Surfactant for Pesticide Formulation.

Supplement Edition,

Dancing Granule, DG, DJG

Japan Agro-Formulation Consulting Co.,Ltd. (J.A.C.)
SK. AgroThink (Shanghai) Corp.,

Shin-Ichi ITOH.

Design of Dancing Granule.

1. Required Physical-Chemical property of DG and its Ingredients.

1-1. What is DG Formulation.

In this report, Dancing Granule will be abbreviated as DG, and it means widely spreading water floating granule which will be applied as water surface application, accompanied with Brownian movement action which dispersed in random direction on water surface under repeating Dispersion / Disintegration.

Regarding appearance of DG, it might be almost same as normal granule, but big size diameter such as 5 to 7 mm, it will be abbreviated DJG in case.

1-2. General Composition of DG.

DG will be composed with following ingredients generally.

Table-1.

Ingredient	Dosage	Comment
Pesticide TC	~30%	Specific gravity, Liquid TC
Carrier Floating agent	~20%	Micro Glass balloon
Other Water soluble	rest	
Water insoluble		White Carbon (WC)
Water surface Spreader	~15%	
Dispersant etc	~ 5%	Anionic Surfactant
Others	Appropriate	Stabilizer, Binder etc

1-2-1. Pesticide, TC

In case DG, mainly TC will be Herbicide, but Fungicide, Insecticide etc will be applied for DG also, there might be no any special limitation. But, actually there are some difficulty for the TC which has big density, liquid TC. Because it might be difficult to keep floating property in case big density TC, might be difficult to keep granule appearance in case liquid TC.

Considering Physical Chemical property of TC, such stabilizer for TC must be studied but Water Solubility, Log P will not affect to Physical Chemical property of DG. In case TC which has low melting point, we need to pay attention because it will affect to Physical Chemical property, production process of DG.

1-2-2. Filler and Carrier for DG.

Filler and/or Carrier is one of most important ingredient of DG. Basically similar Filler/Carrier which used for normal granule can be used for DG also. But because of

special property of DG such as Floating, Water surface spreading, rather special Filler/Carrier must be selected very carefully.

a) Floating Agent

Floating Agent is one of most important ingredient, and it is composed in DG to make DG floating, and generally its dosage is not so small, so it may increase cost of DG. Basically, Inorganic and/or Organic chemical which has small density, or bulk density may use for DG as Floating Agent, but actually, often used Inorganic chemicals for DG. Because it might chemically stable, and easier to purchase product.

In case Inorganic Floating Agent, the foamed mineral (Obsidian, Pearlite) through calcining process such as Perlite, Pumicite, Vermiculite, calcinated Vermiculite is available for DG.

But Micro glass balloon (GBA) which foamed Sodium silicate / Pyroborate through calcining was often used for DG because of quite effective floating performance.

In case Organic Floating Agent, it seldom used as alone but it is used together with Organic chemicals such as mixture of Poly butene / Perlite.

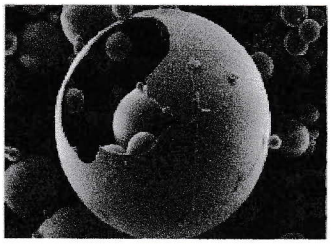
Actually Micro Glass Balloon (GBA) might be one of best product as Floating Agent, and its representative Physical·Chemical property was shown in following Table.

Table-2.

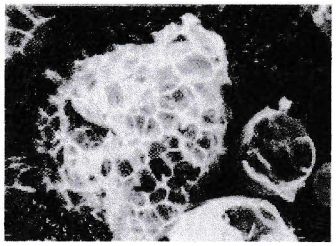
1	Appearance	White Powder
2	True Density	0.39 g/cm^3
3	Bulk Density	0.24 g/cm^3, (0.20 to 0.26)
4	Oil Absorption	3.3 g oil/100cc
5	Particle Size	43 μm (Median, d50), (15 to 75)
6	pH	9.5 (at 5%)
7	Volatile Content	0.5 wt %
8	Glass Thickness	1.16 μm (calculated)
9	Stability	Stable at <600℃

Perlite, Vermiculite maybe available as Floating Agent because of small bulk density, but these Carrier absorb water rather easily when DG applied on water surface, and lose floating property easily. So in case use these carrier, maybe we need pretreatment with Oil to avoid water affinity, and/or it should be used together with GBA.

