

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
20 September 2001 (20.09.2001)

PCT

(10) International Publication Number
WO 01/68602 A1

(51) International Patent Classification⁷: C07D 207/448,
C07C 271/24

(21) International Application Number: PCT/SE01/00511

(22) International Filing Date: 12 March 2001 (12.03.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0000812-8 13 March 2000 (13.03.2000) SE

(71) Applicant (for all designated States except US): **PERSTORP FLOORING AB** [SE/SE]; Strandridaregatan 8, S-231 25 Trelleborg (SE).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **ERICSSON, Jan** [SE/SE]; Rönnebyvägen 83, S-254 43 Helsingborg (SE).

(74) Agent: **STENBERG, Yngve**; c/o Perstorp AB, S-284 80 Perstorp (SE).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

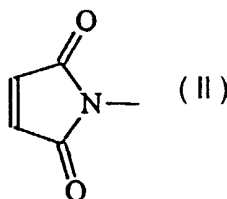
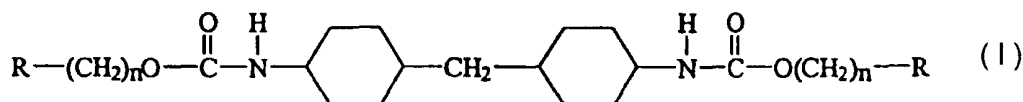
(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: A NEW OLIGOMER COMPOUND AND A USE THEREOF



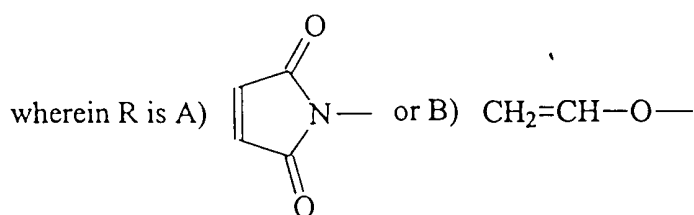
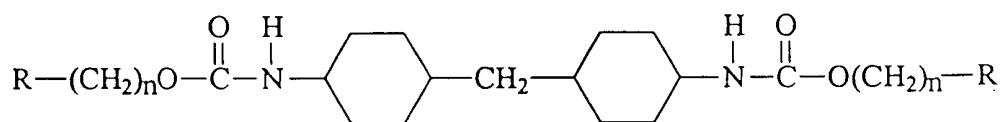
(57) Abstract: A new oligomer compound of formula (I) where a) R is (II) or b) R is $\text{CH}_2=\text{CH}-\text{O}-$ and where n is 2-6 and the use of the oligomer in UV curable lacquers and powder coatings.



WO 01/68602 A1

A NEW OLIGOMER COMPOUND AND A USE THEREOF

The present invention relates to a new oligomer compound having the formula



and wherein n is an integer between 2 and 6 inclusive.

and the use of the oligomer as a reactive component at the production of UV-curable photoinitiator free lacquers and powder coatings.

Such a production has got an increasing importance and means a so-called charge transfer photoinduced co-polymerization of donor/acceptor combinations of monomers.

These systems do not require the presence of a photoinitiator in order to initiate the polymerization process. Practically, the polymerization is induced by irradiation with UV light only, supplied by a high power lamp source. The basic requirement for the curing process to take place is that a suitable monomer/oligomer combination is present in the coating formulation. If such a combination consists of equal amounts of acceptor monomers (contains electron poor double bonds) together with donor monomers (contains electron rich double bonds), an efficient photopolymerization takes place.

