Powder Treatments

In powder conditioning, the powders prepared by various methods are subjected to a variety of treatments to improve or modify their physical, chemical characteristics.

Majority of powders undergo heat treatments prior to compaction like:

i) Cleaning of powders [solid: impurity, liquid: moisture, gas: air]

ii) Grinding/crushing to obtain fine size.

iii) Particle size classification to obtain the desired particle size distribution.

iv) Annealing.

v) Mixing and blending of powders.

vi) Lubricant addition for powder compaction.

vii) Powder coating.

viii) Toxicity of powders.

Cleaning of Powders

Refers to the removal of contaminants - solid, liquid & gaseous, from the powder particles.

• Solid contaminants: Come from several sources like nozzles or crucible linings.

They interfere during compaction and sintering preventing proper mechanical bonding.

Contaminants are non-reactive, but they act as sites for crack nucleation.

Non-metallic solid impurities can be removed from powders by particle separators & metallic electrostatic separation techniques.

• Liquid contaminants: Drying to remove moisture.
Gas contaminants: Gaseous impurities like hydrogen and oxygen get into powders during processing, storage or handling if proper care is not taken.

Finer the powders, contamination will be more because of large powder surface area. These gaseous impurities can form undesirable oxides during processing at relatively high temperature or gets trapped inside the material as pores, reducing the in situ performance of the P/M part.

**Particles Separation**

1. **Classification**

Classification is the separation of particulates into a coarse and fine fractions.

Classification should be distinguished from solid-fluid separation

Classification is usually by:

Size particles, density, particle shape, electric, magnetic, and surface properties.

Classification of particulates gravity, drag, centrifugal, and collision.
Table 1 gives a listing of various classification equipment.

<table>
<thead>
<tr>
<th>Classification</th>
<th>Size range</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Wet</strong></td>
<td></td>
</tr>
<tr>
<td>Screens</td>
<td>1 m–44 μm</td>
</tr>
<tr>
<td>Sedimentation Classifiers</td>
<td>1 mm–10 μm</td>
</tr>
<tr>
<td>Hydrocyclones</td>
<td>500 μm–0.1 μm</td>
</tr>
<tr>
<td>Elbow Classifier</td>
<td>100 μm–0.1 μm</td>
</tr>
<tr>
<td>Centrifuge</td>
<td>50 μm–0.1 μm</td>
</tr>
<tr>
<td><strong>Dry</strong></td>
<td></td>
</tr>
<tr>
<td>Screens</td>
<td>1 m–44 μm</td>
</tr>
<tr>
<td>Expansion chamber</td>
<td>100 μm–10 μm</td>
</tr>
<tr>
<td>Air Classifier</td>
<td>1000 μm–0.1 μm</td>
</tr>
<tr>
<td>Gas Cyclone</td>
<td>500 μm–0.1 μm</td>
</tr>
</tbody>
</table>
Classifier Fundamentals

1-Forces

![Diagram of Classifier](image)

**Figure 1** Forces acting on a particle in a gas classifier

<table>
<thead>
<tr>
<th>Figure2</th>
<th>Figure3</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="image">Diagram of Streamlines and Particle Trajectories</a></td>
<td><a href="image">Graph of Target Efficiency</a></td>
</tr>
</tbody>
</table>

**Figure 2** streamlines and particle trajectories approaching a pin.

2-Collision

3-Particles shape

4-Size Selectivity

![Graphs of Size Selectivity and Size Distributions](image)

**Figure** Size distributions for various types of classifier performance.
A- Dry Classification Equipment

Dry classification equipment uses a gas stream to convey the solids.

The gas used most often is air, is often used to describe this type of equipment (see Fig. 1).

**Figure 4**

**Figure 5**

---

**FIGURE** Air classification equipment: (a) cyclone, (b) expansion chamber, (c) modern complex air classifier, and (d) classifier based on particle inertia.
Wet classification is performed by filtration, settling, centrifugation, and hydrocyclones.

Hydro cyclone The In hydrocyclone design, the particle laden flow enters radially and rotates within the body of the hydrocyclone.

Forces of gravity, centrifugal and drag, act on the particles to force a separation.

The particles larger than the cut size are sent to the underflow, and the particles smaller than the cut size are sent to the overflow along with most of the liquid.

