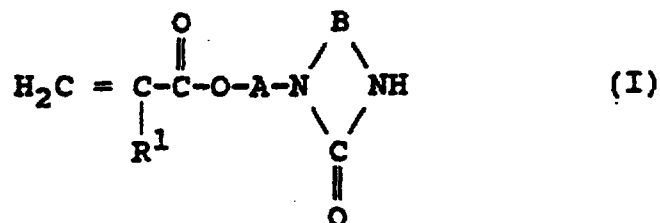


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PROCESS FOR THE MANUFACTURE OF ALKYLIMIDAZOLIDONE (METH) - ACRYLATES

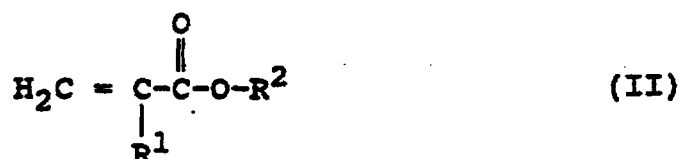
The present invention relates to a process for the manufacture of a compound of formula:



5 in which:

- R^1 represents hydrogen or methyl;
- A and B each independently represent a straight or branched hydrocarbon chain having from 2 to 5 carbon atoms,

10 by reaction of at least one (meth)acrylate of formula:



in which:

- R^1 has the abovementioned meaning; and
 - R^2 represents a C_1 - C_4 alkyl group,
- with a heterocyclic alcohol of formula:



15 in which A and B have the abovementioned meanings.

These compounds of formula (I) are known for their role in the formation of polymers useful as coatings and adhesives, for the treatment of paper and textiles, in particular by United States Patent

US-A-2,871,223, as well as for their uses as leather treatment agents, and in the production of emulsion paints. Ethylimidazolidone methacrylate (EIOM) is mainly used in paints as a wet-adhesion promoter.

5 The synthesis of EIOM by transesterification has already formed the subject of a great many patents, which differ from one another in the nature of the catalyst used. Solid or partly solid catalysts, which make it possible to operate at a temperature below 100°C while
10 giving good results from the viewpoint of the EIOM yield and of the conversion of EIOH (1-(2-hydroxyethyl)imidazolidyl-2-one [sic]), have been discovered. It appears, however, that it might be possible to make the synthesis even easier to operate on an industrial scale if a liquid
15 catalyst offering the same advantages were to be provided for this reaction.

 European Patent Application EP-A-0,236,994 reports the use of sodium methoxide as catalyst of this reaction but with the recommendation of not using it
20 because of its strong propensity to promote side reactions (Michael addition, in particular). However, the Applicant Company has now discovered, surprisingly, that this catalyst can be used very advantageously, giving good results with respect to the EIOM yield and with
25 respect to the conversion of EIOH, without resulting in the predicted disadvantage of promoting side reactions, provided that it is introduced not in a single step (usual conditions of use) at the beginning of the synthesis but distributed throughout the synthesis.

30 The subject of the present invention is thus the process for the manufacture of a compound of formula (I), as it has been defined above, in the presence of sodium methoxide as catalyst, this process being characterized in that the sodium methoxide is gradually introduced, as
35 a solution, throughout the synthesis.

 In accordance with a particularly preferred embodiment of the process according to the invention, a portion of the sodium methoxide is introduced at the beginning of the synthesis and the remainder is intro-

duced, continuously or in fractions, throughout the synthesis. The fraction which is initially introduced advantageously represents from 2 to 40% by weight, preferably from 4 to 20% by weight, of sodium methoxide
5 with respect to the total amount of sodium methoxide employed.

A 1-30% by weight solution of sodium methoxide in a solvent, such as methanol, is generally introduced.

The amount of sodium methoxide used in implementing the process according to the invention is generally
10 between 1×10^{-4} and 2×10^{-3} mol, preferably 5×10^{-4} and 1×10^{-3} mol, per mole of the heterocyclic alcohol of formula (III).

Mention may in particular be made, as examples of
15 reactants of formula (II), of methyl, ethyl, n-propyl, isopropyl, n-butyl and isobutyl acrylates and methacrylates.

