

Surfactant for Pesticide Formulation.

Supplement Edition : EC Formulation

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

Shin-Ichi ITOH.

1. What is EC Formulation

EC is rather old, traditional formulation but still widely used in the world as Pesticide formulation.

Because, production method is rather simple, usually we can get good biological efficacy than other formulation style because of rather small TC particle size, and sometime TC will penetrate into the target rather easily because of solvent.

Recently such solvent has being considered as a kind of Contaminant for environment, for many living things, so, many water based formulation and/or other formulation has being studied now.

But even so, still EC is one of important formulation style, and actually huge volume of EC has been supplied to the market.

For SK company, EC is not so profitable formulation because of price competition of Emulsifier, but EC formulation study might be one of best formulation for surfactant selection training. This is because we summarized important technical points for EC formulation Study.

2. Some technical basic point for EC.

2-1. Solvent selection.

When we consider EC, first we need to decide the solvent. Emulsibility is second problem, because even we found good emulsifier for some EC formulation, we need consider solvent again when it has cold stability problem (crystallization problem).

There might be many conditions as proper solvent for EC, but here we will discuss about just Physical-Chemical properties. Because such as Bio-efficacy, Toxicity, TC decomposition etc are very much complicated, so these factor must be considered as specific problem for each EC formulation.

Simply, also generally speaking, proper solvent should be selected as following order.

- 1) Aromatic, low polarity solvent
(This is because for easy Emulsification)
- 2) When need Polar solvent, it's should be less polarity, its volume should be small
(this is because to prevent re-Crystallization in Emulsion after dilution)

For actual possible solvent for EC, refer to following Table. In that Table, we should pay attention for HLB and log P mainly, because TC solvency will highly depend on these factors.

Table-1. Solvent Property

Solvent Name	HLB (I / O x 10)	Sg	log P	Mp (°C)
Kerosene	0.00	0.80		-40
Ethyl benzene	0.75	0.87	3.15	-95
Xylene	0.94	0.87	3.12	-40
Toluene	1.07	0.87	2.69	-95
Soybean oil	2.55	0.92		-5
Rapeseed oil		0.91		-20
OME (Me-Oleate)	2.36	0.87	7.45	-20
Alkyl dimethylamine (SK-97DM)	2.50	0.79	5.40	-20
Methyl naphthalene	2.73	1.02	3.87	-22
N-Octylpyrrolidone (NOP)	3.41	0.92	4.15	-25
N,N-dimethyldecanamido	6.14	0.92	2.94	
Cyclohexanone	6.25	0.948	0.81	-31
BDG	8.75	0.95	0.30	-68
n-C ₄ H ₉ -OH (n Bu-OH)	12.50	0.811	0.88	-90
iso-C ₄ H ₉ -OH (iso Bu-OH)	14.30	0.803	0.80	-108
PGM	17.10	0.962	-0.49	-96
NMP	14.50	1.028	0.38	-24
DMSO	22.50	1.10	-1.35	18
DMF	33.75	0.94	-1.01	-61
EG	50.00	1.115	-1.36	-13
Water		1.0		0

2-2. Concrete solvent selection method and estimation.

After considering TC properties, select some solvent based on above general principle.

2-2-1. Cold Stability, Heat Stability Test.

- 1) Make some formulation using selected different solvent. In this case, Emulsifier should be just 7 to 10% of SK-50EC and/or SK-51EC
- 2) If the solvent is mainly aromatic, less polar solvent, just SK-50EC might be better as Emulsifier.
- 3) If the solvent is more polar solvent, just SK-51EC might be better as Emulsifier, or maybe we can arrange SK-50EC/SK-51EC mixture as Emulsifier.
- 4) Above both 2), 3), even Emulsibility looks not good, it is no problem, because this test is just select proper solvent, especially for Cold Stability.
- 5) When we select both strongly polar and non-polar solvent, often we need another 3rd

solvent which connecting both polar and non-polar solvent.

2-2-2. Estimation of Cold and Heat Stability Test.

Estimation should be carried out based on following Estimation Standard.

Table-2. Estimation Standard.