2-Hindered settling

When the particles are close together, hindered settling occurs.

\[ V_i = \frac{2R^2(\rho_s - \rho_f)gh(\phi)}{9\eta} \]

we find

<table>
<thead>
<tr>
<th>Unhindered</th>
<th>Hindered, ( \phi = 0.10 )</th>
<th>Hindered, ( \phi = 0.30 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R = 0.1 \mu m )</td>
<td>( V_i = 80 \mu m/hr )</td>
<td>( V_i = 25.7 \mu m/hr )</td>
</tr>
<tr>
<td>( R = 1.0 \mu m )</td>
<td>( V_i = 8 \mu m/hr )</td>
<td>( V_i = 2.57 \mu m/hr )</td>
</tr>
</tbody>
</table>
3- Magnetic and electrical separation

TABLE 1   Classification of Magnetic Separation

- **Top-feed type**: OS vanier, Ferroplan separator
- **Under-feed type**: Crocket wet separator
- **Top-foot type**: YS drum separator
- **Under-foot type**: Grosha drum separator, Multi-stage drum separator
- **Belt type**: Eretz rare earth roll separator
- **Drum type**: Eretz rare earth drum separator, PERMS magnetic separator

**Static-magnetic-field type**
- **High intensity type**
  - Wet high intensity magnetic separator, WHIMS
- **Medium-intensity type**
  - Jones high-intensity separator
- **Low-intensity type**
  - Capco high-intensity wet separator
- **High intensity type**
  - Eretz wet high-intensity separator
- **NY drum separator**
- **Superconductive suspended magnet**
- **Double pole separator**
- **High-gauss separator**
- **DESCOS (superconductive drum-type magnetic separator)**
- **SALA-HGMS**
- **DEM filter**
- **Superconductive HGMS**

**Moving-magnetic-field type**
- **OYB separator**
- **AC spiral separator**
- **OY-table type separator**
- **DS-type separator**

**Electromagnetic induction type**

**FIGURE 9** Drum magnetic separator of the dry type.
Figure 10: Electric conductivity for various materials.

a) Induction charging

b) Particle movement

Table 2: Work Functions for Various Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Work function (eV)</th>
<th>Material</th>
<th>Work function (eV)</th>
<th>Material</th>
<th>Work function (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>3.62</td>
<td>BeO</td>
<td>1.1</td>
<td>Polyethylene</td>
<td>5.24±0.24</td>
</tr>
<tr>
<td>C</td>
<td>4</td>
<td>CaO</td>
<td>1.60±0.2</td>
<td>Polyethylene</td>
<td>5.04±0.47</td>
</tr>
<tr>
<td>Al</td>
<td>4.06±4.26</td>
<td>V₂O₅</td>
<td>2</td>
<td>Polypropylene</td>
<td>5.43±0.16</td>
</tr>
<tr>
<td>Cu</td>
<td>4.25</td>
<td>Nb₂O₅</td>
<td>2.3</td>
<td>Polypropylene</td>
<td>2.49±0.24</td>
</tr>
<tr>
<td>Ti</td>
<td>4.83</td>
<td>ThO₂</td>
<td>2.54</td>
<td>Polyamide</td>
<td>4.77±0.20</td>
</tr>
<tr>
<td>Cr</td>
<td>4.5</td>
<td>SnO₂</td>
<td>2.5</td>
<td>Polystyrene</td>
<td>4.56±0.73</td>
</tr>
<tr>
<td>Ag</td>
<td>5.57±4.74</td>
<td>UO₂</td>
<td>3.15</td>
<td>Polycarbonate</td>
<td>3.85±0.82</td>
</tr>
<tr>
<td>Si</td>
<td>4.60±4.91</td>
<td>FeO</td>
<td>3.85</td>
<td>PMMA</td>
<td>4.30±0.29</td>
</tr>
<tr>
<td>Fe</td>
<td>4.67±4.81</td>
<td>SiO₂</td>
<td>3</td>
<td>Polymethylmethacrylate</td>
<td>6.71±0.26</td>
</tr>
<tr>
<td>Co</td>
<td>5</td>
<td>Al₂O₃</td>
<td>4.7</td>
<td>Polyurethane</td>
<td>4.38±0.06</td>
</tr>
<tr>
<td>Ni</td>
<td>5.04±5.35</td>
<td>MgO</td>
<td>4.7</td>
<td>Polymethylmethacrylate</td>
<td>4.25±0.10</td>
</tr>
<tr>
<td>Pt</td>
<td>5.12±5.93</td>
<td>ZrO₂</td>
<td>5.5</td>
<td>Nito100</td>
<td>4.08±0.06</td>
</tr>
<tr>
<td>Au</td>
<td>5.31±5.47</td>
<td>Fe₂O₃</td>
<td>0.22</td>
<td>Pylex7740</td>
<td>4.84±0.21</td>
</tr>
</tbody>
</table>
Powder Annealing

Heat treatment is generally carried out before mixing or blending the powders.

