Dry mixing and coating of powders[*]

M. Alonso[*] and F.J. Alguacil[*]

Abstract   This paper presents a review on the mixing and coating of powders by dry processes. The review surveys fundamental works on mixture characterization (mixing index definitions and sampling techniques), mixing mechanisms and models, segregation with especial emphasis on free-surface segregation, mixing of cohesive powders and interparticle forces, ordered mixing (dry coating) including mechanism, model and applications and mixing equipment selection.

Keywords   Powder mixing. Powder coating. Segregation. Solids mixer.

Mezclado y recubrimiento de polvos por vía seca

Resumen   En este artículo se presenta una revisión bibliográfica sobre el mezclado y recubrimiento de materiales pulverulentos mediante procesos por vía seca. La revisión incluye trabajos fundamentales sobre caracterización de mezclas (definiciones de índices de mezclado y técnicas de muestreo), mecanismos y modelos de mezclado, segregación con especial énfasis en la segregación de superficie libre, mezclado de polvos cohesivos y fuerzas interpartículas, mezcla ordenada (recubrimiento) incluyendo mecanismo, modelo y aplicaciones, y selección de equipos de mezclado.

Palabras clave: Mezclado de polvos. Recubrimiento de polvos. Segregación. Mezcladores de sólidos.

1. INTRODUCTION

For thousands of years man has been mixing powders for different purposes, mainly by the method of stirring. The earliest mixing operation that could be identified as such was probably the preparation of natural earth pigments in mortars[1]. In this sense, the mixing of solid particles may be regarded as one of the oldest unit operations in the process industry. Solids mixing is an essential operation in the preparation of ceramic and pharmaceutical materials, plastic processing, fertilizer production, food manufacture, mining industry, grain processingand perhaps most importantly in the powder metallurgy industry. The importance of mixing resides in the fact that it is not only the base material, but a mix containing a number of additives, which determines the properties of the end products[2].

In spite of being an ancient operation, solids mixing is a relatively young science. The first fundamental research on the subject was done in 1933 by Oyama[3], who studied the motion of particles in rotating horizontal drums. Forty years later Cooke et al.[4] published a classified list of 650 references on powder mixing, which gives an indication of the increasing interest placed on the matter. In this paper a general vision of previous works on cohesionless powder mixing will first be presented. It will be intentionally made as brief as possible because some exhaustive and excellent reviews are already available[5-17] and there seems little point in duplicating their contents. The remaining part of the review is devoted to the mixing of cohesive powders with especial emphasis on the dry coating process, a special case of powder mixing in which fine cohesive particles of one component cover the surface of coarse particles of another component.

2. CHARACTERIZATION OF SOLIDS MIXTURES

Most of the early investigations on powder mixing were addressed to the assessment of the mixture quality, a topic which has given rise to major theoretical and practical problems. As Enstad[18] pointed out, it is obvious that a powder mixture can never become fully homogeneous on a molecular scale because it consists of discrete powder particles of finite sizes. The degree of homogeneity of a given

http://revistademetalurgia.revistas.csic.es

2.1. Mixing index

In 1970, Fan *et al.*[7] reviewed and discussed over thirty different indices of degree of mixedness proposed by many investigators, all based somehow on the variance of sample compositions. A few more indices have been proposed since then. At the completely unmixed state, the variance of a binary mixture is given by[19] $\sigma_0^2 = p\,(1-p)$, where p is the proportion of one of the components. Ideally, if both constituents have the same physical properties and their particles are geometrically identical, mixing will progress until a state is reached in which the probability of finding a particle of, say, the key component is constant throughout the mixture. This state is commonly referred to as random mixture and its variance is given by[19] $\sigma_R^2 = p\,(1-p)/n$, where n is the number of particles in a sample. At any other time of the mixing process the variance of the sample compositions will lie between these two extreme values. The temporal variation of the variance is thus a measure of the change in the mixture quality during the process. When the components differ in particle size and density and when more than two components are present in the mixture, other expressions for the limiting values of the variance must be used; these have been given by several authors[20-23].

The use of the variance as a measure of the mixture quality has, however, a number of disadvantages: a) a mixture is a very complex assembly of particles and it is not reasonable to expect that it can be described by a single number[6]; b) the use of σ_0^2 to characterize the unmixed state is misleading, since its value is independent of the initial arrangement of the component powders within the mixer[9]; c) although the variance decays inversely as the sample size for a random mixture and is independent of the sample size for a totally segregated mixture, the variance-sample size relationship is unknown for intermediate states so that comparisons between mixing studies in which different sample sizes have been used are of limited value[24]; and d) in using variance as the unique characteristic of a mixture, it is implicitly assumed that the sample compositions are normally distributed, which is far from reality[25]. To overcome these difficulties, Buslik[26] proposed a simple numerical homogeneity index based on the

sample weight required to obtain a standard deviation of 1 %. Although Buslik's index is useful for the comparison of homogeneity of unlike systems[27], its determination in any practical case is, however, a laborious procedure, since it would require repeated campaigns of sampling and analysis to find the sample weight which gives precisely a standard deviation of 1 %[28].

Other mixing indices, not based on the variance of sample compositions, have been reported. Shinnar *et al.*[29-30] proposed the shortest distance between particles of the component present in lower concentration as a test to evaluate the randomness of solid mixtures. Although the test is especially sensitive in detecting clusters of particles, it is obvious that requires a considerable amount of experimental work and thus lacks practicability.

Most of the mixtures encountered in practice are non-random due to incomplete mixing or segregation. A non-random mixture can be described as a mixture in which the compositions of contiguous regions are correlated. As Danckwerts[31] suggested, a mixture might be characterized by its correlogram, i.e. the relationship between the coefficient of correlation of point samples and the distance between the samples. From the correlogram parameters of interest, such as the scale and intensity of segregation, can be deduced. Scale of segregation refers to the state of subdivision of clumps or clusters of particles, whereas the intensity of segregation expresses the differences in composition throughout the mixture. A number of authors[32-41] have used correlation techniques to assess the degree of mixedness. The correlogram, however, becomes difficult to interpret and its calculation is rather lengthy in cases in which diffusion is the predominant mixing mechanism[42].

Akao *et al.*[43-45] presented a mixing index for binary mixtures based on the mean contact number, i.e. the mean number of particles of one component in contact with a given particle of the other component. The idea of contact number was later extended to multi-component mixtures[46-47]. Other works on mixing indices include the use of non-parametric statistical tests (that is, tests which can be performed without knowledge of the population distribution)[48-49], the analysis of the Fourier transform spectrum of the composition data[50] and the application of multivariate statistics[51].

In general, all the theories concerning mixture homogeneity have been developed having in mind

systems of free-flowing, cohesionless powders. If a fine cohesive component is present in the mixture it may stick to the walls of the mixer, resulting in a different mean composition of the system. It has been proposed that the mean concentration of the key component should be checked in addition to the mixing indices[52]. As a concluding remark for this section a recent statement made by Gyenis et al.[53] can be cited: "the problem of finding an uniform and unambiguous definition of the degree of mixing has still not been solved satisfactorily".

2.2. Sampling techniques

Fan et al.[7] reviewed the common sampling techniques that have been employed to assess the homogeneity of solids mixtures. The most common method of sampling is perhaps by thief probe, its main drawback being the disturbance caused by inserting the probe into the mixture[9] and the possibility of removing non-representative samples from segregating mixtures[54].

Another method consists in impregnating the mixture with gelatin which, after setting, allows the whole mass to be sectioned into small elements for analysis[55]. Although in this manner the mixture can be closely examined without distorting its structure, it is a time-consuming technique unuseful for practical purposes.

Radioactive tracer methods[56-59] are simpler to use and can be applied to the continuous assessment of mixing processes. In 1957 Gray[60] used an optic probe to measure the composition of a binary mixture of different colored powders. His method consisted in stopping the mixer at prescribed times and measuring the reflectivity of the mixture at several positions. This same method was used by Miles et al.[61] to evaluate the performance of seven different mixers. Harwood et al.[62] improved the optical technique adapting it to the continuous measurement of the mixture composition. Satoh et al. have also developed a continuous optical method[63, 64] and applied it to the evaluation of continuous powder mixers such as ribbon blenders[65] and batch mixers such as high-speed mixer[66], rotary drum with simultaneous rocking motion[67]and a mixer with a twisted, perforated rotating plate impeller[68]. A review article of some of these works has been published[69]. Optic fiber probes have found other applications, such as in the measurement of particle size and particle velocity of powders in motion[70].

