Surfactant
for Pesticide Formulation.

Supplement Edition : Wet Grinding Process.

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1. Grinding in Pesticide Industry.

Grinding Process in Pesticide formulation is mainly classified into 2 ways, one is Dry, the other is Wet Grinding Process. Here we mainly discuss about Wet Grinding Process which applied for SC and OD mainly. Grinding efficacy depend on a kind of Grinding facility partly but it will not be a subject here, because so called sand grinder is actually only one facility for SC and OD now.

2. Wet Grinding Process.

2-1. General Wet Grinding Process.

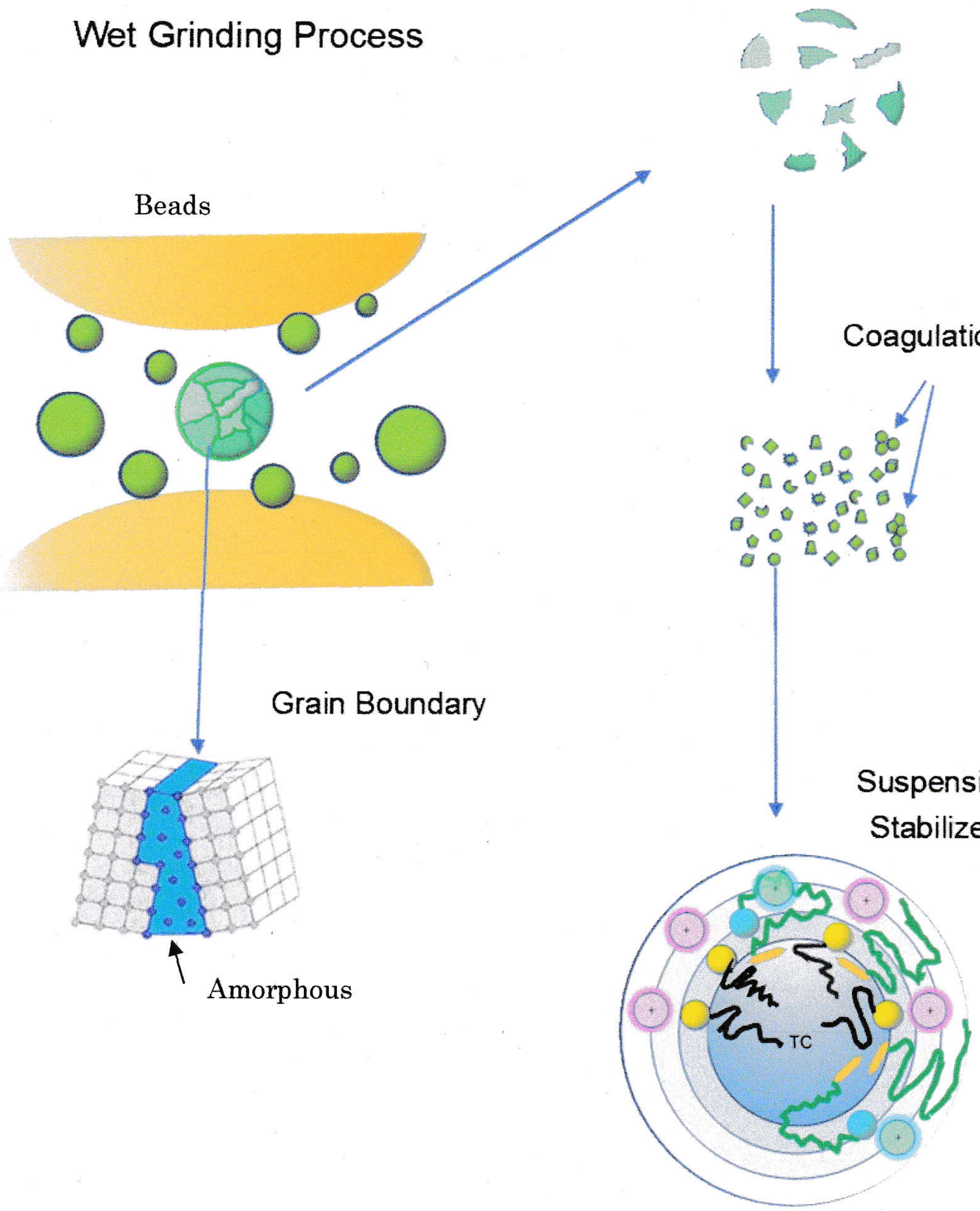
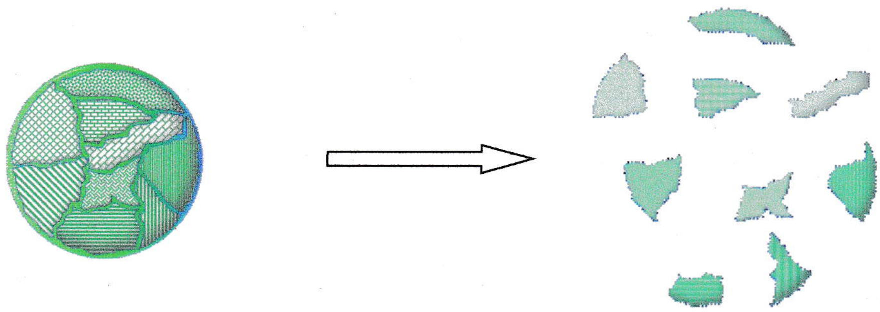


