Chapter II

LITERATURE SURVEY

2.1 Size Enlargement

Scope and applications

Size enlargement is any process whereby small particles are gathered into larger, permanent masses in which the original particles can still be identified.

Applications include formation of useful shapes (e.g., brick and of finely divided materials).

Numerous benefits result from size-enlargement processes (1), as will be appreciated from Table 2.1

Table 2.1 Objectives of Size Enlargement

Reduce dusting losses

Reduce handling hazards, particularly with irritating or obnoxious powders

Render powders free-flowing

Densify materials for more convenient storage or shipment

Prevent caking and lump formation

Provide definite quantity units suitable for metering, dispensing, and administering

Produce useful structural forms

Create uniform blends of solids which do not segregate

Improve the appearance of products

Permit control over properties of finely divided solids (e.g., solubility, porosity, surface/volume ratio, heat-transfer rates)

A wide variety of size-enlargement given in Table 2

Table 2.2 Size-enlargement Methods and Applications

Method	Equipment	Representative applications
Pressure compaction..	Molding press	Plastic preforms, small machine parts from metal powders (cams, gears, gaskets)
	Tableting press	Pharmaceuticals, catalysts industrial chenicals, ceramics, metal powders
	Roll-type press	Clay-type minerals, potassium chloride, sodium chloride, organic compounds, metal powders, ores, charcoal, lime, magnesia, titanium sponge, phosphate rock
	Pellet mill	Pharmaceuticals, plastics, clays, carbon, charcoal, industrial chemicals, fertilizers, rubber products, animal feeds
	Screw extruder	Bauxite, plastics, rare earth fluorides, clays
Agglomeration by tumbling	Inclined pan or disk; rotary drum agglomerator	Fertilizers, iron ores, nonferrous ores, mineral and clay products, carbon black, various finely divided solid waste products
Sintering and heat hardening	Traveling grate (straight or circular), roraty kiln, shaft furnace	Ferrous and non-ferrous ores, minerals, cement clinker, solid waste products
Other techniques:		
Prilling..	Prilling tower	Urea, ammonium nitrates, resins, coal-tar pitch, etc.

Method	Equipment	Representative applications
Sol-gel process....	Spray column	Metal dicarbide spheroids
Fluid-bed processes..	Fluidized bed	Granulations for pharmaceutical tableting, liquid radioactive waste disposal
Agglomeration from liquid		
Suspension..	Various form of agitation	Simultaneous agglomeration and removal of fine solids from liquids
Clustering..	Conical blender	Coffee, dextrin products, non-fat dry milk, starches

2.2 Agglomeration Processes in Food Manufacture

In food manufacture, agglomeration is employed controlling of particle size and particle structure. Approximately 110 processes are revealed for the improvement of dry food ingredients and dry product mixes in terms of dispersibility wettability, solubility, controlled bulk density and other characteristics which depend on completeness of hydration and bulk density.

The production that employs agglomeration can be classified out concerning nonfat dry milk, chocolate drink powders, whole milk and other dairy products, natural sugars and synthetic sweeteners, soluble coffee and soluble tea, flour and cake mixes other agglomeration processes involving beverage mix products, dried egg products and monosodium glutamate. The basic process hired to produce agglomerates can be concluded into two means. First the wet-back method which was originally engaged to carry out agglomerates, it is to add moisture as a spray while the particles are being tumbled or mixed

in bulk. Secondly straight-through processes were developed to
agglomeration during the last stage of dehydration so that it would
not be necessary to add back moisture of agglomerates and then redry
the mixture.

In principle, for a powder to be aggregated it must exhibit
certain properties (6). The first and perhaps the most important
property is that of hygroscopicity, that is the property of readily
sorbing and retaining moisture. The sorption of water is necessary
to obtain a state of surface tackiness which will allow the powder
particles to be randomly adhered to each other. However all hydroscopic
particles do not become sticky when the absorb moisture and those
which do not develop such stickiness are not easily aggregated. A
third property which must be present is that of retention of the
aggregated form when the aggregates are subsequently redried and
packaged. This term may be defined as aggregate strength.

The term "difficult to aggregate particles" refers to
those particles which are substantially lacking one or more of the
above named properties necessary for aggregation. The term
" aggregating agent " may include all those materials which passes
all three of the above named properties. The selection of the
particular aggregating agent to be used will depend on the degree
to which the particular avialable aggregating agents possess the
above properties, the comparative cost of the available agents,
and the particular product which is desired to aggregate. Example
of suitable aggregating agents are amorphous lactose, amorphous
whey, and modified amorphous whey. Such aggregating agents may be
used singly, or in combination or with suitable extenders.

Among the aggregating agents, the one which is perhaps
most often useful is anhydrous lactose. Anhydrous lactose may
be obtained by spray drying dissolved lactose, and exists in the
amorphous or "glass" state. It exhibits all properties of hydrosco-
picity, surface tackiness and aggregate strength. Anhydrous lactose

exhibits a unique property in that while it is very hydroscopic, it is also quite insoluble as compared to other common sugars. Such relatively low solubility makes the anhydrous lactose relatively easy to handle in most conventional aggregators.

The mixture sorption property of anhydrous lactose is due to its strong desire to assume a stable configuration. The most stable form of lactose is that of the monohydrate or crystalline form. The following reaction will show the hydrating process.

$$C_{12}H_{22}O_{11}+H_2O \longrightarrow C_{12}H_{22}O_{11} \cdot H_2O$$
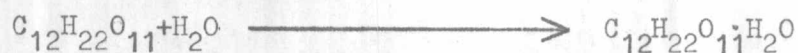
Once the monohydrate is formed, there is no longer any driving force which will cause the lactose to sorb more water. The strong tendency of anhydrous lactose to sorb water is illustrated graphically below.
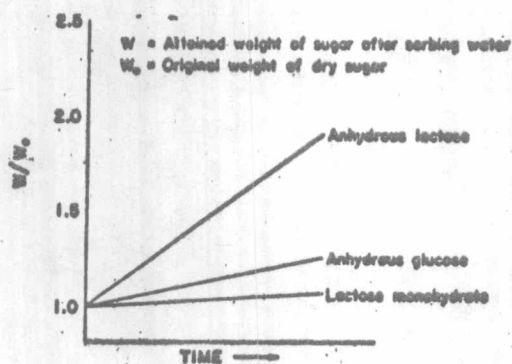

FIG. 2.1   RATE OF WATER SORPTION OF VARIOUS SUGAR

The longer the given quantity of anhydrous lactose is allowed to remain wetted, the more complete will be the conversion of the lactose to the monohydrate or crystalline form.

The effect of the addition of various amounts of anhydrous lactose to several difficult to aggregate materials is also shown graphically below.
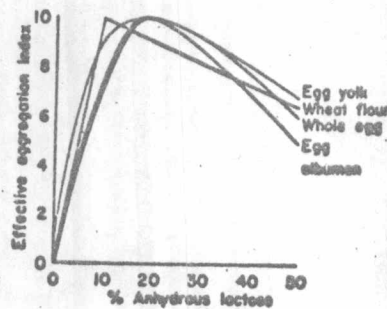
FIG. 2.2 EFFECT OF VARIOUS AMOUNT OF ANHYDROUS LACTOSE IN AGGLOMERATION

It is obvious that among the difficult to aggregate
materials, as examples shown, a mixture containing approximately 20%
anhydrous lactose will produce maximum effective aggregation when
either dried whole egg or dried egg albumen are to be aggregated Dried
egg yolk is most easily aggregated in a mixture containing between 10
and 20% anhydrous lactose.

