

RHEOLOGY (PART 1)

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- ❖ Definition and fundamentals.
- ❖ Newtonian and Non-Newtonian Flows.
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Definition of Rheology

- Rheology is the science/physics that concerns with the flow of liquids and the deformation of solids.
- Study of flow properties of liquids is important for pharmacist working in the manufacture of several dosage forms, viz., simple liquids, gels, ointments, creams, and pastes.
- These systems change their flow behavior when exposed to different stress conditions.

Fundamentals of Rheology

- i. Manufacturing of dosage forms: Materials undergo process such as mixing, flowing through pipes, filling into the containers etc. Flow related changes influence the selection of mixing equipment.
- ii. Handling of drugs for administration: The syringibility of the medicines, the pouring of the liquids from containers, extrusion of ointment from tubes, all depend on the changes in flow behavior of dosage forms.

Newtonian Flow

• Newton was the first to study the flow properties of liquids in quantitative terms. Liquids that obey Newton's law of flow are called as Newtonian fluids. rate of shear(G) \propto shearing stress(F)

$$\tau = \eta G$$

Where

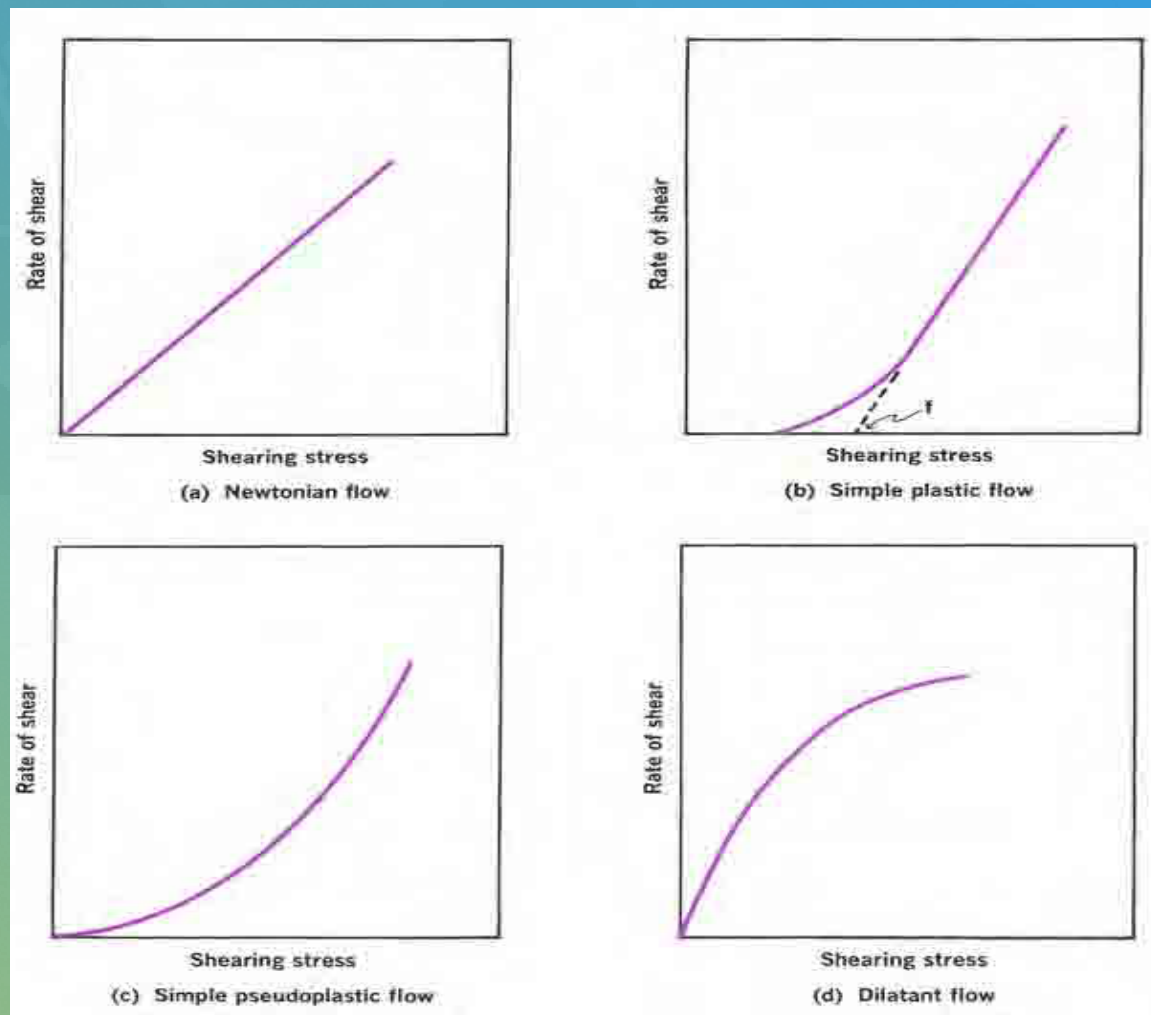
$$F = F' / A$$

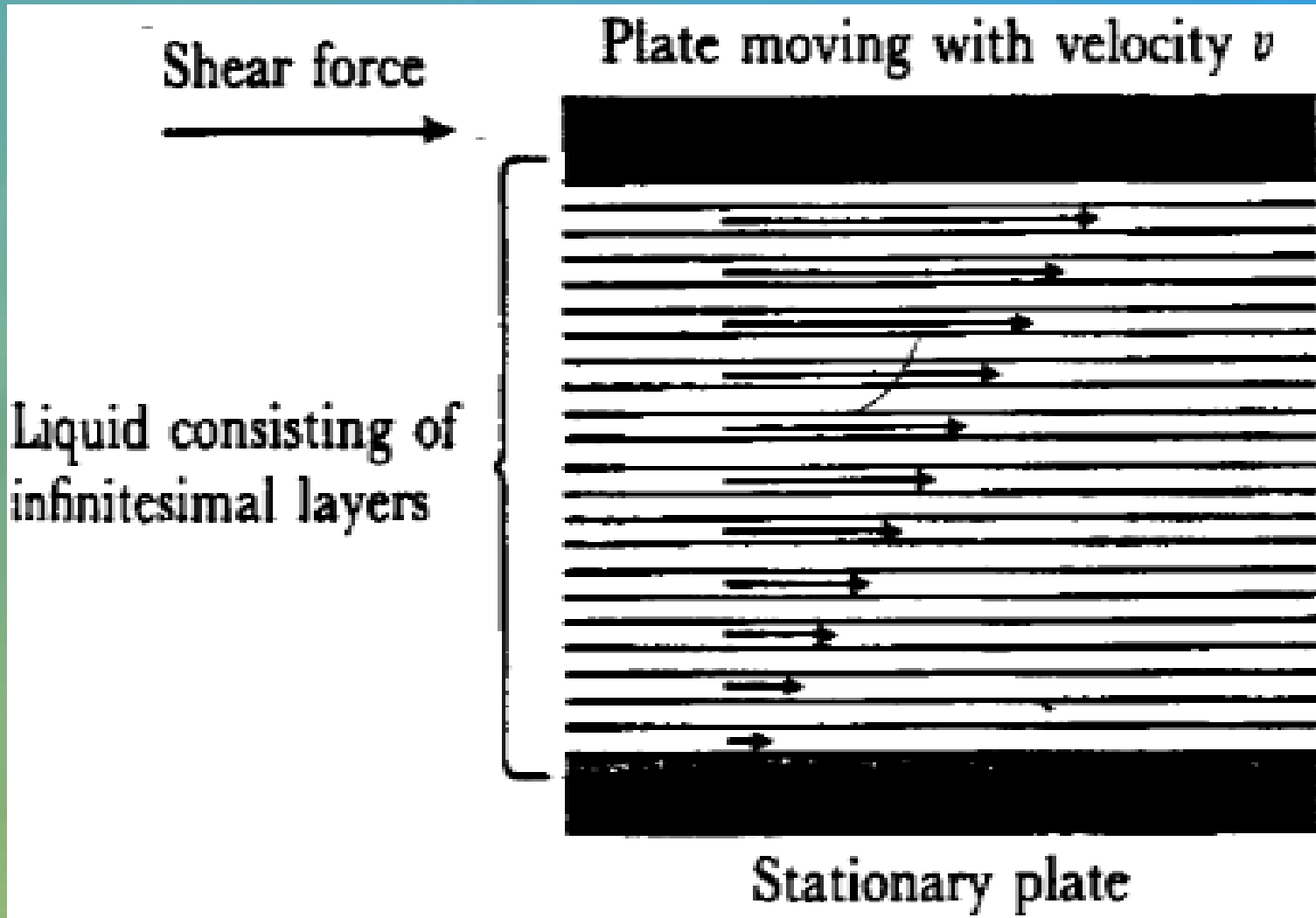
$$G = dv / dr$$

η = viscosity

Examples :

- ☒ Water,
- ☒ chloroform,
- ☒ Castor oil,
- ☒ ethyl Alcohol etc





NON NEWTONIAN FLOW

- A non Newtonian flow is defined as one for which the relation between F and S is not linear.
