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IMPROVED PROCESS FOR THE PREPARATION OF
ADVANCED RESINS

The present invention relates to a process for the preparation of an advanced resin by reaction of a compound having on average more than one epoxy group per molecule and a compound having on average at least one hydroxyl group and preferably aromatic hydroxyl group or carboxyl group per molecule in the presence of a catalyst at elevated temperature, the process comprising mixing the epoxy compound, the compound having at least one nucleophile bearing active hydrogen, and the catalyst and transferring the mixture as a feed stream to a moving surface, the reaction substantially taking place on the moving surface.

Epoxy resins are well known in the art. In combination with a suitable curing agent they result in thermosetting products showing superior toughness, chemical resistance, heat resistance, adhesion and electrical properties.

The most common types of epoxy resins are those which are based on bisphenol-A and which contain 1,2-epoxy groups. These compounds can be made by reaction of bisphenol-A with epichlorohydrin. The reaction is often carried out in such a way that liquid reaction products are obtained, but higher molecular weight semi-solid and solid products are also produced in this way. Another process to produce higher molecular weight semi-solid and solid resinous polyepoxides is a process known as "upgrading" or "advancement". In such an upgrading or advancement process, usually an initially liquid resinous polyepoxide is reacted with a dihydric phenol in the presence of a catalyst until the required amount of the

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dihydric phenol is incorporated in the epoxy chain to increase the molecular weight to the desired level.

It will be appreciated that said upgrading or advancement process as described hereinbefore with reference to dihydric phenol, can also be carried out by using carboxyl compounds or other hydroxyl compounds.

Such upgrading processes have been described in the past both on a batch basis and on a continuous basis, see e.g. US 3,547,881, US 3,919,169 and US 4,105,634. In such known batch and continuous processes, the dihydric phenol and liquid epoxy resin are mixed together at a relatively low temperature and then heated up to the reaction temperature and held at elevated temperature for the time sufficient to produce the resinous epoxy compound of the higher molecular weight. The catalyst is usually added either to the starting reaction mixture at the relatively low temperature or after heating of the reacting mixture to the reaction temperature.

In such known batch and continuous upgrading processes, however, cycle times, including dumping, are typically relatively lengthy. For example, batch processes involving bisphenol-A and a liquid polyepoxide consisting essentially of the diglycidyl ether of bisphenol-A can take from 4 to 20 hours for the reaction to be completed. Further, the homogeneity of temperature in a large kettle reactor is complicated by heat transfer, i.e. the heat of reaction is more difficult to control and localised high heats will cause adverse reactions to occur, e.g. crosslinking and/or gelling. Furthermore, the reaction may continue during dumping when the conditions are less controlled, resulting in different conditions for different batches and thus in different product properties for each batch. The continuous process using a pipe reactor described in US 3,919,169 involves a shorter reaction time in the

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order of about two hours, but in a continuous process it would be highly advantageous if the reaction time could be significantly lower. Also, due to the flow profile in a pipe, the use of pipe reactors often results in a rather broad molecular weight distribution and in a fouling of the reactor wall, ultimately resulting in a thick layer of deposited material which needs regularly cleaning.

In addition to economies of time, long reaction times can lead to a relatively wide molecular weight distribution which may in their turn lead to end use disadvantages. For example, surface coating imperfections due to gel particles (MEK-insolubles, MEK is methyl ethyl ketone) have been observed when molecular weight distribution and concomitant viscosity characteristics are not properly controlled.

Another possibility to produce advanced epoxy resin is the use of an extruder process. However, there are numerous disadvantages to such a process. The investment costs are relatively high, the more because high performance extruders are needed (to avoid any stagnant zones). Further, a relatively high effort is needed to operate the extruder, maintenance is cumbersome and the product quality is not optimal, especially due to gel formation (gel particles which do not dissolve in MEK). These gel particles may result in a low quality cured product. Another disadvantage is the relatively short residence time in an extruder (typically up to five minutes). This short residence time results in the need to use relatively high catalyst concentration to complete the reaction, as illustrated in US patent 4,612,156.

It is in addition observed that, depending on the intended use of the advanced resin, in some cases the upgrading process is preferably carried out in the absence of a solvent in order to avoid solvent stripping

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and vacuum devolatilisation, since even then the final product contains significant amounts of undesirable solvents. These residual solvents may cause numerous problems when the product is fabricated into a usable product, such as films, by coextrusion or moulding. The residual solvents require extensive vacuum drying to prevent voids in the film and moulded articles. The hazard of solvents being released from a product during fabrication could cause a problem unless proper venting is employed. Solvents may have an adverse effect on polymer properties such as stability, colour, haze etc.

