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MANUFACTURE OF VERY ACTIVE ALUMINUM

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The present invention relates to a process for the manufacture of highly active aluminum.

It is known that aluminum dialkyl hydrides which by a reaction with olefins can be further converted on a large scale into aluminum trialkyls can be prepared by reacting finely distributed aluminum with aluminum trialkyls and hydrogen, provided that the surface of the finely distributed aluminum to be reacted is free from oxygen.

It is also known that finely distributed aluminum having a surface that is free from oxygen can be prepared in various ways. It can, for example, be prepared by spraying molten aluminum in the atmosphere of an inert gas into hydrocarbons to which aluminum alkyls have been added. Alternatively, aluminum that has previously been disintegrated, for example aluminum spangle or powder, may be ground in a ball mill in the presence of aluminum alkyls. In the latter case, up to 98% by weight of the aluminum alkyls may be replaced by hydrocarbons, the hydrocarbons serving to avoid the formation of spontaneously inflammable suspensions as far as this is possible. The grinding of the previously disintegrated aluminum involves difficulties which arise both when the aluminum is ground in the presence of pure aluminum alkyls and when it is ground in the solutions diluted with hydrocarbons. Frequently the aluminum cannot be disintegrated to the desired fine grain size of a few μ .

It has been observed that, especially when aluminum triethyl is used, which is the most important aluminum alkyl compound, the aluminum particles that had already been disintegrated to a very fine size are enlarged during the grinding operation. This is due to the fact that several aluminum particles re-unite under the mechanical action of the grinding balls and grow until their size is several hundred μ , in some cases even 2 mm.

The finely dispersed aluminum that has been prepared by one of the above-mentioned known methods is not suitable for use in some syntheses; it is especially inappropriate for the preparation of aluminum trialkyls or aluminum dialkyl hydrides since due to the re-uniting of small aluminum particles which takes place in the grinding process and results in the formation of larger aggregates the reaction takes place at a moderate velocity and, moreover, the flowing capacity of the suspensions obtained is impaired and considerable disturbances of the conveying member occur.

It is also known that in the manufacture of aluminum bronze colors by wet grinding suspensions of extremely finely distributed aluminum in hydrocarbons can be obtained. In this case compounds such as stearic acid, palmitic acid or the aluminum salts thereof are added to the hydrocarbons whereupon aluminum stearate or palmitate is produced on the aluminum surface formed during the grinding. The particles of the products which are prepared in the manner described above and which are commercial products have a diameter within the order of a few μ . This means that in the above-mentioned process an enlargement of the ground aluminum particles by re-combination does not take place. However, suspensions of the above-mentioned kind do not react, as was to be expected, under the conditions of the aluminum alkyl synthesis since the surface of the aluminum particles does not consist of pure aluminum but is covered

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with aluminum stearate and moreover it must be taken into account that layers of oxide may form since the grinding is carried out with the access of air.

In view of the state of the art it has hitherto not been promising to modify the grinding conditions and to carry out the grinding with the exclusion of oxygen by the addition of aluminum alkyls, for under these conditions, too, the surface of the aluminum particles that is produced does not consist of pure aluminum but of aluminum stearate and aluminum palmitate.

Now I have found that highly active aluminum can be prepared by grinding previously disintegrated aluminum in the presence of at least one hydrocarbon, at least one aluminum salt of a higher fatty acid and at least one aluminum alkyl. For example, the aluminum salts of higher fatty acids are added to a suspension of aluminum powder in a hydrocarbon to which aluminum trialkyl has been added. The suspension is then ground for several hours in a mill, preferably a ball mill. In the reaction with aluminum trialkyls and hydrogen, for example, which results in the formation of aluminum dialkyl hydrides the aluminum obtained by the process of the present invention excels an aluminum which has been sprayed into an aluminum alkyl-containing hydrocarbon and which has hitherto been used in the above-mentioned synthesis, by about 20 times with respect to the velocity of the reaction. An aluminum having the same high degree of activity can be obtained by first bringing about the formation of the aluminum salts of fatty acids by reacting free fatty acids with aluminum alkyls in solution and then carrying out the grinding operation. It is of no consequence whether the last-mentioned mode of proceeding, which comprises the preparation of the aluminum salts of fatty acids produced from free fatty acids is carried out inside or outside the mill or in the absence or presence of the aluminum to be disintegrated.