An illustrative example of the use of the on-line optical measuring method is shown in figures 1 and 2. Figure 1 shows a typical high-speed mixer equipped with six optical probes at different heights and radial positions. Each probe contains two optical fibers, one for sending light into the mixture, the other for collecting the light reflected by the mixture and conducting it to a photosensor. In this manner, with the data supplied by the sensors and the previously determined calibration curve of the powder system in consideration, the mixture composition at different points can be continuously measured. Experiments were done with binary mixtures of different-colored powders. One of the components (white) is first placed in the vessel, which is then vibrated at a prescribed frequency N_V while the impeller is set in motion at the desired speed N_R. The second component (colored) is then added at time $t = 0$ onto the bed in the form of a pulse input. The concentration curves and their corresponding mixing curves are shown in figure 2. The degree of mixing appearing
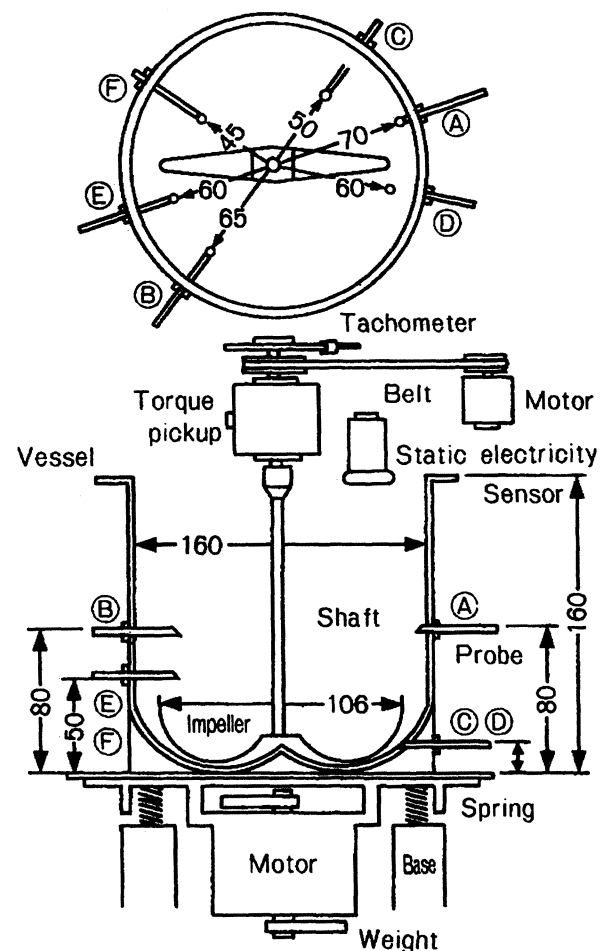

Figure 1. High speed stirred mixer with optical probes.

Figura 1. Mezclador de agitación de alta velocidad con sondas ópticas.

in the y-axis of the mixing curves is defined as $M = 1 -\sigma/\sigma_0$, where σ is the standard deviation of the concentrations measured at the six sampling points and σ_0 is the standard deviation of the completely unmixed state, i.e. at time $t = 0$. Cases 1 and 2 in figure 2 correspond to a binary mixture whose components have identical physical

properties; if the operating conditions are properly selected (case 1) the system attains an ideally perfect mixing state (random mixing); at different conditions (case 2, lower rotation speed and vibration frequency) the circulation of powder within the mixer is very irregular, mixing is poor and a complete mixed state cannot be attained
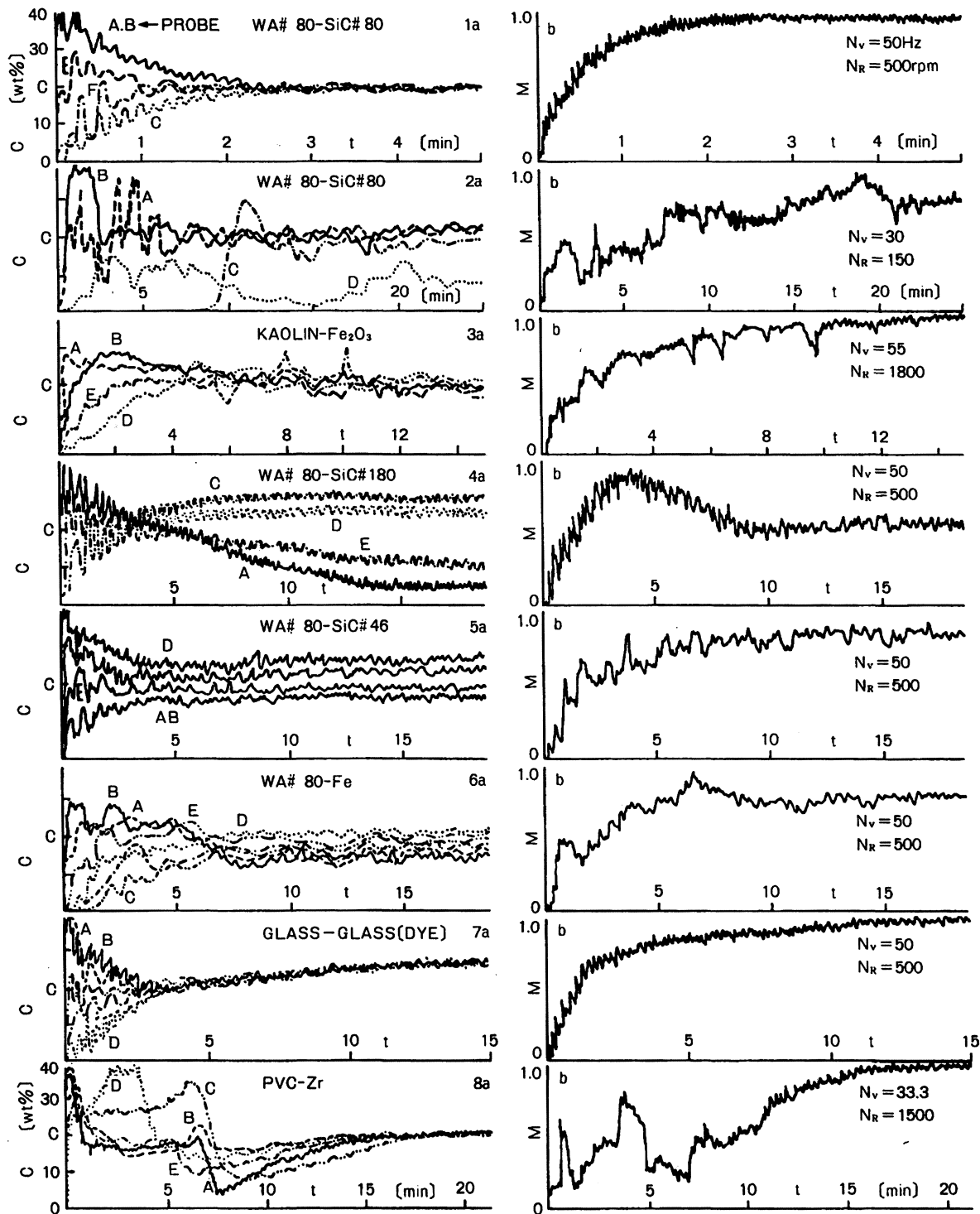

Figure 2. Concentration curves (left) and mixing curves (right) for different types of mixing processes.

Figura 2. Curvas de concentración (izquierda) y curvas de mezclado (derecha) para tipos diferentes de procesos de mezclado.

even after a long mixing time. Case 3 is that of a binary mixture of fine cohesive powders; the time required to attain the random mixing state is larger than in the case of coarse particles (case 1) because fine powders tend to form agglomerates which have to be broken up in order to achieve a good mixture quality at the microscopic level. Cases 4-6 correspond to binary mixtures differing in particle size or density; in these cases, segregation prevents the achievement of complete mixing. Segregation will be discussed below in greater length. Case 7 is that of mixing of coarse particles with the same particles which have been previously coated with dye fine particles; the coating process will also be treated below separately. The last case shown in figure 2 reveals the presence of electrostatic effects in mixing; it is observed a very irregular pattern with brief mixing stages followed by segregation. This example serves to demonstrate the usefulness of the optical method as a practical means to continuously assess the state of mixing and, more importantly, to evaluate the performance of a given mixer and establish the optimum operating conditions.