- In other words when the shear rate is varied, the shear stress is not varied in the same proportion. The viscosity of such a system thus varies as the shearing stress varies.
- It can be seen in liquids and in solid heterogeneous dispersions such as emulsions, suspensions, colloids and ointments.

NON NEWTONIAN SYSTEMS

Three classes:

☒ *PLASTIC FLOW*

☒ *PSEUDOPLASTIC FLOW*

☒ *DILATENT FLOW*

PLASTIC FLOW:

- In which curve does not pass through the origin, the substance behaves initially
- Elastic body and it fails to flow when less amount of stress is applied.
- As increase the stress, leads to non-linear increase in shear rate but after that curve is linear.
- The linear portion extrapolated intersects the x axis at the point called as yield value

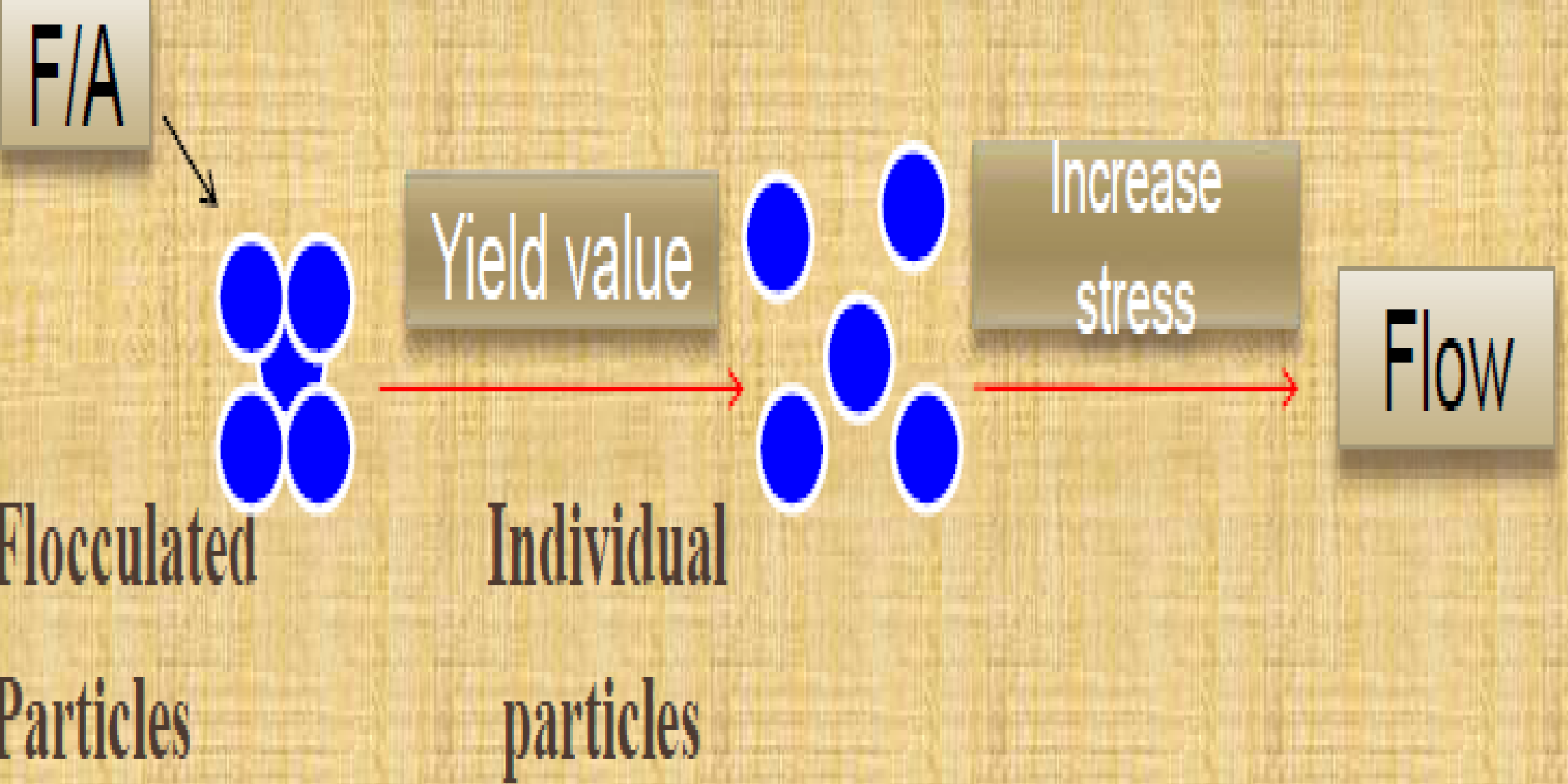
So, plastic flow shows Newtonian flow above the yield value.