Of the aluminum salts of fatty acids those containing 16 to 20 carbon atoms, for example aluminum stearate and aluminum palmitate, taken alone or in admixture with one another have proved particularly effective. The quantities in which the aluminum salts of fatty acids are used may vary within wide limits. It is, however, suitable to use the said salts in a quantity of 0.1 to 10% by weight, preferably 2 to 4% by weight calculated on the quantity of aluminum used as starting material. The quantity of aluminum alkyl compounds which serve to protect against the action of oxygen may likewise vary within wide limits, the aluminum alkyl compounds being preferably used in a quantity of 2 to 5% by weight calculated on the quantity of hydrocarbon used as starting material. Suitable aluminum alkyl compounds are n- and i-alkyl compounds or mixtures thereof, in particular aluminum triethyl, aluminum diethyl hydride, aluminum tri-isobutyl, aluminum di-isobutyl hydride, aluminum trihexyl, aluminum tridodecyl, aluminum trihexadecyl, etc.

Aliphatic hydrocarbons, in particular hexane, heptane, n-octane and mixtures such as gasoline or diesel oil fractions are particularly suitable for use in carrying out the process of the invention. It is, however, particularly advantageous to use iso-octane. Aromatic hydrocarbons, for example benzene and the alkyl derivatives thereof, and cycloaliphatic hydrocarbons, for example cyclohexane, can also be used with a good result.

The highly active aluminum obtained as a suspension by the process of the present invention has a bulk density of 0.3 gram per cc., which is a very low bulk density. The bulk density of the suspension can be considerably increased, for example doubled, by evaporating the hydrocarbon and introducing a fresh portion of the same hydrocarbon or, preferably, a pure aluminum trialkyl compound having the above-mentioned number of carbon

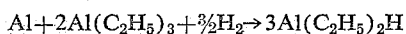
atoms. Such an increase of the bulk density offers the advantage that the flowing capacity of the aluminum suspension is considerably improved and this is in its turn of essential advantage with respect to the introduction of dosed quantities of material by means of pumps and via conduits having small diameters. Besides, when the bulk density is increased less space is required for the reaction of the highly active aluminum with hydrogen which takes place under elevated pressure.

The following examples serve to illustrate the invention but they are not intended to limit it thereto, the parts being by weight.

Example 1

100 parts of aluminum powder are suspended in 150 parts of isooctane and 2 parts of aluminum stearate are added. The resulting suspension is then conveyed into a ball mill under an atmosphere of nitrogen and after the addition of 7 parts of aluminum triethyl the suspension is ground for 3 hours at room temperature. The suspension is let off, the mill is rinsed with isooctane containing aluminum triethyl and subsequently the isooctane is separated by distillation from the aluminum. The distillation is carried out in a vessel provided with a stirrer and the temperature in the distilling flask should not exceed 150° C. After the aluminum that remains behind has cooled such a quantity of isooctane is added as is sufficient to cover the surface of the aluminum. The aluminum paste that has formed after stirring for a short time is very suitable for the conversion into aluminum diethyl hydride as can be seen from the execution of the method described in the following paragraph.

4 mols of aluminum triethyl and an aluminum suspension in isooctane which contains 2.2 mols of aluminum are introduced into an autoclave provided with a stirrer and having a capacity of 1 liter. After heating the whole to 130° C. hydrogen is introduced under 150 atmospheres pressure, this pressure being maintained by introducing further quantities of hydrogen under pressure. After 1 to 1½ hours the absorption of hydrogen is complete. After cooling, the pressure is released from the autoclave. The reaction solution that is obtained contains 85 to 90 mol percent of aluminum diethyl hydride, the percentages being calculated on the quantity of organo-aluminum compound that is present. The aluminum used as starting material has been consumed except for 0.4 to 0.5 mol according to the following equation:



