SOLVAY

asking more from chemistry®

Agrochemical Formulations

About the authors

Leonardo Tagliente has been working for Ametech since 2002. Currently he is in charge of the Export Department. Ametech srl represents and promotes Solvay products by providing marketing, sales and distribution service for various markets, including agrochemical and fertilizers formulations, animal nutrition, emulsion polymerisation and industrial applications.

Valerio Bramati has been working for Rhône- Poulenc, Rhodia and now Solvay since 1977. Currently he is the Technical Manager of the Agro formulation lab in Ospiate di Bollate. Ospiate di Bollate is the main production site of surfactants for agrochemicals of Solvay.

Table of Contents

AMETECH

Main Sales Office
Via Matteotti 62
20092 Cinisello Balsamo (MI)
Italy
www.ametech.it

SOLVAY
asking more from chemistry®

Via Milano, 78/80
I – 20021 Ospiate di Bollate (MI)
Italy
www.solvay.com

Chapter 1

Introduction to Solvay

Asking more from chemistry for 150 years

Established in 1863, Solvay is a global company driven by honored and committed chemists. Having historical anchorage in Europe, Solvay products serve diversified markets worldwide, from consumer goods to energy, with one main aim: to improve quality of life and customer performance. The drive to achieve this aim has resulted in 90 percent of Solvay revenue being generated from businesses that are among the top three global leaders in their fields.

Solvay Novecare

World leader in specialty surfactants, Major player in the polymers, guar and phosphorus derivatives markets.

Main markets

Solvay formulations are used in shampoos, detergents, paints, lubricants, plant protection, mining and oil extraction.

World leader in specialty surfactants

Novecare creates formulations that affect the behavior of fluids. It delivers cleansing, softening, moisturizing, gelling, texturizing, penetrating or dispersing properties. The global network of manufacturing sites and R&I centers allow Solvay to partner with customers in high- growing countries. This continues to focus on developing sustainable solutions. Since 2010, we have been targeting double-digit annual growth. For more information visit www.solvay.com.

Your best partner for tank-mix adjuvants

Solvay is a leading specialty chemical and advanced material, family-owned company, implementing innovative, sustainable, value-creating solutions for its customers.

More than 150 years of rich history and strong expertise

30,000 talented & dedicated employees

Locations in 53 countries to serve customers around the globe

Solid revenues with € 12.4 billion net sales in 2015

Technology leadership to deliver innovations

Wide range of sustainable chemistries

More than 40 years of experience creating high-performance, sustainable solutions in the Agrochemicals market

Solvay innovations improve crop yields with breakthrough formulations applied to plant protection products, fertilizers, seeds and soils.

RIGHT-TO-TARGET TANK MIX

Guar-based, eco-friendly drift-control & tank-mix adjuvants

FORMULATIONS BY DESIGN

- Soprophor® surfactants
- Eco-friendly, safe solvents
- Solutions for oil dispersions
- Glyphosate bio-activators
- Aerosol™

SOIL & WATER MANAGEMENT

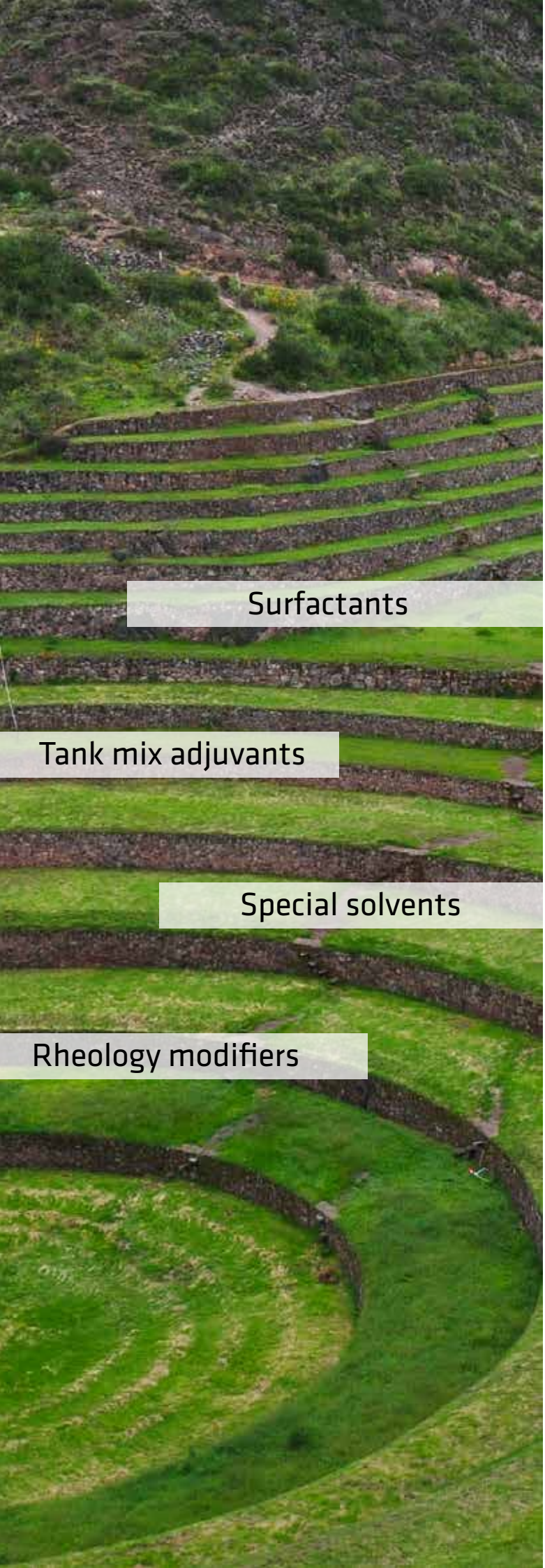
Soil additives to improve plant growth using less water

