Composition comprising polyols

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(54) **Title**: COMPOSITION COMPRISING POLYOLS

(57) **Abstract**: A package for smoking articles comprising an inner shell and an outer shell, the inner shell defining a space for smoking articles and the outer shell defining a cavity to receive the inner shell, the inner and outer shells being hingedly connected such that they pivot relative to each other from a closed position in which the inner shell is received in the outer shell and an open position in which the inner shell extends from the outer shell, wherein the outer shell includes a sidewall that overlaps a sidewall of the inner shell when the inner and outer shells are in their closed position, a recess being formed in the sidewall of one of the inner or outer shells and a tab extending from a corresponding sidewall of the inner or outer shell such that, when the inner and outer shells are in their closed position, the tab locates in said recess.

COMPOSITION COMPRISING POLYOLS

The invention relates to a phenol-based resins and in particular to a heat curable resin composition comprising phenol-glyoxylate (PG) resin and polyol.

Phenol-formaldehyde (PF) resins have many known uses, such as for example, in adhesives for the preparation of particle boards and in binder adhesives for mineral wool isolation products. A disadvantage of these resins is that their use is associated with possible health risks relating to the emission of formaldehyde during resin preparation, resin curing, and in end products. Currently legislation is being enacted in several countries to limit the amount of formaldehyde that may be emitted from such resins. PG resins have been suggested as an alternative to PF resins. PG resins reduce or eliminate the formaldehyde from the product. See for example WO2006/059903, WO2007/140940, and WO2007/140941. While PG resins reduce the amount of formaldehyde that might devolve they can suffer from the disadvantage that the cured PG resins can be too hard or brittle for certain uses and may be prone to hydrolysis.

JP 51-97151 (Japan Synthetic Rubber) (D1) describes photo curable polymers having a repeat unit comprising a carboxylic acid moiety and an aromatic moiety (e.g. represented by Formula 5, paragraph 87). However the meaning of Formula 5 must be read and understood in the context of the complete text of D1. D1 teaches (paragraph 83) that a phenolic compound (such as phenol) is coupled with a glyoxylic acid (in a 2:1 ratio) to form a bis-phenolic compound as shown in Formula 4 (paragraph 84). The next step of D1 (paragraph 86) is a final poly-condensation step stated to produce resins of Formula 5 (paragraph 87). However this step does not use just bis-phenolic compound of Formula 4 alone. Instead compounds of Formula 4 also react with a resol resin (with phenol and formaldehyde as reactants) to build in a bis-phenolic structure into a larger polymer. The formaldehyde is necessary as auxiliary aldehyde to make a polymeric structure. So a skilled person reading D1 would not understand Formula 5 to represent a polymer in an absolute sense where the polymer is built solely (or even substantially) from the repeat unit of Formula 5. A skilled person would appreciate that it is not the 2-oxoethanoic acid with the phenolic compound that gives rise to a polymer network described in D1 but the use of formaldehyde (from the resol resin). Thus it is implicit in the teaching of D1 that the repeat units of Formula 5 must occur within the polymer network together with other repeat units. The process of D1 also has the disadvantage of using formaldehyde.

EP 0779355 (Lubrizol)) (D2) describe lubricants containing a salt additive formed by reacting an optionally hydrocarbyl substituted glyoxylic acid with a hydroxyl aromatic compound. The starting material described in D2 is a molecular adduct formed between two phenolic compounds and one molecular of aldehyde (comparable to a Bisphenol-A: product). This material is not a resin in the sense of a reactive polymer which can form a cured resin network. The final compounds described in D2 are liquids that comprising molecules of two adducts coupled by one diol, they are not polymer networks.

JP 04-001259 (Takeda) (D3) describes molding materials in which carboxylated resol phenol resins are compounded with alkaline metal earth oxides or hydroxides as curability modifiers.

US 5661213 (Rohm & Haas) (D4) describes formaldehyde free curable aqueous binders for non woven fibres such as fibre glass, the binder containing polyacid, polyol and phosphorous containing accelerator. The polyacid used in D4 (polyacrylic acid) does not form a suitable binder itself, as it is a soft polymer that will dissolve when brought into contact with water. D4 teaches cross-linking this polyacid with polyols so the soft soluble polymer turns into a rigid insoluble network suitable as binder.

The invention is concerned with improvements to PG resins suitable for use as binders and relates to the surprising finding that the strength and hydrolytic performance of PG resins may be improved by the addition of polyol.

As used herein, “polyol” refers to any compound comprising two or more hydroxyl groups, including compounds that comprise optional other functional groups besides the hydroxyl groups. The term encompasses diols, including amino-diols and acid-diols, triols including amino-triols, and compounds containing four or more –OH groups.

As used herein, “phenol-glyoxylate resin” refers to resins comprising phenol and/or phenolic compounds and glyoxylic acid and/or glyoxylic compounds as monomers. Glyoxylic compounds include glyoxylate esters or amides, and glyoxylate ester hemiacetals.

As used herein, “phenol-formaldehyde resin” refers to resins comprising phenol and/or phenolic compounds and formaldehyde as monomers. The term encompasses phenol-urea-formaldehyde resins which are resins comprising phenol and/or phenolic compounds, urea or ureic compounds, and formaldehyde as monomers, or blends of “phenol-formaldehyde resins” with “urea-formaldehyde resins”.

