CHAPTER 7

Coating and Encapsulation Processes in Powder Technology

Khashayar Saleh* and Pierre Guigon

Chemical Engineering Department, CNRS-UMR 6067, Compiègne University of Technology, BP 20529, 60205 Compiègne, France

Contents

1. Introduction and Definitions 324
2. Industrial Applications of the Coating Process 326
    2.1. Pharmaceutical industry 326
    2.2. Biological industry 327
    2.3. Food industry 327
    2.4. Other fields 328
3. Principles and Classification of Coating Processes 329
    3.1. Wet coating 330
    3.2. Dry coating 330
    3.3. Melt coating 331
    3.4. Liquid-phase encapsulations 331
        3.4.1. Interfacial polymerisation 331
        3.4.2. Polymer-phase separation 332
        3.4.3. Polyelectrolyte complex formation 332
        3.4.4. Solvent evaporation process 332
4. Fundamental Aspects Involved in Coating 332
    4.1. Phenomena occurring during dry coating process 333
    4.2. Phenomena occurring during wet coating 335
    4.3. Phenomena occurring during melt coating 337
    4.4. Wetting and wettability 338
    4.5. Interparticle forces in the context of coating processes 340
    4.6. Work of adhesion 345
5. Coating Technologies and Equipments 346
    5.1. Fluidised-bed coating 346
        5.1.1. Influence of divers parameters on fluidised-bed coating 347
        5.1.2. Influence of the properties of solid particles 348
        5.1.3. Influence of the properties of the coating liquid 350
        5.1.4. Influence of operating conditions 352
        5.1.5. Influence of the coater's specifications 357
        5.1.6. Design options for fluidised-bed coaters 358
    5.2. Spouted bed coaters 360

---

*Corresponding author. E-mail: Khashayar.Saleh@utc.fr

Granulation
Edited by A.D. Salman, M.J. Hounslow and J.P.K. Seville

5.3. Wurster apparatus 362
5.4. Rotating drum, pan and disc coaters 364
6. Concepts in Modelling the Coating Process 366
Concluding Remarks 372
References 372

1. INTRODUCTION AND DEFINITIONS

Coating of particulate materials is a fundamental operation widely practised in a variety of chemical industries including pharmaceuticals, food, fertiliser, cosmetics, biomedical, nuclear, etc. Generally, the coating process is performed to achieve one or several of the following objectives:

- to protect powders from oxygen, humidity, light or any other incompatible element,
- to delay and/or control the release of active agents involved in core particles,
- to confer desired interfacial properties to the particles making them more proper for the final target applications (e.g. dispersion in plastics, electrostatic pulverisation, etc.),
- to reduce the affinity of powders with respect to aqueous or organic solvents,
- to avoid caking phenomena during storage and transport,
- to improve appearance, taste or odours of products,
- to conserve nutrients contained in food products,
- to functionalise powders (catalysts, enzyme-coated detergents, etc.), and
- to increase the particle size.

In addition, coated particles can be subsequently pelletised or serve as a final product enclosed in a soluble gelatine capsules. The coating process involves the covering of particulate materials including seeds, agglomerates, pellets and powders with a surrounding layer of a coating agent (or coating material). The latter might be composed of a single, or of a multitude of inert or active components, each having a specified function.

The coating process can be applied to a variety of substrates ranging from submicron particles to very large objects. The coating thickness might vary from a few nanometres (chemical deposition) to several micrometres (film coating) or even several millimetres (e.g. sugar coating). According to the particular application, the active component can be contained either in core particles or in the coating material. There are several methods to introduce the coating agent into the system: dispersed or dissolved in an easily evaporable solvent, molten, or applied in the form of a very fine dry powder. In majority of cases, the final deposited layer (or coating layer) is a solid-phase material called a *shell*.

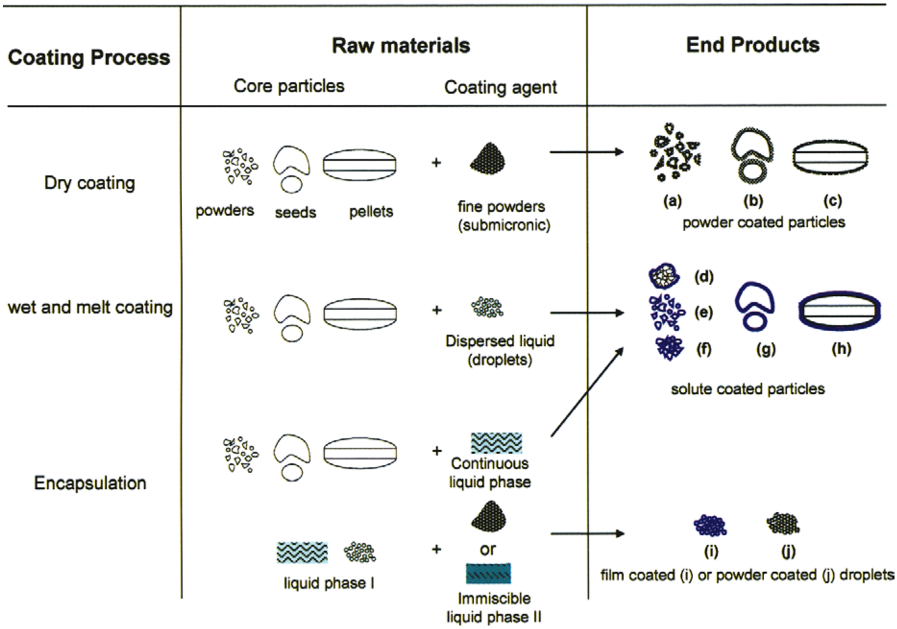


Fig. 1. Survey of coated products.

In a few singular applications the coating layer can also be a liquid film. Some examples of coated products involved in particle technology are schematically depicted in Fig. 1.

Furthermore, the introduction of a liquid into a particulate system leads most often to formation of liquid bridges between wetted particles. This behaviour results in agglomeration phenomenon, which consists of adhesion of several elementary particles to form bigger entities called *agglomerates*. As the coating agent solidifies, liquid bridges are transformed to solid bridges leading to more resistant agglomerates. The solidification is promoted either by heating and evaporation of the solvent when the coating agent is introduced in the form of a solution/suspension or by cooling in the case of melt coating. However, as mentioned by Ormos [1], a lattice distinction between coating and agglomeration is not always possible. Usually, the process is labelled according to its main expected effect. For example, a coating process leading to coated agglomerates (Fig. 1d) or agglomerates constituted of coated particles (Fig. 1f) is called agglomeration if the expected effect is size enlargement and coating if the objective is to cover particles to attain one of the several functionalities mentioned above.

Another term subject to controversy in the technical and scientific literature is *encapsulation*, which is generally admitted to be a special kind of coating. For example, this term has been employed to differentiate either coating process leading to controlled release products or coating for dispersing an active agent on the surface of inert particles. However, in this chapter, the term encapsulation is used to distinguish one of the two following special cases:

- the coating process is performed by immersion in a liquid phase and
- the products core is constituted of a liquid-phase formulation.

2. INDUSTRIAL APPLICATIONS OF THE COATING PROCESS

The coating of particulate products has been accomplished for hundreds of years using techniques as diverse as manually applying coatings to particulate materials to fully automated processing of tablets and compacts in various types of industrial coating devices. Today, a great diversity of products and processes are available for coating particular materials. However, the special functionalities to be achieved might vary basically from one application to another. The objective of this section is to portray an overview of coating operations as practised in various disciplines.

2.1. Pharmaceutical industry

Among all industrial branches concerned with the powder technology, the pharmaceutical industry has without any doubt experienced the most significant developments in coating processes. This is primarily due to high complexity of products and process specifications required in this discipline leading to the development of high-performance coating techniques and agents. Although there are many reasons for coating pharmaceutical products, the main objective of modern coating processes is to manufacture controlled release granules and pellets.

Actually, the principal goal in the pharmaceutical industry has been (and still remains) the synthesis of new and more efficient active agents. It is now generally accepted that the manner in which the drugs are administered is at least as important as the implementation of new drugs: "la manière de donner est plus importante que ce que l'on donne"[1] as states a French proverb.

The earlier applications of coating pharmaceutical products began with sugar coating, a technique largely borrowed from the confectionery industry. Sugar coating consisted of applying a relatively thick layer of sugar around particles. Over decades, the coating had a secondary position in the manufacturing of pharmaceutical products, as its foremost role was to mask the bitter taste of certain drugs "to taste ones medicine"! Indeed, the industrial nature of the coating process began in the 1960s because of the development of a broad variety of polymer-based coating agents, in particular that of cellulose derivatives. These

---

[1] The manner of giving is more important than that one gives.

relatively recent coating products had the particularity to form a very thin coating layer presenting several advantages in comparison to sugar coating. In particular, this so-called film coating process provided better waterproofing and antioxidant effects. In addition, this type of coating allows engraving logo, identification numbers and names on the tablet core [2].

Consequently, since the introduction of polymers the coating process has had a remarkable development. The search for new products and the optimisation of existing ones have led to more and more complex and peculiar formulations. The conception of drugs able to resist to the gastric juices with the setting up of enteric coatings is an obvious example of the advances made possible by film coating. This type of coating permits to protect the stomach from irritant substances on the one hand and to guarantee the full effectiveness of the active principle on the other hand.

Over the last decades, the coating process has become an unavoidable stage of drugs manufacturing. Indeed, one should recognise that if the required amounts (and thus the side effects) of some drugs have decreased considerably, this is partly due to the use of more controlled release and more targeted medications. Currently, the main concern for coating any drug should be to achieve the most adequate mode of its administration, in other words, to bring the right amount of the active ingredient to the right place at the right time.

2.2. Biological industry

For powdery products, the majority of coating process applications in biological areas is similar to those used by the pharmaceutical industry. However, in the biological industry, it is not always possible to extract the active organisms from their native environment in a dry form. For example, to survive, aquatic bacteria require to be enveloped with the aqueous phase containing them. Consequently, in biological industry the coating is frequently performed by liquid-phase encapsulation. The coating agents are usually long-chain molecules, which are formed by polymerisation at the surface of emulsified droplets containing the active agent (Section 3.4).

2.3. Food industry

Compared to other industries, the food industry is characterised by the diversity of both coated and coating materials involved. Furthermore, this field requires the coating of pieces that are much larger and have complex shapes: centres as various as nuts, raisins, cherries, mint patties, crackers and gums are frequently coated with chocolate or hard and soft sugar shells. Breakfast cereals, pet foods and some snacks are often coated with vitamin mixtures and sweeteners. Raisins may be lightly coated with oil to prevent clumping and inhibit drying.

Generally, the requested effects are primarily preserving nutritious elements as well as nutritional value and seasoning foods. For example, fried snacks, such as potato and corn chips, are coated with dry seasoning by hot surface frying fat to help the seasoning adhere but also to reach a moisture protective effect.

As a consequence, the coating layer must provide a good moisture and oxygen protective effect with an immediate release of seasoning agents in the mouth. A recent review of existing technologies for encapsulation of food ingredients can be found in Ref. [3].

2.4. Other fields

There are several other fields concerned by coating process, some of which are presented below:

- Detergent manufacturing

  Detergent industry is a main field of application of coating process. Generally, the objective is to functionalise the detergent particles adhering to active agents such as enzymes, flavours, fabric softeners and conditioners, etc.

- Agricultural products and fertilisers

  Fertilisers are generally coated to obtain a slow release of contained nutritious elements. In fact, the majority, if not all, of fertilisers is very water soluble and in regions with high precipitation the fertiliser may be leached from the soil faster than plants could assimilate it. For example, up to 75% of the nitrogen may be lost in areas with high rainfall [4]. A solution to avoid this problem is to coat the fertiliser granules with low water permeability shells that would retard the release of the fertiliser and therefore give plants more time for assimilation. The earliest application of this type of coating was the production of sulphur coated urea (SCU) which was the first coated fertiliser formulation sufficiently promising to reach large-scale commercialisation. The urea is highly soluble in water whereas sulphur is an advantageous coating material because it is water insoluble, biodegradable, abundant and relatively low cost. In addition, sulphur is an essential plant nutrient, which many soils lack.

  More recently, the use of coating process was extended to other agricultural products. For example, seeds have been coated with protective coat, nutrients, herbicides, bactericidal, insecticides and other materials that attract or repeal moisture.

- Mineral industry
  Coated mineral powders are principally used as solid fillers in plastics manufacturing or in paints. Industrial plastics are usually composite materials, consisting of particles of one or more mineral materials, called solid fillers, suspended in a matrix of plastic materials. Commonly used fillers are clay, talc, calcium carbonate, marble, alumina, titan dioxide and silica. The use of these fillers in plastic systems has two main objectives:
  - diminishing the cost of product by incorporating a high percentage of a low-cost material and
  - granting some desired properties to the system, i.e. opacity, vulcanisation, UV resistance, etc.

Accordingly, coating of mineral powders has one or both of the two following purposes:

  - to improve the ease of dispersion of pigments in nonaqueous media and
  - to control their degree of flocculation in the final dispersion.
- Nuclear field
  The most important use of the coating process in the nuclear field is the neutralisation of radioactive particles by deposit of a thick layer of an inert material.

3. PRINCIPLES AND CLASSIFICATION OF COATING PROCESSES

Coating of solid particles implies two joint conditions: primarily, particles must be thoroughly mixed and secondly the coating agent must be applied to the moving bed of particles in the appropriate manner and form. Powder mixing can be carried out either by mechanical actions (rotating drums and pans) or by pneumatic actions. In some cases, a combination of mechanical and pneumatic action is used (e.g. vibro-fluidised beds). In the particular case of liquid-phase encapsulation the dispersion of core particles is more often performed in stirred vessels.

As for the coating agent it can be introduced into the system in diverse forms i.e. solid, liquid or suspension. Generally, from this point of view, coating processes can be classified as wet coating, dry coating and melt coating (Fig. 2).

Generally, coating processes can be classified according to five main criteria (Table 1): the phase in which core particles are dispersed, physical nature of the coating formulation, the dominant action used to promote the mixing, circulation of core particles and whether or not the process makes use of a solvent. The manner in which the coating formulation is introduced into the system might also be used as a criterion. This criterion concerns essentially wet and melt coating, which in the majority of cases employ a spray nozzle. Although the use of electrostatic pulverisation in dry coating techniques has been experienced recently, its use in industrial units is not yet practised.

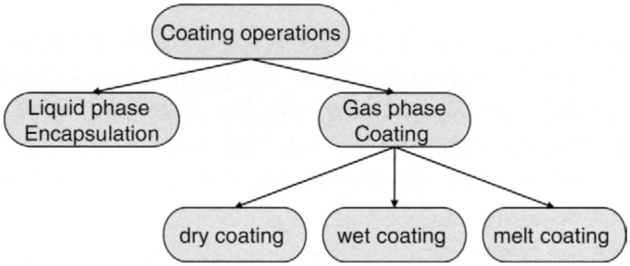


Fig. 2. Classification of coating processes.

Table 1. Criteria in classifying coating operations

Criterion	Possible cases
Dispersing phase	Gas Liquid (encapsulation)
Physical state of coating formulation	Solid (dry coating) Liquid (melt, solution or suspension)
Type of mixing action	Mechanical Pneumatic Combined
Circulation of core particles	Conter-current or co-current single-stage or multi-stage
Use of solvent	Solvent-aided solventless

3.1. Wet coating

In this process, the coating agent is dissolved or suspended in an easily evaporable solvent. The resulting coating mixture is then progressively applied into a mixed bed of particles to be coated. This is usually done by means of a pulverisation system. The solvent is then evaporated, leaving behind a solidified layer of coating agent. The heat necessary to evaporate the solvent can be brought by a hot gas current or through the mixer wall (electric resistance, microwave, etc).

