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(54) Title: LOW EMISSION TIN CATALYSTS

(57) Abstract: Plastic articles with low emission obtainable by polymerization, condensation, and/or cross-linking reaction including the use of metal catalysts wherein said metal catalyst has a low emissivity and is an organotin compound of the general formula R_2SnX_2 wherein R is a C_1 - C_8 -hydrocarbyl, X is a carboxylate group with 14-20 carbon atoms having at least one olefinic double bond. Moreover, the invention relates to the use of an organotin compound in the manufacture of plastic articles with low emissivity of said organotin compound.



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LOW EMISSION TIN CATALYSTS

BACKGROUND OF THE INVENTION

1. Field of the Invention

5 The present invention is related to the use of simple tin catalysts for the manufacturing of polyurethane foams with significantly reduced emission. More particularly, the present invention is related to the use of dialkyltin dicarboxylates R_2SnX_2 which are derived from carboxylic acids with particularly low emissivity, but provide high activity for catalyzing the reaction of isocyanates with polyols and
10 are highly compatible with the components of typical polyurethane formulations.

2. Description of Related Art

Tin compounds are well known as very effective catalysts for the manufacturing of polyurethanes, silicones, and polyesters.

Polyurethanes are basically manufactured by reaction of isocyanates with
15 polyols. Commonly used isocyanates are either aromatic or aliphatic di- or polyisocyanates, commonly used polyols are either polyetherpolyols or polyesterpolyols. Polyurethanes derived from aliphatic isocyanates have the general advantage of a better light stability than polyurethanes derived from aromatic isocyanates. Aliphatic isocyanates are generally less reactive than aromatic isocyanates and hence require
20 particularly strong catalysts; typically organotin catalysts are used, either alone or in combination with other catalysts.

Polymers, and in particular polyurethanes are of increasing importance in the manufacturing of modern car interiors. E.g. US 5656677 teaches the use of polyure-

thane foams derived from aliphatic isocyanates for the manufacturing of light stable car interiors.

A general problem connected with the use of plastics in car interiors is the emission of volatile organic compounds at elevated temperatures; said volatile organic compounds may form condensate films on the car windows, reducing the visual transparency and thereby causing the so called "fogging effect". The emissivity ("fogging") properties of a plastic material are determined either by the amount (by weight) of condensate formed under defined conditions, or by the loss of transparency caused by this condensate on a glass sheet.

Modern plastic materials are formulations of different base materials and additives, which can separately or in combination contribute to the fogging. Several efforts have been undertaken to reduce the fogging from plastic materials by optimising base materials and additives. In manufacturing of polyurethanes, e.g., major achievements have already been made by the introduction of purified polyesters (with reduced contents of volatile cyclic esters), and by the elimination of volatile antioxidant additives (see e.g.: EP 1153951 to Bayer; DE 19611670 to BASF; G. Baatz, S. Franyutti, Paper 9, UTECH '94 Conference, 1994, The Hague).

Facing increasingly tight regulations and consumer demands, further reductions of emission levels are required. After elimination of the previous main contributors, further improvement has to target the so-far neglected minor additives. Among said additives, particularly urethane catalysts contribute to the fogging.

Common catalysts for the urethane reaction are tertiary amines, stannous tin compounds, dialkyltin compounds, and compounds of other metals. The mentioned classes of catalysts may contribute to fogging either because of their own volatility

(e.g. amines), or by formation of volatile reaction products or degradation products.

Attempts have been reported to reduce the fogging properties of said catalysts: using catalysts which are reactive with isocyanates can lead to firm fixation of those catalysts in the polymer matrix and thereby reduce fogging. Examples for isocyanate-reactive amines are given e.g. in EP0799821 (and in the literature cited there).
Examples for isocyanate-reactive dialkyltin catalysts are given e.g. in EP0417605. A general drawback of such isocyanate-reactive catalysts is their reduced catalytic activity. Also, reaction with the isocyanate and incorporation into the polymer matrix changes the polymer properties.

A useful polyurethane catalyst must have high activity for the urethane reaction, and a sufficiently high selectivity for the urethane reaction over undesired side reactions. Furthermore, it should be storage stable, readily soluble in and compatible with the polyols and/or the isocyanates, and best be liquid at ambient temperature.

