

Description

The invention relates to a process for the separation of colloidal barium phosphate or barium sodium phosphate, used as a heterogeneous catalyst in the alkoxylation of an active hydrogen containing organic compound.

In EP-A-398450 it is taught that barium phosphate can be removed from alkoxylation reaction product by physical means, or by treating the product with strong acids, alkali metal carbonates or bicarbonates, solid organic acids, zeolites, clays, or by an aqueous wash at a temperature of about 125°C. In US-A-4329515 it has been described that basic compounds of barium or strontium can be removed from alkoxylation product by mixing the product with certain organic acids.

Removal of barium phosphate can only be carried out at a low temperature with a significant loss of alkoxylation product or with complicated working up procedures. The same applies for barium sodium phosphate, used as an alkoxylation catalyst.

A process has now been found in which these disadvantages are avoided.

The invention relates to a process for the separation of colloidal barium phosphate or colloidal barium sodium phosphate, used as a heterogeneous catalyst in the alkoxylation of an active hydrogen containing organic compound, from the alkoxylation product which comprises contacting the alkoxylation product at a temperature of from 40°C to 95°C with of from 15% by weight or more of water such as to break the colloidal state of the barium phosphate or barium sodium phosphate and collecting the phosphate.

The term colloidal is applied to two-phase systems in which one of the phases is dispersed in the other in the form of finely divided particles. In the above case the phosphate is dispersed in the reaction mixture in the form of finely divided particles. The particles have a size of less than 0.2 µm and they flow easily through filter paper.

Generally colloids have the property that they flocculate out when subjected to an electrostatic field. They generally have the tendency to flocculate when acids, bases or salts are added to the two-phase system. In the process for the separation of barium phosphate or barium sodium phosphate the amount of water to be added, preferably is less than 50 per cent by weight on the weight of the alkoxylation product. The broken colloidal barium phosphate or barium sodium phosphate may be collected by filtration, centrifugation, decantation of the reaction product or other physical means. The barium phosphate and barium sodium phosphate, which were used as a heterogeneous catalyst in the alkoxylation reactions, are still present after the alkoxylation reaction chemically unchanged. Consequently they may be reused after separation. The high temperatures in the alkoxylation reaction have caused them to be in the form of colloids which must first be broken.

It is very surprising that the colloidal barium phosphate and barium sodium phosphate are broken by

water. It has been found that under the conditions described according to the invention slurries of barium phosphate or barium sodium phosphate can be obtained, which can be easily worked up in an economical manner.

The invention preferably relates to a process for the separation of barium phosphate or barium sodium phosphate, used as a heterogeneous catalyst in the alkoxylation of an active hydrogen containing organic compound which comprises adding to the alkoxylation product from 15 to 35 per cent by weight, calculated on the weight of the alkoxylation product, of substantially water, the temperature being in the range of from 40 °C to 95 °C, and allowing the colloidal barium phosphate or barium sodium phosphate to break.

The reaction in which the barium phosphate or barium sodium phosphate has been used as heterogeneous catalyst, started with an alkylene oxide and an active hydrogen containing organic compound.

The alkylene oxides are particularly lower alkylene oxides, more particularly those in the range of from 2 to 4 carbon atoms. Preferred are ethylene oxide, propylene oxide or mixtures thereof, more preferred is ethylene oxide.

The active hydrogen containing organic compounds include alcohols, phenols, thiols (mercaptans), amines, polyols or carboxylic acids. A preferred group of compounds are the alcohols, specifically the primary mono-hydric alkanols, having carbon numbers in the range of from 6 to 24. The alkoxylation reactions and products (alkoxylation) have been described in US patent specification 4,967,016 and the contents of which are included by reference.

Acyclic aliphatic mono-hydric alcohols (alkanols) form a most preferred class of reactants, particularly the primary alkanols, although secondary and tertiary alkanols are also very suitably utilized in the process of the invention. Preference can also be expressed, for reason of both process performance and commercial value of the product, for alkanols having from one to 30 carbon atoms, with C₆ to C₂₄ alkanols considered more preferred and C₈ to C₂₀ alkanols considered most preferred. As a general rule, the alkanols may be of branched or straight chain structure, although preference further exists for alkanol reactants in which greater than 50 per cent, more preferably greater than 60 per cent and most preferably greater than 70 per cent of the molecules are of linear (straight-chain) carbon structure.

The general suitability of such alkanols as reactants in alkoxylation reactions is well recognized in the art. Commercially available mixtures of primary mono-hydric alkanols prepared via the oligomerization of ethylene and the hydroformylation or oxidation and hydrolysis of the resulting higher olefins are particularly preferred.

