Surfactant for Pesticide Formulation.

Supplement Edition : OD (Oil base SC)

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1. What is OD Formulation

SC is a formulation which active ingredient was dispersed in liquid medium, and it will be applied directly and/or applied after diluted with water. Also liquid medium is not limited just water only. On the contrarily OD is, active ingredient dispersed in organic medium, and it will be applied directly or it will be applied after dilute with organic solvent. In this point of view, Oil based SC formulation which will be diluted with water before application, it might be belongs to SC. But currently dispersion medium of SC is usually Water, so here we will definite Oil based SC as OD. Such OD some time it will be called as OF (Oil Flowable) also.

Why OD formulation considered beside SC ? Because at least OD has two important characteristics as follows.

1) Some TC will be easily decomposed (Hydrolysis) in Water, to prevent such decomposition, non-aqueous solvent will be used as dispersion medium.
2) Very often a kind of Oil is able to enhanced Bio-Efficacy of TC, this is because such oil will be combined together with TC, and formulated in OD.

2. Physical-Chemical property of OD

2-1. General

Simply said, Physical-Chemical property of OD is almost same as SC, but the difference might be caused by dispersion medium difference. Because dispersion medium is a kind of Oil in case OD, so formulation viscosity might be little bit higher than SC, and OD must be Emulsified when it was diluted with water.

2-2. Formulation Stability

Cold Stability, Heat Stability should be same as water based SC, but usually Cold Stability some time looks not so good as SC because of kind of Solvent (dispersion medium). Heat Stability some time looks not so good as SC also, this is because viscosity difference for temperature change is quite big, so suspending TC in a medium is rather difficult.

Usually normal Dispersant is Anionic Surfactant but such Dispersant can't work well in non-aqueous medium because it can't dissolve into the non-aqueous medium, also it is rather difficult for us to find so called thickener for non-aqueous medium.

Because of these difficulty, keep high Suspencibility of formulation might be little bit difficult, so Surfactant must be selected very carefully.

2-3. Emulsibility

OD will be diluted with water before application, so it must be emulsified very well. Adjusting the Emulsibility itself is essentially not so difficult but because of rather small dosage of Emulsifier, because of Cationic Surfactant modified thickener, some time these factors cause difficulty.

3. General Composition of OD and its Ingredients.

3-1. General Composition

The OD composition is basically similar with normal SC but dispersion medium is non-aqueous medium. General OD composition is as follows.

Table.3-1. General Composition of OD.

	Dosage (wt %)	Characteristic
Technical	~ 30	Active Ingredient, usually < 20
Solvents	Rest	Suspending TC, consider Sg, Viscosity
Dispersant / Emulsifier	~ 20	Suspending TC, Emulsify Solvent (TC)
Thickener	0.5 to 5	Affinity with Solvent

3-2. Solvent

Regarding Solvent selection for OD, there might be no strict limitation but at least we need consider its cost, specific gravity, viscosity, cold/heat stability, TC solubility, water content (TC stability) etc., except its bio-efficacy.

Typically, often used solvent and its character might be as follows.

1) Kerosene (Hydrocarbon)

   No chemically active functional group, Low viscosity, Good cold stability, Emulsifying difficulty.

2) Fatty acid ester (OME, Oleic acid methyl ester)

   Low viscosity, Good cold stability (depend on Fatty acid composition), Easy emulsifying, Less chemically active functional group. Some commercial product freezing easily, so we need to select good product.

3) Edible oil (Soy bean oil)

   High viscosity, Cold stability problem, Emulsifying difficulty, Easy oxidization, Small Water contained,

Table.3-2 show Physical-Chemical Property of potential solvent for OD.

Table.3-2, Physical-Chemical Property of Solvent.

