PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C09D 167/02	A1	(11) International Publication Number: **WO 99/60067** (43) International Publication Date: 25 November 1999 (25.11.99)

(21) International Application Number: PCT/US98/27920

(22) International Filing Date: 30 December 1998 (30.12.98)

(71) Applicant: EASTMAN CHEMICAL COMPANY [US/US]; 100 North Eastman Road, Kingsport, TN 37660 (US).

(72) Inventors: NEWSOM, Mi, Kyong; 541 Southridge Circle, Yardley, PA 19067 (US). CHOU, Chun-tzer; 1056 Rotherwood Drive, Kingsport, TN 37660 (US).

(74) Agent: LINDEMAN, Jeffrey, A.; Morgan, Lewis & Bockius LLP, 1800 M Street, N.W., Washington, DC 20036-5869 (US).

(81) Designated States: European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published

With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

Upon the request of the applicant, before the expiration of the time limit referred to in Article 21(2)(a).

(54) Title: THE USE OF 1,4-CYCLOHEXANEDICARBOXYLIC ACID AS A MEANS OF IMPROVING FLOW PROPERTIES AND BROADENING CURE WINDOW OF POLYESTER POWDER COATING ENAMEL

(57) Abstract

The invention describes a powder coating composition based on a polyester resin containing 1,4-cyclohexanedicarboxylic acid. Such powder coating compositions exhibit improved flow properties during curing and a broadened cure window.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	**ES**	Spain	**LS**	Lesotho	**SI**	Slovenia
AM	Armenia	**FI**	Finland	**LT**	Lithuania	**SK**	Slovakia
AT	Austria	**FR**	France	**LU**	Luxembourg	**SN**	Senegal
AU	Australia	**GA**	Gabon	**LV**	Latvia	**SZ**	Swaziland
AZ	Azerbaijan	**GB**	United Kingdom	**MC**	Monaco	**TD**	Chad
BA	Bosnia and Herzegovina	**GE**	Georgia	**MD**	Republic of Moldova	**TG**	Togo
BB	Barbados	**GH**	Ghana	**MG**	Madagascar	**TJ**	Tajikistan
BE	Belgium	**GN**	Guinea	**MK**	The former Yugoslav Republic of Macedonia	**TM**	Turkmenistan
BF	Burkina Faso	**GR**	Greece			**TR**	Turkey
BG	Bulgaria	**HU**	Hungary	**ML**	Mali	**TT**	Trinidad and Tobago
BJ	Benin	**IE**	Ireland	**MN**	Mongolia	**UA**	Ukraine
BR	Brazil	**IL**	Israel	**MR**	Mauritania	**UG**	Uganda
BY	Belarus	**IS**	Iceland	**MW**	Malawi	**US**	United States of America
CA	Canada	**IT**	Italy	**MX**	Mexico	**UZ**	Uzbekistan
CF	Central African Republic	**JP**	Japan	**NE**	Niger	**VN**	Viet Nam
CG	Congo	**KE**	Kenya	**NL**	Netherlands	**YU**	Yugoslavia
CH	Switzerland	**KG**	Kyrgyzstan	**NO**	Norway	**ZW**	Zimbabwe
CI	Côte d'Ivoire	**KP**	Democratic People's Republic of Korea	**NZ**	New Zealand		
CM	Cameroon			**PL**	Poland		
CN	China	**KR**	Republic of Korea	**PT**	Portugal		
CU	Cuba	**KZ**	Kazakstan	**RO**	Romania		
CZ	Czech Republic	**LC**	Saint Lucia	**RU**	Russian Federation		
DE	Germany	**LI**	Liechtenstein	**SD**	Sudan		
DK	Denmark	**LK**	Sri Lanka	**SE**	Sweden		
EE	Estonia	**LR**	Liberia	**SG**	Singapore		

THE USE OF 1,4-CYCLOHEXANEDICARBOXYLIC ACID AS A MEANS OF IMPROVING FLOW PROPERTIES AND BROADENING CURE WINDOW OF POLYESTER POWDER COATING ENAMEL

This disclosure demonstrates how incorporating 1,4-cyclohexanedicarboxylic acid (1,4-CHDA) into a polyester resin for powder coating applications improves coating flow during cure and broadens the cure window, a function of the time and temperature at which cure occurs. As a result, coating properties are fully developed at either lower cure temperatures or shorter cure times, and the cure variables do not require such precise control as coatings based on other diacids.