As used herein, “urea-formaldehyde resin” refers to resins comprising urea and/or ureic compounds and formaldehyde as monomers. Phenolic compounds are for example resorcinol, cresol, natural lignines and tannins, and bisphenol-A. Ureic compounds are, for example, glycouril, guanamine, benzoguanamine, and melamine.

As used herein ‘’curable resin’’ means a reactive polymer which can form a cured resin network. As used herein ‘’heat curable resin’ means a resin that forms an insoluble, solid polymer network by itself on heating without the addition of other compounds.

The term “comprising” as used herein means that the list that immediately follows is non-exhaustive and may or may not include any other additional suitable items, for example one or more further feature(s), component(s), ingredient(s) and/or substituent(s) as appropriate. ‘’Substantially comprising’’ as used herein means a component or list of component(s) is present in a given material in an amount greater than or equal to about 90%, preferably ≥ 95%, more preferably ≥ 98% by weight of the total amount of the given material. The term “consisting of” as used herein mean that the list that follows is exhaustive and does not include additional items.

For all upper and lower boundaries of any parameters given herein, the boundary value is included in each range for each parameter. All combinations of minimum and maximum values of the parameters described herein may be used to define the parameter ranges for various embodiments of the invention.

It will be understand that the sum of each parameter expressed herein as a percentage will total 100%, for example the amount of all the ingredients that comprise a composition of the invention (or part thereof) when expressed as a percentage of the composition (or the same part thereof) will total 100%.

Broadly the present invention provides a heat curable resin composition comprising at least one phenol-glyoxylate resin and at least one polyol.

Preferred PG resins used herein substantially comprises, more preferably consist of, phenolic and glyoxylic repeat units. Most preferably the PG resin used herein and/or composition of the invention are obtained without adding any aldehydes and/or resols in addition to phenolic and/or glyoxylic compounds.

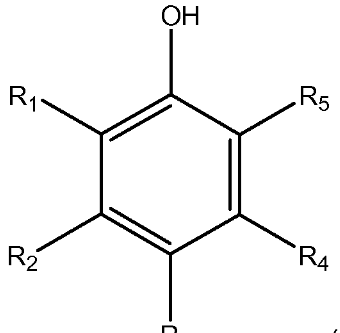
Compositions of present invention can use carboxy functional cross-linked PG resins which already form rigid binders In one aspect of the invention the applicant has discovered that surprisingly, cross-linking such binders with polyol forms an interpenetrating network, in which the resistance to fracture may decrease so the network becomes tough rather than brittle. The present invention is inventive over D3 combined with D4. A reader of D3 would have no reason to consult D4 as the resins described in D3 are already rigid binders. The fact that D4 teaches how to modify soft polymers to form rigid networks would be irrelevant to a reader of D3.

Preferred compositions comprise greater than or equal to 1%, more preferably ≥ 10%, most preferably ≥ 20% of PF resin by weight of the composition.

Any suitable PG resin may be used herein. Preferred PG resins are selected from those disclosed in WO2006/059903, WO2007/140940, and WO2007/140941.

Preferred PG compounds herein include resins obtained and/or obtainable from phenolic monomers and glyoxylic acid and/or glyoxylic ester monomers. Conveniently the respective molar ratio of glyoxylic (acid/ester) to phenol is a ratio from 0.5 to 1 to a ratio of 3 to 1, more conveniently a ratio from 0.6 to 1 to a ratio of 2 to 1, most conveniently a ratio from 1 to 1 to a ratio of 1.5 to 1. Usefully PG compounds according to the invention are resins that are obtained from the monomers glyoxylic acid and phenol, where the respective molar ratio of the monomers is a ratio from 1 to 1 to a ratio of 1.5 to 1.

Preferably the PG resin is prepared from a hydroxy-aromatic compound according to formula (I):



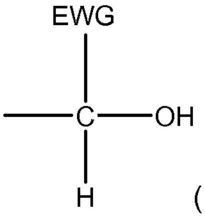
(I)

wherein:

at least one of the set consisting of R_1, R_3, and R_5 is a group of formula (II); any remaining one or two of the set consisting of R_1, R_3, and R_5 being H, OH, a C_1-C_{12} alkyl group or an oligomeric or polymeric system;

R_2 and R_4 are H, OH, a C_1-C_{12} alkyl group, or an oligomeric or polymeric system.

Formula (II) is the following group:



$$-\overset{\displaystyle EWG}{\underset{\displaystyle H}{C}}-OH \qquad (II)$$

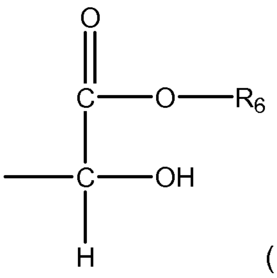
wherein EWG is an electron-withdrawing group.

As is known in hydroxy-aromatic chemistry, the positions on the aromatic ring adjacent to and opposite the hydroxy group (i.e., ortho and para) have a different reactivity than the remaining two meta-positions. In formula (I), therefore, the groups R_1, R_3, and R_5 could be regarded within a similar context and are herein referred to as a set.

