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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : **C08G 63/60**	**A2**	**(11) International Publication Number:** **WO 98/42768** **(43) International Publication Date:** 1 October 1998 (01.10.98)

(21) International Application Number: PCT/EP98/01903

(22) International Filing Date: 24 March 1998 (24.03.98)

(30) Priority Data:
97200904.7 25 March 1997 (25.03.97) EP
(34) Countries for which the regional or international application was filed: GB et al.

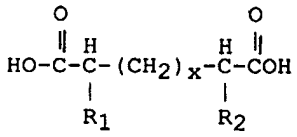
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(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
Without international search report and to be republished upon receipt of that report.

(54) Title: ACID FUNCTIONAL AND EPOXY FUNCTIONAL POLYESTER RESINS



(I)

(57) Abstract

Carboxyl functional polyester resins obtainable by reaction of (a) at least a compound of formula (I) wherein $x \geq 1$ wherein R_1 and R_2 each may represent an alkyl group having from 1 to 4 carbon atoms or wherein R_1 and R_2 may form together the remainder of cyclic cycloalkyl group (A1), optionally mixed with minor amounts of a corresponding compound of formula (I) wherein x=0, or anhydride thereof (A2), (b) at least one diol compound B, comprising two aliphatic hydroxyl groups, which may each independently be a primary or a secondary hydroxyl group; (c) optionally one dihydroxymonocarboxylic acid compound C, comprising a tertiary aliphatic carboxyl group and two aliphatic hydroxyl groups which may each independently be primary or secondary hydroxyl, and (d) optionally a trihydroxyalkane (D1) or tetrahydroxyalkane (D2); the molar ratio of compounds (A1+A2):B:C:D1:D2 being X+Y+2Z+3Q+P:X:Y:Z:Q, wherein X ranges from 1 to 8, Y ranges from 0 to 8, Z ranges from 0 to 4 and Q ranges from 0 to 3 and wherein P ranges from 1 to 5, preferably from 1 to 3 and is most preferably equal to 1, at a temperature of from 100 to 240, until essentially all the hydroxyl groups as initially present in the reaction mixture have been reacted; linear or branched polyglycidyl esters derived therefrom and powder coating compositions comprising one or both type of these ester types.

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ACID FUNCTIONAL AND EPOXY FUNCTIONAL POLYESTER RESINS

The present invention relates to carboxyl functional polyester resins, to a process for the preparation of the resins, to polyglycidylester resins obtainable by glycidating said carboxyl functional polyester resins, to coating compositions, and in particular powder coating compositions or liquid coating compositions comprising said carboxyl functional polyester resins or said polyglycidylester resins, and to cured products obtained by using the indicated coating compositions.

Powder coating compositions based on the solid reaction products of 2,2-bis-(4-hydroxyphenyl)propane and epichlorohydrin are known already for a long time. The cured products prepared on the basis of these compositions are resistant against hydrolysis, however, they show a low ultraviolet resistance and are therefore not suitable for applications requiring a high degree of outdoor durability such as building parts or automotive topcoats.

Triglycidylesters which can be used in good quality outdoor durable coatings and in moulding compositions are disclosed in European Patent Application No. 447360A (EP-A-447,360). Due to the anhydride half ester nature of the terminal carboxyl functions present in the tricarboxylic acid adduct precursors, strong alkaline conditions should be avoided during glycidation of these tricarboxylic acid adducts to avoid hydrolysis of the glycidylester formed and/or hydrolysis of one or more ester groups in the resin

backbone. As a result thereof the triglycidylester produced will contain a relatively high level of hydrolizable chlorine and/or will contain low molecular weight hydrolysis products which might cause toxicity problems, as may be derived from "Water based coatings with excellent saponification stability XIIIth Int. Conf. 1987, Athens, Greece, p. 175.

