COATING OF NANOPARTICLE AGGLOMERATES VIA SAS IN FLUIDIZED BED

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ABSTRACT

A coating process of nanoparticle agglomerates has been developed by supercritical antisolvent (SAS) technique in a fluidized bed. Titanium oxide has been covered with a solution of Pluronic F-127. The bed has been fluidized with supercritical carbon dioxide. The preliminary results show a good cover quality and particle size distribution between 7 and 10 µm when the fluid rate is 2.5 times higher than fluidization velocity.

INTRODUCTION

Currently, nanoparticles are one of the most important topics in science and technology research due to the wide range of applications that they can offer in fields like biotechnology, medicine, electronics, catalysis or food industry. Their interesting properties, which derive from their size and specific surface area, can be improved by the addiction of a fine covering layer. Some physical characteristics are enhanced, such as hygroscopicity, shape, apparent density, compressibility and mechanical strength, by this coating. [1] Furthermore, these coverings can protect high added value products, encapsulate hydrophobic or toxic compounds, or modify drug release profiles.

Combining the fluidized bed technology with a supercritical antisolvent mechanism is a good option to carry out the deposition of these coverings over the nanoparticles. Although this technique uses organic solvents, it offers a huge variety of compounds that can be used as coating agent due to its solubility is not limited by the CO_2. Inside the coating chamber, the nanoparticles are suspended in supercritical carbon dioxide. A solution formed by the coating material and an organic solvent, which must be soluble in the supercritical carbon dioxide, is introduced into the chamber by a nozzle. As the solution enters in the chamber, the precipitation process takes place, the solvent is dissolved by the carbon dioxide, producing the supersaturation. Consequently, the coating material is settled over the surface of the nanoparticle agglomerates.

Working with nanoparticles and their agglomerates in fluidized bed offers a huge range of advantages: the heat and material transference is enhanced inside the bed. Also, nanoparticles tend to form large agglomerates due to the cohesive forces (Van der Waals or electrostatic forces), which can be reduced using supercritical fluid fluidized bed [2].

The aim of this work consists on study the main process operation variables in order to obtain a favorable coating quality, trying to keep the particle size as low as possible and a narrow size distribution.

MATERIALS AND METHODS

Materials

Titanium dioxide under the trade name AEROXIDE TiO2 P 25 from Evonik Industries has been chosen as model particle. The powder properties can be observed in Table 1. As coating agent, Pluronic F-127 was supplied by Sigma. Ethanol was chosen as organic solvent, with a purity of 99.5% supplied by Panreac. Carbon dioxide, the fluidization fluid, was provided by Carburos Metalicos S. A. with a purity of 99.95%.

Table 1: Titanium oxide properties

Particle	size (nm)	Skeletal density (Kg/m^3)	Bulk density (Kg/m^3)	Tapped density (Kg/m^3)
TiO_2	21	3800	90	130

Experimental device

The carbon dioxide is pumped to the desired operating pressure (100 bar) inside the coating chamber once it has been previously heated (36ºC) in the first tank. Inside the coating chamber, the nanoparticle agglomerates are suspended with a constant known fluid velocity of carbon dioxide, which is higher than the minimum fluidization velocity of the particles in these conditions [3]. The solution formed by the coating agent and the organic solvent is introduced inside the coating chamber by a chromatography pump. When the solution enters the fluidized bed, the antisolvent process takes place: the organic solvent is dissolved in the supercritical carbon dioxide and the coating agent precipitates over the surface of the nanoparticle agglomerates. The carbon dioxide, which carries the ethanol, is expanded in a third tank that acts as a flash where the two phases are separated. The carbon dioxide gets off through the top meanwhile the ethanol is gathered at the bottom.

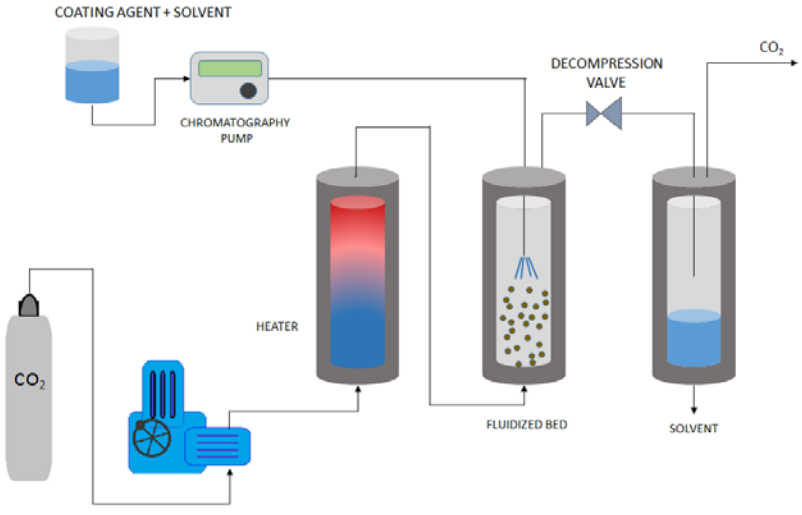

Figure 1: schematic diagram of the experimental set-up.

After a predefined period of time, the flow of solution is ceased and a constant flow of carbon dioxide crosses the coating chamber during 20 minutes in order to dry the final product and

eliminate the possible traces of ethanol. Finally, the system is depressurized and the final agglomerates can be collected and analyzed.