The amount of lactose added to the mixture has a great influence
of reconstitution time of the product. The effect of which the addition
of lactose has on the reconstitution time of the product was shown in
the figure 2.3 It can be seen that an aggregated mixture of 80%
dried egg albumen and 20% anhydrous lactose will reconstitute in about
one-fifth the time necessary to reconstitute unaggregated egg albumen
powder. An aggregated mixture of about 20% anhydrous lactose and 80%
dried whole egg or dried egg yolk will reconstitute less than one-tenth
the time the time necessary to reconstitute unaggregated dried whole
egg or dried egg yolk. A mixture of about 10% anhydrous lactose and
90% wheat flour has a reconstitution time of about one-twentieth that
of unaggregated wheat flour. As the percentages of anhydrous lactose
present in the dry mixture increases above the values mentioned above,
the reconstitution time remains substantially the same.

As mentioned lactose is among the goodaggregating agents.

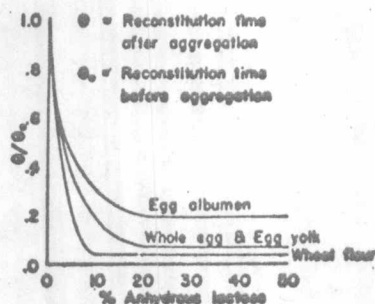hereby we should know a number of ways in which the agent may function.

FIG.2.3 EFFECT OF THE ADDITION OF LACTOSE ON THE RECONSTITUTION TIME

    1. The agglomerating agent may be any liquid which when it cantacts the material in bed will cause the particle to become tacky or sticky and adhere together in clusters by solubilizing part or all of the material or otherwise transforming it to create this condition

    2. The agglomerating agent may be a solution or suspension of some ingredient in a liquid, so that the ingredient will it_self perform the bonding function and, therefore, make it possible to agglomerate materials,

    3. The agglomerating agent may be material which when heated becomes a liquid which performs the function described in and by a modification of theprocess in which a cool gas is used to fulidize the material, the wetting agent would be caused to solidify after it contacts the material in the bed, thereby causing agglomerates to form and

    4. The agglomerating agent may be a combination of one or more material in the form of liquid mixtures which may be combined with the powdered material fed into the process. One or more of the individual materials in the combination may or may not play a part in the agglomerating function, but it may become incorporated into the agglomerates instead of being evaporated by the fluidizing gas. Thus, the process provides a means of combining materials while simultaneously producing an agglomerated product.

The wetting agent may also provide a means of combining materials, which are not readily available in a dry form, with powdered materials and obtaining a dry free-flowing product.

2.3 Wet Back Process in Industries

2.3.1 Application of fluidization to Chocolate Drink Powders. The pillsbury fluidized bed process is the process(4) used for chocolate drink powders, angel food cake and flour-sugar mixtures. The process involves the use of a moving fluidized bed of powdered material. The bed is successively treated with vapor and carrying gas to form
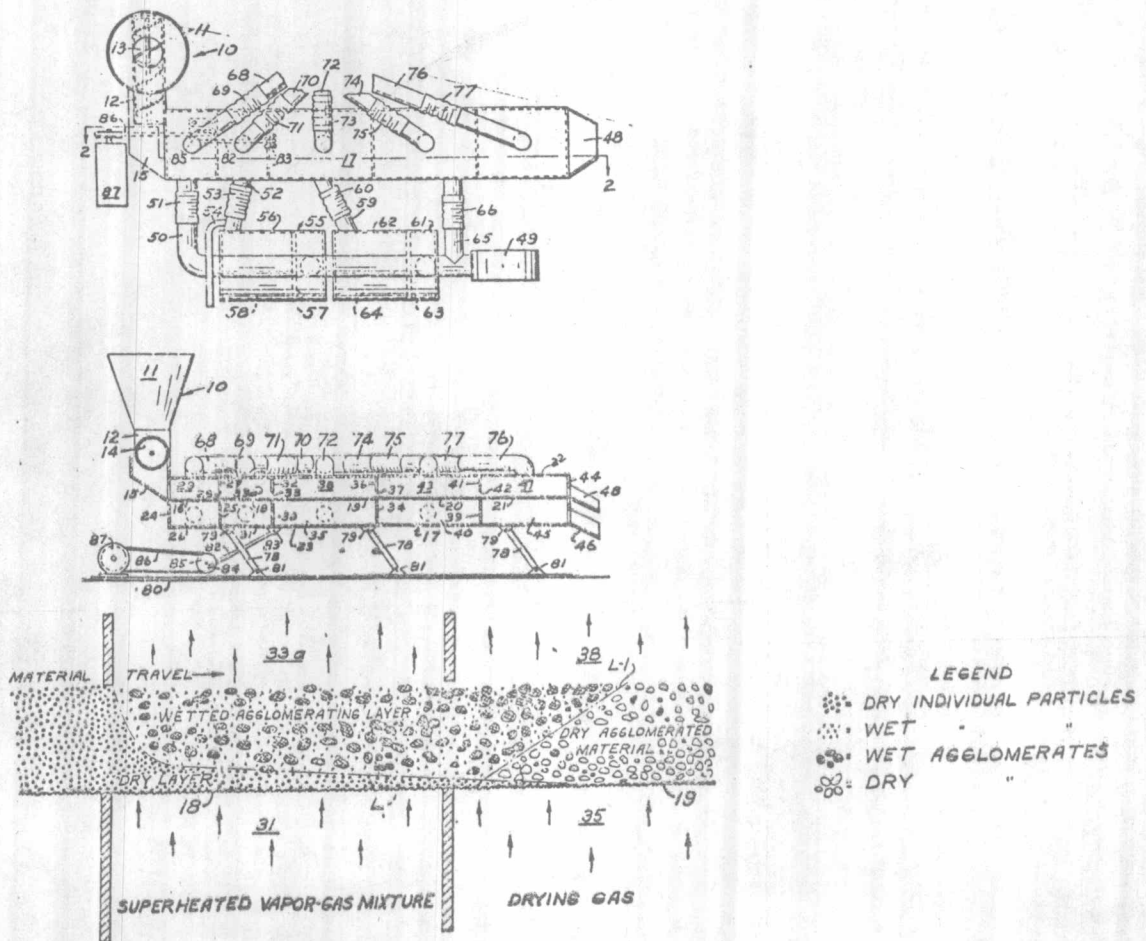
FIG. 2.4 PILLSBURY FLUIDIZED BED PROCESS

.agglomerates through contacting and colliding particles.

An important feature of the process resides in the continual agitaion of preferably all of the pervious sheets and chambers to keep the individual powdered particles as well as the agglomerates in continually dispersed and fluidized condition. The combined agitation of the pervious sheets together with the upward flow of the various pressurized gas and vapor-gas streams effects proper treatment of the powder and the agglomerates while in highly concentrated and fluidized bed and contributes to maintain the entire machine in nonfouling condition.

The terms which shael be defined clearly are

1. Gas, which means an essentially inert gas which serves as a carrier for the agglomerating agent which is vapor may transfer heat or mass to the solids being treated and preferably provides the force necessary to fluidize or sufficiently agitate the bed of solids so as to cause the solid particles to be partially suspended and dispersed in the bed. The requisite gas in most cases is not condensable within the range of temperatures employed and is inert toward the material being treated.

2. Vapor, which is either condensable or absorbable on the surface of the particles being agglomerated within the range of temperatures employed and, when so condexsed and/or absorbed upon surfaces, causes adhesive films to be formed so that particles will adhere together. The vapor is introduced into the gas to provide a gas-to-vapor ratio which, within the range of temperatures employed, will result in surface condensation and/or absorption of the vapor upon the particles in the upper zone or strata of the bed of moving particles.

