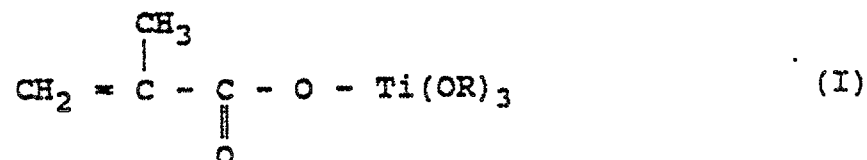


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UNSATURATED ORGANOMETALLIC COMPOUNDS DERIVED FROM
TITANIUM AND PROCESS FOR THEIR PREPARATION

The present invention relates to new unsaturated organometallic compounds derived from titanium and to a process enabling them to be prepared. These new compounds can be applied to the manufacture of new polymers which can in particular form part of the formulation of paints, in particular of marine paints.

The subject-matter of the present invention is therefore firstly unsaturated organometallic compounds derived from titanium, denoted by the formula (I):



in which R denotes a tert-butyl, tert-amyl or 2-ethylhexyl radical.

To prepare the compounds (I) methacrylic acid is reacted with a tetraalkoxytitanium $\text{Ti}(\text{OR})_4$, where R = isopropyl or tert-butyl, to obtain the corresponding compound (I), or with $\text{Ti}(\text{OR})(\text{OtAm})_3$, where R = isopropyl or tert-butyl and tAm = tert-amyl, to obtain a compound (I) with R = tert-amyl, the compounds (I) with R = isopropyl or tert-butyl furthermore denoting intermediate synthesis products which can be reacted with tert-amyl alcohol or with 2-ethylhexanol, to obtain a compound (I) in which R denotes tert-amyl or 2-ethylhexyl respectively.

In particular, methacrylic acid is reacted with $\text{Ti}(\text{OR})_4$ or $\text{Ti}(\text{OR})(\text{OtAm})_3$ with R = isopropyl or tert-butyl and tAm = tert-amyl in stoichiometric conditions at a temperature of 40-80°C, at a pressure of 13.3-66.7 kPa (100-500 mmHg), the methacrylic acid being added to $\text{Ti}(\text{OR})_4$ or $\text{Ti}(\text{OR})(\text{OtAm})_3$, if appropriate in a solvent

such as toluene, the alcohol ROH or the ROH-solvent azeotrope released by the reaction being gradually distilled, and, when it is intended to obtain the compound of formula (I) with R = tert-amyl or 2-ethyl-hexyl from the synthesis intermediates, the reaction is continued by introducing tert-amyl alcohol or 2-ethyl-hexanol into the mixture in a proportion of approximately 3 moles per 1 mole of intermediate compound (I) at a pressure of 13.3-66.7 kPa (100-500 mmHg) and at a temperature of 40-80°C, while distilling the isopropanol or the tert-butanol released by the reaction.

$\text{Ti}(\text{OR})(\text{OtAm})_3$ (R = isopropyl or tert-butyl and tAm = tert-amyl) can be obtained by reacting $\text{Ti}(\text{OR})_4$ with tert-amyl alcohol in a proportion of 3 moles of the latter per 1 mole of $\text{Ti}(\text{OR})_4$, at a pressure of 13.3-66.7 kPa (100-500 mmHg), at a temperature of 40-80 °C, while distilling the isopropanol or tert-butanol released by the reaction.

The following examples illustrate the present invention without, however, limiting its scope.

EXAMPLE 1 : Preparation of tri-tert-butoxytitanium methacrylate

Into a 100-ml three-necked round bottom flask equipped with an isobaric dropping funnel, a thermometer and a distillation column are introduced 25.53 g of tetra- tert-butoxytitanium. The reaction is successfully conducted at 18 kPa (135 mmHg), the reaction flask being placed in an oil bath at 55°C. 6.13 g of methacrylic acid are added dropwise with magnetic stirring. The tert-butanol released by the reaction is gradually distilled (boiling point: 41°C/19 kPa (140 mmHg)). The reaction is followed by weighing the distillate released. At the end of the reaction tri-tert-butoxytitanium methacrylate is recovered in the round bottom flask: it is a slightly viscous, pale yellow liquid.

Yield : 97.5 %

^1H NMR analysis

δ_{H} (C_6D_6) in ppm :

1.4 [S, 27H, $-\text{CH}_3$]

1.7	[s, 3H, -CH ₃]
5.2 and 6.3	[t, 2H, =CH ₂].

