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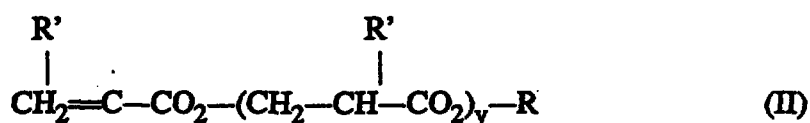
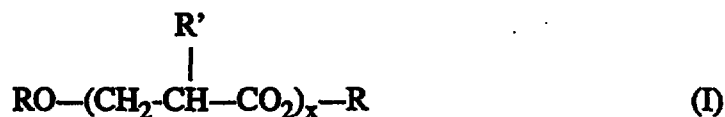
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Esterification of (meth)acrylic acid with an alkanol

The invention relates to a process for the esterification of (meth)acrylic acid with an alkanol in the presence of an esterification catalyst, in which unreacted starting compounds and the (meth)acrylic ester formed are separated off by distillation and a bottom product comprising oxy esters is obtained. The term (meth)acrylic acid here denotes, as is customary, acrylic or methacrylic acid.

The preparation of alkyl esters of (meth)acrylic acid is usually carried out by esterification of (meth)acrylic acid with alkanols at elevated temperature in the liquid phase in the presence or absence of solvent and in the presence of acid as catalyst (DE-A 23 39 519). A disadvantage of this method of preparation is the secondary reactions occurring under the abovementioned esterification conditions, viz. as yet unreacted starting alcohol adds onto the double bond of alkyl (meth)acrylate already formed (Michael addition) to give a compound of the general formula I below and as yet unreacted (meth)acrylic acid adds onto the double bond of the ester formed to give a compound of the general formula II. Multiple addition is also possible. In addition, mixed types can occur. These adducts (alkoxy esters and acyloxy esters) are abbreviated as oxy esters.



where $x,y = 1-5$

$R = \text{alkyl}$

$R' = \text{H or CH}_3$

When $R' = \text{H}$, the esterification is of acrylic acid, when
5 $R' = \text{CH}_3$, the esterification is of methacrylic acid.

The problem of oxy ester formation is particularly acute in the preparation of esters of acrylic acid, with the main oxy esters formed being alkoxypropionic esters and acyloxypropionic esters where $x,y = 1$. In the preparation of esters of methacrylic acid, oxy ester formation occurs to a
10 lesser extent. The formation of oxy esters is described in DE-A 23 39 529. This indicates that the formation of oxy esters occurs essentially independently of the specific esterification conditions. Of very particular importance is oxy ester formation in the preparation of acrylates of $\text{C}_1\text{-C}_8$ -alkanols, in particular $\text{C}_4\text{-C}_8$ -alkanols, very particularly in the preparation of n-butyl
15 acrylate and 2-ethylhexyl acrylate.

It is a characteristic of the oxy esters that their boiling point is above the boiling point of starting acid, starting alcohol, target ester formed and any organic solvent also used.

The work-up of any such esterification reaction mixture is normally
20 carried out by separating unreacted starting compounds and the target ester from the reaction mixture by distillation, with the acid catalyst used for the esterification being able to be removed beforehand, if appropriate, by extraction with water and/or aqueous alkali (cf. for example, Ullmann's Encyclopedia of Industrial Chemistry, Vol. A1, 5th Ed., VCH, p. 167 ff.). The
25 bottom product remaining in such a distillative work-up contains the oxy esters which result in a considerable loss in yield.

For this reason, various further methods have been examined in order to solve the problems resulting from formation of the oxy esters. Thus, JP-A-82/62229 describes the alkaline saponification of the high-boiling
30 esterification residues. In this way, part of the alcohol used and acrylic acid



and β -hydroxypropionic acid or their salts are recovered. A simple and economical return of the products to the esterification reaction is therefore not possible. JP-B-72/15936 describes the preparation of acrylic esters by reacting β -alkoxypropionic esters with acrylic acid in the presence of strong acids (transesterification). However, this forms as by-product equimolar amounts of β -alkoxypropionic acid which cannot be returned to the esterification reaction and therefore represent waste material. JP-A-93/25086 describes the dissociation of the Michael addition product butyl β -butoxypropionate (see formula I, $x = 1$, $R = \text{butyl}$) at elevated temperature and in the presence of sulfuric acid and an excess of water. However, the yield is only about 30%. Finally, JP-A-94/65149 describes the dissociation of the Michael addition products I and II (see above, $x = y = 1$) in the presence of titanium alkoxides. In this reaction, the conversion is likewise low ($< 60\%$) and large amounts of titanate are necessary. This process is therefore uneconomical and environmentally unfriendly because of the large amounts of titanate to be disposed of.

