cyclic anhydride is preferably an anhydride according to formula (II):



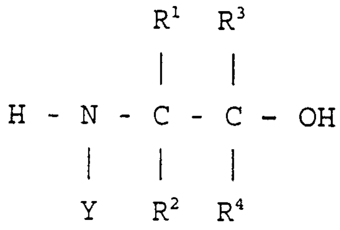
(II)

In which B has the same meaning as mentioned before.

Examples of appropriate cyclic anhydrides are phthalic anhydride, tetrahydro phthalic anhydride, hexahydro phthalic anhydride, 5-norbornene-2,3-dicarboxylic anhydride, norbornane-2,3-dicarboxylic anhydride, 2-dodecene-1-yl-succinic anhydride, maleic anhydride, (methyl)- succinic anhydride, glutaric anhydride, 4-methylphthalic anhydride, 4-methylhexahydro phthalic anhydride and 4-methyltetrahydro phthalic anhydride. The anhydride can also contain other functional groups.

In a preferred form is besides the anhydride also a carboxylic acid group present. An example thereof is trimelitic anhydride.

The alkanolamine is preferably an alkanolamine according to formula (III).



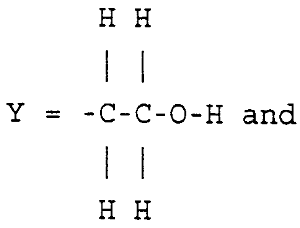
$$\mathrm{H-N(Y)-C(R^1)(R^2)-C(R^3)(R^4)-OH} \qquad \text{(III)}$$

Of which R^1, R^2, R^3, R^4 and Y have the same meaning as mentioned before.

The alkanolamine can be a monoalkanolamine, dialkanolamine, trialkanolamine or a mixture thereof.

Examples of appropriate alkanolamines are (di)ethanolamine, 1-(m)ethylethanolamine, n-butylethanolamine, 1-(m)ethylisopropanolamine, 3-amino-1, 2-propanediol, 2-amino-1,3-propanediol, tris(hydroxymethyl)aminomethane.

Preferably, diethanolamine is applied. In this case are in formula (I)



$$Y = \mathrm{-C(H)(H)-C(H)(H)-O-H} \text{ and} \qquad \text{(I)}$$

$R^1, R^2, R^3, R^4 = H$

The reaction between the anhydride and the alkanolamine can proceed without a solvent, in water or in an organic solvent. Preferably, the reaction starts in the presence of < 40 weight % of water compared to the monomers.

The distillation of the water can, if desired, proceed at 1 bar, under vacuum or azeotropically.

The equivalent ratio anhydride: alkanolamine lies generally between 1,8:1,0 and 1,0:1,8. Preferably, this ratio lies between 1.5:1,0 and 1:1,5.

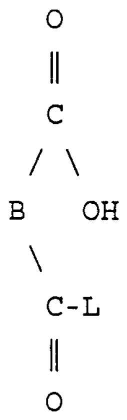
In case a high crosslink density is desired, di- or trialkanolamines or carboxylic acid functional anhydrides can be applied as starting materials.

The reaction of diethanolamine with an activated ester, such as a cyclic anhydride, can also result in a ester amine.

However, the same product can also be formed out of the ß-hydroxyalkylamide because of an internal rearrangement. The inventors have measured that the ß-hydrocyalkylamide and the ester-amine form an equilibrium with each other in a 85/15 ratio. In case the ester-amine reacts further with a cyclic anhydride another ß-hydroxyalkylamide is formed, see figure 3, for example.

The applied compound can also be obtained by reaction between an alkanolamine, such as for instance described above, and a compound having one or more carboxylic acid groups and an activated carboxylic acid group.

The compound having a carboxylic acid group and an activated carboxylic acid group is preferably a compound according to formula (IV):

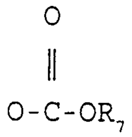


(IV)

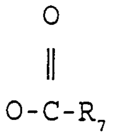
In which

- B has the meaning as mentioned before.

- L =



$O-\overset{O}{\overset{\|}{C}}-OR_7$ or



$O-\overset{O}{\overset{\|}{C}}-R_7$ or

OR_7

In which R^7 is a (C_1-C_{12}) branched or linear alkyl group is.