¹³C NMR analysis

δ_C (C₆D₆) in ppm :

17.0	[-CH ₃]
32.1	[-CH ₃]
79.4	[Ti-O-C]
127.2	[=CH ₂]
136.8	[=C]
185.2	[-CO ₂ -]

IR analysis (film)

2972,	2926 cm ⁻¹ :	-CH ₃ (s)
	1645 cm ⁻¹ :	C=C (w)
1588,	1525 cm ⁻¹ :	-COO- asym (m)
	1426 cm ⁻¹ :	-COO- sym (m)
	1005 cm ⁻¹ :	C-O (s, broad)
	638 cm ⁻¹ :	Ti-O (m)

EXAMPLE 2 : Preparation of tri(2-ethylhexoxy)titanium methacrylate

A first stage is conducted, which consists in preparing triisopropoxytitanium methacrylate as synthesis intermediate according to a procedure described in Tr. Inst. Khim., Akad. Nauk. SSR Ural. Filial. 13 39-47 (1968).

The second stage of the synthesis is carried out immediately following the first, at a reduced pressure of 15 kPa (110 mmHg): 19.54 g of 2-ethylhexanol are introduced dropwise with heating and with magnetic stirring, using the second dropping funnel, into the reaction flask containing the synthesis intermediate. The isopropanol released by the reaction is distilled rapidly.

The expected product is recovered in the reaction flask; it is liquid, viscous and pronounced yellow in colour.

Yield: 98.5 %

¹H NMR analysis

δ_H (C₆D₆) in ppm :

0.9-1.1	[m, 18H, -CH ₃]
1.1-1.9	[m, 25H, -CH ₂ - and CH]
2.1	[s, 3H, -CH ₃]
4.6	[t, 6H, -CH ₂ -]
5.4 and 6.5	[t, 2H, =CH ₂]

¹³C NMR analysis

δ_C (C₆D₆) in ppm :

11.4	[-CH ₃]
14.4	[-CH ₃]
18.9	[-CH ₃]
23.5	[-CH ₂ -]
23.7	[-CH ₂ -]
29.8	[-CH ₂ -]
30.6	[-CH ₂ -]
43.2	[CH]
79.6	[O-CH ₂]
124.8	[=CH ₂]
139.2	[=C]
173.9	[-CO ₂ -]

IR analysis (film) :

2958, 2928, 2872 and 2859 cm ⁻¹	: -CH ₂ - and -CH ₃ -(S)
1644 cm ⁻¹	: C=C (w)
1559 cm ⁻¹	: -COO- asym (m)
1423 cm ⁻¹	: -COO- sym (m)
1088 cm ⁻¹	: C-O (m, broad)
673, 618 cm ⁻¹	: Ti-O (m)

EXAMPLE 3 : Preparation of tri-tert-amyl oxytitanium methacrylate

First stage

14.21 g of tetraisopropoxytitanium are introduced into a 100-ml three-necked round bottom flask equipped with a multiple adaptor with two isobaric dropping funnels, a thermometer and a distillation column. A reduced pressure of 20 kPa (150 mmHg) is then applied to the assembly and the flask is placed in a bath at 55°C. 13.22 g of alcohol are added dropwise with magnetic

stirring and the isopropanol released by the reaction is distilled.

Second stage

The second stage of the synthesis is carried out immediately following the first, at a reduced pressure of 20 kPa (150 mmHg): 4.30 g of methacrylic acid are introduced dropwise with heating and with magnetic stirring, using the second dropping funnel. The isopropanol released by the reaction is distilled rapidly.

At the end of the reaction the round bottom flask contains a slightly viscous, light yellow liquid.

Yield: 95.8 %

^1H NMR analysis

δ_{H} (C_6D_6) in ppm :

1.0	[t, 9H, $-\text{CH}_3$]
1.3	[s, 18H, $-\text{CH}_3$]
1.5	[m, 6H, $-\text{CH}_2-$]
1.8	[s, 3H, $-\text{CH}_3$]
5.2 and 6.3	[t, 2H, $=\text{CH}_2$]

^{13}C NMR analysis

δ_{C} (C_6D_6) in ppm :

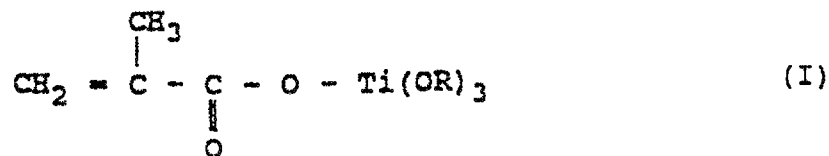
9.1	$[-\text{CH}_3]$
17.0	$[-\text{CH}_3]$
29.6	$[-\text{CH}_3]$
37.2	$[-\text{CH}_2-]$
80.0	$[\text{Ti}-\text{O}-\text{C}]$
127.1	$[=\text{CH}_2]$
136.8	$[=\text{C}]$
185.1	$[-\text{CO}_2-]$