In the present PG compound, at least one of the groups in the set consisting of R_1, R_3, and R_5 is a group according to formula (II); the other one or two groups in the said set - in case not all three of the said set is a group according to formula (II) - is/are H, OH, or C_1-C_{12} alkyl group, preferably H, OH, a C_1-C_9 alkyl group, or an oligomeric or polymeric system. If there are two groups not according to formula (II) then they may be the same or may be different. The oligomeric or polymeric system may be a hydroxy-aromatic resin, either of the resol or of the novolac type, preferably of the novolac type; or it may be a different type of thermosetting or thermoplastic system. For example, the set according to R_1, R_3, and R_5 consist of: R_1 is a group according to formula (II), R_3 is H, and R_5 is H; R_1 is a group according to formula (II), R_3 is H, and R_5 is CH_3; R_1 is H, R_3 is a group according to formula (II), and R_5 is H; R_1 and R_3 are a group according to formula (II), R_5 is H; R_1, R_3, and R_5 are all a group according to formula (II).

In the present PG compound, R_2 and R_4 are H, OH, a C_1-C_{12} alkyl group, or an oligomeric or polymeric system; preferably R_2 and R_4 are H, OH or a C_1-C_9 alkyl group. R_2 and R_4 may be the same or may be different. Some preferred embodiments of R_2 and R_4 are: R_2 is OH and R_4 is H; R_2 is CH_3 and R_4 is H; R_2 is CH_3 and R_4 is CH_3; R_2 is H and R_4 is C_4H_9. R_1 and R_2 may be part of a multicyclic compound; the same holds mutatis mutandis for R_2 and R_3, R_3 and R_4, or R_4 and R_5.

The group according to formula (II) is an integral part of the compound; it is R_1, R_3, or R_5 in formula (I), or two of those, or all three. In formula (II), EWG is an electron-withdrawing group. EWG's are as such known to the skilled person. Examples of an EWG are acid-, ester-, cyano-, di-alkylacetal-, aldehyde-, substituted phenyl-, or trihalomethyl groups. Hydrogen is not an EWG. In a preferred embodiment, the group of formula (II) is a group according to formula (III):

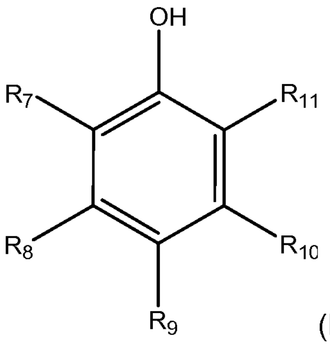


(III)

wherein R_6 is H, a C_1-C_{12} alkyl group, aryl group, aralkyl group or cycloalkyl group. Preferably R_6 is H or a C_1-C_{12} alkyl group; examples hereof are methyl, ethyl, propyl, butyl, pentyl, hexyl; more preferably, R_6 is H, a methyl group or an ethyl group.

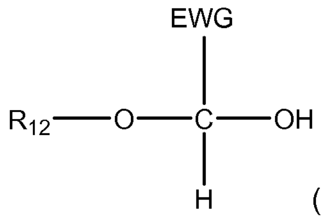
In a preferred embodiment of the present PG compound, at least one of the set consisting of R_1, R_3, and R_5 is H. This has the advantage that the hydroxy-aromatic compound is better suitable for the preparation of the oligomeric or polymeric structures typical for resins. In another preferred embodiment, two of the set consisting of R_1, R_3, and R_5 are H. This has the advantage that such a compound can be used to create three-dimensional networks, an ability often desired in resins. The same ability of the compound to create three-dimensional networks is present in those embodiments where all of R_1, R_3, and R_5 are either H or a group according to formula (II).

The compound as described above may be prepared by bringing a compound of formula (IV) into contact with a compound according to formula (V), optionally in the presence of a catalyst, and allowing them to react whereby formula (IV) is:



(IV)

wherein R_7, R_8, R_9, R_{10} and R_{11} are H, OH, a C_1-C_{12} alkyl group or an oligomeric or polymeric system, whereby at least one and preferably two or even three of the set consisting of R_7, R_9, and R_{11} is or are H; and formula (V) is:

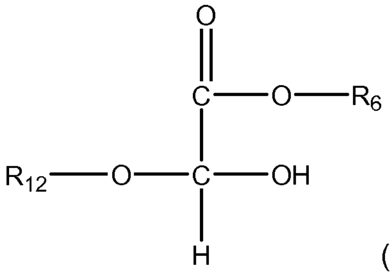


$$\begin{array}{ccccccc} & & & \text{EWG} & & \\ & & & | & & \\ R_{12} & - & O & - & C & - & OH \\ & & & | & & \\ & & & H & & \end{array}$$

(V)

wherein EWG is an electron-withdrawing group and wherein R_{12} is H, a C_1-C_{12} alkyl group, aryl group, aralkyl group or cycloalkyl group.

In another preferred embodiment, the compound according to formula (V) is an alkanol hemiacetal according to formula (VI):



$$\begin{array}{ccccccc} & & O & & & & \\ & & \| & & & & \\ & & C & - & O & - & R_6 \\ & & | & & & & \\ R_{12} - O & - & C & - & OH & & \\ & & | & & & & \\ & & H & & & & \end{array}$$

(VI)

wherein R_6 is H or a C_1-C_{12} alkyl group, aryl group, aralkyl group or cycloalkyl group and wherein R_{12} is H, a C_1-C_{12} alkyl group, aryl group, aralkyl group or cycloalkyl group. Preferably R_6 and R_{12} are C_1-C_{12} alkyl groups. Examples thereof are methyl, ethyl, propyl, butyl, pentyl, hexyl, and heptyl. R_6 and R_{12} are in particular a methyl group or an ethyl group.