Following Figure is SEM microscopic photography of some carrier. GBA is aggregate of complete independent micro glass balloon, it is complete different from other mineral, and also we will know, such balloon will be broken under some conditions.



Micro Glass Balloon



Perlite

Vermiculite

Fig-1. Microscopic structure of some Carrier (SEM)

b) Carrier (Water soluble / Water insoluble)

The DG formulation in this study, in order to avoid disadvantage of inadequate performance of Surfactant which adsorbed by Carrier, we considered Water soluble Carrier as necessary condition for DG Carrier.

Basically Water Soluble Carrier was not affected water surface property of DG. The preferable Water Soluble Carrier might be KCl, Na Benzoate, Na gluconate, Salt of Phospholic acid etc, but also we need to consider other factor such as easy granulation, hardness of DG etc., Generally, maybe we can say KCl might be most preferable carrier for DG. But some time particle size of carrier affect DG hardness, Dancing action of DG, so we need carefully studied about carrier.

In case Na Benzoate, it will improve the hardness of DG, but pH will become little bit high. In case Salt of Phospholic acid, it can be arrange the pH by combination of Salt of Phospholic acid but it is not so good for easy granulation.

c) Water Insoluble Carrier.

As Water Insoluble Carrier, White Carbon (WC), $CaCO_3$ will not affect for water surface property of DG even Surfactant such as Water Surface Spreader absorbed on carrier, but Inorganic carrier such as Clay, Bentonite, Talk etc affected water surface property of DG. Also in case Corn Starch affected water surface property of DG bit, but maybe it can be apply for DG under some conditions.

In case liquid TC applied for DG, because of less oil adsorption ability of Water Soluble Carrier, WC was partly combined in DG but inorganic normal carrier such as Clay, Bentonite should not be applied for this DG. Obviously, Dancing action was affected when such normal inorganic carrier applied.

A. Kajiyama (Improvement Disintegration time of Tablet by adding Inorganic Salt, Chiba University, Feb. 2008) had been studied Disintegration of Tablet which contains Inorganic Salt, and found the Inorganic Salt which has positive Heat of Dissolution

shorten the disintegration time obviously (In the Table, there is more than 10 times difference of Disintegration time in case $NaHCO_3$ and Na_2CO_3, inorganic salt which has negative Heat of Dissolution make disintegration time longer).

DG related Data including other Inorganic, Organic Salt etc., are summarized in the Table-3.

Table-3.

	Density	pH	Heat of Dissolution (KJ/mol)	Water solubility (g/100ml)	DG Hardness	Drying process
$NaHCO_3$	2.20	↓	19.1	70		CO_2 ↑
KH_2PO_4	2.34	↓	19.6	22		
K_2SO_4	2.66		23.7	111		
KCl	1.99		17.2	28	H	
NaCl	2.16		3.9	36		
Na_2SO_4	2.70		− 2.4	5		
Na_2CO_3	2.54		−26.7	22		CO_2 ↑
NaH_2PO_4	2.36	↓		60	H	
Na_2HPO_4	1.70	↑		8	H	
$(NH_4)_2SO_4$	1.77		6.6	71		NH_3 ↑
$CaCO_3$	*2.71	↑	−13.1	Insol		
Na Benzoate	1.44	↑		66	H	
Na Gluconate	1.80	↑		58		
Lactose	*1.52			22	S	
Corn Starch	*1.50			Insol	S	

＊ : Bulk density might be less than 1.0 usually.

1-2-3. Surfactant (Dispersant, Other Surfactant).