Solvent Name	Sg	HLB (I / O x 10)	*log P*	Viscosity (CP)	Mp (℃)
Kerosene	0.80	0.00		3.3(38)	-40
Ethyl benzene	0.87	0.75	3.15	0.68(20)	-95
Xylene	0.87	0.94	3.12	0.84(20)	-40
Toluene	0.87	1.07	2.69	0.56(25)	-95
Soybean oil	0.92	2.55		26.2(38)	-5
Rapeseed oil	0.91			46.2(38)	-20
OME (Me-Oleate)	0.87	2.36	7.45	5.8(25)	-20
Methyl naphthalene	1.02	2.73	3.87		-22
Cyclohexanone	0.948	6.25	0.81	2.3(20)	-31
BDG	0.95	8.75	0.30	5.85(20)	-68
n-C4H9-OH (n Bu-OH)	0.811	12.50	0.88	2.46(20)	-90
iso-C_4H_9-OH (iso Bu-OH)	0.803	14.30	0.80	3.37(20)	-108
PGM	0.962	17.10	-0.49	1.81(20)	-96
NMP	1.028	14.50	0.38	1.62(25)	-24
DMSO	1.10	22.50	-1.35	2.0(25)	18
DMF	0.94	33.75	-1.01	0.79(25)	-61
EG	1.115	50.00	-1.36	19.9(20)	-13
Glycerin	1.26	50.00	-1.76	1,500(20)	18
Water	1.0			1.0	0

Usually, specific gravity (Sg) of many organic solvent is less than 1.0, on the contrarily Sg of TC is bigger than 1.0, so sedimentation of TC will be easily detected especially at high temperature.

Also, solvent should not dissolve the TC, otherwise TC will recrystallize by temperature change. And if solvent contains some Water, it may cause Hydrolysis of TC (depend on TC character), so we need pay attention about it. In this point of view, even the solvent does not contains water but such as Hydroxy Group (-OH) of solvent may cause TC decomposition, so we should pay attention for it when apply such hydroxy group contains solvent.

And such as edible oil, these are solidified at low temperature easily (its highly depend on Fatty acid composition of oil), so we also should consider this point when apply edible oil as solvent.

Another important technical point about solvent is its Viscosity. It is easily understand that high viscosity solvent keep the TC suspensibility very well, but also we should pay attention for Viscosity change at High/Low temperature.
Following Fig.3-1 shows Viscosity change of representative solvent under temperature changed.

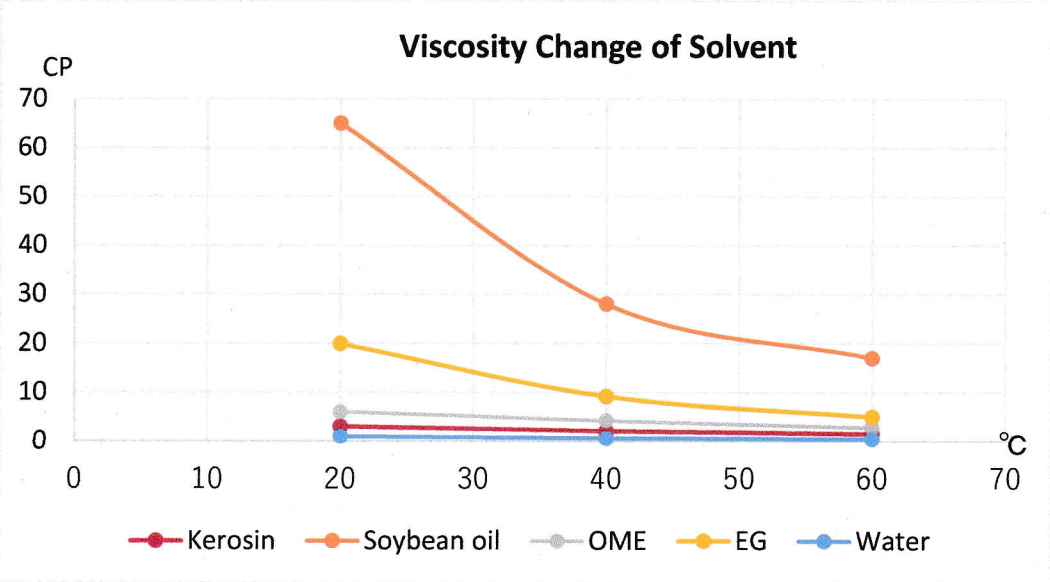

Fig.3-1. Viscosity Change of Solvent at Various Temperature.

As shown in Fig.3-1, Viscosity change of Water is very small, so generally water based normal SC has no suspensibility problem in a sense of viscosity change. In case paraffin, viscosity itself looks rather small but it depend on molecular weight of Paraffin, and its viscosity change at various temperature looks rather small, it means Viscosity Index is very small.