Examples of preferred compounds according to formula (IV) are phenol, (2, 3, or 4-)cresol, resorcinol, (2, 3, or 4-)tert-butylphenol, (2, 3, or 4-)nonylphenol, (2,3- 2,4- 2,5- 2,6- or 3,4-)dimethylphenol, (2, 3, or 4-)ethylphenol, bisphenol A, bishenol F, and hydrochinon. Examples of compounds according to formula (V), in particular of the preferred alkanol hemiacetals according to formula (VI), are methylglyoxylate methanol hemiacetal (GMHA^{TM}, DSM Fine Chemicals, Linz); ethylglyoxylate ethanol hemiacetal (GEHA^{TM}, DSM Fine Chemicals, Linz); ethylglyoxylate methanol hemiacetal; butylglyoxylate butanol hemiacetal; butylglyoxylate methanol hemiacetal; butylglyoxylate ethanol hemiacetal; isopropylglyoxylate isopropanol hemiacetal; propylglyoxylate propanol hemiacetal; cyclohexylglyoxylate methanol hemiacetal, 2-ethylhexylglyoxylate methanol hemiacetal, and combinations thereof.

Further examples of compounds suitable for reacting with the compounds of Formula (I) are oxoethanoic acid (glyoxylic acid hydrate), methylglyoxylate hydrate, ethylglyoxylate hydrate, and combinations thereof.

Preferred compounds for reacting with the compounds of Formula (I) include oxoethanoic acid, methylglyoxylate methanol hemiacetal, ethylglyoxylate ethanol hemiacetal, and combinations thereof.

It may be beneficial to execute the reaction step according to the invention in a solvent or dispersant. As solvents, those compounds are suitable in which the reactants dissolve sufficiently to let the reaction take place. Examples of such solvents are water and various organic solvents. Depending on the specific compound or compounds of formula (IV) and (V), it may well be possible to use one or more of the reactants as solvent; in such a case, it can be possible to forego on the use of a solvent that is essentially a non-reactant and to execute the reaction step in bulk. In particular, many of the compounds according to formula (V) and in particular according to formula (VI) are a liquid at temperatures between 10°C and 100°C and can act as dispersant/solvent as well as reactant.

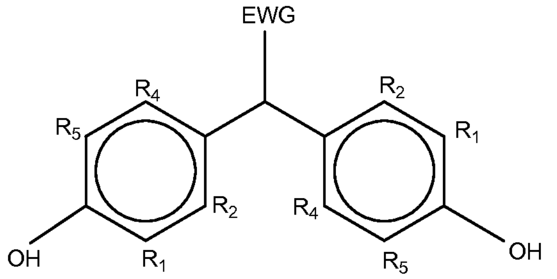
Although the reaction step may proceed spontaneously once the respective compounds have been brought together, it may be useful to bring the compounds together in the presence of a catalyst in order to accelerate the reaction. As catalyst, preferably an acid or a base is used; in particular, a Lewis or a Brønsted type of acid is preferred - such as for example sulphuric acid - whereby the pH is reduced to between 0 and 5, preferably to between 1 and 4, in particular to between 2 and 3. Suitable examples of acid catalysts are sulphuric acid, methanesulfonic acid, nitric acid, hydrochloric acid, phosphoric acid, boric acid, tetrafluoroboric acid, paratoluene sulphonic acid, formic acid, ammonium sulphate, ammonium chloride, ammonium nitrate. Suitable examples of basic catalysts are ammonia, trimethyl amine, triethyl amine, DABCO (diaza-bicyclo-octane), DBU (diaza-bicyclo-undecene), DMAP (4-dimethylaminopyridine), sodium hydroxide, potassium hydroxide.

The temperature in the reaction step of present process can vary within wide limits, and preferably lies between 10°C and 100°C. More preferably the process is carried out at between 40°C and 90°C. The pressure in the present process preferably is between 0.005 MPa and 1.0 MPa, preferably between 0.02 MPa and 0.2 MPa; most preferably, the pressure is atmospheric.

As consequence of the reaction step, a compound according to formula (I) is formed; additionally, other compounds may released as by-products. It may be desirable to isolate such compound according to formula (I); this may be achieved through techniques that are as such known, such as for example a combination of pH change, solvent exchange, evaporation and/or precipitation. If the compound according to formula (I) is not isolated, it may still be desirable to remove $R_{12}OH$; this may be achieved through techniques that are as such known, such as for example distillation. It may, however, also be acceptable or even desirable to let $R_{12}OH$ remain in the presence of the compound according to formula (I).