Examples of appropriate compounds with one carboxylic acid group and one activated carboxylic acid groups are alkyl esters, such as for instance mono(m) ethyladipate and mono(m)ethylsebacate. Activated carboxylic acid groups are for instance anhydrides and thioesters.

The compound applied in the invention can also be obtained by reaction between a cyclic anhydride, such as described above, and an alcohol after which the obtained reaction product in situ reacts with an alkanolamine.

Examples of appropriate alcohols are (C_1-C_{10}) alcohols. Preferably methanol or ethanol are applied.

Another binder composition according to the invention can be obtained by reacting linear polyanhydrides with alkanolamines or derivatives.

It is also possible that the carboxylic acid groups and the ß-hydroxy alkylamide groups are not located on the same compound.

Examples of such ß-hydroxy alkylamide containing compounds can be obtained by reaction of activated or non-activated carboxylic acid groups, as described above, with alkanolamines, as described above.

According to a further aspect of the present invention, there is provided a composition suitable for use as a binder, said composition containing one or more compounds with carboxylic acid groups or ß hydroxyalkylamide groups. Suitable water soluble molecules having ß-hydroxyalkylamides can be obtained as shown in figure 4 and 5, wherein the starting materials are dimethyl adipate and caprolactone respectively. Because no salt formation is possible with these molecules, it is known that predominantly (>70 %) the amides are formed.

Another example is the substitution product of dimethylsuccinate with diethanolamine. This reaction can proceed in the presence of a catalyst such as for instance sodium methanolate. If no catalyst is used, the reaction has to be performed at a higher temperature, such as for instance 160°C.

The carboxylic acid containing compounds are fully or partially water soluble compounds, such as maleïc acid, glutaric acid, adipic acid, 2-methyl adipic acid, succinic acid, citric acid and tartaric acid.

The carboxylic acid groups containing compounds can also be obtained by partial or full reaction of high functional alcohols, such as sucrose or polyvinylalcohol, with cyclic anhydrides as described above.

Water soluble compounds are compounds which can homogeneously be divided in water. Eventually, emulsions or dispersions can be applied. It is important that the binder containing solution does not vary much in composition and that the binder composition is sprayable.

To further improve the water solubility of the carboxylic acid functional compounds, a base can be added. Preferably, a base is added which evaporates during the curing reaction. Examples of such bases are amines such as ammonia, methylamine, diethylamine and triethylamine.

In another preferred form of the invention mixtures of the above described products are used.

Water can be added to the binder compounds according to the present invention to further improve their sprayability, however, which results in compounds having a lower viscosity, but still having a desired sprayability. It is possible to use the compounds without water, resulting in a higher viscosity. A decrease of the viscosity can be achieved by heating up the binder composition. Generally, temperature will not be higher than 110°C to prevent condensation reaction.

The composition applied in this invention can also contain additives, such as aminopropyl siloxane to improve the adhesion on glass, stabilizers to prevent thermal or UV degradation and surface-active compounds. Fillers, such as clay, silicates, titanium dioxide, magnesium sulfate and pigments can also be applied.

The binder applied in this invention can also be applied in combination with other binder compositions such as for instance phenol-formaldehyde resins.

The binder composition is preferably sprayed onto the fibers just after the spinning of the mineral wool. The curing of the binder composition proceeds by bringing the sprayed fibers into an oven. The curing time is mainly dependent on the components used in the binder and on the desired oven temperature. ß-hydroxy alkylamide groups attached to an aromatic group, for instance, will react slower with carboxylic acids than the ones attached on an aliphatic group and aromatic carboxylic acids will react faster with ß-hydroxy alkylamides than aliphatic carbonxylic acid groups. The curing temperatures lie mostly between 150°C and 300°C and preferably between 200°C and 300°C. The curing times lie mostly between 10 sec and 600 sec, preferably between 10 and 60 sec.

When spraying binder composition to the fibers some binder does not end in the wool but is collected in process water either directly or when cleaning walls and ducts in the spinning chamber system. This water may be used as dilution water for the binder, where by loss of binder is avoided/reduced.

The invention is illustrated by the following, non-restricting examples, and figures wherein figures 2 and 7 schematically show a reaction process for providing compounds according to the present invention, and figure 6 shows mixtures of different compounds according to the present invention obtained by reacting functional ß-hydroxyalkyl amides partially with cyclic anhydrides.