Fig.-1, General Wet Grinding Process.

2-2. Property of Solid Particle (Pesticide Technical, TC,).

Usually TC is Polycrystal solid which composed with monocrystals, and there are Grain boundary between each monocrystal (Fig.-1, Fig.-2). The strength of Bond Energy of Crystal will depend on a kind of TC but generally it is too strong enough to cut bonding. Also Grain boundary of Polycrystal, it is a kind of Amorphous state so Polycrystal will be ground along with grain boundary in a initial state of grinding.



Polycrystal (TC) Monocrystals

Fig.-2 Initial Grinding situation.

Physically, actual TC particle is not surface smooth sphere but it is very rough surface irregular form, and often has many small hole. These Physical properties of TC highly related to grinding process also.

Not only Physical property but Chemical property is very important character. Simply said, TC is Organic chemical which composed with different functional chemical group, and generally its water solubility is low. And, it is not easy for us to grasp all chemical property of TC, but log P is one of important indicator to understand chemical property of TC. Especially F (Fluorine) atom containing TC shows rather strong water repellent property, so such TC will not wetting easily in water media. These chemical properties also highly related to grinding process.

2-3. Further grinding Process.

Each monocrystal will be ground continuously, and its particle size became small and small. At the same time specific surface area increase along with ground small particles. Because of specific surface area increase, system energy become very high, it means unstable system, then Coagulation of particles, absorption to the beads will be found to decrease system energy.

Surface energy increase simply depend on surface area increase. Simply calculation showed in Table-1, but actual surface area and Number of particles difference before/latter grinding will be bigger than simple calculation because of rough surface and small hole in a surface.

Table-1. Simply calculation of Surface area and Number of particles.

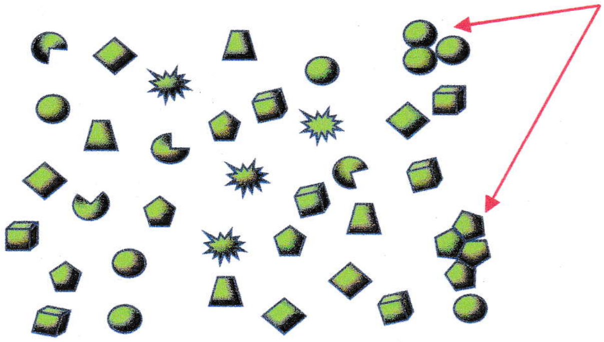
- Surface Area of Sphere : $4\pi \times r^2$
- Volume of Sphere : $(4\pi/3) \times r^3$

Example, radius 100μ → 1μ (Volume no change under same sg)

Surface Area Change : $(4\pi \times 100^2)/(4\pi \times 1^2) = 40{,}000/4 = 10{,}000$

Number of Particles : $((4\pi/3) \times 100^3)/((4\pi/3) \times 1^3) = 100^3$

Because of Coagulation, particle Adsorption on a vessel etc, particle size will not become small continuously than specific particle size. Usually it will be 3μm in case Dry grinding process but it will be smaller in Wet grinding process, because solvent such as Water will stabilize unstable situation also.



Some Coagulation, Absorption will be found in a latter part of Grinding.

Fig.-3, Latter grinding situation.