IR analysis (film)

2970, 2926 cm^{-1}	: $-\text{CH}_3$ (s)
1644 cm^{-1}	: $\text{C}=\text{C}$ (w)
1587, 1554, 1517 cm^{-1}	: $-\text{COO}-$ asym (m)
1423 cm^{-1}	: $-\text{COO}-$ sym (m)
1003 cm^{-1}	: $\text{C}-\text{O}$ (s, broad)
668, 623, 587 cm^{-1}	: $\text{Ti}-\text{O}$ (m)

CLAIMS

1 - Unsaturated organometallic compound derived from titanium, denoted by the formula (I) :



in which R denotes a tert-butyl, tert-amyl or 2-ethylhexyl radical.

2 - Process for manufacture of a compound of formula (I) as defined in Claim 1, characterized in that methacrylic acid is reacted with a tetraalkoxytitanium $\text{Ti}(\text{OR})_4$, where R = isopropyl or tert-butyl, to obtain a corresponding compound (I), or with $\text{Ti}(\text{OR})(\text{OtAm})_3$, where R = isopropyl or tert-butyl and tam = tert-amyl, to obtain a compound (I) with R = tert-amyl, the compounds (I) with R = isopropyl or tert-butyl furthermore denoting intermediate synthesis products which can be reacted with tert-amyl alcohol or with 2-ethylhexanol, to obtain a compound (I) in which R denotes tert-amyl or 2-ethylhexyl respectively.

3 - Process according to Claim 2, characterized in that methacrylic acid is reacted with $\text{Ti}(\text{OR})_4$ or $\text{Ti}(\text{OR})(\text{OtAm})_3$ with R = isopropyl or tert-butyl and tAm = tert-amyl in stoichiometric conditions at a temperature of 40-80°C, at a pressure of 13.3-66.7 kPa (100-500 mmHg), the methacrylic acid being added to $\text{Ti}(\text{OR})_4$ or $\text{Ti}(\text{OR})(\text{OtAm})_3$, if appropriate in a solvent such as toluene, the alcohol ROH or the ROH-solvent azeotrope released by the reaction being gradually distilled, and, when it is intended to obtain the compound of formula (I) with R = tert-amyl or 2-ethylhexyl from synthesis intermediates, the reaction is continued by introducing tert-amyl alcohol or 2-ethylhexanol into the mixture in a proportion of approximately 3 moles per 1 mole of intermediate compound (I) at a pressure of 13.3-66.7 kPa



(100-500 mmHg) and at a temperature of 40-80°C, while distilling the isopropanol or the tert-butanol released by the reaction.

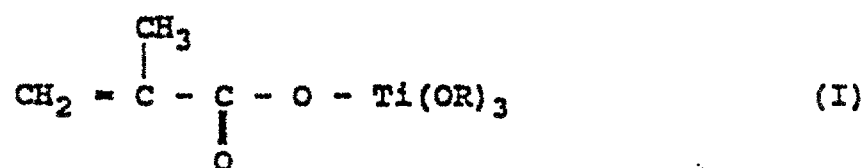
4 - Process according to Claim 3, characterized in that $\text{Ti}(\text{OR})(\text{OtAm})_3$ (R = isopropyl or tert-butyl and tAm = tert-amyl) is obtained by reacting $\text{Ti}(\text{OR})_4$ with tert-amyl alcohol in a proportion of 3 moles of the latter per 1 mole of $\text{Ti}(\text{OR})_4$, at a pressure of 13.3-66.7 kPa (100-500 mmHg) at a temperature of 40-80 °C, while distilling the isopropanol or tert-butanol released by the reaction.



ABSTRACT

UNSATURATED ORGANOMETALLIC COMPOUNDS DERIVED FROM
TITANIUM AND PROCESS FOR THEIR PREPARATION

These compounds are denoted by the formula (I) :



in which R denotes a tert-butyl, tert-amyl or 2-ethylhexyl radical.

To prepare them, methacrylic acid is reacted with a tetraalkoxytitanium $\text{Ti}(\text{OR})_4$, where R = isopropyl or tert-butyl, to obtain a corresponding compound (I), or with $\text{Ti}(\text{OR})(\text{OtAm})_3$, where R = isopropyl or tert-butyl and tAm = tert-amyl, to obtain a compound (I) with R = tert-amyl, the compounds (I) with R = isopropyl or tert-butyl furthermore denoting intermediate synthesis products which can be reacted with tert-amyl alcohol or with 2-ethylhexanol, to obtain a compound (I) in which R denotes tert-amyl or 2-ethylhexyl respectively.