It will be appreciated that depending on the relative amounts of epoxy compound and the compound having at least one hydroxyl compound or carboxyl compound the end product is an epoxy compound or a hydroxyl or carboxyl compound. The above described problems, however, hold for all end products.

The process of the present invention solves the above described problems. Short reaction times are sufficient (reaction times are usually in the order of up to 1 hour at most), relatively low capital requirements are necessary and a constant product consistency is obtained. Operational costs are low when compared with the known processes. These advantages are obtained by mixing the reactants, transferring the mixture, to a moving surface at a suitable temperature to form a reacting layer and allowing the components to react on the moving surface. Optionally further heating and/or cooling may be applied to the reaction mixture on the moving surface to create the desired temperature profile. It will be appreciated that an ideal plug flow is obtained in this way, resulting in the high product quality.

Thus, the present invention relates to a process for the preparation of an advanced resin by reaction of a compound having on average more than one epoxy group per

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molecule and a compound having on average at least one hydroxyl group or carboxyl group per molecule, in the presence of a catalyst at elevated temperature, the process comprising (1) mixing the epoxy compound, with
5 the compound having at least one hydroxyl compound or carboxyl compound and the catalyst, and (2) transferring the mixture, as a feedstream to a surface which is at least intermittently moving with respect to the feedstream.

10 It will be clear that the above described process has numerous advantages over the prior art processes. The process is a continuous process using short reaction times only. The necessary equipment is relatively cheap. No back mixing is possible. No continuous fouling of the
15 equipment occurs. High quality advanced resin can be made of equally consistent quality.

It will be appreciated that the reaction between components to be transferred on the moving surface may alternatively have partially taken place. However,
20 according to preferred embodiments, substantial reaction between the components before transferring to the moving surface, is avoided.

In the above process the mixing of the epoxy compound and the hydroxyl compound (preferably phenolic compound) or carboxyl compound is preferably carried out as a
25 continuous process. The two components are preferably mixed as liquid components. Mixing may be carried out by methods well known in the art, e.g. in one or more simple mixing chamber, but is preferably carried out in a device which mixes the ingredients intensively in a short time,
30 e.g. a conventional mixer, an impingement mixer, an extruder, a high shear mixer or static mixer. It will be appreciated that the mixing of reactants and catalyst may be performed in more than one mixing stages using more
35 than one mixers, which may be the same or different. It

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is possible to mix the three components at the same time, but it is also possible to use a mixture of one of the reactants and the catalyst, followed by mixing with the second component. Another possibility is to mix the two reactants, followed by addition of the catalyst. Mixing may be carried out at another location provided that reactions only occur to a minor degree (less than 50% of the original epoxy groups have reacted), followed by transport to the location where the reaction is carried out. Mixing is suitably carried out at a temperature between 60 and 240 °C, preferably between 80 and 220 °C, more preferably between 100 and 190 °C at least partly by using preheated reactants. Heating may be applied during mixing (including heat generated by the mixing process) or thereafter. In the case that one of the components is a solid, the temperature of the two components may be chosen such that a solution is obtained having a temperature as mentioned above. For instance solid hydroxy reactant of ambient temperature may be mixed with liquid epoxy compound of e.g. 150 °C. In the case that the two components are mixed at the minimum reaction temperature or above this temperature, it will be clear that mixing and deposition should be carried out fast to prevent any premature reaction as much as possible.

After mixing, the reaction mixture is transferred to the moving surface, preferably in a continuous way. The mixture may be simply poured onto the surface or may for instance be sprayed or dropped onto the surface. A convenient way is a simple pipe or a number of pipes, which pipe or pipes may be fixed or moving. Another possibility is a single or multiple nozzle system, which may distribute the feedstream as a flow or as a spray. In general these techniques are known in the art. The thickness of the layer is suitably between 1 and 20 mm, preferably between 2 and 5 mm, especially 3 to 4 mm.

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In the new process it is possible that the surface is a fixed surface, while the feedstream is moved above the surface. This is possible in batch or semi continuous processes, as after deposition of the reaction mixture and completion of the reaction, the reaction mixture has to be removed from the surface. Preferably the feedstream has a fixed position and the surface is a moving surface. This makes it possible to carry out the reaction in a continuous way. It is of course possible that the feedstream as well as the surface are moving.

The moving surface is preferably a continuously moving surface, although an intermittently moving surface is also possible. More preferably, the surface is continuously moving at the same speed. The surface itself may have every possible shape, for instance it might be a drum or a plate, but preferably the surface is a flat surface e.g. a plate, a moving belt (the top layer being the moving surface), a disk or a flat ring. Preferably the surface is a continuous belt or endless conveyer belt, as described in e.g. US 4,389,357. Preferably a continuous stainless steel belt is used. The dimensions of the belt are not relevant for the principle of the invention. The width of the belt may be from a few centimetres to several meters, depending on the desired capacity. The length of the belt may be between several meters up till several hundreds of meters, depending on speed of the belt, reaction time and desired capacity. Usually a belt width of 0.2 till 5 meters, especially between 0.4 and 3 m, and a belt length of 10 to 100 meters, especially between 40 and 80 m, will be suitable. The moving surface is in at least one direction preferably horizontal or substantially horizontal, i.e. less than 3 degrees deviating from the horizon, preferably less than 1 degree. In the case of an endless conveyer belt this holds also for the other direction.