On the contrarily, viscosity change of EG, Soybean oil looks rather big. In case OME, viscosity change might be not so big also.
Considering viscosity change, Soybean oil looks not so good solvent, but maybe OME, Paraffin might be better solvent for OD because of rather small viscosity change.

Also we should consider how to change the viscosity of solvent chemically. Because, some time a kind of additive change the viscosity of solvent sharply. Normally such additives are known as Thickener which increase viscosity but also we should consider others such as solvent, Inorganic salt etc., which is able to adjust the viscosity also.

Not only Additives but, maybe we should think about simple solvent combination to improve viscosity itself, viscosity change problem. And, such solvent combination is not only related to viscosity problem but it will change the solvent HLB, affinity between TC and solvent. These factors will affect the suspensibility of TC also.

We can't say about best solvent for OD, but maybe we can suggest better solvent system such as OME/Paraffine based system. Freezing point of good OME is around -20℃ but some commercial product freezing just around 0℃, in this case Paraffine improve Freezing point, and OME/Paraffine is rather easily emulsified.

3-3. Dispersant / Emulsifire

The normal SC contains 1)water as dispersion medium, 2)dispersive (dispersoid) as colloidal particle which usually has oily property, and 3)surfactant which easily dissolved into water medium. So, there are so many different kinds of surfactant which work well in two different mediums, we can select proper surfactant rather easily.

But in case OD which dispersion medium is oil, surfactant selection is not so easy. Because many anionic surfactant which essentially water soluble are not soluble into the oil, simply said such surfactant is just dispersive (dispersoid), colloidal particles in oil medium. In case Nonionic surfactant, simply said it might be able to dissolve into the oil medium, but there is no water in OD but just single oily medium as solvent and TC mixture, so such surfactant might tend to be just solute in oil medium, in this case it is not easy to work as surfactant.

The difficulty of surfactant selection in OD system is simply explained as above, but even non-aqueous oil medium, there are difference of Hydrophilic / Hydrophobic property difference, so we need to apply surfactant under considering difference property of oil medium, surfactant property difference very carefully.

As a Dispersant, we have oil soluble Anionic surfactant such as SK-53CA and SK-560EP. SK-53CA is low HLB, SK-560EP is high HLB surfactant, it can be absorbed onto TC which has Hydrophilic / Hydrophobic property even in oil medium, and work as Dispersant. As Nonionic surfactant, it should have proper Hydrophilic / Hydrophobic property, it should have rather low HLB because of often used low HLB oil medium, then it will be absorbed onto TC, and it will work as Dispersant also. But just as Dispersant, sometime Anionic surfactant will work well than Nonionic surfactant, because Anionic surfactant will be absorbed onto TC more strongly in case TC has a kind of polar group. Actually, even we said Non-Aqueous system, OD system contains small amount of water.

As a Emulsifire, we can't expect much for single Anionic surfactant, it should be mainly depend on Nonionic surfactant and mixture of Nonionic / Anionic surfactant mixture. The balance of Nonionic / Anionic surfactant to get good emulsibility, it will highly depend on difference of oil, but our SK-5110 can be apply rather widely for various kind of oil.

Fortunately, OD is not transparent but a kind of suspension, so even Surfactant can't

dissolve into the oil, it can be dispersed into the oil medium uniformly as Emulsifire.

For example, SK-5218CP which is Nonionic, high HLB surfactant can't dissolved into Kerosin, but it can be apply as Emulsifire.

The HLB (affinity for Ingredients) of surfactant which often used in OD is shown in following Table.3-3.