The curve represents plastic flow, such materials are called as Bingham bodies.

- Bingham bodies does not flow until the shearing stress is corresponding to yield Value exceeded.
- So, yield value is important property of certain dispersions.
- The reciprocal of mobility is Plastic viscosity

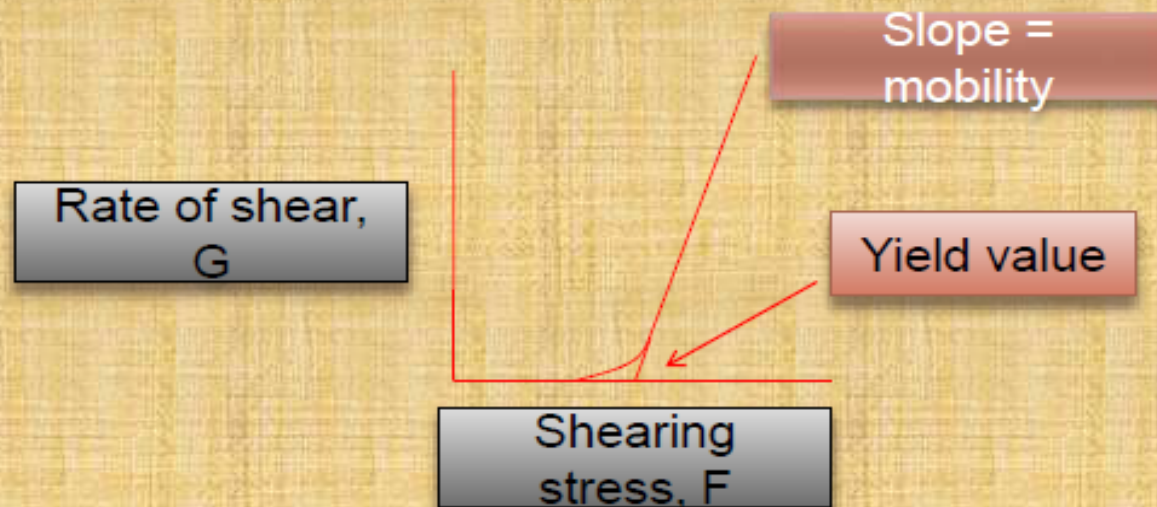
☒EXAMPLES: ZnO in mineral oil, certain pastes , paints and ointments.

Plastic flow explained by flocculated particles in concentrated suspensions, ointments, pastes and gels



PLASTIC FLOW

The curve for the plastic flow is as follows.