The high level of hydrolizable chlorine is reflected in example 2 of EP-A-447,360 which relates to the glycidation of the 2:1 adduct of hexahydrophthalic anhydride and dimethylolpropionic acid. The product obtained has a chlorine content of 1.5%. Such a high level of residual chlorine is generally undesirable in coating compositions. In addition, due to the fact that the triglycidylesters reported in EP-A-447,360 are liquid, they can not be applied in powder coating compositions.

In e.g. International Application WO 96/11238, it was taught to a person skilled in the art of this specific area of curable coatings, that epoxy resins containing cycloaliphatic nuclei had the disadvantage that they could only provide brittle coating films when cured. This brittleness made them unsuitable for coating applications, as brittleness often led to poor adhesion.

From European patent application No. 0634434A2 was known a process for the preparation of linear tertiary aliphatic carboxyl functional polyester resins, by reacting:

(a) at least one compound A' comprising one mono-functional primary- or secondary hydroxyl group and/or at least one compound A" comprising one primary- or

secondary hydroxyl group and one tertiary aliphatic carboxyl group;

(b) at least one aromatic or cycloaliphatic dicarboxylic acid compound B comprising two aromatic- or secondary aliphatic carboxyl groups or the anhydride thereof;

(c) at least one diol compound C comprising two aliphatic hydroxyl groups, which may independently be a primary or a secondary hydroxyl group; and

(d) at least one dihydroxymonocarboxylic acid compound D comprising a tertiary aliphatic carboxyl group and two aliphatic hydroxyl groups, which may each independently be primary or secondary hydroxyl,

the molar ratio of compounds A':A":B:C:D being

M:N:X+Y+1:X:Y

wherein M+N=2, X ranges from 2 to 8 and Y ranges from 2-N to 8, at a temperature of from 100 to 240 °C, until essentially all the non-tertiary carboxyl groups as initially present in the reaction mixture have been reacted.

Moreover in this application were disclosed polyglycidylester resins obtainable by reacting said linear tertiary aliphatic carboxyl functional polyesters with an excess epihalohydrin in the presence of a suitable base and optional catalyst. Preferably, the polyesters were reacted with epichlorohydrin. Both the specified linear polyesters and the corresponding polyglycidylesters derived therefrom were used with a cross-linking agent for powder coating compositions.

From the European patent application No. 0720997A2, linear tertiary carboxyl functional polyesters and epoxy functional polyester resins were known. These polyester resins were obtainable by reaction of:

a) at least one aromatic and/or cycloaliphatic carboxylic acid compound A comprising two aromatic- and/or secondary aliphatic carboxyl groups or the anhydride thereof,

b) at least one hydroxyl compound B comprising two aliphatic hydroxyl groups, which groups each independently may be primary or secondary hydroxyl groups,

c) at least one hydroxyl substituted carboxylic acid compound C comprising at least one tertiary aliphatic carboxyl group and two aliphatic hydroxyl groups, which groups each independently may be primary or secondary hydroxyl groups, and

d) optionally one carboxylic acid compound D comprising one carboxyl group,

the molar ratio of compounds A:B:C:D being

$$(X+Y-1):X:Y:Z,$$

wherein X ranges from 2 to 8, Y ranges from 2 to 8, and Z ranges from 0 to 2.

These polyester resins could be used together with a suitable curing agent for the production of powder coatings, or could be converted into the corresponding glycidylesters, which in combination with a suitable curing agent could be used for the production of powder coatings.

Although the linear tertiary aliphatic carboxyl functional polyester resins and the polyglycidylesters thereof enabled a certain progress as to the requirements of excellent outdoor durability (UV stability) and resistance against hydrolysis in the cured state, with reference to their use in modern economically applied powder coatings, there is still a

need for further improvement of this combination of properties.

On the other hand novel powder coating binders for the exterior durable powder coating market derived from carboxylated polyester resins, cured with epoxy functional acrylate polymers, have been proposed during the Waterborne, Higher Solids and Powder Coatings Symposium, February 5-7, 1997, New Orleans LA, USA, T Agawa and E D Dumain, p. 342-353, "New Two-component Powder Coating Binders: Polyester acrylate hybrid as TGIC Cure Alternative.