2-4. Surfactant to stabilize high energy system.

The huge high energy system, it is unstable energy system, will be stabilized by some way, but use Surfactant is one of most effective way.

Newly created surface area which has high energy, will be stabilized easily by adsorption of surfactant molecule. Coagulation of particles will be avoid by surfactant adsorption, also surfactant will help as grinding agent, and finally Dispersion System (Suspension) will be stabilized and became stable suspension.

Anionic surfactant will form Electric Double Layer and make particle dispersed stable in a system by Static Electric Repulsion, also Nonionic surfactant make particle disperse stable by Steric Hindrance Effect.

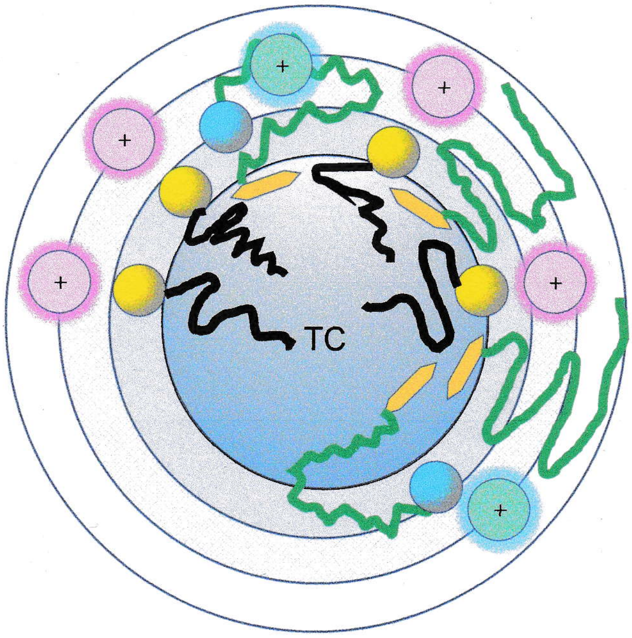


Fig-4. Illustrative image of Surfactant adsorption on TC.

Surfactant adsorption highly depend on TC property and kind of surfactant. Usually Hydrophobic part of surfactant which used for SC, it is composed with poly aryl group, and/or long chain alkyl group which has strong organic property. And rough surface, newly created surface which has rather high energy, surfactant will be absorbed on TC easily.

2-5. Other Factors for Grinding Process.

Usually solid TC is Polycrystal which composed with Monocrystal (Crystal). Many crystal has one crystal structure but some has different structure (Polymorphism) also. And, even the TC has only one crystal structure, it contains Amorphous part, and/or Lattice defects of crystal (Fig.-1, Fig.-2).

During grinding process of TC, Crystal structure might be changed some time, and it will make Grinding fairly difficult because of unfavorable polymer like behavior.
This kind of phenomena is one of most difficult technical problem in grinding process, and there are many reasons for such phenomena, but Crystal Structure Change might be one of important reason (Amorphization in following Figure) for difficult grinding.