However, even if satisfactory mixing is achieved in the mixer, it cannot be assumed that the quality of mixing will remain unchanged during subsequent handling and storage[12]. This is especially true in the case of mixtures of cohesionless powders except those consisting of identical monosized materials. In industry, the interest is in the quality of the mixture leaving the mixer and therefore, as suggested by Harnby[71], samples should be taken from the outlet stream. In almost all of the laboratory studies on mixing, samples have been, however, removed from inside the mixer.

3. MIXING MECHANISMS

Two fundamental processes take place in a mixer[72]: first, a transport of groups of particles from one region to another and, second, a random motion of individual particles relative to one another. These processes have been referred to as convective and diffusive mixing, respectively. In the convective mechanism groups of particles move relative to each other with different velocities, leaving a thin layer (about 10 particle diameters in thickness) between them, termed the *failure zone*[73]. The presence of these shearing planes have led a number of authors to propose shearing as another mixing mechanism, but it

accounts for essentially the same phenomenon occurring in the convective process and there is no need to make a distinction between them.

If a smaller component is present in the failure zone it may be able to move downwards (*inter-particle percolation*[74]) provided the particle weight is much greater than the inter-particle cohesive force. This phenomenon will occur even if the sizes of the particles do not differ appreciably, because the velocity gradient existing in the failure zone favors the formation of a loosely-packed local structure within which the particles have a greater mobility. Inter-particle percolation, a mechanism of both mixing and segregation, has been extensively studied by Bridgwater et al.[73-85]. They have proposed[76] this mechanism as an explanation of the overmixing, that is, the deterioration in mixture quality with time if the mixing time is too long, a phenomenon that Rose[86] described in terms of a demixing potential. Inter-particle percolation ʼis controlled primarily by particle diameter ratio and shear strain in the failure zone[83]; other factors, such as particle density, particle elasticity, strain rate and friction, appear to be less important[78, 83]. Whilst small particles tend to drain downwards through the failure zone, large particles move towards the region in which there is more mobility of the smaller ones, i.e. in the direction of increasing strain rate, where the frequency of voids occurrence is greatest. This process by which large particles move small distances through the voids has been termed *particle migration*[84]. Inter-particle percolation and particle migration are some of the micromechanical processes which together constitute the mixing or segregation action.

Whenever the component powders differ in size, shape or density, mixing and demixing processes caused by the mechanisms described above take place simultaneously and if the process is prolonged an equilibrium between mixing and segregation is reached, after which the quality of the mixture remains unchanged[87].

3.1. Mixing models

The first fundamental studies on powder mixing were carried out using horizontal rotating drums, which are probably the simplest mixing vessels. In this type of mixer, mixing proceeds almost exclusively by diffusion and, accordingly, it has been modeled by means of Fick's diffusion equation by several workers[88-93]. The diffusion model is,

however, restricted to ideal mixtures of identical cohesionless powders[94, 95] and additional terms in Fick's equation are needed in the case of segregating systems[96, 97].

Other autors have used a stochastic approach to model the mixing process. Inoue *et al.*[98] modeled mixing in a V-type tumbling mixer as a discrete steady-state Markov process. The Markov chain model has also been used to describe mixing in motionless mixers, both for binary ideal[99] and multi-component non-ideal[100] systems. In continuous form, the Markov chain model leads to the so-called Kolmogorov diffusion equation[1, 101] in which, besides a diffusive term similar (but not identical) to that of Fick's equation, there is an additional drift (convective) term. The stochastic models can predict the concentration distribution and its variation with time from prior knowledge of the one-step transition probabilities (which are obtained experimentally)and can be applied to any class of mixer regardless the mechanism(s) by which mixing proceeds[102]. The stochastic approach can also be employed to model more complex mixing processes, such as those carried out in mixers having moving mechanical elements (impellers, screws, ribbons).

4. SEGREGATION

In any process involving the motion of particles relative to one another, differences in properties such as particle size, density, shape and particle resilience[12] will cause the separation of the bulk mass into regions, each of them containing only like particles. Among the properties just enumerated, particle size seems to be the most important factor determining the segregating behavior of granular materials. On the one hand, smaller particles may percolate downwards through the interstices between larger particles. But on the other hand, if the particles are too small the particle-particle cohesive force may overcome the body force (e.g. gravity) acting upon the particle, thus decreasing its mobility and hindering segregation. Furthermore, if one component consists of coarse cohesionless particles and the other is a fine cohesive powder, the fine particles may adhere to the surface of the larger particles, yielding a fairly homogeneous mixture which does not tend to segregate[103]. Also, small additions of liquids such as water (possibly with surface-active agents) can remarkably reduce the flowability of the powders and thus prevent segregation. It may be accepted as a general rule that

segregation problems arise only in systems of cohesionless free-flowing materials.

When powder beds are vibrated, the larger particles rise to the surface and the fines percolate downwards. In this case, it seems that segregation persists even if the larger particles are much denser than the smaller ones[104] and this experimental fact suggests that segregation in vibrated beds can be explained on the basis of geometrical considerations alone[105].

However, if the separation of particles takes place by the so-called free surface segregation mechanism[106], the origin of segregation is not of a geometrical nature alone and the effect of the size ratio (related to the tendency of smaller particles to percolate) may be compensated for by an appropriate density ratio (which is a measure of the tendency of the particles to sink in a medium of lower density). Free surface segregation is the process by which powders segregate when poured into a heap[106] and the same mechanism is the cause of segregation in tumbling mixers operating under certain conditions.

Based on a simple analysis, a parameter was developed which has shown to be useful for correlating mixing data in free-surface segregating systems. The segregation parameter S is given by[107]

$$S = \frac{\rho}{d} \cdot \frac{1 + v_c(d-1)}{1 + v_c(\rho-1)} f(\varepsilon)$$

where ρ and d are the coarse-to-fine density and size ratios, respectively, v_c is the solid volume fraction of coarse particles and $f(\varepsilon)$ a certain function of the bed porosity ε. Figure 3 shows the relationship between the mixing index and the segregation parameter for experiments carried out in a rotary drum with binary mixtures of components differing in size and/or density. The mixing index M is defined so that it ranges between 0 and 2; values of M between 0 and 1 describe the situations in which the coarse particles float and accumulate at the outer region of the bulk, whereas values of M between 1 and 2 correspond to the case where the coarse component sinks and concentrates at the core. A value of M equal to either 0 or 2 means complete component segregation. For M = 1 the tendency of floating equals that of sinking and the large particles (or the fines for that matter) are distributed evenly within the bulk of the mixture. As demonstrated in figure 3, the segregation parameter S defined above is useful to predict the segregating behavior of binary mixtures: the coarse particles behave as floaters if S < 1 and as sinkers if S
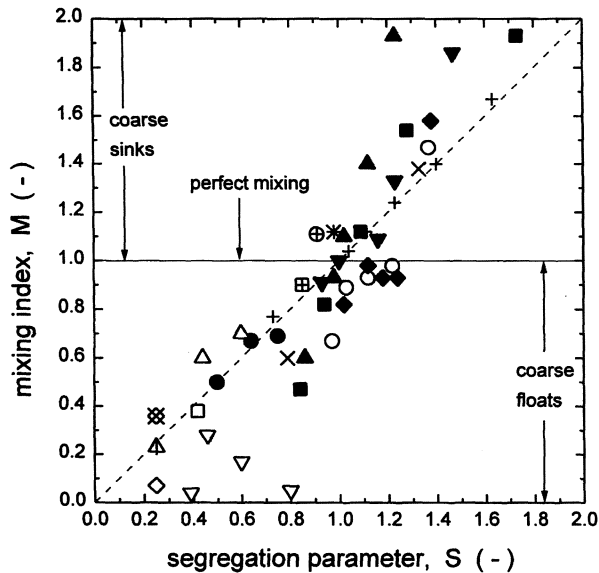
Figure 3. Mixing index as a function of the segregation parameter. Different symbols correspond to different binary mixtures.

Figura 3. Índice de mezclado en función del parámetro de segregación. Símbolos diferentes corresponden a mezclas binarias diferentes.

> 1; ideally, the sinking and floating tendencies will be balanced if $S = 1$ (perfect mixing). The validity of the model has also been confirmed by later experiments[108, 109].