Note that most of industrial coating processes rely on wet coating. Generally, a large variety of coated forms can be obtained. Some examples are sugar coating as well as film coating of drugs, colouring and flavouring of foods, etc.

3.2. Dry coating

In this case, the coating agent is added to the system in the form of fine solid particles. The adherence of the coating layer on the substrate is guaranteed by van der Waals forces or by electrostatic forces (Section 4.4) although in some cases small amounts of binders are added to intensify the adhesion of coating powder. Consequently, the particle size of coating agent must be small enough (often less than 1 μm) to allow adhesion forces to overcome disruptive ones. This process is used for coating of powder paints or some mineral powders to improve their flowability. Another example is the incorporation of anti-caking additives to foods, fertilisers and mineral powders before their storage in hoppers.

3.3. Melt coating

This kind of coating uses a coating agent molten either prior to or during the coating step. Compared to wet processing, here the solidification of the deposited coating layer is carried out by cooling rather than drying. In addition, melt-coating processes use no solvent. The most widely used agents in this category are high-molecular-weight compounds such as polyethylene glycols, silicones, paraffins, etc.

Melt coating can be carried out via two different procedures. The first one consists of spraying a hot melted agent in a cooled bed of particles at which it has sufficient time to spread before solidification. In the second procedure, the coating agent is introduced in the system prior to coating operation in a powdery form. The mixture is then heated up to a temperature close to the melting point of the coating agent at limited regions of the bed. This results in the coating agent being softened and spread over the substrate particles. Further cooling then solidifies the deposited coating layer.

A representative example of melt-coating application is the production of sulphur-coated urea. Melt coating for taste masking, gastric resistance, acid resistance, sustained release or bioavailability enhancement by polymers is also frequently used.

3.4. Liquid-phase encapsulations

Liquid-phase encapsulation has been the object of intense development over the past 20 years essentially due to increasing interest in the immobilisation of viable enzymes, live cells and biocatalyst systems. In liquid-phase encapsulation the active liquid to be coated is dispersed in an immiscible liquid (continuous phase). A continuous microcapsule wall is then formed by in situ polymerisation reactions surrounding the active liquid phase. There are four main techniques used in liquid-phase encapsulation, which are summarised below. For more details see Ref. [5].

3.4.1. Interfacial polymerisation

In this technique the aqueous phase containing the active agent to be encapsulated plus one or more reactants is dispersed in an immiscible organic solvent.

Once dispersion is well established, a co-reactant soluble in the organic phase is added to the system. The reaction between co-reactants contained in each phase leads to the formation of a polymer membrane on the aqueous/organic solvent interface. The most commonly used membranes are polyamides or nylons resulting from reaction of diamines (water soluble) with diacid chlorides (organic solvent soluble). The organic phase is usually a solution of chloroform and cyclohexane with compositions ranging from 20% to 35% v/v [5].

3.4.2. Polymer-phase separation

This technique relies on the so-called interfacial precipitation phenomenon, which occurs at the interface of an aqueous/organic solvent system when each phase contains an appropriate polymer chain, e.g., 10% haemoglobin under alkaline conditions for aqueous phase and nitrocellulose as well as polystyrene for organic solvent (diethyl ether or benzene). From a process point of view polymer-phase separation is quite similar to the interfacial polymerisation (IFP) technique. The main difference concerns the nature of member-forming reagents.

3.4.3. Polyelectrolyte complex formation

In this process, an aqueous solution containing sodium alginate and the active substance to be encapsulated is dropped into an aqueous solution of calcium chloride. This leads to formation of a calcium alginate membrane, which rapidly appears around the droplet's surface. The calcium alginate beads are then transformed into microcapsules through a series of washes and treatments.

3.4.4. Solvent evaporation process

Also called in-liquid drying process or complex emulsion method, the solvent evaporation technique is based on the dispersing of active liquid phase in an immiscible volatile solvent, which contains a coating agent. Subsequent evaporation of volatile solvent from the resulting emulsion produces microcapsules.

4. FUNDAMENTAL ASPECTS INVOLVED IN COATING

Coating is a complex operation including a number of elementary phenomena, which take place in a multi-phase medium. Generally, several consecutive and competitive elementary steps such as particle mixing, liquid spreading, solvent evaporation, agglomeration, abrasion and fragmentation affect the coating process. Each of these phenomena could interfere with the others. Therefore, the successful use of a coating process requires the understanding of the mechanisms that govern the critical issues in coating, e.g. adhesion, uniformity, texture of the coating and surface appearance, particle growth and stability of operation.

In this section, we will describe some theoretical aspects of phenomena involved in coating operations.

4.1. Phenomena occurring during dry coating process

In dry coating, fine (guest) particles are attached onto the surface of relatively larger (host or core) particles by mechanical means without any liquid or binder [6,7]. Both discrete and continuous coating can be achieved depending on operating conditions (processing time, weight ratio of guest to host particles), properties of both coating and coated particles and interactions between them. Furthermore, a homogeneous coating consists of either a particle layer (monolayer or multilayer), which is porous, or a continuous film coating, which is generally non-porous. In the majority of cases, if a continuous coating is expected the dry deposited layer must undergo a further treatment such as melting, polymerisation, etc.

Also it is important to note that an even coating is not always desirable. For example, in dry coating of cohesive powders by flow conditioners (glidants) the optimum flowability is achieved before the host particles are completely covered [8–9]. This is related to the mode of action of glidants. In an intermediate coverage level, coating particles lead to a higher roughness of host particles. This results in a decrease of the interaction forces because the presence of asperity on the particles surface increases the distance between interacting particles. Consequently, a more homogeneous coating characterised by a reduced surface roughness decreases the flow properties.

A successful dry coating process requires two conditions to be satisfied: a good mix between guest and host particles and adhesion forces high enough to overcome the disruptive forces. The former governs the homogeneity of coating on both a microscopic and macroscopic scale and the latter is responsible for a stable coating. In order to achieve a homogeneous and efficient coating the size of guest particles must be orders of magnitude smaller than that of host particles. In addition, as the main forces promoting the adherence of coating particles are the long action forces (van der Waals, electrostatic), generally the size of guest particles must not exceed a few micrometers. This condition guarantees that the adhesion force between particles prevails over the weight of the smaller particle, which will not be easily removed from the host.

Because the main step of a dry coating operation is the mixing process, these two processes are closely related. In order to better understand the phenomena occurring during dry coating the literature on powder mixing, which is much more abundant than the literature on dry coating, should not be overlooked (e.g. [10,11]). Ideally, a mixing process should intimately blend the two species so that any sample taken from the mixture would hold the same fraction of the two constituents. This is usually referred to as ordered mixing. However, achieving this ideal state of mixing is very difficult (if not impossible). In addition, dry coating is a more sophisticated procedure because, besides the requirement for ordered mixing, some complementary conditions must be fulfilled. In particular, the guest particles must adhere onto the surface of host particles and be evenly distributed.

Because the size of guest particles is very small the coating powder is often cohesive and naturally forms agglomerates. Hence, a convenient coating requires breaking-up of agglomerates and rearrangement of elementary coating particles. This is accomplished by means of a mechanical action, which progressively splits the agglomerates on smaller fragments until a homogeneous covering of core particles is reached.

The kinetics and the quality of coating depend on the relative magnitude of inter-particle forces exerting between host and guest particles. These forces depend above all on the size of the interacting particles. However, the chemical nature of particles plays also an important role. For example, Meyer and Zimmermann [9] found that the coating process is more efficient when the interfacial nature of guest particles is the opposite to that of the core particles: hydrophobic coatings spread easier over a hydrophilic substrate. Generally, the dry coating process involves the following consecutive–competitive phenomena:

- Coating or spreading: Coating occurs when primary guest particles adhere to the surface of host particles. As mentioned earlier, the spreading depends also on the chemical nature of particles. The surface covering occurs either after a collision between individual guest and host particles or by spreading of agglomerates of guest particles already adhered to a host particle.
- Crushing or squashing: Crushing takes place as a result of the force of impact due to mixing. Agglomerates of the coating powder break apart at structurally weaker areas and spread over the surface of host particles either in the individual form or in the form of small agglomerates.
- Peeling or abrasion: If during mixing relatively strong forces are applied to the particles, the fine particles may be peeled off from the surface of core particles because of insufficient adhesive strength. The detached particles might be transferred to the surface of other host particles or adhere to each other. However, due to low proportion of guest particles with respect to host particles, the second phenomenon is less probable.
- Embedding: When relatively severe operating conditions are applied, the characteristics of host and guest particles change due to their deformation. In some cases, because of stronger forces exerted onto colliding bodies the guest particles are immobilised on the surface of host particles by embedding.

However, for embedding to occur the guest particles must be harder than the host and also host particles should be deformable. An example of a model system reported by Iwasaki *et al.* [12] is spherical copper particles as host and submicron-sized alumina as guest particles. In addition, a minimum energy is required for the immobilization, which depends on the desired feature of particles and must be provided by a proper choice of operating conditions.

- Mechanofusion: In some cases, a considerable amount of thermo-mechanical energy is generated due to the mixing action. This can result in high local temperatures due to dissipated energy. If local temperatures higher than the melting point of the coating agent are attained, guest particles become softened and molten. The coating agent can then spread over the host particle's surface through fusion–solidification cycles. Compared to other dry coating mechanisms, mechanofusion can lead to a continuous coating shell.

4.2. Phenomena occurring during wet coating

A common characteristic of wet coating processes is the use of a hot gas stream, which permits the evaporation and evacuation of the solvent. Several authors [13–17] have reported a description of the different phenomena occurring during wet coating. These phenomena are summarised in Fig. 3 and described below:

Coating liquid containing a binder is applied, usually by means of a spray nozzle, into a moving bed of particles, which are wetted by liquid droplets. If excessive liquid is present or it is unevenly distributed so that the liquid droplets are larger than the particles, wet agglomerates develop by formation of liquid bridges. When the operation is performed in a fluidised bed, if wet agglomerates are too strong to be fragmented and too large to be fluidised then large regions of the bed may de-fluidise and stick together as large wet clumps. This phenomenon is termed *wet quenching*. Note that if the break-up forces exerted by the environment exceed liquid bridge strength, the wet clumps will be transformed into smaller wet agglomerates. Alternatively, if the droplet size is less than particle size, two situations are distinguished:

- Fast drying before a collision between wet particles. Consequently, the growth occurs by layering.
- Collision of two or more wet particles leading to the formation of a moving liquid bridges and wet agglomerates.

If the cohesion strength is weak in comparison with the break-up forces induced by the moving action, the break-up of the bridges could lead to the formation of individual wet particles that can be dried and grow by the layering mechanism. On the contrary, the solidification of liquid bridges occurs due to

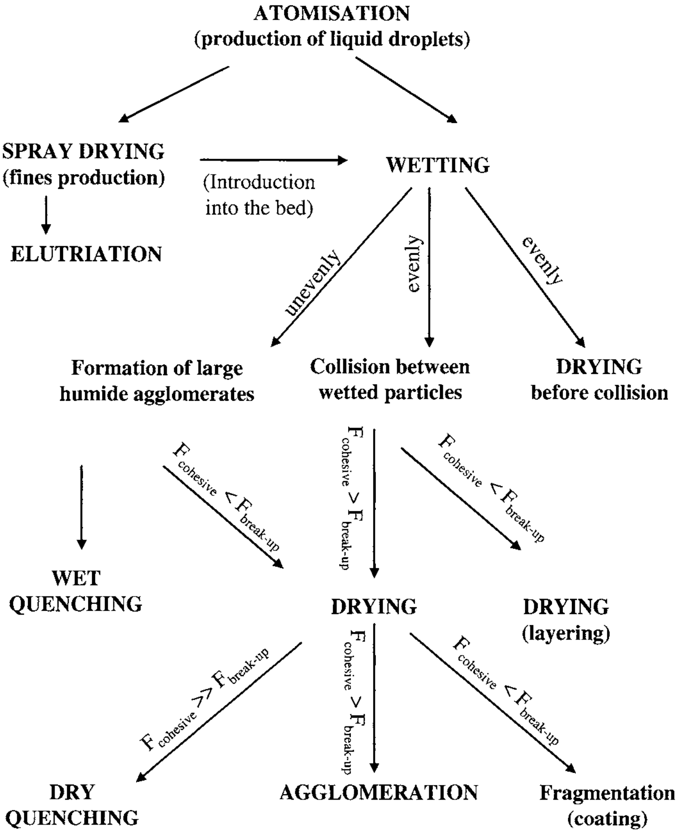


Fig. 3. Phenomena occurring during wet coating.

evaporation of the solvent and agglomerates become stabilised. Whether or not the particles remain together depends on the relative magnitude of the binding forces and the break-up forces arising from the movement of particles throughout the bed. If the cohesive forces are larger than the break-up forces, particle growth occurs by agglomeration. Once again, in the case of fluidised-bed coating if excessive particle growth occurs, the minimum fluidisation velocity of particles will exceed the operating velocity and "dry quenching" of the bed will follow. However, if the break-up forces completely predominate, the agglomerate may break down into smaller agglomerates or individual particles with a small amount of coating material attached to the surface of each.

Note that a parasite phenomenon takes place during the spraying of the liquid corresponding to the droplets drying before the particles surface is attained (spray drying). This step favours the formation of fine solid particles that can be carried out by the drying gas or introduced in the bed and, in turn, grow or adhere to other particles.

In addition, another parasite phenomenon taking place during spray coating is the rebound of droplets after their collision with particles. This phenomenon depends on the wetting parameters of the solid–liquid system used and the operating conditions. Whether or not the rebound of droplets occurs depends on the relative magnitude of the droplet inertia and dissipation and spreading energies [18].

Another common feature of wet coating operations is the existence of a local wetting region in the neighbourhood of the introducing point of the coating liquid. This leads to formation of a localised zone of relatively low temperature within the moving bed, the "wetting zone", which has a crucial role on the hydrodynamic aspect of the operation as well as the uniformity of deposition. The presence of such a local wetted zone was initially established experimentally by Smith and Nienow by establishing the temperature contours in a fluidised-bed coater (Fig. 4a) [19]. Experimental works of some other authors [20–22] confirmed this observation. Recently, in a remarkable work Heinrich *et al.* [22] established a mathematical model of the fluidised-bed coating taking into account the principal transport phenomena i.e. momentum, heat and mass transfer. The simulation results obtained by these authors showed that the model could reproduce the temperature gradients close to the spray zone (Fig. 4b).

4.3. Phenomena occurring during melt coating

There are two common ways to achieve melt coating. The first one corresponds to the injection of a molten coating agent onto the particles surface, which is cooled by a cold gas stream. This case is analogous to wet coating provided that the heating is replaced by cooling and drying by solidification. In the second case,

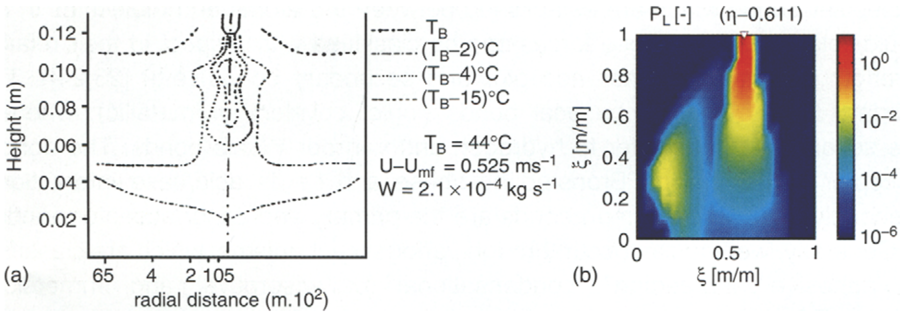


Fig. 4. Temperature gradients in a fluidised-bed coater. (a) Measured temperature profile in a diametrical plane of a bed of fluidised-bed coater established by Smith and Nienow [15]. (b) Calculated two-dimensional dimensionless local liquid loading of a start-up period in a liquid-sprayed fluidised bed (from Heinrich et al. [22]).

the coating agent is added to particles in the solid state. The heating of the bed at temperatures close to the melting point of the coating agent causes the fusion and further spreading of the agent. Generally, the heating of the bed occurs locally and the rest of the bed is at a lower temperature, which permits the solidification of deposited coating layer. Therefore, the coating is carried out by successive wetting of particles by molten coating agent and the solidification of the deposited layer.