2.3.2 All Purpose Sugar Process.
An all-purpose sugar agglomeration is accomplished in two different and successive steps. In the first step a downwardly flowing curtain of the powdered material is subjected to balanced downwardly directed and converging jets of steam or, alternatively, to horizontally directed and balanced opposing jets of steam, in either case solely to effect

moistening of the powdered material. There after, the powdered material is subjected, in a separate age agitation stage, to the action of downwardly directed or horizontally directed and opposed jets of either substantially dry steam or air to act on the powder after it has been moistened and to cause it to move in a turbulent manner within an agglomerating zone, so that there will be a sufficient number of collisions between the particles in order that agglomerates there of will be built up there from.
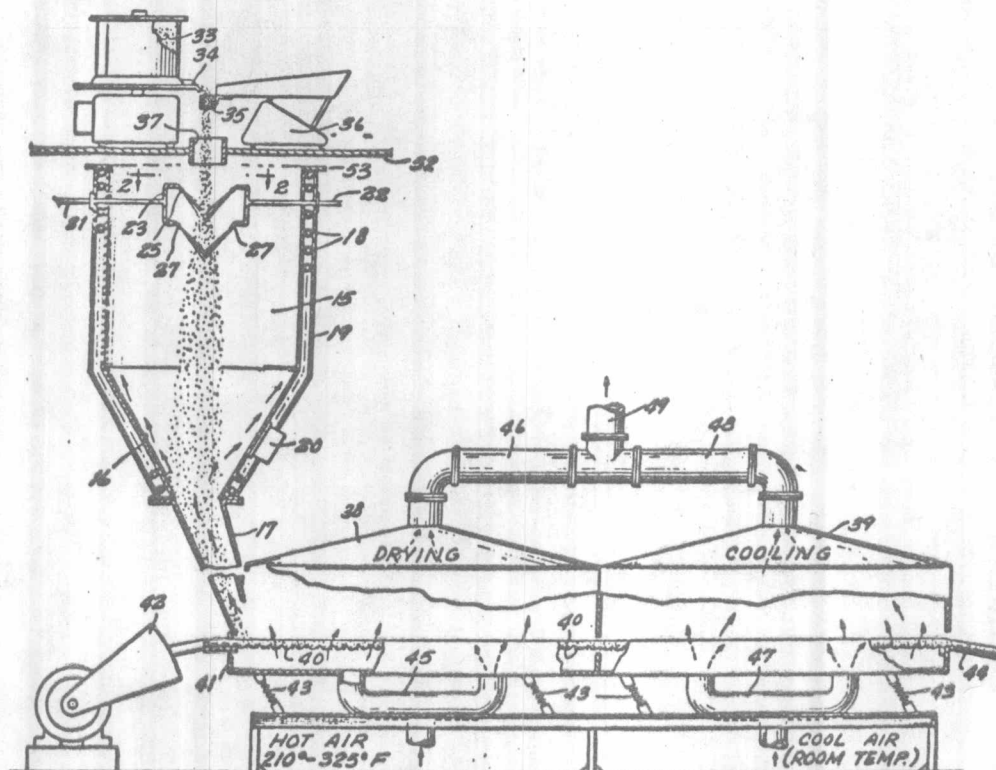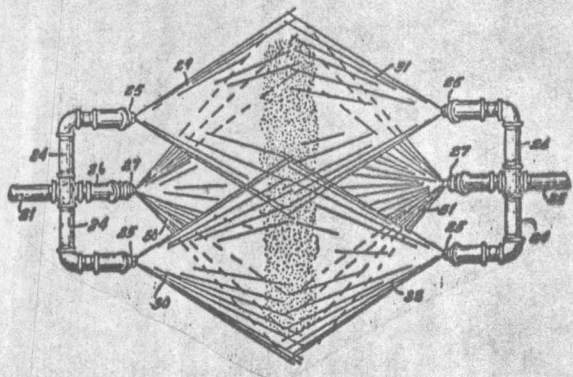
FIG. 2.5 ALL-PURPOSE SUGAR PROCESS

FIG.2.6   ARRANGEMENT OF STEAM NOZZLES IN THE ALL PURPOSE SUGAR PROCESS

2.4 Agglomerate Properties

Three-dimensional masses of powder, whether compacted pellets or loose assemblages of particles, exhibit a characteristic behavior when deformed. One property, termed dilatency, has far reaching consequences in regard to powders generally and to agglomerate strength in particular.

2.4.1 Dilatency of Powders

A mass of powder such as sand tightly packed and enclosed in a flexible envelope invariably increases in volume when the envelope is deformed. The mass dilates, or expands—hence the phenomenon is termed
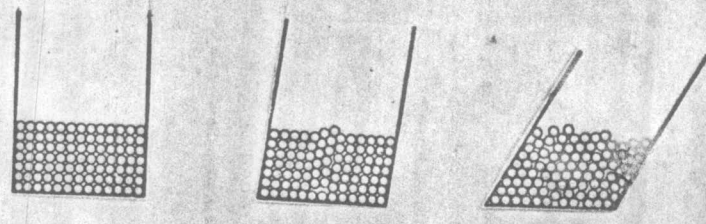

FIG.   2.7 DILATENCY IN AN IDEALIZED POWDER.

dilatency. The most common situation under which dilatency is encountered is when one walks along a damp beach. The sand appears to become momentarily dry in the vicinity of each footprint. It does so because of a local increase in the volume occupied by the sand. The water present, which earlier filled the interstices of the undeformed bed of sand, then becomes insufficient to fill the expanded bed. The sand appears dry because a little time is required for water from surrounding regions to filter back intothe expanded area. What actually happens on the particle-to-particle level is that certain of those particles that previously were intermeshed and in closely packed contact are made to separate and enter into a more loosely packed condition.

The dilatency of a powder is most easily visualized with an enclosure in which single layers of spherical particles can be con-fined and deformed (18). This idealized situation is depicted in Fing. 2.7. An initial cubical arrangement of the spheres is chosen for convenience, but similar effects prevail with staggered or even random arrangements. On the figure the left-hand illustration shows each sphere contacting four others (or three and the wall). The center shows that, following a slight deformation, a column of spheres has risen near the center section, leaving a void deep within the packing. Any column might have been lifted, depending upon chance irregularities. The lifting is induced by frictional force arising from the right figure the initial expansion has been followed by a collapse as many of the spheres shift into a regular honeycomb or tightest-packing condition. The illustration shows that there is a tendency for local, tightly packed regions to develop and to remain so, never "meshing" ideally with one another. Loose, irregular regions, or zones, exist between the more tightly packed ones. These serve as slip planes when further deformation is induced.

Dilatency is a universal phenomenon among particles, even those of different shapes and sizes. It is purely a consequence of the geometry of the packing and depends on the nature of the particles

themselves only insofar as this determines the packing geometry. Internal friction does not alter the occurrence of dilatency; the same behavior has been found whether air, water, oil, or soap-and-water solutions fill the voids. Dilatency is, of course, most evident in tightly packed powders.

2.4.2 Strength Testing

In practice, only experimental investigation of agglomerate strength can establish whether or not a granule prepared in a certain way will hold together during the service required of it. Accordingly, granules are subjected to compression, tension, impaction, shear, bending, and abrasion by being squeezed, dropped, abraded, and tumbled in a drum with others of its kind. Such tests serve their intended purposes and are by no means to be degraded. However, only carefully controlled compression, tension. and adhesion tests are readily subject to scientific analysis.

In testing for tensile strength the primary problem is one of fastening onto a granule. For this, adhesives have been employed after first smoothing off opposed faces of the agglomerate and treating them with a lacquer coating to prevent penetration of the adhesive into the agglomerate itself. Provided the granule pulls apart within its unaltered body, its tensile strength is calculated again as the product of the failing force and the cross-sectional area.