Overall, the two reactants are utilized in quantities which are predetermined to yield an alkoxylation product of the desired mean or average adduct number. Such products commonly have an average adduct number in the range from less than one to 30 or greater, although

the invention is also suitable for alkoxylation of reactants, such as polyols, for which substantially higher average adduct number products are often desired. In particularly preferred embodiments, the invention is applied for the manufacture of ethylene oxide adducts of primary monohydric alkanols in the carbon number range from 6 to 24, having an average of between 1 to 15, more preferably between 2 and 12, oxyethylene groups per ethoxylate molecule, and characterized by very desirable adduct distribution.

In general terms, suitable and preferred process temperatures and pressures for purposes of this invention are the same as in conventional alkoxylation reactions between the same reactants, employing conventional catalysts. A temperature of at least 90 °C, particularly at least 120 °C and most particularly at least 130 °C, is typically preferred from the standpoint of the rate of reaction, while a temperature less than 250 °C, particularly less than 210 °C, and most particularly less than 190 °C, is typically desirable to minimize degradation of the product.

Superatmospheric pressures, e.g. pressures between 0.7 and 11 barg, are preferred, with pressure being sufficient to maintain the active hydrogen reactant substantially in the liquid state.

When the active hydrogen reactant is a liquid and the alkylene oxide reactant is a vapour, alkoxylation is then suitably conducted by introducing alkylene oxide into a pressure reactor containing the liquid active hydrogen reactant and the catalyst. For considerations of process safety, the partial pressure of a lower alkylene oxide reactant is preferably limited, for instance, to less than 4 bar, and/or the reactant is preferably diluted with an inert gas such as nitrogen, for instance, to a vapour phase concentration of 50 per cent or less. The reaction can, however, be safely accomplished at greater alkylene oxide concentration, greater total pressure and greater partial pressure of alkylene oxide if suitable precautions, known to the art, are taken to manage the risks of explosion. A total pressure of between 3 and 7 barg, with an alkylene oxide partial pressure between 1 and 4 barg, is particularly preferred, while a total pressure of between 3.5 and 6.5 barg, with an alkylene oxide partial pressure between 1.5 and 3.5 barg, is considered more preferred.

Under the conditions of the alkoxylation reaction the barium phosphate or the barium sodium phosphate are present at the end of the reaction in colloidal form in the alkoxyated product and breaking of the colloid is necessary to separate the catalysts from the alkoxyated product.

In principle the obtained colloid of barium (sodium) phosphate is broken in a slurry, a foam, a soft gel or a wax plus slurry.

In the Figure on the vertical axis is given the temperature in degrees Celsius and on the horizontal axis the weight percentage of water, calculated on the weight mixture of alkoxyated DOBANOL-1 (DOBANOL is a trade mark) and water. In the figure several areas are depicted:

colloid area	A
slurry area	B
foam area	C
soft gel area	D
wax/slurry area	E
solid area	F

The colloid area A represents the area wherein the obtained hot alkoxylation reaction mixture is cooled to about 40 °C to 95 °C, and wherein a low water percentage does not break the colloid.

The slurry area B represents the area wherein the amount of water is sufficient to break the colloid into a slurry. The obtained particles have a diameter of 0.5-2 mm and can be separated by filtration or centrifugation.

The foam area C represents the area wherein the colloid is broken to a foam because of the high temperatures, generally above 95 °C.

The soft gel area D is the area wherein independent of the temperature by addition of much water a soft gel exists.

The wax/slurry area E is the area wherein at temperatures below 40 °C wax and slurry area formed, whether a low percentage of water is added or a normal percentage.

The solid area F is present below about a few degrees Celsius.

In a preferred process for the separation of barium phosphate or barium sodium phosphate, the amount of water ranges from 15 to 35 per cent by weight, calculated on the weight of the alkoxyated product. This corresponds in the figure with area B (the amount of water herein being based on the total amount of alkoxyated product and water).

It has been found that unless the amount of added water is small, the colloid is always broken. For the separation it is best that the slurry contains particles of about 0.5 to 2 mm, which latter can be collected by filtration or centrifugation.

Example 1

In a 5-litre autoclave were introduced 1000 g of DOBANOL-1 (a C₁₁-alcohol) and 15 g of barium phosphate. The mixture was kept under a nitrogen atmosphere of 2.5 bar (250 kPa) and stirred at 750 rpm, while the temperature in the autoclave was raised to 155 °C. Ethylene oxide gas was then introduced into the autoclave, the total pressure being held at 4 bar (400 kPa). The ethylene oxide partial pressure was 1.5 bar (150 kPa), so that the gas cap contained always less than 40% ethylene oxide.