Note that compared to wet coating processes, in melt coating the control of the heat transfer rate and the bed temperature is more important.

4.4. Wetting and wettability

From the physicochemical properties playing a role in the wet and melt coating process, the wetting parameters are probably the most important especially when using low viscosity liquid binders. In fact, both bonding and adhesive forces, which govern the growth mechanism and the coating efficiency respectively, depend on the liquid surface tension and liquid–solid contact angle. Wetting parameters mainly govern the mechanisms by which particles are coated and hence the resulting coating quality and morphology of the final product. Wettability describes the ability of a liquid to spread over the surface of a solid material. The wettability of a solid with respect to a liquid is a direct consequence of molecular interactions between phases coming into contact. Considering a liquid drop deposited on a flat solid surface; for wetting to occur, liquid molecules situated in the three phase interface must break off with their surrounding liquid molecules, push away the gas or vapour molecules adsorbed at the solid surface and adhere the solid by forming bonds with the solid's molecules. If the solid–liquid adhesive forces are stronger than both liquid cohesive and solid/gas adhesive forces, then spontaneous wetting occurs. Adhesive forces arise from different interatomic and intermolecular bonds which are established between the atoms and molecules in the liquid/solid interface. These forces can be classified with respect to their relative strength as primary, donor–acceptor and secondary bonds (e.g. [23,24]). The primary bonds involve chemical bonds (ionic, covalent or metallic), whereas the secondary bonds refer to hydrogen and van der Waals bonds. The donor–acceptor forces include Bronsted acid/base and Lewis acid/base interactions. Generally, the most common bonds are the primary and donor/acceptor bonds.

Generally, wetting can occur through various mechanisms, which are classified as "adhesive", "spreading", "condensational" (or "adsorptive") and "immersion" wetting [23]. However, sole spreading wetting is involved in wet coating process and is discussed below.

Spreading wetting is a process in which a given amount of a liquid spreads over a solid substrate. The most widely used description of this type of wetting is the concept of sessile drop. Consider a horizontally positioned, ideally planar, smooth and chemically homogeneous solid surface in equilibrium with the vapour phase. When a liquid drop is deposited on such a surface, spreading wetting occurs during which the liquid forms a spherical cap and the solid/liquid interface, delimited by the so-called "three-phase contact line", stretches pushing away the solid/vapour interface. The included angle formed at a given time at a point on the three-phase contact line between the solid/liquid interface and the tangent to liquid/vapour interface is known as the contact angle, θ (Fig. 5).

The spreading continues until an equilibrium contact angle, θ_e, is reached for which cohesion interactions, which tend to conserve the spherical form of the drop, equal the adhesive interactions, which are responsible for liquid spreading. If the drop size is small enough such that the gravitational forces can be neglected, the relation between surface energies and the contact angle at equilibrium is given by the classical Young equation [23–27]:

$$\cos\theta_e = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \tag{1}$$

where γ_{AB} represents the interfacial tension defined as the energy required to create a contact interface of unity between the two phases A and B, initially completely separated. The subscripts S, L and V refer to solid, liquid and vapour, respectively. Equation (1) indicates that the equilibrium contact angle is unique and depends only on the three interfacial tensions of the considered solid/liquid/vapour system. Consequently, this parameter is an adequate quantitative measure of the wettability of solids with respect to a given liquid. Low contact angles imply that the liquid wets the surface and will spread readily across it, whereas high contact angles imply that the liquid does not wet the surface and will tend to form beads. For the special case when $\theta_e = 0$, the deposited liquid will spread spontaneously and wet completely the substrate. Hence, the wetting is called total or infinite.

The liquid is called "wetting" or "non-wetting" if the contact angle is less than or greater than 90°, respectively.

An important problem when using the Young equation to determine the contact angle is that γ_{SV} and γ_{SL} are not easily measurable. In order to overcome this

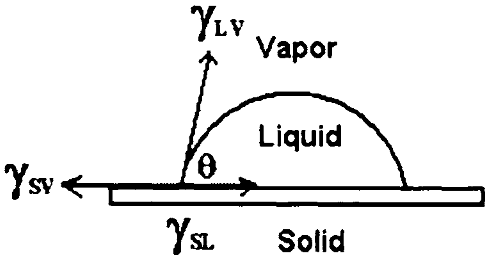


Fig. 5. Sessile drop spread wetting.

problem, several authors have proposed models to reduce the number of variables in equation (1). Antonow [25] and alternatively Bertholot [26], using two different approaches showed that equation (1) can be transformed to the following:

$$\cos\theta_e = -1 + 2\frac{\gamma_{SV}}{\gamma_{LV}} \tag{2}$$

For planar compact solid surfaces, the equilibrium contact angle can be determined quite simply from direct measurements by microscopical methods using goniometric techniques or indirect force-based methods using microbalances, e.g., Whilhelmy plate method, tilt-plate method and capillary rising method [27].

In contrast to planar surfaces, for finely divided solids, the contact angle and therefore the wettability assessment is not a trivial task even for ideally smooth and homogeneous surfaces. Nevertheless, both direct and indirect methods exist to assess the wettability of powders with respect to liquids. For example, Fig. 6 shows a micrograph of a glass bead wetted by water further to water vapour condensation in the observation chamber of an environmental scanning electronic microscope (ESEM). It is out of the scope of this chapter to detail these different techniques but valuable information can be found in a recent review article [27].

4.5. Interparticle forces in the context of coating processes

As was emphasised in previous sections, the interaction between build-up and break-up forces and consequently the strength of solid and liquid bridges

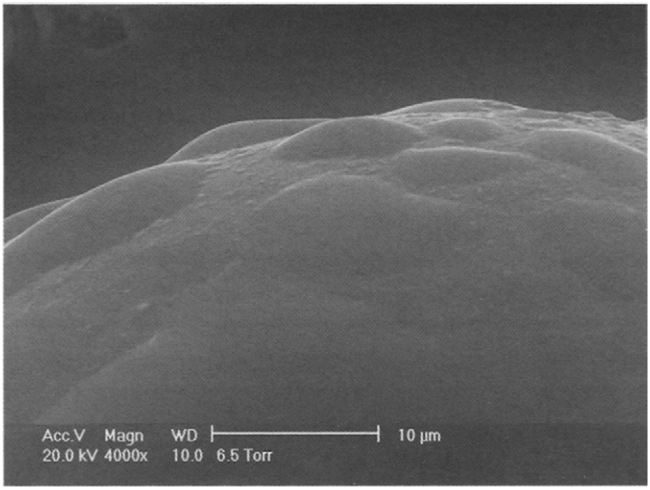


Fig. 6. Micrograph of a glass bead wetted by water further to steam condensation in the observation chamber of an environmental scanning electronic microscope (ESEM).

between particles plays a crucial role in determining the mechanism of growth. In 1958, Rumpf [28] presented a state of knowledge in the agglomeration field together with a complete synopsis of bonding mechanisms causing agglomerate cohesion. Rumpf used bonding mechanisms with and without material bridges as the basis of classification. Based on theoretical considerations Rumpf plotted the tensile strength of agglomerates due to different bonding forces as a function of particle size (Fig. 7).

Bonding mechanisms without material bridges, i.e. van der Waals and electrostatic forces, only are significant in the case of very fine particles (<100 μm). These forces can be neglected in the presence of binding agents (liquid and solid bridges) which are at least greater by one order of magnitude.

The crystallisation of salts or drying of a deposited binder can form solid bridges. The strength of the bond arises from the molecular or atomic attraction in the solid state. Unfortunately, these types of forces are not so amenable to a theoretical approach and have been often estimated experimentally. As paradoxical as it may appear, this is not a real handicap where coating and agglomeration processes are concerned. In fact, the formation of solid bridges passes through liquid bridge formation. Generally, solid bridges are several orders of

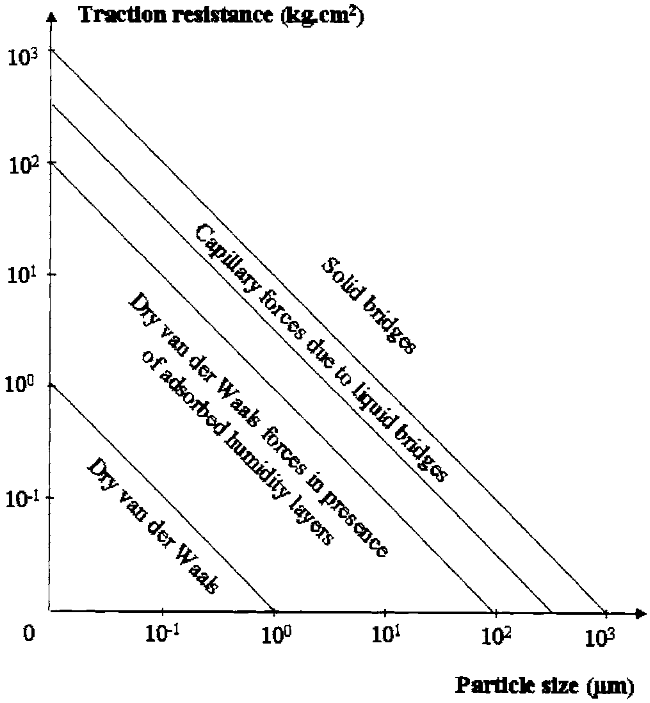


Fig. 7. Tensile strength of binary agglomerates due to different bonding forces as a function of particle size [28].

magnitude stronger than liquid bridges. Consequently, if the liquid bridges are strong enough to withstand the break-up forces, so are the solid bridges.

It is out of the scope of this chapter to detail all attractive forces involved in particulate systems. Substantial literature exists on this subject and valuable information can be found in a number of excellent books and papers (e.g. [24,28,29]). Here, we will limit ourselves to a brief description of attractive interparticle forces involved in coating process i.e. the van der Waals forces which are responsible for dry coating and liquid bridge bonding forces occurring during wet and melt coating.

- Van der Waals forces and dry coating

  In dry coating, the adhesion of coating agent on the surface of core particles is usually ensured by attractive van der Waals forces. These forces exist between molecules of any nature within very short distances up to 100 nm. Van der Waals attractive forces have been extensively described in the scientific literature. Several physical models have been established for well-defined geometries (see e.g. Ref. [29]). Considering a perfectly spherical and smooth guest particle attached to a core particle (spherical and smooth as well) according to Lifshitz theory the van der Waals force can be calculated from the equation

$$F_{\mathrm{vdw}} = \frac{C}{8\pi Z^2}\left(\frac{R_1 R_2}{R_1 + R_2}\right) \tag{3}$$

where C is the "Lifshitz–van der Waals constant" which depending on the material characteristics and physical model used, takes values in the order of 10^{-20}–10^{-19} J. R_1 and R_2 are the radii of the guest and the core particles, respectively. Z is the gap width between two particles which is equal to 4.10^{-10} m for two particles in close contact [29]. This equation shows that the van der Waals attractive force is proportional to the particle size and inversely proportional to the squared gap width.

As long as the attractive forces remain superior to disruptive ones the particles stay together. In the absence of external forces, disruptive forces result from the gravity exerting on detachable particle which is considered to be the guest particle. Although the van der Waals forces increase with increasing particle size (equation (3)) the dependency of the gravitational force, F_g, on this factor is more pronounced ($F_g \propto R_1^3$). Therefore, increasing the size of the guest particle, a critical size is reached where the gravitational force is just equated to the attractive force. The balance between the attractive and disruptive forces is a criterion to predict whether or not the adhesion takes place:

$$\frac{F_{\mathrm{vdw}}}{F_g} = \frac{\frac{C}{8\pi Z^2}\left(\frac{R_1 R_2}{R_1+R_2}\right)}{\frac{4}{3}\pi\rho_p g R_1^3} \tag{4}$$

or

$$\frac{F_{\mathrm{vdw}}}{F_{\mathrm{g}}}=\frac{3C}{32\pi^2 Z^2 \rho_{\mathrm{p}} g R_1^2}\left(\frac{1}{1+\alpha}\right) \tag{5}$$

where ρ_{p} is the particle density and α is taken as the ratio R_1/R_2. This equation shows that for given values of Z and ρ_{P}, the ratio between attractive and disruptive forces is inversely proportional to the term $(\alpha + 1)$ as well as to squared particle size (R_1^2). $F_{\mathrm{vdw}}/F_{\mathrm{g}}$ ratios greater than unity mean that in the absence of any other disruptive force than that of gravity, the guest particle will spontaneously adhere to the core particle.

Obviously, the model presented here is an over-simplification and should not be used for design purposes. However, it does enable us to see how changes in some parameters affect the $F_{\mathrm{vdw}}/F_{\mathrm{g}}$ ratio, thereby increasing the tendency of guest particles to adhere. In particular, the two following important points can be drawn from this model:

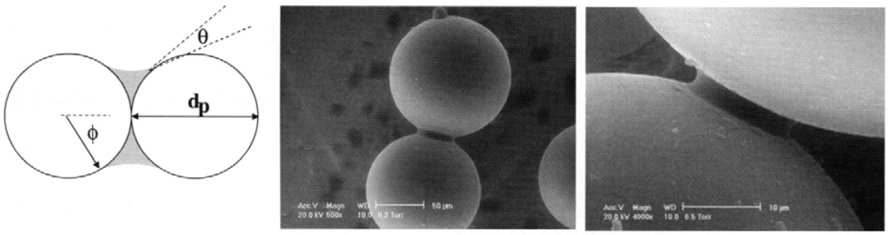
1. For a given particle size, $F_{\mathrm{vdw}}/F_{\mathrm{g}}$ ratio increases with decreasing α. This evolution is however insignificant for α ratios smaller than 0.1 as the change becomes negligible compared to unity (see equation (5)). This means that the bonding forces between a guest particle and a core particle are higher than that of the two guest particles (for which $\alpha = 1$).
2. For a fixed α ratio, the probability of adhesion decreases significantly with the size of guest particles. The $F_{\mathrm{vdw}}/F_{\mathrm{g}}$ ratio becomes smaller than unity for particle sizes of a few micrometers (whatever the value of other parameters is) even at very favourable conditions for adhesion (i.e. low density and narrow gap). This is the reason why the dry coating agents are always submicron powders.

Note that a major difficulty when dealing with real systems lies in the high dependency of van der Waals forces on the distance between particles. In fact, the surface roughness and the presence of dust largely affect the attractive forces being exerted on the particles. In addition, the external forces imposed by the mixing system are not easily amenable to a mathematical description. Finally, depending on the nature of powders, the Lifshitz–van der Waals constant, C, can vary by an order of magnitude. These facts taken as a whole make it extremely difficult to establish reliable physical models to predict the behaviour of industrial units used for dry coating.

- Liquid bridge bonding forces

  According to models described by Rumpf [28] and by Newitt and Conway-Jones [30], for two identical touching spherical particles (Fig. 8) the bond strength due to a static liquid bridge can be related to the liquid surface tension, γ,

- Liquid bridge bonding forces



(a) Rumpf's model. (b) ESEM micrographs of a binary agglomerate (glass beads/water).