Since an agglomerate is oreinarily not an elastic body, rupture by tensile test can take place without relative motion among the particles. Such motion is necessary as explained in the preceding section if failure is to occur due to compression forces, however. It follows, then that compression must overcome friction among particles and that a linear relationship between the vompressive and tensile and compressive strengths are great, closer correspondence between the two measures may be anticipated
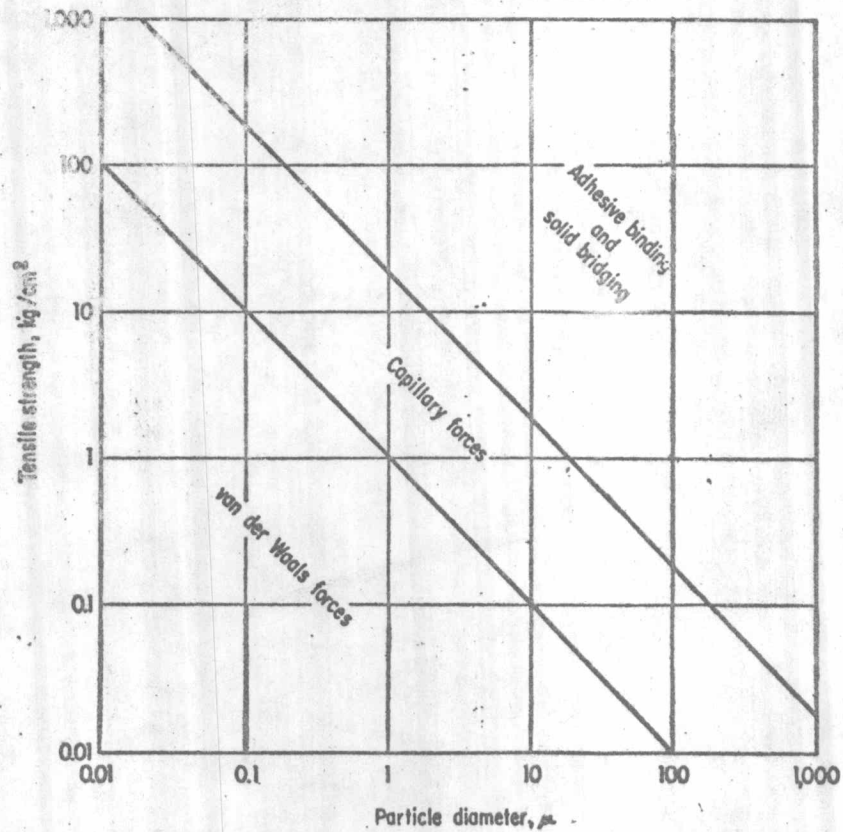
FIG. 2.8 PARTICLE SIZE AND AGGLOMERATE STRENGTH REGIONS IN WHICH
VARIOUS BINDING MECHANISMS PREDOMINATE (AFTER H. RUMF THE STRENGTH
OF GRANULES AND AGGLOMERATES IN W.A. KNEPPER(ED), AGGLOMERATION
(NEW YORK WILEY, 1972 P. 399)

Fig. 2.8 indicates agglomerate tensile strength values to
be expected for the various binding mechanisms as a function of
particle size.

2.5.1 Particle Packing

The greatest density for powder is obviously obtained when
the voids among the largest particles are just filled with smaller

particles, and these voids are in turn filled with still smaller
particles, and so on. Arrangements of particles in this as well as
in less dense configurations is of basic importance in numerous
endeavors besides agglomeration, among the latter being soil geology,
hydraulic engineering, concrrete design etc.

2.5.1 Uniform-Size Spheres

Spherical particles of uniform size may be packed in five
different arrangements as shown in Fig 2.9. They are designated
cubical. orthorhombic(cubical tetrahedral), tetragonal, pyranidal,
and tetrahedral. If the volume of the solid figure bounding the
cubical arrangement, for example, is V; if Nx,Ny, and Nz are,
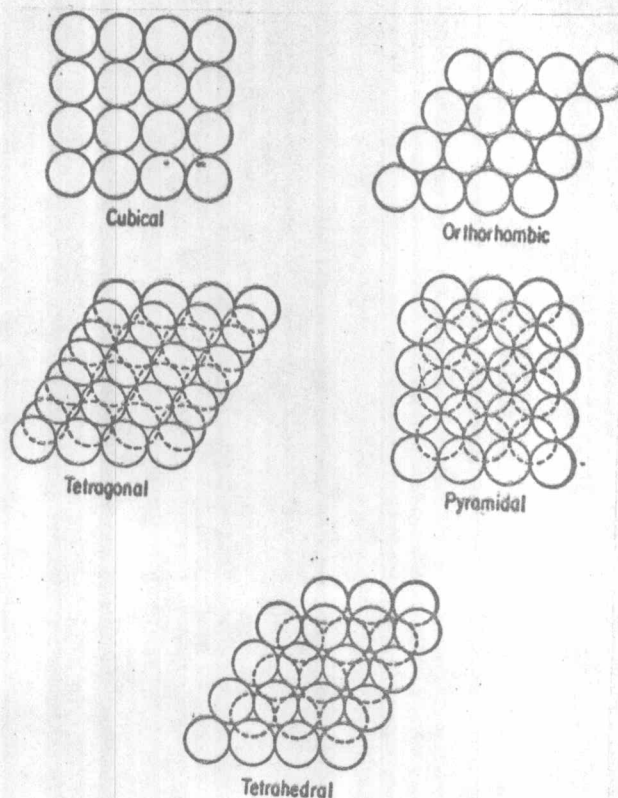

Cubical

Orthorhombic

Tetragonal

Pyramidal

Tetrahedral

FIG. 2.9 PACKING ARRANGEMENTS FOR SPHERES.

respectively, the number of spheres along each of the axes x,y, and z, and if r is the sphere radius then V is equal to

$$2rNx \cdot 2rNy \cdot 2rNz.$$

The volume of the spheres, on the other hand, is $\frac{4}{3} r^3 Nx \cdot Ny \cdot Nz.$ Therefore, the volume of the void space expressed as a percentage of the total volume occupied by the arrangement of spheres is $(8r^3 - \frac{4}{3}\pi r^3)/8r^3$ 100 or. 47.6 per cent. In other words, the spheres actually occupy 100-47.6 or 53.4 per cent of the included volume, or, stated another way, the space has 53.4 per cent of theoretical density. In a similar vein, the percentage void volume of the orthorhombic packing is 39.5 per cent (=60.5 per cent of theoretical density), of the tetragonal 30.2 per cent (=69.8 per cent of theoretical density), and of the pyramidal and tetrahedral 25.9 per cent (=74.1 per cent of theoretical density), the latter two being identical.

Absolute sphere size is theoretically irrelevant in the above cases. In actual practice, however, complete independence of absolute particle size does not hold for the very small sizes (10). The void fraction increases with a decrease in particle size in the small-size range. This behavior apparently arises because large, heavy particles exert a sufficiently great force through their points of contact when vibrated or otherwise disturbed to breakdown arching and bridging effects. Small particles, on the other hand, do not exert such a force since the number of contacts per particle remains the same as long as the same type of packing is preserved.

The cubical packing is unstable and does not occur in nature. The tetragonal, pyramidal, and tetrahedral cases represent systematic nesting systems and should not be expected except in highly idealized situations. This leaves the orthorhombic system as the one most likely to be encountered with uniform-size spheres. Somewhat greater densities may be obtained of special efforts are made. For example, densities for closely sized spheres put into a cylindrical container and vibrated for an extended period attained about 62.5 per cent,

indicating that only something like $\frac{1}{5}$ of all possible double nestings are actually produced.

2.5.2 Selected-Size Spheres

For systems composed of two or more sizes of components, the optimum amounts of each to give the densest arrangement could be readily calculated from geometric consideration if no expansion of the mass resulted from the mixing. In practice, expansion always occurs to some extent even though the powder sizes are of identical density. The phenomenon is termed dilatency as earlier described and occurs because a mass of static spheres forms a rigid system that must be separated slightly by vibration or agitation for one sphere to slide over another. Comparison of theoretical and experimental densities for mixtures through quaternary are given in Table 2.4 (9)

Table 2.3

Density of One-Sized, Binary, Ternary, and Quaternary Mixtures of Spheres

| Fractional Composition of Spheres of Diameters (in). of | | | | PerCent of Theoretical | |
0.505	00.061	0.011	0.0016	Calculated	Experimental
1.000	—	—	—	60.5	58.0
0.726	0.274	—	—	84.8	80.0
0.647	0.244	0.109	—	95.2	89.8
0.607	0.230	0.102	0.061	97.5	95.1

After R.K.McGeary, "Mechanical Packing of Spherical Particles," J. Amer. Ceram. Soc., 44,521 (1961).