When in this experiment the aluminum that has been prepared by a grinding operation according to the process of the invention is replaced by a suspension that has been prepared according to a known process by spraying aluminum in the atmosphere of an inert gas, for example nitrogen or argon, there is obtained after hydrogen has been introduced under pressure for 1 hour and the operation has been carried out under the same conditions as described above a reaction solution which contains but 4 to 5 mol percent of aluminum diethyl hydride, that is to say the velocity of reaction of the said suspension is only about 1/20 of the velocity of reaction of the ground aluminum used according to the present invention.

The aluminum diethyl hydride that has formed can subsequently be easily converted in known manner into aluminum triethyl by a reaction with ethylene.

Example 2

In the process described in Example 1 the aluminum triethyl is replaced by aluminum triisobutyl. The process is carried out in the manner described in Example 1 with the use of a highly active aluminum prepared by the process of the invention. There is obtained, under the action of hydrogen, aluminum diisobutyl hydride which

can be further converted by a reaction with isobutylene into aluminum triisobutyl.

Example 3

100 parts of aluminum powder are suspended in a mixture of 7 parts of aluminum triethyl and 150 parts of isooctane. 2 parts of stearic acid are introduced in the course of a few minutes. The aluminum stearate forms in solution with the evolution of ethane. The whole of the suspension is then conveyed into a ball mill and ground for 3 hours at room temperature. The process is continued as described in Example 1. A highly active aluminum is obtained which is just as suitable for the reaction resulting in the formation of aluminum dialkyl hydrides as the aluminum prepared according to the preceding examples.

I claim:

1. A process for the manufacture of highly active aluminum which comprises grinding previously disintegrated aluminum in the presence of at least one hydrocarbon having at least 6 carbon atoms and being liquid at room temperature, 0.1–10% by weight—calculated on the quantity of the aluminum used as starting material—of at least one aluminum salt of a fatty acid containing 16–20 carbon atoms, and at least one aluminum alkyl compound whose alkyl group contains 2–16 carbon atoms.

2. A process for the manufacture of highly active aluminum which comprises grinding previously disintegrated aluminum in the presence of isooctane, 0.1–10% by weight—calculated on the quantity of aluminum used as starting material—of at least one aluminum salt of a fatty acid containing 16–20 carbon atoms, and aluminum triethyl.

3. The process of claim 2 wherein the aluminum salt is aluminum stearate.

4. The process of claim 2 wherein the aluminum salt is aluminum palmitate.

5. A process for the manufacture of highly active aluminum which comprises reacting an aluminum alkyl compound and at least one fatty acid containing 16–20 carbon atoms to form the aluminum salt of that fatty acid and then grinding the reaction mixture with previously disintegrated aluminum in the presence of (1) a hydrocarbon having at least 6 carbon atoms and being liquid at room temperature, and (2) at least one aluminum alkyl compound whose alkyl group contains 2–16 carbon atoms.

6. The process of claim 5 wherein the alkyl aluminum compound and the fatty acid are used in an amount such that the quantity of the aluminum salt formed is 0.1–10% by weight—calculated on the quantity of aluminum used as starting material.

7. A process for the manufacture of highly active aluminum which comprises (1) preparing a suspension of finely divided aluminum by grinding previously disintegrated aluminum in the presence of (a) at least one hydrocarbon having at least 6 carbon atoms and being liquid at room temperature, (b) at least one aluminum alkyl compound whose alkyl group contains 2–16 carbon atoms, and 0.1–10% by weight, based on the quantity of aluminum used as the starting material, of at least one aluminum salt of a fatty acid containing 16–20 carbon atoms, (2) distilling off the hydrocarbon from the aluminum, and (3) suspending the remaining highly active aluminum in a liquid selected from the group consisting of a hydrocarbon, an aluminum alkyl compound and mixtures thereof, the number of the carbon atoms in the hydrocarbon and in the alkyl radicals of the aluminum alkyl compounds being within the range given above.

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