A NEW PRODUCTION PROCESS OF POWDERS WITH DEFINED PROPERTIES BY ELECTROHYDRODYNAMIC ATOMIZATION OF LIQUIDS AND POST-PRODUCTION ELECTRICAL MIXING

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ABSTRACT: a new electrical process to produce powders with defined chemical composition, size distribution, and morphology (shape and structure) is presented; first, the production of charged droplets with defined mass of solute per unit charge is achieved by electrosprays of two liquids in opposite polarities. Then, electrostatic forces lead to neutral droplets with defined relative amounts of reactants arising from the initial compositions of solutions. Due to the homogeneous mixing of liquid droplets, the same chemical reaction is induced in separate droplets considered as homogeneous micro-reactors. The first part of the paper is devoted to the validation of these principles (neutralisation, homogeneous liquid mixing and reactivity at the micro-reactor scale).

The final dried powder is shown to exhibit well defined properties with reference to macroscopic experimental parameters. The final size distribution varies with the solute concentration in the liquids to be sprayed and with their respective flowrates. The morphology (surface to volume ratio, hollow-dense) mainly depends on the reactivity of mixed compounds from droplets of opposite polarities (i.e. mainly on the products of eventual chemical reactions) but also on the evaporation and heating/cooling rates. Before any optimisation of the reactor, the massic yield of the process varies from 10 to 30% for different experimental conditions.

1 INTRODUCTION

Powders are widely used for their high surface/volume ratio, for sintering and for coating of surfaces [1]. Interest of powders is then closely related to the way they are made, which defines the quality of the powder in terms of size distribution, chemical and structural homogeneity. In order to achieve these requirements, aerosol routes are often used for their low energy cost and especially droplet-to-particle routes. One promising way of monodisperse droplets production is the breaking-up of a liquid jet by Electro-HydroDynamic Atomisation of liquids (EHDA). Then, these droplets are converted to particles by evaporation of the solvent. The droplets/particles so-produced are charged, so that, up to now, the EHDA was only used for thin films deposition on earthed electrodes (painting, printers, coating [2]).

Charged powders are hardly suitable for industrial purposes because of losses encountered during transport in tubes and because of surface reactivity. Thus, different means have been tried to neutralise the sprays produced by EHDA with either unipolar gaseous ions produced by electrical discharge in reverse polarity [3] or with bipolar gaseous ions produced by radioactive material[4]. Nevertheless, the electrical neutrality is only true at the macroscopic

scale due to a bipolar charge distribution of droplets. This uncompleted discharging limits the industrial use of the EHDA by low massic yield of neutralisation (<7% of dissolved solutes[4]).

Moreover, the initial composition of the sprayed liquid determines the final droplet composition. In that respect, it was, up to now, impossible to spray chemically reactive solutions if crystallisation, precipitation, polymerisation or more generally chemical reactions creating viscous or even solid products were started in the solution, leading to clogging of spraying nozzles. Thus, the actual way to induce chemical reactions in suspensions of droplets is based on heterogeneous reactions so as to bring into the liquid phase the needed amount of gaseous reactants. Such reactions with interfacial steps are most often kinetically limited by the dynamic of gas diffusion, adsorption on the surface, dissolution and diffusion in the liquid.

To fulfill the needs for neutralising charged droplets (so as to get a free aerosol) and for inducing the same chemical reaction in separate droplets considered as micro-reactors, without any more limiting steps of reactants mixing, we present a new electrical principle for homogeneous powder production. EHDA of liquids (containing the reactants to be mixed) initially deliver two sprays of charged droplets with defined composition and reverse polarities.

After a description of the experimental set-up, the first part of the results will be devoted to the validation of the principles: (i) Most of the resulting droplets are neutral ; (ii) the mixing of two liquid droplets leads to an homogeneous liquid mixture in the resulting droplet ; (iii) this electrical bipolar mixing can be applied to induce the same chemical reaction in separate droplets considered as micro-reactors. The second part of the results will show that the final particle properties are connected to macroscopic regulation parameters of the process.

II EXPERIMENTAL SET-UP AND SPECIFICATIONS (Figure 1)

Reactor specifications: the positive and negative sprays are created at the top of a mixing chamber, in which droplet neutralisation is achieved by electrostatic forces acting on droplets of reverse polarities. An extra mixing force arise from the gas flow in the mixing chamber.

Electro-spray characteristics: the high voltage electrodes are nozzles, which contain the liquid to be sprayed by EHDA ($\pm10 < V_{nozzle} < \pm15kV$). Due to the acceleration of charges at the liquid surface, the liquid takes a conical shape which ends in a filament of liquid (also referred as the jet). This jet breaks up in small droplets in the micron range with narrow size, charge and velocity distributions[3].
The earthed electrode is a ring located a few centimetres away from the nozzle. First, it creates the high electric field required for the EHDA process, and then it constitutes a shielding electrode which is needed to reduce the space charge influence on the electric field in the production volume (i.e. around the jet) and thus enables mixing and accumulation of space charges a few centimetres away from the spray heads.