Fig. 8. Binary agglomerate due to a liquid bridge. (a) Rumpf's model. (b) ESEM micrographs of a binary agglomerate (glass beads/water).

and solid–liquid contact angle, θ, as follows:

$$F = \pi\gamma d_\mathrm{p}^2 \sin^2\psi + \pi\gamma d_\mathrm{p} \sin\psi \;\sin(\psi + \theta) \tag{6}$$

where d_p is the particle diameter and ψ the liquid filling angle which depends on the volume of the liquid bridge.

Recently, Mehrotra and Sastry [31] presented a review of existing models dealing with the tensile strength of binary agglomerates. They also extended the application of the Rumpf's theory to the case of not equally sized particles.

Furthermore, experimental results from Adams *et al.* [32], Mazzone *et al.* [33] and more recently theoretical and experimental studies from Ennis *et al.* [34,35] demonstrated that the cohesive strength of the dynamic liquid bridges may exceed that of the static by at least an order of magnitude due to the additional energy dissipation resulting from binder viscosity. According to Ennis *et al.* [34] both the capillary and viscous contributions were found to significantly affect the bonding mechanism of colliding particles. The Ennis' findings underlined that the capillary viscous number, Ca_vis, which is a measure of relative magnitude of viscous forces to capillary forces, permits the estimation of the magnitude of the strength of a dynamic pendular bridge. For Ca_vis of less than 10^{-3}, the dynamic bridge strength is of the order of a static bridge and is insensitive to liquid viscosity. As a result, the strength of the dynamic pendular bridge is a superposition of Laplace–Young capillary and viscous dissipation forces. In contrast, bridge strength is insensitive to surface tension and linearly related to Ca_vis for capillary number in excess of 10. That is, bridge strength is only a function of viscosity at high Ca_vis. Note that under agglomeration conditions Ca_vis ranges from 1 to 100 and as a result the capillary contribution to the pendular bridge force can be neglected in this case. In contrast, for coating operations, generally low-viscosity liquids are employed and consequently the role of the viscous forces becomes secondary.

Ennis *et al.* [35] linked these identified microlevel mechanisms to the macroscopic process variables and presented a significant understanding of different granulation regimes from an engineering point of view. In order to establish regimes of granulation, Ennis *et al.* defined the viscous Stokes number, St_v, as the ratio of the relative kinetic energy between colliding particles to the viscous dissipation brought about by pendular bonds:

$$St_v = \frac{8\rho d_p U_0}{18\mu} \tag{7}$$

where U_0 is the relative velocity of particles, ρ_p the particle density and μ the viscosity of the binding liquid. It is to be noted that the calculation of St_v presumes knowledge of the interparticle velocity, U_0, which reflects the effect of break-up forces imposed by granulation system. Ennis established some mathematical models to estimate this parameter for some of currently used techniques. For example, in the case of a fluidised bed U_0 was estimated to be equal to $12U_B dp/d_B$ as a maximum, and to $12U_B dp/d_B\delta^2$ on average, where δ is the dimensionless bubble spacing and U_B and d_B are bubble velocity and bubble size, respectively.

A critical viscous number $St_v{}^*$ must be surpassed for rebound of colliding particles to occur:

$$St_v^* = \left(1 + \frac{1}{e}\right)\ln\left(\frac{h}{h_a}\right) \tag{8}$$

where e is the particle coefficient of restitution, h the thickness of the binder layer and h_a a measure of the particle's surface asperities.

Three granulation regimes were defined in terms of the magnitude of St_v in comparison with St_v^*:

$St_v \ll St_v^*$	non-inertial regime (all collisions successful),
$St_v \approx St_v^*$	inertial regime (some collisions succesfull), and
$St_v \gg St_v^*$	coating regime (no collisions successful).

Despite the limitation of theoretical analysis of Ennis due to a number of simplifications, this theory can be used, at least qualitatively, with experimental results for fluidised-bed granulation.

4.6. Work of adhesion

Taking into account the analysis of phenomena governing layering, it can be concluded that for a given set of operating conditions, the coating efficiency depends on physicochemical properties which condition the liquid spreading and adhesion on the particles surface. According to Dupré's equation, the thermodynamic work of adhesion, W_A, required to separate a unit area of a solid and a liquid phase forming an interface may be expressed by:

$$W_A = \gamma_{LV}(1 + \cos\theta) + \pi_s \tag{9}$$

π_s is called the equilibrium spreading pressure which represents the difference between solid surface energies under operating pressure and under vacuum. For an isobaric operation, the value of this term can be considered constant. Dupré's equation strictly only applies to a solid/liquid interface but by assuming that the surface free energy of a liquid does not change significantly when it solidifies isothermally and ignoring any shrinkage stresses, it may be applied to solid/substrate interfaces [23].

The term π_s in equation (9) is defined as $\gamma_S - \gamma_{SV}$, often referred to as the equilibrium spreading pressure. It is a measure of surface energy reduction by vapour adsorption of the contacting liquid. For practical purposes π_s is frequently considered negligible, mainly due to difficulties in its accurate measurement.

5. COATING TECHNOLOGIES AND EQUIPMENTS

Several coating technologies exist and a is variety of industrial equipments commercially available. These could be divided into two categories: systems using mechanical agitation and those that use pneumatic solid mixing. Examples of the first category of apparatus are drums, pans and impeller mixers. The mixing of the solid is achieved by the movement of the apparatus itself or by use of an agitator. As for the second category, some examples are the fluidised-bed, spouted-bed or Wurster apparatus.

Throughout this section we will be referring to these various coating technologies. Emphasis is however given to fluidised-bed coaters because this type of equipment is by far the most widespread in the industry to perform the coating of solid particles. In addition, the majority of trends relative to the influence of different variables on operation criteria holds up for other pneumatic agitation techniques. Note that the dry coating technologies are not detailed here as they fall under powder mixing discipline and are described in several excellent works (e.g. [6,10,11]).

5.1. Fluidised-bed coating

Employed as early as 1926 for catalytic cracking of hydrocarbons, fluidised beds have successfully been used for coating solid particles such as pellets, granules and powders. However, it was not until the early 1970s that its widespread use began, in particular due to its introduction in the pharmaceutical industry in the United States. Since then, this technique has been used on an industrial scale in the manufacture of many products, including detergents, fertilisers, foods, etc.

In a fluidised-bed coater, core particles are fluidised by hot air in which the coating liquid in a solution or a suspension form is applied either directly into or onto the bed. This is often performed using a spraying nozzle. The nozzle may be positioned either above or inside the fluidised bed.

In the case of solutions or suspensions, the solvent will be evaporated leaving behind the deposited solid material as thin solid layers. The heat of vaporisation of the solvent is mainly brought by the fluidising medium, which can be air, inert gas or solvent vapour.

In addition to desirable characteristics of conventional fluidised bed such as isothermicity, high heat and mass transfer rates and good particle mixing, fluidised-bed coating permits several elementary operations such as wetting, mixing evaporation and drying and sometimes granulation and classification to be carried out in a single piece of apparatus. Therefore, contrary to coating technologies relying on mechanical mixing (rotating drums and pans), there is no need for subsidiary drying units to evaporate the added solvent. However, these advantages, responsible for the successful use of fluidised beds in industrial operations, may be upset by some disadvantages when operating in the presence of spraying liquids, by de-fluidisation phenomena occurring due to formation of large agglomerates. Another problem when operating fluidised beds is the attrition phenomenon, which results in losses in coating agent deposition and then operation efficiency. The latter, is an important parameter in the case of costly binders and indicates whether or not the operation is economically acceptable.

This is a potentially serious problem that must be kept in mind for coating and agglomeration processes because when it occurs the behaviour of fluidised bed can change drastically and result in whole batches being rejected.

5.1.1. Influence of divers parameters on fluidised-bed coating

For optimal process development, it is imperative to understand the influence of process parameters and design as well as product properties on the process performance and the fundamental mechanisms controlling the process. In this section, the influence of various parameters on the mechanism of growth based on works reported in the literature is reviewed.

In fluidised-bed coating the growth mechanism and the properties of the end product depend on a variety of parameters. These parameters can be classified in four main groups: the properties of solid particles, the properties of the coating liquid, the geometry of the coater and the operating conditions. Note that the complexity of the process lies in the interactions between these various parameters. Accordingly, it is difficult to highlight the effect of each parameter in an independent way as none of them are autonomous.

Prior to analysing the effect of process and products variables, it is helpful to introduce some important coating criteria. Generally, the extent of the growth is characterised by one of the two following criteria:

- Particle mean diameter: Generally, any characteristic diameter can be used but the Sauter mean diameter, d_{32}, and the median mean diameter, d_{50}, are the most widely used.
- Growth rate: This dimensionless parameter determines the percentage of the particle size increase. This can be obtained by dividing the difference between the instantaneous diameter and the initial one by the initial mean diameter.

In addition, the following criteria take into account the efficiency of deposition and the loss of the coating agent by attrition and spray drying:

- Solute content: The solute content is defined as the mass fraction (or percentage) of the deposited coating agent to the support particles.
- Coating efficiency: This criterion is the ratio of the quantity of solute deposited on the solid particles during the time t to that introduced in the bed for the same duration.

5.1.2. Influence of the properties of solid particles

- Size and particle size distribution.
  Reported works in the literature agree on the fact that the dominant mechanism of the growth depends strongly on the initial particles size distribution. The presence of fine particles in the bed supports the growth by agglomeration [15,36–38]. For example Smith and Nienow [15] using a system having a weak tendency to agglomerate (i.e. glass beads-acid benzoic) showed that the increase in the initial size of the particles allows a change of the mechanism of growth from agglomeration to layering. The same phenomena were observed when a more agglomerating coating solution (polyethylene glycol) was used but the growth rate was somewhat higher. Hence, the growth rate has, on the whole, a tendency to increase with decreasing particle size.

As for the influence of the initial particle size distribution, Jackson *et al.* [39] and Vanacek *et al.* [40] noted that using a narrow particle size distribution leads to an excessive formation of agglomerates. On the contrary, in the case of a relatively broad distribution, the particle growth is mainly controlled by the layering mechanism.

In addition, the smaller the mean particle size, the greater the efficiency of operation [41]. This can be explained by the fact that smaller particles capture more binder than larger particles because of their greater specific area and more frequent contact with the spray in the atomizing zone.

- Particle porosity
  Some authors [15,19,37,42–44] observed that the porosity of the support have a considerable influence on the mechanism of growth in fluidised-bed coating at low temperature. For example, Song *et al.* [44], carried out experiments using both porous (sodium tripolyphosphate) and non-porous (glass beads) particles. The coating liquid was a mixture of mono- and diorthophosphate of sodium. They observed that the effects of the fluidising velocity and the concentration of the solution on the growth rate are more significant for the porous particles than for the compact beads.

Smith and Nienow [15,19] carried out coating experiments with porous alumina particles using solutions of benzoic acid (10% w/w). They noted that contrary to compact particles, the size of alumina particles remains practically constant throughout a long time called *no-growth period*. Beyond this period, the particle mean size increases noticeably either by agglomeration or by layering. These authors demonstrated that the no-growth period corresponds to the partial filling of the pores. Indeed, the specific surface area of particles decreased during the no-growth period and remained practically constant during the growth regime. Other workers [42–44] reported similar observations using other model systems. These works pointed out that the duration of the no-growth period is a function of a multitude of parameters such as the pore size distribution, the concentration and the viscosity of the solution, wetting parameters and the drying rate.

Recently, Desportes [43] used the fluidised-bed coating technique to produce supported catalysts using highly porous silica particles as support and a coating solution containing organo-metallic precursors. He carried out a systematic study on the influence of the operating parameters on the coating of coarse porous particles in a fluidised bed. The reported results highlight that the coating process is governed by the balance between two elementary processes: drying and impregnation by capillary wetting. This author defined two characteristic times, the first one relative to drying, t_{dry}, and the second to penetration by capillarity, t_{cap}. He postulated that for $t_{\mathrm{dry}}/t_{\mathrm{cap}}$ ratios higher than 10 the deposition occurs uniformly at the internal surface of particles provided that the moisture content of particles remains greater than 10%. The deposition at the peripheral surface of particles begun when volume of pores is filled either by saturated coating solution or by solidified coating agent.

- Solubility of particles in the coating liquid
  Dencs and Ormos [45] carried out coating experiments in fluidised beds of six types of solids with aqueous solutions containing the same material that those constituting the bed. These authors noted that in the case of urea, the nitrate of sodium and potassium dihydrate carbonate, primarily layering develops the growth. The particle size distributions of obtained products at the end of the

operation were narrow. On the other hand, the coating of the sodium dichromate, ammonium nitrate and potassium phosphate led to products having broad size distribution, lying between 0.2 and 5 mm. In this case, the growth is carried out mainly by agglomeration.

In addition, during the coating of sodium and iron sulphates, Mortensen and Hovmand [46] noted that the growth is done by layering for the first case, whereas in the case of ferrous sulphate it is controlled by the mechanism of agglomeration. In order to highlight the effect of the solubility and the absorptivity of the solid support on the mechanism of coating, Ormos *et al.* [47] studied the coating of various materials with an aqueous solution containing gelatine (6% w/w). These materials of initial size ranging between 0.1 and 0.2 mm are different by their solubility and their absorptivity (Table 1). These authors noted that the growth of the particles is more marked for the soluble solids in the solvent (water), as is the case for sodium chloride and nitrate. On the contrary, the growth is less marked for the glass beads and silica sand, both having good absorptivity. Finally, the speed of growth is very low when the material used has a low absorptivity, case of polyethylene.

5.1.3. Influence of the properties of the coating liquid

- Liquid density

  The literature reveals no significant effect of the liquid density on the coating criteria. The only effect of this parameter concerns the coating of porous particles, in particular when the starting point for the growth regime is determined by the filling of pore volume by the coating liquid. In this case, the higher the liquid density, the longer the period of no growth.

- Wetting parameters

  First of all note that the wetting parameters are not inherent properties of the liquid but result from localised interactions between liquid and solid molecules (Section 4.4). Several works show that the extent of wetting is one of the most important parameters in controlling the quality of deposited layer. Indeed, the growth kinetics as well as the operating efficiency are strongly dependent on the distribution of the liquid on the surface of the particles characterised by the contact angle. In addition, this parameter has an influence on the morphology of the final product.

Generally, the wetting of the solid substrate by the coating liquid is a function of three parameters, which are the contact angle, the surface tension of the liquid and its viscosity. The two first parameters govern the maximum (equilibrium) wetting which can be attained, whereas the third determines the wetting kinetics.

The surface tension of the liquid governs the droplet size distribution as well as the distribution of the liquid on the surface of the particles.

Aulton and Banks [48] were the first to study the effect of the wettability on the fluidised-bed coating process. To modify the wettability, these authors used mixtures of two solid components, the first one being hydrophilic (lactose) and the second hydrophobic (salicylic acid). The coating liquid was an aqueous solution containing 5% in weight of polyvinylpyrrolidone (PVP). These authors noted that the increase in the mass fraction of the hydrophobic component results in a reduction of agglomeration extent.

Recently, Saleh *et al.* [49] carried out a systematic study of the influence of wetting parameters on the coating criteria by two types of experiments. The first one consisted of using hydrophobic glass beads prepared by a chemical grafting treatment. This type of operation has an advantage in being able to modify homogeneously the surface properties of solid particles without changing any other properties of solid particles (density, size, surface roughness) or of binder liquid (surface tension, viscosity, etc.). The second type of experiment consisted of adding different types of surfactant to aqueous solutions of lactose (10% w/w). In this case, both untreated and chemically treated glass beads were used. The results showed that the coating efficiency increases with the product of the liquid surface tension and $(1+\cos\theta)$. These results do indicate the direct relationship that exists between the coating efficiency and the adhesion work (see equation 9).