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After depositing the reaction mixture on the surface there is no need for physical agitation of the mixture, e.g. stirring or mixing. Thus, no back mixing occurs, resulting in a product quality of extreme high
5 uniformity. If desired ultrasonic, sonic or subsonic radiation may be used to improve the homogeneity.

The reaction mixture usually will have a temperature between 20 and 260 °C, preferably between 80 and 220 °C, more preferably between 100 and 190 °C. To control the
10 reaction rate additional heating means may be installed to increase the temperature of the reaction mixture. In this respect it is observed that the reaction is exothermic, and provided that the temperature is sufficiently high, the temperature of the mixture will
15 increase. In the case that the temperature of the reaction mixture is too low to start the reaction, additional heating means are necessary. In the particular case of bisphenol A and the diglycidyl ether of bisphenol A, the starting temperature sufficiently high
20 to reach the exothermic phase is between 110 and 125 °C, usually about 120 °C. After a first set of additional heating means, a second set of additional heating means may be used, especially to keep the reaction temperature sufficiently high to finish the reaction in a relatively
25 short time. Suitably the temperature of the deposited layer is heated in such a way that the temperature is between 120 °C and 220 °C, preferably between 140 and 200 °C. It will be understood that the temperature increase of the deposited layer will be the combined
30 effect of the heating and cooling means and the exothermic reaction. Depending on the thickness of the layer and the own cooling capacity of the moving surface, it might be necessary to install additional cooling means in order to prevent that the temperature reaches values
35 at which decomposition of the product could occur. In

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general cooling means should be used in the case the reaction temperature exceeds 240 °C, especially 220 °C, more especially 200 °C. Near the end of the moving surface the reaction product is preferably cooled to a temperature suitably below 100 °C, especially below 60 °C, more especially below 30 °C. Thus, the solid product which is usually obtained after cooling can easily be removed from the surface.

Suitable heating means are infra red radiators, a hot gas oven or heating means at the back side of the surface using heated steam, oil or electricity. Suitable cooling means are (inert) gasses or oil or water applied to the back side of the surface. Heating means and cooling means which can be used are known in the literature, for instance in J.H. Perry, the Chemical Engineer's Handbook.

The reaction between the epoxy compound and the hydroxyl compound or the carboxyl compound should preferably take place on the moving surface. Preferably less than 50 percent of the epoxy groups of the starting epoxy compound have reacted before the mixture is deposited onto the moving surface, preferably less than 20 percent, more preferably less than 5 percent, even more preferably less than 2 percent. Depending on the specific type of the resins to be advanced a certain degree of pre-reaction may be allowable.

If necessary, an easy way to prevent reaction before deposition onto the moving surface is to keep the temperature sufficiently low, e.g. below 120 °C. The temperature profile applied to the reaction mixture, and depending on the starting temperature of the mixture, the heating and cooling means and the reaction heat, should be such that at least 80 percent of the theoretical conversion has been achieved, preferably at least 95 percent, more preferably at least 98 percent, at the end of the reaction cycle.

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When the reaction is complete or substantially complete, the reaction mixture is allowed to come off from the surface. In the case of an endless belt this may happen automatically. Otherwise mechanical means may be used to remove the reaction product. A suitable way to reach the end temperature is by cooling the moving surface at the underside with water, but other cooling means can also be used.

The epoxy resins used as starting material in the present invention generally have on average more than one, suitably at least 1.5, preferably at least 1.7, reactive 1,2-epoxy groups per molecule. These epoxy compounds generally have on average up to 6, preferably up to 5, more preferably up to 2.5, reactive 1,2-epoxy groups per molecule. These epoxy compounds can be monomeric or polymeric, saturated or unsaturated, aliphatic, cycloaliphatic, aromatic or heteroaromatic and may be substituted, if desired, with other substituents in addition to the epoxy groups, e.g. hydroxyl groups, alkoxyl groups or halogen atoms, especially bromine atoms. It will be appreciated that also mixtures of epoxy compounds can be used.