Example I

Preparation of the addition product of phthalic anhydride with diethanolamine

In a double jacketed glass reactor, heated with mineral oil, provided with a mechanical stirrer and a nitrogen inlet, are brought 300 g phthalic anhydride, 100 g water and 212 g diethanolamine. The reaction mixture was steadily heated while stirred to ca. 70°C. After two hours the phthalic anhydride is completely dissolved and the reaction product is ready. The reaction product is a clear, colorless, low viscous solution.

Example II

Preparation of the addition product of succinic anhydride with diethanolamine

In a double jacketed glass reactor, heated with mineral oil, provided with a mechanical stirrer and a nitrogen inlet, are brought 300 g succinic anhydride, 100 g water and 315 g diethanolamine. The reaction mixture was steadily heated while stirred to ca. 70°C. After two hours the succinic anhydride is completely dissolved and the reaction product is ready. The reaction product is a clear, colorless, low viscous solution.

The compounds obtained according to Experiments I and II are cured on a glass plate in an oven during 60 sec at 250°C.

The cured compounds had very good properties with respect to hardness, scratch resistance, chemical resistance, mechanical properties and adhesion to glass.

CLAIMS

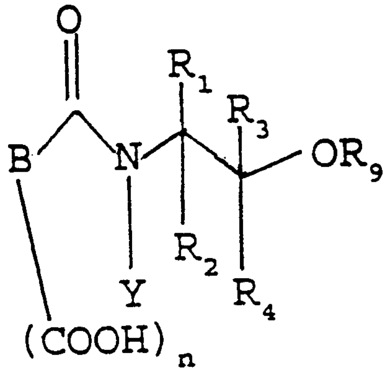
1. Use of a water soluble binder composition for the production of glass or stone wool, characterized in that the binder composition contains one or more compounds with carboxylic acid groups and ß-hydroxyalkyl amide groups.

2. Use of a water soluble binder composition for the production of glass or stone wool, wherein the binder composition contains one or more compounds with carboxylic acid groups or ß-hydroxyalkylamide groups.

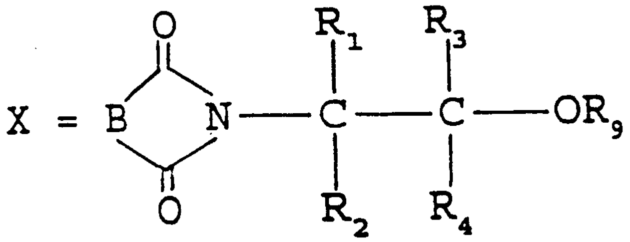
3. Use according to claims 1 or 2 characterized in that the equivalent ratio of the carboxylic acid groups and ß-hydroxyalkyl groups lies between 1.0 : 5.0 and 5.0 : 1.0.

4. Use according to claim 3, characterized in that the equivalent ratio of the carboxylic acid groups and ß-hydroxyalkyl groups lies between 1.0 : 3.0 and 2.0 : 1.0.

5. Use according to one of the claims 1-4, characterized in that the binder contains a compound according to formula (I) or (X):



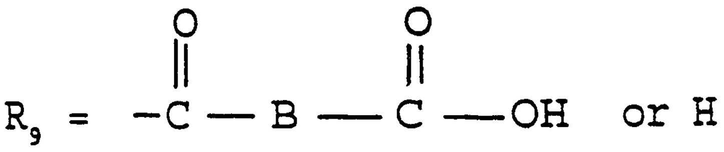
(I)



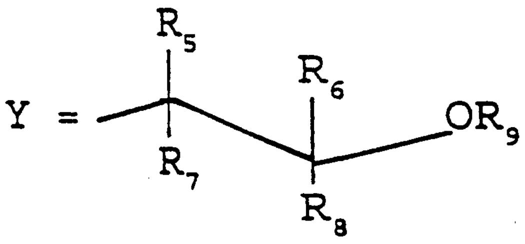
n = 1,2,3

B = (C_2-C_{20}) eventually substituted, aryl or (cyclo) alkyl aliphatic radical.