The powder coating industry is challenged to develop finished coatings comparable in appearance to that of solvent-borne coatings. Without solvent, the nonuniform powder particles must be able to flow to a similar degree of smoothness in order to match the appearance of a solution coating. In order to achieve the desired effect, the powder coating must melt within a particular temperature range permitting timely and ample flow of the polymeric material prior to crosslinking. It was previously determined that 1,4-CHDA reduces resin melt viscosity thus enhancing flow properties of the enamel during cure. Results of the current study indicate that the presence of increasing amounts of 1,4-CHDA in powder coating resins improves cure response of the resin during crosslinking as well. It is resonable to expect that lower viscosity resins are more mobile; therefore, they interract more readily with the crosslinker.

The reduction in resin melt viscosity of 1,4-CHDA, 1,3-CHDA, HPHP and BEPD has been described in Eastman Publication Number N-343. It is anticipated that these would provide similar effects on flow properties and cure response. An example resin composition is given in Table I where 1,4-CHDA replaces terephthalic acid (TPA) at 0, 6, 9, 12, 18 and 24 mole percent. Components of the resin may include, but are not restricted to *NPG*® Glycol, 1,4-cyclohexanedimethanol, 2-butyl-2-ethyl-1,3-propanediol (BEPD), 3-hydroxy-2,2-dimethylpropyl 3-hydroxy-2,2-dimethylpropanoate (HPHP), 3-methyl-1,5-pentanediol, 2-methyl-1,3-propanediol, 1,4-butanediol, 1,2-butanediol, 2,2-diethyl-1,3-

pentanediol, 1,4-CHDA, 1,3-cyclohexanedicarboxylic acid (1,3-CHDA), hexahydrophthalic anhydride, isophthalic acid, terephthalic acid, trimethylolpropane, trimellitic acid, or combinations thereof. Since the ultimate performance of the crosslinked coating is dependent upon binder composition, the monomeric effects apply to both polymeric compositions of hydroxyl and acid terminated polyester resins for polyester-isocyanate, polyester-epoxy hybrid, polyester-triglycidylisocyanurate (TGIC), and combinations of polyesters with other crosslinkers.

Resin properties, such as acid number, hydroxyl number, glass transition temperature (Tg), and molecular weight are summarized in Table II. The results demonstrate that an increase in the mole percent of 1,4-CHDA decreases resin Tg and viscosity (Figure 1). The powder coating enamel formulation and physical properties are given in Tables III & IV, respectively. A 9% molar replacement of TPA with 1,4-CHDA achieves an optimal balance between enamel flow and Tg. 1,4-CHDA improved impact resistance, t-bend and orange peel at various cure conditions (Figures 2-4).

Table I

Resin Composition[1]

	Moles
NPG® Glycol	8.18
Trimethylolpropane	0.62
Diacid:	8.18
1,4-CHDA	
Terephthalic Acid	

[1]0.1% Fascat 4100 catalyst based on total charge.