Because DG is a kind of Granule, so maybe normal surfactant for Granule can be available also. But because of special function of DG, so called Dancing Action, Water surface spreader is necessary ingredient for DG, also other ingredient such as Carrier, Disintegrating agent, Binder and Dispersant etc should be carefully selected under considering affinity with Water surface spreader.

Generally TC is Lipophilic organic chemical, and its biological efficacy might be expected by uniform TC dispersion in a water, and following formation of TC treatment layer on a soil. This is because Dispersant might be necessary ingredient for DG, but also we need consider Surfactant combination in DG formulation. Actually in DG formulation, not only Dispersant but also Water Surface Spreader is another necessary

surfactant in DG. Under these conditions, Dispersant has to be selected very carefully to avoid inadequate effect of Surfactant combination. In other word, Dispersant must not affect performance of Water surface spreader.

In a result, we found that good Dispersant should not decrease surface tension, and also it might be high molecular weight Dispersant. When Dispersant decrease surface tension, performance of Water Surface Spreader was affected very much. (hereafter, Surface, Surface Tension means Statistic Surface Tension, it must be discriminated from Dynamic Surface Tension).

In case this DG, SK-24 and SK-20GR was used as Dispersant. SK-20GR is a kind of Binder, and it had another function to make DG more hard.

When general Dispersants such as Na-Alkylbenzene sulfonate, Salt of Alkyl sulfate, Nonionic surfactant modified sulfate, Nonionic surfactant modified phosphate, Sulfosuccinate type Anionics were used together with Water Surface Spreader, DG will lose Dancing Action on a water, this is because, Water Surface Spreader might lost its Dynamic Surface Tension lowering ability.

The excellent Water Surface Spreader should have following property.

1) Dynamic Surface Tension lowering ability
2) Molecular weight should be around several hundred
3) Rather linear molecular structure
4) Balanced Hydrophilic-Lipophilic

Regarding Hydrophilic-Lipophilic Balance, surfactant which HLB(I/O) is around 5 to 10 might be a good Water Surface Spreader, such as SK-45EH (5.8), BG (10), BDG (8.8). (About BG and BDG, its BP is rather low, so DG lose Water Surface Spreading ability during Drying process)

1-2-4. Other Ingredients.

The other composite of DG which specific for each DG, such as Stabilizer for TC must be studied carefully as same as other general granule. Except such stabilizer, Improver for water surface action, hardness of DG might be one of rather important ingredients.

a) Improvement of Water Surface Action.

As Improver for Water Surface Action, especially such as Dancing Action, including Carrier, Filler, liquid / Solid, sometime such as Water repelling chemicals are used.
As carrier, filler, $CaCO_3$ might be one of possible chemical because also not expensive, but be careful about pH increase.

Also, such as higher Fatty acid salt help water surface action improve with just small amount in DG. In this case we can find Scum on a water surface if dosage increased.

Moreover, hydrocarbon such as Liquid / solid Paraffin, polybutene, fatty acid ester like OME (Methyl oleate) also improve water surface action sometimes.

b) Improvement of DG Hardness.

Granule hardness of DG affected by several factors, but Carrier, Filler is one of important factor for hardness. The specific salt of Organic acid such as Na-Benzoate, Inorganic acid such as NaH2PO4, Na2HPO4 often make DG more hard easily.

And a kind of binder such as high molecular weight PVA, also improve the hardness of DG. But because of aqueous solution of PVA, adding process of PVA aqueous solution must be considered. Because we need consider kneading water, compatibility of other water soluble surfactant and PVA.

Because of rather big diameter of DG, more long time are needed for Drying Process. If Drying is not enough, the hardness of DG will easily decreased. On the contrarily, too much hard DG will not easily spreading on water surface, so including Package selection of DG, the condition of Drying process should be considered carefully.

2. Production of DG (Kneading, Granulation, Drying).

In case normal size DG, just normal granule production process can be available mostly. But, especially big size DG, DJG, "How widely spreading DG on water surface" might be one of most important point for DG. For this purpose DG required special Disintegration・Spreading on water surface. This is because, we need pay special attention for each Kneading, Granulation, Drying process mainly.