GB 923 595 describes the recovery of monomers from the residue of the esterification of acrylic acid with alkanols in the absence of molecular oxygen. It recommends, inter alia, the removal of all volatile monomers prior to the dissociation, dissociation in the presence of sulfuric acid and removal of the dissociation products by means of a stream of inert gas. According to the examples, the dissociation is always carried out at at least 300°C . Coke is formed as residue (17-40%) and this has to be dug out of the reactor. This process is therefore neither economical nor can it be carried out on an industrial scale. A further disadvantage is the need to exclude oxygen.

CN-A 1,063,678 describes the dissociation of the alkoxypropionic ester present in the esterification residue in the presence of sulfuric acid in a cascade, with temperature and catalyst concentration (0.8-1.5%) being different in each reactor. Coupled with the dissociation is a distillation to





separate alkanol and acrylate. The process is very cumbersome and does not achieve high conversions.

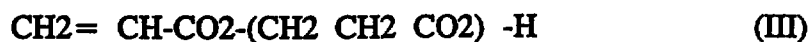
Finally, CN-A 1,058,390 describes the dissociation of alkoxypropionic esters in the presence of sulfuric acid, etc., into alkanols and acrylic esters. This is carried out stepwise. The dissociation is first carried out under reflux and the reaction products are subsequently distilled off. The dissociation of the acrylic acid-containing ester residues from the preparation of ethyl/methyl acrylate (ethyl ethoxypropionate, methyl methoxypropionate) is carried out in the presence of ethanol or methanol. Here too, the process is complicated and does not achieve high conversions.

It is an object of the present invention to carry out the redissociation of the oxy esters present in this bottom product and to reuse the starting acid, starting alcohol and target ester obtained thereby for the purposes of the esterification without the disadvantages of the processes of the prior art.

We have found that this object is achieved by a process for esterifying (meth)acrylic acid with an alkanol in the presence of an esterification catalyst in which unreacted starting compounds and the (meth)acrylic ester formed are separated off by distillation and a bottom product containing oxy esters is obtained, wherein the bottom product is separated off and either (a) the bottom product is admixed directly with oligomeric (meth)acrylic acid and the oxy esters present in the bottom product are dissociated at an elevated temperature in the presence of acid catalysts different from oligomeric (meth)acrylic acid or (b) the oxy esters are first separated by distillation from the bottom product, the distillate is admixed with oligomeric (meth)acrylic acid and is dissociated at an elevated temperature in the presence of acid catalysts different from oligomeric (meth)acrylic acid. The alkanol is preferably n-butanol or 2-ethylhexanol. In general, from 10 to 50% by weight, preferably from 10 to 40% by weight, based on the amount of bottom product in (a) or distillate in (b), of oligomeric (meth)acrylic acid is added. Oligomeric acrylic acid is normally employed in a form known per se, stabilized by means of polymerization inhibitors. Advantageously, the oligomeric (meth)acrylic acid used for this purpose is the bottom product obtained in the



distillative purification of raw acrylic acid; this bottom product comprises mainly compounds of formula III below (see, for example, DE 22 35 326):



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$$x = 1 - 5$$

The (meth)acrylic acid oligomers can be added to the mixture to be dissociated prior to the dissociation. They can also be fed separately into the dissociation reactor.

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These oligomers are not free-radical oligomers, but Michael adducts of the acid with itself, as are obtained as by-products in, for example, the distillation of (meth)acrylic acid. These oligomers are usually burnt as nonrecyclable by-products from (meth)acrylic acid production. Under the redissociation conditions, these oligomeric (meth)acrylic acids are also redissociated, continuously generating free (meth)acrylic acid in statu nascendi.

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Compared with a prior addition of (meth)acrylic acid, this has the advantage that the (meth)acrylic acid added does not immediately distill off together with the dissociation products, but the dissociation proceeds continuously in the presence of (meth)acrylic acid, which results in reduced formation of by-products (dialkyl ethers, olefins). According to an advantageous embodiment of the invention, the process of dissociation is carried out in the presence of molecular oxygen.

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According to a further advantageous embodiment of the invention, the product to be dissociated has added to it, in addition to the acid esterification catalyst which is different from oligomeric (meth)acrylic acid and may already be present, further acids selected from the group consisting of mineral acids such as sulfuric acid or phosphoric acid, and organic acids different from oligomeric (meth)acrylic acid, for example alkyl- or arylsulfonic acids such as methanesulfonic acid or p-toluenesulfonic acid. The total amount of acid different from oligomeric (meth)acrylic acid which is then

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present can be from 1 to 20% by weight, preferably from 5 to 15% by weight, based on the amount of the bottom product in (a) or distillate in (b). It is particularly useful if a stripping gas preferably containing molecular oxygen is passed through the bottom product in (a) or the distillate in
5 (b) as an entrainer for the dissociation products. Air or mixtures of air with inert gas (e.g. nitrogen) are advantageously used as stripping gas.