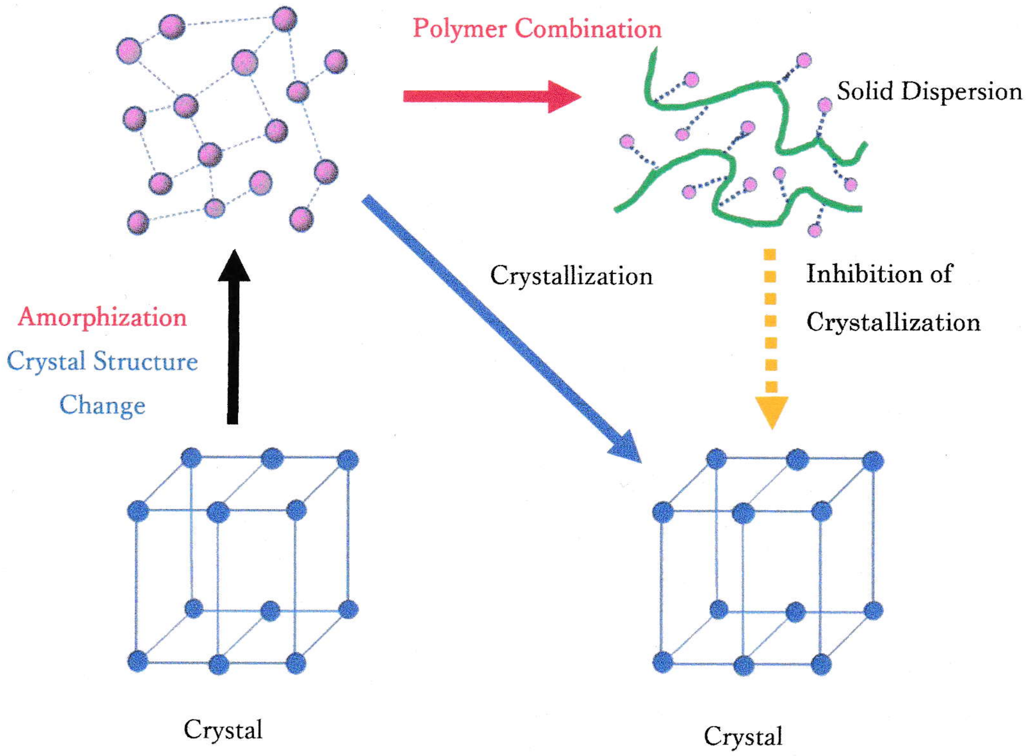


Fig-5. Crystal Structure Change.

These Polymer like behavior, Structure change, will be caused by mechanical, chemical, and other reasons as follows.

1. Mechanical reason : Grinding speed, Beads, Vessel shape ....
2. Chemical / Physical reasons :
   a) Melting Point of TC (Lowering MP, Liquid crystal, easy Amorphization)
   b) TC Solubility in Water, Organic solvent (easy Amorphization, pH)
   c) TC Chemical property (Surfactant absorption, Lowering MP, Liquid property, pH)
   d) Temperature increase (Frictional heating generated)
   e) Affinity between Surfactant / TC (stable Dispersion, easy Amorphization)
   f) Absorption property of Surfactant (stable Dispersion, easy Amorphization)
   g) Affinity between TC / Thickener (stable Dispersion, Polymer like property)
   h) Affinity between Surfactant / Thickener (stable Dispersion, Polymer like property)
   i) Others

Many times, Surfactant, Polymer will disperse the TC stably, but some time such additives will be a reason for polymer like undesirable phenomena. So, we should consider above reason carefully, and need take action to avoid crystal structure change.

2-6. Other Factors Stabilizing / Unstabilizing Dispersion System (Suspension)

2-6-1. Stokes's Law

- $\mathcal{V}_S = D_p^2 (\rho_p - \rho_f) \cdot g \times (1/18\eta)$

  $\mathcal{V}_S$: Terminal velocity

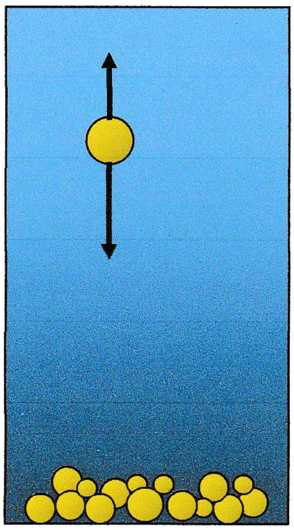
  D_p : Particle diameter

  ρ_p : Particle density ρ_p

  ρ_f : Media density ρ_f

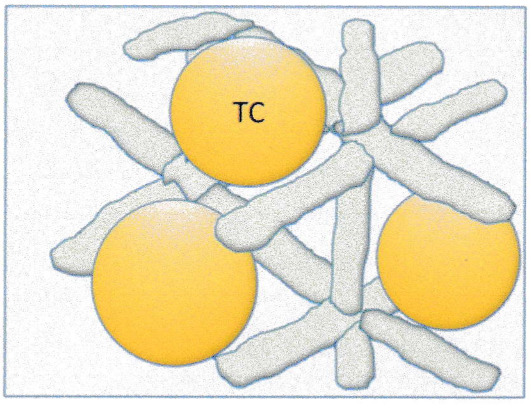
  g : Acceleration of gravity g

  η : Viscosity of media



2-6-2. Thickener

- Suspending by Structuring
- Viscosity Increase of Water



2-6-3. Coagulation and Particle size growth (Crystal growth)

- Creaming, Flocculation, Coalescence (Van der Waals attraction)
- Ostwald Ripening