Table.3-3 Surfactant Property

Surfactant	HLB	HLB(I/Ox10)	ION	Solubilization	Comment
SK-5935	4.30	6.08	N	(M/B)	Empirical HLB might be appropriate
SK-53CA	8.0	8.82	A	(M/B)	
SK-5110	8.30	9.14	N	M/B	
SK-58DL		9.29	N/A	M/B	Nonionic, Anionic combined
SK-58DH		11.61	N/A	M/B	Nonionic, Anionic combined
SK-94S7	11.80	10.61	N	M	
SK-5218CP	13.00	11.56	N	B	I/O x 10 might be appropriate
SK-33SC	(12.00)	12.07	N-A	B	Water, EG contained
SK-5945	15.00	14.74	N	M/B	
SK-34SC	(15.00)	16.10	N-A	B	PG contained
SK-560EP		17.62	A	M	Paraffine contained

SK-58DL, DH is composed with SK-5110 / SK-53CA / SK-560EP / SK-5218CP

Table.3-4 shows surfactant combination to get good emulsibility for various oil.
In case Soybean oil, it is rather difficult to get good emulsibility, so surfactant dosage is rather big. Also in case White Oil (Paraffine), some Nonionic surfactant can't dissolved into the oil, so we should be careful about it. In case OME, it is rather easy to get good emulsibility, but sometime market product of OME has cold stability problem because of fatty acid composition.

Table.3-4 Surfactant Combination for Different Oil

	Soybean Oil	Methyl Oleate	White Oil-1	White Oil-1
Oil	80.0	85.0	85.0	90.0
SK-5110	13.0	11.1	10.0	3.2
SK-5935	7.0			
SK-560EP		3.3		
SK-53CA		0.6		3.6
SK-94S7			5.0	3.2

Table.3-5 shows surfactant combination for OME / Paraffine system with PGM. Some time OME has cold stability problem, so Paraffine was combined to improve cold stability. Also PGM was combined together, it is because not only to improve cold stability, but also it make HLB of system higher, and then it make emulsibility of system easy.

Table.3-5 Surfactant Combination for OME / Paraffine

	1	2	3	4	5	6
OME	38.64	38.64	38.64	38.64	38.64	38.64
Paraffine	38.64	38.64	38.64	38.64	38.64	38.64
PGM	7.73	7.73	7.73	7.73	7.73	7.73
SK-58DH	15.00		7.00	11.00	10.00	11.00
SK-58DL		15.00	8.00			
SK-5110				4.00		4.00
SK-53CA					5.00	
SK-35PQ						2.00
Emulsibility	B / C	C / D	B / A	A	B / A	Excellent

3-4. Thickener

Regarding Thickener for OD system, representative product might be Organoclay, Castor Oil Derivatives, Polymer such as Polyamide, and Fumed Silica.

According to our study, Organoclay might be most effective to thicken the system but it often cause flocculation when OD diluted into the water. In case Castor oil derivatives, it make OD thicken rather easily but viscosity became very lower especially at high temperature, it is rather difficult to get stable viscosity at various temperature. Also such as Polyamide, Fumed Silica, generally it will not thicken the OD strongly like Organoclay do, sometimes it need big dosage to thicken OD.

Generally speaking, all these Thickener has more or less problems such as Flocculation when OD diluted into the water. This is because, maybe we can say that proper Thickener selection is key for OD.

Under these conditions, all other methods must be used together to obtain a viscosity stable OD. But there are so many factors which affect property of OD, so here we will discuss about some Thickener only.

3-4-1. Organoclay (Organic bentonite), Dosage : 0.5%～2%

Organoclay is Cationic surfactant absorbed clay, so we should try some different product, and we should check viscosity stability of OD at various temperature and

Flocculation (Scum) after OD diluted with water.

Bentonite has easily exchangeable Positive charge of its surface, and such positive charge will be easily intercalated. Such intercalation order will be,

$Li^{+}<Na^{+}<K^{+}<Mg^{2+}<Ca^{2+}<Ba^{2+}<Al^{3+}<Fe^{3+}<$Organic Cation.

Organic Bentonite is Organic Cation intercalated Bentonite, and there are different type of Organic Cation such as,

1) $R-N^{+}(CH_3)_3$, 2) $R-N^{+}(CH_3)_2-CH_2-\Phi$, 3) $(R)_2-N^{+}(CH_3)_2$, 4) $R-N^{+}CH_3-(CH_2CH_2-OH)_2$

Organic charactors of Organic Bentonite, simply said it will be increased in a order 1) to 3), and 4) has more hydrophilic property. These Cation difference will affect Thickening property, but it will depend on another ingredient also.

Thickening mechanism of Organic bentonite was considered as follows.

