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(54) WATER-REPELLENT ALUMINIUM OXIDES AND HYDRATED OXIDES

(71) We, SWISS ALUMINIUM LTD., a Company organised under the laws of Switzerland, of Chippis, Canton of Valais, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for producing water-repellent, finely divided $Al_2O_3 \cdot xH_2O$, in which x is from 0 to 3.

Water-repellent materials are employed, for example, as antiblocking agents in PVC, as water-repelling fillers in plastics materials and for giving a waterproof finish to paper and textiles. In comparison with corresponding materials that are not water-repellent, the water-repellent ones are easier to incorporate into organic substances. In plastics materials, for example PVC, the water-repellent materials result in lower increases in viscosity than in the case of the corresponding materials that are not water-repellent.

It is known to produce, in crystalline or gel form, inorganic substances which have been rendered water-repellent by treatment of the corresponding hydrophilic compounds. Thus, German Patent specification No. 1,004,596 describes how finely divided inorganic oxides containing free OH groups may be rendered water-repellent by treatment with alcohols in the vapour phase. U.S. Patent specification No. 3,699,041 describes the coating of the surface of aluminium hydroxide with surface-active substances, such as ethoxylated fatty acid amides and amino alcohols, by a simple mixing operation. The treated aluminium hydroxide is said to be of use in latices. It is known from U.S. Patent specification No. 3,031,418 to combine aluminium hydroxide with acetic acid; the acetic acid is however, only used as an aid for preparing a special form of boehmite.

Other specifications, for example U.S. Patent specification No. 2,944,914 deal with the pressure-catalysed surface esterification of

$AlOOH$ for preparing organophilic products; in this case the treatment is carried out in the absence of water, the water formed during the esterification being adsorbed or distilled off.

German Patent Specification No. 1,049,027 describes the treatment of hydrophilic substances having hydroxyl, amino or amido groups with isocyanates in non-aqueous media, to render them water-repellent. Offenlegungsschrift No. 1,964,094 describes the modification of china clays with amines in organic solvents.

All the above processes have disadvantages e.g. complexity, the use of health-endangering or explosive substances and costliness.

According to the present invention, a process for producing water-repellent, finely divided, crystalline $Al_2O_3 \cdot xH_2O$, in which x is from 0 to 3, comprises mixing an organic lyophilic compound which is a carboxylic acid, or an alkali or alkaline earth metal salt thereof, an aldehyde, a ketone or an alcohol and which contains only one functional group and only hydrocarbon matter other than the functional group and which has at least 6 carbon atoms, in the form of an emulsion, dispersion or fine powder, with an aqueous dispersion of $Al_2O_3 \cdot xH_2O$, in which x is from 0 to 3 and the surface area per mass is at least $0.1m^2/g$, to obtain a non-acidic aqueous system, separating the solids present from the non-acidic aqueous liquid and drying the solids. The mixing, e.g. stirring, is preferably conducted at from 30 to $90^\circ C$.

The process can be performed simply, safely and economically. In particular, the process has the advantage that it does not require any organic solvent or water-removing procedure, as it is carried out in an aqueous system. Another advantage is that the process is applicable to the liquor containing precipitated aluminium hydroxide that is formed in the Bayer process and thus compared with the processes which require the use of finished, dried products, two process steps, such as intermediate filtration and drying of the $Al_2O_3 \cdot xH_2O$, can be saved.

The finely divided, water-repellent products formed by the present process have a coating of the lyophilic compound used and will float on water, where they will not agglomerate because of their substantially uniform coating. The particles do not lose their water-repelling properties even after contact with boiling water or organic solvents. After filtration and drying the particles are still water-repellent and their ability to float may be retained indefinitely.

The coating process is apparently not a matter of esterification of the $Al(OH)_3$, but of an addition by means of strong electrostatic bonding between the electronegative radicals of the molecules of the lyophilic compound, on the one hand, and the $Al_2O_3 \cdot xH_2O$, e.g. $Al(OH)_3$, partially positively charged by virtue of its high zeta potential, on the other hand.

The lyophilic compound, particularly when it contains a carboxy or hydroxy group, preferably has at least 8 carbon atoms. The lyophilic compound should be water-insoluble and preferred compounds are aliphatic straight chained and cyclic carboxylic acids, aldehydes, ketones and alcohols.