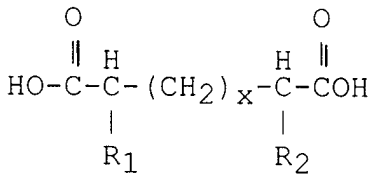
However, as indicated on page 353 already, further improvements have to be made to provide smoother films, lower cure temperatures and UV durability to rival that of automotive topcoating or outdoor building panel topcoating.

Therefore, it is an object of the invention to provide, acid functional polyester resins, which can be readily glycidated so as to form a polyglycidylester resin. Said carboxyl functional polyester resin and said polyglycidylester resin must show further improved properties when used in outdoor durable powder coating compositions, which are relatively environmentally friendly.

As a result of extensive research and experimentation said carboxyl functional polyester resins aimed at have been now surprisingly found.

Accordingly, the invention provides carboxyl functional polyester resins obtainable by reaction of:

a) at least a compound of the formula



I

wherein x ≥ 1

wherein R_1 and R_2 each may represent an alkyl group having from 1 to 4 carbon atoms or wherein R_1 and R_2 may form together with the group ~CH-$(CH_2)_x$-CH~ a cycloalkyl group and preferably 1,4-cyclohexane dicarboxylic acid (A1), optionally mixed with minor amounts of a corresponding compound of formula I, wherein x=0 or anhydride thereof (A2),

b) at least one diol compound B comprising two aliphatic hydroxyl groups which may each independently be a primary or a secondary hydroxyl group;

c) optionally a dihydroxymonocarboxylic acid compound C, comprising a tertiary aliphatic carboxyl group and two aliphatic hydroxyl groups, which may each independently be primary or secondary hydroxyl; and

(d) optionally a trihydroxyalkane (D1) or tetrahydroxy-alkane (D2),

the molar ratio of compounds (A_1+A_2):B:C:D1:D2 being X+Y+2Z+3Q+P:X:Y:Z:Q, wherein X ranges from 1 to 8, Y ranges from 0 to 8, Z ranges from 0 to 4 and Q ranges from 0 to 3 and wherein p ranges from 1 to 5, and preferably 1-3 and is most preferably equal to 1, at a temperature of from 100 to 240 °C, and preferably from 180 to 210 °C if any compound C is present, until essentially all the hydroxyl groups as initially present in the reaction mixture have been reacted.

With the term "minor amounts" as used the optional component A2 are meant amounts of from 0 to 10 mole%, relative to the total molar amount of A1 and A2.

Preferably carboxyl functional polyester resins are aimed at wherein Y > 0 if Z + Q = 0, or wherein Z + Q > 0 if Y = 0.

It will be appreciated that the aliphatic carboxyl functional polyester resins thus produced may only contain tertiary carboxyl groups pendant of the main chain, whereas only at each end of the main chain secondary carboxyl groups originating from 1,4-cyclohexane dicarboxylic acid, are present.

Dependent on the actual presence of components (D1) or (D2) the main chain will be linear (components D are absent) or branched (component D1 and/or D2 is present).

It will be appreciated by those skilled in the art that the molecular weight distribution and number average molecular weight of the resin produced will depend on the specific reactants and the ratios applied in the process of the invention.

Whilst the tertiary aliphatic carboxyl groups optionally present in compounds C practically do not react under the esterification conditions employed, glycidation of these non-terminal tertiary aliphatic carboxyl groups and the terminal secondary carboxyl groups with epihalohydrin can be performed under standard alkaline conditions, whereby a polyglycidyl-ester resin can be obtained which contains a low hydrolizable halogen content, usually lower than 1% by weight and preferably lower than 0.7% by weight, based on the total weight of the composition.