	Conditions	Check Items	Estimation Standard
Heat Stability	54°C, 1 to 7 days	Color change	No appearance change
	54°C, 1 to 7 days	Precipitation	No appearance change
	54°C, 1 to 7 days	Others	No appearance change
Cold Stability	-5°C, 1 to 7 days	Crystallization	No crystallization
	-10°C, 1 to 7 days	Crystallization	No crystallization
	Freeze Thaw	Crystallization at < -20°C	
		Recover situation at R.T.,	Thaw completely
		Recover time at R.T.,	Short time

Just for initial solvent selection test, only 1 or 2 days estimation might be OK, especially for cold test, but for the final estimation, at least 7 days estimation needed. Regarding Estimation Standard, basically it will be decided by registration holder under considering all possible situation, but simply said above conditions will be accepted widely. Also such as WHO, CIPAC standard should be consulted.

For Cold Stability, No Crystallization at -5 Celsius or at -10 Celsius, moreover for the safety, seedling should be carried out. Also Freeze-Thaw estimation should be carried out, because Crystallization will be founded at actual conditions even we can't find Crystallization at -5 and/or -10 Celsius at laboratory estimation. These are because we can't control the field condition completely.

When temperature is very low, sure there might be Crystallization, so Crystallization itself at very low temperature, this is not essential problem, but such Crystal must be dissolved again (Thaw, Recover) when temperature increased to somewhat which almost same as field temperature. This is a reason of importance of Freeze-Thaw estimation. But Freeze-Thaw test highly depend on the vessel size, its quality also, so when we carried out this at laboratory, we should pay attention for recover time especially, it must be very short.

For Heat Stability, actually it is carried out for check TC decomposition. But we can't check TC decomposition, so we should pay attention for appearance any change of EC.

2-3. Emulsification Adjustment.

After solvent system was almost decided, next we need to adjust Emulsibility. For Emulsibility adjustment, we should consider following general principals.

- 1) If we have similar EC formulation (Kind of TC, its dosage, kind of Emulsifier), just we should adjust Original Emulsifier system.
- 2) We should consider just similarity of solvent system of other formulation, and follow that Emulsifier system (especially low dosage TC)
- 3) In case aromatic solvent used mainly and combined rather small amount of polar solvent also, SK-50EC/SK-51EC system can be available as Emulsifier. When polar solvent increased gradually, required emulsifier HLB will be increased. Then mainly use SK-51EC and/or adjust SK-5218CP, SK-92FS1 accordingly.
- 4) In case Paraffine base, edible oil solvent system, main Emulsifier should be SK-5110, and SK-94S7, SK-5945 for more higher HLB, SK-5935 for lower HLB as HLB adjusting surfactant. When we need Anionic surfactant for emulsion stabilizer, sometime SK-560EP can be used but its dosage should not be so much.

Following Table is a list of Emulsifier which used for EC mainly. SK-5110, SK-50EC, SK-51EC, SK-58DL and SK-58DH is already formulated Nonionics and Anionics mixture, the other is single component (some contains solvent).

Table-3 Emulsifier List often used for EC

Surfactant	HLB I/Ox10	ION Type	Solubilization	Comment
SK-5935	6.08	N	(M/B)	Use together with Nonionics
SK-5110	8.19	N	B	
SK-53CA	8.82	A	(M/B)	Use together with Nonionics
SK-58DL	9.29	N/A	M/B	SK-5110, SK-53CA, SK-560EP, SK-5218CP
SK-50EC	9.50	N/A	B	
SK-94S7	10.61	N	M	
SK-5218CP	11.56	N	B	
SK-51EC	11.59	N/A	B	
SK-58DH	11.61	N/A	M/B	SK-5110, SK-53CA, SK-560EP, SK-5218CP
SK-33SC	12.07	N-A	B	Some Water contained
SK-92FS1	13.54	N	B	
SK-5945	14.74	N	M/B	
SK-34SC	16.10	N-A	B	
SK-560EP	17.62	A	M	Paraffine contained as solvent

ION Type, N : Nonionics, A : Anionics, N/A : Nonionics Anionics mixture

N-A : Nonionics modified to Anionics

Solubilization, B : Big, M : Medium, M/B : Medium to Big

2-4. How to optimize Emulsifire for individual formulation.

Here, we will discuss about Emulsifire adjustment, but in case extremely bad Emulsibility, such situation must be already improved (Emulsion particle size, flowering etc) before Emulsifier adjustment based on above 2-3. When HLB of Emulsifire is far from EC system required HLB, it is not Emulsifire optimization problem, but we should consider 2-3 again.