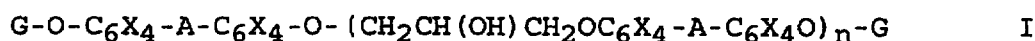
Suitable epoxy compounds are the reaction products of polyphenols and epihalohydrins, polyalcohols and epihalohydrins, amines and epihalohydrins, sulphur containing compounds and epihalohydrins, polycarboxylic acids and epihalohydrins or mixtures thereof.

Preferred epoxy compounds are the reaction products of polyphenols and epihalohydrins, of polyalcohols and epihalohydrins, polycarboxylic acids and epihalohydrins or mixtures thereof, the reaction products of polyphenols and epihalohydrins especially preferred. Illustrative examples of epoxy compounds are described in for instance The Handbook of Epoxy Resins by H. Lee and K. Neville, McGraw-Hill, New York (1967), Epoxy Resins, Chemistry and

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Technology, edited by C.A. May, Marcel Dekker (1988) and Chemistry and Technology of Epoxy Resins, edited by B. Ellis, Blackie Academic & Professional (1993).

5 Epoxy compounds of particular interest in the practice of the present invention include diglycidyl ethers of bisphenol compounds, particularly those compounds represented by general formula I,



10 in which G represents a glycidyl group, and wherein each A independently is a divalent hydrocarbon group having 1 to 8 carbon atoms, preferably methylene or isopropylidene, -C(O)-, -O-, -S-, -S-S-, -S(O)-, -S(O)₂- or a covalent bond, each X independently is hydrogen, an alkyl group having 1 to 4 carbon atoms, preferably methyl, or halogen, preferably chlorine or bromine, and n has an average value of 0 to 12, preferably 0 to 2. More preferably A is isopropylene, X is hydrogen or bromine, especially hydrogen, and n is up to 0.2.

15 The average epoxy equivalent weight (EEW, weight of resin in grams containing one mol equivalent epoxy) is suitably from 140, preferably from 160, up to 3000, preferably up to 950, more preferably up to 450, still more preferably 185.

20 Especially preferred examples of the epoxy compounds are bisphenol A and bisphenol F, especially bisphenol A, type epoxy compounds having an average epoxy equivalent weight of from 160 to 200. They are commercially available from Shell Chemicals Europe and Shell Chemicals Corporation (USA) under the trade names EPIKOTE and EPON. Further especially preferred examples are brominated
25 bisphenol A compounds which for example have an epoxy equivalent of from 200 to 800.
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Further useful epoxy compounds are epoxy novolac resins. The epoxy novolac resins can be obtained by reacting, preferably in the presence of a basic catalyst, e.g. sodium or potassium hydroxide, an epihalohydrin, e.g. epichlorohydrin, with the resinous condensate of an aldehyde, e.g. formaldehyde, and either a monohydric phenol, e.g. phenol itself, or a polyhydric phenol. Further details concerning the nature and preparation of these epoxy novolacs resins can be obtained in Handbook of Epoxy Resins and the other references mentioned above.

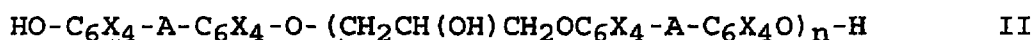
The above-mentioned epoxy compounds can be obtained by means known for the preparation of epoxy resins from a compound containing hydroxyl groups by reacting such compounds with an epihalohydrin in the presence of a suitable catalyst and reacting the resultant intermediate halohydrin ether with a basic acting substance such as an alkali metal hydroxide. It is observed that many of the epoxy compounds to be used for the production of the modified resins of this invention are commercially available.

The preferably used aromatic hydroxyl group containing starting compounds in the present invention have on average more than one, suitably at least 1.5, preferably at least 1.7, reactive hydroxyl groups per molecule. Preferably the number of aromatic hydroxyl groups is between 1.8 and 2.3, more preferably between 1.9 and 2.1. These aromatic hydroxyl compounds may be monomeric or polymeric and may be substituted, if desired, with other substituents in addition to the hydroxy groups, e.g. alkoxy groups or halogen atoms, especially bromine atoms. It will be appreciated that also mixtures of hydroxy compounds can be used. Further, it is also possible to use mono-aromatic hydroxyl compounds, resulting in (partial) end-capping of the epoxy compound.

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Illustrative examples of aromatic hydroxy compounds are described in for instance The Handbook of Epoxy Resins by H. Lee and K. Neville, McGraw-Hill, New York (1967), Epoxy Resins, Chemistry and Technology, edited by C.A. May, Marcel Dekker (1988) and Chemistry and Technology of Epoxy Resins, edited by B. Ellis, Blackie Academic & Professional (1993).