Liquid flowrate is regulated by syringe pumps feeding the nozzles from 1 to 50 ml/h

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depending on liquid properties (conductivity, surface tension, density, viscosity). The liquid flowrate and the voltage determine the droplet composition per unit charge (0,1 to 10 mol/C).

Gas conditioning system: on the one hand, gas flow is required to continuously extract from the reactor the neutral droplets so-produced. On the other hand, the partial pressure of solvent in the reactor is controlled by the ratio of flowrates of saturated air produced with the saturation device (bubblers filled with solvent) and of "clean" air (see figure 1).

Drying/heating step : in our case, it consists of a classical oven tube in quartz where droplets/particles blown away from the production and neutralisation reactor by the gas flow are then heated to different temperatures (100 to 800°C). The residence time in the oven has been kept constant to ten seconds in this set of experiments.

Collection step : the final particles are collected onto an inorganic alumina membrane filter , with a pore size of 0,22 µm, because it could withstand the high temperature range.

Analysis step : the aerosol concentration was monitored either just at the exit of the reactor or after the oven tube with a Condensation Nuclei Counter (CNC model 3022 from TSI™). The shape as well as the size distribution of the collected particles were determined by SEM. The internal structure of the particles was observed by TEM and the chemical composition were observed by local Energy Dispersive X-Ray measurements and mapping.
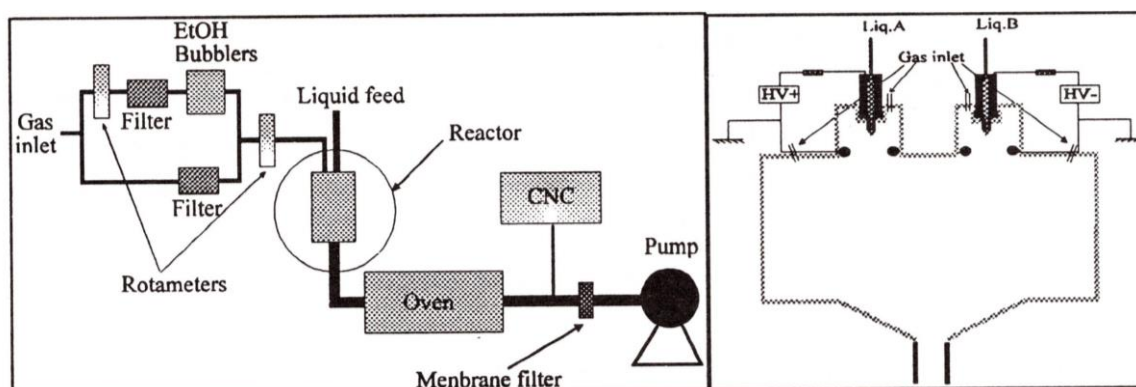

Figure 1: Synoptic view of the experimental set-up and reactor for production (EtOH=Ethanol).

III RESULTS AND DISCUSSION
III.1 Validation of the basic Principles of bipolar mixing
Neutralisation:: From figure 2, can be seen that the numeric concentration of particles at the exit of the reactor is increased by almost two orders of magnitude when droplets of both polarities are sprayed simultaneously compared to when only one spray is producing charged droplets. Moreover, the numeric concentration is not altered with more than 10% when the connection tube from the reactor to the CNC is earthed. Thus, less than 10% of the number of particles coming from the mixing chamber are charged, which confirms the efficiency of the neutralisation. Finally, before any improvement of the mixing and of the flow patterns in the reactor, the massic yield of neutralisation varies from 10 to 30%w for different conditions.
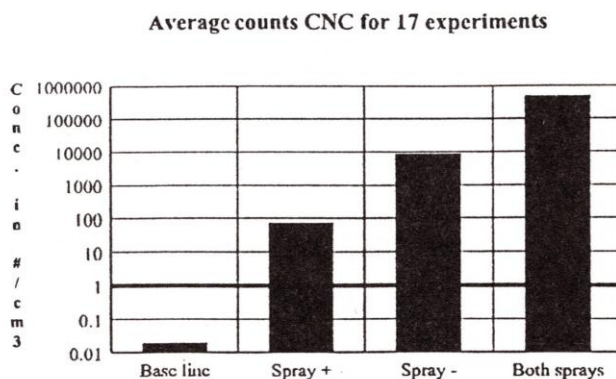
Borra, J. P., Camelot, D., Marijnissen, J., & Scarlett, B. (1997a). A new production process of powders with defined properties by EHD atomization of liquids and electrical mixing. *Journal of Electrostatics, 40-1*, 633-638.