Some of the important objectives are,

i) Improving the purity of powder: Reduction of surface oxides from powders by annealing in hydrogen or other reducing atmosphere. Dissolved gases like hydrogen and oxygen, other impurities are removed by annealing of powders.

Lowering impurities like carbon results in lower hardness of the powder and hence lower compaction pressures & lower die wear during compaction. For eg., atomized powders having a combined carbon and oxygen content as high as 1% can be reduced after annealing to about 0.01% carbon and 0.2% oxygen. Heat treatment is done at protective atmosphere like hydrogen, vacuum.

ii) Improving the powder softness: Aim is to reduce the work hardening effect of powders that has be crushed to obtain fine powders; while many powders are made by milling, crushing or grinding of bulk materials. Powder particles are annealed under reducing atmosphere like hydrogen. The annealing temperature is kept low to avoid fusion of the particles.

iii) Modification of powder characteristics: The apparent density of the powders can be modified to a higher or lower value by changing the temperature of treatment.
Mixing and blending of powders

The various types of mixing methods are,

(i) convective mixing: transfer of one group of particles from one location to another.

(ii) diffusive mixing: movement of particles on to newly formed surface,

(iii) shear mixing: deformation & formation of planes within the powders

Depending on the extent of mixing, mixing can be classified as

(i) perfectly mixed or uniform mixing,

(ii) random mixed, &

(iii) totally un-mixed.

The mixing should be stopped when random mixture is achieved. Over mixing leads to reduced flow characteristics of the mix.

Table 3 shows a classification of various powder mixers, based on the manner by which the powders are set in motion. This table also lists rough ranges of powder properties appropriate to each type of mixer.
Although mixer performance should be evaluated on the basis of the powder properties being handled, operating conditions, and the application purpose, the general features of each mixer are as described below.

### Table 3: Classification of Powder Mixers and Range of Their Services

<table>
<thead>
<tr>
<th>Classification</th>
<th>Mixer</th>
<th>Typical Powder Properties</th>
<th>Operation</th>
<th>Range of Particle Diameter (mm)</th>
<th>Flowability Angle at Repose (deg)</th>
<th>Cohesion/cohesion Properties</th>
<th>Water Content</th>
<th>Viscosity</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotary vessel</td>
<td>Horizontal</td>
<td>Horizontal cylinder</td>
<td></td>
<td>Over 1.0</td>
<td>15-0.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>inclination</td>
<td>Inclined cylinder</td>
<td></td>
<td>15-0.1</td>
<td>15-0.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>V-type</td>
<td>V-type</td>
<td></td>
<td>8-4.5</td>
<td>5-3.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Double-cones</td>
<td>Double-cones</td>
<td></td>
<td>8-4.5</td>
<td>5-3.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cube</td>
<td>Cube</td>
<td></td>
<td>8-4.5</td>
<td>5-3.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S-type</td>
<td>S-type</td>
<td></td>
<td>8-4.5</td>
<td>5-3.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Continuous V-type</td>
<td>Continuous V-type</td>
<td></td>
<td>8-4.5</td>
<td>5-3.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Rotary Vessel Type

The rate of mixing is rather low in a rotary vessel, but a good final degree of mixedness can be expected.

The powders to be mixed are charged up to 30–50% of the vessel volume. The rotational speed is set at 50–80% of the critical rotational speed, NCR, given as

\[
N_C = \frac{0.498}{\sqrt{R_{\text{max}}}} \quad \text{(s}^{-1})
\]

Where

- \(R_{\text{max}}\) (m) is the maximum radius of rotation of the mixer.
Lubricant powder

Lubricants added to the powders for better compaction has to be removed for desirable final P/M part

A normal body binder must have several characteristics:

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>It must leave a minimal amount of ash after firing</td>
<td>Its dispersion must be easy</td>
</tr>
<tr>
<td>It must easily burn out at low temperature</td>
<td>It cannot be toxic</td>
</tr>
<tr>
<td>It cannot be abrasive</td>
<td>It does not affect the glazing stage of manufacturing</td>
</tr>
<tr>
<td>It must improve the mechanical strength of dry pieces</td>
<td>It must be as inexpensive as possible.</td>
</tr>
<tr>
<td>It does not cause bodies to stick to mold</td>
<td></td>
</tr>
</tbody>
</table>

Types:

Inorganic Binders, Sodium Silicate, Magnesium Aluminum Silicates, Bentonite, Polyacrylates, Paraffins, Wax.

Powder Coating

Spray coating can be used for all fluid systems, be it in batch or continuous operation or if the film is applied from a sprayed solution, suspension or hot melt.