In addition, the work of Saleh *et al.* demonstrated that the agglomerate strength due to a liquid bridge (equation 6) can suitably describe the extent of agglomeration. This is mainly because the coating agent used by these authors was a low viscosity liquid. Another remarkable finding of these authors was that for contact angles higher than 90° the efficiency remained negligible ($<$4–5%) whatever the exact value of the contact angle was. This observation was attributed to the rebound phenomena, which become preponderant when the contact angle exceeds 90° [18].

- Liquid viscosity

  The viscosity of the coating liquid has a major effect on the predominant mechanism of the growth. Several experimental and theoretical works show that the extent of agglomeration increases with increasing the liquid viscosity (e.g. [15,19,32–35,50]). Generally, as described in Section 4.5 at high liquid viscosity the capillary forces do not govern the agglomeration and give up their place to viscous dissipation forces. Furthermore, the viscosity has a noticeable influence on atomisation behaviour of the liquid and the resultant droplet size. The latter has a tendency to increase with increasing the liquid viscosity.

In addition, the liquid viscosity plays a role in the quality of deposition. In the case of high viscosity liquids, the evaporation takes place before the liquid has time to reach the equilibrium contact angle. This phenomenon, similar to a poor wettability, alters the quality of deposition and the formation of nonuniform and rough coating layers.

- Concentration of the liquid

  The solution concentration is a parameter that affects the duration of the operation as well as the mechanism of the growth. However, while operating with highly concentrated solutions, the degree of saturation during drying can reach elevated levels. This leads to an increase of crystallisation or solidification rate of the solution on the surface of the particles.

In some cases, the concentration of the coating agent considerably affects its viscosity. For example, this is the case when using agglomerating liquids such as aqueous solutions containing polymers (i.e. CMC, PVP, gelatine, etc.). For this type of coating solution the effect of the concentration appears through the variation of the liquid viscosity.

In the same manner, if the concentration affects the surface properties of the coating solution, the effect of the concentration becomes secondary compared to that of surface tension and contact angle.

Generally, when growth by layering is the dominant mechanism (nonviscous liquids) the growth rate after a given time varies linearly with the concentration [44,45,51,52]. For fixed operating conditions and for a given amount of coating agent introduced in the bed, the concentration seems to have no significant effect on the growth rate [17]. However, with high concentrations, evaporation and spray drying of atomised droplets becomes so fast that the coating efficiency deteriorates.

5.1.4. Influence of operating conditions

- Atomising conditions

  The atomization air and liquid flow rates constitute key parameters in the fluidised-bed coating process. These parameters determine the droplet size, which in turn influence the mechanism and quality of deposition. Generally, it is accepted that the mean droplet size decreases with increasing atomising air flow rate or decreasing liquid flow rate.

Liquid flow rate

The liquid flow rate is an important parameter in the coating process especially in batch operations, because it determines the duration of the operation and consequently the rate of production. Heating power must be taken into consideration when choosing suitable parameters.

In addition, it should be noted that, for a given atomising air flow rate, the increase in the liquid flow rate leads to an increase in droplet size [53–56].

The effect of this factor on the particle growth rate has been studied in two different ways: the first one is to keep the duration of the operation constant and the second one is to keep the amount of the liquid (reduction in operation time) constant.

For the first case, several works showed [45,57–61] that the increase in the liquid flow rate allows an increase in the particles size. This could be explained by an increase in the droplet size on the one hand and the enhancement of the amount of the coating liquid brought to the system on the other hand. These two phenomena support the growth by agglomeration.

As for the second case, the results reported in the literature are not conclusive. Indeed, according to the physical properties of the liquid and in particular the liquid viscosity, two cases can be distinguished. In the case of highly viscous binders having a strong tendency to agglomerate, the increase in the flow of the solution allows an increase in the particle growth rate and a reduction in their brittleness [59]. For less viscous solutions, Saleh *et al.* [17] reported that for a given ratio of the solute introduced to the initial particle mass, the increase of the liquid flow rate influences neither the particle growth rate nor the operating efficiency [17,62]. This was explained by the fact that, in their operating conditions, the droplet mean size did not vary significantly with the liquid flow rate.

These results show that the influence of the liquid flow rate on the growth rate cannot be disconnected from the physicochemical properties of liquid and solid particles.

Atomising air flow rate

Generally, the effect of this parameter is expressed by means of NAR ratio, which represents the ratio of the volume or mass flow rate of the atomising air to that of the liquid.

Several researchers [44,57,59,63] studied the effect of the air flow rate at constant liquid flow rate on the particle growth rate. The results showed that the increase in the atomising air flow rate results in a reduction of the average particle size.

In addition, Shinee *et al.* [51] studied the kinetics of growth during the injection of a solution of sodium chloride in a bed constituted from NaCl crystals. These authors noticed that for low air flow rates (voluminal NAR = 500) the growth of the particles occurs by agglomeration, while for relatively high values of this parameter (NAR = 1000) the growth by layering becomes dominant.

Ormos *et al.* [64], using a solution of gelatine (6% in weight) and silica sand as support noted that the size of the particles increases for values of NAR (mass) ranging between 1.13 and 1.7 then decreases between 1.7 and 2.5 and remains constant beyond this value.

As for the effect of the atomizing air on the coating efficiency, Saleh *et al.* [17] revealed the existence of an optimum air flow rate. They showed that starting from low atomising gas flow rates the operation efficiency first increases to attain a maximum value and decreases afterwards. It is interesting to note that the same trend was reported by Link and Schlünder [65] concerning the coating of a single freely suspended aluminium sphere with a 10 wt.% of hydrated lime ($Ca(OH)_2$) suspension. These researchers supposed that the binder deposition on the particle surface occurs in two steps: collision between liquid droplets and solid particles followed by droplet adhesion on the surface of particles. According to Löffler [66], the ability of a droplet to come into contact with the particle is determined by the impingement efficiency. After collision, the droplet can bounce or be captured. The efficiency can be calculated as the product of impingement efficiency and adhesion probability, which governs the second step. By increasing the atomising gas flow rate at a constant liquid flow rate, impingement efficiency increases. In fact, due to both higher velocity and higher number of droplets more of them reach the particles surface before spray drying occurs. On the other hand, the adhesion probability is equal to unity (up to a critical velocity) because all kinetic energy possessed by the droplets is dissipated during contact. Beyond this critical value, the adhesion probability decreases because the collisions become inertial and the reflection and bounce of the liquid droplets occurs. However in the work of Saleh *et al.* [17,67] the efficiency decrease after the maximum point was not as pronounced as in Link's experiments because in a fluidised bed the bounced droplets from primary particles can still encounter other particles.

In addition, Saleh *et al.* demonstrated that the quality of deposition can be significantly improved by increasing the atomising air flow rate. This was attributed to the decrease of droplet size in the one hand and to the increase of droplet momentum on the other, which lead to a more homogeneous and more impact deposition.

- Bed temperature

  The analysis of studies related to the effect of the temperature on the growth mechanism results in two distinct types of size evolution according to the range of temperatures used. For temperatures lower than 100°C, the results of various works are agreed on the fact that the size of the particles decreases with the temperature [59,60,68]. This effect was explained by the reduction in the solid moisture due to faster drying, which reduces the possibility of formation of liquid bridges between particles. Thus, higher temperatures tend to encourage the growth by layering [40]. However, Song et al. [44] attributed the reduction in the average size of the particles to the temperature gradient existing around the wetting zone of the coater, which leads to a fragmentation of the particles due to thermal shocks. This gradient is more important when the temperature is higher. In addition, in the range of higher temperatures, other researchers [62,69] observed the same phenomena: the average size of particles decreases slightly with the temperature of the bed. During the drying and coating of calcium tetrahydrate nitrate, Markvart *et al.* [69] noted that for a bed temperature of 163°C, the dominant mechanism is agglomeration, whereas beyond 200°C, the layering mechanism prevails. For temperatures in between, the growth is done simultaneously by the two mechanisms.

It is notable that, for temperatures higher than 300°C (temperature range used for radioactive waste processing and calcinations), the majority of the studies agree on the fact that the growth is governed by layering and that the average size of the particles increases with temperature [39,70–83]. For example, in the case of de-nitrification of uranyl nitrate, Philoon *et al.* [72] noted that the average size of the particles at a temperature of around 700°C is 2.5 times larger than that obtained at 600°C. This result was explained by the increase in the porosity of the bed with the temperature.

Also, Jonke *et al.* [52] noted that the size distribution of the coated particles strongly depends on the temperature. At 310°C, the percentage of large particles is appreciably reduced, and that of fines (between 74 and 147 μm) is increased. According to these authors, at low temperature, the evaporation of part of the liquid is done in the porous solid leading to a fragmentation of the particles and a consequent formation of fines. On the other hand, at high temperature, the evaporation of the liquid takes place only on the external surface of particles.

In an experimental study Saleh and Hemati [41] studied the coating behaviour of model particles (silica sand and glass beads) with aqueous solutions containing NaCl as the coating agent. They observed that the increase of the bed temperature from 50°C (relatively wet conditions) to 130°C (relatively dry conditions) led to a highly porous and rough surface with sharp-edged crystal structures. This can be due to high drying rate in the system that causes the droplets to be saturated (or over saturated) when reaching the particle surface. This diminishes the wettability considerably and hence the spreading of liquid on the particle surface. In addition, an increase in the bed temperature has a negative effect on the coating efficiency because the loss of solute due to spray drying increases. Also the effect of the bed temperature is more pronounced for porous particles than compact particles.

- Fluidisation gas velocity

  The fluidising gas velocity is a parameter that influences both the operation stability and coating parameters. Hydrodynamic behaviour of the fluidised-bed coater is strongly dependent on the fluidising gas velocity. A proper choice of this parameter is essential to avoid unplanned agglomeration and to keep a stable operation for long periods. According to some authors [15,44,51] the fluidisation velocity can be considered as the principal parameter in the control of the growth of the particles. Generally, for low values of U/U_{mf} ($= 2$), the growth is mainly governed by agglomeration. As the ratio of U/U_{mf} increases, growth by layering becomes more and more prominent. However, if the agglomeration must be totally avoided fluidisation ratios between 10 and 50 are needed [83].

In addition, Smith and Nienow [15] showed that the choice of the fluidisation velocity depends primarily on the nature of the support and that of the coating solution. For example, when a methanol solution containing 10% of benzoic acid was injected into a bed of glass beads (270 μm) fluidised with a gas excess of 0.15 m s^{-1}, bed quenching took place after 5 min. Increase in the excess of gas to 0.65 m s^{-1} made it possible to maintain a stable operation up to 600 min. In the latter case, the dominant mechanism was layering.

Also, it is worthwhile to mention the work of Cherif [84] who studied the effect of fluidising gas velocity on the stability of the operation as well as on the coating criteria. The operation stability was followed by means of the time evolution of total pressure drop. In fact, it is well known that bed quenching is characterised by a rapid decrease in pressure drop, because most of the gas goes through the slumped bed. Consequently the bed quenching point can be determined by measuring the pressure drop through the bed [84]. The results showed that the lower the gas velocity, the faster the bed quenching takes place. To maintain a stable operation with layering as the predominant mechanism, fluidising gas velocities higher than 6 times the minimum fluidisation velocity of initial particles was needed. However, a drop of about 30% in the coating efficiency was observed when increasing the fluidisation velocity from 2 to 6 U_{mf}. This was attributed to the increase of attrition rate with increasing fluidising gas velocity. Several workers [15–17] have reported a direct relationship between the attrition rate in fluidised beds and the excess gas velocity. In addition, a higher fluidising gas velocity results in higher spray drying rate.

- Mass of the bed

  Experiments carried out by Dencs and Ormos [45] during the production of urea in a continuous fluidised-bed coater, showed that the average size of particles increases with the height of the bed up to a value close to 1.25 times the diameter of the column. Beyond this ratio the growth rate became independent of this factor. These observations were explained by the fact that an increase in the bed height entail on the one hand, an increase in the average residence time of particles in the bed and on the other hand, by the development of the mechanical constraints which support a more marked attrition of the solid particles in the bed. For the bed heights higher than 1.25 times the diameter of the column, these authors postulated that there is a dynamic balance between the growth and the disintegration of the formed particles.

During batch coating, Ormos *et al.* [64] studied the influence of the bed height between 40 and 130 mm. The initial size of the support varied between 100 and 200 μm. During tests, they kept the ratio of the mass of the aqueous solution injected with that of the support constant. They noted that the average size of the particles decreases significantly with the height of the layer between 40 and 80 mm to remain constant beyond that.

In addition, according to Saleh *et al.* [17] for a given ratio of the introduced mass of solute to initial bed mass, the growth rate and the coating efficiency are independent of the initial bed mass. These results together with those related to the effect of liquid flow rate indicate that particles wetting in a fluidised-bed spray coater occurs only in a limited volume of bed called "atomisation zone", which is independent of total mass of particles. The penetration depth of the spray determines the size of this zone. This is a function of gas velocity, the nozzle position, physical properties of atomising and fluidising gas and particles momentum. The existence of such a zone in the coater was reported by Smith *et al.* [15] by measuring the temperature gradients near the nozzle. Since the total bed weight has no effect in the penetration depth of the spray there is no effect of this parameter in the coating criteria.

5.1.5. Influence of the coater's specifications

Aside from general requirements to ensure a suitable fluidisation [85] additional conditions must be fulfilled to maintain a stable coating operation. In particular, the introduction of the coating liquid within the bed renders the operation much more delicate than the conventional fluidisation. Among all coater's specifications the characteristics and the position of the spraying system and the use of auxiliary mixing aids are the most important parameters.

Dencs and Ormos [45] studied the effect of mechanical agitation on coating and granulation in a fluidised bed equipped with a vertical agitator. They observed that increasing the number of revolutions leads to a linear reduction of the particle size. However, beyond a critical value of 180 rpm, the size varied moderately with this factor.

The position of the spray is also a design parameter which can have an on the duration of a stable operation and on the mechanism of growth and the efficiency of the operation.

Some researchers [57,59] announced that a rise in the spray height with respect to the bed surface led to a reduction of the size of the coated particles. This was attributed to spray drying of atomised droplets. For example, the results of Rankell *et al.* [57] obtained in a fluidised-bed coater of 0.3 m diameter showed that the average size of the particles passes from 500 to 250 μm when the position of the spray with respect to the distributor increases from 0.75 to 1.5 m.

According to Mortensen and Hovmand [86] the size of the particles is maximised when the spray is immersed in the bed.

Ormos *et al.* [64] studied the influence of the position of the spray with respect to the distributor in the range between 0.09 and 0.24 m. They noted that, under their operating conditions, this factor does not have any influence on the average size of the particles, but it influences the particle size distribution.

Cherif [84] studied the influence of the characteristics of the pulverisation system (i.e. the type of the spraying nozzle and the angle of dispersion of the spray) on the mechanism of growth. Both internal mixing and external mixing nozzles producing similar dispersion angles were studied. The results showed that the external mixing atomiser led to a slower growth rate due to a finer atomisation. However, the operation becomes less stable as the external mixing nozzles present a higher risk of filling of the liquid nozzle's opening. The influence of the spray dispersion angle was studied by using two internal mixing systems providing two angles of 15 and 70°respectively. It was observed that an increase in the angle of dispersion favours the agglomeration extent and hence the growth rate. Cherif showed that the height of the spray nozzle has a considerable effect on the efficiency of the operation without modifying the growth mechanism. Finally, several authors reported that the most adequate position of the nozzle is that for which the end of the tube is immersed in the bed. Doing so, the scouring action of the bed particles permits to avoid cakes formation on the outside of the nozzle.