The alkoxylation reaction was continued with 1.8 kg of ethylene oxide was reacted with the alcohol, which was after 2 hours.

After the ethylene oxide gas stream was stopped the autoclave was kept for a further thirty minutes at 155 °C. The alkoxylation reaction product was then cooled to 80

°C and kept under nitrogen atmosphere. It still contained the barium phosphate.

1000 g of the alkoxyated product/barium phosphate was admixed with 200 g of water of 80 °C. The barium phosphate flocculated out within 5 minutes in 0.5-2 mm particles, which were partly removed from the alkoxyated product by filtration and partly by centrifugation at the temperature of 80 °C. The alkoxyated product was dried and contained the narrow range ethoxylate $C_{11}H_{23}(OC_2H_4)_6-7OH$ with less than 1 ppm of barium phosphate.

Remarks: When alkoxyated product/barium phosphate of 80 °C was not blended with water and directly filtered, the barium phosphate slipped through cotton filters of all pore diameters of 0.5 micron and higher.

Even precoating the filters with Decalite or Celite did not prevent the barium phosphate colloid from running through the filter. This indicated that the colloid particles were less than 0.1 µm in diameter.

No substantial barium phosphate separation from the colloid could be achieved using centrifuges with centrifugal forces up to 12000 g.

The alkoxyated product/barium phosphate was brought in an electrical field (two 10 cm x 10 cm electrodes, potential difference 6000 V, positive electrode connected to earth) the barium phosphate flocculated on the negative electrode as coarse 0.5 to 2 mm particles.

From the above experiments it was concluded that the barium phosphate was present in the ethoxylate product as a colloid.

Example 2

Similar to the process described in Example 1, 1000 g of DOBANOL-45 (C_{14} - C_{15} -alcohol) and 15 g of barium phosphate were charged to the reactor. 1.5 kg of ethylene oxide was reacted with the alcohol.

1000 g of ethoxylated product/barium phosphate of 80 °C was admixed with 200 g of water of 80 °C. The barium phosphate flocculated out within 5 min and was removed by centrifugation or filtration.

Example 3

Similar to the process described in Example 1, 1000 g of DOBANOL-91 (C_9 to C_{11} -alcohol) and 15 g of barium phosphate were charged to the reactor. 1.9 kg of ethylene oxide was reacted with the alcohol.

1000 g of ethoxylated DOBANOL-91/barium phosphate was admixed with 200 g of water of 80 °C. The barium phosphate flocculated out within 5 min and was removed by centrifugation or filtration.

Example 4

Similar to the process described in Example 1, barium sodium phosphate was used as a catalyst instead of barium phosphate.

1000 g of ethoxylated product/barium sodium phosphate of 80 °C was admixed with 200 g of water of 80 °C. Also this colloid was broken and $BaNaPO_4$ flocculated out, when 200 g of water at 80 °C was added. It was removed by centrifugation or filtration.

Example 5

Barium phosphate obtained after filtration in the process of Example 1 was charged to the reactor with 1000 g of fresh DOBANOL-1. The alcohol was reacted with ethylene oxide as described in Example 1. The recycled barium phosphate had the same activity as the fresh barium phosphate used in the process described in Example 1. The obtained alkoxyated product had the same properties as that in Example 1.

Example 6

Hereinafter are described some working-up techniques with alkoxyated DOBANOL-1/barium phosphate blends, prepared according to the first part of Example 1:

Cooling to 80 °C, addition of water 10% : remained colloid.

Cooling to 80 °C, addition of water 30% : colloid broken, soft gel.

Cooling to 40 °C, addition of water 20% : colloid broken, could be filtered or centrifuged. waxy.

Cooling to 100 °C, addition of water 20% : colloid broken, difficult to be filtered or centrifuged because of foaming.

Cooling to 20 °C, addition of water 20% : colloid broken, could be filtered or centrifuged. partly solid.

Claims

1. A process for the separation of colloidal barium phosphate or colloidal barium sodium phosphate, used as a heterogeneous catalyst in the alkoxylation of an active hydrogen containing organic compound, from the alkoxyated product, which comprises contacting the alkoxyated product with water, characterized in that the alkoxyated product is contacted at a temperature of from 40 °C to 95 °C with of from 15% by weight or more of water, calculated on the weight of the alkoxyated product, such as to break the colloidal state of the barium phosphate or barium sodium phosphate, and collecting the phosphate.
2. A process as claimed in claim 1, wherein the amount of water is in the range of from 15 to 35 per cent by weight, calculated on the weight of the alkoxyated product.
3. A process as claimed in claim 1 or 2, wherein the broken colloidal barium phosphate or barium

°C and kept under nitrogen atmosphere. It still contained the barium phosphate.