Dry state of Organic Bentonite construct layered crystal structure which spacing 2 to 4 nm. And such space will expand to around 5 nm based on solvent Solvation to hydrophobic part of quaternary compound, also Hydroxy group (-OH) which existed in end of layered crystal will form Hydrogen bonding, and constructing structure. This mechanism cause viscosity increase.

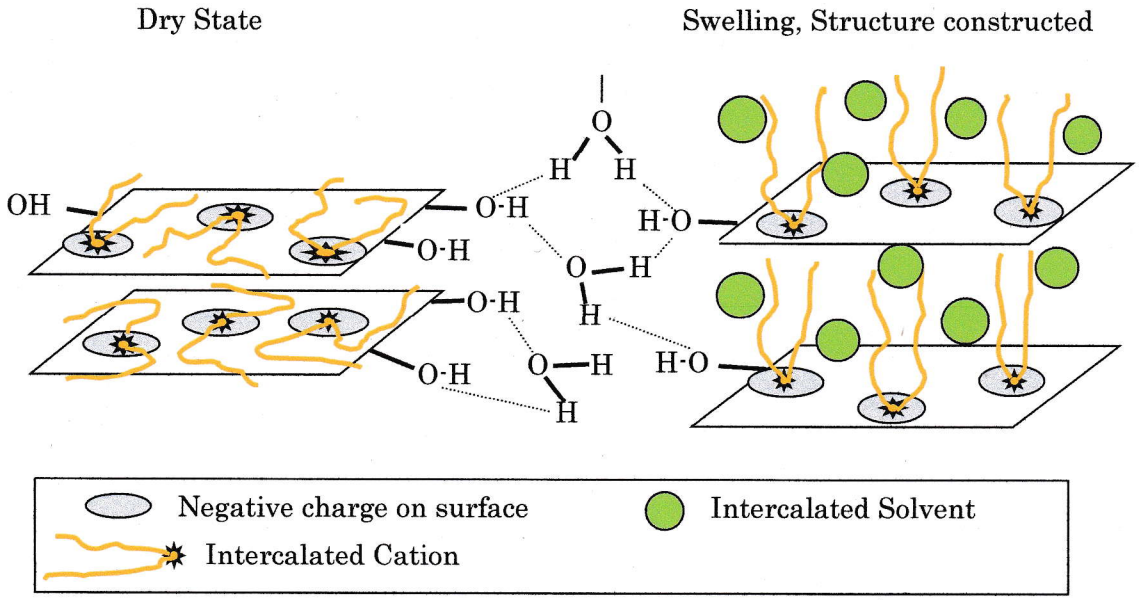

Fig 3-2. Illustrative Organic Bentonite Structure

Usually, Solvation is not so easy process for swelling compare with water base, so such as small amount of alcohol (MeOH, EtOH, IPA) addition in Solvent make swelling rather easy

3-4-2. White Carbon (Precipitated silica), Fumed Silica (Dry process), : ～ 5%

Silica has silanol group (Si-OH) on its surface, and tri dimensional network structure based on Hydrogen bonding of silanol group make viscosity increase. Following Table shows comparison of Physical property of Precipitated, Fumed Silica.

Table.3-6 Comparison of Physical property of Precipitated, Fumed Silica

Property	Unit	Precipitated Silica	Fumed Silica
Bulk density	g/l	～ 260 ～	～ 50 ～
Specific surface area (BET)	m^2/g	～ 170 ～	～ 200 ～
Absorbed moisture	%	～ 6 ～	< 1.5
pH (4%)		5 ～ 9	3 ～ 5
SiO_2	%	98	>99.9
HCl	%	< 0.1	< 0.005
Mean primary particle size	nm	5 to 100	5 to 50
Pore diameter	nm	>30	Non-porous
Pore diameter distribution			Very broad
Structure of aggregate and agglomerate		Structure aggregated, strongly coagulated	Chain-like, branched structure, softly coagulated
Thickening effect		Exist	Very remarkable

Important difference in above Table are, Moisture content and Structure of agglomerate, these will affect for OD properties.