There are several very attractive general characteristics connected with this new chemistry and among the most important are:

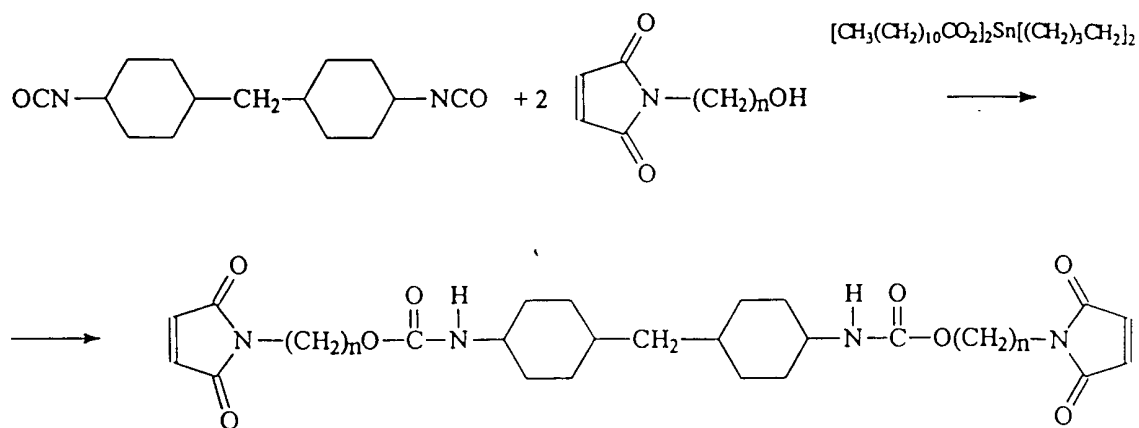
- * The inhibition of oxygen in the polymerization process is minimized.
- * Photoinitiator free; means that no residual fragments from the initiator are left in the cured coating. This is extremely important for outdoor stability and for materials in food contact.
- * The coating becomes photobleached upon curing, which basically means that the remaining photoactivity within the cured coating is minimized. This also means that thicker coatings can be cured more efficiently.

- * The adhesion can be expected to be optimized due to created covalent bonding between the coating and the coated surface. This is a consequence of the polymerization mechanism (curing) in charge transfer induced polymerization, where hydrogen abstraction is considerably involved. In particular, it is well known that hydrogens adjacent to heteroatoms like oxygen, nitrogen, etc. are easily abstracted. Consequently this is likely to take place if for example cellulose is included in the surface being coated by this polymerization process.
- * Non-yellowing coatings can be obtained.
- * The polymerization may be carried out at any optional temperature, which is advantageous for applications on heat sensitive materials and surfaces (furniture, etc.).
- * The polymerization may be carried out locally through a mask (compare photoimaging).
- * The total polymerization time for this type of system is relatively fast, and is in the order of fractions of seconds up to minutes for total conversion of reactive groups.
- * The investment cost is considered to be rather low.
- * The space occupied by the UV equipment is relatively at a minimum.

The performance determining unit(s), which represents the main part of the molecular weight, gives the main contribution to the final mechanical properties of the cured coating. Improvements regarding abrasion, scratch and water resistance, and also improved gloss and finish in general can be obtained by surface coating modification by UV technology. The final properties of the surfaces will be given by the characters of the functional groups within the molecules and their distribution, molecular weight, flexibility, etc.

It was quite surprising that the novel oligomer according to the present invention would work as a reactive component at the production of UV curable photoinitiator free lacquers and powder coatings.

A novel bis-maleimide oligomer according to one embodiment of the invention can be produced as schematically shown in fig. 1 below.

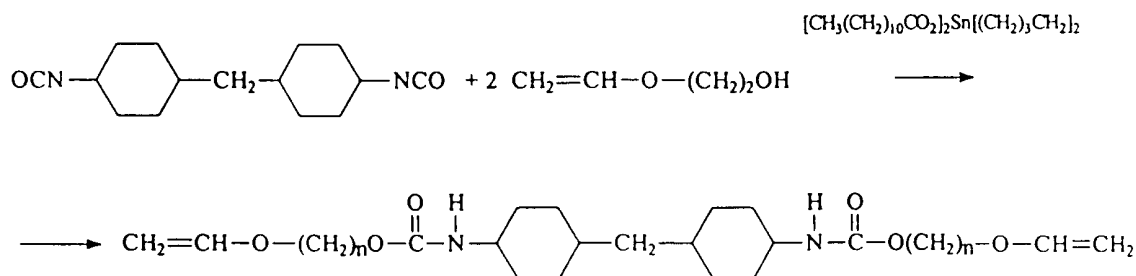
Fig. 1

where n is 2-6, preferably 2.