Analysis methods

Some techniques have been used in order to determinate the coating quality and the process efficiency:

- Fourier transform infrared spectroscopy (FT-IR): The fingerprint of the pure components and the samples has been determined to check the presence of the coating agent on the particle surface and whether it covers the core particles completely. The equipment used was Alpha fabricated by Bruker.
- Gravimetric analysis: the samples have been introduced in a furnace at a temperature of 550 ºC for the period of 72 hours with the purpose of determinate the covering substance quantity.
- Laser diffraction: Malvern Mastersize 2000 equipment has been used to obtain the particle size distribution to know the process effect in the product size.

RESULTS

One of the studied operating parameters was the velocity of the fluidization fluid. Table 2 shows the operating conditions of the experiments and the efficiency of the process determined by gravimetric analysis. This efficiency is high and it increases - with the velocity of the fluidization fluid, which means that the particles contain almost all the polymer used during the experiment.

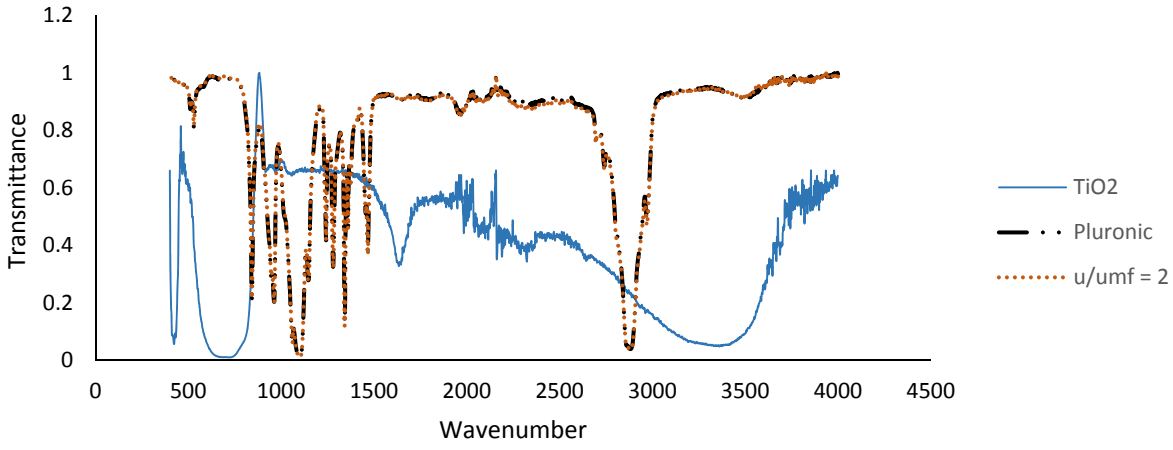

Figure 2: FT-IR spectra of the experiment working at $u/u_{mf} = 2$

Further, as shown in Figure 2, at a fluid velocity twice the minimum fluidization velocity, there is a complete overlap (match) of the FTIR spectra of the pure polymer and of the sample surface that indicates that the polymers covers completely the Titanium dioxide surface.

Table 2: operating conditions and efficiency of the process

u / u_{mf}	Solution flow (ml/min)	$C_{solution}$ (mg/ml)	Ratio (pol/par)	d0.1 (µm)	d0.5 (µm)	d0.9 (µm)	yield (w/w %)
1.5	1	0.060	0.9	4.60	651.35	1389.43	79.95
2	1	0.060	0.9	1.83	11.25	1027.99	94.11
2.5	1	0.060	0.9	1.31	8.45	442.50	95.15

After the fluidization and the coating process it was observed a change in the initial particle size distribution, finding two different fractions; the principal fraction with particles between 7 and 10 µm and the other one between 400-1400 µm. This proportion, which is presented in Figure 3, varies whit the fluidization fluid velocity; the higher the velocity is, the smaller the agglomerates are.

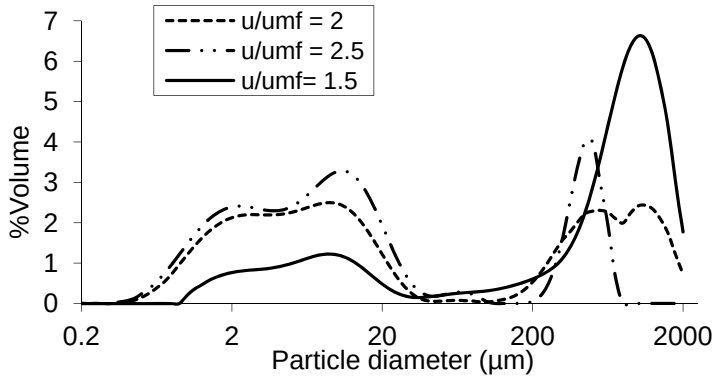

Figure 3: particle size distribution of the final product

CONCLUSIONS

In conclusion, supercritical antisolvent technique in fluidized bed is a good coating method as preliminary results shows. Fluidization fluid velocity is a critical parameter that can modify the product particle distribution, it is necessary to optimize all the operation parameters, such as ratio particle/polymer, CO_2 density or solution flow rate, in order to achieve narrow distributions and improve the coating quality.

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