Aromatic hydroxy compounds of particular interest for the present invention include bisphenol compounds, particularly those compounds represented by general formula II,



wherein each A independently is a divalent hydrocarbon group having 1 to 8 carbon atoms, preferably methylene or isopropylidene, -C(O)-, -O-, -S-, -S-S-, -S(O)-, -S(O)₂- or a covalent bond, each X independently is hydrogen, an alkyl group having 1 to 4 carbon atoms, preferably methyl, or halogen, preferably chlorine or bromine, and n has an average value of 0 to 12, preferably 0 to 2. More preferably A is isopropylene, X is hydrogen or bromine, especially hydrogen, and n is up to 0.2. Aromatic hydroxy compounds which are very suitable for the process of the present invention are commercially available, for instance under the general names bisphenol A and bisphenol F.

The average hydroxy equivalent weight is from 140, preferably from 170, up to about 3000, preferably up to 950, more preferably up to about 450. Especially preferred examples are bisphenol A and bisphenol F, especially bisphenol A, having an average hydroxy equivalent weight of 160 to 200.

Illustrative examples of suitable carboxyl compounds are described in for instance The Handbook of Epoxy

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Resins by H. Lee and K. Neville, McGraw-Hill, New York (1967), Epoxy Resins, Chemistry and Technology, edited by C.A. May, Marcel Dekker (1988) and Chemistry and Technology of Epoxy Resins, edited by B. Ellis, Blackie Academic & Professional (1993).

Carboxyl compounds of particular interest for the present invention are aromatic and aliphatic carboxylic acids. Very suitable are aromatic di- and tri-carboxylic acids and aliphatic dicarboxylic acids. Especially suitable are phthalic acid, terephthalic acid or an alpha,omega dicarboxylic aliphatic acid in which the aliphatic group is a linear alkyl group containing 1 to 12 carbon atoms.

It will be appreciated that optionally mono-epoxy compounds, mono-aromatic hydroxyl compounds and/or mono-carboxylic compounds may be added to the reaction mixture in order to control the amount of reactive end groups in addition to one or more polyfunctional compounds. For instance, the amount of epoxy groups in an advanced epoxy resin may be controlled by the addition of a certain amount of phenol or cresol or benzoic acid. Examples of mono-epoxy compounds are glycidyl esters of carboxylic acids, especially tertiary carboxylic acids as VERSATIC acids (VERSATIC is a trademark), and optionally substituted benzoic acids. Examples of mono-phenol compounds are p-tert.-butyl phenol and nonyl phenol. Examples of mono-carboxylic compounds are optionally substituted benzoic acids and tertiary carboxylic acids as versatic acids.

Suitable catalysts which can be employed in the reaction of the present invention include quaternary ammonium compounds, quaternary phosphonium compounds, sulphonium compounds and mixtures thereof. Suitable quaternary ammonium compounds include tetramethyl ammonium chloride, benzyl trimethyl ammonium chloride,

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triethanol ammonium chloride, tetraethanol ammonium hydroxide and dodecyl dimethylbenzyl ammonium naphthenate. Suitable quaternary phosphonium catalysts include for example ethyl triphenyl phosphonium

5 -chloride, -bromide or -iodide, or -acetic acid complex, benzyltriphenyl phosphonium-chloride or -bromide or -iodide, tetrabutyl phosphonium -chloride-bromide or -iodide, and mixtures thereof. Suitable sulphonium catalysts include thio urea catalysts as tetramethyl

10 thiourea, N,N'-dimethyl thiourea, N,N'-diphenyl thiourea and mixtures as well as thioethanol and other sulfonium precursors. For further details reference is made to the catalysts mentioned in the above mentioned handbooks and in US 5,310,854, EP 467,278, US 5,360,886, US 3,919,169,

15 US 3,341,580, US 3,477,990 and the references cited in these documents. A suitable group of catalysts are also peralkylated amino imino diaza phosphorin compounds such as 2-t-butylimino-2-diethylamino-1,3-dimethyl perhydro-1,3,2-diazaphosphorin. See e.g. US 5,063,252. The

20 catalyst is employed in any amount which is satisfactory to catalyse the reaction between the epoxy compound and the hydroxyl compound. Suitable amounts are from 0.01 to 3 weight percent, more suitable between 0.01 and 1 weight percent. More preferred amounts are between 0.01 and

25 0.2 weight percent of catalysts based on the combined weight of the reactants. The catalyst is preferably used in the form of a concentrated solution, for example in an alcohol. It will be appreciated that also mixtures of catalysts can be used.

30 A preferred group of catalysts is formed by quaternary phosphonium compounds and quaternary ammonium compounds. A more preferred group is formed by the quaternary phosphonium compounds and most preferably ethyltriphenyl phosphonium halide.

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After the solid epoxy resin has been prepared by the process of the present invention, it is then processed in the conventional manner for ultimate use, i.e. it is crushed, sieved, classified and/or diluted with suitable solvents and reactants to prepare solution resins useful as coatings and the like. The epoxy resin products suitably have an EEW of between 300 and 50,000, preferably from 400 to 10,000 and a weight average molecular weight between 600 and 100,000, preferably from 800 to 20,000.