Table II

Resin Properties

Mole % of 1,4 -CHDA	Acid Number	OH Number	Tg, °C (midpoint)	Mn	Mw
0	8	49	60	2900	10262
6	7	48	58	3065	11054
9	8	48	55	2965	10290
12	4	47	57	3313	12785
18	4	48	53	3378	13941
24	3	47	48	3305	12678

Table III

Powder Coating Enamel Formulation

Components		Weight, g
Polyester Resin		560
Huls B 1530 blocked diisocyanate		140
Dupont R-960 TiO_2 pigment		280
Benzoin (1% based on binder)		7
Dibutyltin dilaurate, DBTDL (1% based on binder)		7
Modaflow 2000 (1% based on binder)		7
	TOTAL	1001

Table IV
Reactivity and Stability Characteristics

Percent of 1,4-CHDA	Gel Time (@204°C, sec)	Pill Flow (mm)	Caking Test (% Passing)
0	96	131	94
6	98	138	81
9	95	159	62
12	49	124	13
18	60	119	13
24	56	137	0

We Claim:

1. A powder coating composition comprising:
a polyester resin comprising 1,4-cyclohexanedicarboxylic acid; and
a binder.

2. A powder coating composition of claim 1, wherein said 1,4-cyclohexanedicarboxylic acid is present in an amount of between about 6-24 mol% based on the total number of moles of diacid present in said polyester resin.

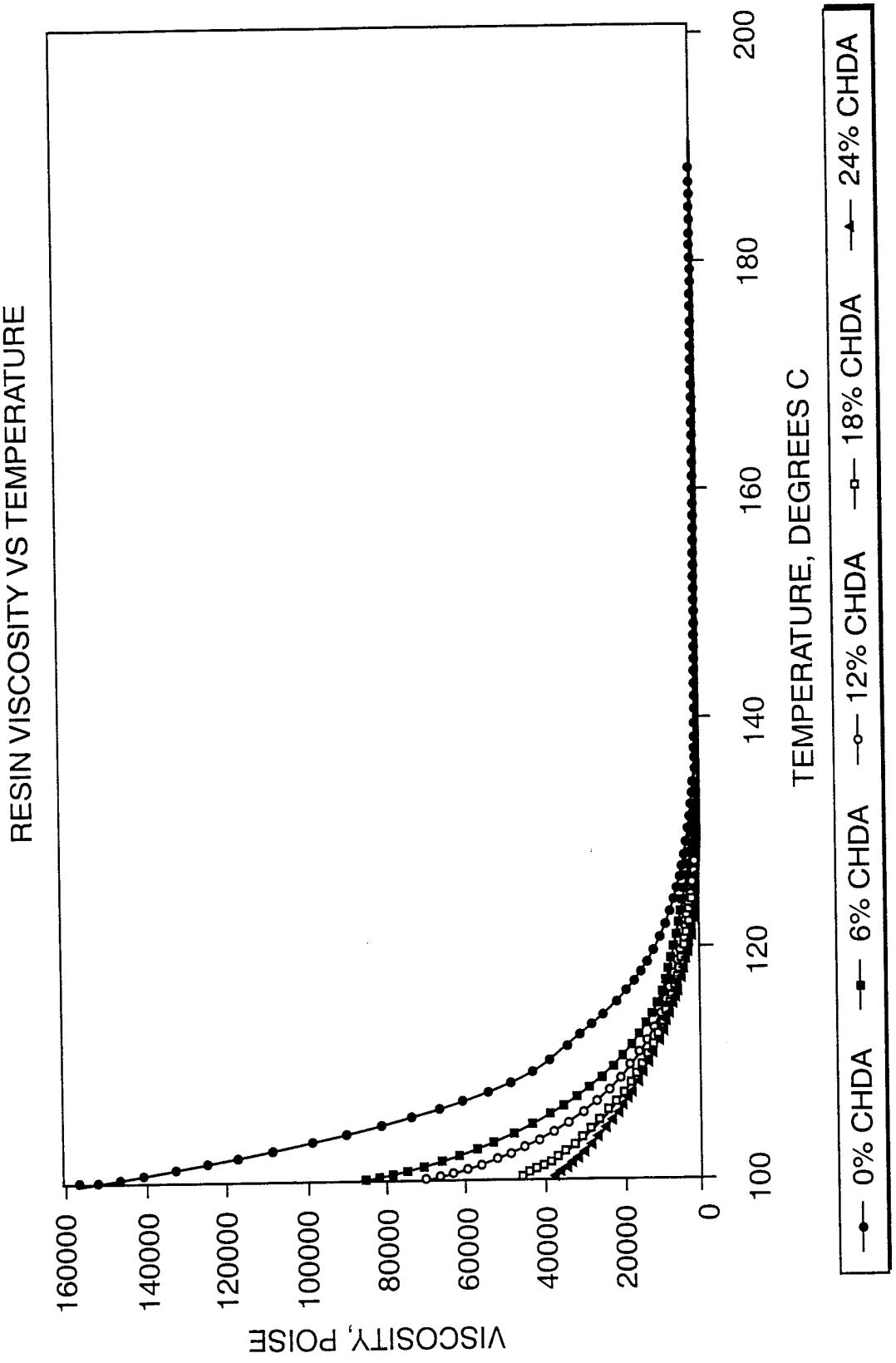
RESIN VISCOSITY VS TEMPERATURE
VISCOSITY, POISE
160000
140000
120000
100000
80000
60000
40000
20000
0
100
120
140
160
180
200
TEMPERATURE, DEGREES C
0% CHDA
6% CHDA
12% CHDA
18% CHDA
24% CHDA