Dialkyltin compounds are well known for their strong catalytic power in polyurethane reactions, and are often indispensable in order to achieve the required material properties. Particularly useful are dialkyltin dicarboxylates. Among the dialkyltin dicarboxylate polyurethane catalysts, dimethyltin dicarboxylates are the strongest.

The most common carboxylate types for dialkyltin dicarboxylate catalysts are acetate, 2-ethylhexanoate, neodecanoate, and laurate. All dialkyltin carboxylates containing these carboxylate types contribute to fogging, not only by their own volatility, but particularly by the volatility of their degradation products, the most important being the corresponding carboxylic acids.

It can be reasonably expected that dialkyltin dicarboxylates derived from car-

carboxylic acids with longer alkyl chain than lauric acid would contribute less to fogging.

When simply the length of the carboxylate alkyl chain of a dialkyltin carboxylate is further increased (e.g. to saturated C₁₃ – C₁₇), one significant drawback is a decrease in the catalytic activity. Even more important drawbacks are the higher melting points (e.g. dimethyltin dimyristate approx. 70°C, dimethyltin dipalmitate approx. 80°C), the limited solubility in the typical main components of polyurethane formulations (i.e. polyols and/or isocyanates), and the limited compatibility with said main components.

Certain dialkyltin dicarboxylates having 13 or more carbon atoms and at least one olefinic double bond in the carboxylate alkyl chain are liquid at ambient temperature. Example are oleates, ricinoleates, linolates, and linoleates of dimethyltin and dibutyltin.

E.g., dimethyltin dioleate has been described as a heat stabiliser for PVC. No reference to polyurethane catalysis was made. Furthermore, GB1250498 teaches the use of a “basic dimethyltin oleate” as a curing catalyst for silicone rubbers. Said “basic dimethyltin oleate” is described as a “Harada complex” R₂SnA₂*R₂SnO; according to the modern state-of-the-art, it would be called 1,1',3,3'-tetramethyl-1,3-oleoyloxo-1,3,2-stannoxane.

E.g., dibutyltin dioleate has been described as a heat stabiliser for PVC, as solvent extraction agent for arsenate ions, as catalyst for esterifications, as catalyst for curing of silicones and as catalyst for curing of electrodeposition coatings. One publication (R. V. Russo, J. Cell. Plast. 12, (1976), 203) reported comparative testing of dibutyltin dioleate as polyurethane foam catalyst, but said article teaches

that dibutyltin dioleate is a particularly poor catalyst. No reference to emissivity was made.

E.g., use of dioctyltin diricinoleate has been reported as a polyurethane gelation catalyst, having reduced toxicity (US4332927 to Caschem). No reference to
5 emissivity was made.

SUMMARY OF THE INVENTION

The present invention is directed to low emission organotin compounds of the general formula



wherein R is C₁-C₈-hydrocarbyl, preferred are methyl and butyl, particularly preferred is methyl. X is a carboxylate group with 14-20 carbon atoms having at least one olefinic double bond, optionally substituted; preferred are oleate, ricinoleate, linoleate and linolenate; particularly preferred is oleate.

15 These compounds can be used as low emission catalysts in all fields of applications where organotin compounds are known to be useful as catalysts. Such fields include, but are not limited to, catalysis of esterification and transesterification reactions, condensation curing of RTV II silicones, curing of cataphoretic electrodeposition coatings, deblocking of blocked isocyanates, and, especially, curing of the
20 synthesis of polyurethanes by the reaction of isocyanates with polyols. Advantageous is particularly the low emissivity, but high activity for catalyzing the reaction of isocyanates with polyol, and high compatibility with the typical components of polyurethane formulations.

The invention is further directed to the use of said organotin compounds as catalysts for the production of low emission polyurethanes, particularly for use in car interiors. Especially preferred is the use of said catalysts for the production of polyurethanes derived from aliphatic isocyanates. The inventive catalysts can be
5 used alone or in combination with other catalysts.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is directed to low emission dialkyltin dicarboxylates of the general formula



R is a C₁-C₈-hydrocarbyl group. Typically, R is an aliphatic, saturated, unbranched, and not further substituted alkyl group, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl and octyl,.

Preferred alkyl groups are methyl, butyl, and octyl. Particularly preferred is methyl.