2-1. Pretreatment

Including each ingredient, it must be dispersed uniformly in DG. But especially from view point of excellent Dancing Action on water surface, macroscopic uniformity must be maintained in DG but microscopic ununiformity should be accepted in some extent. These ununiformity related to Kneading method in a process, and kneading method relate to floating property of DG because of distraction of GBA.

In this point of view, all ingredients except GBA and water soluble carrier KCl, should be mixed very well after grinding.

Regarding about water soluble carrier KCl, because it is highly relate to Dancing Action, so whether Grind or not it must be consider very carefully.

Also about GBA, it should be mixed with Spreading Agent independently/separately

from other ingredients but other carrier can be mixed together with GBA/Spreader because Oil absorbing property of GBA is not so big.

2-2. Kneading Process

In current our DG, there are no Filler/Carrier which has big Oil absorbing capacity, moreover Water must be added for Granulation, so Kneading machine must be selected very carefully. The kneading machine which give rather high granulation pressure, such facility must be avoided.

The Ribbon Mixer as Kneading facility, it might be a one of proper facility for Kneading. When we can't apply such as Ribbon mixer, in this case we need to decide Kneading Conditions carefully to avoid distraction of GBA, high Granulation Pressure for long time.

2-3. Granulation Process

In case normal size granule, Extruder such as Basket type extruder might be one of best facility for granulation because of excellent yield, but we need pay attention for granulation pressure, and it should be lower for production.

In case small size DG, just same as normal granule, same facility is available for granulation and best diameter might be around Φ 2mm into consideration of Disintegration and Spreading on water surface. Also about such DG, normal carrier such as Clay, Bentonite etc., might be available, because such carrier will not affect to water surface behavior so much.

In case big size DJG which has diameter around Φ5mm, Basket type extruder is not good facility, molding is rather difficult. For these DJG, Twin Dies Pelletizer (TD-P) might be one of best facility as granulator. The characteristic of TD-P are, low granulation pressure and high yield.

Table-4.

Production Capacity	200kg/h～1,000kg/h
Diameter of Dies	Φ20mm～Φ60mm
Dies Dimension	Φ4mm～Φ10mm

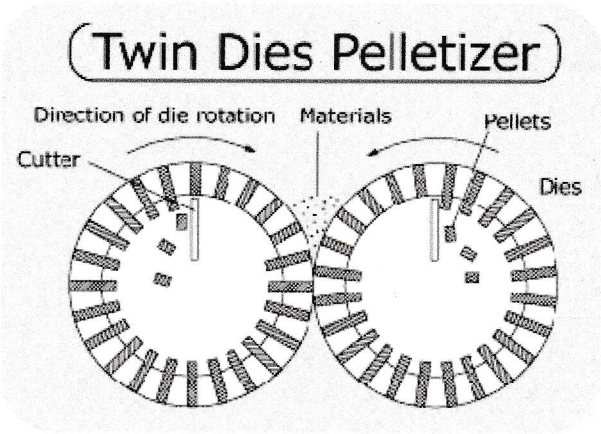


Fig-2. Image of Granulator

Figure and Table shows schematic illustration of TD-P, and representative specification.

Sometime, shape adjusting, grading machine is used for DJG but we should be careful about this process. Because surface of DJG is not very smooth, there are singular point such as many small pore, rough surface, and these physical singular point might have relation with water surface behavior of DJG, so make DJG surface too smooth should be avoided (see Fig-3, -4)

2-4. Drying Process

Just after granulation, DJG contains water, so such DJG will be easily broken during Drying process. This is because Drying method/facility must be considered very carefully. Fluidal bed facility is one of representative Drying facility but because of drying method, grains will vigorously moving in a vessel. At the result, DJG will be broken and yield will be decreased, so this kind of facility must be avoided.

The appearance and internal image of DJG are showed in following figures. DG is designed to perform Appropriate Disintegration, Water Surface Spreading with Brownian movement, and these properties might be related to DJG structure also.