The equation describing plastic flow is,

$$\mathbf{U} = \mathbf{F} - \mathbf{f} / \mathbf{G}$$

Where,

f = Yield value

F = Shearing stress

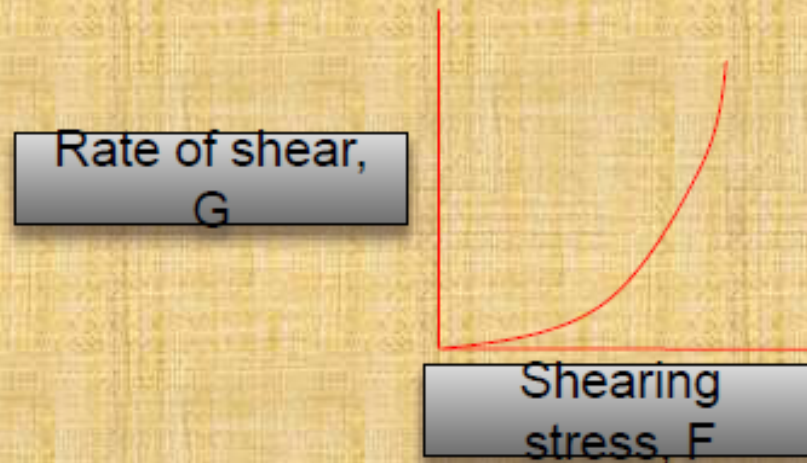
G = Rate of shear

PSEUDO PLASTIC FLOW

Many Pharmaceutical products liquid dispersion of natural and synthetic gums shows pseudo plastic flow.

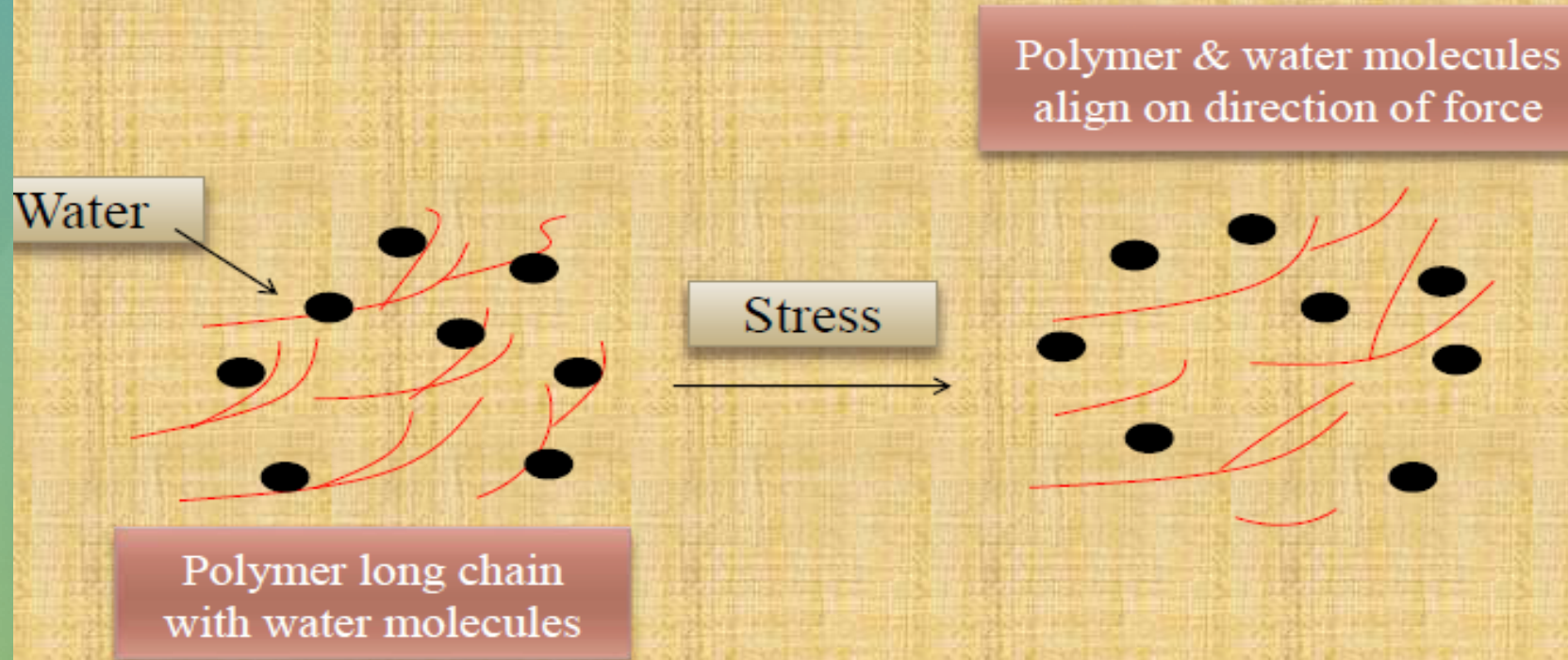
- eg. 1. Tragacanth in water
- 2. Sod. Alginate in water
- 3. Methyl cellulose in water
- 4. Sodium CMC in water