FIG. 1

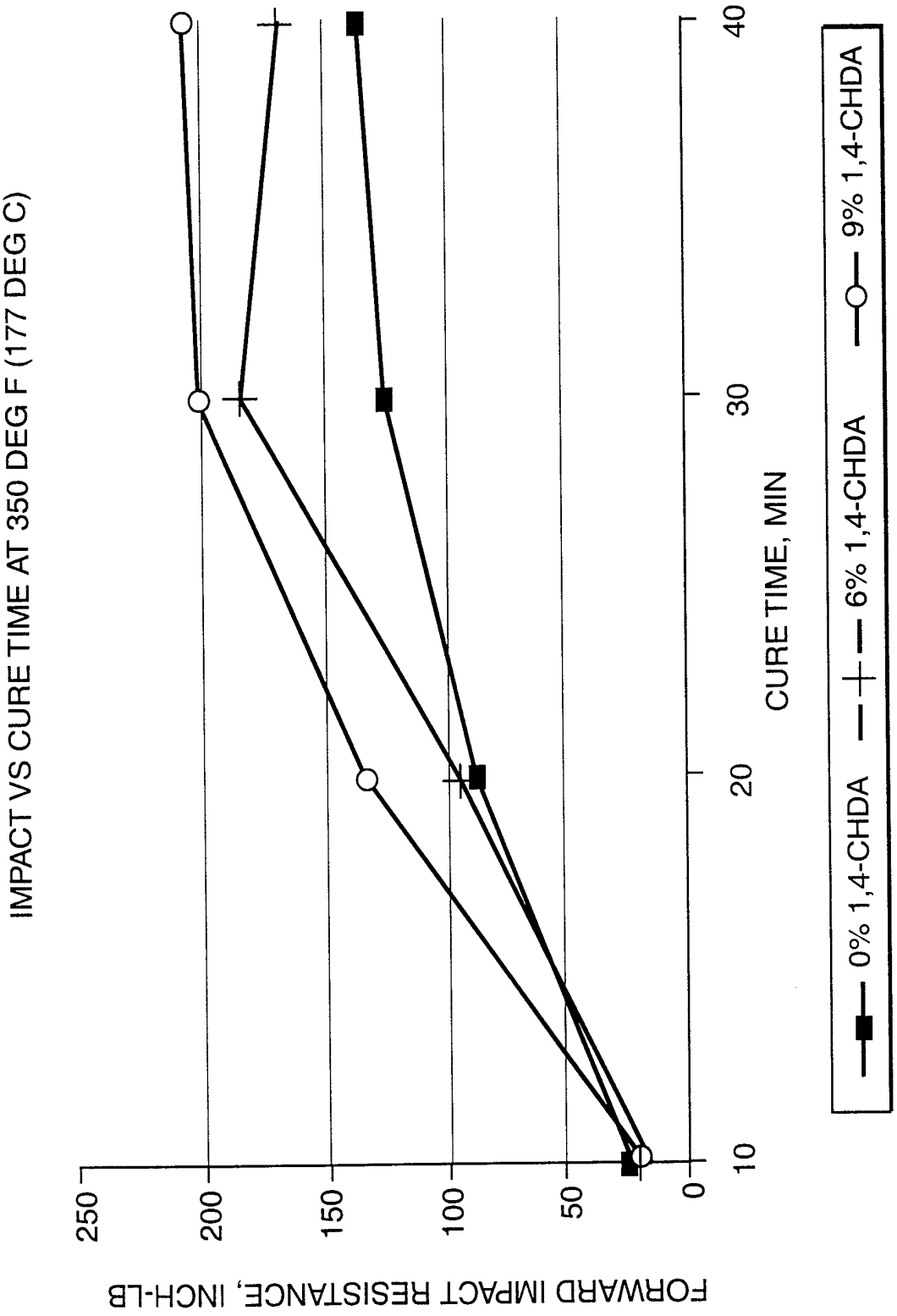
IMPACT VS CURE TIME AT 350 DEG F (177 DEG C)
FORWARD IMPACT RESISTANCE, INCH-LB
250
200
150
100
50
0
10
20
30
40
CURE TIME, MIN
0% 1,4-CHDA
6% 1,4-CHDA
9% 1,4-CHDA