During Drying Process, the appearance, inside micro structure of DJG might be changed by water evaporation process, and Anionic Surfactant will migrate to surface of DG. At the result there might be small pore, surface will be rough surface.

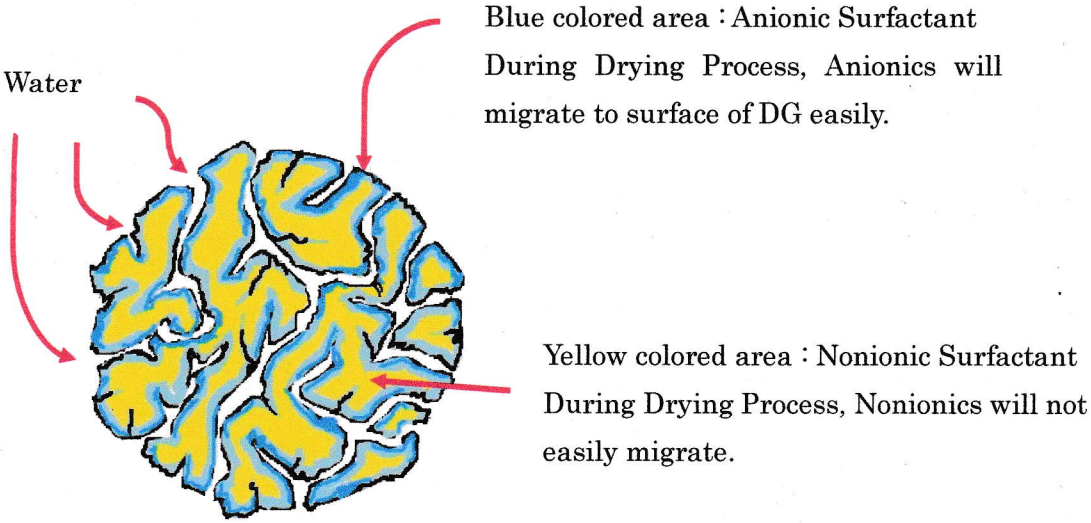


Fig-3 : Surfactant localization image in DG

Also Water Soluble Carrier dispersed in DJG, these carrier will be dissolved into water easily and will make vacant space which will be next singular point for Disintegration.

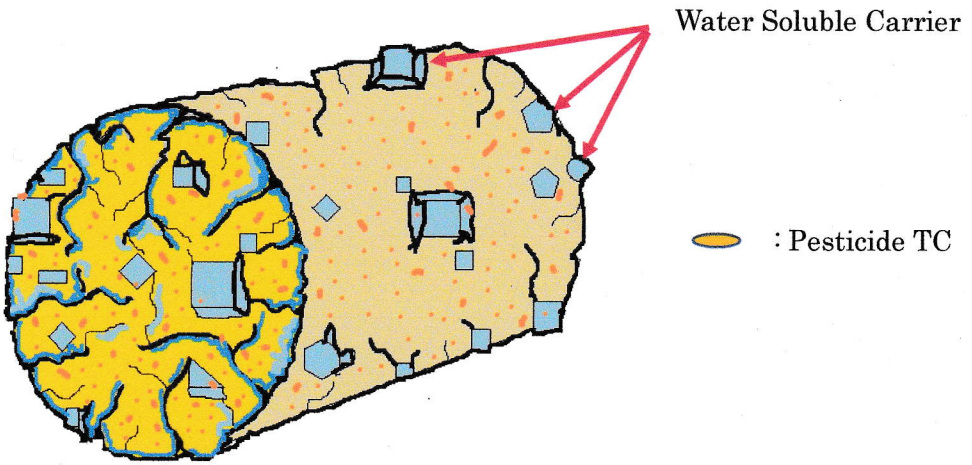


Fig-4 : Water Soluble Carrier in DG

3. Estimation of DG.

3-1. Water Surface Spreadability and Dancing Action of DG.

Water surface spreader for DG is quite important and necessary functional material that will affect performance of DG. Water surface spreader in this DG is, its function will be relate to other ingredient, a kind of Nonionic Surfactant which designed to perform full Dancing Action on water surface.