15 X is a carboxylate group derived from a carboxylic acid of the type



wherein R' is a C₁₃-C₁₉-hydrocarbyl group having one or more olefinic double bonds. Typically, R' is an aliphatic and unbranched alkenyl group; it may be further substituted, e.g., with one or more hydroxy groups. The alkenyl group may be
20 present in the cis-form, or in the trans-form, or a mixtures of both forms.

Preferred carboxylate groups are oleate, ricinoleate, linoleate and linolenate.

Particularly preferred is oleate.

Said low emission dialkyltin dicarboxylates can be synthesised from commercially available raw materials using standard synthesis methods for dialkyltin dicarboxy-

lates; e.g. by reaction of dialkyltin oxides with carboxylic acids, or by reaction of dialkyltin dichlorides with alkali carboxylates, or by reaction of dialkyltin dichlorides with carboxylic acids and bases, etc.

Said low emission dialkyltin dicarboxylates are liquid at room temperature, or melt at a low temperature slightly above room temperature. They are well soluble or mixable with polyetherpolyols and/or polyesterpolyols, which are widely used in the manufacturing of polyurethanes. Several of said low emission dialkyltin dicarboxylates are soluble in aliphatic and/or aromatic isocyanates, which are widely used in the manufacturing of polyurethanes. When dissolved, they have an excellent compatibility with said polyols and isocyanates, and do not precipitate from solution when stored at ambient temperature. When dissolved in isocyanates, they do not promote the formation of isocyanurates (isocyanate trimers), which is a common side-reaction of several other organotin catalysts.

Said low emission dialkyltin dicarboxylates have only very low volatility, and when degraded by hydrolysis, alcoholysis, acidolysis, or related reactions, the degradation products formed therefrom also have only very low volatility.

Said low emission dialkyltin dicarboxylates have a high but at least sufficient catalytic activity for catalyzing the reaction of isocyanates with alcohols to form urethanes.

20

The present invention is further directed to the use of said low emission dialkyltin dicarboxylates as catalysts for the production of low emission polyurethanes or polysilicones.

Said low emission polyurethanes or polysilicones produced by the use of said low emission dialkyltin dicarboxylates may appear in any form generally applicable to polyurethanes or polysilicones, as foams (rigid, flexible, high resiliency, integral, microcellular), RIM, RRIM, elastomers, coatings, etc.

5 By use of said low emission dialkyltin dicarboxylate catalysts, any general type of low emission polyurethane or polysilicone may be produced: foams (rigid, flexible, high resiliency, integral, microcellular ...), RIM, RRIM, elastomers, coatings, etc.

Preferred low emission polyurethanes are polyurethane foams.

10 Also preferred low emission polyurethanes are light stable polyurethanes derived from aliphatic isocyanates.

In manufacturing of low emission polyurethanes, the inventive low emission dialkyltin dicarboxylate catalysts can be used either alone or in combination with other catalysts. Especially, the well known synergy of dialkyltin compounds with
15 tertiary amines in the catalysis of the urethane reaction may be used to enhance the catalytic power of the inventive dialkyltin dicarboxylate catalysts. Also, in the production of water blown foam, tertiary amine catalysts may be used to speed and direct the reaction of isocyanates with water. Examples of further common catalysts which may be used together with the inventive catalysts include metal compounds
20 of stannous tin, Ti, Pb, Hg, Bi, Fe, Ni ...

In production of a polyurethane, the inventive low emission dialkyltin dicarboxylate catalysts can be either added prior to the reaction to the polyol component, or to the isocyanate component, or it can be admixed with other additives to form a master blend, or it can be added directly to the reaction mixture.

The isocyanates commonly used in the production of polyurethanes are well known to those skilled in the art. Examples include TDI (toluene diisocyanate, typically mixtures of the para-isomer, and the ortho-isomer), MDI (4,4'-diphenylmethane diisocyanate), polymeric MDI, IPDI (isophorone diisocyanate),
5 HDI (hexamethylene diisocyanate). The isocyanates are either used as such, or can also be used in a blocked form; when used in a blocked form, the blocking agent has to be cleaved of the isocyanate shortly before or during the processing.

The polyols commonly used in the production of polyurethanes are also well known to those skilled in the art. The most important classes are polyesterpolyols
10 and polyetherpolyols, which are basically polyester resp. polyether chains, terminated and optionally further substituted with isocyanate-reactive hydroxyl groups. E.g., the most commonly used polyetherpolyols are derived from ethylen oxide and/or propylene oxide.