A density 95.1 per cent of theoretical as shown for a quaternary mixture is about that obtained with pressed and high-fired ceramic

objects. Such a mixture is remarkable in that, instead of being an apparently hard solid body, it can be poured from a container. Approximately a sevenfold difference in spherical component diameters is necessary for efficient agglomerate packing.

2.5.3 Continuous Distribution of Sizes

The great majority of particle systems are composed of a more or less continuous distribution of particle sizes extending down from some maximum value. These will not necessarilly pack so as to give minimum voids; more likely than not they will segregate instead when vibrated. Stable systems, or those that tend toward minimum voids, are those that tend toward minimum voids, are those in which the number of particles in each size interval increases as the particle size decreases. Their particle diameters follow generally the distribution expression

$$\text{Cumulative weight fraction less than } d = \left(\frac{d}{d_{max}}\right)^q$$

where d is the particle diameter, d_{max} the maximum particle diameter of the system, and q an exponent having values between $\frac{1}{2}$ and $\frac{1}{3}$

When the bulking or packing characteristics of one powder must be correlated with the same properties of other powders, the mean volume surface, or Sauter, diameter d_{vs} will usually be found most appropriate.

2.5.4 Effect of Particle Shape, Density, and Roughness

In general, the greater the deviation of a smooth-surfaced particle's shape from spherical, the denser will be the packing that can be prepared from it by vibration or moderate-pressure compaction. This is undoubtedly attributable to the particle's orienting themselves so that the projections on some tend to fit into the indentations of others.

Solid-material density has little effect except when the particles are very small or when the continuous-medium density is relatively large. In either case, the result is a slight increase

in the void fraction. Under pressure compaction the difference in
voids is insignificant as the effect is primaray one related to
sedimentation rate, buoyancy, and fluid viscosity.

Greater voidage, finally, is promoted by any factor, such
as surface roughness or cohesiveness, which creates difficulty in one
particle's sliding past another. The degree of surface roughness is
an especially important consideration with dry powders. A roughness
coefficient defined as the total exterior .surface area divided by the
gross exterior surface area has been suggested for correlating purposes.

2.6 Binding Mechanisms

The forces existing between pairs of small particles have
never been directly measured because of their very low magnitude.
What is understood about the phenomena of attachment among particles
is deduced largely from observations on larger bodies and on powder
masses or is calculated from well-known physical principles. That
there are forces, however, between particles and surfaces is revealed
every day by the tenacity with which dust adheres to furniture,
automobiles, and all other common objects. Two highly polished and c
optically flat glass plates are reported to require forces of as much
as much as 650 psi to pull them apart if brought into intimate contact,
while gold leaf has been shown to adhere to glass with a force of as
much as 46,000 pasi. When a solid bar is broken under high-vacuum
conditions (also under mercury) and the parts replaced rapidly in their
correct relative position, they adhere, and the bar will be found .
subsequently to be ssentially as strong as it was before having been
broken. In fact, absolutely clean surfaces will adhere with the bulk
strength of the parent material. Actual powders exist with their
surfaces contaminated with adsorbed moisture or gases, oxide layers,
grease, etc. For this reason agglomerates rarely incorporate a
physically cohesive bond, Pressure compaction and attrition, however,

sometimes produce a penetration of these covering layers so that real welding can occur.

There are four distinct mechanisms by which particles are held in agglomerates and each of these can be subdivided into several categories. Mechanical interlocking of particles is not one of them as it is generally conceded to be only a minor contributor to overall agglomerate strength in most instances. The major mechanisms all involve bonding through atomic forces.

2.6.1 Solid Bridging

The strongest binding among particle masses usually is achieved when a distinct fusion occurs across points of contact. Fusion can be brought about (1) by partial or incipient melting as described in connection with sintering, (2) by solid diffusion, (3) through added agents called binders which set or harden, (4) through chemical reaction between the solids and/or the binding compounds, and (5) by crystallization of dissolved materials.

Fusion through melting is produced by elevated temperatures and is aided by high pressure and by impurities, particularly if the latter provide eutectic compositions. When the solids are hard or exhibit high melting points, bridging is restricted to the tips of roughness peaks. Larger bridges are formed when the solids are plastic. Even though temperatures insufficient to cause melting may be attained, some materials, notably metals, form bridges across contact points by solid diffusion. Diffusion is accelerated, of course, by higher temperatures and is enhanced by pressure. Compression itself, when it represents an input of considerable energy and is borne by points of contact of very small cross-sectional area may contribute greatly to local melting and fusion.

Commonly employed binders which set or harden to form bridges across particle are Portland cement and sodium silicate. The process of using binders is often termed curing. Chemical reactions contribute

significantly to bridge growth in the iron are and mixed fertilizer industries. Bridging is effected, for example, in the former when Fe_3O_4 is converted to Fe_2O_3 and in the latter when ammonia is reacted with superphosphate.(8)

Small crystals often form across the points of contact among larger crystals creating pinding bridges while the latter are being dried. Bridging in this situation is a considerable nuisance because it produces caked crystals when a free-flowing product is desired. Small crystal formation also occurs with deliquescent crystals or when slightly water soluble crystals are exposed alternately to high and low relativehumidities.

2.6.2 Low-Viscosity Liquid Binding

Adhesion among particles is created by the presence of mobile but low-viscosity liquids. The mechanism is identical with the strong attraction exhibited by two planes of glass with a drop of water placed between them. In both cases the interfacial tension peripheral to the liquid boundary draws the solids together. The relative amount of liquid, its properties, and the shape of the particles actually determine the resulting force.
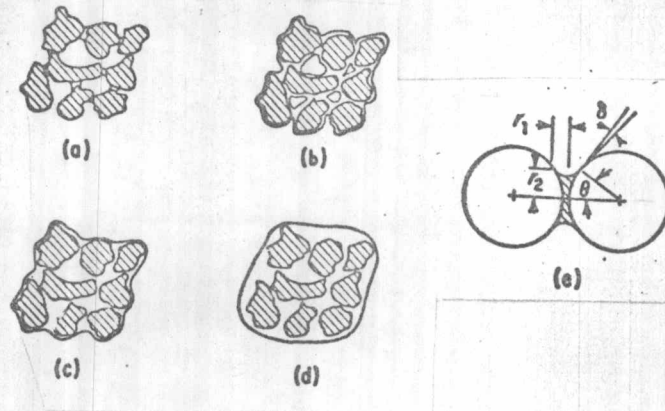

FIG. 2.10 STATES OF LIQUID IN ASSOCIATION WITH AGGLOMERATES.

When the void spaces among grains are only partially filled
as in Fig. 2.10, the pendular state is said to exist. At the solid-
liquid-gas contact line, the liquid tension is directed along the
liquid surface if the solid is wetted, while within the liquid bridge
a negative capillary pressure is created. Both effects result in a
mutual pulling together of the particles. It arises, it should be
noted, solely from the gas-liquid interfacial tension. If the void
space is completely filled with liquid, the interfacial force still
exists but at the granule surface only. As long as the liquid does
not extend to the particle's edges and there are concave cavities in
its surface, a negative capillary pressure exists internally and the
granule retains a certain tensile strength. This situation is
illustrated at Fig.2.10c and is termed the capillary state.
A transition condition called the funicular state, as at Fig 2.10 b,
is defined as one with gas spaces present but one in which liquid
still forms a contiuous network. As the liquid completely envelopes
the particles. Fig.2.10 d, the concavities intergranular binding forces
vanish, and only the interfacial tension of the liquid tends to hold
the particles captive.