5.1.6. Design options for fluidised-bed coaters

The operating arrangement of a fluidised-bed coater varies according to application, feed type (melt, slurry, solution, etc.), spraying nozzle configuration and solid throughput. However, all of the possible configurations are modifications of a basic idea: particles to be coated are suspended by a hot gas stream and the coating liquid is applied as homogeneously as possible onto particles surface.

Figure 9 assembles a survey of diverse design options available for fluidised-bed coaters. Regarding the spraying of coating agent, three possible elementary configurations are commonly used which are top-spray, bottom-spray and side-spray equipment. In some cases a combination of these options is used. The bottom spray configuration promotes a more regular circulation of particles through the wetting zone but its disadvantage is the clogging of the nozzle(s) that cannot be remedied easily since removal of the nozzle during a run is not possible. Side-spray systems are frequently used for waste and sludge incineration but rarely for coating operations.

Heat for evaporation of the solvent is either supplied as sensible heat in the fluidising air or through the walls and/or by means of heat transfer surfaces inserted inside the bed. In some cases, the exiting air is recycled after dehumidification in order to reduce energy consumption of the unit (Fig. 9).

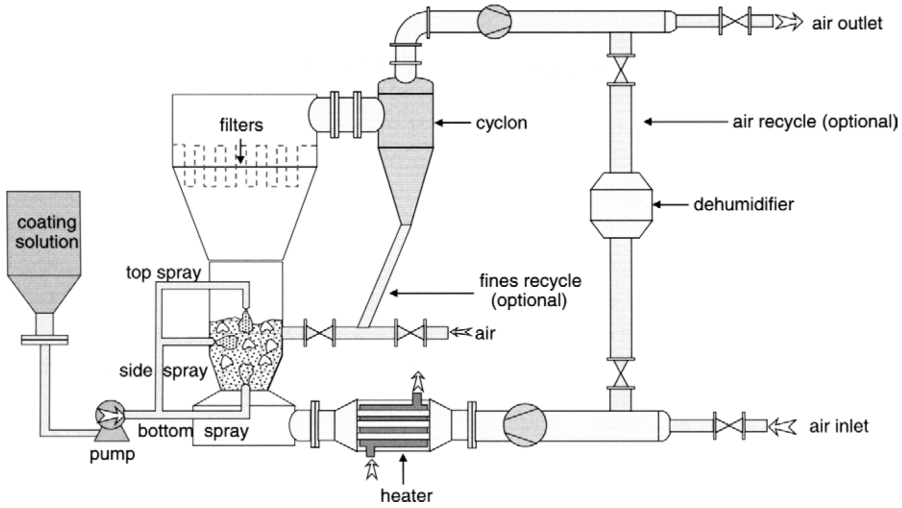


Fig. 9. Typical fluidised-bed coater.

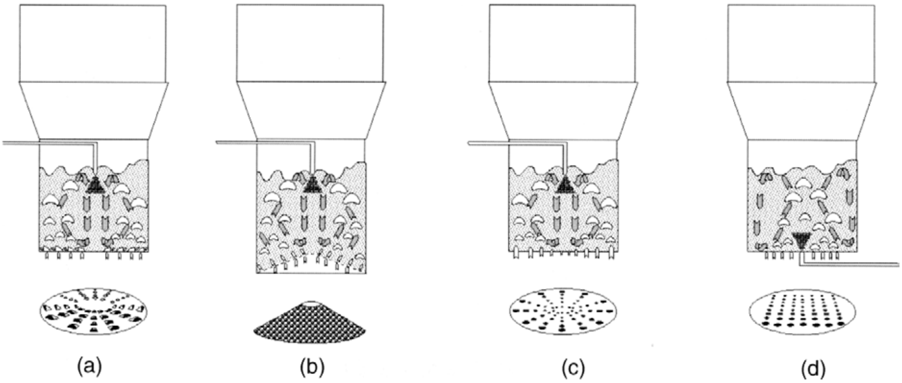


Fig. 10. Examples of specially designed distributors to improve particle circulation.

Dust removal systems (cyclones and/or filter bags or a combination of both) are usually used to separate fine dusty powder from the exit gases.

Coating units can either be carried out continuously or in batches. Batch units are used for low solid throughputs but are versatile since the same apparatus might treat several types of solids. The coating mass distribution is however not as good as that obtained by continuous operations. This is because all particles do not have the same residence time in the wetting zone of the bed. The residence time distribution (RTD) of particles within the spray zone can be tightened by a proper design of the column or the air distributor. For example, distributor designs presented in Fig. 10 provide a more regular circulating of solid particles within the bed and thereby a more uniform coating mass distribution. Continuous operations can be performed either in a single piece of apparatus or in a cascade of different pieces of apparatus. The former is easier and less costly but the latter results in a more uniform coating mass distribution because the RTD of particles shifts from mixed flow to plug flow as the number of coating chambers increases. In the case of a single unit, partitioning the coating cell as illustrated in Fig. 11 could tighten the RTD. Note that option B is more adequate for agglomeration process because the passage of products from one compartment to another occurs through the gap distance between the air distributor and partition plates. Hence, due to segregation, coarser agglomerates have more possibility to leave a given compartment than finer agglomerates, which are retained during longer times.

5.2. Spouted bed coaters

Fluidised-bed coating would be a good choice for coating powders having small to medium sizes (up to 1 mm). Even though this technique can be used for larger particle sizes, its advantages will be largely disrupted as far as energy considerations are concerned. For large particles (Geldart's class D), the energy consumption (calculated by the product of the gas flow rate and its temperature drop through the bed) is determined by the minimum fluidisation velocity rather than the net energy required to eliminate the solvent. Spouted beds have been developed into an effective alternative to fluidised beds for handling coarse particles, i.e. particles that exceed about 1 mm in diameter [87,88]. Since then they have been commercially used as a substitute for the fluidised bed, to process a great variety of coarse solid materials.

A typical spouted bed consists of a cylindrical vessel usually with a conical base and a central orifice in the cone's bottom. The vessel is filled with solid particles and spouting gas is injected through the orifice with relatively high

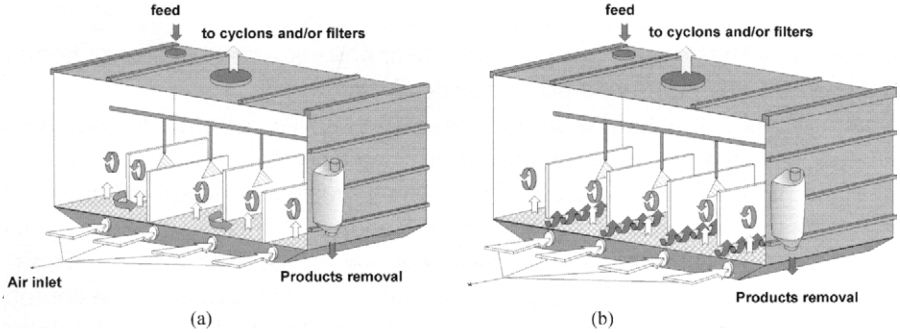


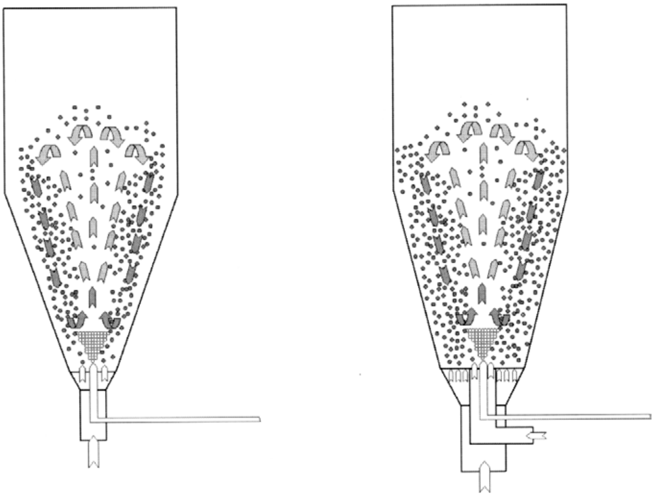
Fig. 11. Schematic view of continuous fluidised-bed coating units.

velocities, typically between 1 and 30 m s^{-1}. The gas also flows into and upwards through the annulus. The high gas velocity causes a stream of solid particles to rise rapidly in a dilute central zone within the bed referred to as the *spout*. In the reason of diverging form of the spout the gas and solid velocities decrease along the bed height. Therefore, having reached a given height entrained particles fall back forming a fountain above the annular space around the spout. The particles form a loosely packed bed within the annulus space and slide down slowly and reenter the spout during their descending at different levels of the bed. Hence, a spouted bed has three well-defined characteristic regions (Fig. 12):

- The spout, characterised by relatively high velocities of both solids and gas stream, short contact times between gas and solid phases, high bed voidage and co-current solids movement with respect to upward gas stream.
- The fountain, where the solids movement with respect to the gas stream is nearly crosscurrent.
- The annulus (also called the down-comer) which, compared to the spout, is characterised by high solids concentrations, low gas and solids velocities, higher contact times and a counter-current solids movement.

In a spouted bed, a well-defined cyclic movement is thereby imposed on the solid particles. In order to avoid any lateral exchange between the spout and the annulus the latter is sometimes delimited by means of a draft tube.

Both top-spray and bottom-spray spouted-bed coating processes can be used. However, the most commonly used configuration is the bottom-spray configuration.



(a) spouted bed coater (b) spouted-fluid bed

Fig. 12. Spouted-bed coating apparatus.

In this case, the coating liquid is sprayed in the lower region of the spout where the spray droplets collide with the bed particles. Each time a particle passes through the spray zone, it acquires an additional amount of coating material. The deposited coating liquid should solidify or dry outside the spray zone, either in the spout or in the annulus. This circulation of solid particles is repeated until the desired coat amount is deposited on the solid particles. Repetitive passages through the wetting zone increase the coating content and reduce coat deficiencies due to uneven deposition on the surface. Consequently, the amount of coating content of each particle depends on the coating applied in each pass and the total number of passes executed by the particle during the operation. In almost all experimental works reported in the published literature, particle growth by layering is the dominant growth mechanism.

Industrial spouted-bed coating processes operate either continuously or discontinuously. The former is better matched for high production rates but produces less uniform coating mass distribution due to the variation in the RTD of particles in the wetting zone. Unfortunately, despite its importance, experimental data on RTD in continuous spouted beds are not known.

As for batch processes, heterogeneity in coating distribution do exist due to variations in the number of passages through the spray zone and the amount of the coating liquid deposited in each pass. However, recent works of Cheng [89,90] showed that the coating per pass distribution is responsible for the majority of the variation in the spouted-bed coating process. Note that the use of a draft tube could however lead to a more uniform coating.

Regarding the top-spray spouted-bed coating process, Robinson and Waldie [90] reported that the growth rate is dependent on particle size. They postulated that larger particles spend a greater percentage of their time in the spray zone.

Finally, note that the modification of standard spouted beds to include the characteristics of fluidised bed, called spouted-fluid bed, has also received attention due to its better solids mixing and heat and mass transfer rates. This kind of apparatus involves a substantial fluid flow through a single central inlet orifice, as in spouted bed, and an auxiliary fluid flow through a distributor surrounding the central orifice, as in fluidised bed (Fig. 12b). The auxiliary gas stream thereby keeps the annular zone lightly fluidised. Both flat based or conical based columns can be used.

5.3. Wurster apparatus

Wurster apparatus is perhaps the most common configuration used for film coating. This apparatus is an air suspension coating introduced in the early 1950s by Wurster. Industrial exploitation of Wurster coaters is more recent than fluidised beds and spouted beds. This system is a combination of the concepts of fluidised bed and spouted bed techniques (Fig. 13). A draft tube insert (Wurster partition or column) is placed coaxially in the bed to order the circulation of particles. The particles are carried by an upward gas stream in the draft tube and fall downward around it at the top of the tube. The coating solution is sprayed upward through a nozzle in the centre of the distributor plate placed at the bottom of the bed. The gas velocity inside the draft tube is significantly higher (generally between 3 and 20 ms^{-1}) than inside the annulus (0.1–1.0 ms^{-1}).

A gap between the distributor plate and the bottom of the draft tube allows powder to be picked up at this interface and accelerated by the high-velocity gas stream. Generally, the distributor is a perforated plate, with the size of perforations decreasing from the centre outward. The fraction of open areas of the

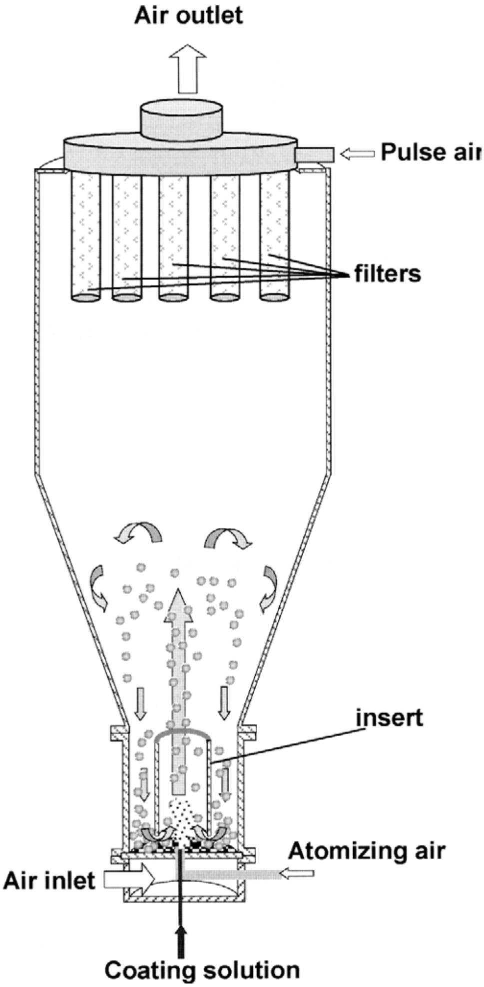


Fig. 13. Wurster coating apparatus.

distributor beneath the draft tube and the annulus determine the relative amount of air flowing into these two sections. The liquid droplets are moving faster than the solid particles so the particles can be wetted and dried in the draft tube but the drying can also take place in the annulus. The solid movement in a Wurster coater is very similar to that of a spouted bed. The size of particles is however much smaller, close to that used in fluidised-bed coaters. Compared to conventional fluidised-bed coaters, in the Wurster apparatus growth by layering is encouraged. This is due to low solids concentrations and elevated heat and mass transfer rates within the draft tube.

Industrial Wursters can be used for handling up to 500 kg of solids. The process is extensively used in the pharmaceutical industry for precision coating and modified release drugs, e.g., sustained release, enteric release and temperature-controlled release.

The literature on Wurster coating processes is less abundant than fluidised-bed coating. The fundamental mechanisms controlling the process are not yet well understood and the optimisation is often based on operator experience. However, the knowledge from fluidised-bed coating could be used as guidelines as the majority of phenomena occurring are comparable in both operations. For example, it has been reported that, similar to fluidised-bed coating, in the Wurster apparatus the smaller particles capture more coating than the larger particles [91]. In addition, the effect of the particle porosity is analogous to that observed in fluidised beds.

Note also that the circulation time distribution can vary considerably depending on the particle properties, coater configuration and process variables such as air flow rate, partition gap, loading, atomisation air velocity, and distributor design.