R^1, R^2, R^3, R^4, R^5, R^6, R^7, and R^8 = H, (C_1-C_8) aryl- or (cyclo) alkyl radical or CH_2-OR, in which R = H. aryl or (cyclo) alkylradical,



$$R_9 = -\overset{\overset{\displaystyle O}{\|}}{C} - B - \overset{\overset{\displaystyle O}{\|}}{C} - OH \quad \text{or H}$$



6. Use according to claim 5, characterized that the molecular weight of the compound according to

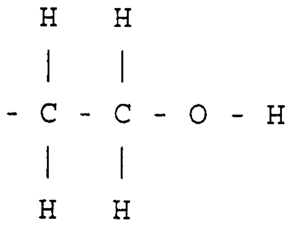
formula (I) is lower than 1000, preferably lower than 600.

7. Use according to claim 5, characterized that B is part of a polymer.

8. Use according to claims 4, 5 or 6 characterized that B is a 1,2-ethylene, 1,2-ethylidene, 4-carboxyl 1,2-phenylene, 1,3-propylene, 1,2-cyclohexyl, 1,2-phenylene, 1,3-phenylene, 1,4-phenylene or 1,2-cyclohex-4-enyl radical.

9. Use according to claim 5, characterized that in formula (I):

Y =

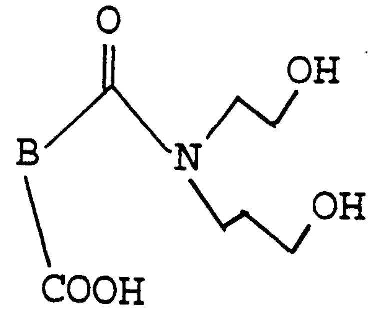


$$-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{O}-\mathrm{H}$$

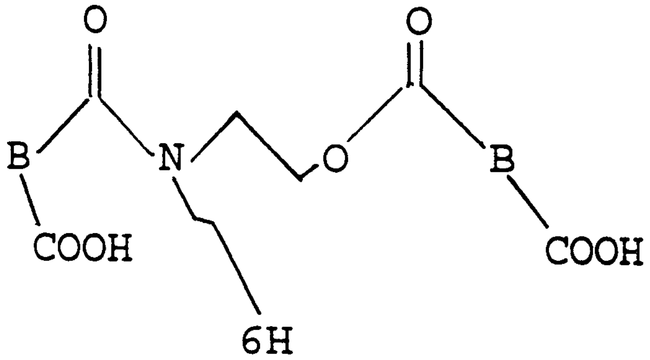
and

R^1, R^2, R^3, R^4 = H

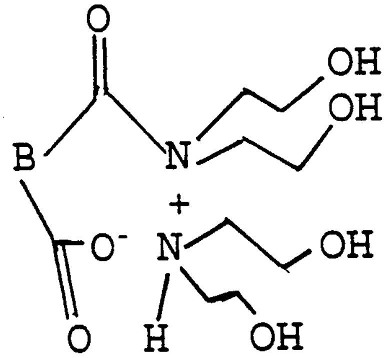
10. Use according to any of the claims 1-9, wherein the binder contains a compound selected from the group comprising the following compounds A-K:


O
OH
B
N
OH
COOH

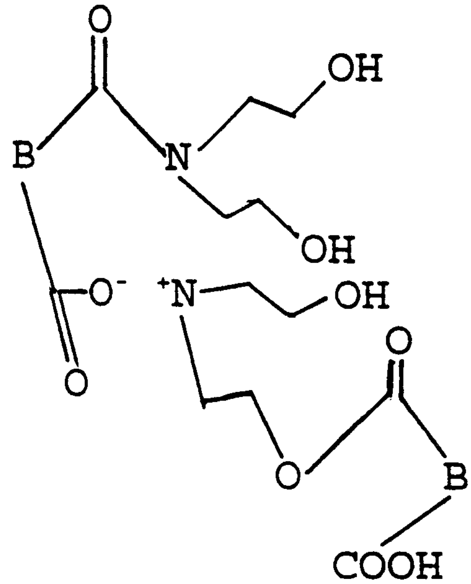
(A)