It will be appreciated that other aspects of the present invention are formed by polyglycidylesters of the hereinbefore specified carboxyl functional poly-esters and by coating compositions and more in

particular powder coating compositions or liquid coatings, comprising said carboxyl functional polyester resins and/or said polyglycidylesters derived therefrom and by cured products, obtained by using these coating compositions.

The process for preparation of the aliphatic carboxyl functional polyester may in general be carried out according to conventional esterification methods, preferably by azeotropic condensation, taking care that the terminal secondary carboxyl groups are only originating from 1,4-cyclohexane dicarboxylic acid. In particular, the condensation is carried out by charging the compounds A, B, optionally C and optionally D1 or D2, simultaneously to the reactor whereafter the temperature is increased from room temperature to a temperature in the range of from 180 to 240 °C, preferably from 180 to 210 °C in the presence of any compound B, during a period of 3 to 8 hours, thus allowing the reaction to initiate and to proceed under continuous azeotropic removal of water. Generally the azeotropic removal of water is being continued until at least 90% of the original hydroxyl groups have reached and more preferably at least 95% of the original hydroxyl groups have reacted. An esterification catalyst known in the art, such as for example dibutyltinoxide, paratoluenesulphonic acid, tinoctoate, zincoctoate and lithium ricinoleate may be used in the esterification process, but is in general not required.

In order to be sure that the terminal secondary carboxyl groups have originated from the structure of formula I dicarboxylic acid wherein $x \geq 1$, and in particular 1,4-cyclohexane dicarboxylic acid, and not from the corresponding 1,2-structure (x=0) and in

particular 1,2-dicyclohexane dicarboxylic acid, a part of the total batch of e.g. 1,4-cyclohexane dicarboxylic acid to be included, may be added during the reaction and more preferably in its last stage.

Suitable compounds B for use in the process of the present invention include branched aliphatic-, cycloaliphatic-, or araliphatic compounds, containing two aliphatic hydroxyl groups, each individually being either a primary or a secondary hydroxyl group, such as for example propylene glycol, neopentyl glycol, hydrogenated diphenylolpropane (HDPP), hydrogenated 4,4'-dihydroxydiphenyl, 1,4-cyclohexanedimethylol, 1,4-dihydroxycyclohexane, hydroxypivalylhydroxypivalate and 2-butyl-2-ethyl-1,3-propanediol or mixtures thereof; of which HDPP is particularly preferred.

A typical example of a suitable compound C for use in the process of the present invention is dimethylol propionic acid.

A typical and preferred example of compound D1 to be used for the preparation of the branched carboxyl functional polyesters of the present invention, is trimethylol propane and a preferred example of compound D2 is pentaerythritol.

As indicated above the aliphatic carboxyl functional polyester resin obtainable according to the process of the present invention can be easily converted to a polyglycidylester resin according to methods known in the art i.e. by reaction with an excess epihalohydrin in the presence of a suitable base and optionally a catalyst. Most conveniently epichlorohydrin is used.

It will be appreciated that due to the polymeric nature of the polyglycidylester resin of the present

invention a relatively low level of toxicity can now be combined with excellent coating properties. More in particular an excellent weatherability and acid resistance in combination with an attractive film flow, giving a coherent and smooth appearance, very attractive hardness-flexibility balance, have been reached.

It was found that those polyglycidylester resins derived from the carboxyl functional polyester resins of the invention wherein Y ranges from 1 to 4, X simultaneously ranges from 1 to 6, Z ranges 0 to 2 and Q ranges 0 to 2, can provide the most preferred outdoor durable powder coating compositions. More preferably polyglycidylester resins are used wherein x = 3, Y = 1.5, Z = 0, Q = 0.

The curable powder coating compositions of the invention may be prepared by addition of a cross-linking resin to either the hereinbefore specified linear or branched or star shaped aliphatic carboxyl functional polyester resins of the present invention or to the polyglycidylester resin obtainable by glycidating said linear or branched aliphatic carboxyl functional polyester resin.