At very low concentration of coarse particles, mixing/demixing is controlled by the ability of the coarse material to open voids in the layers below due to its specific weight. Fines percolation does not play any role at this level of concentration, in agreement with the findings of Arteaga and Tüzün[110] and Nikitidis et al.[111] concerning the segregation of different-sized particles in silos. At the other extreme, at very high concentration of coarse particles, segregation is controlled by fines percolation, which means that the coarse particles will invariably behave as floaters regardless of their density.

Alternative models of free-surface segregation have also been proposed by other authors[112, 113] but their predictions have not been checked with experimental results. Segregation in continuous mixers has been studied by Weinekötter et al.[114] using an optical probe to continuously assess the mixture composition.

Another demixing mechanism is the so-called trajectory segregation, which may occur when the particles are dispersed in a fluid medium. In this case, segregation occurs because the drag force on the particle depends on its size, density and shape. This is the main segregation mechanism, though not the only one, in gas fluidized beds [115-121].

In some instances, particle segregation is a desirable phenomenon. Thus, Izumikawa et al.[122] used shape segregation to recover copper from integrated circuit panels. These panels are made of copper, epoxi resin and glass fiber. During grinding of the panels, the particles of the three components attain different shape: spherical copper particles, flake-like epoxi particles and fibrous glass particles. After grinding, the mixture is conveyed by an inclined belt conveyor, whereby the spherical copper particles roll downwards and segregate from the other components. In this simple manner, up to 80 % of the initial copper can be recovered. Separation of differently shaped particles can also be achieved in rotating vibrating conical disks[123, 124].

5. MIXING OF COHESIVE POWDERS

Cohesive forces such as van der Waals force, moisture bonding, electrostatic force, solid bridging and mechanical interlocking, promote the agglomeration of powder particles. If the particle body force (gravity, centrifugal force) is greater than the inter-particle cohesive force, the agglomerates will be dispersed into their primary constituent particles and the powder will flow freely. Powders exceeding 100 μm in diameter usually show cohesionless behavior, although some powders, presumably closely sized ones, show it down to 30 μm[10]. The micro-processes and mixing-demixing mechanisms discussed above would apply to aggregates of cohesive materials rather than individual particles. There is an additional factor that must, however, be taken in consideration, namely, the innate and finite cohesion of the agglomerate that comprises many individual particles. The flow behavior of cohesive materials has been studied and reviewed extensively by Molerus[125-127] and, in spite that a complete theory is still not available, two basic points appear to have been definitively established, at least qualitatively: a) the action range of the cohesive forces depends fundamentally on particle size, in such a way that for large particles the range of inter-particle attraction (i.e. that within which the cohesive forces exceed the body forces) is comparable with the scale of surface roughness and would prevent effective bonding[128]; b) a decrease in contact area will result in lower cohesion, so that particle shape[129] and particle surface texture[130] play significant roles in the cohesive behavior of the powder.

Due to the absence of long-range segregation, a mixture of cohesive powders is usually of good

quality when analyzed at a large scale of scrutiny, but at a small scale of scrutiny a high intensity of segregation can occur[128]. The role of the mixer in this case is to provide enough energy to repeatedly break the agglomerates down to the scale of the constituent particles[131]. Comparatively, few studies have been done on the mixing of cohesive powders. In contrast, the mixing of coarse cohesionless powders with fine cohesive particles has received relatively more attention, especially because of the peculiarities and applicability of the resulting so-called *ordered mixtures*.

5.1. Inter-particle forces

The mechanisms of inter-particle adhesion may be classified into two groups[132]: a) those which require no material bridges (van der Waals, electrostatic and magnetic attraction forces, mechanical interlocking and chemical forces) and b) those which operate through material bridges (solid bridges, capillary bonding forces and inmobile liquid bridges[133]). The forces of the first group are the only ones to consider when the powder is in equilibrium with a dry atmosphere and those of the second group become important as humidity increases[134].

The van der Waals forces are related to electromagnetic fluctuation phenomena in solids. These forces originate when the random movement of electrons on a particle's surface momentarily concentrate to form dipoles which, in turn, are attracted to other dipoles nearby[135]. The van der Waals forces are only noticeable when the particles can come sufficiently close together, at separation distances of the order of the size of a molecule, 0.2 to 1 nm[136]. Whilst the gravitational force is proportional to the cube of the particle diameter, the van der Waals force is proportional to the diameter and, therefore, the magnitude of the attractive van der Waals force becomes negligible compared with that of the body force when the particle size exceeds a certain value (of the order of a few microns)[136]. The van der Waals force between two smooth spheres of radii r_1 and r_2 is[135] $F = AR/6H^2$, where H is the distance between the spheres, $R = r_1r_2/(r_1+r_2)$, and A is the Hamaker constant of the material. A list of Hamaker constants of many materials can be found in reference[137]. The most important parameter determining the van der Waals attraction force is the interparticle separation distance H; in turn, H is affected by the surface roughness and the

presence of spacers (small molecules or fines adsorbed) on the particle surface[136]. Due to elastic and/or plastic deformation at the point of contact, the contact area between the interacting solids increases and this results in an increase in the van der Waals force[132], in such a way that the total force is given by [136] $F = (A/6H^2)(R+r^2/H)$, where r is the radius of the extended contact area. The adhesion force between flattened particles may become 20 times that of unflattened particles[138], although this effect is negligible for materials with hardness above 10^8 $dyn/cm^{2[139]}$. In the above equations for the estimation of the adhesion force it is common to use a value of 0.4 nm for the interparticle separation distance H[140].

Electrostatic forces arise, for instance, when two solids are in rubbing contact (tribo-electric charging). In this situation, they will charge each other electrostatically and electrons are transferred until, at equilibrium, a contact potential difference is ʻestablished[128]. In general, the magnitude of electrostatic forces on particles are quite small[135] and some orders of magnitude smaller than the omnipresent van der Waals force[136]. Electrostatic and van der Waals forces both promote the deformation of particle surface, augmenting the contact area and, thus, the adhesion force[129]. The other mechanisms belonging to the first group cited above are far less important.

Among the adhesion mechanisms which occur through the formation of material bridges, moisture bonding is perhaps the most important. At low relative humidities, moisture is in the form of adsorbed water vapor. At a critical value of the relative humidity (between 65 and 80 %), condensation of water vapor occurs at the contact points generating liquid bridges[141]. Below a relative humidity of 65 %, capillary forces play no part in inter-particle adhesion[142], but in the range of effective moisture bonding they can become about one order of magnitude larger than the van der Waals force[139]. The effect of humidity is, however, to increase the magnitude of the van der Waals force[134] because of the decrease in interparticle distance. On the other hand, electrostatic forces decay rapidly with humidity because humidity causes the surrounding air to become conductive and promotes the discharge of the particles[134].

6. DRY COATING OF POWDERS

As mentioned previously, when a fine cohesive powder is mixed with a coarser granular material,

322

the structure of the resulting mixture consists in a layer of fines adhered on the surface of the larger particles. Hersey[143] coined the term *ordered mixture* for this kind of mixture, to distinguish it from the random mixture that results when cohesionless powders are mixed.

There exist several factors peculiar to ordered mixtures, not found in random systems: a) it has been found[144] that in ordered mixtures the variance is not affected by the sample size as would be the case in a random mixture; b) the degree of homogeneity attainable in ordered mixtures is far larger than in random mixtures[18, 143, 145, 146]; c) provided that the number of fines does not exceed that of adherence sites on the carrier (larger) particles' surface, ordered mixture are more stable than random mixtures to constituent segregation under vibration, handling and conveying[54, 143, 145-151]. Although resistant to constituent segregation, ordered mixtures can exhibit a type of segregation that has been termed *ordered unit segregation*[152-156], consisting in the appearance of fractions rich and poor in the fine component due to the polydisperse nature of the coarse powder.