An expression for the tensile strength i of an agglomerate of
spheres in terms of particle diameter d, the porosity of the agglomerate
, and the binding force b at the contact points can be written if
the simplifying assumptions are made that the agglomerate is
microscopically homeogeneous and that the fracture cross section
contains a great number of points of contact, or points of binding.
When an agglomerate of spheres is pulled into two pieces, the spheres
must, of course, go with one or the other of the two parts. Assuming
those in the fracture zone choose to remain with the part in which
they are most deeply buried, the effective fracture region about these
spheres can be as much as one-half a sphere's area and as little as zero
Stated another way, some spheres may be expected to protrude above the
plane of fracture so as to expose a full hemisphere while others are

immersed to all intermediate degrees between hemispherical exposure
and complete submergence. From geometrical considerations it can be
shown that the mean exposed surface area of the spheres extending
abovethe plane of fracture is $\pi d^2/4$. This is the area over which bonds
were broken in severing the original agglomerate. Also from geometrical
analyses it can be shown that a mean area of $\pi d^2/6$ would have been
exposed had the agglomerate been sliced along the plane of fracture
and that the mean spherical surface area may be described as that
area enclosedby a cone with a half angle of 60° having its apex at
the mean sphere's center and its base in the fracture plane.

Since the spheres are taken as being statistically
distributed throughout the agglomerate, their average number N per
unit of fracture cross section is $(1-\epsilon)/A$, where A is the mean area
of an average particle. Utilizing the previous geometric relations,
this makes

$$N = 6(1-\epsilon)/(\pi d^2) \tag{2.1}$$

The average number of points of bonding per particle in the
fracture area j, is related to that portion of an average sphere in
the fracture zone, i.e.,

$$j = \left(\frac{\pi d^2/4}{\pi d^2}\right) j \tag{2.2}$$

where j is a coordination number describing the average number of
contact points between one sphere and its neighbors in the agglomerate.

Since, on the average, the directions of the bonds between
spheres are distributed uniformly throughout an agglomerate, their
projections perpendicular to the plane of fracture are just $\sin^2 60^{\circ}$
($= 3/4$) as great. The agglomerate tensile strength i is therefore

$$i = \frac{3}{4} N j_f b \tag{2.3}$$

where b is the binding force of a point contact. Substituting from Eqs.(2.1) and (2.2) then yields

$$i = \frac{9j}{8\pi} \left(\frac{1-\epsilon}{d^2}\right) b \tag{2.4}$$

The coordination number, obviously depends on porosity and the product of the coordination and porosity, i.e., on $j\epsilon$. The product is approximately equal to 3.1 or π, but not greater than 5.1

When the liquid content of an agglomerate is such as to make it conform to the pendular state, the binding force b is established largely by the interfacial tension of the liquid and the particle diameter but also a function of δ, the angle which the liquid surface makes with the particle surface, as shown on Fig. 2.10e. and with θ, the sector angle of the liquid ring. The result is expressed

$$b = adf (\delta, \theta) \tag{2.5}$$

The function $f(\delta, \theta)$ is between 2.8and 2.2 when the liquid completely wets the solid (i.e., $\delta = 0$) and when θ has values between 10 and 40°. Therefore, substituting Eq. (2.5) with Eq. (2.4) gives for the approximate tensile strength of a pendular state agglomerate

$$i_p = 2.78\left(\frac{1-\epsilon}{\epsilon}\right) \frac{\sigma}{d} \tag{2.6}$$

Contrary to the usual first expectations, an agglomerate is stronger when lesser amounts of pendular moisture are present. By Fig. 2.10. the radius r_1 on the diagram reduces faster than the radius r_2 and, therefore, produces a more rapid increase in the curvature of the liquid. This creates a very high-pressure deficiency within the binding liquid.

To describe capillary-state agglomerates, use may be made of the capillary potential or capillary pressure P_3 which is a measure of the tendency of granular masses to fill with water. It is expressed by

$$P_s = \frac{S_v(1-\epsilon)}{\epsilon} \cos\delta \qquad (2.7)$$

where S_v is the specific surface area. Since for uniform spheres S_v is equal to $6/d$,

$$P_s = \frac{6\delta}{d}\left(\frac{1-\epsilon}{\epsilon}\right)\cos\delta \qquad (2.8)$$

An applied tensile force has to overcome the interfacial tension of the liquid along the edge of the agglomerates as well as the internal pressure. This means that the tensile strength of a capillary-state agglomerate i_c is

$$i_c = P_s + \frac{C\sigma}{A} \cos\delta = \frac{6}{d}\left(\frac{1-\epsilon}{\epsilon}\right) + \frac{C\sigma}{A}\cos\delta \qquad (2.9)$$

where C is the agglomerate circumference and A is cross-sectional area. With sand, for example, that is completely wet by water the contant in Eq. (2.8) is about 8 instead of 6. On the basis of Eq. (2.6) and (2.8), a capillary-state agglomerate would be expected to be some two to three times stronger than a pendular one of the same material. The capillary forces operating within an agglomerate are not necessarily small; calculations show they can create the same effect as a compressive force of up to 200 psi.

Because the funicular state has bonds of both types, a funicular-state agglomerate should exhibit a tensile strength ranging between those of the pendular and capillary states.

2.6.3 High-Viscosity Liquid Binding

When the interstices of an agglomerate are filled, or partially filled, a highly viscous material such as asphalt, the strength of the agglomerate is enhanced, depending on the cohesional strength of the filling substance and the adhesion force with which it attaches

to the solids phase. In practice the adhesion between the binding
medium and the solid is almost always greater than the cohesive
strength of the binder, possibly due to particle-surface irregularities
and the physical interlocking of medium and solid. The lesser of the
two, the cohesive strength of the filler, thus establishes the
agglomerate's strength. The full or theoretical value seldom is
attained, however, due to flaws in the medium bridging between the
particles and to viscous and plastic flow within the medium which
precedes fracture

Some particle materials in humid atmospheres adsorb
sufficient moisture to promote cohesion among the grains. When the
adsorbed layer is very thin, as around a point of contact, it may
very well serve to transmit intermolecular forces from one particle to
another. This has led to an adsorbed film being classed as a high-
viscosity binder.

2.6.4 Intermolecular and Electrostatic Forces

The forces that bind molecules into discrete particles
project beyond the particle's surface and tend to hold particles in
contact also. For nonmetallic materials they are called van der Waals
forces. Metals are bound by forces that are not quite van der Waals
type and yet they are not pure chemical or valence forces. For
purposes here they will not be distinguished as a force apart but will
be considered in the general context of van der Waals forces. In
addition to chemical and van der Waals forces, electrostatic forces
develop as a result of electron deficiencies or excesses on particles.
These ionic charges result from chemical reactions at the surface
unequal chemical compositions, and the like. Charges of opposite
polarity, of course, result in particle attraction.

Agglomerates bound by van der Waals and/or electrostatic
forces are orders of magnitude weaker than those held by any of the
previously described binding mechanisms. The latter types of forces

really are significant only with quite small particles. Nevertheless, van der Waals forces are basic to many phenomena and their magnitude is now reasonably well known

2.7 Fluidization

Fluidization is the operation by which fine solids are transformed into a fluidlike state through contaction with a gas or liquid. This method of contacting has a number of unusual characteristics, and fluidization application is concerned with efforts to take advantage of this behavior and put it in good use.

2.7.1 The Phenomena of Fluidization

A fluidized bed is considered a layer of solid particles displayed in a vertical column, the bottom of which is closed by a porous plate (distributor) which supports the solids. If a rising fluid flow is established through the bed of particles, different phenomena may happen: —

1. For low fluid flows, the bed of particles remains fixed. This is a fixed bed.

2. With an increment of flow rate, particles move apart and a few are seen to vibrate and move about in restricted regions. This is the expanded bed.

3. At a still higher velocity, a point is reached when the particles are all just suspended in the upward-flowing gas or liquid. At this point the frictional force between a particle and fluid counterbalances the weight of the particle, the vertical component of the compressive force between adjacent particles disappears, and the pressure drop through any section of the bed about equals the weight of fluid and particles in that section. The bed is considered to be just fluidized and is referred to as an incipiently fluidized bed or a bed at minimum fluidization.