In one specific embodiment where n in above formula is 2, dicyclohexyl methane diisocyanate (Desmodur®W) was reacted with 2-hydroxyethylmaleimide (HEMI) in an organic solvent at catalytic conditions to form a novel bismaleimide oligomer called Bis-MI-DW below.

HEMI can per se be produced according to our copending Swedish patent application.

A novel vinyl ether oligomer according to another embodiment of the invention can be produced as schematically shown in Fig. 2 below.

Fig. 2

n is 2-6, preferably 2-4.

In one specific embodiment where n in above formula is 2, the vinyl ether oligomer was obtained by mixing Desmodur® W and 2-hydroxyethyl vinyl ether in an organic solvent at catalytic conditions to form a vinyl ether oligomer called BIS-VE-DW below.

The invention is further illustrated by the embodiment examples 1-3 below of which example 1 then relates to a reaction between Desmodur® W and HEMI. Example 2 illustrates a reaction between Desmodur® W and 2-hydroxyethyl vinyl ether. Example 3 illustrates the use of the new oligomers of examples 1 and 2 as reactive components at the production of a UV curable photoinitiator free lacquer.

Example 1

HEMI (5 g, 35.4 mmoles) was dissolved in acetone. The known catalyst shown on Fig. 1 was added and then dicyclohexylmethane diisocyanate (Desmodur® W) (4.45 g, 17 mmoles) was added dropwise at room temperature while stirring. The reaction mixture was then stirred over night. The acetone was evaporated and the remaining crude product was recrystallized from ethanol/acetone. The product was filtered and washed with ethanol and finally dried at vacuum. ¹H NMR (CDCl₃) confirmed (Table 1 below) the pure bismaleimide (BIS-MI-DW) of Fig. 1 where n is 2. The yield was 4.6 g (50 % based on Desmodur W).

Table 1

	Mw	mp °C	C %	H %	N %	O %
Measured value	544.6	35-75	59.9	6.9	10.3	23.7
Theoret. value			59.6	6.7	10.3	23.5

Example 2

2-hydroxyethyl vinyl ether (3.2 g, 35.4 mmoles) was dissolved in acetone. The reaction mixture was treated under dry conditions for 2 hours. The known catalyst shown on Fig. 2 was added and then dicyclohexylmethane diisocyanate (Desmodur® W) (4.45 g, 17 mmoles) was added dropwise while stirring at room temperature. The reaction mixture was then stirred over night. The acetone was evaporated and the remaining crude product was recrystallized from ethanol/acetone. The product was filtered and washed with ethanol and finally dried at vacuum. ¹H NMR (CDCl₃) confirmed (Table 2 below) the pure vinyl ether oligomer BIS-VE-DW of Fig. 2 where n is 2. The yield was 3.2 g (43 % based on Desmodur W).

Table 2

	Mw	mp °C	C %	H %	N %	O %
Measured value	438.2	30-55	63.3	8.9	6.5	21.9
Theoret. value			63.0	8.7	6.4	21.9

Example 3

A 50/50 molar ratio mixture was prepared from BIS-MI-DW and BIS-VE-DW.

Typically 5 mg of this mixture was loaded into an aluminium DSC sample pan. The temperature of the sample was increased from 0°C to 130°C at a rate of 100°C/min. The polymerization temperature was 130°C and this temperature was kept for 15 s, 30 s and 45 s respectively and then the lamp source was turned on for 60 s. A slight decrease in the polymerization exotherms could be seen, which means that the polymerization continuously proceeded with time above the melting temperature without additional initiation by the UV source.