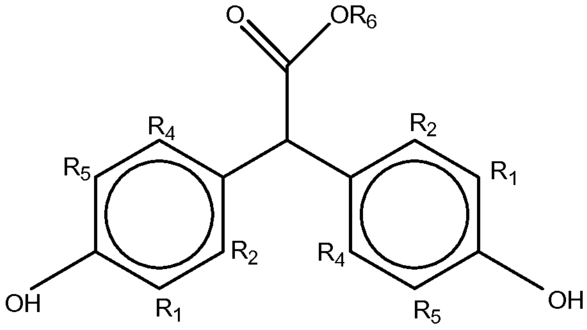
In the process for the preparation of the hydroxy-aromatic compound according to the invention, the molar ratio between the EWG-containing compound according to formula (V) (E) and the hydroxy-aromatic compound according to formula (IV) (H), herein referred to as E/H ratio, may vary between wide limits. Preferably, the E/H ratio lies between about 0.1 and about 10, more preferably between about 0.5 and about 3. If the E/H ratio is about 0.5 or lower, the resulting hydroxy-aromatic compound according to the invention can be a mixture having a significant amount of a compound according to formula (I) in which one of the set consisting of R_1, R_3, and R_5 is a group of formula (II). If the E/H ratio is about 3 or higher, the resulting hydroxy-aromatic compound according to the invention can be a mixture having a significant amount of a compound according to formula (I) in which all three of the set consisting of R_1, R_3, and R_5 are a group of formula (II). If the E/H ratio is about 1 or 2, the resulting hydroxy-aromatic compound according to the invention can be a mixture in which compounds according to formula (I) in which one, two or all three of the set consisting of R_1, R_3, and R_5 are a group of formula (II) are all clearly represented.

When executing the reaction step as described above, it was found that a further reaction can also be made to take place, namely the formation of a compound according to formula VII:



(VII)

In case the EWG is according to formula (VI), the compound according to (VII) will be as in formula (VIII):

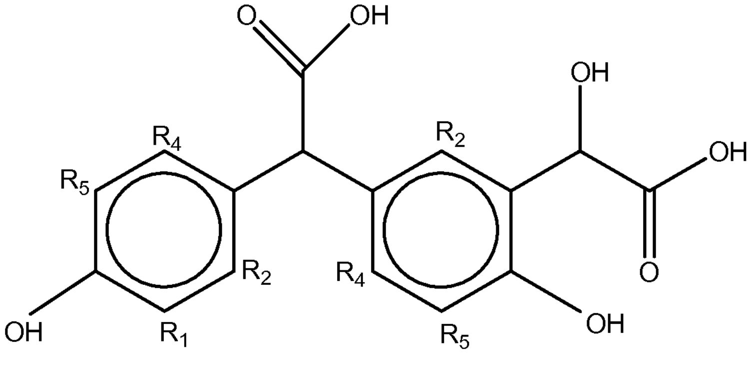


(VIII)

It was found that when executing the reaction step according to the invention, many hydroxy-aromatic compounds have a preference to first react on the para location of the aromatic moiety before doing so on the ortho location; hence the creation of compounds according to formula (VII) or (VIII). The present invention therefore also relates to compounds of formula (VII), in particular of formula (VIII), most preferably with R_1, R_2, R_4 and R_5 being all H and R_6 being methyl.

The compounds according to formula (VII) and (VIII) can typically be made by prolonged execution of the reaction step as described above for the preparation of compounds according to formula (I), whereby the E/H molar ratio preferably lies between 0.3 and 0.7, more preferably between 0.4 and 0.6.

Alternatively, using oxoethanoic acid as the preferred compound according to Formula V, and an E/H molar ratio of between 0.8 and 2.0, preferably between 1.0 and 1.5, compounds according to formula IX and formula X are typically formed after prolonged reaction time.



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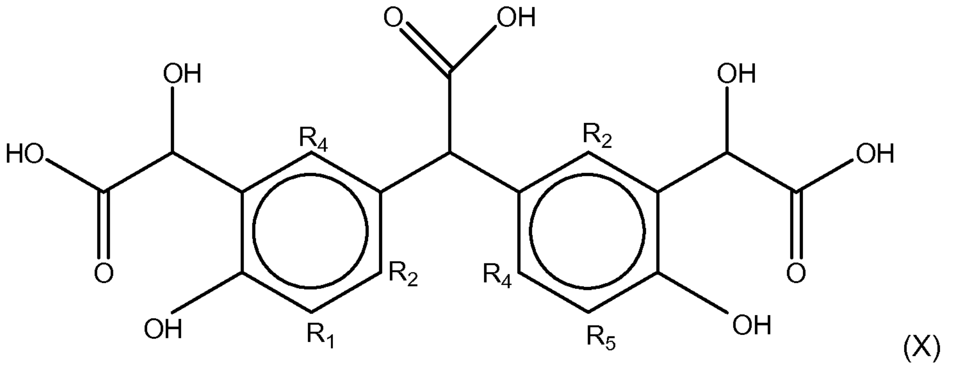


(X)

The PG resins herein may be prepared via condensation reactions between a hydroxy-aromatic compound and a compound such as an aldehyde, and typically also subsequent condensation reactions; an example of such a process is the process for preparation of a phenol-formaldehyde resin. In the process according to the invention, a compound according to formula (I) is used in the (subsequent) condensation reactions. The (subsequent) condensation reactions may be executed in the same fashion and under similar conditions as described above for the preparation of the compound according to formula (I), (VII) (VIII), (IX)and (X), although typically for a - further - prolonged period of time. The compound falling within the scope of formula (V) and in particular formula (VI) may be - aside from the hydroxy-aromatic compound according to formula (I) and/or the already formed oligomeric or polymeric structures - the sole other compound participating in the condensation reactions in the resin; it may also be possible to use other compounds such as aldehdyes like formaldehyde or furfural ($C_5H_4O_2$) in combination with the compound according to formula (V). Preferably, however, at least 5 or 10 mol.% of the compounds participating in the condensation reactions with a hydroxy-aromatic moiety in the resin are one or more compounds according to formula (V); more preferably, this is at least 20 or 30%; in particular, this is at least 40 or 50%; with strong preference, at least 60 or 70 mol.% of the compounds reacting with a hydroxy-aromatic moiety in the resin are one or more compounds according to formula (V); most preferably, this is at least 80 or 90% or even essentially 100%.