O
O
B
N
O
B
COOH
COOH
6H

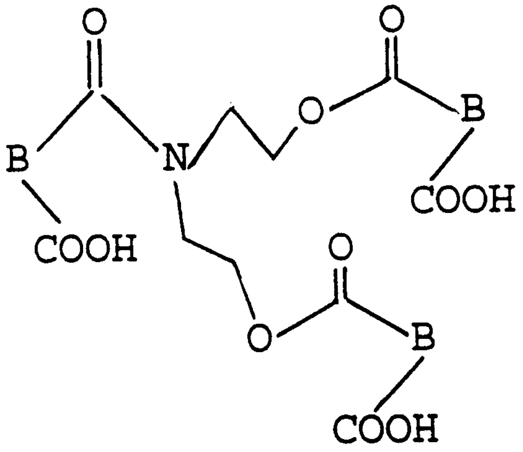
(B)


O
OH
OH
B
N
+
O⁻
N
OH
O
H
OH

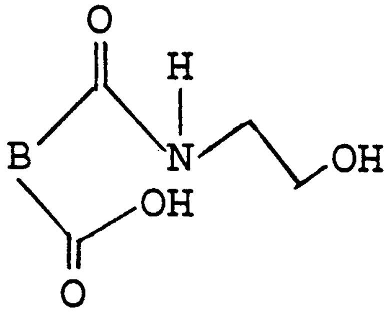
(C)


O
OH
B
N
OH
O⁻
⁺N
OH
O
O
O
B
COOH

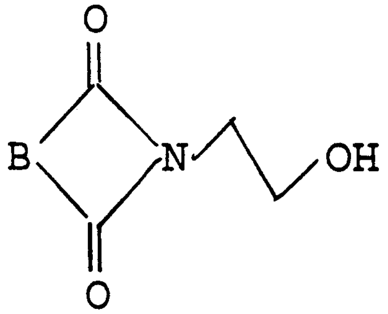
(D)


O
O
B
N
O
B
COOH
COOH
O
O
B
COOH

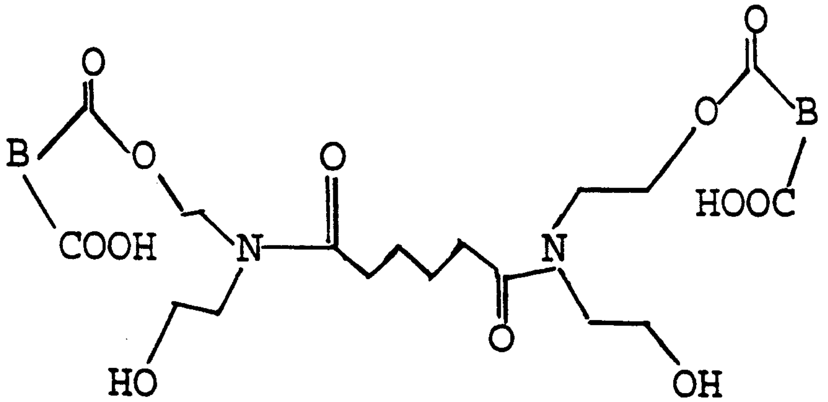
(E)


O
H
B
N
OH
OH
O

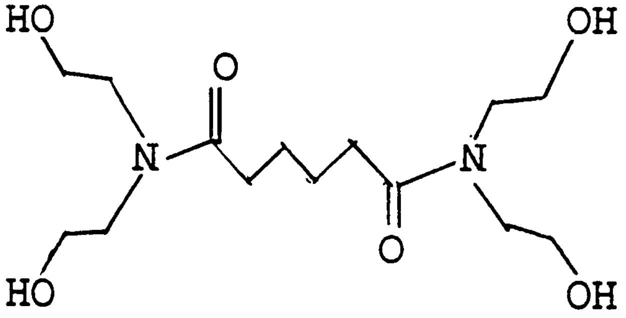
(F)


O
B
N
OH
O

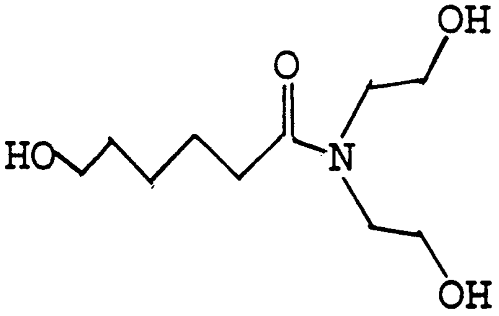
(G)