FIG. 2

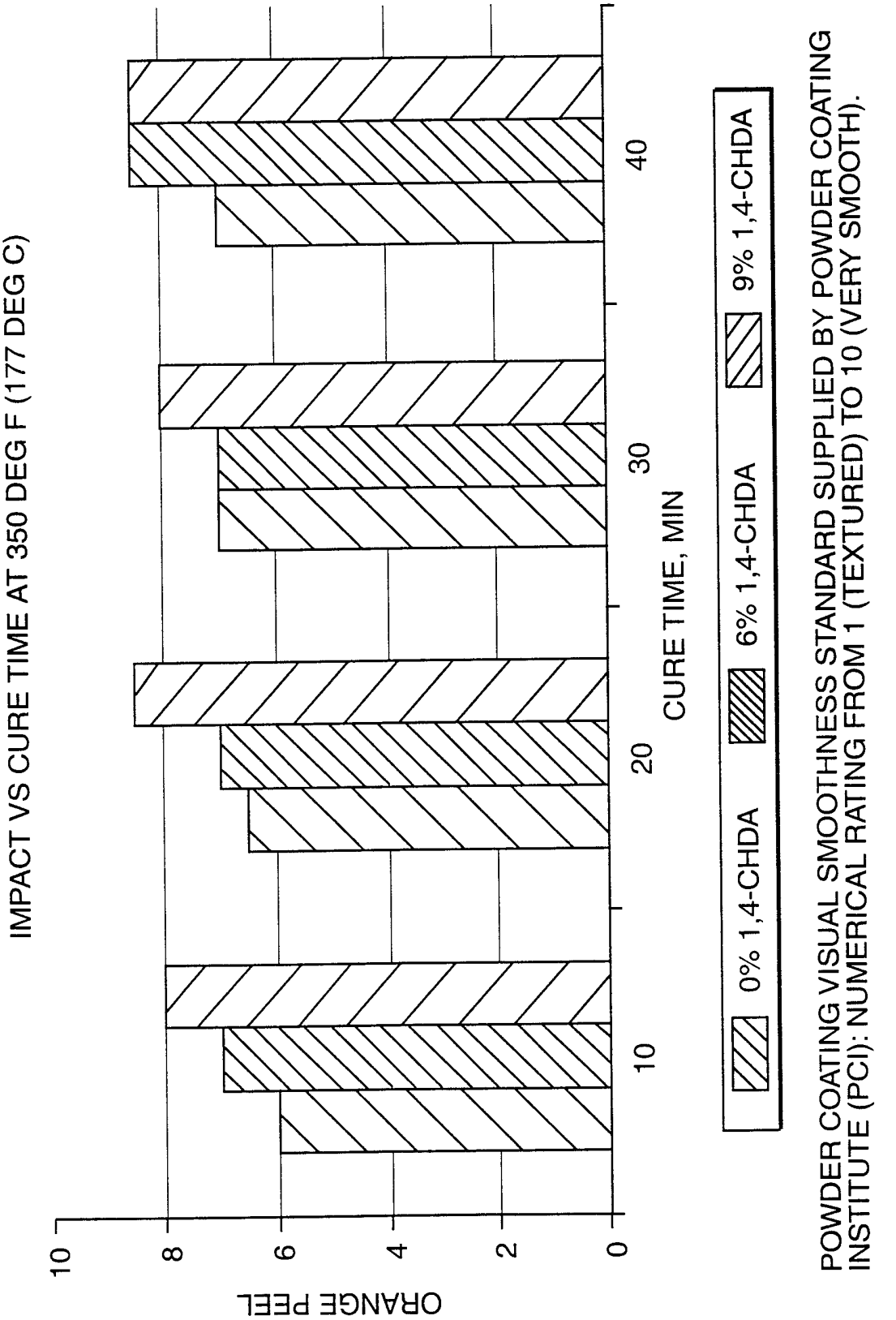
IMPACT VS CURE TIME AT 350 DEG F (177 DEG C)
ORANGE PEEL
0
2
4
6
8
10
CURE TIME, MIN
10
20
30
40
0% 1,4-CHDA
6% 1,4-CHDA
9% 1,4-CHDA
POWDER COATING VISUAL SMOOTHNESS STANDARD SUPPLIED BY POWDER COATING INSTITUTE (PCI): NUMERICAL RATING FROM 1 (TEXTURED) TO 10 (VERY SMOOTH).