Graph for pseudo plastic flow is like this



- In which curve is passing from origin (Zero shear stress), so no yield value is Obtained.
- As shear stress increases, shear rate increases but not linear.

Pseudo plastic flow can be explained by **Long chain molecules of polymer.**



In storage condition, arrange randomly in dispersion.

The exponential equation shows this flow

$$F^N = \eta G$$

N = no. of given exponent

η = Viscosity coefficient

➤ In case of pseudo plastic flow, $N > 1$.

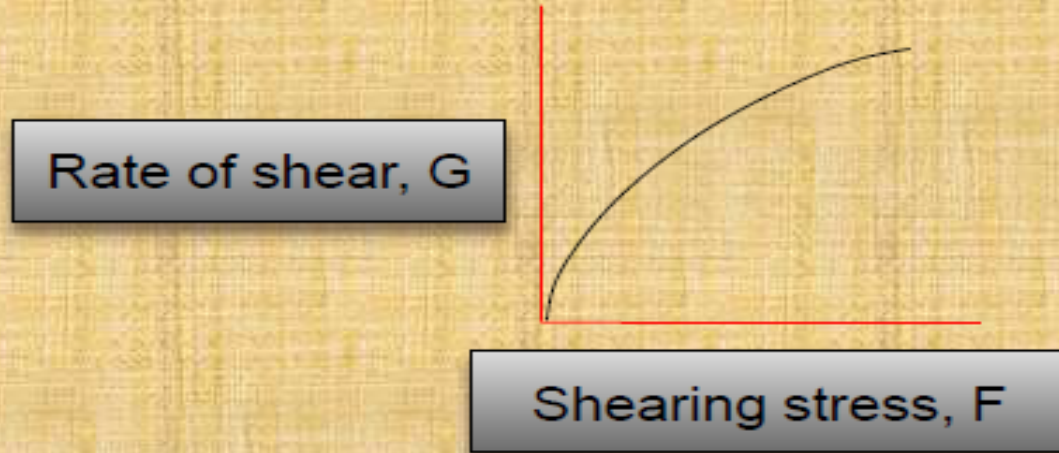
i.e. More $N > 1$, the greater pseudo plastic flow of material.

➤ If $N = 1$, the flow is Newtonian.

DILATANT FLOW

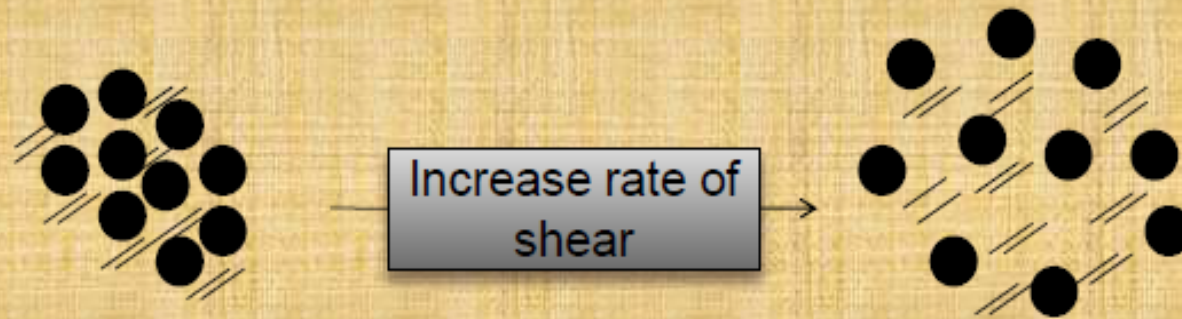
- * Certain suspensions with high % of dispersed solids shows an increase in resistance to flow with increasing rates of shear, such system increase in volume when sheared, such system called as dilatant flow.
- * Also, called as “ **Shear thickening system**” i.e. when stress is removed, dilatant system return to its original position