The polyurethane may contain further additives (like blowing agents, foam
15 stabilisers, chain extenders, flame retardants, fillers, pigments etc.), known to those skilled in the art.

The present invention is further directed to the use of said low emission polyurethanes for use in car interiors.

The advantages and the important features of the present invention will be
20 more apparent from the following examples.

EXAMPLES

Glossary:

Polyol 1 is a 3500 MW polyether polyol, (OH-No. approx. 38) available from

Elastogran as Lupranol 3032.

Polyol 2 is a 4700 MW polyether polyol (OH-No. approx. 36), available from Shell Chemicals as Caradol ET 36-17.

Polyol 3 is a 6000 MW polyether polyol (OH-No. approx. 28), available from DOW Chemicals as Voranol CP 6001.

Polyol 4 is a 6000 MW polyether polyol (OH-No. approx. 32-35), available from DOW Chemicals as Voranol CP 1421.

Isocyanate 1 is toluene diisocyanate (TDI, mixture of 80% para, and 20% ortho).

Isocyanate 2 is Isophorone diisocyanate (IPDI).

Isocyanate 3 is 4,4'-Diphenylmethane diisocyanate (MDI 2447).

Foam stabiliser 1 is a silicone, available from Crompton Corp. as Niox RS-171.

Amine cocatalyst 1 is Diethanolamine (DEOA).

Amine cocatalyst 2 is blend of bis(dimethylaminoethyl)ether and dipropylene glycol, available from Crompton Corp. as Niox A-1.

15

Example 1

Preparation of the Catalysts

1 a) Preparation of dimethyltin dioleate from dimethyltin dichloride

Into a 3-neck glass flask, equipped with a mechanical stirrer, thermometer, dropping funnel, and pH glass electrode, were placed 44 g of dimethyltin dichloride (0.2 mol) and 44 g of water. The mixture was stirred until the dimethyltin dichloride is completely dissolved. 113 g of oleic acid (0.4 mol) were added and the mixture was heated to 60°C.

An aqueous NaOH solution (35.5% by weight) was placed into the dropping

funnel. While stirring, the NaOH solution was slowly added to the reaction mixture.

NaOH addition was stopped when a pH of approx. 6 had been reached.

The mixture was heated to approx. 80 °C, then the stirrer was stopped and the phases allowed to settle.

5 The phases were separated and the lower (aqueous) phase discarded. The organic phase was dried in a rotary evaporator at approx. 80°C / 1 mbar, and subsequently further dried with Na₂SO₄. Finally, 1% of Celite (a filter aid) were added and the product was filtered.

Yield: 136.6 g of dimethyltin dioleate (96.0% of theor.). The product was a
10 clear yellow liquid, and contained 15.8% Sn (theor. 16.7%), and 0.0% Cl (theor. 0.0%).

1 b) Preparation of dimethyltin dioleate from dimethyltin oxide

Into a 3-neck glass flask, equipped with a mechanical stirrer, thermometer, and a vacuum connector, were placed 57.7g of dimethyltin oxide (0.35 mol) and
15 197.6 g of oleic acid (0.7 mol). While stirring, the mixture was heated to 40°C, and a vacuum of 10 mbar was applied. During 1 hour the temperature was slowly risen to 70°C, and was subsequently held for another hour. Subsequently a vacuum of 1 mbar was applied, and the reaction mixture was further stirred for 1 more hour.

The vacuum was broken, and the reaction mixture was allowed to cool to
20 room temperature. Finally, 1% of Celite (a filter aid) were added and the product was filtered.

Yield: 245.8 g of dimethyltin dioleate (98.7% of theor.). The product contained 16.5% Sn (theor. 16.7%).

It was a clear yellow liquid, having a viscosity of 100 mPa*s. It was miscible with Polyols 1, 2, and 3. It was readily soluble in Isocyanates 1, 2, and 3.

A 1% solution (by weight) of the product in Isocyanate 2 was prepared and stored at 25°C. After 3 weeks the solution was still clear, no solid material had formed and the infrared spectrum of the solution did not show the carbonyl band of an isocyanurate.