The process of the present invention is suitably carried out at a molar ratio of the epoxy groups of the epoxy compound and the hydroxyl groups of the hydroxyl compound between 5.0/1.0 and 1.0/5.0, preferably between 2.5/1.0 and 1.0/1.0, more preferably between 2.2/1.0 and 1.1/1.0.

The invention is illustrated by the following examples.

The reactive ingredients e.g. bisphenol A (diphenylol-propane, DPP), the diglycidylether of bisphenol A (commercially available from Shell Chemicals Europe under the name EPIKOTE-828, EPIKOTE is a trademark) and the catalyst are mixed at or slightly below the reaction temperature using high speed stirrer in a reaction vessel.

Example 1

A model experiment was set up to demonstrate the inventive concept of the present invention. A homogeneous feed was prepared by dissolving 18 g of bisphenol A in 45 g of liquid diglycidyl ether of bisphenol A (EEW 182, Epikote-828) at 135 °C. The epoxy group content (EGC) of the mixture was 3817 mmol/kg, which theoretically should result in a reaction product having an EGC of 1350 mmol/kg. After cooling till 70 °C the catalyst (1 mmol/kg ethyl triphenyl phosphonium iodide, ETPPI) was added as an aqueous ethanolic solution (30 wt%). The

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mixture was divided over various thin-walled aluminium trays (approx. 6.5 g per tray, diameter = 5 cm, layer thickness ~ 2.5 mm). Two series of experiments were carried out:

- 5 a: isothermal; the content of the tray was kept at 180 °C by means of infra-red heating above the tray.
b: exothermal; the bottom of the tray was heated in such a way that an inert material would become 180 °C in 4 min. and kept at that temperature thereafter (in the reactive mixture higher temperatures were measured in view of the exothermal reaction).
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After a certain period the trays were cooled till -78 °C (and analysed at room temperature). Arbitrarily the time that the reactive mixture was above 150 °C was taken as the reaction time. Analysis showed that the target EGC value was reached within 30 minutes irrespective of the type of reaction conditions. The phenolic-OH content of the 30 min. product was 17 mmol/kg (for all reaction mixtures).

15

20 Example 2

In a series of similar experiments an alternative catalyst, 2-tert-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diaza-phosphorine, was used. The target EGC values were also reached within 30 min., again irrespective of the applied reaction conditions.

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Example 3

A mixture of bisphenol A and the diglycidyl ether of bisphenol A (EEW 182, Epikote-828) with an EGC value of 3825 mmol/kg prepared in the same way as described in example 1 and containing 1 mmol/kg of ETPPI was, as a 3 mm layer, placed in an oven at 170 °C with surround air heating. After 30 min, the target EGC value of 1350 mmol/kg was found.

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Example 4

A mixture of bisphenol A and the diglycidyl ether of bisphenol A (EEW 182, Epikote 828) with an EGC value of 3548 mmol/kg prepared in the same way as in example 1 and containing 3 mmol/kg of ETPPI was, as a 3 mm layer, placed in an oven at 170 °C with surround air heating. After 30 min. the target EGC value of 600 mmol/kg was found. The product had a phenolic-OH content of 11 mmol/kg.

Examples 5-7

Bisphenol A, liquid diglycidyl ether of bisphenol F (EPIKOTE 862 and ETPPI were mixed in the mutual weight ratios of example 1 in a 5 kg batch in a prereactor.

The final temperature of the mixture after stirring during at most 10 minutes was 80 °C.

The mixture was poured on a flat moving endless belt which had a width of 15 cm, a length of 5 m and upper edges on which had been mounted, while the layer thickness was 1, 2 and 5 mm respectively. Over a length of three meters of the endless belt an electrical heating was applied, while a roof had been mounted over that belt area.

The belt moved continuously with a speed of about 6 m/hr, whereas the temperature of the belt surface was 180 °C

The mixture was cooled after leaving the roof for about 20 minutes. The solid resin mass could be broken off from the end of the belt after 50 minutes.

The obtained resins showed a phenolic value of less than 50 mmol/kg.

Example 8

A 5 kg batch of a mixture of the same ingredients in the same mutual weight ratios as in example 1 was stirred during about 45 minutes at 90 °C, during which about 1/3

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of the original amount of available epoxy groups had been reacted.

5 The prereacted mass was poured on the same moving endless belt of examples 5-7, except that a layer of a thickness of 1 cm was formed. The speed of the endless belt was about 6 m/hr.

10 The mixture was cooled after leaving the roof for about 20 minutes. The solid resin mass could be broken off from the end of the belt after 50 minutes. The obtained resin showed a phenolic OH value of 18 mmol/kg.