6.1. Mechanism of ordered mixing

The coating process of powders follows in general the three following stages[157, 158] (Fig. 4): (i) at the beginning of the operation, the fine aggregates adhere to the coarse particles in their immediate vicinity; (ii) when a coarse particle carrying fines adhered onto its surface collides with a non-coated particle, it transfers part of its fines to the latter; (iii) by friction and collision between particles, the agglomerates of fines are gradually dispersed onto the surface of the carriers, which results in an increase in the coated surface area. The dispersion of fines is actually occurring from the earlier stages of the process. The dispersion rate and the degree to which the agglomerates are broken up depend strongly on the mechanical energy input and, therefore, on the type of mixer used. There exists a especial type of mixer, the Angmill® Mechanofusion System, which imparts such a high level of mechanical energy to the particles that the particle surface texture is greatly modified, it melts locally and a partial or total penetration of the fine component into the body of the larger particles takes place (last stage in Fig. 4).

The exchange of fine particles (either individually or as agglomerates) between carriers resulting in the uniform distribution of the minor
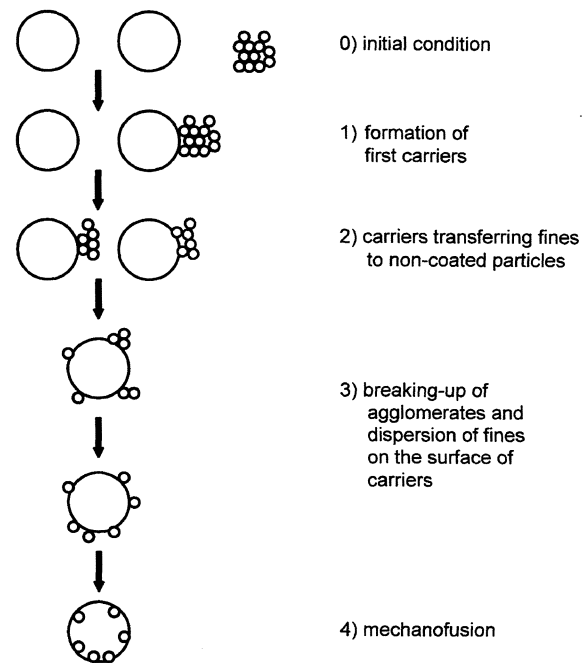

Figure 4. Mechanism of the coating-mechanofusion process.

Figura 4. Mecanismo del proceso de recubrimiento-mecano-fusión.

constituent within the bulk of the mixture is a stochastic process which can be modeled by a Fokker-Planck type equation which, based on certain exchange-probability functions, describes the temporal evolution of the distribution of fines within the carriers as a convective-diffusion process[159-163].

In an actual process, the maximum number of fines in a coating monolayer lies between two limits. The upper limit corresponds to the case of hexagonal-close packing, which gives a coated surface fraction of about 0.91 (or, equivalently, average distance between centers of contiguous fines equal to one fine diameter). The lower limit corresponds to a completely random packed monolayer, that is, a layer formed in the absence of external forces and in this case the coated surface fraction is approximately equal to 0.51 (average distance between centers of neighboring fines equal to 4/3 times their diameter)[164-165].

The presence of fines on the surface of the coarse particles affect the flow and packing characteristics of the latter. These properties are controlled by two factors[158]: a) the surface texture of the non-coated portion of the carriers, which changes as a consequence of the inter-particle friction occurring during mixing and, b) the amount and degree of dispersion of the coating agent over the bulk material.

6.2. Applications of ordered mixing

Ordered mixing was originally applied almost exclusively to the pharmaceutical industry, where a finely-divided active drug ingredient is adsorbed onto the surface of a coarse excipient to prepare a solid drug delivery system[166]. The presence of the drug in finely-divided non-agglomerated form results in high dissolution rates[167-168]. On the other hand, the coarse carrier particles give the mixture the required flowability and tabletting characteristics[166-168].

The dry coating of powders offer attractive possibilities for the preparation of composites which, however, have remained relatively unexplored until quite recently. A peculiarity of ordered mixtures, not found in random ones, is that the fine component occupies specific and fixed positions throughout the system. This has two immediate effects: first, it prevents segregation of the constituents during handling and compounding. Second, compaction of ordered mixtures results in a regular distribution of the fine component within the matrix formed by the coarse particles. Furthermore, the minor component, even at very low concentration, can form a continuous three-dimensional network imbedded in the matrix material. The regularity of the network can be controlled by selecting an appropriate size distribution for the core particles. The properties of the composite will depend also upon the degree of dispersion of the coating agent on the surface of the core particles, which in turn depends on mixing time and on the level of mechanical energy imparted by the mixer to the powder. Therefore, the preparation of new materials via powder coating permits, in principle, easy control of the structural characteristics of the product. An example is the preparation of electroconductive plastics by compaction of metal-coated plastic powders[169-170]. Figure 5 shows silver-coated polymethyl methacrylate (PMMA) particles prepared with the Angmill® Mechanofusion System; hot-pressing of the coated particles yields a structure (Fig. 6) in which the silver particles form a 3-D network imbedded in the plastic matrix. The conductivity of this structure follows the laws of typical percolating systems: only above a certain critical concentration of metal, continuous metal paths spanning the composite are formed and the material becomes conductor. It is worthwhile to point out that this compounding method via dry coating permits preparation of electroconductive plastics with metal loadings much lower than in the case of
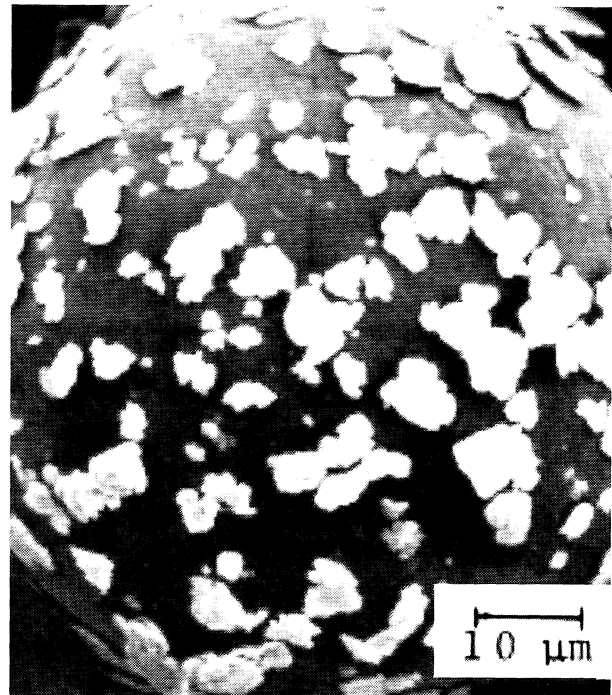

Figure 5. Silver-coated PMMA.

Figura 5. PMMA recubierto con partículas de plata.

conventional compounding via powder mixing. The method has been put into practice in an industrial scale, for manufacturing high-efficiency contact materials to be used in the electrical industry[171].

Dry powder coating has been also applied to the dispersion of ceramic powders into superplastic alloys[172]. Another interesting application of powder coating is the preparation of porous structures[173] with possible use in, for instance, the catalyst industry. An example is shown in figure 7. First, NaCl crystals are coated with plastic fine particles (PMMA). The coated powder is then hot-pressed (yielding a structure similar to that shown in Fig. 6), and placed in stirred water; after the salt
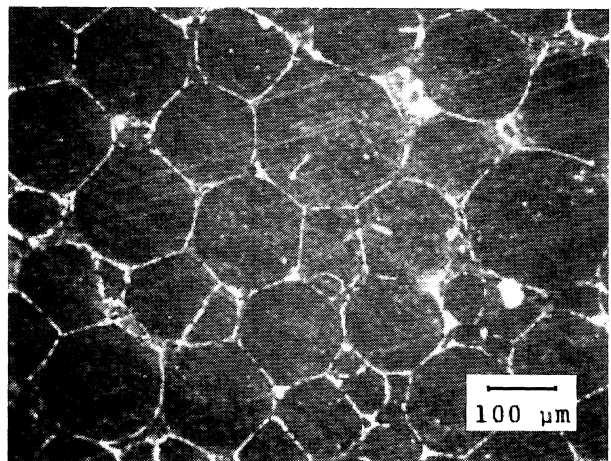

**Figure 6.** 3-D silver network imbedded in PMMA matriz.

Figura 6. Red tridimensional de plata en la matriz de PMMA.

has dissolved, a highly porous structure (porosity above 90 %) remains (Fig. 7).

7. MIXING EQUIPMENT SELECTION

The selection of the most appropriate mixer for a given duty must take into account several aspects[14, 174]: loading, the mixing operation itself, discharge, cleaning, contamination, wear, space requirement, noisiness and capital, fixed and variable operational costs. Regarding the mixing operation itself, the factors to be considered include [86, 175] the degree of homogeneity attainable in the mixer, the time required to achieve this degree and the energy consumption (mixing time × power input).