Mention may be made, as examples [sic] of heterocyclic alcohol of formula (III), of EtOH.

The reaction of the process according to the
20 invention can be carried out in the presence of an excess of one or other of the reactants. However, it is advisable for the (meth)acrylate of formula (II)/heterocyclic alcohol of formula (III) molar ratio to be between 2 and
25 5 approximately, preferably between 2.5 and 3.5. By carrying out the reaction with a large molar excess of (meth)acrylate with respect to the heterocyclic alcohol, a solution of compound of formula (I) in the (meth)acrylate is obtained, on conclusion of the reaction, which can
30 be used directly in certain applications, such as the production of paints and coatings or alternatively the treatment of leather.

The reaction of the process according to the invention is preferably carried out in the presence of at
35 least one polymerization inhibitor used, for example, in the proportion of 300 to 1800 ppm, preferably of 600 to 1300 ppm, with respect to the heterocyclic alcohol of formula (III). Mention may in particular be made, as examples of polymerization inhibitors which can be used,

of phenothiazine, hydroquinone methyl ether, di-tert-butylcatechol, hydroquinone, p-anilinophenol, para-phenylenediamine and their mixtures in all proportions.

5 The reaction of the process according to the invention is preferably carried out under a pressure not exceeding atmospheric pressure, for example a pressure of between 0.3 and 1 bar. The reaction is advantageously carried out while bubbling air through, in order to improve the effectiveness of the stabilizers. It is
10 carried out by mixing the (meth)acrylate of formula (II) and the heterocyclic alcohol of formula (III) and by heating the reaction mixture generally to a temperature of between 60 and 90°C approximately, preferably between 70 and 85°C approximately, this temperature obviously
15 being dependent on the exact nature of the alcohol and of the (meth)acrylate.

 In the implementation of the process according to the invention, it is advisable to wait for maximum dehydration before adding the catalyst, so as to prevent
20 deactivation of the latter by the water. This result can be achieved, for example, by heating the starting mixture of (meth)acrylate of formula (II), of heterocyclic alcohol of formula (III) and of polymerization inhibitors at reflux while separating therefrom, by dissolution, the
25 azeotrope of (meth)acrylate and of water when an azeotrope of (meth)acrylate and of water is formed. At this stage, after separation of the distillate, the starting catalyst fraction is introduced into the hot reaction mixture.

30 The duration of the reaction according to the invention clearly depends on the reaction conditions, such as the temperature, the pressure and the amount of catalyst used, but is generally between 5 and 10 hours approximately. It clearly also depends on the nature of
35 the reactants employed.

 The reaction mixture is thus heated at reflux until the head temperature reaches the distillation temperature of the azeotrope of the (meth)acrylate and of the alcohol of formula R_2OH formed by the reaction, when an azeotrope

is formed.

The possible excess (meth)acrylate can then be removed by evaporation, so as to isolate the compound of formula (I) from the reaction mixture, generally in the solid state: thus, the acrylate of 1-(2-hydroxyethyl)-imidazolidyl-2-one [sic] is a white crystalline solid with a melting temperature of 43°C, which is soluble under cold conditions in ketones, alcohols, aromatic hydrocarbons and water and which are [sic] insoluble under cold conditions in saturated hydrocarbons, and which precipitates at 0°C from ethyl acrylate. The methacrylate of 1-(2-hydroxyethyl)imidazolidyl-2-one [sic] is a white crystalline solid with a melting temperature of 47°C possessing the same solubility properties as the above acrylate. On conclusion of the evaporation operation, the solid crystalline product can additionally be purified by filtration, then washing with petroleum ether, and drying.

The compound (I) can also be isolated by partial evaporation of the (meth)acrylate, then crystallization at a sufficiently low temperature (preferably less than or equal to 0°C) and for a sufficiently long period of time (which can reach up to 15 hours), then filtration, followed by the purification stages described above.

Finally, a third method for isolating the compound of formula (I) from the solution containing it consists in extracting with water, followed by separating by settling, concentrating the (meth)acrylate and purifying by the stages described above.

The following Examples illustrate the invention without, however, limiting it. In these Examples, the percentages are shown by weight, except when otherwise indicated.