2-4-1. How to know HLB adjustment direction.

First, check the both Emulsibility at condition of the actual lowest required HLB and the highest required HLB. Generally, such condition is,

HLB lowest condition : Lowest water temperature, highest dilution times,
Use 10°C water, 2,000 times dilution for example.

HLB highest condition : Highest water temperature, lowest dilution times,
Use 30°C water, 20 times dilution.

Table-4. Emulsibility at extreme condition and Emulsifire HLB adjustment direction.

Emulsibility at 10°C 2,000 times dilution	Emulsibility at 30°C 20 times dilution	Emulsifire Adjust direction
Good	Poor	HLB → High Ex, Add SK-5218CP etc, high HLB Emulsifire SK-50EC/SK-51EC=5/5 → 3/7
Poor	Good	HLB → Low Ex, Add SK-53CA etc, low HLB Emulsifire SK-50EC/SK-51EC=5/5 → 7/3

2-4-2. How to decrease the Emulsifire.

When we optimize Emulsifire and it showed Good Emulsibility, some time we will be requested dosage change of Emulsifire, maybe it might be dosage decrease of Emulsifire. In this case, Emulsifire HLB adjustment will be as followed.

Table-5. Emulsifire HLB adjustment for its Dosage decreased.

Proper HLB of Emulsibility adjusted Emulsifire	Emulsifire Adjust direction
Ex, SK-50EC/SK-51EC=5/5 (10%)	Ex, SK-50EC/SK-51EC=5/4 (9%)
SK-51EC/SK-53CA=8/2 (10%)	SK-51EC/SK-53CA=7/2 (9%)
SK-58DH/SK-5218CP=8/2 (10%)	SK-58DH/SK-5218CP=7/2 (9%)
SK-5110/SK-560EP=9/1 (10%)	SK-5110/SK-560EP=8/1 (9%)

2-4-3. How to adjust Emulsifire for Aromatic/Polar solvent system.

In case Aromatic solvent rich system, basic Emulsifier system might be SK-50EC / SK-51EC as shown in Table-6.

Table-6. Emulsibility Adjustment for Aromatic Solvent Rich System.

Main Emulsifire	Adjustable Surfactant
SK-50EC, SK-51EC	For HLB up
	SK-5218CP, SK-58DH, SK-5945, SK-94S7, SK-560EP
	For HLB down
	SK-58DL, SK-5110, SK-5935, SK-53CA

In case Polar solvent combined system, basic Emulsifier system might be same as SK-50EC / SK-51EC, and adjustable surfactant might be also same as above Table-6. But in this case, we have another important technical point which we need pay attention about it. That is re-crystallization problem in Emulsion after dilution. This mechanism will be understood as rather strong water affinity of polar solvent. These polar solvent which initially solubilized in inside of micelle together with TC, will be easily diffusing into the bulk water phase of Emulsion, at a result of this phenomena, TC will start the Crystallization in micelle, and finally such crystal will be phase out as precipitation (Crystal) in a Emulsion.