A general reliable design method is still lacking, mainly because the scale-up problem is yet unsolved[16]. In order to preserve geometric similarity between the particles and the equipment, even if the practical problem of making smaller particles to study their mixing behavior in a laboratory scale mixer can be overcome, will frequently result in changes in the physical properties of the materials. Thus, while a powder may originally have been cohesionless, reducing its particle size in proportion to the reduction in mixer size may result in it becoming cohesive. If, alternatively, the particle size is mantained but the mixer size is reduced, geometric similarity does not exist and the model mixer cannot be assumed to be representative of a larger mixer[80]. Bridgwater[10] concludes that laboratory tests for mixers are of restricted value and suggests that work should concentrate on industrial scale studies.
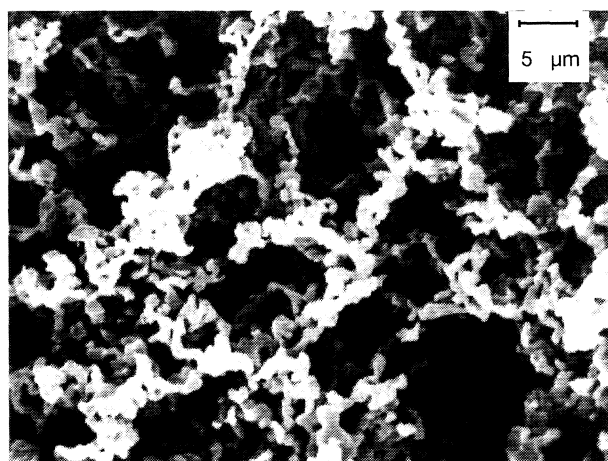
Figure 7. Porous structure resulting after salt extraction from PMMA-coated NaCl crystals.

Figura 7. Estructura porosa resultante tras la extracción de la sal de una estructura de cristales de NaCl recubiertos con PMMA.

Concerning the mixing of cohesionless powders, Williams[6] classifies the mixers into two general broad types: *segregating* and *non-segregating* mixers. Segregating mixers are those which rely mainly on diffusive mixing (e.g. tumbling mixers), whereas non-segregating (or less segregating) are those which rely on convection rather than on surface effects (e.g. mixers with mechanical stirrers). Segregation can, however, occur after mixing, i.e. during discharge, transportation or storage. Williams[6] recommends to carry out mixing as near as possible to the part of the process where the mixture is to be used, with as little intermediate handling as is practicable.

In the case of cohesive powders, as for instance in powder coating, the mechanical energy input characteristics of the mixer constitute the primary factor affecting the rate and degree of mixing attainable. Thus, tumbling mixers are not capable of breaking the agglomerates down into their constituent primary particles and, hence, are not suitable for mixing cohesive powders.

A number of studies comparing the performance of different types of mixers[2, 5, 16, 25, 61, 71, 128, 176-179] and their economic aspects[180] are available, but most of them have been done using cohesionless free-flowing materials and their conclusions might not be valid for other types of powders.

8. CONCLUDING REMARK

The fact that there are no general rules for selecting the appropriate mixer for a given duty clearly indicates that, in spite of being among the oldest unit operations, our present state of knowledge of powder mixing is still very far from satisfactory and that a lot of work remains to be done.

Acknowledgments

REFERENCES

[1] K. SOMMER, Instn. Chem. Engrs. Symp. Series, 65 1981 S1/A.

[2] J. BORNEMANN, Instn. Chem. Engrs. Symp. Series, 65 1981 S1/E.22

[3] Y. OYAMA, Int. Chem. Eng. 20 (1980) 36.

[4] M.H. COOKE, D.J. STEPHENS and J. BRIDGWATER, Powder Technol. 15 (1976) 1.

[5] K.W. CARLAY-MACAULY and M.B. DONALD, *Chem. Eng. Sci.* 17 (1962) 493.

[6] J.C. WILLIAMS, *Powder Technol.* 2 (1968) 13.

[7] L.T. FAN, S.J. CHEN and C.A. WATSON, *Ind. Eng. Chem.* 62 (1970) 53.

[8] J.C. WILLIAMS and M.A. RAHMAN, *J. Soc. Cosmetic Chemists*, 21 (1970) 3.

[9] C. SCHOFIELD, *Powder Technol.* 15 (1976) 169.

[10] J. BRIDGWATER, *Powder Technol.* 15 (1976) 215.

[11] J.C. WILLIAMS, *Powder Technol.* 15 (1976) 237.

[12] J.C. WILLIAMS, *Powder Technol.* 15 (1976) 245.

[13] T. YANO, M. SATOH and K. TERASHITA, *Powder Technol.* 20 (1978) 9.

[14] H.B. RIES, *Int. Chem. Eng.* 18 (1978) 426.

[15] P.J. LLOYD, *Instn. Chem. Engrs. Symp. Series*, 65 1981 S3/K.

[16] W. MÜLLER, *Ger. Chem. Eng.* 5 (1982) 263.

[17] S. KANG, *3rd Korea-Japan Powder Technology Seminar* 1989, p. 1.

[18] G.G. ENSTAD, *Instn. Chem. Engrs. Symp. Series*, 65 1981 S2/H.

[19] P.M.C. LACEY, *Trans. Instn. Chem. Engrs.* 21 (1943) 53.

[20] D. BUSLIK, *Bull. Am. Soc. Test. Mater.* 165 (1950) 66.

[21] K. STANGE, *Chemie. Ingr. Tech.* 26 (1954) 331.

[22] K.R. POOLE, R.F. TAYLOR and G.P. WALL, *Trans. Instn. Chem. Engrs.* 42 (1964) T305.

[23] N. HARNBY, *Trans. Instn. Chem. Engrs.* 45 (1967) CE270.

[24] H.G. KRISTENSEN, *Powder Technol.* 7 (1973) 249.

[25] M.D. ASHTON and F.H.H. VALENTIN, *Trans. Instn. Chem. Engrs.* 44 (1966) T166.

[26] D. BUSLIK, *Powder Technol.* 7 (1973) 111.

[27] J.A. HERSEY, *Powder Technol.* 10 (1974) 97.

[28] J.A. DUKES, *Powder Technol.* 8 (1973) 311.

[29] R. SHINNAR and P. NAOR, *Chem. Eng. Sci.* 15 (1961) 220.

[30] R. SHINNAR, A. KATTAN and I. STEG, *Chem. Eng. Sci.* 18 (1963) 677.

[31] P.V. DANCKWERTS, *Appl. Sci. Res.* A3 (1953) 279.

[32] J.R. BOURNE, *Chem. Eng. Sci.* 22 (1967) 693.

[33] J.R. BOURNE, *Chem. Eng. Sci.* 23 (1968) 339.

[34] N .HARNBY, *Powder Technol.* 5 (1971) 155.

[35] H.G. KRISTENSEN, *Powder Technol.* 8 (1973) 149.

[36] A.M. SCOTT and J. BRIDGWATER, *Chem. Eng. Sci.* 29 (1974) 1789.

[37] H.G. KRISTENSEN, *Powder Technol.* 13 (1976) 103.

[38] P.M.C. LACEY and F.S.M.A. MIRZA, *Powder Technol.* 14 (1976) 25.

[39] M.H. COOKE and J. BRIDGWATER, *Chem. Eng. Sci.* 32 (1977) 1353.

[40] H.G. KRISTENSEN, *Chem. Eng. Sci.* 33 (1978) 555.

[41] J.R. TOO, L.T. FAN and R.M. RUBISON, *Proc. Int. Symp. Powder Technol.*, Kyoto 1981, p. 712.

[42] C. SCHOFIELD, *Trans. Instn. Chem. Engrs.* 48 (1970) T28.

[43] Y. AKAO, H. SHINDO, N. YAGI, L.T. FAN, R.H. WANG and F.S.LAI, *Powder Technol.* 15 (1976) 207.

[44] Y. AKAO, H. KUNISAWA, L.T. FAN, F. LAI and R.H. WANG, *Powder Technol.* 15 (1976) 267.

[45] H. SHINDO, T. YOSHIZAWA, Y. AKAO, L.T. FAN and F. LAI, *Powder Technol.* 21 (1978) 105.