Figure 2: Average number concentration of particles per cubic centimetre
at the exit of the mixing chamber for different conditions of production.

Homogeneous liquid droplets mixing: by spraying different alcoholic solutions of metal organic compounds in positive and negative polarity (Tin tetraacetate and Titanium tetrabutylate) in saturated air, we have observed with EDX mapping analysis of final dried particles constituting the powder, that they all contain both compounds in each particle volume. This confirms the efficiency of homogenisation of the droplet resulting from neutralisation of two liquid droplets of opposite polarity with different composition.

Reactivity at the micro-reactor scale: we mixed positive metal organic dissolved in alcoholic solvent with negative ethanol-water droplets to induce sol-gel reactions i.e. the formation of a metal hydroxide, leading to oxides with typical ceramic properties by inorganic polymerisation and calcination [1]. Chemical analysis still have to be performed. However, as can be seen from figure 3, when neutralising the metal organic droplets by only ethanol droplets, i.e. by preventing from reaction with water, the shrivelled morphology has always been observed (fig. 3a), whereas by inducing the reaction with water-ethanol droplets, it has never been observed (fig 3b). This indicates that for reactive mixing, the crust properties (formed during the same heating treatment in the oven) were different than for non reactive mixing. The reproducibility of this observation confirms that the reaction has taken place in the case of reactants mixing (3b) leading to different liquid products and thus to different crust properties.
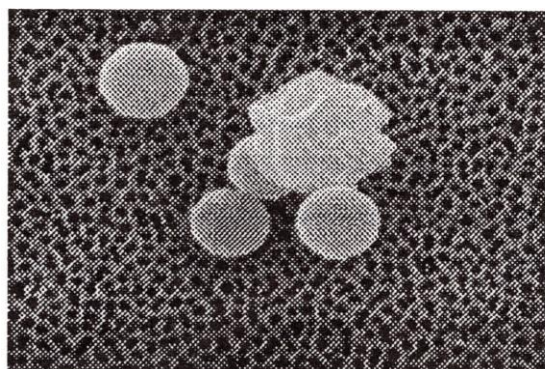

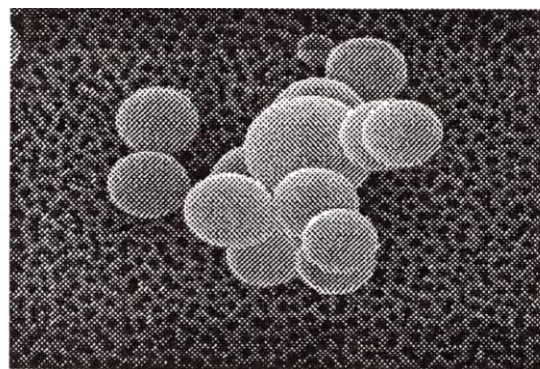Figure 3a: Particle morphology
for non reactive mixing.

Figure 3b: Particle morphology
for reactive mixing

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III.2 Parametric study related to the droplet/particles properties

Particles size: the final size distribution of the powder is tri-modal so that it is thought that, added to the classical bi-modal size distribution reflecting the production of main mode by regular break-up of the jet (5-20 µm) and the random satellites formation in between two drops (0,5-3 µm) [3], an extra intermediate multiple-mode is formed by the Rayleigh break-up i.e. by the electrical disruption of initially highly charged droplets. Note that evaporation rate is then an important parameter which has also to be controlled (see below).

Liquid flowrate: for given conditions of concentration and by varying the liquid flow rates from 5 to 20 ml/h, we succeeded to produce dried particles from 2,4 to 5 µm.

Solute concentration: by decreasing the solute concentration, it is possible to decrease the mean particle size down to a few nanometres only if the air is saturated with solvent to prevent from Rayleigh explosion. Actually, it has been proved to be necessary to regulate the evaporation rate to prevent from post-production break-up of droplets by increasing electrical surface stress as the droplet size decreases by evaporation. This alteration of the size distribution is cancelled by preventing from evaporation i.e. by saturating the air with solvent.

Morphology: **Reactive-non reactive mixing:** from figure 3 can be seen that, depending on the development of a reaction in the drop, the liquid products properties are modified to such an extent that the thermic crust properties influence the powder morphology and homogeneity.