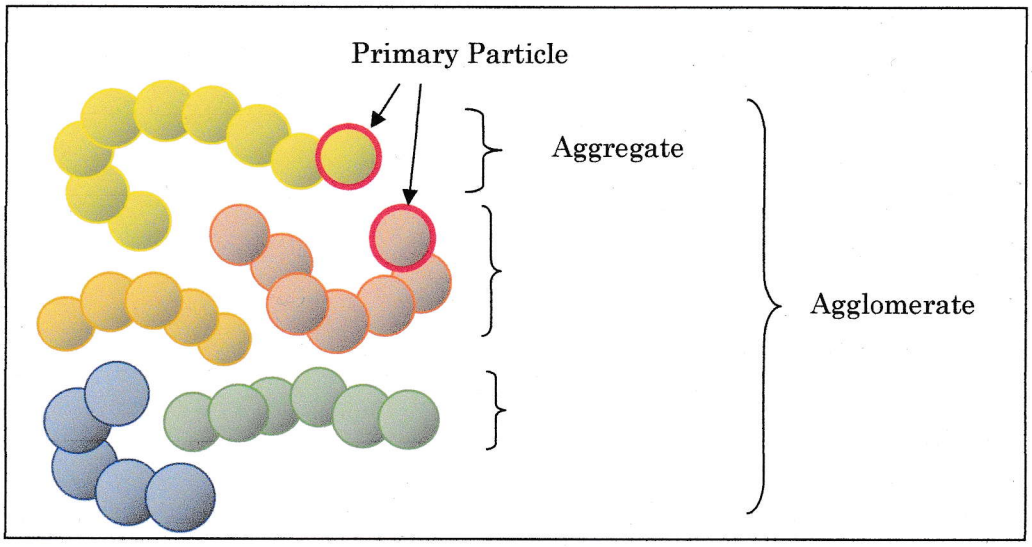

Fig.3-3. Illustrative Primary particle, Aggregate, and Agglomerate of Fumed Silica.

Fig.3-3 show illustrative Primary particle, Aggregate and Agglomerate of Fumed

Silica and Fig.3-4 is SEM image of exact Fumed Silica.

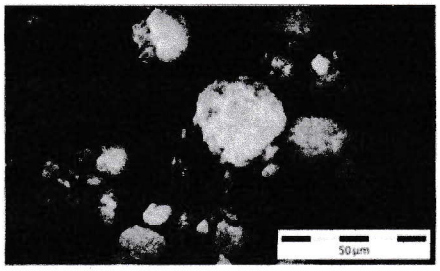

Fig.3-4-1, Agglomerate

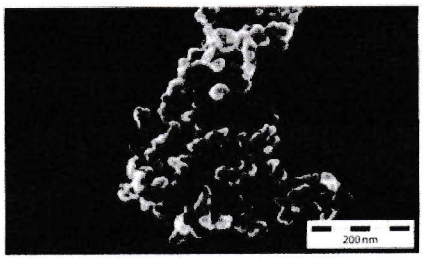

Fig.3-4-2 Aggregate

In Agglomerate, Aggregate of Precipitated Silica (White Carbon), each primary particle, each aggregate coagulated rather strongly than Fumed Silica, so usually Fumed Silica perform better thickening effect in OD system.

Regarding Thickening mechanism, it might be based on hydrogen bonding of Silanol group basically, it was illustratively showed in following Fig.3-4.

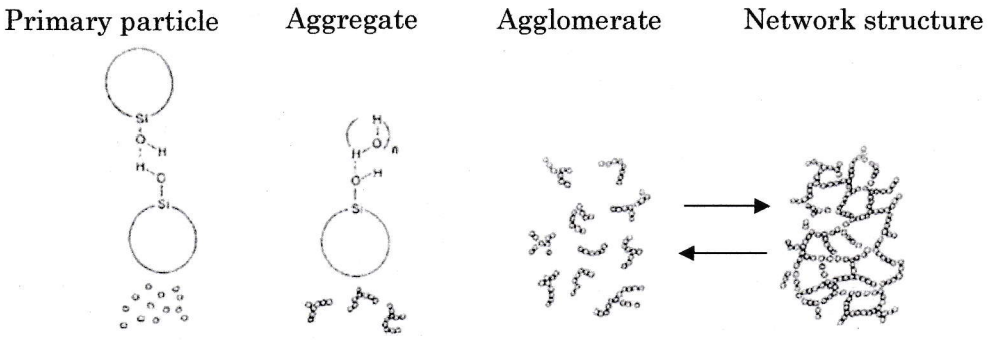

Fig.3-5, Thickening mechanism of Fumed Silica.