[46] L.T. FAN, J.R. TOO, F.S. LAI and Y. AKAO, *Powder Technol.* 22 (1979) 205.

[47] J.R. TOO, R.M. RUBISON, L.T. FAN and F.S. LAI, *Powder Technol.* 23 (1979) 99.

[48] F.S. LAI, R.H. WANG and L.T. FAN, *Powder Technol.* 10 (1974) 13.

[49] J.R. TOO, L.T. FAN, R.M. RUBISON and F.S. LAI, *Powder Technol.* 26 (1980) 131.

[50] S.H. SHIN and L.T. FAN, *Powder Technol.* 19 (1978) 137.

[51] R.H. WANG, L.T. FAN and J.R. TOO, *Powder Technol.* 21 (1978) 171.

[52] Z.T. CHOWHAN and E.E. LINN, *Powder Technol.* 24 (1979) 237.

[53] J. GYENIS and J. ARVA, *Powder Handling Processing* 1 (1989) 165.

[54] W.J. THIEL and P.L. STEPHENSON, *Powder Technol.* 31 (1982) 45.

[55] P.M.C. LACEY and F.S.M.A. MIRZA, *Powder Technol.* 14 (1976) 17.

[56] L.T. FAN, S.J. CHEN, N. ECKHOFF and C.A. WATSON, *Powder Technol.* 4 (1970) 345.

[57] F.S. LAI and L.T. FAN, *Powder Technol.* 13 (1976) 73.

[58] A. MERZ and R. HOLZMÜLLER, *Instn. Chem. Engrs. Symp. Series* 65 (1981) S1/D.

[59] C.J. BROADBENT, J. BRIDGWATER, D.J. PARKER, S.T. KENINGLEY and P. KNIGHT, *Powder Technol.* 76 (1993) 317.

[60] J.B. GRAY, *Chem. Eng. Prog.* 53 (1957) 25.

[61] J.E.P. MILES and C. SCHOFIELD, *Trans. Instn. Chem. Engrs.* 48 (1970) T85.

[62] C.F. HARWOOD, R. DAVIES, M. JACKSON and E. FREEMAN, *Powder Technol.* 5 (1971) 77.

[63] M. SATOH, Y. DEGUCHI, S. KOMURA and K. MIYANAMI *J. Res. Assoc. Powder Technol. Japan* 22 (1985) 79.

[64] M. SATOH and K. MIYANAMI, *Bull. Univ. Osaka Pref. Ser. A* 36 (1987) 141.

[65] K. MIYANAMI, M. SATOH and T. YANO, *J. Powder Bulk Solid Technol.* 2 (1978) 47.

[66] M. SATOH, Y. DEGUCHI, H.TSUMURA and K. MIYANAMI, *J. Soc. Powder Technol. Japan* 24 (1987) 707.

[67] M. ALONSO, M. SATOH and K. MIYANAMI, *Powder Technol.* 59 (1989) 65.

[68] M. SATOH, M. ALONSO, T. SHIGEMURA, K. MIYANAMI and T. SUZUKI, *Trans. Instn. Chem. Engrs.* 68 (1990) 149.

[69] M. ALONSO, M. SATOH and K. MIYANAMI, *KONA* 7 (1989) 97.

[70] K. OKI, T. AKEHATA and T. SHIRAI, *Powder Technol.* 11 (1975) 51.

[71] N. HARNBY, *Powder Technol.* 1 (1967) 94.

[72] R. HOGG, G. MEMPEL and D.W. FUERSTENAU, *Powder Technol.* 2 (1968) 223.

[73] J. BRIDGWATER and N.D. INGRAM, *Trans. Instn. Chem. Engrs.* 49 (1971) 163.

[74] A.P. CAMPBELL and J. BRIDGWATER, *Trans. Instn. Chem. Engrs.* 51 (1973) 72.

[75] J. BRIDGWATER, N.W. SHARPE and D.C. STOCKER, *Trans. Instn. Chem. Engrs.* 47 (1969) T114.

[76] J. MASLIYAH and J. BRIDGWATER, *Trans. Instn. Chem. Engrs.* 52 (1974) 31.

[77] J. BRIDGWATER and A.M. SCOTT, *Trans. Instn. Chem. Engrs.* 52 (1974) 317.

[78] A.M. SCOTT and J. BRIDGWATER, *Ind. Eng. Chem. Fundam.* 14 (1975) 22.

[79] A.M. SCOTT and J. BRIDGWATER, *Powder Technol.* 14 (1976) 177.

[80] D.J. Stephens and J. Bridgwater, *Powder Technol.* 21 (1978) 17.

[81] D.J. Stephens and J. Bridgwater, *Powder Technol.* 21 (1978) 29.

[82] M.H. Cooke, J. Bridgwater and A.M. Scott, *Powder Technol.* 21 (1978) 183.

[83] J. Bridgwater, M.H. Cooke and A.M. Scott, *Trans. Instn. Chem. Engrs.* 56 (1978) 157.

[84] W.S. Foo and J. Bridgwater, *Powder Technol.* 36 (1983) 271.

[85] J. Bridgwater, W.S. Foo and D.J. Stephens, *Powder Technol.* 41 (1985) 147.

[86] H.E. Rose, *Trans. Instn. Chem. Engrs.* 37 (1959) 47.

[87] R.H. Wang and L.T. Fan, *Chem. Eng. Sci.* 32 (1977) 695.

[88] P.M.C. Lacey, *J. Appl. Chem.* 4 (1954) 257.

[89] R. Hogg, D.S. Cahn, T.W. Healy and D.W. Fuerstenau, *Chem. Eng. Sci.* 21 (1966) 1025.

[90] D.S. Cahn and D.W. Fuerstenau, *Powder Technol.* 1 (1967) 174.

[91] D.S. Cahn and D.W. Fuerstenau, *Powder Technol.* 2 (1968) 215.

[92] R. Hogg, G. Mempel and D.W. Fuerstenau, *Powder Technol.* 2 (1968) 223.

[93] C. Wightman and F.J. Muzzio, *Powder Technol.* 98 (1998) 113.

[94] J. Koga, K. Yamaguchi and I. Inoue, *Powder Technol.* 26 (1980) 127.

[95] R. Hogg and D.W. Fuerstenau, *Powder Technol.* 6 (1972) 139.

[96] F. Strek, A. Rochowiecki and J. Karcz, *Powder Technol.* 20 (1978) 243.

[97] A. Rochowiecki, *Proc. Int. Symp. Powder Technol.,* Kyoto, 1981, p. 718.

[98] I. Inoue and K. Yamaguchi, *Int. Chem. Eng.* 10 (1970) 490.

[99] S.J. Chen, L.T. Fan and C.A. Watson, *AIChE J.* 18 (1972) 984.

[100] F.S. Lai and L.T. Fan, *Ind. Eng. Chem. Process Des. Dev.* 14 (1975) 403.

[101] L.T. Fan and S.H. Shin, *Chem. Eng. Sci.* 34 (1979) 811.

[102] L.T. Fan and J.R. Too, *Proc. Int. Symp. Powder Technol.,* Kyoto, Japón, 1981, p. 697.

[103] J.A. Hersey, *Powder Technol.* 15 (1976) 149.

[104] J.C. Williams, *Fuel Soc. J.* 14 (1963) 29.

[105] A. Rosato, F. Prinz, K.J. Standburg and R. Swendsen, *Powder Technol.* 49 (1986) 59.

[106] J.A. Drahun and J. Bridgwater, *Powder Technol.* 36 (1983) 39.

[107] M. Alonso, M. Satoh and K. Miyanami, *Powder Technol.* 68 (1991) 145.

[108] T.J. Fiske, S.B. Railkar and D.M. Kalyon, *Powder Technol.* 81 (1994) 57.

[109] C. Wightman and F.J. Muzzio, *Powder Technol.* 98 (1998) 125.

[110] P. Arteaga and U. Tüzün, *Chem. Eng. Sci.* 45 (1990) 205.

[111] M.S. Nikitidis, U. Tüzün and N.M. Spyrou, *Chem. Eng. Sci.* 53 (1998) 2335.

[112] L. Progozhin, *Chem. Eng. Sci.* 48 (1993) 3647.

[113] A.A. Boateng and P.V. Barr, *Chem. Eng. Sci.* 51 (1996) 4167.