The amount of cross-linking compound used in the powder coating compositions of the invention will normally be such so as to provide about equal amounts of reactive groups of the cross-linking compound and of the aliphatic carboxyl groups present in the linear or branched aliphatic carboxyl functional polyester resin or of the epoxy groups present in the polyglycidylester resin.

Suitable cross-linking resins for use in combination with the aliphatic carboxyl functional

polyester resins of the present invention are for example outdoor durable epoxy resins, such as for example the polyglycidylester resins according to the present invention, the diglycidylesters of alpha, alpha'-dibranched dicarboxylic acids as disclosed in European Patent Application publication number 518,408 and the polyglycidylesters based on polycarboxylic acids carrying two alkyl substituents on each of the alpha carbon atoms as disclosed in European patent application publication number 366,205.

Suitable cross-linking resins for use in combination with the polyglycidylester resins of the present invention are for example the (corresponding) acid functional polyester resin of the present invention; solid polyacids such as sebacic acid, 1,12-dodecanedioic acid; anhydrides such as polyazeleic polyanhydride; acid functional polyesters such as the reaction product of one mole of trimethylolpropane and 3 moles of hexahydrophthalic anhydride, the reaction product of 1,6-hexanediol with a molar excess of 1,12-dodecanedioic acid, the reaction product of 4 moles 1,10-decanedicarboxylic acid, 1.49 mols hexanediol, 0.47 mols 1,1,1-tris-(hydroxymethyl)-propane and 0.27 mols pentaerythritol, the reaction product of 4 mols 1,10-decanedicarboxylic acid, 1.2 mols hexanediol, 0.45 mols trimethylolpropane, 0.29 mols pentaerythritol and 0.21 mols dimethylol-propionic acid and the reaction product of one mole of hexamethoxymethylmelamine and 3 moles of hydroxypivalic acid and amine-type curing agents.

Most preferred are combinations of the aliphatic carboxyl functional polyester resins and the polyglycidylesters derived therefrom.

The powder coating compositions of the present invention may further comprise a catalyst and optionally other additives, as known in the art to be suitable for use in powder coating compositions.

Suitable catalysts are for example quaternary ammonium and phosphonium salts; metal salts/compounds such as for example stannous(II)octoate; basic compounds such as for example the imidazoles; and tertiary amines such as for example diazabicycloundecene.

The amount of catalyst used will usually be somewhere in the range of from 0.1 to 2% by weight based on the weight of the total powder coating composition.

Suitable cure times and cure temperatures of the powder coating compositions of the invention are those conventionally applied in connection with powder coating systems.

The invention is illustrated by the following examples, however without restricting its scope to these specific embodiments.

Example 1

Preparation of aliphatic carboxyl functional polyesters 1 to 6 according to the invention.

Compounds A1 to D2 were charged in molar amounts as indicated in Table 1 in a round bottom glass reactor, equipped with a condenser, temperature control, nitrogen inlet, stirrer and vacuum inlet.

The mixture was then heated to 150 °C in 30 minutes. The temperature of the reaction mixture was increased in two hours to 210 °C and kept at 210 °C until at least 94% of the original hydroxyl groups have reacted. The acid functional polyester thus formed was

discharged and allowed to cool down to room temperature.

Table 1 1) 2)

Carboxyl functional poly-ester resin	1	2	3	4	5	6	7	8
1,4-CHCA (A1)	9	9	9	7	21	6	5.5	6.5
HHPA (A2)	-	-	-	-	-	-	-	-
DMPA (C)	2.5	2	1.2	-	-	-	1.5	1.5
HDPP (B)	5.5	6	6.8	4	8	1	3	4
TMP (D1)	-	-	-	1	3	1	-	-
PENTA (D2)	-	-	-	-	1	-	-	-
1,4-DMCH (B)	-	-	-	-	-	2	-	-

1) Numbers given represent the amount of moles of a particular compound charged to the reactor in the process of example 1 for the preparation of the linear tertiary carboxyl functional polyester resins 1 to 5.