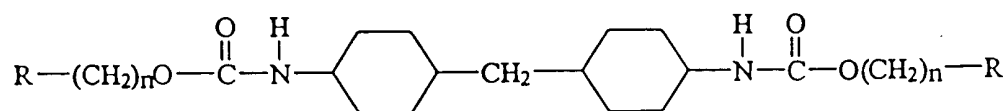
The polymerization proceeded efficiently without the addition of a photoinitiator system.

The products obtained were transparent and not discolored.

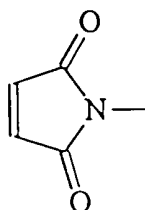
The invention is not limited to the embodiments shown since these can be modified in various ways within the scope of the invention. For instance a new oligomer of the present invention can be combined with another complementary compound when used for UV curable photoinitiator free lacquers and/or powder coatings.

CLAIMS

1. A new oligomer compound having the formula



where a) R is



or b) R is $\text{CH}_2 = \text{CH} - \text{O}$

and where n is 2-6

2. A compound according to claim 1, alternative a) where n is 2
3. A compound according to claim 1 alternative b) where n is 2-4.
4. Use of the compound according to any one of claims 1-3, as a reactive component in UV curable photoinitiator free lacquers and powder coatings.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 01/00511

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C07D 207/448, C07C 271/24

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)

IPC7: C07D, C07C

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

SE,DK,FI,NO classes as above

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

EPO-INTERNAL, WPI DATA, PAJ, CHEM.ABS DATA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 9939247 A1 (FIRST CHEMICAL CORPORATION), 5 August 1999 (05.08.99), page 8; page 9, claims 5,6 --	1-4
A	US 4217396 A (HECKLES, JOHN S.), 12 August 1980 (12.08.80), column 4, line 65 - column 5, line 18, the claims --	1-4
A	US 5387367 A (HAEBERLE, KARL ET AL), 7 February 1995 (07.02.95) --	1-4



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	"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
"A" document defining the general state of the art which is not considered to be of particular relevance	"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
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"&" document member of the same patent family
"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	

Date of the actual completion of the international search

11 June 2001

Date of mailing of the international search report

19-06-2001

Name and mailing address of the ISA

Swedish Patent Office
Box 5055, S-102 42 STOCKHOLM
Facsimile No. +46 8 666 02 86

Authorized officer

Gerd Strandell/EÖ
Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 01/00511

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0878482 A1 (DAINIPPON INK AND CHEMICALS, INC.), 18 November 1998 (18.11.98), the claims; the examples --	1-4
A	US 4751273 A (LAPIN, STEPHEN C. ET AL), 14 June 1988 (14.06.88) -- -----	1-4

INTERNATIONAL SEARCH REPORT

Information on patent family members

28/05/01

International application No.

PCT/SE 01/00511

Patent document cited in search report			Publication date	Patent family member(s)		Publication date
WO	9939247	A1	05/08/99	AU	2485199 A	16/08/99
				BR	9908044 A	28/11/00
				EP	1051665 A	15/11/00
				US	6066510 A	23/05/00
US	4217396	A	12/08/80	CA	1132290 A	21/09/82
				DE	3009988 A,C	13/11/80
				GB	2048913 A,B	17/12/80
				JP	55151027 A	25/11/80
US	5387367	A	07/02/95	CA	2055419 A	21/05/92
				DE	4036927 A	21/05/92
				DE	59108532 D	00/00/00
				EP	0486881 A,B	27/05/92
				ES	2096612 T	16/03/97
EP	0878482	A1	18/11/98	JP	11124403 A	11/05/99
				JP	11124404 A	11/05/99
				AU	1586499 A	18/10/99
				EP	1073685 A	07/02/01
				WO	9948928 A	30/09/99
US	4751273	A	14/06/88	CA	1304394 A	30/06/92
				US	RE33211 E	08/05/90