For water surface normal granule, water surface spreader which has low surface tension were used generally. When granule applied on water surface, action of water surface spreader might be considered that, first water surface spreader in a granule will be dissolved into the water, and it might be oriented on water surface. Together with water surface spreader movement, granule will be spreading on a water.
For such water surface spreader, surfactant which has around 30mN/m will be often used.

DG is also a kind of water surface spreading granule, so similar design idea might be necessary for DG in view point of water surface spreading.
Exact water surface spreader in this DG has surface tension of 32mN/m, and it is lower enough, it is considered as well spreading performance.

In case normal water surface spreading granule has no time requirement for spreading, and normally granule disintegration on a water will not be observed.
On the contrary, physically its diameter will be 3 to 10 times bigger than normal granule, moreover DG will be spreading on water surface accompany with contentious Irregular movement (Dancing Action) of DG itself and continuously disintegrating DG within short time. (resemble to Brownian movement)

Also, this continuous irregular movement, it is quite strong, active and more widely spreading compare with normal water surface spreading granule which spreading by just surface tension.

Analysis of Irregular movement on water surface might be not so easy because DG is composed with many other ingredient, but based on many different water surface spreader comparison, we considered one of Driving Force for such movement might be Surface Tension itself and Difference of Statistic and Dynamic Surface Tension.

Surfactant shows its surface tension but usually it takes fairly long time to show steady surface tension, it is depend on a kind of surfactant, concentration etc but usually it need few minute.

Meantime, Dynamic Surface Tension is kinetic tension to reach steady surface tension (statistic surface tension), so in case Dynamic Surface Tension is lower some extent and Difference of Static and Dynamic Surface Tension is small enough, then we considered DG will move some extent.

Following Table showed surface tension together with typical water surface spreader SK-551.

Surface Tension of 0.1% aqueous solution of Surfactant. Table-5.

	Statistic surface tension	Dynamic surface tension	Difference
SK-45EH,	32.5 mN/m	35.5 mN/m	3.0 mN/m
SK-551	30.2 mN/m	39.5 mN/m	9.3 mN/m

Also as another Driving Force for Irregular movement of DG on water surface, solubility speed difference of carrier which has particle distribution, intentionally applied special process (SK-45EH adsorption process) in DG production which might cause microscopic irregularity, might be considered as Driving Force.

3-2. Performance oF DG and its Estimation.

Except Biological Estimation item, general physical-Chemical estimation item might

be apply for DG also. But we should be very careful about some estimation items which considered special for DG such as Water Floating Property, Disintegration, Water Surface Spreading, DG hardness. These item must be set as new estimation items for DG, but so far there is no official, standard estimation method.

Especially Biological estimation is very important for DG, but also it is difficult to carry out Bio-Efficacy test for all formulation on formulation study.
Even so, we need to check Physical-Chemical property, so temporary we established our own Estimation method based on our experience.

Followings are our current estimation method for DG.

SKIS-T-001-1	Disintegration Time for Floating Granule.
SKIS-T-001-2	Floating Ratio of Floating Granule.
SKIS-T-001-3	Arrival Distance for Floating Granule.
SKIS-T-001-4	Time for Arrival Distance for Floating Granule.
SKIS-T-001-5	Dancing Action for Floating Granule.
SKIS-T-001-6	Estimation Unit for Floating Granule.

SKIS-T-001-1

Disintegration Time for Floating Granule.

1. Preface.

   This Estimation method is applied for Floating Granule.

2. Definition.

   Disintegration Time is Time in Second that starting from granule is placed onto the water surface until all Granule disintegrated.

3. Test Method.

   Prepare 1000 mL beaker charged with 800 mL of 20 Celsius Tap water, Regulated grams of Granules is put onto the Water surface, and check the Time until all Granule disintegrated into fine particle, and beyond recognize original form.
   Repeat the estimation 3 times, and average must be recorded in second.