Example 9

15 A homogeneous feed was prepared by dissolving 290.5 g of bisphenol-A in 509.5 g of liquid-ether of bisphenol-A (EEW 182, EPIKOTE 828) at 120 °C. The EGC of the mixture is 3389 mmol/kg, which theoretical should result in a reaction product having a EGC of 204 mmol/kg. After cooling till 90 °C 5 mmol/kg ETPPI (see example 1) was added. The mixture was poured on a flat moving belt like in examples 5-7, while the layer was 1 and 3 mm. After 1 hour at 180 °C the EGC was 248 mmol/kg and the phenolic value of less than 100 mmol/kg.

Examples 10-15

25 The proceedings of example 9 were repeated under the same conditions except that instead of ethyltriphenyl phosphonium iodide (ETPPI) the corresponding ethyl triphenyl phosphonium-chloride, -bromide, tetra-n-butylphosphonium-chloride, -bromide and -iodide and tetramethylammonium chloride were used, providing advanced resins having an EGC in the range of from 230-270 mmol/kg and a phenolic value of less than 100 mmol/kg.

Examples 16-20

35 The proceedings of example 5 were repeated under the same conditions except that instead of ethyltriphenyl-phosphonium iodide (ETPPI), the corresponding ethyl triphenyl phosphonium-chloride and -bromide, tetra-n-butyl

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phosphonium-chloride, -bromide and -iodide, and tetramethylammoniumchloride were used. Advanced resins were obtained, having an EGC in the range of from 1500 to 1900 mmol/kg and a phenolic value of less than 50 mmol/kg.

5 Example 21

 A homogenous feed was prepared by dissolving 16 g of PRIPOL 1022 (Mixture of di- and tri-carboxylic fatty acid) in 34 g of liquid diglycidyl ether of bisphenol A (EEW 182, EPIKOTE-828) at 70 °C, the EGC of the mixture was
10 3621 mmol/kg, which theoretically should result in a EGC of 2517 mmol/kg, the catalyst tri-ethanolammoniumborate was added and the mixture was divided over various thin-walled aluminium trays. The trays were placed on the belt at a temperature of 160 °C. Two experiments were carried out, of
15 a 1 mm and 2 mm layer. After respectively 2 hours a EGC of 2528 mmol/kg was found.

Example 22

 The proceedings of example 21 were repeated except that the mixture contained 17.39 g of E828 and 12.64 g of
20 PRIPOL 1022 (trademark) respectively, and had an theoretical EGC of 1632 mmol/kg. After two hours the EGC was 1705 mmol/kg.

Example 23

 The proceedings of example 9 were repeated except that
25 the epoxy resin EPIKOTE 828 was replaced by an amount of EPIKOTE 834 resin of 682.5 g, resulting after about one hour at 180 °C in an EGC of 240 mmol/kg and a phenolic value of less than 100 mmol/kg.

Example 24

30 The proceedings of example 9 were repeated except that the epoxy resin EPIKOTE 828 resin was replaced by an amount of EPIKOTE 1001 resin of 1363.5 g, resulting after about one hour at 180 °C in an EGC of 240 mmol/kg and a phenolic value of less than 100 mmol/kg.

C L A I M S

1. A process for the preparation of an advanced resin by reaction of a compound having on average more than one epoxy group per molecule and a compound having on average at least one hydroxyl group or carboxyl group per molecule, in the presence of a catalyst at elevated temperature, the process comprising (1) mixing the epoxy compound, the hydroxyl compound or the carboxyl compound and the catalyst, and (2) transferring the mixture, as a feedstream to a surface which is at least intermittently moving with respect to the feedstream.
2. A process according to claim 1, in which the mixing process and the transferring process is a continuous process.
3. A process according to claim 2, in which the moving surface is continuously moving at the same speed.
4. A process according to any of claims 1 to 3, in which the surface is a continuous belt.
5. A process according to any of claims 1 to 4, in which no physical agitation is applied to the deposited layer.
6. A process according to claims 1-5, in which an aromatic hydroxyl group containing compound is used.
7. A process according to claims 1-6, in which the epoxy compound has the general formula I

$$\text{G-O-C}_6\text{X}_4\text{-A-C}_6\text{X}_4\text{-O-(CH}_2\text{CH(OH)CH}_2\text{OC}_6\text{X}_4\text{-A-C}_6\text{X}_4\text{O)}_n\text{-G} \quad \text{I}$$
in which G represents a glycidyl group, and in which A is methylene or isopropylene, each X independently is hydrogen or bromine, n has an average value of 0 to 12.
8. A process according to claim 6, in which the aromatic hydroxyl compound has the general formula II

$$\text{HO-C}_6\text{X}_4\text{-A-C}_6\text{X}_4\text{-O-(CH}_2\text{CH(OH)CH}_2\text{OC}_6\text{X}_4\text{-A-C}_6\text{X}_4\text{O)}_n\text{-H} \quad \text{II}$$





* C L M S *

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in which A is methylene or isopropylene each X independently is hydrogen or bromine, n has an average value of 0 to 12.