EXAMPLE 1

1458 g of EIOH, 1823 g [sic] of phenothiazine (PTZ) as stabilizer and 3827 g of methyl methacrylate (MMA) are introduced into a 5 litre jacketed glass reactor equipped with a probe for measuring the tempera-



ture, a variable speed mechanical stirrer and a packed adiabatic column surmounted by a reflux ratio head. The column head is stabilized with a 0.1% solution of hydroquinone methyl ether (HQME) in MMA.

5 The contents of the reactor are brought to boiling point, while bubbling air through and under reduced pressure, at a temperature of 75°C for 1 hour and the water is removed by azeotropic distillation with MMA.

 2.12 g of sodium methoxide (MeONa), as a 1%
10 solution in methanol (MeOH), are then introduced into the reactor in a single step. The remainder of the MeONa, as a 1% solution in MeOH, i.e. 40.82 g, is introduced over 7 hours using a metering pump. The pressure is adjusted in order to maintain a temperature of 75°C in the
15 reactor. The withdrawal of the MMA/MeOH azeotrope is regulated by a column-head set temperature equal to that of the boiling point of the azeotrope at the pressure under consideration, plus 3°C. When the amount of methanol withdrawn corresponds to the expected amount, the
20 reaction is extended by 1 hour, until formation of MeOH is no longer observed (column-head temperature measured at total reflux = boiling temperature of MMA at the pressure under consideration).

 After cooling, crude, solid-free EIOM is
25 recovered.

 The EIOM yield and the conversion of EIOH are determined from analysis by liquid phase chromatography (HPLC) of the reaction crude, using the following equations:

$$\text{Conversion of EIOH C (\%)} = \frac{(\text{starting EIOH} - \text{final EIOH})}{\text{starting EIOH}} \times 100$$

$$\text{EIOM yield Y (\%)} = \frac{\text{Number of moles of EIOM formed}}{\text{Number of moles of starting EIOH}} \times 100$$

30 The results are reported in the Table below, which also includes the data and results of Comparative Example 2.

COMPARATIVE EXAMPLE 2

The same test as in Example 1 is repeated, except that all of the MeONa catalyst is introduced in a single step at the beginning of the synthesis.

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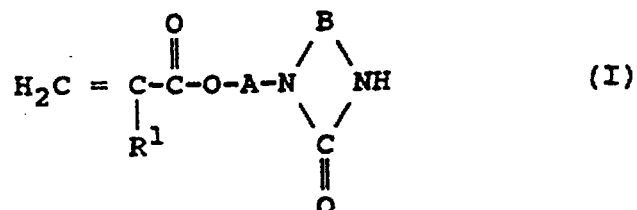
Table 1

Example	HPLC analysis of the crude mixture obtained (%)			Y (%)	C (%)
	MMA	EIOH	EIOM		
1 (of the invention)	43.58	1.44	41.66	77	95.9
2 (comparative)	Not analysed: the mixture has two phases, synonymous with a conversion of less than 50%				<50



CLAIMS

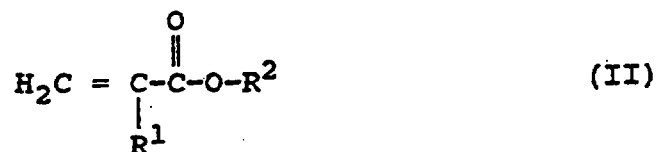
1. Process for the manufacture of a compound of formula:



in which:

- 5
- R^1 represents hydrogen or methyl;
 - A and B each independently represent a straight or branched hydrocarbon chain having from 2 to 5 carbon atoms,

by reaction of at least one (meth)acrylate of formula:



10 in which:

- R^1 has the abovementioned meaning; and
 - R^2 represents a C_1 - C_4 alkyl group,
- with a heterocyclic alcohol of formula:



15 in which A and B have the abovementioned meanings, in the presence of sodium methoxide as catalyst, characterized in that the sodium methoxide is gradually introduced, as a solution, throughout the synthesis.