4. For an increment of flow rate above minimum fluidization, both gas and liquid fluidized beds are considered to be

dense phase fluidized beds. However, at a sufficiently high fluid flow rate the terminal velocity of the solids is reached, the upper surface of the bed disappears. It is the phenomena of pneumatic or hydraulic transport at the higher fluid flow rate.

2.7.2 Minimum Fluidization

The onset of fluidization occurs when

$$\left\{\begin{array}{c}\text{Drag force by}\\\text{upward moving gas}\end{array}\right\} = \left\{\begin{array}{c}\text{Weight of}\\\text{particles}\end{array}\right\} \qquad 2.10(a)$$

or

$$\left[\begin{array}{c}\text{Pressure drop}\\\text{across bed}\end{array}\right] \cdot \left[\begin{array}{c}\text{Cross-sectional}\\\text{area of tube}\end{array}\right] = \left[\begin{array}{c}\text{Volume}\\\text{of bed}\end{array}\right] \left[\begin{array}{c}\text{Fraction}\\\text{of}\\\text{solids}\end{array}\right] \cdot \left[\begin{array}{c}\text{Specific}\\\text{weight}\\\text{of solids}\end{array}\right]$$

$$2.10(b)$$

or

$$\Delta p \cdot A_t = W = (A_t L_{mf}) \left[(\rho_s - \rho_g)\ \frac{g}{g_c}\right] \qquad 2.10(c)$$

by rearranging, we find for minimum fluidizing conditions that,

$$\frac{\Delta p}{L_{mf}} = (1 - \epsilon_{mf})(\rho_s - \rho_g)\frac{g}{g_c} \qquad 2.11$$

In a bed at onset of fluidization the voidage is a little larger than in a packed bed, and it actually corresponds to the loosest state of a packed bed of hardly any weight. Thus we may estimate U_{mf} from random packing data, or, better still, it should be

measured experimentally, since this is a relatively simple matter. U_{mf}, the superficial velocity at minimum fluidizing conditions, is found related as

$$\frac{1.75}{\phi_s \epsilon_{mf}^3}\left(\frac{d_p U_{mf}\rho_g}{\mu}\right)^2 + \frac{150(1-\epsilon_{mf})}{\phi_s^2 \epsilon_{mf}^3}\left(\frac{d_p U_{mf}\rho_g}{\mu}\right) = \frac{d_p^2 \rho_g(\rho_s-\rho_g)g}{2} \qquad 2.12$$

If U_{mf} and/or ϕ_s are unknown, the following modification of these expressions, suggested by Wen and Yu can be used. First it was found for a wide variety of systems that

$$\frac{1}{\phi_s \epsilon_{mf}^3} \cong 14 \quad \text{and} \quad \frac{1-\epsilon_{mf}}{\phi_s^2 \epsilon_{mf}^3} \cong 11 \qquad 2.13$$

and for small particles

$$U_{mf} = \frac{d_p^2(\rho_s-\rho_g)g}{1650\mu} \qquad Re_p < 20 \qquad 2.14$$

and for large particles

$$U_{mf}^2 = \frac{d_p(\rho_s-\rho_g)g}{24.5\rho_g} \qquad Re_p > 1000 \qquad 2.15$$

These simplified expressions, Eqs.2.14 and 2.15, give U_{mf} in terms of the usually specified variable of densities, particle size, and gas viscosity; and for 284 data points in a Reynolds number range of 0.001 to 4000 the expressions have been found to give predictions of U_{mf} with a standard deviation of 34%.

2.7.3 Pressure Drop in Fluidized Beds.

For the relatively low flow rates in a packed bed the pressure drop is approximately proportional to gas velocity usually reaching a maximum value Δp_{max} slightly higher than the static pressure of the bed. With a further increase in gas velocity, the packed bed suddenly "unlocks"; in other words, the voidage increases from ϵ_m to ϵ_{mf}, resulting in a decrease in pressure drop to the static pressure of the bed, as given by Eq. 2.10 With gas bubbles are seen to rise with resulting nonhomogeneity in the bed. Despite

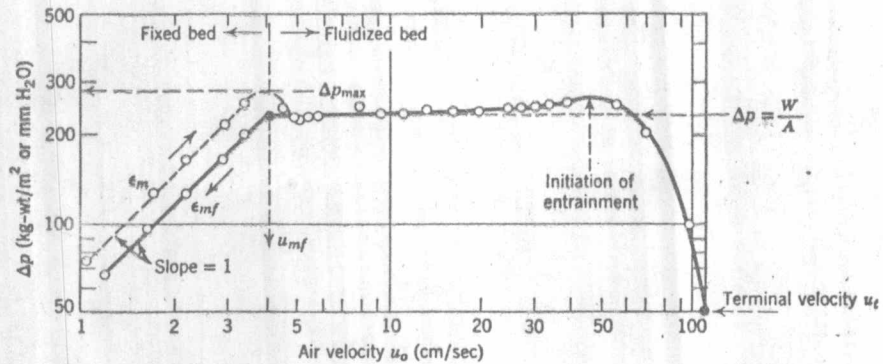this rise in gas flow, the pressure drop remains practically unchanged.

FIG. 2.11 PRESSURE DROP VERSUS GAS VELOCITY FOR A BED OF
UNIFORMLY SIZED SAND PARTICLES.

The constancy in pressure drop in thetwo situations, the bubbling
liquid and the bubbling fluidized bed, may be taken intuitively to be
analogous.

A pressure drop versus velocity diagram is useful as a rough
indication of the quality of fluidization, especially when visual
observation is not possible. Thus a well fluidized bed will behave as in
Fig. 2.11. Note here that observed pressure drop data may deviate slightly
from the calculated value of Eq. 2.11. This can be attributed to the energy
loss by collision and friction among particles as well as between particles
and the surface of container.

2.7.4 Terminal Velocity of Particles.

The gas flow rate through a fluidized bed is limited on one
hand by U_{mf} and on the other by entrainment of solids by the gas. When
entrainment occurs these solids must be recycled or replaced by fresh
material to maintain steady-state operations. This upper limit to gas flow
rate is approximated by the terminal or free-fall velocity of the particles,
which can be estimated from fluid mechanics by

I15A87A65.

$$U_t = \left[\frac{4gd_p(\rho_s - \rho_g)}{3\rho_g C_d} \right]^{1/2} \qquad (2.16)$$

where C_d is an experimentally determined drag coefficient.

For both spherical and nonspherical particles the terminal velocity U_t can be obtained from Fig.2.12 an experimental correlation of the dimensionless groups $C_d \, Re_p^2$ versus Re_p, where

$$Re_p = \frac{d_p \rho_g U_t}{\mu} \qquad (2.17)$$

and the velocity independent group

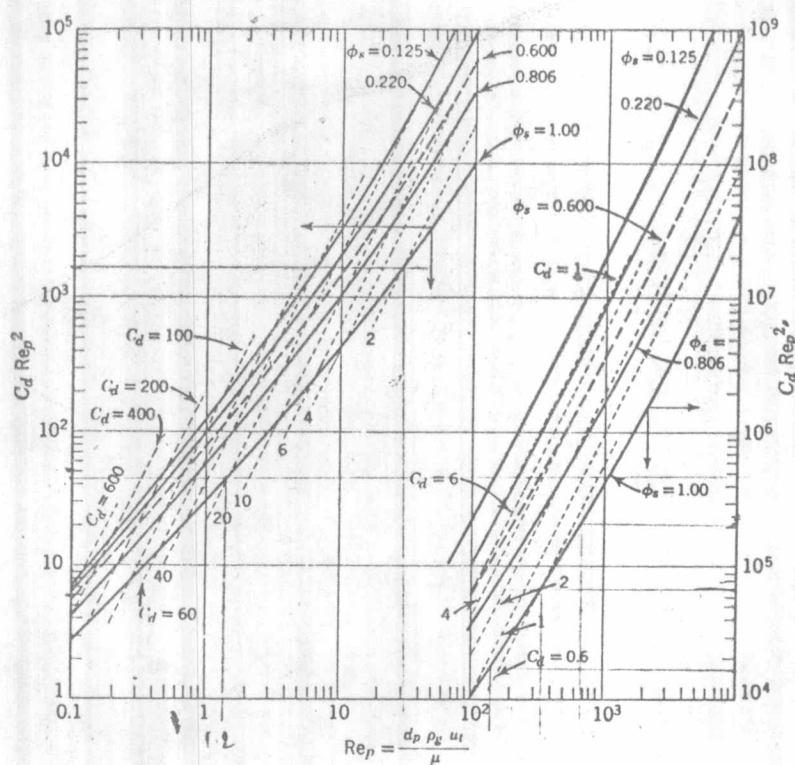FIG. 2.12. CHART FOR CALCULATING THE TERMINAL VELOCITY OF PARTICLES FALLING THROUGH FLUIDS