Graph for dilatant flow is like this



- ❖ In which curve is passing from origin (Zero shear stress), so no yield value is Obtained.
- ❖ Non-linear increase in rate of shear.
- ❖ Increase resistance to flow on increase rate of shear

- In which, particles are closely packed with less voids spaces, also amount of vehicle is sufficient to fill the void volume.



At rest close packed Less
void volume Sufficient
vehicle Low consistency

Open packed High void
volume Insufficient
vehicle High
consistency

This leads particles to move relative to one another at low rate of shear.

- So therefore, dilatant suspension can be poured from bottle because in these condition it is fluid.
- When stress is increased, the particles shows the open packing and bulk of system (void volume is increase) is increased.
- But the amount of vehicle is insufficient to fill this void space.
- Thus particles are not wetted or lubricated and develop resistance to flow.
- Finally system show the paste like consistency.

- Because of this type of behavior, the dilatant suspension can be process by high speed mixers, blenders or mills.

The exponential equation shows this flow

$$F^N = \eta G$$

N = no. of given exponent

η = Viscosity coefficient

In which $N < 1$, and decrease as the dilatancy increase.

If $N = 1$, the system is Newtonian flow

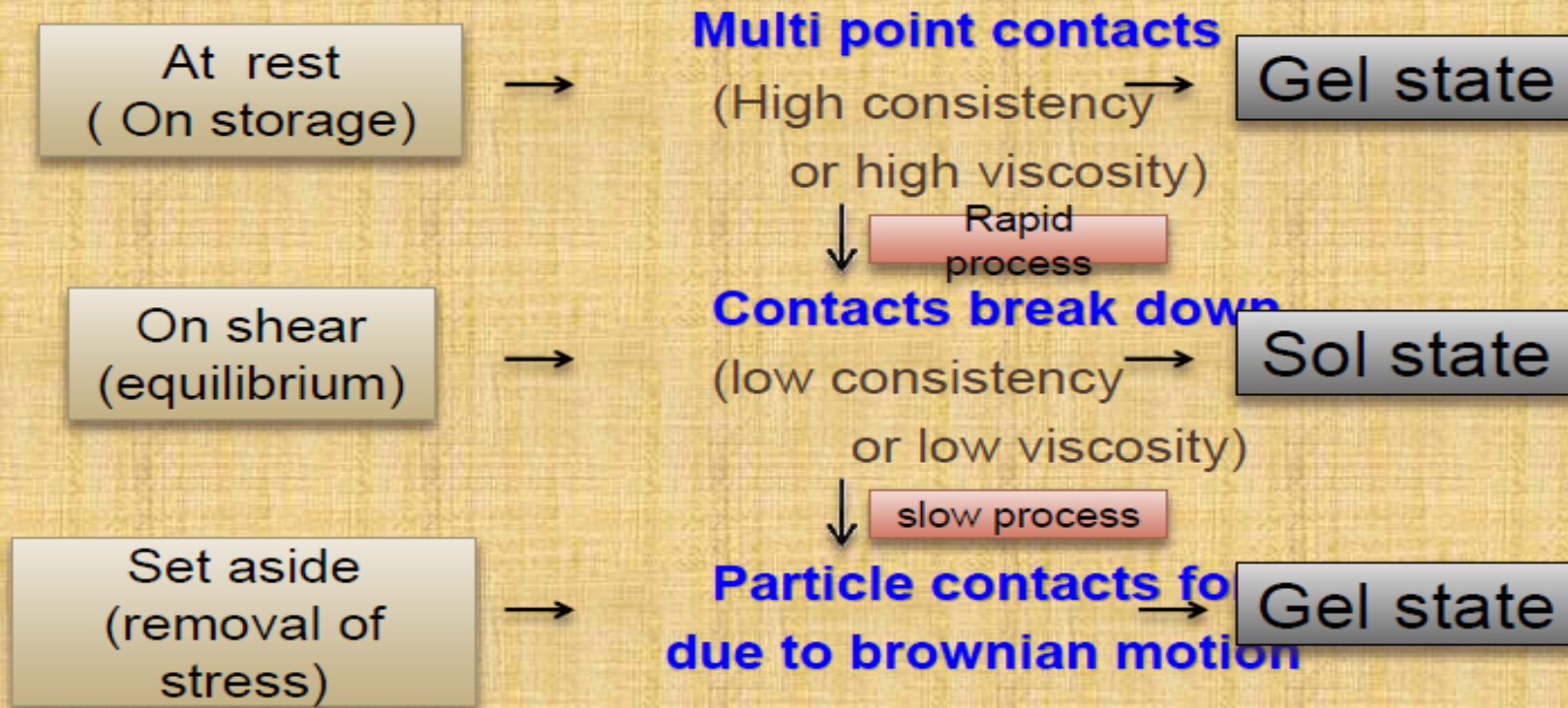
THIXOTROPY (GEL-SOL-GEL)