For this processing option the parameters have to be chosen to avoid agglomeration,

For hot melt coating the droplets must be small enough not to form solid bridges.

The quality of the coating extensively depends on the statistical residence time of the particles in the coating zone.
Top-Spray Coating
To produce perfect film, care must be taken that the droplets:
1. Do not become too viscous before touching the substrate, in order to maintain a good spread ability.
2. The particle motion.
3. The travel distance of droplet from nozzle to substrate are uniform.

Bottom-Spray Coating
This processing consists of a perforated bottom screen with defined free areas. Most of the process air is channeled through the center via a tube, as such producing a venturi effect, which sucks the product from outside the partition past the spray nozzle.

Tangential Spray Coating
This processing technique is the production motion is provided by a motor-driven rotor disc.

The coating material is sprayed concurrently inside the rotating product.

The film structure is generally rather porous.
Toxicity of powders

• Toxicity leads to undesirable health effects like eye, skin irritation, vomiting, respiratory problems, blood poisoning etc.

• Powder like lead, nickel are highly toxic & Al, iron are less toxic

• Precautions: Use of protective gloves, respiratory masks, protective clothing etc.; use of well ventilated storage, workplace; careful handling, disposal of wastes

• Flammability & reactivity data is required

• Health effects: Inhalation – disturbs the respiratory track; remedial measures include moving the person to fresh air. Artificial breathing is required if patient not breathing properly.

Skin, eyes – Brushing, washing skin and eyes with water and soap. Clean eyes with fresh water for 15 mts.

• Sb, Ba, V, Be, Se, Co, Zn, Cd oxide.

• Borax (or gerstle borate), copper, chromium (chrome), manganese, nickel, potassium dichromate.
Green Body Drying

This section discusses the kinetics of drying for various conditions of temperature and solvent partial pressure in the atmosphere.

INTRODUCTION

To remove the solvent used to suspend the ceramic powder for green body fabrication, the green body is heated or placed in an atmosphere where the solvent evaporates.

Depending on the type of ceramic powder used and the green body fabrication process different solvents are used.

LUBRICANT ADDITION

Solvents are typically organics or water. Organic solvents are chosen to easily wet the ceramic powder surface and easily evaporate during drying. This means that a low enthalpy of vaporization and a reasonably high vapor pressure is important for a solvent to be easily evaporated.

The weight loss during drying is shown in Figure 1.

This figure shows a constant rate period where the surface of the green body is always wet by the flow of liquid to the surface.

This flow emanates from the rearrangement of particles in the green body, which is caused by the compressive capillary pressure at the surface of the green body. At some point, the particle network becomes rigid and no more shrinkage can take place.

This critical point is referred to as the leather hard point in clay ceramics nomenclature. With particulate ceramics, this rigidity threshold takes place at high volume fraction where the particles come into contact. With gels, the particle network exists at the start of drying—shrinkage occurs as a result of this compliant network stopping at the rigidity threshold of the network. After this critical point, the liquid-vapor interface starts to recede into the pores.

At this stage, surface tension driven flows in the direction of the free surface attempt to keep a monolayer of solvent on the surface of all the ceramic powder. Such capillary flow will continue as long as there is a continuous pathway from the liquid front to the green body surface.
FIGURE 1: Diagram of the drying of a ceramic green body showing the weight loss and shrinkage with time.

FIGURE 2: The drying front in a green body composed of mono sized 0.5 mm SiO₂ particles. In this photo, saturated pores are white and empty pores are black.

TABLE 1: List of Polymers That Depolymerize during Thermal Degradation.

---

As Cast

Green Body Shrinkage and Deformation

Particle Contact with Liquid Filling the Pores

Completely Dry

Weight

Constant Rate Period

Decreasing Rate Period

Time
**Drying Mechanism (Drying Process)**

1. **Heat Transfer**

   The flux of heat, \( q \), into a green body is given by the boundary layer heat transfer:
   \[
   q = \frac{Q}{A} = h (T_B - T_S)
   \]

   where \( Q \) is the quantity of heat transferred per unit time, \( A \) is the surface area of the green body at temperature \( T_S \) exposed to the bulk gas at temperature \( T_B \), and \( h \) is the heat transfer coefficient which is a function of the gas flow rate around the green body.

   ![Diagram of evaporation](image)

   *FIGURE 3* diagram of evaporation in a porous network (a) liquid partial pressure profile, (b) temperature profile.