O
O
B
O
O
O
B
COOH
N
N
HOOC
HO
O
OH

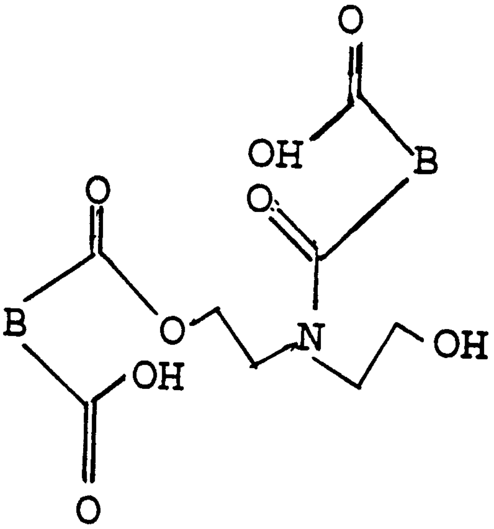
(H)



(I)



(J)



(K)

11. Procedure to prepare glass or stone wool by spraying spun glass or stone with the binder composition according to one of the claims 1-10 and subsequently to cure these at temperatures between 150 and 300°C during 600 and 10 seconds.

12. Glass wool or stone wool covered with cured binder described in one of the claims 1-10.

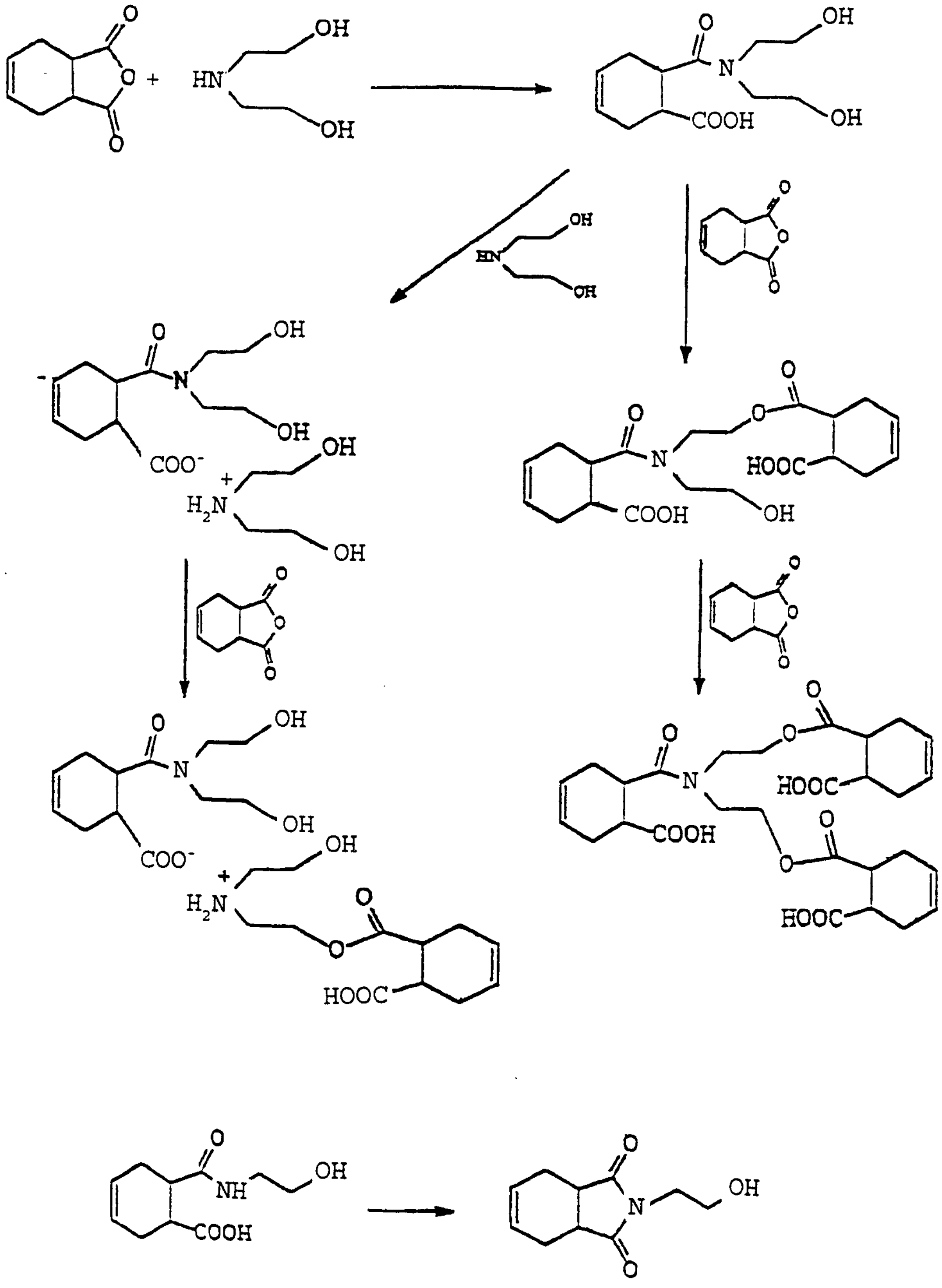


FIG. 1

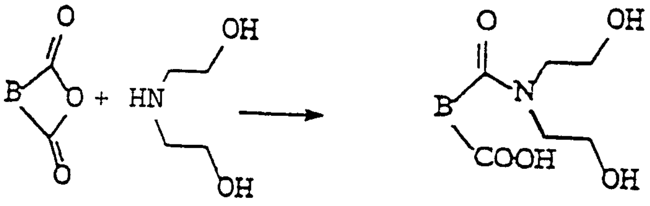

O
B
O
O
OH
HN
OH
O
OH
B
N
COOH
OH

FIG. 2