Partial vapour pressure of solvent in the reactor: from figure 4 can be seen that, depending on partial vapour pressure of solvent in the reactor (before the drying step), the final particle morphology can be varied from "multi-cup" shape in air free of solvent to nearly spherical shape in air with 2% v/v ethanol (i.e. p(Et-OH) = 13,2 mm Hg). This effect is already known and can be attributed to the modification of the evaporation rate, because it determines the ratio of time constants of variation of concentration at the evaporating surface on the diffusion in the liquid. The "multi-cup" shape is obtained when a crust is formed in the initial step of solid formation leading to an empty volume in the centre of a hollow particle, which will collapse during the heating treatment. The nearly spherical particles are obtained when the evaporation rate is reduced because it prevents from the crust formation and leads to a more dense particle which is then dried without major modification of the morphology.
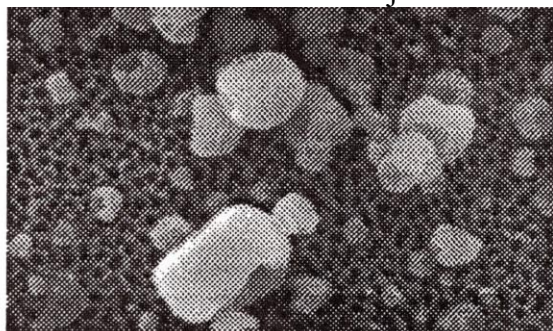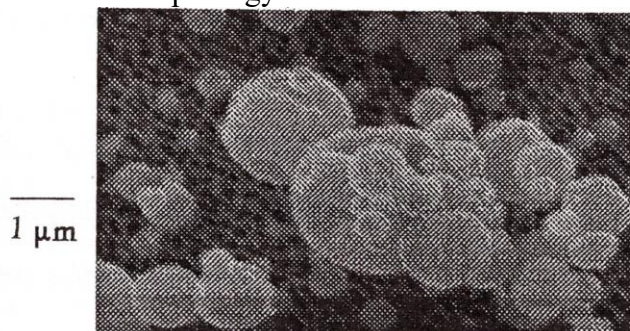

1 µm

Fig. 4a: Particle morphology in air   Fig. 4b: Particle morphology in partially saturated air

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IV CONCLUSIONS

For the first time, this bipolar mixing principle enables the homogeneous mixing of two droplets with a preliminary massic yield i.e. before any improvement of the mixing and of the flow patterns in the reactor, varying from 10 to 30%w for different conditions. It can thus be used to achieve the micro-reactors concept to produce different types of powders with defined size, shape, structure and chemical composition [5]. Moreover, this process has been shown to be flexible with reference to macroscopic experimental parameters.

It has been found that the size of particles so-produced remains closely similar for a given set of production conditions. The size distribution is controlled by the liquid flowrate and the initial liquid composition from a few nanometres to micrometres.

It has been proved to be necessary to regulate the evaporation rate of charged droplets to get liquid droplets at the moment of neutralisation, so that the mixing in the droplet is complete and that the resulting neutral micro-reactor is homogeneous. This is extremely important when a chemical reaction has to arise from mixing of reactants which have thus to be in the same liquid phase. The evaporation rate is also a key parameter for Rayleigh explosion probability.

The final powder structure (homogeneous /multi-layers, specific surface area or surface to volume ratio, hollow/dense, crystalline /amorphous) mainly depends on the reactivity of mixed compounds from droplets of opposite polarities (i.e. on the liquid product properties from eventual chemical reactions) and also on the evaporation and heating/cooling rates.

The final composition of droplets results from the respective amounts of material brought by the initial droplets of opposite polarities which have been mixed. As it is known that the charge of droplets generated by these sprays is related to their size, the final composition of droplets after mixing should depend on their final charge level. Thus, to control the composition of final droplets/particles cloud, it is important to select only one mode (i.e. one charge level) of the droplet population. As most of the droplet are neutralised, it is now interesting to get rid of the still charged droplets by an electrostatic selector. Thus the neutral powder so-produced should accurately be adjust to any specified composition. Finally, after the neutralisation step by bipolar mixing, to a given level of charge corresponds a defined chemical composition of the partially discharge or completely neutralised droplets. Thus, for the future, an electrostatic selection of particles could be used to select other charge levels so as to study the relation between final stochiometry and charge of droplets so-produced.

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The structure (porosity, dense/hollow, surface to volume ratio) of the particles mainly depends on the type of liquid compounds which are brought into contact in the final neutral droplet, because this will define the eventual reactions induced in the drop:
- For non reactive solutes mixed by neutralisation of droplets, the process leads to homogeneous droplets with controlled stochiometry of the final particle.
- For reactive species mixed by neutralisation of droplets, we claim for new processes of homogeneous powders production. When the solutes and/or organic liquid compounds are dissolved in miscible solvents, the resulting neutral droplets are homogeneous and the final size and structure of the particles and powders are closely related to the crystallisation, precipitation or chemical reaction leading to solid products in a tri-dimensional dry network after evaporation whose structure (hollow/dense, porosity, eventual post production break-up) mainly depends on evaporation and drying conditions. Actually, this process has been proved to be an efficient way for manufacturing dense spherical precursor oxide particles by controlling stochiometric amount of reactants brought in droplet of reverse polarities.