4. Estimation.

   Time for Disintegration is depend on Granule performance, but usually it should be less than 5 to 15 min.

SKIS-T-001-2

Floating Ratio of Floating Granule.

5. Preface.

   This Estimation method is applied for Floating Granule.

6. Definition.

   Floating Ratio is Ratio of Floating Granule number to all Granule number which put onto water surface.

7. Test Method.

   Prepare 1000 mL beaker charged with 800 mL of 20 Celsius Tap water, Regulated number of Granules (it is depend on Granule size etc but at least 10 granules) is put onto the Water surface, and check the number of Granules that is sinking into the water within 30 second.

   Repeat the estimation 3 times, and average must be recorded in second.

8. Estimation.

   Floating Ratio is expressed as following equation.

   ((A – B) / A) X 100 = Floating Ratio (%)

   A : Total charged Granule number

   B : Sinking Granule number

   Example : ((10-2)/10) X100 = 80%

SKIS-T-001-3

Arrival Distance for Floating Granule.

9. Preface.

   This estimation method is applied for Floating Granules.

10. Definition.

    Arrival Distance is Longest Spreading Distance of Granule in Unit which regulated in SKIS-T-006.

11. Test Method.

    Use estimation unit which regulated in SKIS-T-001-6, Water (every estimation, Water

Hardness, Temperature must be controlled as same condition) charged into the Unit.
Regulated grams of Granule is put onto Water surface, and check the Spreading Materials (Disintegrated particle, Oil Film etc) until the Spreading Materials no more spreading.
Usually, 20 Celsius Tap Water used, and Depth of Water should be around 3 to 5 cm.

12. Estimation.
Arrival Distance is expressed as Spreading Distance (cm) for Theoretical Distance (240cm).
Example : 180/240.

SKIS-T-001-4

Time for Arrival Distance for Floating Granule.

13. Preface.
This estimation method is applied for Floating Granule.

14. Definition.
Time for Arrival Distance is Time in Second that starting from Granule put onto water surface until Granule arrived at Longest Arrival Distance in Unit which regulated in SKIS-T006. When Granule spreading to opposite edge of Unit, then the time until arrived opposite side will be estimated.

15. Test Method.
Use estimation unit which regulated in SKIS-T-001-6, Water (every estimation, Water Hardness, Temperature must be controlled as same condition) charged into the Unit.
Regulated grams of Granule is put onto Water surface, and check the Time until Spreading Materials (Disintegrated particle, Oil Film etc) no more spreading.
Usually, 20 Celsius Tap Water used, and Depth of Water should be around 3 to 5 cm.

16. Estimation.
Needed Time until Longest Arrival Distance must be recorded in Second.
At the same time, Dispersing Speed must be calculated based on Longest Arrival Distance.
Example : Time for Arrival Distance, 360 sec (6 min).
Arrival Distance, 190 cm
Dispersing Speed, 32 cm/min (190 / 6 = 31.6)

SKIS-T-001-5

Dancing Action for Floating Granule.

17. Preface.

This estimation method is applied for Floating Granule.

18. Definition.

Dancing Action is Brownian Movement like Irregular and Active Movement of Original Granule and/or disintegrated second grain on Water surface.

19. Test Method.

Prepare 1000 mL beaker charged with 800 mL of 20 Celsius Tap water, Regulated number of Granules (it is depend on Granule size but 1 or 2 Grains at laboratory test) is put onto the Water surface, and check the Dancing Action.

Repeat the estimation 3 times.

20. Estimation.

Dancing Action is recorded in 5 Scale, from most actively moving to no such movement.

A : Very active Dancing Action

B : Less than A

C : Less than B

D : Less than C

E : No Dancing Action.

Dancing Action itself is not related to Spreading Property, sometime no Dancing Action but spreading very widely, it depend on recipe of Granule.

SKIS-T-001-6

Estimation Unit for Floating Granule.

21. Preface.

This unit is apply for property estimation of Floating Granules.

22. Facility

50 cm X 50 cm

Calculated Spreading Distance : 240 cm