1 c-g) Preparation of further dialkyltin dicarboxylates

Following the procedure described in example 1 b, the following materials were synthesised (see table 1):

10

Table 1

Experiment	Dialkyltin oxide	Carboxylic acid	Product	Yield (% of theor.)
1c	Dibutyltin oxide	Oleic acid	Dibutyltin oleate	97.6
1d	Dioctyltin oxide	Oleic acid	Dioctyltin oleate	97.2
1e	Dimethyltin oxide	Ricinoleic acid	Dimethyltin ricinoleate	96.3
1f	Dimethyltin oxide	Linoleic acid	Dimethyltin linoleate	96.9
1g	Dimethyltin oxide	Linolenic acid	Dimethyltin linolenate	98.1

Example 2

Catalyst Activity Tests

Viscosity Measurement in Elastomers based on aromatic Isocyanates (TDI)

80 g of Polyol 1 were placed at room temperature into a dry 100 mL wide-neck glass bottle. 0.0002 mol of the respective organotin catalyst were added. The mixture was stirred for 2 minutes to dissolve the catalyst.

0.036 mol of Isocyanate 1 were added, and the mixture stirred for 2 more minutes. The bottle was then placed under a Brookfield rotary viscosimeter. The raw mixture had a Brookfield viscosity of $\ll 1$ Pa*s. Sample temperature and viscosity were recorded until the mixture became too viscous for further measurement (> 25 Pa*s). In each experiment, the time of isocyanate addition to the polyol considered as the start of the reaction ($t = 0$ min). Results are summarised in table 2.

Table 2

Example Catalyst	2a Dimethyltin dioleate	2b Dibutyltin dilaurate (comparison)	2c Dimethyltin dineodecanoate (comparison)	2d No Catalyst
Time (min)	Viscosity (mPa*s)	Viscosity (mPa*s)	Viscosity (mPa*s)	Viscosity (mPa*s)
0				
2				
4	800	600	1100	600
6	1000	800	1300	600
8	1300	1000	1900	600
10	1800	1400	2900	600
12	2400	1800	4700	600
14	3200	2200	7800	600

16	4100	2900	14000	600
18	5300	3600	> 25000	600
20	7200	4400		600
22	9200	5500		600
24	12100	6800		600
26	16100	8400		600
28	21700	10300		600
30	> 25000	13100		600

Example 3

Catalyst Activity Tests

Viscosity Measurement in Elastomers based on aromatic Isocyanates (TDI)

5 Example 2 was repeated with the difference that after mixing of all components at room temperature the glass bottle was immersed in an oil heating bath. The oil bath was heated at a nearly constant rate from room temperature to 100°C, and was then held at this temperature (heating to 100°C takes typically approx. 20 minutes). In each experiment, the time of isocyanate addition to the polyol considered as the start of the reaction (t = 0 min). Results are summarised in table 3.

10

Table 3

Example Catalyst	3a Dimethyltin dioleate		3b Dibutyltin dilaurate (comparison)		3c Dimethyltin dineodecanoate (comparison)		3d No Catalyst	
	Viscosity (mPa*s)	Temp. (°C)	Viscosity (mPa*s)	Temp. (°C)	Viscosity (mPa*s)	Temp. (°C)	Viscosity (mPa*s)	Temp. (°C)
0								
2								
4	800	38	900	37	1200	34	600	34
6	900	48	1000	46	1300	40	500	42
8	900	58	1000	54	1500	48	500	51
10	1000	65	1000	63	1900	59	400	59
12	1300	72	1400	73	3200	71	200	67
14	2400	80	3100	83	6800	83	<200	77
16	5000	90	6600	87	> 25000	91	<200	84
18	> 25000	95	> 25000	91			<200	92
20							<200	95

Example 4

Viscosimetric Catalyst Activity Tests

Elastomer based on aliphatic Isocyanate(IPDI)

5 75 g of Polyol 2 were placed at room temperature into a dry 100 mL wide-neck glass bottle.

 In a dry glass flask, 0.00016 mol of the respective organotin catalyst and 5,6 g of Isocyanate 2 are mixed by stirring.