2) The chemical compounds represented by the abbreviations used are:

1,4-CHCA: 1,4-cyclohexanedicarboxylic acid
HHPA : hexahydrophthalic anhydride
DMPA : dimethylolpropionic acid
HDPP : hydrogenated diphenylolpropane
TMP : trimethylol propane
PENTA : pentaerythritol
1,4-DMCH: 1,4-dimethylolcyclohexane

Example 2

Preparation of aliphatic carboxyl functional polyester 9 according to the invention.

Compounds HHPA, HDPP, TMP in a molar ratio of 1:8:2 were charged in a round bottom glass reactor, equipped with a condenser, temperature control nitrogen inlet, stirrer and vacuum inlet. The mixture was heated to 190 °C and kept at this temperature until the acid value was below 0.1 meq/g. Subsequently 1,4-CHCA was added in an amount according to a molar ratio 1,4-CHCA + HHPA, HDPP, TMP and 1,4-DMCH of 13:8:1:2, and the mixture was further reacted until at least 94% of all original hydroxyl groups had reacted. The acid functional polyester thus formed was discharged and allowed to cool down to room temperature.

Example 3

Preparation of corresponding polyglycidylester resins A, B, C, D, E, and F.

An amount equalling 1 carboxyl group equivalent of linear tertiary and partly secondary aliphatic carboxyl functional polyester resins obtained as samples 1, 2, 3, 4, 7, and 8 respectively in Table 1, was dissolved in 16 moles epichlorohydrin (ECH), 15.5 moles iso-propylalcohol (IPA) and 15.5 moles of demi-water. The solution was charged to a glass-reactor equipped with a temperature control, stirrer and reflux condenser. Next, the temperature was raised to 70 °C, followed by gradual addition of an 50 %wt aqueous solution of 0.16 moles of NaOH over a period of 20 min. The temperature is increased during this caustic addition from 70 to 80 °C. At this temperature the mixture is stirred until virtually all acid groups are converted (approx. 50 min.). Subsequently, the mixture is cooled

to 55 °C. At this temperature, gradual addition of an 50 %wt aqueous solution of 0.92 moles of NaOH over a period of 60 min. followed. After a post-reaction of 5 min., 15 moles of water was added and the mixture was stirred for 5 min. The reactor content was allowed to settle and subsequently the brine was separated from the organic phase. The excess of ECH, the IPA and some remaining water was flashed off with vacuum.

The resulting crude resin A, B, C, D, E, and F was dissolved in methyl isobutyl ketone (MIBK) (MIBK/resin=5/1 v/v) and washed 4 times with water (water/resin=1/1 v/v) at 70-75 °C. The MIBK is removed by vacuum flash and the polyglycidylester was discharged from the reactor and allowed to cool down.

The epoxy resins obtained showed the following properties:

Table 2

Resin	A	B	C	D	E	F
EGC (mmol/kg)	1360	1214	996	1355	1400	1250
Tot. Cl(cor.) (mg/kg)	5640	5338	5029	6212	7500	6500
ICI-viscosity (Poise, 200 °C)	9	11	16	14	9	16
Tg (°C) (DSC, second scan, mid. val.)	35	39	47	38	32	39

Table 3

Ingredients*	P1	P2	P3	P4	P5
Polyglycidyl-ester resin (1) A	600	-	-	-	-
" B	-	750	-	-	-
" C	-	-	750	-	-
" D	-	-	-	738	-
" E	-	-	-	-	1000
Carboxyl functional resin (2) 6	397	450	369	500	724
Titaniumdi-oxide	299	360	336	371	517
Modaflow (3)	19.4	23.4	21.9	24.8	33.6
Benzoin	8.0	9.6	9.0	9.9	14.8
Catalyst	3.0	3.6	3.4	3.7	5.2
Powder characteristics					
Extrusion behaviour	←.....good.....→				
Storage stability @ 30 °C	moderate	good	good	moderate	good
Coatings (4)					
Appearance	←.....smooth.....→				
Gloss (5)	85	89	85	86	87
Reverse Impact (6)	>60	>20	>10	>40	>40
Accelerated weather resistance (7)	>1800	>1800	>1800	1500	>1800

* all amounts in grams

(1) Prepared as described in Example 3

(2) Prepared as described in Example 1

(3) Modaflow III is an acrylic based flow aid available from Monsanto Co.