The PG resin comprises hydroxy-aromatic moieties (H) derived from hydroxy-aromatic compounds used as starting materials. The resin also comprises EWG-derived moieties and possibly aldehyde-derived moieties, together referred to as A. The resin thus has a molar A/H ratio. The molar A/H ratio in the resin preferably lies between 0.5 and 3, more preferably between 0.75 and 2. If the molar A/H ratio lies above 1, resol-type of resins can be formed whereby reactive ‘A’-derived hydroxy groups are available. If the molar A/H ratio lies below 1, novolac-type of resins can be formed, in which essentially all ‘A’-derived hydroxyl functionality has reacted away to form C-C and C-O ether bonds.

According to an embodiment of the invention, a hydroxy-aromatic resin can be prepared directly from raw materials comprising a compound according to formula (IV) as hydroxy-aromatic compound, and a compound according to formula (V). The conditions for achieving this are similar to those given above for the process or preparing the compound according to formula (I), and can be established by the skilled person via simple routine experimentation and using also his knowledge of the preparation of phenol-formaldehyde resins.

The compositions herein comprise polyol. Any suitable polyol may be used. Preferably the polyol is added during or after the manufacture of the PG resin but before it is cured. While not wishing to be bound by theory it believed that the polyol reinforces the cured resin by increasing the network density. It has been found that, in general, the higher the number of –OH groups and the shorter the chain of atoms between the -OH groups, the harder the cured resin becomes. Therefore, when a more flexible product is required it would be prudent to chose a polyol containing less –OH groups, a longer polyol, or a combination thereof.

Preferably the ratio of OH from the polyol to COOH from the PG resin is from 0.01:1 to 1.2:1, more preferably from 0.1:1 to 0.8:1.

Preferred polyols for use herein have from 2 to 10 –OH groups. More preferably from 2 to 5. Examples of preferred polyols include diols such as ethylene glycol, diethylene glycol, triethylene glycol, 1,6 hexane diol, neopentylglycol; amino-diols such as diethanolamine and diisopranolamine, acid diols such as dimethylolpropionic acid and dimethylolethanoic acid, polymer diols such as polytetrahydrofuran, polyethylene glycol; triols such as trimethylol-propane; amino-triols such as triethanolamine, triisopropanolamine, and trishydroxymethylmethanamine (“TRIS”), polyols such as pentaerythritol, dipentaerythritol, tripentaerythritol and polymeric polyols such as polyvinyl alcohol, poly-hydroxyethyl(meth)acrylate and copolymers with similar hydroxyfunctional monomers.

Preferred polyols include pentaerythritol, ethylene glycol, diethylene glycol, triethylene glycol and glycerol.

The polyol is preferably added during or after the synthesis of the phenol-glyoxylic resin. More preferably the polyol is added after the synthesis of the resin. Even more preferably the polyol is added to the finished gyloxylate resin reaction mixture while still hot, after which the resin is cooled and collected. Without wishing to be bound by theory it is believed that the polyol already partly reacts with the carboxylic acid groups in the resin without leading to gelation or a substantial increase in viscosity.

The compositions herein may also comprise PF resins. Preferably the present composition comprise 10% or more of PF resin. More preferably the compositions herein comprise 20% or more of PF resin. Even more preferably the composition herein comprise 50% or more of PF resin.

The ratio of PG:PF is preferably in the range 1:100 to 1:1. More preferably the ratio is from 1:50 to 1:2. Even more preferably the ratio is from 1:40 to 1:5. Any suitable PF resin may be used herein. Suitable PF resins are described in e.g. A. Knop, L.A. Pilato, Phenolic Resins, Springer Verlag Berlin 1990. Suitable PF resins include for example resol resins (having a molar ratio of formaldehyde of higher than 1), novolac resins (having a molar ratio of formaldehyde of smaller than 1, to which crosslinker has been added such as hexamethylene tetramine), and modified phenolic resins. Preferred PF resins include urea modified phenolic resins, more preferably urea modified phenolic resins with a urea content of between 30 and 40%. An example of a preferred PF resin is BAKELITE® PF 1764 M, which is used in the manufacturing of mineral wool insulation materials.

The preparation of a blend according to the invention may be effected by mixing at ambient temperature the PF resin and the PG resin. Preferably the pH is adjusted to 5-10. Adjustment of the pH may, for example, be effected by adding a base. Examples of suitable bases include metal hydroxides, metal carbonates and amines. Examples of suitable hydroxides are potassium hydroxide, sodium hydroxide, potassium carbonate, potassium bicarbonate, sodium carbonate, sodium bicarbonate. Examples of suitable amines are ammonia, ethanolamine, diethanolamine, triethanolamine, 2-dimethylamino-ethanol, triethylamine. Preferred bases are sodium hydroxide.and potassium hydroxide.

The invention moreover relates to the use of the present compositions for the preparation of coatings, adhesives or shaped articles such as wood-based panels like particle boards, strand boards, plywood and laminates, or mineral wool such as stone wool or glass wool, or shaped textile articles such as automotive interior parts, or in the foundry industry (for example as a binder for sand or the like to form moulds used at high temperatures to make articles from molten materials such as metals). To this end, the resins may be used by methods and under conditions similar to those known *per se* for phenol-formaldehyde resins.