$$C_d Re_p^2 = \frac{4gd_p^3 \, \rho_g(\rho_s - \rho_g)}{3 \cdot 2}$$

To determine u_t first find $C_d \, Re_p^2$ from the known values of d_p, ρ_g, ρ_s and μ then in Fig. 2.12 look up the corresponding value of Re_p, From which u_t is calculated using Eq. 2.17

2.7.5 Mode of Fluidization.

Two main types of fluidization have been noted experimentally. In cases where the fluid and solid densities are not too different, where the particles are small, and therefore where the velocity of flow is low, the bed fluidizes evenly with each particle moving individually through a relatively uniform mean free path. The solid phase has many of the characteristics of a gas. This is called particulate fluidization. Where the fluid and solid densities are greatly different or the particles are large, the velocity of flow must be relatively high. In this case, fluidization is uneven, and the fluid passes through the bed mainly in large bubbles. These bubbles burst at the surface spraying solid particles above the bed. Here, the bed has many of the characteristics of a liquid with the fluid phase acting as a gas bubbling through it. This is called aggregative fluidization. It appears that particulate fluidization occurs when the Froude number ($Fr_{mf} = \frac{Umf^2}{d \, g}$) at the point of fluidization is less than one, whereas aggregative fluidization occurs when the Froude number at the point of fluidization is greater than one.

2.8 Polystyrene

The term polystyrene (3.) is applied to materials in which 95% or more of polymeric mass is derived from styrene monomer. The polymer itself can be made by polymerizing the monomer in solution or as emulsion. A suspension technique is sometimes employed industrially but most polystyrene is made by polymerization in bulk. The product is a linear,largely amorphous polymer and has outstanding optical properties, high refractive index. However two properties tend to limit the range of application of the material,they are its high brittleness and its relatively low heat-distortion temperature ($82-88^{\circ}c$). In addition polystyrene is not stable to outdoor weathering and it is readily attacked by many solvents including those used in dry-cleaning. Certain organic materials such as essential oils, unsaturated hydrocarbons and petroleum can cause crazing in polystyrene and other organic solvents, notably aromatic hydrocarbons chlorinated hydrocarbons, ketones and esters swell or dissolve polystyrene. Other properties vary with grade, and can best be considered in relation to individual grades.

Polystyrene materials can be divided into three categories

a) General purpose materials. These are rigid materials having comparatively low shock resistance, excellent electrical properties, susceptible to stress and solvent crazing.

b) Specialist materials such as heat resistant or low static are very smimilar to (a)

c) Expanded polystyrene has very low density, very low thermal conductivity enabling its use ih buoyancy, packing and thermal insulation applications and this is the material to be used in this experiment.

The major physical properties of expanded polystyrene and the way that these vary with density are given in Table2.5

Table 2.4 Properties of Expanded Polystyrene

Density (lb/ft^3)	1	2	4	6 .	8	10
Thermal conductivity ($Btu/in/h/ft^2/deg.F$)	0.24	0.24	0.25	0.25	0.27	0.30
Compressive strength (lbf/in^2)	10	25	60	100	140	180
Flexural strength (lbf/in^2)	20	45	120	190	250	340

For chemical structure, we can see the formation of polystyrene from styrene as

$$n \underset{}{\overset{CH=CH_2}{\bigcirc}} \longrightarrow \left[\overset{CH-CH_2}{\bigcirc} \right]_n$$
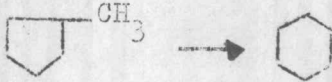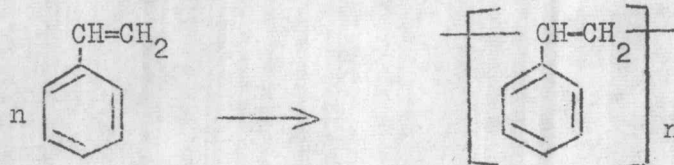
2.9 Gasoline

Gasoline in the commercial line can be divided into two grades, the low and high octane gasoline. Their physical properties are shown in table2.6. For the chemical properties, it is revealed that there is no certain composition of solvents or chemical substances in blending gasoline. It depends on the processing line in the petroleum plant to adjust any fraction in the distillation tower for gasoline blending to meet the physical psoperties as shown before. However, three major chemicals are combined together to produce gasoline, they are reformate, naphtha and a certain limit of C_4 to C_6

Table 2.5 Physical Properties of Gasoline (Esso Standard THailand)

Physical Property	Low Octane	High Octane
GRAVITY, SPECIFIC @ $60^{\circ}F$	0.697	0.738
APPEARANCE	CLEAR & BRIGHT	CLEAR & BRIGHT
COLOUR	ORANGE	RED
DOCTOR TEST	NEGATIVE	NEGATIVE
GUM, mg./100 ml.	1.0	1.0
OCTANE NUMBER, RESEARCH METHOD	84.4	95.5
SULFUR, WT. %	0.03	0.03
LEAD CONTENT, g.Pb/USG	1.6	2.0

Table 2.6 Major Powerforming Reactions

Type of Reactions		Chemical Change
DEHYDROGENATION		$\bigcirc \longrightarrow \bigcirc + 3H_2$
ISOMERIZATION		
—NAPHTHENE		
—PARAFFIN	$CH_3\!-\!CH_2\!-\!CH_2\!-\!CH_2\!-\!CH_2\!-\!CH_3 \longrightarrow CH_3\!-\!CH\!-\!CH\!-\!CH_3$ with CH_3 branches	
DEHYDROCYCLICIZATION		$CH_3\!-\!CH_2\!-\!CH_2\!-\!CH_2\!-\!CH_2\!-\!CH_3 \longrightarrow \bigcirc + H_2$
HYDROCRACKING		$CH_3\!-\!CH_2\!-\!CH_2\!-\!CH_2\!-\!CH_2\!-\!CH_3 \longrightarrow n\,(CH_3\!-\!CH_2\!-\!CH_3)$

Reformate is the end products of chemical fractions in the distillation tower which are adjusted their octane number higher in the powerformer. The important reactions occured are shown in Table 2.7

As an additional information, by the Polish investigation(27) of the gasoline fraction at the B.P. 117-123°c, twentythree individual hydrocarbons were detected : 60% cycloparaffins, 20% isooctanes and 20% n-octane. The presence of 1,1-dimethylcyclohexane was also confirmed. Besides that, the greatest amount of 6 membered naphthenes were found in the 95-122°c fraction (23). Its highest amount (15%) were found in the gasoline from crude oils with small S and tars content but from the crude oils with high S and tars content, the amount was smaller (7%)

Generally in order to improve the gasoline efficiency. Tetraethyl lead is presented about 0.15% as an antiknock(22) which is associated with the other substances in a combination of tetraethyl lead, Ethylenedibromide, Ethylenechloride by the ratio of Pb: Br_2:Cl_2 = 1: 0.39: 0.34 by weight or it can be said that there is 2-3 gm lead in 1 gallon of gasoline

Gasoline used in this experiment will be the high octane gasoline which possessesmore aromatic compounds and of course dissolves the PFD faster because polystyrene is very sensitive to aromatic hydrocarbons as described in 2.8