(4) Coatings: Q-panel AL-36, cured at 200 °C for 15 minutes and thickness 40-60 micrometres.

(5) Measured with Gardner micro-TRI-gloss apparatus, angle 60°.

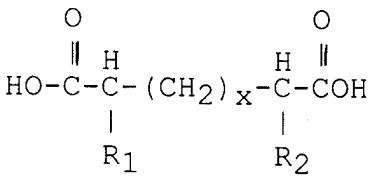
(6) Measured in inch/pounds according to Ericksen type 304 ISO-TR-6272/1979-DIN-55669.

Hours in Atlas Weather-OMeter, running SAE J1960 test method before 50% reduction in gloss.

C L A I M S

1. Carboxyl functional polyester resins obtainable by reaction of

(a) at least a compound of the formula



I

wherein $x \geq 1$

wherein R_1 and R_2 each may represent an alkyl group having from 1 to 4 carbon atoms or wherein R_1 and R_2 may form together with the group $\sim CH-(CH_2)_x-CH\sim$ a cycloalkylgroup (A1), optionally mixed with minor amounts of a corresponding compound of formula I wherein x=0, or anhydride thereof (A2),

(b) at least one diol compound B, comprising two aliphatic hydroxyl groups, which may each independently be a primary or a secondary hydroxyl group;

(c) optionally one dihydroxymonocarboxylic acid compound C, comprising a tertiary aliphatic carboxyl group and two aliphatic hydroxyl groups which may each independently be primary or secondary hydroxyl, and

(d) optionally a trihydroxyalkane (D1) or tetrahydroxyalkane (D2);

the molar ratio of compounds (A1+A2):B:C:D1:D2 being X+Y+2Z+3Q+P:X:Y:Z:Q, wherein X ranges from 1 to 8, Y ranges from 0 to 8, Z ranges from 0 to 4 and Q ranges from 0 to 3 and P ranges from 1 to 5, preferably from 1 to 3 and is most preferably equal to 1, at a

temperature of from 100 to 240, until essentially all the hydroxyl groups as initially present in the reaction mixture have been reacted.

2. Carboxyl functional polyester resins according to claim 1, characterized in that component A1 is 1,4-cyclohexyl dicarboxylic acid, optionally mixed with minor amount of 1,2-cyclohexane dicarboxylic acid or anhydride thereof.

3. Carboxyl functional polyester resins according to claims 1-2, characterized in that component B is hydrogenated diphenylolpropane (HDPP).

4. Carboxyl functional polyester resins according to claims 1-3, characterized in that component C is dimethylol propionic acid.

5. Carboxyl functional polyester resins according to claims 1-4, characterized in that component D1 is trimethylol propane.

6. Carboxyl functional polyester resins according to claims 1-5, characterized in that component D2 is pentaerythritol.

7. A linear or branched polyglycidylester resin obtainable by reacting carboxyl functional polyester resins according to claims 1-6, with an excess epihalohydrin in the presence of a suitable base and optionally a catalyst.

8. A powder coating composition comprising a linear or branched aliphatic carboxyl functional polyester resin claims 1-6 and a cross-linking agent.

9. A powder coating composition comprising a polyglycidyl ester resin of claim 7 and a cross-linking agent.

10. A powder coating composition according to claim 9, characterized in that the cross-linking agent is a

linear or branched polyester resin according to claims 1-6.