1000 g of the alkoxyated product/barium phosphate was admixed with 200 g of water of 80 °C. The barium phosphate flocculated out within 5 minutes in 0.5-2 mm particles, which were partly removed from the alkoxyated product by filtration and partly by centrifugation at the temperature of 80 °C. The alkoxyated product was dried and contained the narrow range ethoxylate $C_{11}H_{23}(OC_2H_4)_8-7OH$ with less than 1 ppm of barium phosphate.

Remarks: When alkoxyated product/barium phosphate of 80 °C was not blended with water and directly filtered, the barium phosphate slipped through cotton filters of all pore diameters of 0.5 micron and higher.

Even precoating the filters with Decalite or Celite did not prevent the barium phosphate colloid from running through the filter. This indicated that the colloid particles were less than 0.1 µm in diameter.

No substantial barium phosphate separation from the colloid could be achieved using centrifuges with centrifugal forces up to 12000 g.

The alkoxyated product/barium phosphate was brought in an electrical field (two 10 cm x 10 cm electrodes, potential difference 6000 V, positive electrode connected to earth) the barium phosphate flocculated on the negative electrode as coarse 0.5 to 2 mm particles.

From the above experiments it was concluded that the barium phosphate was present in the ethoxylate product as a colloid.

Example 2

Similar to the process described in Example 1, 1000 g of DOBANOL-45 (C_{14} - C_{15} -alcohol) and 15 g of barium phosphate were charged to the reactor. 1.5 kg of ethylene oxide was reacted with the alcohol.

1000 g of ethoxylated product/barium phosphate of 80 °C was admixed with 200 g of water of 80 °C. The barium phosphate flocculated out within 5 min and was removed by centrifugation or filtration.

Example 3

Similar to the process described in Example 1, 1000 g of DOBANOL-91 (C_9 to C_{11} -alcohol) and 15 g of barium phosphate were charged to the reactor. 1.9 kg of ethylene oxide was reacted with the alcohol.

1000 g of ethoxylated DOBANOL-91/barium phosphate was admixed with 200 g of water of 80 °C. The barium phosphate flocculated out within 5 min and was removed by centrifugation or filtration.

Example 4

Similar to the process described in Example 1, barium sodium phosphate was used as a catalyst instead of barium phosphate.

1000 g of ethoxylated product/barium sodium phosphate of 80 °C was admixed with 200 g of water of 80 °C. Also this colloid was broken and $BaNaPO_4$ flocculated out, when 200 g of water at 80 °C was added. It was removed by centrifugation or filtration.

Example 5

Barium phosphate obtained after filtration in the process of Example 1 was charged to the reactor with 1000 g of fresh DOBANOL-1. The alcohol was reacted with ethylene oxide as described in Example 1. The recycled barium phosphate had the same activity as the fresh barium phosphate used in the process described in Example 1. The obtained alkoxyated product had the same properties as that in Example 1.

Example 6

Hereinafter are described some working-up techniques with alkoxyated DOBANOL-1/barium phosphate blends, prepared according to the first part of Example 1:

Cooling to 80 °C, addition of water 10% : remained colloid.

Cooling to 80 °C, addition of water 30% : colloid broken, soft gel.

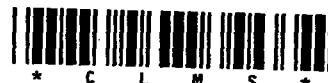
Cooling to 40 °C, addition of water 20% : colloid broken, could be filtered or centrifuged. waxy.

Cooling to 100 °C, addition of water 20% : colloid broken, difficult to be filtered or centrifuged because of foaming.

Cooling to 20 °C, addition of water 20% : colloid broken, could be filtered or centrifuged. partly solid.

Claims

1. A process for the separation of colloidal barium phosphate or colloidal barium sodium phosphate, used as a heterogeneous catalyst in the alkoxylation of an active hydrogen containing organic compound, from the alkoxyated product, which comprises contacting the alkoxyated product with water, characterized in that the alkoxyated product is contacted at a temperature of from 40 °C to 95 °C with of from 15% by weight or more of water, calculated on the weight of the alkoxyated product, such as to break the colloidal state of the barium phosphate or barium sodium phosphate, and collecting the phosphate.
2. A process as claimed in claim 1, wherein the amount of water is in the range of from 15 to 35 per cent by weight, calculated on the weight of the alkoxyated product.
3. A process as claimed in claim 1 or 2, wherein the broken colloidal barium phosphate or barium



* C L M S *

sodium phosphate is collected by filtration or centrifugation.