The advantages of the process of the present invention are, in particular, that the dissociation proceeds more quickly and that a smaller amount of by-products such as ethers or olefins is formed. Thus, among
10 other things, smaller losses of starting materials, particularly of alcohols, occur than in known processes. In addition, high dissociation yields can be achieved. The direct return of the dissociation mixture does not adversely affect the purity of the (meth)acrylic ester and leads to a low ether content. For this reason, no complicated separation of the ether from the easily
15 polymerizable (meth)acrylic ester is necessary. All in all, this also means reduced environmental pollution, since smaller amounts of residue are obtained.

In the distillative separation of the oxy esters from the bottom product, the distillation conditions depend on the type of alcohol component
20 used in the esterification. In general, a temperature of from 100 to 300°C and a pressure of from 1 to 50 mbar are employed. Any conventional distillation apparatus is suitable for the distillation process. Since only a simple separation task is to be performed, a simple splash guard is generally sufficient, i.e. a column is not normally required.

25 For the dissociation of the oxy esters separated off by distillation or present in the bottom product, a simple heatable stirred reactor with jacket heating or heating coil, or else a forced-circulation evaporator, for example a falling-film evaporator or flash evaporator, coupled with a residence time vessel, can be used. To achieve better separation of the dis-
30 sociation products, it may be advantageous to use a rectification attachment

Catalyst: at least one acid selected from the group consisting of mineral acids, for example sulfuric acid and phosphoric acid, and organic acids different from oligomeric (meth)acrylic acid, for example alkyl- or arylsulfonic acids such as methanesulfonic or p-toluenesulfonic acid

Amount of oligomeric (meth)acrylic acid: 5-50% by weight, preferably 10-40% by weight, based on the amount of bottom product in (a) or of the oxy ester distillate separated from the bottom product in (b)

Pressure: preferably at atmospheric pressure or under reduced pressure (so that the dissociation products immediately vaporize) (< 1 atm)

30 Conversion: $\geq 90\%$

The reaction is carried out, for example, by the bottom product to be dissociated being taken continuously from the distillative work-up of the esterification mixture and fed together with the dissociation catalyst to the dissociation reactor. However, the reaction can also be carried out batchwise. It is also possible to use a semicontinuous reaction procedure in which the product to be dissociated is continuously fed to the dissociation reactor (which contains the dissociation catalyst), and the bottom product is removed batchwise from the dissociation reactor only after the dissociation is complete. The dissociation products are separated off continuously by distillation.

The applicability of the dissociation process described is not restricted to a specific type of esterification process from which the oxy esters, i.e. the addition compounds I and II, are obtained as by-products. In general, the esters are prepared by customary methods (see Ullmann's Encyclopedia of Industrial Chemistry, Vol. A1, 5th Ed., VCH, p. 167 ff.).

A typical example of the conditions under which the esterification preceding the dissociation of the oxy esters can take place can be briefly presented as follows:

Alcohol:	(meth)acrylic acid	1:0.7-1.2 (molar)
Catalyst:	sulfuric acid or sulfonic acids	
Amount of catalyst:	0.1-10% by weight (preferably 0.5-5% by weight) based on starting material	
Stabilization:	200-2,000 ppm of phenothiazine (based on the weight of the starting materials)	
Reaction temperature:	80-160°C, preferably 90-130°C	
Reaction time:	1-10 hours, preferably 1-6 hours	

If desired, an entrainer (e.g. cyclohexane or toluene) may be used to remove the water of esterification. The esterification can be carried out



at atmospheric pressure, under superatmospheric pressure or subatmospheric pressure, either continually or batchwise.

In the acid-catalyzed esterification of acrylic acid with alkanols, the bottom product obtained after separating off the acid esterification catalyst, the unreacted starting materials and the acrylic ester generally has the following composition:

- 1-20% by weight of acrylic ester
- 50-80% by weight of alkoxypropionates (see formula I)
- 5-30% by weight of acyloxypropionates (see formula II)
- 10 remainder: mainly stabilizers (phenothiazine) and polymers

Further details and advantages of the process of the present invention may be taken from the examples described below.

Firstly, a result achieved using a process not according to the present invention will be described by means of a comparative example.

15 COMPARATIVE EXAMPLE

A glass circulation reactor (volume: 1 l) heated by means of a heating plug was charged with 500 g of an oxy ester distillate obtained from an esterification residue from n-butyl acrylate production which has been freed of the acid esterification catalyst, together with 40 g of p-toluenesulfonic acid. The oxy ester distillate comprised

- 20 11.0% by weight of butyl acrylate,
- 64.8% by weight of butoxy ester I ($R = C_4H_9$)
- 20.5% by weight of acyloxy ester II ($R = C_4H_9$).