The lyophilic compound is preferably used in the form of an emulsion and suitable aqueous emulsions may be formed by vigorous stirring of the compounds in water, at a temperature above its melting point and in the presence of an appropriate emulsifier. In the emulsion the concentration of organic material is usually between 5 and 40 g/l of water (preferably deionised) and the concentration of the emulsifier is preferably 20 – 40% by volume, referred to the organic phase. Aromatic compounds, e.g. of the types mentioned above, may be employed as the lyophilic compound but are usually less suitable than the aliphatic compounds as they tend to be more difficult to emulsify.

Stearic acid is the most preferred lyophilic compound. The preferred emulsion is prepared by stirring stearic acid together with an emulsifier comprising sodium alkyl benzene sulphionate (preferably in a slightly acid mixture also containing non-ionogenic substances and solvents) and water at a temperature above 80°C.

The $Al_2O_3 \cdot xH_2O$ to be treated may be the $Al(OH)_3$ that crystallises out in conventional manner in the Bayer process. Preferably, the initial $Al_2O_3 \cdot xH_2O$ has a surface area per mass of at least $3m^2/g$.

The suspension of $Al_2O_3 \cdot xH_2O$ used in the present process is preferably liquor from the Bayer process, consisting of a strongly alkaline sodium aluminate solution (110–180 g of Na_2O per litre of solution) containing $Al(OH)_3$ which has crystallised out from the solution. In a particularly preferred procedure the emulsion of the lyophilic compound, prepared by intensive stirring at temperature of 50 to 80°C, is added at temperatures of 30 to 90°C, preferably 40 to 70°C, at any desired time, preferably in the last third of the crystallisation process, to the alkaline suspension of sodium aluminate

and crystallising $Al(OH)_3$, care being taken to ensure rapid distribution of the emulsion in the suspension by stirring strongly. If the stirring is too slow, the coating of the particles may be uneven.

Surprisingly, the addition of the emulsion does not disturb the process of crystallisation of the $Al(OH)_3$ and the yield also is not affected. Thus, the emulsion may be added before all the $Al(OH)_3$ has crystallised out. In contrast to other processes, for example that described in U.S. Patent specification No. 2,944,914, the water-repellent product is resistant to the strong alkali content of the suspension.

After the stirring, the solid product is separated from the liquid, e.g. by filtration, preferably then washed, and dried, preferably at a temperature of 105–130°C.

A variation of the above procedure involves suspending in water at room temperature the filter cake obtained in the production of finely divided $Al(OH)_3$, usually at a solids content of up to 65% by weight (e.g. in an amount of 400 g/l, H_2O), adding an appropriate amount of the emulsion of the lyophilic compound while stirring, and filtering off and drying the solid product. Alternatively, the suspension of the filter cake may be mixed with a suitable lyophilic compound, e.g. stearic acid, in fine powder form, stirred, filtered off and then dried.

Another modification of the process, which can be used for coating aluminium oxide (Al_2O_3) as well as the hydroxide ($Al(OH)_3$), involves suspending the dry powder at room temperature in water, for example 200 g/l H_2O , and then adding, and mixing in, an appropriate amount of an emulsion of lyophilic compound. As in other versions of the process, the suspension may be very strongly alkaline when the emulsion is added without the coating process being impaired.

In all the specific versions of the process given above, the end products from the same starting material and lyophilic compounds are substantially the same.

If the starting material is aluminium hydroxide, the $Al(OH)_3$ produced has, for example, the following characteristics:

Loss on ignition	about 35%
Organic carbon	0.42%
X-ray photograph	same lines as for the starting substance

The resistance of the products to acids and alkalis corresponds to that of the starting substance. Also, the products do not normally contain any coarse portions, as the coated material, in contrast to the uncoated material, on drying does not form any agglomerates.

The most characteristic feature of the products is that they are not wetted by water. Even after shaking for several hours, the product will float on water: this is an indication

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of the uniformity of the coating, as uncoated particles of an inhomogeneous product sink to the bottom when shaken with water.

The present process can be used to make products in which the coating is of a water-insoluble salt, e.g. a calcium salt, of a carboxylic acid, e.g. an aliphatic acid such as stearic acid. When the coating is, for example, of calcium stearate this has the advantage that the surface layer has a higher melting point than, for example, when the coating is of stearic acid. This is an advantage when the coated particles are to be employed as a filler in plastics materials whose processing temperatures are above the melting point of the carboxylic acid e.g. stearic acid. The products of this type may conveniently be made by first mixing an emulsion of the carboxylic acid with the suspension of $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ and then mixing in a water-soluble salt of the desired metal, e.g. in the form of an aqueous solution.

The invention is illustrated by the following Examples. In the Examples, all samples of aluminium hydroxide which were used had a surface area per mass of at least $0.1\text{ m}^2/\text{g}$.