 The isocyanate/catalyst mixture is added to the polyol at room temperature,
10 and the mixture stirred for 2 more minutes. The glass bottle was immersed in an oil heating bath, placed under a Brookfield rotary viscosimeter. The oil bath was heated at a nearly constant rate from room temperature to 100°C, and was then held at this temperature (heating to 100°C takes typically approx. 20 minutes). The raw mixture had a Brookfield viscosity of $\ll 1$ Pa*s. Sample temperature and viscosity were
15 recorded until the mixture became too viscous for further measurement (> 25 Pa*s).
In each experiment, the time of isocyanate addition to the polyol considered as the start of the reaction ($t = 0$ min). Results are summarised in table 4.

Table 4

Example Catalyst	4a Dimethyltin dioleate		4b Dibutyltin dioleate		4c Dibutyltin dilaureate (comparison)		4d Dimethyltin dineodecanoate (comparison)		3e No Catalyst	
	Viscosity (mPa*s)	Temp. (°C)	Viscosity (mPa*s)	Temp. (°C)	Viscosity (mPa*s)	Temp. (°C)	Viscosity (mPa*s)	Temp. (°C)	Viscosity (mPa*s)	Temp. (°C)
0										
1										
2										
3	600	34	900	35	700	33	500	38	400	36
4	500	39	800	40	500	38	700	43	<200	39
5	400	41	600	43	700	43	600	48	<200	42
6	400	47	200	49	700	50	500	54	<200	47
7	700	55	700	57	700	58	800	61	<200	53
8	900	64	1100	66	600	67	1100	69	<200	60
9	1300	72	1100	72	1200	74	1800	76	<200	66
10	2100	78	1800	78	1800	80	3400	81	<200	71
11	4300	83	4200	83	2600	84	8400	85	<200	76
12	9700	87	7900	87	5200	87	>25000	88	<200	80
13	>25000	89	>25000	90	11900	90			<200	83
14					>25000	92			<200	86
15									<200	88

Example 5

Preparation of Polyurethane Foams

Water blown Foams from Polyether Polyols and aromatic Isocyanate (MDI)

100 g of Polyol 3 and 2 g of Polyol 4 were mixed and placed into a cardboard cup.

A master blend was made of 3.6 g of water, 0.5 g of Foam stabiliser 1, 0,6 g of Amine cocatalyst 1, and 0.15 g of Amine cocatalyst 2. The blend was added to the polyol and mixed.

0.5 g of the resp. organotin catalyst was added to the mixture and the mixture was stirred for 2 minutes.

61.8 g of Isocyanate 3 (index 100) were quickly added to the mixture. The mixture was stirred for 10 seconds, and than poured into a cardboard box.

A polyurethane foam formed and expanded. Cream time and rise time of the foam were recorded.

Results are summarised in Table 5.

Table 5

Example Catalyst	5a Dimethyltin dioleate	5b Dibutyltin dilaurate (comparison)	5c Dimethyltin dineodecanoate (comparison)
Cream Time (s)	10	10	8
Rise Time (s)	54	44	45

Example 6

Determination of the Fogging of Catalysts by Gravimetry

A dry, clean round piece of aluminum foil (diameter 103 mm, thickness 0.03 mm) was weighed. 5 g of the resp. liquid organotin catalyst and 0.5 g of water were placed onto the bottom of a dry and clean glass beaker (inner diameter 80 mm, outer diameter 90 mm).

A silicone rubber ring was fitted to the neck of the beaker, the aluminum foil was placed on top of it, and covered with a glass sheet (110 x 110 x 3 mm). The beaker was hang into a thermostated glycerol heating bath in such a way, that the glass sheet was 60 mm above the glycerol level. An aluminum cooling block (connected to another thermostat) was placed onto the glass sheet. For 16 hours, a glycerol bath temperature of 100°C, and a cooling block temperature of 21°C was maintained. Subsequently, the aluminum foil was placed into a dessicator and kept there for 1 hour at room temperature over silica.

The aluminum foil was then weighed again, and the weight difference (in mg) was recorded as mg of fogging condensate.

Results are summarised in Table 6.

Table 6

Example Catalyst	6a Dimethyltin dioleate	6b Dibutyltin dilaurate (comparison)	6c Dimethyltin dineodecanoate (comparison)
Fogging condensate (mg)	21.5	194.2	234.4

Example 7**Determination of the Fogging of Polyurethane Foams by Gravimetry****Foams based on Polyether Polyols and aromatic Isocyanate (MDI)**

The foam samples prepared in Example 5 were cut into round disks (each 80 mm in diameter, and 10 g of weight). Example 6 was repeated with the difference, that instead of 5 g of the resp. liquid organotin catalyst and 0.5 g of water, now the resp. foam disks were placed onto the bottom of the glass beaker.