5 9. A process according to claims 1 to 8, in which the catalyst is a quaternary ammonium or phosphonium compound.

10. A cured composition obtained by using an advanced resin according to any of claims 1 to 9.

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(May 1998)

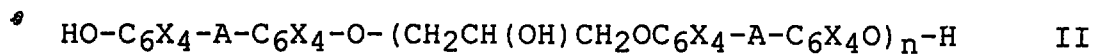
REVISED SET OF CLAIMS

1. A process for the preparation of an advanced resin by reaction of a compound having on average more than one epoxy group per molecule and a compound having on average at least one hydroxyl group or carboxyl group per molecule, in the presence of a catalyst at elevated temperature, the process comprising (1) mixing the epoxy compound, the hydroxyl compound or the carboxyl compound and the catalyst, and (2) transferring the mixture, as a feedstream to a second independent moving surface which is at least intermittently moving with respect to the feedstream and on which second independent moving surface the advancing reaction takes substantially place.
2. A process according to claim 1, in which no backmixing occurs in the deposited layer on the second independent moving surface.
3. A process according to claims 1 and 2, in which the mixing process and the transferring process is a continuous process.
4. A process according to claim 3, in which the separate moving surface is continuously moving at the same speed.
5. A process according to any of claims 1 to 4, in which the surface is a continuous belt.
6. A process according to any of claims 1 to 5, in which no physical agitation is applied to the deposited layer.
7. A process according to claims 1-6, in which the epoxy compound has the general formula I
- $$\text{G-O-C}_6\text{X}_4\text{-A-C}_6\text{X}_4\text{-O-(CH}_2\text{CH(OH)CH}_2\text{OC}_6\text{X}_4\text{-A-C}_6\text{X}_4\text{O)}_n\text{-G} \quad \text{I}$$
- in which G represents a glycidyl group, and in which A is methylene or isopropylene, each X independently is hydrogen or bromine, n has an average value of 0 to 12.

AMENDED SHEET



8. A process according to claims 1-6, in which an aromatic hydroxyl group containing compound is used, which has the general formula II



5 in which A is methylene or isopropylene each X independently is hydrogen or bromine, n has an average value of 0 to 12.

9. A process according to claims 1 to 8, in which the catalyst is a quaternary ammonium or phosphonium
10 compound.

10. A cured composition obtained by using an advanced resin according to any of claims 1 to 9.

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AMENDED SHEET



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(21) International Application Number: PCT/EP97/02003 (22) International Filing Date: 18 April 1997 (18.04.97) (30) Priority Data: 96201053.4 19 April 1996 (19.04.96) EP (34) Countries for which the regional or international application was filed: GB et al. (71) Applicant: SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. (NL/NL); Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL). (72) Inventors: BEEREPOOT, Johannes Petrus, Jozef, Badhuisweg 3, NL-1031 CM Amsterdam (NL). BLOM, Johannes, Jozias, Badhuisweg 3, NL-1031 CM Amsterdam (NL). DE JONG, Feike, Badhuisweg 3, NL-1031 CM Amsterdam (NL). VAN LIEMPT, Virgilius, Christiaan, Johannes, Nicolaas, Badhuisweg 3, NL-1031 CM Amsterdam (NL). VAN DER LINDEN-LEMMERS, Wilhelmina, Johanna, Maria, Badhuisweg 3, NL-1031 CM Amsterdam (NL). RAAS, Paulus, Egidius, Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL). BJARDIJN, Willem, Badhuisweg 3, NL-1031 CM Amsterdam (NL).		(81) Designated States: AU, BR, CA, CN, JP, KR, <u>SG</u> , European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report.
(54) Title: IMPROVED PROCESS FOR THE PREPARATION OF ADVANCED RESINS (57) Abstract The invention relates to a process for the preparation of an advanced resin by reaction of a compound having on average more than one epoxy group per molecule and a compound having on average one or more than one nucleophile bearing active hydrogen such as aromatic hydroxyl group, carboxyl group or amino group, per molecule, in the presence of a catalyst at elevated temperature, the process comprising (1) mixing the epoxy compound, the aromatic hydroxyl compound or the carboxyl compound and the catalyst, and (2) transferring the mixture, as a feedstream to a surface which is at least intermittently moving with respect to the feedstream. In a preferred embodiment an endless conveyor belt with additional heating means and optional cooling means are used.		