4. A process as claimed in claims 1-3, wherein the alkoxylation reactant is ethylene oxide or propylene oxide.
5. A process as claimed in claim 4, wherein the active hydrogen containing organic compound is an alcohol, a phenol or a polyol.
6. A process as claimed in claim 5, wherein the alcohol is a primary mono-hydric alkanol having carbon numbers in the range of from 6 to 24.
7. A process as claimed in any one of the claims 1-6, wherein the barium phosphate or barium sodium phosphate is reused.

Patentansprüche

1. Verfahren zur Abtrennung von als heterogener Katalysator bei der Alkoxylierung einer aktiven Wasserstoff enthaltenden organischen Verbindung verwendetem kolloidalem Bariumphosphat oder kolloidalem Bariumnatriumphosphat von dem alkoxylierten Produkt, bei dem das alkoxylierte Produkt mit Wasser in Berührung gebracht wird, dadurch gekennzeichnet, daß das alkoxylierte Produkt bei einer Temperatur von 40°C bis 95°C mit 15 Gew.-% oder mehr, berechnet nach dem Gewicht des alkoxylierten Produkts, Wasser in Berührung gebracht wird, so daß es zum Brechen des kolloidalen Zustands des Bariumphosphats oder des Bariumnatriumphosphats kommt, sowie das Phosphat gesammelt wird.
2. Verfahren nach Anspruch 1, wobei die Wassermenge im Bereich von 15 bis 35 Gew.-% liegt, berechnet nach dem Gewicht des alkoxylierten Produkts.
3. Verfahren nach Anspruch 1 oder 2, wobei das gebrochene kolloidale Bariumphosphat oder Bariumnatriumphosphat durch Filtrieren oder Zentrifugieren gesammelt wird.
4. Verfahren nach Ansprüchen 1-3, wobei es sich bei dem Reaktionspartner um Ethylenoxyd oder Propylenoxyd handelt.
5. Verfahren nach Anspruch 4, wobei es sich bei der aktiven Wasserstoff enthaltenden organischen Verbindung um einen Alkohol, ein Phenol oder ein Polyol handelt.
6. Verfahren nach Anspruch 5, wobei es sich bei dem Alkohol um ein primäres einwertiges Alkanol mit Kohlenstoffzahlen im Bereich von 6 bis 24 handelt.

7. Verfahren nach einem der Ansprüche 1-6, wobei das Bariumphosphat oder Bariumnatriumphosphat wiederverwendet wird.

Revendications

1. Procédé de séparation de phosphate de baryum et de sodium colloïdal ou de phosphate de baryum colloïdal, utilisé à titre de catalyseur hétérogène au cours de l'alkoxylation d'un composé organique contenant de l'hydrogène actif, d'avec le produit alcoxylé, conformément auquel on met le produit alcoxylé en contact avec de l'eau, caractérisé en ce que l'on met le produit alcoxylé en contact, à une température de 40°C à 95°C, avec de 15% en poids et plus d'eau, calculés sur le poids du produit alcoxylé, de manière à briser l'état colloïdal du phosphate de baryum ou du phosphate de baryum et de sodium, et on recueille le phosphate.
2. Procédé suivant la revendication 1, caractérisé en ce que la proportion d'eau varie de 15 à 35% en poids, calculés sur le poids du produit alcoxylé.
3. Procédé suivant la revendication 1 ou 2, caractérisé en ce que le phosphate de baryum ou le phosphate de baryum et de sodium, colloïdal, est recueilli par filtration ou centrifugation.
4. Procédé suivant l'une quelconque des revendications 1 à 3, caractérisé en ce que le réactif d'alkoxylation est l'oxyde d'éthylène ou l'oxyde de propylène.
5. Procédé suivant la revendication 4, caractérisé en ce que le composé organique contenant de l'hydrogène actif est un alcool, un phénol, ou un polyol.
6. Procédé suivant la revendication 5, caractérisé en ce que l'alcool est un alkanol monohydroxylé primaire comportant de 6 à 24 atomes de carbone.
7. Procédé suivant l'une quelconque des revendications 1 à 6, caractérisé en ce que l'on réutilise le phosphate de baryum ou le phosphate de baryum et de sodium.