EXAMPLE 1

Finely divided $\text{Al}(\text{OH})_3$ was crystallised out from 10 litres of alkaline aluminate liquor from the Bayer process. After a crystallisation time of 48 hours, an emulsion made in the following way was added.

To 1.4 litres of water at a temperature of 80°C there were added 5.6 g of Cefax emulsifier S (a mixture of sodium alkyl benzene sulphonate, non-ionogenic substances and solvents) and 20 g of stearic acid. The emulsion was dispersed for 10 minutes by means of a high-speed disperser.

During the addition of the emulsion to the alkaline suspension the latter was stirred vigorously; the temperature of the suspension was 40°C . The time of addition was 15 minutes. After the addition had been completed, the suspension was stirred for another 1 to 2 hours, the solid material filtered off, washed with hot water at about $50 - 60^\circ\text{C}$ and then dried at 105°C . A very finely divided, water-repelling aluminium hydroxide that would float on water was obtained.

EXAMPLE 2

2 kg of filter cake consisting of $\text{Al}(\text{OH})_3$ and having a solids content of about 50% were suspended in 5 litres of H_2O at room temperature. As in Example 1, an emulsion of 20 g of stearic acid and 4 g of Cefax emulsifier S in 1 litre of water, at a temperature of 70 to 80°C , was added to the suspension over a period of about 20 minutes while stirring. The suspension was stirred for another 20 to 30 minutes, the solid material filtered off, washed briefly and dried at 105°C . A finely divided, water-repelling product what would float on water was obtained.

EXAMPLE 3

1 kg of dry finely divided $\text{Al}(\text{OH})_3$ was suspended in 5 litres of H_2O and then treated as in Example 2. A finely divided, water-repelling

product that would float on water was obtained.

EXAMPLE 4

1 kg of dry finely divided $\text{Al}(\text{OH})_3$ was suspended in 5 litres of H_2O . An emulsion of 20 g of cyclohexanecetic acid and 4 g of Cefax emulsifier S in 1 litre of water, at a temperature of 70 to 80°C , was added as in Example 2 and the suspension treated as described in that Example. A finely divided, water-repelling aluminium hydroxide that would float on water was obtained.

EXAMPLE 5

1 kg of dry finely divided Al_2O_3 was suspended in 5 litres of H_2O and then treated as in Example 2. A finely divided, water-repelling product that would float on water was again obtained.

EXAMPLE 6

2 kg of finely divided $\text{Al}(\text{OH})_3$ filter cake with a solids content of about 50% were suspended in 5 litres of H_2O . To this suspension there was added an emulsion consisting of 20 g of commercial stearic acid, 4 g of Cefax emulsifier S and 100 ml of H_2O , prepared as described in Example 1. The time of addition was 45 minutes. After adding the emulsion, a solution of 8.6 g of CaCl_2 in 250 ml of H_2O , which had been brought to a pH value of $8 - 9$ by adding NaOH , was added in the course of about 15 minutes. The solid material was filtered off, washed until it was free from chlorine ions and dried at about 110°C ; it had a CaO content of 0.1%. It was finely divided, water-repelling and would float on water.

WHAT WE CLAIM IS:-

1. A process for producing water-repellent, finely divided, crystalline $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, in which x is from 0 to 3, which comprises mixing an organic lyophilic compound which is a carboxylic acid, or an alkali metal or alkaline earth metal salt thereof, an aldehyde, a ketone or an alcohol and which contains only one functional group and only hydrocarbon matter other than the functional group and which has at least 6 carbon atoms, in the form of an emulsion, dispersion or fine powder, with an aqueous suspension of $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, in which x is from 0 to 3 and the surface area per mass is at least $0.1\text{ m}^2/\text{g}$, to obtain a non-acidic aqueous system, separating the solids present from the non-acidic aqueous liquid and drying the solids.
2. A process according to claim 1 in which the lyophilic compound is used in the form of an emulsion and the suspension is a suspension of $\text{Al}(\text{OH})_3$ in alkaline sodium aluminate solution obtained in the Bayer process.
3. A process according to claim 1 in which the suspension is a suspension of the filter cake obtained in the Bayer process and has a solids content of up to 65%.
4. A process according to any preceding claim in which the lyophilic compound is aliphatic or alicyclic.
5. A process according to claim 4 in which the lyophilic compound is stearic acid.

6. A process according to any preceding claim in which the mixing is conducted at from 30 to 90°C.
7. A process according to claim 1 substantially as described in any of the Examples.
8. Water-repellent, finely divided $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, in which x is from 0 to 3, produced by a process according to any preceding claim.

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