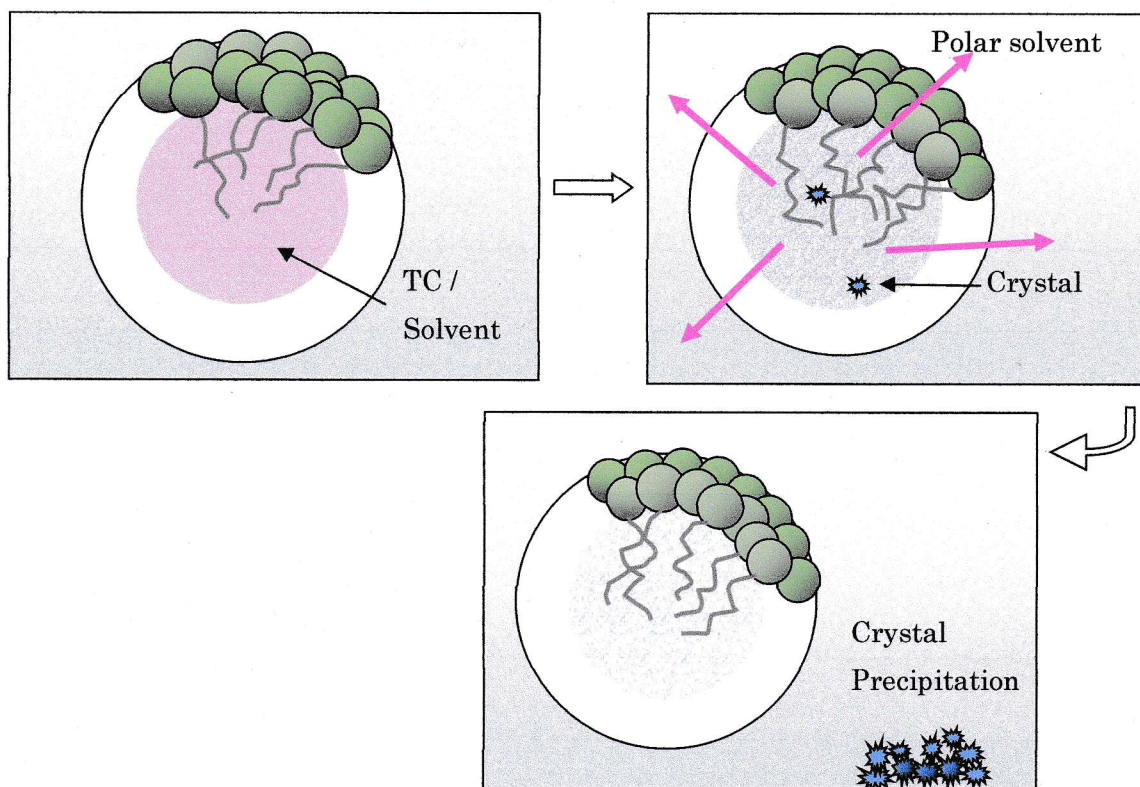


Fig-1. Recrystallization Mechanism in Emulsion.

So, in case combine polar solvent, we should pay attention about kind of polar solvent and its dosage in a formulation.

Generally speaking, Recrystallization often happened in case excellent emulsibility. Because excellent emulsibility means very fine emulsion particle size, and above Recrystallization mechanism (Fig.-1) will be easily happen in this case. So, Emulsibility should be optimize considering this point also.

2-4-4. How to adjust Emulsifire for Paraffine base solvent system.

In case Paraffine rich solvent system, basic Emulsifier and adjustable surfactant are shown in Table-7.

Table-7. Emulsibility Adjustment for Paraffin Rich System

Main Emulsifire	Adjustable Surfactant
SK-5110	For HLB up SK-58DH, SK-5945, SK-94S7, SK-560EP For HLB down SK-58DL, SK-5935, SK-53CA

3. Estimation of EC.

3-1. Formulation Stability Test.

Formulation stability test should be carried out based on International Standard which provided by WHO, CIPA C and/or customer's request. But general conditions might be,

Cold Stability : at -5 and/or -10°C for 2 weeks, and Freeze-Thaw test.

Heat Stability : at 54°C, for 2 weeks.

Regarding Cold Stability, we must be careful about Crystallization which highly depend on kind of Solvent. The solvent must have biggest solubility for TC (such solvent might be Polar solvent usually) but also we should pay attention for Re-crystallization of TC in a emulsion. (so, not only polar solvent, additional Co-solvent should be combined to avoid Re-Crystallization in diluted emulsion).

Regarding Heat Stability, we mainly pay attention for Appearance change of formulation. Usually we are not sure about TC decomposition, but we should be careful about any change which suggest TC decomposition.

3-2. Emulsification Test.

These estimation should be carried out based on International Standard and/or customer's requirement, but we should carry out estimation at actual dilution time also.

Usually, we should check Flowering (Blooming), Emulsibility and Emulsibility Stability (Separation, Precipitation etc).

Regarding Flowering, it is highly depend on kind of solvent, and no longer White-Cloudy blooming but almost transparent in case polar solvent rich formulation.

About Emulsibility, fine excellent emulsion shows Fluorescent Color like Red to Blue, so we should master emulsion estimation work through experimental. Also, emulsibility will be affected by Water Temperature, Water Hardness and Dilution Times. So, emulsibility must be optimize under considering these points.