Results are summarised in Table 7.

Table 7

Example Foam sample	7a Foam prepared with Dimethyltin dioleate	7b Foam prepared with Dibutyltin dilaurate (comparison)	7c Foam prepared with Dimethyltin dodecanoate (comparison)
Fogging condensate (mg)	1.15	1,51	3.45

In view of the many changes and modifications that can be made without departing from principles underlying the invention, reference should be made to the appended claims for an understanding of the scope of the protection to be afforded the invention.

Claims

1. Plastic articles with low emission obtainable by polymerization, condensation, and/or cross-linking reaction including the use of metal catalysts wherein said metal catalyst has a low emissivity and is an organotin compound of the general formula



wherein R is a C₁-C₈-hydrocarbyl, X is a carboxylate group with 14-20 carbon atoms having at least one olefinic double bond with the proviso that

- a) said plastic article is not made of polyvinyl chloride including dimethyltin dioleate or dibutyltin dioleate as heat stabilizer,
 - b) said organotin compound is not dibutyltin dioleate and said plastic article is not a polyurethane foam,
 - c) said organotin compound is not dibutyltin diricinoleate and said plastic article is not a polyurethane,
 - d) said organotin compound is not dibutyltin dioleate and said plastic article is not polyester or cured silicone.
2. Plastic article according to claim 1, wherein in said organotin compound R is an aliphatic, saturated alkyl group.
 3. Plastic article according to claim 2, wherein in said organotin compound at least one alkyl group is methyl, butyl, or octyl.

4. Plastic article according to anyone of claims 1 to 3, wherein in said organotin compound X is a carboxylate group derived from a carboxylic acid of the type



wherein R' is a C₁₃-C₁₉-hydrocarbyl group having one or more olefinic double bonds.

5. Plastic article according to claim 4, wherein said olefinic double bonds are isolated double bonds.
6. Plastic article according to claim 4 or 5, wherein R' is an aliphatic, substituted or unsubstituted alkenyl group.
7. Plastic article according to anyone of the preceding claims, wherein in said organotin compound said hydrocarbyl and/or carboxylate group is a linear group.
8. Plastic article according to anyone of the preceding claims, wherein in said organotin compound the carboxylate group is selected from:
- oleate, ricinoleate, linoleate and linoleate.
9. Plastic article according to anyone of the preceding claims, wherein said organotin compound is liquid at room temperature (20-25°C).
10. Plastic article according to anyone of the preceding claims, wherein said plastic article is made of polyurethane or polysilicone.
11. Plastic article according to anyone of the preceding claims, wherein said plastic article is a foamed article.

12. Plastic article of claim 11, wherein the polyurethane foam is derived from aliphatic isocyanate.
13. Use of an organotin compound according to anyone of claims 1 to 10 in the manufacture of plastic articles with low emissivity of said organotin compound.
14. The use of claim 13, wherein said plastic article is a foamed article.
15. The use of claim 13 or 14, wherein said plastic article is made of polyurethane or polysilicone.
16. The use of any of claims 13 to 15 wherein said organotin compound is dioctyltin dicarboxylate.
17. The use of claim 16 wherein the carboxylate group is selected from:

oleate, ricinoleate, linoleate and linoleate.
18. The use of claim 17 wherein the organotin compound is dioctyl dioleate.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/06265

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G18/24 C08G77/00

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 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)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	US 4 332 927 A (SIMONE DOMINIC) 1 June 1982 (1982-06-01) cited in the application Run No. 33-35 column 2, line 29 ---	1-18
X	GB 1 250 498 A (COSAN CHEMICAL CORPORATION) 20 October 1971 (1971-10-20) cited in the application claim 6 claim 1 ---	1-18
X	GB 1 141 708 A (ALLIED CHEM) 29 January 1969 (1969-01-29) page 3, line 27 - line 55 --- -/--	1-18

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

☒ Patent family members are listed in annex.

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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

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INTERNATIONAL SEARCH REPORT

International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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