Because Fumed Silica show Thixotropic property, Network structure will be composed at Standing but it will be collapse by shaking rather easily.

The Viscosity will be affected by pH of system, usually we can get highest viscosity around 5 to 9 (6 to 8), also viscosity will be affected by Solvent Polarity.
Especially in polar solvent, Silanol group modified Hydrophobic Fumed Silica work well better than normal Fumed Silica.

$$Si-OH \quad \rightarrow \quad Si-O-Si-(CH_3)_2$$

Fig.3-5, Example of Hydrophobic Fumed Silica

3-4-3. Glucose Derivatives, and Others. ~5%

Some Glucose ester, Alkylated cellulose can be dissolved into the oil, and thicken the system. Such most representative product are Dextrin palmitate, Ethyl cellulose.
These products can be applied for OD but usually its dosage looks rather high and viscosity change at various temperature is rather big.

A kind of fatty acid such as 12-hydroxy stearic acid (12-HAS) also make oil Gel easily, and higher fatty acid metal salt are famous as thickener for oil and make Grease. But in case these fatty acid and/or derivatives as thickener will affect emulsibility seriously when OD diluted into the water, and it is not so easy to control viscosity stability as same as Glucose derivatives.

Because of these point, single use of glucose derivative, fatty acid derivative for OD, it looks not easy. But maybe we should consider combination use together with other thickener.

4. Direction for Actual Formulation Study.

4-1. Viscosity stabilization of Solvent at Temperature Change.

For actual OD formulation, maybe we need Thickener, but here we mainly discuss other factors. Following Table shows Theoretical Density Calculation when additives mixed with basic oil OME.

Table-4-1. Calculated density, OME (87g) additives mixture.

Chemicals	Density g/cm^3	Mw	Water content %	Calculated Density, Added Chemical to OME 87g (100ml)				
				1g	2g	5g	10g	20g
OME	0.870			—	—	—	—	—
KCl	1.987			0.875	0.881	0.897	0.924	
$CaCl_2$	2.150	110.98		0.878	0.882	0.899	0.927	
$CaCl_2 \cdot 2H_2O$	1.835	147.01	24.51	0.875	0.880	0.896	0.920	
$MgCl_2$	2.325	95.21		0.876	0.882	0.901	0.930	
$MgCl_2 \cdot 6H_2O$	1.569	203.3	53.17	0.874	0.879	0.892	0.912	
Gluconate Na	1.800					0.895	0.918	0.963
Lactose	1.520					0.891	0.910	
Glycerin	1.260			0.873		0.885	0.897	0.923
Urea	1.320				0.877	0.886	0.902	

The density change of OME mixture is not so big when additives amount is practical range, but some additives make original density of OME bigger as above, sometime we

should consider these additive.

Such as Glycerin, Lactose has Hydroxy group (-OH), sometime it may affect for TC stability, so we should carefully check this point when apply these chemicals.

In case KCl, $CaCl_2$, $MgCl_2$, these are essentially not soluble into the Oil, but these has fairly big solubility into Nonionic surfactant, and viscosity of its mixture will be increased, sometime it will be just like Grease. And such Nonionics / Salt mixture are known as kind of Thickener for Oil, so we sometimes should apply this idea for OD formulation.

Fig 4-1 shows Hydration of water and it is considered as oxonium ion formation.