A catalyst and other additives may be added to the composition before it is used for processing in its final application. Examples of customary additives include mould release agents, antistatic agents, adhesion promoters, plasticizers, colour enhancing agents, flame retardants, fillers, flow promoters, colorants, diluents, polymerization initiators, UV-stabilizers, heat stabilizers, and combinations thereof. Examples of fillers include glass fibres, mica, carbon fibres, metal fibres, clay, aramide fibres, polyethylene fibres, and combinations thereof.

The composition according to the invention may be used as such; however, it is also possible to subject the resin to a modification step; this is a reaction step designed to alter or enhance its functionality in a specific way. An example of an altered functionality is the solubility of the resin in water. An example of an enhanced functionality is the addition of a reactive group. An example of a modification step is to bring the resin in contact with compounds that react with the -OH groups; an example of such a compound is epichlorohydrin. Another example of a modification step is to bring the resin in contact with compounds that hydrolyze the ester groups; an example of such a compound is water; the hydrolysis of ester groups into a -COOH group increases the solubility of the resin in water. Also, the modification step may be achieved through a transesterification reaction between the $-OR_6$ groups and suitable compounds such as amines.

Further aspects of the invention and preferred features thereof are given in the claims.

The present invention is illustrated with the following examples, which are non-limiting.

<u>Comparative Example</u>

Phenol (104 g, 90 wt% in H_2O; 1 mol) and glyoxylic acid (252g, 40 wt% in H_2O; 1.4 mol) were placed in a 500 ml 3-necked round bottom flask equipped with a condenser. At a temperature of 80°C, 4 g methane sulphonic acid was slowly added to the reaction mixture. Temperature increases and was maintained at approximately 100°C (reflux). After 8 hours reaction time the reaction was stopped by cooling the reaction mixture to room temperature. After cooling down a light viscous resin was obtained

For determining strength a sandbar test was used. Sand with size between 0.25 and 0.6 mm was used to produce sandbars with dimensions

140 mm * 25 mm * 10 mm. For eight sandbars the procedure was as follows: 500 g sand was mixed with 100 ml 15 wt% in water resin mixture. This mixture was poured into a mould. The sandbars were cured at approx. 160°C for 2 hours. The bending strength was determined by breaking the bars in a measuring device which had a support span of 100 mm and a velocity of compressing of 10 mm/min after a preload of 0.2 N is applied.

34.4 g H_2O is added to 15.6g of this resin and stirred to a homogeneous mixture. 250 g sand (sufficient for 4 sandbars) was added to the mixture and evaluated in the sandbar test. The average weight of the sandbars was 54.2 g and the average bending strength was 0.3 N/mm^2.

Example 1

104 g phenol (90 wt% in H_2O; 1 mol) and 252 g glyoxylic acid (40 wt% in H_2O; 1.4 mol) was placed in a 500 ml 3-necked round bottom flask equipped with a condenser. At a temperature of 80°C, 4 g methane sulphonic acid was slowly added to the reaction mixture. Temperature increases and was maintained at approximately 100°C (reflux). After 2 hours 57g of pentaerythritol was added to the mixture and dissolved. After dissolving the pentaerythritol the reaction was stopped by cooling to room temperature. After cooling a light viscous resin was obtained.

35.6g H_2O is added to 14.4g of this resin and stirred to a homogeneous mixture. 250g sand (sufficient for 4 sandbars) was added to this mixture and evaluated as described in the Comparative Example. The average weight of the sandbars was 53.3 g and the average bending strength was 2.3 N/mm^2.

Example 2

A resin was prepared as described in Comparative Example except that the reaction was allowed to go for 16 hours instead of 8. After cooling down a light viscous resin was obtained. 6.8 g of this resin, 0.7 g triethyleneglycol and 17.5 g H_2O was mixed to a homogeneous mixture. This mixture was mixed with 125 g sand (sufficient for 2 sandbars) and evaluated as described in the Comparative Example. The average weight of the sandbars was 54.8 g and the average bending strength was 1.4 N/mm^2.

Example 3

104 g phenol (90 wt% in H_2O; 1 mol) and 252 g glyoxylic acid (40 wt% in H_2O; 1.4 mol) was placed in a 500 ml 3-necked round bottom flask equipped with a condenser. At a temperature of 80°C, 4 g methane sulphonic acid was slowly added to the reaction mixture. Temperature increases and was maintained at approximately 100°C (reflux). After 8 hours reaction time the reaction was stopped by cooling the reaction mixture to room temperature. After cooling down a light viscous resin was obtained.

50 g of this resin was mixed with 8g of glycerol and stirred until homogeneous. 52.5g H_2O was added to 22.5g of this mixture and stirred until homogeneous (mixture 2). 375 g sand (sufficient for 6 sandbars) was added to mixture 2 and evaluated as described in the Comparative Example. The average weight of the sandbars was 54.3 g and the average bending strength was 1.3 N/mm^2.

Example 4

104 g phenol (90 wt% in H_2O; 1 mol) and 252 g glyoxylic acid (40 wt% in H_2O; 1.4 mol) was placed in a 500 ml 3-necked round bottom flask equipped with a condenser. At a temperature of 80°C, 4 g methane sulphonic acid was slowly added to the reaction mixture. Temperature increases and was maintained at approximately 100°C (reflux). After 8 hours reaction time the reaction was stopped by cooling the reaction mixture to room temperature. After cooling down a light viscous resin was obtained.