2. **Mass Transfer**

   The mass flux, \( j \), is related to the heat transfer flux, \( q \), required to evaporate those molecules at the point of vaporization by the following expression:

   \[
   q = \Delta H_{vap} \cdot j
   \]
Where $\Delta H_{\text{vap}}$ is the enthalpy of reaction. This relation requires that the two differential equations for the two fluxes be linked for their simultaneous solution, the mass transfer flux $j$.

**Drying Rate**

Once the drying front enters the green body, the drying rate decreases. Because water evaporates on the material surface during the constant drying-rate period, the drying rate $R_c$ is apparently equal to the evaporation rate from the free water surface.

$$ \theta_d = \int_{w_1}^{w_2} \frac{d\theta}{R_d} $$

The drying time $\theta_d$, drying rate $R_d$, water content $w$.

**Stages of Drying**

As shown in Figure, the drying process consists of the following three stages:

1) Preheating period.

2) Constant drying-rate period: free water exists on the surface of the material.

3) Decreasing drying rate period.

Figure shows the drying rate $R$ in relation to the water content $w$.

**Drying Stresses**

The local effective stress $\sigma_e$ is given by the sum of the gas pressure, $P_g$, the capillary pressure, $P_c$, and stress within the solid $\sigma_s$. 
\[ \sigma_e = \sigma_e + P_g + P_c \]

The net stress is given by the difference between the effective stress and the average stress:
\[ \sigma = \sigma_e - \langle \sigma \rangle \]

Where \( \langle \sigma \rangle \) is the average stress integrated over the pore volume of the green body, \( V_p \) given by
\[ \langle \sigma \rangle = \frac{1}{V_p} \int_0^{V_p} \sigma_e \, dV \]

The stress within the solid is often to be constant over the green body, thus it disappears from the net stress. If, however, there is a temperature profile in the green body.

In the initial stage of drying, when the liquid fills the pores and there is a temperature profile in the green body, the thermal expansion of the liquid will add another stress, that can be substantial.

However, this liquid expansion stress is either

1. not Important because the liquid filling the pores transfers heat relatively fast and eliminates thermal gradients.
2. relieved by flow if the permeability of the particle network is high.

**CRACKING, AVOIDANCE OF CRACKING**

A small amount of polymer can produce an enormous volume of gas, which must be removed from the porous green body.

The flow of this gas in the porous network of the ceramic green body can create a pressure build-up which puts stress on the green body.

The stress induced by flow and temperature gradients in the green body, so that binder fatigue conditions can be selected to prevent cracking of the green body.

To remove the polymeric binder, the green body is heated often in an oxidizing atmosphere. During this process the polymer degrades along many possible degradation pathways, which include

1. Separation of the main chain,
2. Reaction with side chains and substituents,
3. Cross-linking and cyclization ending in carbon formation.
Vapors leach out the binders without causing the part distortion, warping, or cracking that frequently occur in thermal debinding.

A dislocation or carrier gas is circulated through the debinding cell to prevent binder deposit on cold chamber walls.

The vapors are condensed by passing them through a distillation column and reused. Solvent and thermal debinding are slow (10 to over 30 h) processes, but catalytic debinding is faster and usually takes 2-4 hours for completion.

Large, bulky parts present considerable difficulty in binder removal and are not good.

**QUANTITY OF HOT AIR REQUIRED FOR DRYING PROCESS,**

From equation:

\[
b \ \text{P(s)} + \ n\text{O}_2(g) \rightarrow v\text{V(g)} + s\text{S(s)} + \Delta H
\]

where \(b\) moles of polymer, \(P\), react with \(n\) moles of \(O_2\) to produce \(v\) moles of volatile(s), \(V\), vapor, and \(s\) moles of solid residue(s), \(S\), solid; \(\Delta H\) is the enthalpy of reaction.

**TYPES OF COMPRESSED AIR DRYERS**

- Regenerative Desiccant Type
- Heat of Compression Type
- Single Tower Type
- Membrane Type
<table>
<thead>
<tr>
<th>Types of Dryers</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tray dryer</td>
<td></td>
</tr>
<tr>
<td>Turbo dryer</td>
<td></td>
</tr>
<tr>
<td>Spray dryer</td>
<td></td>
</tr>
<tr>
<td>Drum dryer</td>
<td></td>
</tr>
<tr>
<td>Tunnel dryer</td>
<td></td>
</tr>
<tr>
<td>Screen conveyor dryer diagram</td>
<td>Quantity of hot air required for drying process, quantity of heat required for heat the drying air.</td>
</tr>
</tbody>
</table>

- Tray dryer
- Turbo dryer
- Spray dryer
- Drum dryer
- Tunnel dryer
- Screen conveyor dryer diagram

Quantity of hot air required for drying process, quantity of heat required for heat the drying air.