5.4. Rotating drum, pan and disc coaters

Rotating drum, pan and disc coaters are among the oldest and the simplest techniques used for coating particulates. Rotary pans were originally developed in the confectionery industry and adopted by pharmaceutical industry for sugar coating of drugs. The main characteristics of rotational coaters are their versatility, flexibility, large throughputs and ability to handle a wide range of products. The common principal point of these techniques is that the motion of particles is maintained in a mechanically rotated vessel, while spraying liquid onto the moving bed of particles carries out coating. Figure 14 illustrates a schematic view of rotary coaters. These techniques are suitable for coating large particles, from a few millimetres to some centimetres.

A main drawback of rotational coating techniques is the poor heat and mass transfer rates. Unlike the air suspension methods (fluidised beds, spouted beds, Wurster) a suitable control of the temperature is not possible when using

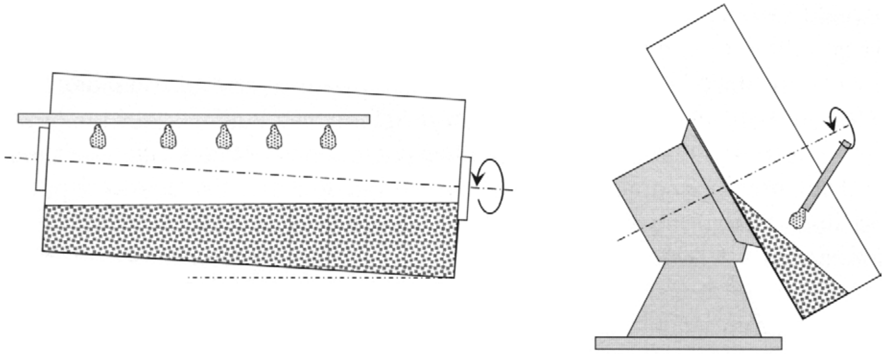

(a) rotary drum (b) rotary disc

Fig. 14. Schematic view of rotary coaters.

rotational apparatus. In addition, the holdup of rotary coaters is small which results in bigger shell volumes compared to pneumatic-based apparatus. Because of the large size of apparatus substantial filters must be used to collect the dust if necessary.

Generally, coating pans operate discontinuously, whereas discs and drums can be used either in batch or in continuous modes.

A conventional rotary pan consists of an ellipsoid vessel made usually of stainless steel and mounted on a gearbox shaft which is driven by an electric motor. A hot air blower is usually used to irrigate the particles bed and improve the drying. The selection of a coating pan depends on manufacturer specifications and may range from a simple modification of the conventional copper pan to specialised high-volume vessels.

The operating mode of coating discs and pans are very similar. The only major difference is the geometric design of the vessel, which makes rotary discs suitable for continuous operation. The diameter of industrial discs varies between 3 and 10 m and the height to diameter ratios between 0.1 and 0.3. Continuous discs are only suitable for short residence times. For longer residence times or when a controlled RTD is required rotary drums are preferred. Rotary drums are usually equipped with one or more ribbon-like baffles mounted to the inside surface of the front wall. In continuous rotary drums coating agent is sprayed onto the bed, wetting the particles as they pass through the drum. Coating agent may be sprayed either at the entire length of the drum or only during the first sections. The last compartments of the drum are used for evaporation and drying and in some cases for cooling. A hot and dry gas stream generally traverses the drum. In some industrial designs, the drum may have a perforated or mesh wall for drying of the tablets. In this case, the hot gas stream is directed through the drum wall as the drum and the bed of particles are being rotated. This kind of design enhances gas to particle heat transfer and is suitable when high drying rates are needed.

Note that rotary coaters are more suited to narrow size distributions. In the case of large particle size distributions, the coating distribution is less uniform due to natural segregation as separation takes place: fines concentrate near the bottom of the kidney-shaped cross-section of the bed and the coarsest particles travel near the surface. The sizing of rotary drums is based on the average residence time *t*, which is calculated from the ratio of total mass of particles contained in the vessel (holdup), *m*, and mass throughput, *C*. The holdup, *m*, is a function of drum volume and drum loading, which varies between 0.1 and 0.3. Residence time depends mainly on three operating parameters: the angle of inclination of the drum's axis against the horizontal, the rotational speed and the drum's length. However, the angle of inclination is rather small (2–5°and only serves to provide the required axial movement. The rotational speed is usually fixed between 25% and 40% of the critical speed beyond which tumbling and centrifugation occurs.

Unfortunately, the lack of the knowledge does not allow carrying out a priori sizing of rotary drums. For a given set of coating agent and substrate the sizing is based on experimental runs in pilot plants during which the appropriate operating conditions (angle of inclination, rotational speed, holdup, liquid flow rate, concentration) are determined. The scale-up is then performed by know-how from the equipment manufacturer but some useful guiding rules exist [92].

6. CONCEPTS IN MODELLING THE COATING PROCESS

Rational scale-up of coating units requires modelling of the growth phenomena by layering and agglomeration. A successful modelling requires knowledge of both mechanical and physicochemical phenomena occurring during the coating process and presented in previous sections. Generally, the two main parameters that are chosen as modelling variables are either the particle size or the coating content of particles. Existing models in literature, aimed at predicting the evolution of these target variables during simultaneous coating and agglomeration processes, may be broadly classified into two main categories: empirical and theoretical models. The first group involves models of "black box" type where the relationship between the particle mean size and key parameters in the process environment expected to govern the particle growth (i.e. operating conditions and physical properties of solid and liquid) is given by an empirical expression. These models are quite simple but their use is restricted to the special cases and the domain of operating conditions at which the phenomena are studied.

A very different process is used for theoretical models where one tries to take into account the physical phenomena occurring during the operation. Among the various theoretical modelling works on coating and agglomeration, two different approaches can be distinguished: simple approach and "fundamental" approach. The simple approach neglects the variations in particle size and solute content distributions considering that all particles have the same size as well as the same residence time in the system. In other words, it is assumed that the size and the solute content of a single particle can be representative of the bulk properties of the powder. In this case, the targeted parameters can be predicted using conventional heat and mass balances established for solids. In the case of mono-size spherical particles with a uniform distribution of solute over particles the simple layering model leads to the following relations for estimating of the evolution of the solute content and the mean particle size as a function of time:

- solute content

$$\tau_s(t) = \frac{\dot{w}_L C\eta}{\rho_L M_0} t \tag{10}$$

- particle mean diameter

$$d_p = \left[d_{p0}^3 + \frac{\eta}{100}\frac{\dot{w}_L C}{\rho_L}\frac{\rho_p}{\rho_s}\frac{d_{p0}^3}{M_0} t\right]^{\frac{1}{3}} \tag{11}$$

where ρ_s, ρ_p and ρ_L are solute (coating agent) density, particle density and liquid density, respectively. $\dot{w}_L$ the coating liquid mass flow rate, t the operating time, M_0 the initial mass of the bed, η the coating efficiency and C the concentration of the coating agent. d_{p0} and d_p are the initial particle size and particle size at time t, respectively.

An important limitation of any theoretical model of coating processes is the difficulty of relating the coating efficiency to the process and product-related parameters. Note that this type of model is suitable and frequently used in the coating process by a solute but is not reliable when agglomeration is pronounced because the total number of particles varies with time. In the latter case a simple model proposed by Sherrington could be used [93].

If the distribution of a given coating criterion rather than its mean value is to be predicted, more detailed description must be used based on a coupling conventional heat and mass balances and population balance equations (PBEs). This is particularly the case for the film coating of drugs where even small deviations in the thickness of the polymer film can significantly alter the properties of the final product.

The population balance is a statement of continuity that describes how a given property of the population of particles changes with time and in space. In principle, any common property of particles can be used but as mentioned above in coating processes the more interesting parameters are the particle size and the coating content.

PBEs were first introduced based on statistical mechanisms by Hulburt and Katz (1964) [94]. Since, the PBEs were successfully applied for different particulate systems such as crystallisation, granulation, mixing, fluidisation, etc. PBEs describe how the rate of variation of the number of particles in a given interval of the target property (particle size, coating content, etc.) can be related to the rate at which particles enter and leave that interval by different phenomena occurring (i.e. bulk flow into and out of the system, coating, agglomeration, breakage, etc.). In the most general case, for a continuous particulate system, the macroscopic population balance leads to the following expression [94,95]:

$$\frac{1}{N_T}\frac{\partial(N_T f)}{\partial t} = -\frac{\partial(Gf)}{\partial x} - \frac{Q_{\mathrm{out}}f_{\mathrm{out}} - Q_{\mathrm{in}}f_{\mathrm{in}}}{N_T} + B - D \tag{12}$$

where $G = \partial x/\partial t$ designates the mono-dimensional particle growth rate and f the population density function of particles defined on a number basis. More precisely f is a function of the spatial coordinates in the system, of the target property x of the particles and of the time, t. f is defined as the ratio of the number of particles, ∂N, in a differential neighbourhood around x, to the size of the neighbourhood, ∂x Q designates the number-based particle flow rate and the subscripts *in* and *out* specify the inlet and outlet flows. The variables B and D are the birth and death rates of particles number variation in a given x interval by such events as agglomeration and breakage which change population density in a discontinuous fashion. The application of PBEs for modelling the simultaneous growth by layering and agglomeration in coating processes are abundant. These models can be classified in two main categories:

- Single-zone models: In single-zone models it is assumed that the particles are homogeneously mixed and the coating agent is evenly distributed throughout the bed volume. Equation (12) is directly applicable for single zone models. Generally, in a coating apparatus due to high intensity mixing of the particles the population density, f, is independent of spatial coordinates. In addition, usually the breakage rate is not detailed separately. This means that B and D in equation (12) correspond to the net variation of particles number by combined effect of agglomeration and breakage.
- Twin-zone models: Sheroney [96] and Wnulowski and Setterwall [97] were the first to propose a twin-zone model based on the PBEs for the fluidised-bed coating. In a twin zone model, the volume of the bed of particles is divided into two distinct regions: an active zone surrounding the spray nozzle and a mixing zone. This type of model is more reliable as it has been experimentally confirmed that such a distinct zone exists near the nozzle where the deposition of the spray on the particles and bulk evaporation of the solvents take place

[15,17,19,21,22]. The size of this region is determined by the penetration depth of the spray, which depends in turn to operating conditions.

It is considered that the coating mass deposited on the particles is directly proportional to the residence time of the particles in the spray zone, so that the coating mass distribution can be regarded as the RTD function.

In a twin zone model the PBEs are applied separately for each distinct zone taking into account the internal flow of particles circulating between them:

- For the spray zone:

$$\frac{1}{N_{T,\text{spray}}}\frac{\partial(N_{T,\text{spray}}f_{\text{spray}})}{\partial t} = -\frac{\partial(G \cdot f_{\text{spray}})}{\partial x} - \frac{\alpha Q_{\text{out}}f_{\text{out}} - \beta Q_{\text{in}}f_{\text{in}}}{N_{T,\text{spray}}} - \frac{Q_{\text{c}}(f_{\text{spray}} - f_{\text{dry}})}{N_{T,\text{spray}}} + B - D \tag{13a}$$

In this equation, α is the number fraction of the spray zone and Q_c the circulating rate of particles between spraying and drying zones, which is considered to be the same for entry and exit flow. Note that even for a batch operation ($Q_{\text{in}} = Q_{\text{out}} = 0$) the internal zones must be considered as open systems as $Qc \neq 0$.

- For the drying zone there is no growth by layering nor by agglomeration:

$$\frac{1}{N_{T,\text{dry}}}\frac{\partial(N_{T,\text{dry}}f_{\text{dry}})}{\partial t} = -\frac{(1-\alpha)Q_{\text{out}}f_{\text{out}} - (1-\beta)Q_{\text{in}}f_{\text{in}}}{N_{T,\text{dry}}} - \frac{Q_{\text{c}}(f_{\text{dry}} - f_{\text{spray}})}{N_{T,\text{dry}}} \tag{13b}$$

Simultaneous resolving of equations (13a) and (13b) results in the determination of f_{spray} and f_{dry}.

Note also that if it is supposed that all particles have the same residence time in the wetting-evaporation zone (i.e. the particles pass regularly through a well-defined spray zone) twin-zone models leads to the same predictions as single-zone models.

A difficult task while modelling the growth phenomena results from the complexity of the PBEs. Although analytical methods of solving PBEs exist their use is limited to simple cases. Actually, analytical solutions are most often used to verify the persistence of numerical methods. Actually, numerical methods present two obvious advantages. First of all particle size distributions of any type can be dealt with and secondly discontinuous processes such as sequential feeding and solid removal can be taken into account.

Extensive literature relative to numerical methods of solving PBEs is available. For a detailed review see Hounslow et al. [98] and Hogg [99]. The basic idea consists in breaking up the particle size distribution into a number of discrete x ranges. The population balance, described by an ordinary differential equation, is then established for each x interval and the resulting set of equations are solved by numerical methods.

The most popular numerical method is that proposed by Hounslow *et al.* [98] mainly because it guarantees to predict the correct rate of change for first four moments; i.e. total particle number, length, surface and volume (or mass).

Note that the modelling of simultaneous growth by layering and agglomeration requires the introduction of the appropriate formulas for the particle growth rate, G, and agglomeration terms (B–D) into PBEs.

- Agglomeration term: In the majority of coating operations the main growth mechanism is the layering and agglomeration can be neglected. This is particularly true when the particle size exceeds a few hundreds of micrometers. In this case, the PBEs can be considerably simplified because both B and D are nil. For finer particles, the agglomeration can hardly be avoided and must be taken into account. Smoluchowski [100] was the first to develop a mathematical expression for birth and death rates by agglomeration. Considering that particle coalescence results from a series of binary collisions between them, he established the following equations:

$$B = \int_0^{v/2} \beta(v-w,v)f(v-w)f(w)\partial w \tag{14a}$$

$$D = f(v)\int_v^{\infty} \beta(v,w)f(w)\partial w \tag{14b}$$

where v and w are the volumes of the coalescing particles. The asterisk is used to signify that volume rather than size or coating content is chosen as the internal coordinate. The conversion of this equation to a length-based or a mass-based form is straightforward.

If particle mass or coating content is chosen as x coordinate the equation (14) is directly applicable as:

$$u = m/\rho = m_\mathrm{p}(1+\tau_\mathrm{s})/\rho \tag{15}$$

In contrast, if the particle size is used as x variable equation (14) can be expressed as follows (see Hounslow *et al.* [98]):

$$B(L) = \frac{L^2}{2}\int_0^L \frac{\beta\left((L^3-\lambda^3)^{1/3},\lambda\right)\psi\left((L^3-\lambda^3)^{1/3}\right)\psi(\lambda)\mathrm{d}\lambda}{(L^3-\lambda^3)^{2/3}} \tag{16a}$$

$$D(L) = \psi(L)\int_0^{\infty} \beta(L,\lambda)\psi(\lambda)d\lambda \tag{16b}$$

Besides the fact that this model considers only binary collisions, its main drawback is that it suggests that the total volume of agglomerating particles is conserved.

In equations (14) and (16), β is a measure of agglomeration extent and is called the coalescence kernel, which defines the rate at which binary particle collisions result in successful coalescence. In general, this parameter is subdivided into two parts:

$$\beta(v, w) = KE \tag{17}$$

where K is the frequency of binary particle collisions between particles of volumes v and w. This parameter is a function of such parameters as apparatus geometry and operating conditions, which influence the hydrodynamic behaviour of the system. E is the probability of successful coalescence following collision between two particles of volumes v and w. This parameter is mainly conditioned by the balance between disruptive and attractive forces exerted during particle collisions. Generally, both K and E are size-dependent parameters but it is usually assumed that equation (17) contains two distinct parts, one independent of the particle size and the second dependent on it:

$$\beta(v, w) = K_0 E_0 K_1(v, w) E_1(v, w) = \beta_0 \beta_1(v, w) \tag{18}$$

where β_1 includes the functional dependency of the agglomeration kernel on the sizes of the colliding particles.