It is defined as, isothermal and comparatively slow recovery on standing of material of a consistency lost through shearing.

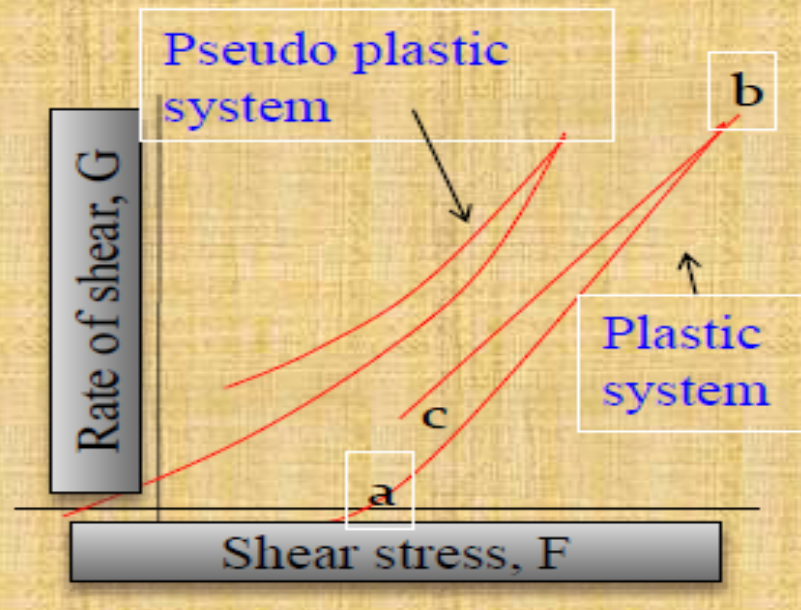
It is shear thinning system, when agitated and kept aside it is expected to return its original state of fluidity, but takes longer time to recover compared to the time taken for agitation.

Thixotropic behavior can be shown by plastic and pseudo plastic system.

THIXOTROPY CONCEPT (PARTICLE – PARTICLE INTERACTIONS) (GEL – SOL – GEL TRANSFORMATION)



The thixotropy phenomena can be observed by constructing consistency curves.



- From the graph up curve ab is obtained, up to maximum point b.
- If the rate of shear is reduced, then down curve bc is obtained.
- In **Non-Newtonian system**, the **down curve** is displaced to **left of the up curve**.
- In this graph, the material has **low consistency** at any rate of shear on **down curve** compared to that shown on **up curve**.
- Ily, **thixotropic curves** constructed for **pseudo plastic system** .
- In **Newtonian system**, down curve superimposed to up curve.

ANTI-THIXOTROPY (-VE THIXOTROPY)

Anti-thixotropy represents an **increase in consistency (high viscosity)** rather than a decrease in consistency in the **down curve**.

The **increase in thickness or resistance to flow with increase time of shear** is observed for (magnesia magma).

Anti – thixotropy is **flocculated system** containing **low solid content (1 – 10 %)**.

Dilatancy system is **deflocculated system** containing **solid content ($> 50\%$)**.