2. Process according to Claim 1, characterized in that a portion of the sodium methoxide is introduced at



the beginning of the synthesis and the remainder is introduced, continuously or in fractions, throughout the synthesis.

3. Process according to Claim 2, characterized in that 2 to 40% by weight, preferably 4 to 20% by weight, of sodium methoxide are introduced initially with respect to the total amount of sodium methoxide employed.

4. Process according to one of Claims 1 to 3, characterized in that a 1-30% by weight solution of sodium methoxide in a solvent, such as methanol, is introduced.

5. Process according to one of Claims 1 to 4, characterized in that the sodium methoxide is used in an amount of 1×10^{-4} to 2×10^{-3} mol, preferably of 5×10^{-4} to 1×10^{-3} mol, per mole of the heterocyclic alcohol of formula (III).

6. Process according to one of Claims 1 to 5, characterized in that the reaction is carried out at a temperature of between 60 and 90°C, preferably between 70 and 85°C.

7. Process according to one of Claims 1 to 6, characterized in that a molar ratio of the (meth)acrylate of formula (II) to the heterocyclic alcohol of formula (III) is used which is between 2 and 5, preferably between 2.5 and 3.5.

8. Process according to one of Claims 1 to 7, characterized in that the reaction is carried out for a period of time of between 5 and 10 hours at a pressure not exceeding atmospheric pressure.

9. Process according to one of Claims 1 to 8, characterized in that the reaction is carried out in the presence of at least one polymerization inhibitor chosen from phenothiazine, hydroquinone methyl ether, di-tert-butylcatechol, hydroquinone, p-anilinophenol, para-phenylenediamine and their mixtures in all proportions.

10. Process according to Claim 9, characterized in that the polymerization inhibitor or inhibitors is or are used in the proportion of 300 to 1800 ppm, preferably of 600 to 1300 ppm, with respect to the heterocyclic alcohol



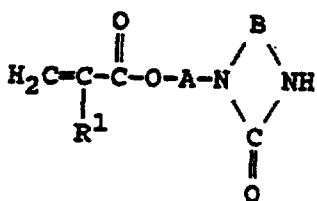
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of formula (III).

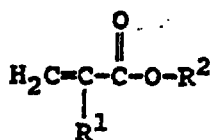
ABSTRACT

PROCESS FOR THE MANUFACTURE OF ALKYLIMIDAZOLIDONE (METH) -
ACRYLATES

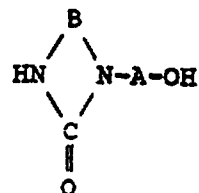
Process for the manufacture of a compound of formula (I) by reaction of at least one (meth)acrylate of formula (II) with a heterocyclic alcohol of formula (III) in the presence of sodium methoxide as catalyst, characterized in that the sodium methoxide is gradually introduced, as a solution, throughout the synthesis:



(I)



(II)



(III)

R^1 = hydrogen or methyl; A and B each independently represent a straight or branched hydrocarbon chain having from 2 to 5 carbon atoms; R^2 = C_1 - C_4 alkyl group.

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- 5 -

is formed.

The possible excess (meth)acrylate can then be removed by evaporation, so as to isolate the compound of formula (I) from the reaction mixture, generally in the solid state: thus, the acrylate of 1-(2-hydroxyethyl)-imidazolidyl-2-one [sic] is a white crystalline solid with a melting temperature of 43°C, which is soluble under cold conditions in ketones, alcohols, aromatic hydrocarbons and water and which are [sic] insoluble under cold conditions in saturated hydrocarbons, and which precipitates at 0°C from ethyl acrylate. The methacrylate of 1-(2-hydroxyethyl)imidazolidyl-2-one [sic] is a white crystalline solid with a melting temperature of 47°C possessing the same solubility properties as the above acrylate. On conclusion of the evaporation operation, the solid crystalline product can additionally be purified by filtration, then washing with petroleum ether, and drying.

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Finally, a third method for isolating the compound of formula (I) from the solution containing it consists in extracting with water, followed by separating by settling, concentrating the (meth)acrylate and purifying by the stages described above.

The following Examples illustrate the invention without, however, limiting it. In these Examples, the percentages are shown by weight, except when otherwise indicated.

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