Several attempts have been made to develop a generalised expression for agglomeration kernel. However, despite the plenty of experimental results reported in the literature none of these representations is completely reliable. Proposed expressions are based on probabilistic considerations rather than a rigorous description of the collision phenomenon [101]. At the moment, the most commonly used expression is the following generic form proposed by Kapur [102,103]:

$$\beta_1(v, w) = \frac{(v + w)^a}{(vw)^b} \tag{19}$$

In this expression, the numerator and denominator are approximate measures of the binary collision frequency, K, and the probability of successful collision, E, respectively.

- Coating term: For size-based PBEs the particle growth rate, G, in equation (12) is the rate of increase in particle size resulting from the deposition of the coating agent into the surface of particles. Assuming that particles belonging to different interval sizes receive all the same amount of coating agent, G is given by

$$G = \frac{\eta}{100} \frac{w_{\mathrm{liq}} C}{\rho_{\mathrm{liq}} \rho_b} \frac{2}{S} \tag{20}$$

This equation states that the coating rate is inversely proportional to the total surface area of particles in the system, S. This is a fairly realistic hypothesis because the coating process is a surface-dependent phenomenon.

Note that equation (20) can also be written in a discretised form [36] more adequate for numerical solutions:

$$G_i = \frac{\eta_i}{100}\frac{w_{\text{liq}}C}{\rho_{\text{liq}}\rho_b}\frac{2}{\sum_j \pi N_j L_j^2} \tag{21}$$

G_i is the growth rate in the ith size interval. The efficiency η depends, more often than not, to the mean particle size inside the interval. The term $\sum \pi N_j L_j^2$ is a measure of total surface

CONCLUDING REMARKS

The industrial scale-up and practise of coating powder materials can be successfully performed provided that the optimal operating conditions and required residence time is determined prior to exploitation. Currently, a proper determination of operating conditions is only possible by conducting coating experiments in bench scale units. Although existing literature provides highly useful information on the effect of different variables on the coating process, its use is limited to qualitative rather than quantitative analysis of phenomena. In particular, the effect of operating variables on the coating efficiency and agglomeration extent is not yet well described. Consequently, an accurate and reliable determination of these parameters cannot be performed by theoretical considerations and more investigations should be carried out in this orientation. Finally, another major difficulty is the control of the coating quality and homogeneity both on a microscopic and a macroscopic scale.

REFERENCES

[1] Z. Ormos, Handbook of powder technology, vol. 9, in: D. Chulia, A. Deleuil, Y. Pourcelot (Eds.), Powder Technology and Pharmaceutical Processes, Elsevier, Amsterdam, 1994.
[2] G. Cole, J. Hogan, M. Aulton, Pharmaceutical Coating Technology, Taylor & Francis, UK, 1995.
[3] S. Gouin, Trends Food Sci. Tech. 15 (2004) 330–347.
[4] O.R. Lundt, J. Agric. Food Chem. 19 (5) (1971) 797–800.
[5] C. Thies, in K.L. Kadam (ed.), Granulation Technology for Biproducts, CRC Press, 1989, Boca Raton, FL, Chap. 7, Microencapsulated Enzymes and Live Mammalian Cells, pp. 179–206.
[6] R. Pfeffer, R.N. Dave, D. Wei, M. Ramlakhan, Powder Technol. 117 (2001) 40–67C.
[7] A. Mujumdar, D. Wei, R.N. Dave, R. Pfeffer, C-Y. Wu, Powder Technol. 140 (2004) 86–97.
[8] C. Conesa, K. Saleh, A. Thomas, P. Guigon, N. Guillot, Prediction of flow properties of powder coatings used in automotive industry, “KONA” Powder Sci. Technol. Japan, No. 22 (2004) 94–106.
[9] K. Meyer, I. Zimmermann, Powder Technol 139 (2004) 40–54.

[10] N. Harnby, M.F. Edwards, A.W. Nienow, Mixing in the Process Industries, 2nd edition, Butterworth & Heinmann, London, 1997.
[11] F.J. Muzzio, A. Alexander, C. Goodridge, E. Shen, T. Shinbrot, K. Manjunath, S. Dhodapkar, K. Jacob, in Chapt. 5. Solids mixing, E.L. Paul, V.A. Atiemo-Obeng, S.M. Kresta (eds), Handbook of Industrial Mixing: Science and Practice, Wiley, Inc., Hoboken, New Jersey, 2004.
[12] T. Iwasaki, M. Satoh, T. Ito, Powder Technol. 123 (2002) 105–113.
[13] S.P. Nalimov, J. Appl. Chem. USSR (Engl. Trans.) 50 (1977) 1682.
[14] T. Schoefer, O. Worts, Arch. Pharm. Chem. Sci. 6 (1978) 69.
[15] P.G. Smith, A.W. Nienow, Chem. Eng. Sci. 38 (8) (1983) 1223–1240.
[16] A. Maroglou, A.W. Nienow, Powder Metall. 29 (1986) 291.
[17] K. Saleh, R. Cherif, M. Hemati, Adv. Powder Technol. 10 (3) (1999) 255–277.
[18] T. Mao, D.C.S. Kuhn, H. Tran, AIChE J. 43 (9) (1997) 2169–2179.
[19] P. G. Smith, A. W. Nienow, Proc. of Int. Symp. on Particle Technol., I. Chem. E. Symp. Ser., No. 63 (1981), D2/k/1–D2/k/14
[20] K. Saleh, D. Steinmetz, M. Hémati, in: Fluidisation, G. Flamant, D. Gauthier, M. Hemati, D. Steinmetz (eds), Lavoiser Tec & Doc, Paris, 14 (75) (2000) 229–236.
[21] S.J. Maronga, P. Wnulowski, Powder Technol. 94 (1997) 181–185.
[22] S. Heinrich, J. Blumschein, M. Henneberg, M. Ihlow, M. Peglow, L. Mörl, Chem. Eng. Sci. 58 (2003) 5135–5160.
[23] A.J. Kinloch, Adhesion and Adhesives, Chapmann & Hall, UK, 1987.
[24] J.N. Israilachvili, Intermolecular & Surface Forces, 2nd edition, Academic Press, New York, 1992.
[25] G.J. Antonow, Chim. Phys. 5 (1907) 372.
[26] D. Bertholot, Compt. Rend. 126 (1898) 1857.
[27] M. Lazghab, K. Saleh, I. Pezron, P. Guigon, L. Komunjer, Powder Technol. 157 (2005) 79–91.
[28] H. Rumpf, Chem. Ing. Tech. 30 (1958) 144.
[29] W. Pietch, Size enlargement by agglomeration, in M.E. Fayed, L. Otten (Eds.), Handbook of Powder Science & Technology, 2nd edition, Chapman & Hall Ltd., London, 1997.
[30] D.M. Newitt, J.M. Conway-Jones, Trans. I. Chem. Eng. 36 (1958) 422–441.
[31] V.P. Mehrotra, K.V.S. Sastry, Powder Technol 25 (1980) 203–214.
[32] M.J. Adams, V. Perchard, Inst. Chem. Eng. Symp. Ser. 91 (1984) 12.
[33] D. Mazzone, R. Pfeffer, G.I. Tardos, Powder Technol. 51 (1987) 71.
[34] B.J. Ennis, G.I. Tardos, R. Pfeffer, Chem. Eng. Sci. 45 (1990) 3071.
[35] B.J. Ennis, G.I. Tardos, R. Pfeffer, Powder Technol. 65 (1991) 257.
[36] K. Saleh, D. Steinmetz, M. Hemati, Powder Technol. 130 (2003) 116–123.
[37] K. Saleh, Ph.D. thesis, Institut National Polytechnique de Toulouse (France) 1998.
[38] D.D. Dunlop, L.I. Griffin, J.F. Moser, Chem. Eng. Prog. 54 (8) (1958) 39–43.
[39] J.D. Jackson, H.A. Sorgenti, G.A. Wilcox, R.S. Brodkey, Ind. Eng. Chem. 52 (No. 9) (1957) 795–798.
[40] V. Vanacek, M. Markvart, R. Drbohlav, Fluidised Bed Drying, Leonard Hill, London, 1966.
[41] K. Saleh, M. Hemati, 11th International Drying Symposium, IDS'98, Greece, 1998.
[42] S. Desportes, D. Steinmetz, M. Hemati, K. Philippot, B. Chaudret, In press Powder Technolol. XX (2005) .
[43] S. Desportes, Ph.D. Thesis, Institut National Polytechnique de Toulouse (France) 1998.
[44] B.H. Song, G.S. Lee, S.D. Kim, J. Chem. Eng. Japan 23 (No. 2) (1990) 148–155.
[45] B. Dencs, Z. Ormos, Powder Technol. 31 (1982) 85–99.
[46] S. Mortensen, S. Hovmand, Engineering Foundation Conference on Fluidisation, California, 1975, pp. 519–544.
[47] Z. Ormos, M. Machacs, K. Pataki, Hungarian, J. Ind. Chem. 7 (1979) 341–350.

[48] M. E. Aulton, M. Banks, Conference on Powder Technology in Pharmacy, Basel, Switzerland, Powder Advisory Centre, 1979.
[49] K. Saleh, I. Pezron, L. Komunjer, P. Guigon, 4ème Colloque Science et Technologie des poudres, 4–6 mai 2004, Compiègne.
[50] K. Saleh, L. Vialatte, P. Guigon, Chem. Eng. Sci. 60 (2005) 3763–3775.
[51] K. Shinee, Y. Poong, K.L. Won, J. Chem. Eng. Jpn. 22 (5) (1989) 469–476.
[52] A.A. Jonke, E.J. Petkus, J.W. Loeding, S. Lawrowski, Nucl. Sci. Eng. 2 (1957) 303–319.
[53] S. Nukiyama, Y. Tanasawa, Trans. Soc. Mech. Eng. Jpn. 5 (18) (1939) 1–4.
[54] W. R. Marshall, Chem. Eng. Prog., 1954, monograph series, no. 2, 50.
[55] K.Y. Kim, W.R. Marshall, AIChE. J. 17 (3) (1971) 575–584.
[56] T. Schoefer, O. Worts, Arch. Pharm. Chem. Sci. Ed. 5 (1977) 1232–1247.
[57] A.S. Rankell, M.W. Scott, H.A. Lieberman, F.S. Chow, J.V. Battista, J. Pharm. Sci. 53 (1964) 320–324.
[58] M.W. Scott, H.A. Lieberman, A.S. Rankell, J.V. Battista, J. Pharm. Sci. 53 (3) (1964) 314–324.
[59] W.L. Davies, W.T. Gloor Jr., J. Pharm. Sci. 60 (1971) 1869–1874.
[60] M.J. Crooks, H.W. Schade, Powder Technol. 19 (1978) 103–108.
[61] B. Waldie, Chem. Eng. Sci. 46 (1991) 2781–2785.
[62] N.N. Bakhshi, A. Nihalami, Proc. Int. Symp. Fluidisation Toulouse, 1–5 (1973) 534–544.
[63] S. Mortensen, S. Hovmand, Chem. Eng. Prog. 79 (4) (1983) 37–42.
[64] Z. Ormos, K. Pataki, B. Csukas, Hung. J. Ind. Chem. 1 (1973) 475–492.
[65] C. Link, E-U. Schlün.der, Chem. Eng. Process, 36 (1997) 443–457.
[66] F. Löffler, Staubabscheiden, Thieme Verlag, 1988.
[67] M. Hemati, R. Cherif, K. Saleh, V. Pont, Powder Technol. 130 (2003) 18–34.
[68] T. Schoefer, O. Worts, Arch. Pharm. Chem. Sci. Ed. 6 (1978) 202–213.
[69] M. Markvart, V. Vanecek, R. Drbohlav, Brit. Chem. Eng. 7 (7) (1962) 503–508.
[70] A. A. Jonke, N. M. Levitz, E. J. Petkus, R. J.Taecker, ANL 5363 A E C R & D Report (1954)
[71] E. Hawthorn, L.P. Shorts, J.E. Lioyd, Trans. Inst. Chem. Eng. 38 (1960) 197–215.
[72] W.C. Philoon, E.F. Sanders, W.T. Trask, Chem. Eng. Prog. 56 (4) (1960) 106–112.
[73] B.S. Lee, J.C. Chu, A.A. Jonke, S. Lawrowski, AIChE J 8 (1) (1962) 53–58.
[74] J.A. Buckham, A.L. Ayers, J.A. Mc Bide, Chem. Eng. Prog. Symp. Ser. 62 (65) (1964) 52–63.
[75] E.S. Grimmett, Chem. Eng. Symp. Ser. 62 (67) (1966) 93–100.
[76] H. J. Flamm, USAEC Report ORNL-TM-2113, 1968.
[77] J.E. Hanway, Chem. Eng. Symp. Ser. 66 (105) (1970) 253–259.
[78] T. Fukomoto, K. Maeda, Y. Natagi, Nucl. Sci. Eng. 7 (3) (1970) 137–144.
[79] W.J. Bjorkland, G.F. Offutt, AIChE Symp. Ser. 69 (128) (1973) 123–129.
[80] J. C. Wall, J. T. Graves, E. J. Roberts, J. Chem. Eng. (April 14) 82 (8) (1975) 77–82.
[81] E.S. Grimmett, AIChE J 10 (No. 5) (1964) 717–722.
[82] F. N. McDonald, ENICO Report 1123, 1982.
[83] A. W. Nienow, P. N. Rowe, in: Fluidization, J. Davidson (Ed), Academic Press, London, 1985.
[84] R. Cherif, Ph.D. thesis, Institut National Polytechnique de Toulouse, France, 1998.
[85] D. Kunii, O. Levenspiel, Fluidisation Engineering, Wiley, New York, 1991.
[86] S. Mortensen, S. Hovmand, Engineering Foundation Conference on Fluidisation, California, 1975, pp. 519–544.
[87] K.B. Mathur, H. Epstein, Spouted Beds, Academic Press, New York, 1974.
[88] W. Sutanto, N. Epstein, J.R. Grace, Powder Technol. 44 (1985) 205–212.
[89] X. X. Cheng, Ph.D. thesis, University of West Virginia, 1993.
[90] T. Robinson, B. Waldie, Trans. Inst. Chem. Eng. 57 (1979) 121–127.
[91] W.J. Iley, Powder Technol. 65 (1991) 441–445.

[92] R. Turton, X.X. Cheng, Powder Technol. 150 (2005) 78–85.
[93] P. J. Sherrington, Chem. Eng. July/August (1969) 201–215.
[94] H.M. Hulburt, S. Katz, Chem. Eng. Sci. 19 (1964) 555–574.
[95] A.D. Randolph, M.A. Larson, Theory of Particulate Processes, Academic Press, New York, 1971.
[96] D.F. Sheroney, Chem. Eng. Sci. 36 (1981) 845–848.
[97] P. Wnulowski, F. Setterwall, Chem. Eng. Sci. 44 (3) (1989) 493–505.
[98] M.J. Hounslow, R.L. Ryall, V.R. Marshall, AIChE 34 (11) (1988) 1821–1832.
[99] R. Hogg, Powder Technol. 69 (1992) 69–76.
[100] M. Smoluchowski, Z. Phys. Chem. 92 (1917) 129.
[101] F.Y. Wang, I.T. Cameron, Powder Technol. 124 (2002) 238–253.
[102] P.C. Kapur, Adv. Chem. Eng. 10 (1978) 55–123.
[103] P.C. Kapur, D.W. Fuerstenau, I & EC Process Des. Dev. 8 (1969) 56–62.