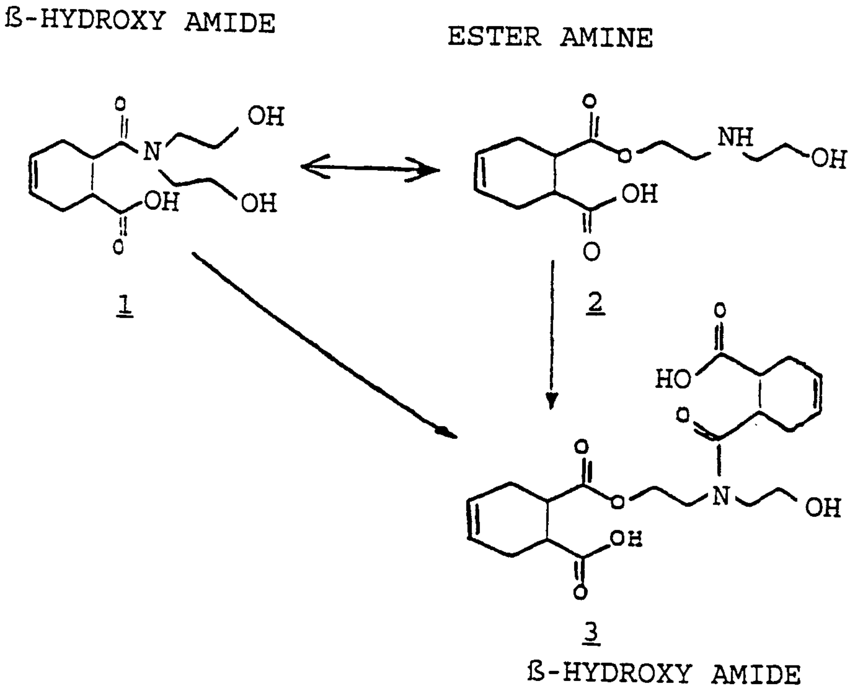

ß-HYDROXY AMIDE
ESTER AMINE
O
N
OH
OH
OH
O
1
O
O
NH
OH
OH
O
2
O
HO
O
O
O
N
OH
OH
O
3
ß-HYDROXY AMIDE

FIG. 3

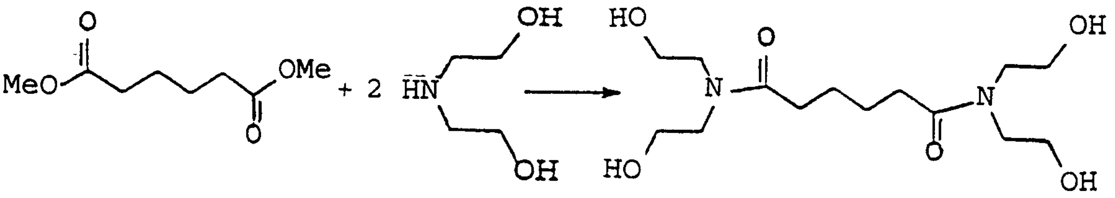


FIG. 4

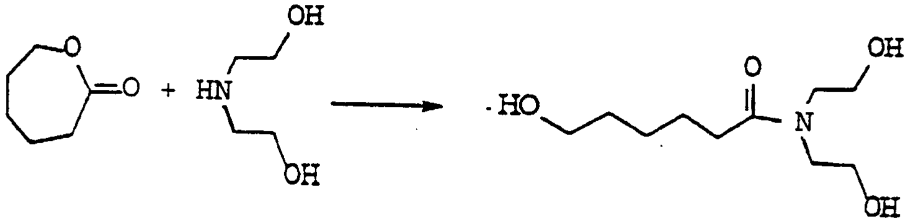


FIG. 5

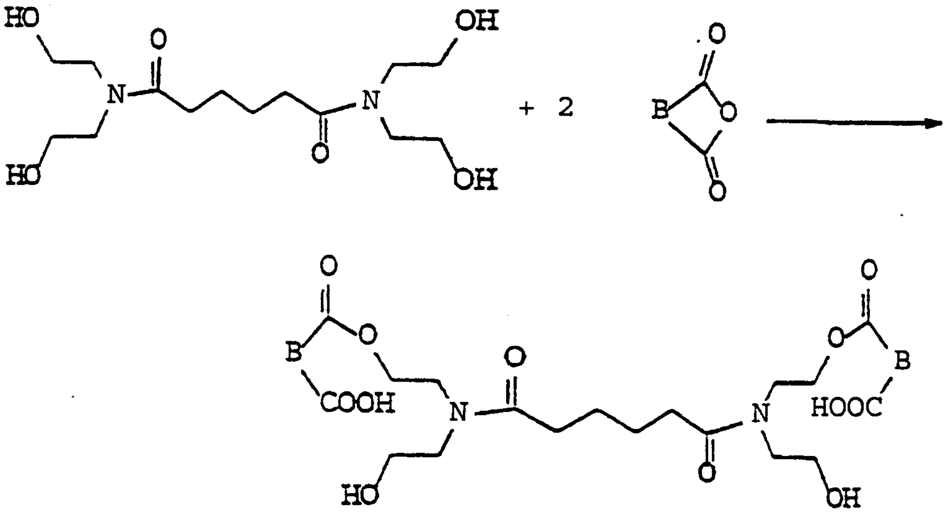


FIG. 6

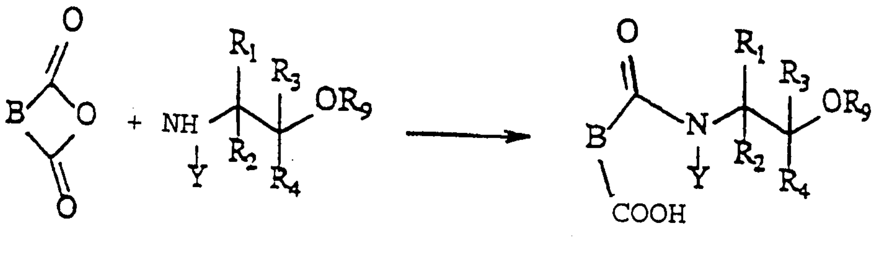


FIG. 7

INTERNATIONAL SEARCH REPORT

In ıtional Application No
PCT/NL 99/00030

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C03C25/02 C08K7/14 D04H1/64

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 C03C C08K D04H C09D C07C C08F C08L

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	US 5 340 868 A (C.R. STRAUSS ET AL.) 23 August 1994 see the whole document ---	1-12
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A	US 4 115 637 A (H.J. CENCI ET AL.) 19 September 1978 see column 5, line 57 - line 69 --- -/--	1-12

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search 23 April 1999	Date of mailing of the international search report 04/05/1999
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Reedijk, A

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