The dissociation temperature was 195°C and the operating pressure was 1 atm.

During the dissociation, the esterification residue to be dissociated was continuously fed to the dissociation reactor, regulated by the level in the reactor.

The dissociation products were taken off in vapor form and condensed at the top of the column (50 cm × 2.8 cm, empty) superposed



on the dissociation reactor. Over a period of 119.5 hours, 7,401 g of mixture were fed to the dissociation reactor and 7,080 g of dissociation products were condensed.

According to analysis by gas chromatography, the condensate
5 comprised:

72.0% by weight of	butyl acrylate
13.9% by weight of	butanol
4.8% by weight of	acrylic acid
1.4% by weight of	dibutyl ether
10 6.6% by weight of	butenes
0.2% by weight of	butyl butoxypropionate

Conversion: 96% by weight based on oxy esters.

The dissociation bottoms were still readily handleable (pumpable) at 25°C and contained no solids.

15 EXAMPLE OF THE PROCESS OF THE PRESENT INVENTION

A glass circulation reactor (volume: 1 l) heated by means of a heating plug was charged with 500 g of the oxy ester distillate from the Comparative Example, with addition of 40 g of p-toluenesulfonic acid and 10 g of a distillation residue obtained in the production of a pure acrylic
20 acid distillate and having the following composition:

5.5% by weight of	acrylic acid
54.0% by weight of	diacrylic acid
14.5% by weight of	dodecylbenzenesulfonic acid

remainder: mainly polymers of acrylic acid and phenothiazine.

25 The dissociation temperature was 195°C and the operating pressure was 1 atm.

The oxy ester distillate and the corresponding amount of acrylic acid distillation residue (20% by weight) were continuously fed to the reactor, regulated by the level in the reactor. 10% by weight of the feed
30 flow was continuously removed from the reactor.



Over a period of 302 hours, 23,985 g of the mixture of oxy ester distillate and acrylic acid distillation residue was fed to the dissociation reactor and 21,580 g of product mixture were condensed. According to analysis by gas chromatography, the condensate comprised:

- 5 69.5% by weight of butyl acrylate
- 6.1% by weight of butanol
- 19.5% by weight of acrylic acid
- 0.6% by weight of dibutyl ether
- 3.1% by weight of butenes

- 10 Conversion: 96% by weight based on oxy esters.

It can be seen from the above example of the process of the present invention that this process is able to achieve higher conversions and results in smaller losses of starting material than in known processes.





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We claim:

1. A process for esterifying (meth)acrylic acid with an alkanol in the presence of an esterification catalyst in which unreacted starting compounds and the (meth)acrylic ester formed are separated off by distillation and a
5 bottom product containing oxy esters is obtained, wherein the bottom product is separated off and either
 - (a) the bottom product is admixed directly with oligomeric (meth)acrylic acid and the oxy esters present in the bottom product are dissociated at an elevated temperature in the presence of acid catalysts different
10 from oligomeric (meth)acrylic acid or
 - (b) the oxy esters are first separated by distillation from the bottom product, the distillate is admixed with oligomeric (meth)acrylic acid and is dissociated at an elevated temperature in the presence of acid catalysts different from oligomeric (meth)acrylic acid.
- 15 2. A process as claimed in claim 1, wherein the amount of oligomeric (meth)acrylic acid added is from 5 to 50% by weight, preferably from 10 to 40% by weight, based on the amount of bottom product in (a) or distillate in (b).
- 20 3. A process as claimed in claim 1 or 2, wherein the process of dissociation is carried out in the presence of molecular oxygen.
4. A process as claimed in any of claims 1 to 3, wherein the process of dissociation is carried out at from 150 to 250°C, preferably from 180 to 230°C.
- 25 5. A process as claimed in any of claims 1 to 4, wherein the acid catalyst added is an acid selected from the group consisting of mineral acids such as sulfuric acid or phosphoric acid, and organic acids different from

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oligomeric (meth)acrylic acid, for example alkyl- or arylsulfonic acids such as methanesulfonic acid or p-toluenesulfonic acid.

6. A process as claimed in claim 5, wherein the added amount of added acid catalyst is from 1 to 20% by weight, preferably from 5 to 15%
5 by weight, based on the amount of bottom product in (a) or distillate in (b).

7. A process as claimed in any of claims 1 to 6, wherein the dissociation is carried out under reduced pressure (< 1 atm).

8. A process as claimed in any of claims 1 to 7, wherein a stripping
10 gas is passed through the bottom product in (a) or distillate in (b) in order to remove the dissociation products.

9. A process as claimed in claim 8, wherein the stripping gas used is an oxygen-containing gas.

10. A process as claimed in any of the preceding claims, wherein the
15 dissociation products obtained are returned directly to the esterification.

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