FIG. 3

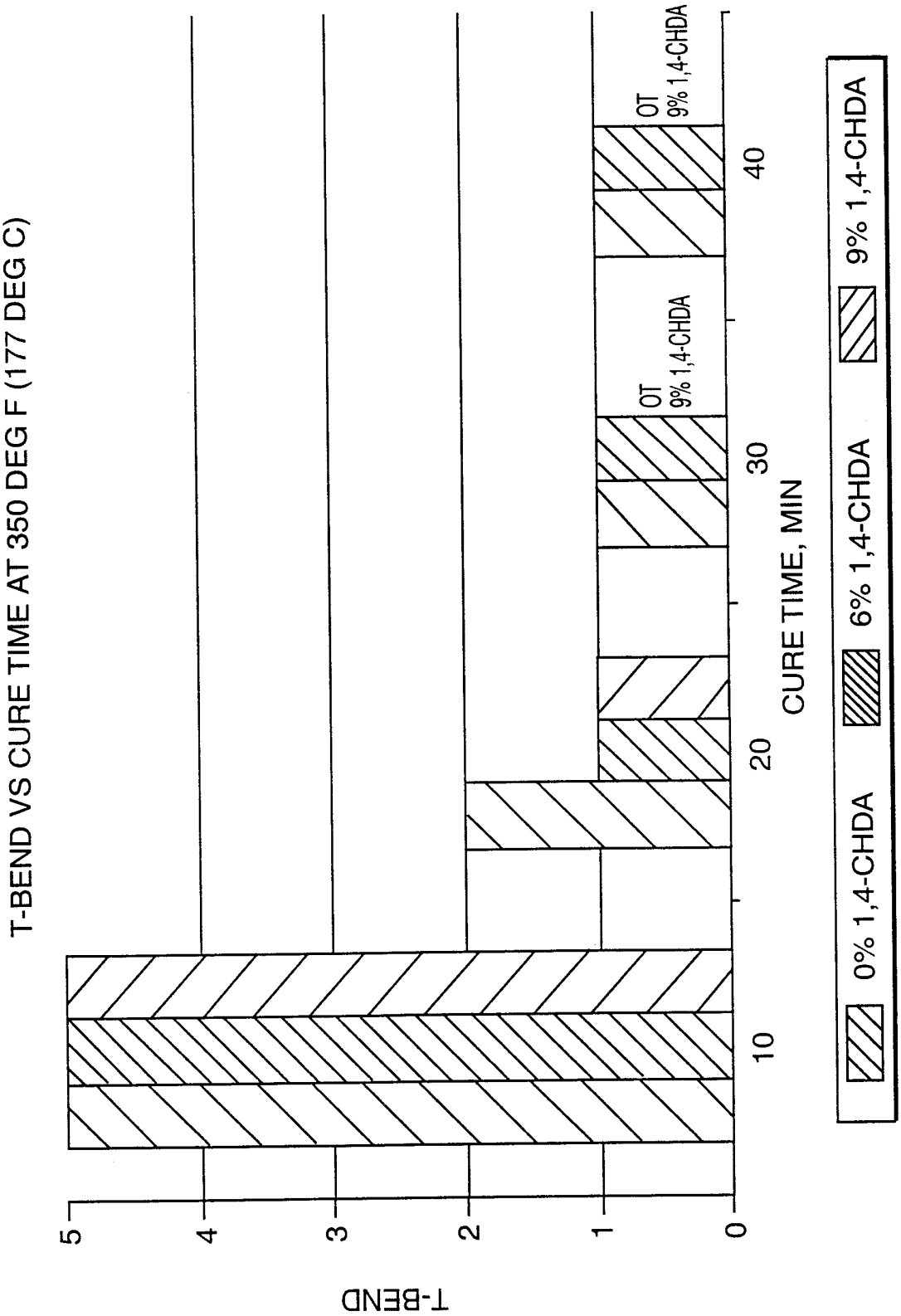
T-BEND VS CURE TIME AT 350 DEG F (177 DEG C)
T-BEND
0
1
2
3
4
5
10
20
30
40
CURE TIME, MIN
OT
9% 1,4-CHDA
OT
9% 1,4-CHDA
0% 1,4-CHDA
6% 1,4-CHDA
9% 1,4-CHDA

FIG. 4

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/27920

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09D167/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09D C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 26 11 691 B (CHEMISCHE WERKE HÜLS) 21 April 1977 (1977-04-21) claims 1-3	1,2
X	EP 0 408 465 A (EASTMAN KODAK CO) 16 January 1991 (1991-01-16) page 2, column 2, line 13 -page 3, column 3, line 39; claim 1	1,2
X	JOHNSON L K ET AL: "NEW MONOMERS FOR POLYESTER POWDER COATING RESINS" JCT. JOURNAL OF COATINGS TECHNOLOGY, vol. 65, no. 826, 1 November 1993 (1993-11-01), pages 19-26, XP002057331 ISSN: 0361-8773 page 20, right-hand column, line 17 -page 21, right-hand column, line 4	1,2

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

☒ Patent family members are listed in 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	Date of mailing of the international search report
7 October 1999	20/10/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Decocker, L

1

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 98/27920

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 2611691 B	21-04-1977	CH 628674 A	15-03-1982
		ES 456974 A	16-08-1978
		FR 2344609 A	14-10-1977
		GB 1573818 A	28-08-1980
		JP 52112631 A	21-09-1977
		US 4173658 A	06-11-1979
EP 0408465 A	16-01-1991	AT 102230 T	15-03-1994
		CA 2058760 A,C	27-12-1990
		DE 69006953 D	07-04-1994
		DE 69006953 T	22-09-1994
		DK 408465 T	28-03-1994
		EP 0479851 A	15-04-1992
		ES 2062472 T	16-12-1994
		JP 4505939 T	15-10-1992
		WO 9100306 A	10-01-1991