[114] R. Weineкötter and L. Reh, *Part. Part. Syst. Charact.* 12 (1995) 46.

[115] A.W. Nienow, D.J. Cheesman, J.R. Grace and J.M. Matsen (Eds.), *Fluidization,* Plenum Press, New York, EE.UU., 1980, p. 373.

[116] A.W. Nienow, P.N. Rowe and L.Y.L. Chung, *Powder Technol.* 20 (1978) 189.

[117] A.W. Nienow and T. Chiba, *Fluidization,* 2ª ed., Academic Press, 1985, p. 9.

[118] S. Chiba, A.W. Nienow, T. Chiba and H. Kobayashi, *Powder Technol.* 26 (1980) 1.

[119] N.S. Naimer, T. Chiba and A.W. Nienow, *Chem. Eng. Sci.* 37 (1982) 1047.

[120] P.N. Rowe, A.W. Nienow and A.J. Agbim, *Trans. Instn. Chem. Engrs.* 50 (1972) 310.

[121] S.Y. Wu and J. Baeyens, *Powder Technol.* 98 (1998) 139.

[122] C. Izumikawa, H. Sasaki, H. Ohya, S. Endoh and H. Iwata, *J. Soc. Powder Technol. Japan* 32 (1995) 378.

[123] K. Yamamoto, Y. Tamao and M. Sugimoto, *J. Soc. Powder Technol. Japan* 32 (1995) 612.

[124] K. Yamamoto, M. Tohyama and M. Sugimoto, *Powder Technol.* 99 (1998) 1.

[125] O. Molerus, *Powder Technol.* 12 (1975) 259.

[126] O. Molerus, *Powder Technol.* 20 (1978) 161.

[127] O. Molerus, *Chem. Eng. Commun.* 15 (1982) 257.

[128] N. Harnby, *Mixing in the Process Industries,* ch.5. Butterworths, London, Inglaterra, 1987.

[129] K.W. Montz, J.K. Beddow and P.B. Butler, *Powder Technol.* 55 (1988) 133.

[130] D. Tabor, *Tribology in Particulate Technology,* ch. 3.1. Adam Hilger, Bristol, Inglaterra, 1987.

[131] F. Lai and J.A. Hersey, *Instn. Chem. Engrs. Symp. Series,* 65, 1981, S1/C.

[132] H. Rumpf, K. Sommer and K. Steier, *Int. Chem. Eng.* 18 (1978) 558.

[133] S. Moser and K. Sommer, *Powder Technol.* 17 (1977) 191.

[134] M.C. Coelho and N. Harnby, *Powder Technol.* 20 (1978) 201.

[135] J.K. Beddow, *Particulate Science and Technology.* Chemical Publishing Co., New York, EE.UU., 1980.

[136] J. Visser, *Powder Technol.* 58 (1989) 1.

[137] J. Visser, *Adv. Colloid Interface Sci.* 3 (1972) 331.

[138] R.C. Tsiang, C. Wang and C. Tien, *Chem. Eng. Sci.* 37 (1982) 1661.

[139] L. Massimilla and G. Donsi, *Powder Technol.* 15 (1976) 253.

[140] H. Krupp, *Adv. Colloid Interface Sci.* 1 (1967) 111.

[141] M.C. Coelho and N. Harnby, *Powder Technol.* 20 (1978) 197.

[142] G.A. Turner and M. Balasubramanian, *Powder Technol.* 10 (1974) 121.

[143] J.A. Hersey, *Powder Technol.* 11 (1975) 41.

[144] C.C. Yeung and J.A. Hersey, *Powder Technol.* 22 (1979) 127.

[145] C.W. Yip and J.A. Hersey, *Powder Technol.* 16 (1977) 189.

[146] P. Bannister and N. Harnby, *Powder Technol.* 36 (1983) 275.

[147] M.J. Crooks and R. Ho, *Powder Technol.* 14 (1976) 161.

[148] L. BRYAN, Y. RUNGVEJHAVUTTIVITTAYA and P.J. STEWART, *Powder Technol.* 22 (1979) 147.

[149] P.L. STEPHENSON and W.J. THIEL, *Powder Technol.* 25 (1980) 115.

[150] F. LAI and J.A. HERSEY, *Chem. Eng. Sci.* 36 (1981) 1133.

[151] J.N. STANIFORTH, *Powder Technol.* 45 (1985) 73.

[152] C.W. YIP and J.A. HERSEY, *Powder Technol.* 16 (1977) 149.

[153] P. THANOMKIAT, P.J. STEWART and P.S. GROVER, *Powder Technol.* 24 (1979) 97.

[154] J.A. HERSEY, W.J. THIEL and C.C. YEUNG, *Powder Technol.* 24 (1979) 251.

[155] F. LAI, J.A. HERSEY and J.N. STANIFORTH, *Powder Technol.* 28 (1981) 17.

[156] W.J. THIEL, L.T. NGUYEN and P.L. STEPHENSON, *Powder Technol.* 34 (1983) 75.

[157] M. ALONSO, M. SATOH and K. MIYANAMI, *Powder Technol.* 56 (1988) 135-141.

[158] M. ALONSO, M. SATOH and K. MIYANAMI, *Powder Technol.* 59 (1989) 45.

[159] M. ALONSO, M. SATOH and K. MIYANAMI, *Powder Technol.* 59 (1989) 217.

[160] M. ALONSO, M. SATOH and K. MIYANAMI, *Adv. Powder Technol.* 2 (1991) 49.

[161] K. SHINOHARA, K. TAKAYASIKI, M. OTANI and T. UCHIYAMA, *Kagaku Kogaku Ronbunshu* 22 (1996) 356.

[162] K. SHINOHARA, Y. OTOMURA, T. UCHIYAMA and H. MINOSHIMA, *J. Soc. Powder Technol. Japan* 35 (1998) 111.

[163] K. SHINOHARA, Y. OTOMURA, T. UCHIYAMA and M. OTANI, *J. Soc. Powder Technol. Japan* 35 (1998) 271.

[164] M. ALONSO, M. SATOH and K. MIYANAMI, *Powder Technol.* 62 (1990) 35.

[165] M. ALONSO, M. SATOH and K. MIYANAMI, *Can. J. Chem. Eng.* 70 (1992) 28.

[166] P.L. STEPHENSON and W.J. THIEL, *Powder Technol.* 26 (1980) 225.

[167] J.A. HERSEY, *J. Pharm. Sci.* 6 (1977) 29.

[168] K.F. LAI and J.A. HERSEY, *J. Pharm. Pharmacol.* 31 (1979) 800.

[169] M. ALONSO, M. SATOH, K. MIYANAMI, K. HIGASHI and T. ITO, *Powder Technol.* 63 (1990) 35.

[170] M. ALONSO, M. SATOH, K. MIYANAMI, K. HIGASHI and T. ITO, *Powder Technol.* 67 (1991) 11.

[171] M. SATOH, K. HIGASHI, K. MIYANAMI, S. TANIMURA, K. TSUJI, H. INADA and K. KOJIMA, *Powder Technol.* 70 (1992) 71.

[172] M. SATOH, F. HAMANO, K. MIYANAMI, K. HIGASHI, T. ITO and H. YOSHIDA, *Proc. 2nd World Congress Particle Technology*, Kyoto, Japón, 1990, p. III-432.

[173] M. ALONSO, M. SATOH and K. MIYANAMI, *Proc. 2nd World Congress Particle Technology*, Kyoto, Japón, 1990, p. III-345.

[174] W.C. PECK, *Trans. Instn. Chem. Engrs.* 34 (1956) 100.

[175] H. RUMPF and W. MUELLER, *Trans. Instn. Chem. Engrs.* 40 (1962) 272.

[176] J.F.E. ADAMS and A.G. BAKER, *Trans. Instn. Chem. Engrs.* 34 (1956) 91.

[177] K.W. CARLEY-MACAULY and M.B. DONALD, *Chem. Eng. Sci.* 19 (1964) 191.

[178] C.F. HARWOOD, K. WALANSKI, E. LUEBCKE and C. SWANSTROM, *Powder Technol.* 11 (1975) 289.

[179] A.W. NIENOW and T. CHIBA, *Instn. Chem. Engrs. Symp. Series*, 65 (1981) S2/F.

[180] N. HARNBY, *Chem. Proc. Eng.* (dic.) (1968) 53.