15g of this resin was mixed with 3.9g of triethyleneglycol and stirred until homogeneous. 26.25g H_2O was added to 11.25g of this mixture and stirred until homogeneous (mixture 2). 187.5g sand (sufficient for 3 sandbars) was added to mixture 2 and evaluated as described in the Comparative Example. The average weight of the sandbars was 53.1g and the average bending strength was 2.6 N/mm^2.

Example 5

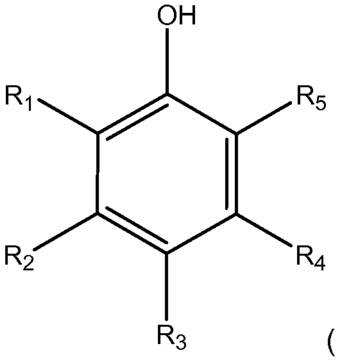
104 g phenol (90 wt% in H_2O; 1 mol) and 252 g glyoxylic acid (40 wt% in H_2O; 1.4 mol) was placed in a 500 ml 3-necked round bottom flask equipped with a condenser. At a temperature of 80°C, 4 g methane sulphonic acid was slowly added to the reaction mixture. Temperature increases and was maintained at approximately 100°C (reflux). After 8 hours reaction time the reaction was stopped by cooling the reaction mixture to room temperature. After cooling down a light viscous

resin was obtained.

15g of this resin was mixed with 1.6 g ethyleneglycol and stirred until homogeneous. 26.25g H_2O was added to 11.25g of this mixture and stirred until homogeneous (mixture 2). 187.5g sand (sufficient for 3 sandbars) was added to mixture 2 and evaluated as described in the Comparative Example. The average weight of the sandbars was 51.9g and the average bending strength was 1.5 N/mm^2.

CLAIMS

1. A heat curable resin composition comprising at least one phenol-glyoxylate resin (PG resin) and at least one polyol.
2. A composition according to Claim 1 wherein the ratio of OH from the polyol to COOH from the PG resin is a ratio from 0.01 to 1 to a ratio from 1 to 1.2.
3. A composition according to any preceding claim wherein the polyol has 2 to 5 hydroxy groups.
4. A composition according to any preceding claim wherein the polyol is selected from ethylene glycol, diethylene glycol, triethylene glycol, 1,6 hexane diol, neopentylglycol, diethanolamine, polytetrahydrofuran, polyethylene glycol, trimethylolpropane, pentaerythritol, dipentaerythritol, tripentaerythritol, glycerol, and combinations thereof.
5. A composition according to any preceding claim wherein the polyol is selected from pentaerythritol, ethylene glycol, diethylene glycol, triethylene glycol, diethanolamine, glycerol, and combinations thereof.
6. A composition according to any preceding claim wherein phenol-glyoxylate resin comprises the reaction product of a hydroxy-aromatic compound of formula (I):



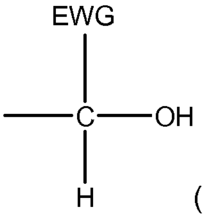
(I)

wherein:

at least one of the set consisting of R_1, R_3, and R_5 is a group of formula (II); any remaining one or two of the set consisting of R_1, R_3, and R_5 being H, OH, a C_1-C_{12} alkyl group or an oligomeric or polymeric system;

R_2 and R_4 are H, OH, a C_1-C_{12} alkyl group or an oligomeric or polymeric system;

and a compound according to formula (II):



$$\mathrm{-}\overset{\displaystyle EWG}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}\mathrm{-OH}$$

(II)

wherein EWG is an electron-withdrawing group.

7. A composition according to Clam 6 wherein the compound according to formula (II) is selected from oxoethanoic acid, methylglyoxylate methanol hemiacetal, ethylglyoxylate ethanol hemiacetal, and combinations thereof.
8. A composition according to any preceding claim wherein the phenol-glyoxylate resin comprises the reaction product of phenol and oxoethanoic acid.
9. A composition according to any preceding claim wherein the PG resin is obtained without using any aldehyde and/or resol in addition to phenolic and/or glyoxylic compounds.
10. A composition according to any preceding claim wherein the PG resin consists of phenolic and glyoxylic repeat units.
11. An article comprising a composition according to any preceding claim.
12. Use of a composition according to any of claims 1 to 10 to produce mineral wool.
13. Use of a composition according to any of claims 1 to 10 in foundry applications.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/053182

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G8/28 C03C25/34 C08L61/14 B22C1/22 C08K5/053

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)
C08G C03C C08L B22C C08K

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)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 05 197151 A (JAPAN SYNTHETIC RUBBER CO LTD) 6 August 1993 (1993-08-06) cited in the application paragraph [0083] - paragraph [0088] paragraph [0095] - paragraph [0097]	1,6,7,11
Y	WO 2007/140940 A (DSM IP ASSETS BV [NL]; BOONEN JOZEF JOHANNES CATHERIN [NL]; BOESTEN WI) 13 December 2007 (2007-12-13) cited in the application page 1, lines 14-16 page 6, line 23 - page 7, line 2; claims	1-13

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

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family.

Date of the actual completion of the international search
13 July 2009

Date of mailing of the international search report
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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