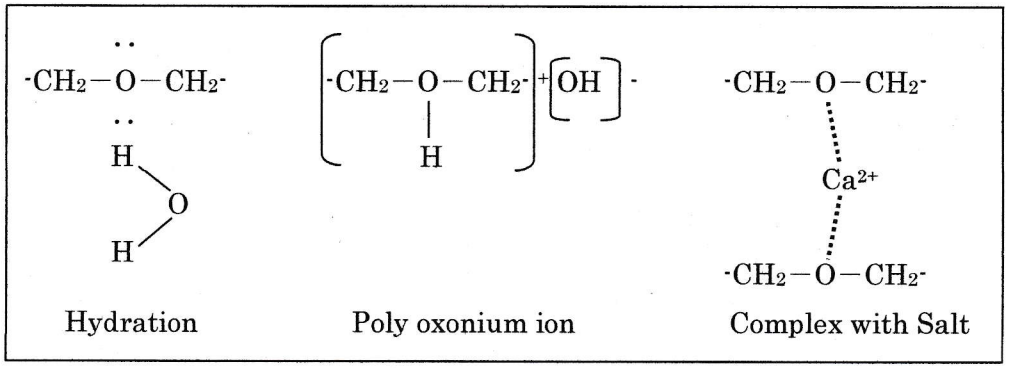

Fig 4-1 Ether Oxygen of Polyoxyethylene type Nonionics

Maybe almost same as above, such as $CaCl_2$ will make complex with Ether Oxygen of oxyethylene group, and make a kind of structure. This mechanism will be supported by reported Crown Ether like Chelating for Metal ions also.

Regarding Emulsifier, dosage for OD is rather big compare with such as normal EC etc., This is because, Emulsifier itself will increase the viscosity of OD system, it will assist some for viscosity stabilization.

4-2. Emulsification of OD.

As we already discussed some at section 3-3, we have HLB different Emulsifier (Tab 3-3), so we can arrange Emulsifier combination under considering HLB of oil (Solvent).

Practically, first we can apply SK-58DH (high HLB), SK-58DL (low HLB) for OME based OD, both Emulsifier contains Anionics (SK-53CA, SK-560EP) and Nonionics (SK-5935, SK-5945,SK-5218CP and Ethoxylated Castor oil).

For Paraffin based oil Emulsification, main emulsifier should be SK-5110 which composed different Nonionics (SK-5935, SK-5945, Castor oil ethoxylated), and some Anionics such as SK-560EP or Anionics contained SK-58DH, SK-58DL.

Following Table is recent OD examples.

Table 4-2, Example of OD, Relation with Solvent, Thickener and Emulsifier.

	1	2	3	4	5	6	7
Dinotefuran	21.00						
Glufosinate		21.00					
Mesotrione			15.50				
Metsulfuron				3.00			
Penoxaden					20.30		
Penoxsulam						5.30	
Pretilachlor							31.60
Pyrazosulfuron							2.06
OME	57.00	61.00		65.60	35.20	68.20	20.84
Soybean oil			55.50				
White oil					30.00		10.00
Glycerin			15.00	13.00		10.00	15.00
OB 838B	1.00	0.50	0.50	0.70	0.50	0.50	1.50
SK-26CR	3.00					3.00	
WC		2.00	0.50	0.70			2.50
Urea	5.00	1.00		2.00			
CaCl2	1.00				1.00	1.00	
12-HAS							0.50
SK-58DH	12.00			12.00	6.00	12.00	8.00
SK-5110		3.00	12.00		7.00		
SK-560EP		5.10					
SK-5218CP		4.00					6.00
SK-5935			1.00				
SK-53CA		2.40					
SK-355							5.00
SK-21K				1.00			
SK-800				1.00			
SK-805				1.00			
Total	100	100	100	100	100	100	103

OB 838B : Organic Bentonite, SK-26CR : Acrylic polymer,
12-HAS : 12 hydroxy stearic acid

Examples are not perfect formulation but we can understood some different way to make solvent thicken, Emusifier arrangement for different solvent combination.

Regarding about TC, usually it is insoluble into the oil, then it might have no relation

with other ingredient in OD. But practical situation might be not so simple, sometime TC will have interaction with other ingredients in OD, we should be very careful about these points also.

5. Estimation of OD.

5-1. Cold Stability

Cold stability (Solidification of Solvent) highly depend on kind of Solvent. Sometime solvent should be combined to perform good cold stability.

5-2. Heat Stability

Heat Stability should be carried out at proper temperature (usually 54 Celsius). Solvent viscosity rather easily become lower at high temperature, and it may cause TC sedimentation easily. So, all possible method should be combined to stabilize viscosity.

5-3. Emulsification into the Water.

OD will be diluted with water before its use, so it must perform good emulsibility into the water. Especially Thickener will affect emulsibility, and it might cause flocculation easily in emulsion. So proper thickener selection, Emulsifier arrangement should be considered carefully.