ENHANCE EFFICIENCY FERTILIZERS

Eco-friendly liquid formulations for nitrogen fertilizer protection

SEED BOOSTING

Unique seed treatment to secure crop potential



Solvay Novecare Agricultural Formulations Business Unit offers a complete range of additives for the crop protection industry to meet your specific needs in terms of performance, cost-effectiveness, safety and environmental protection.

Our R&I Team, either independently or in cooperation with our customers, works to improve the quality and the efficacy of agricultural protection products.

We have been serving the agrochemical industry for more than 40 years and today retain a market leading position. We continue to expand our range of products introducing new, safe, environmentally respectful and cost-effective additives and adjuvants.

Chapter 2

Surfactants and Specialties in Plant Protection

Categories of surfactants

Ethoxylated Castor Oils

Denomination	Ionic Character	Physical form (20° C)	EO Moles	Active Content (%)	HLB Value	Water Content (% Max)	Pour & Melting point (°C)	Applications	Function
Alkamuls R/81	Nonionic	VL	18	100	9.2	0.5	< 0	EC - SE	E
Alkamuls RC	Nonionic	L	22	100	10.5	0.5	< 0	EC - SE	E
Alkamuls 696	Nonionic	VL	13.5	100	8.2	0.5	< 0	EC - SE	E
Alkamuls 14/R	Nonionic	W	58	100	14.9	0.3	35	EC - EW - ME - SE	E
Alkamuls B	Nonionic	L	33	96	11.8	5	5	EC - EW - ME - SE	E
Alkamuls BR	Nonionic	VL	33	100	12.6	0.3	15	EC - EW - SE	E
Alkamuls OR/36	Nonionic	VL	36	100	13.1	0.5	12	EC - EW - ME - SE	E
Alkamuls OR/40	Nonionic	VL	40	100	13.5	0.5	16	EC - EW - ME - SE	E

Ethoxylated Fatty Acids

Denomination	Ionic Character	Physical form (20° C)	EO Moles	Active Content (%)	HLB Value	Water Content (% Max)	Pour & Melting point (°C)	Applications	Function
Alkamuls A	Nonionic	L	6	100	10	0.5	< 0	EC	E
Alkamuls AP	Nonionic	L	4	100	8	0.3	< 0	EC	E

Ethoxylated Sorbitan Esters

Denomination	Ionic Character	Physical form (20° C)	EO Moles	Active Content (%)	HLB Value	Water Content (% Max)	Pour & Melting point (°C)	Applications	Function
Alkamuls T/20	Nonionic	L	20	97	16.7	3	< 0	SL - EC	E - BA
Alkamuls T/80	Nonionic	L	20	97	15	3	< 0	SL- EC-EW	E - BA
Alkamuls T/85-V	Nonionic	VL	20	100	11	1	< 0	EC - EW	E

Dodecylbenzene Sulphonates

Denomination	Ionic Character	Physical Form (20° C)	Active Content (%)	HLB Value	Water Content (% Max)	Pour & Melting point (°C)	Applications	Function
Rhodacal 70/B	Anionic	VL	70	8.6	1	0	EC - ME - EW - SE	E
Rhodacal 60/B	Anionic	VL	60	8.6	1	0	EC - ME - EW - SE	E
Rhodacal 60/BE	Anionic	VL	60	8.3	1	0	EC - ME - EW - SE	E

Adjuvants for Glyphosate

Denomination	For Salt	Ionic Character	Physical Form (20° C)	High Loading Formulation (g/l)	Active Content (%)	Pour & Melting point (°C)	Chemical Family	Function
Geronol CF/AR-E	IPA	Anionic	L	450	70	< 0	Alkylethoxy-phosphate, amine salt	360 SL, 450 SL
Geronol CF/AS 30	IPA	Amphoteric	L	360	40	< 0	Ammonium quaternary	360 SL, 450 SL
Geronol CF/AS 30 HL	IPA	Amphoteric	L	up to 540	40	< 0	Ammonium quaternary	500 SL from IPA salt; 540 SL from acid
Agrho FKC 1500	IPA	Amphoteric	L	up to 540		< 0	Special blends	500 SL from IPA salt; 540 SL from acid
Geronol CF/82 CC	K, IPA	-	L	up to-600 for K	82	-5	Special blends	540 K and all IPA
Geronol CF/010	K, IPA	Cationic	L	up to-540 for K	40	< 0	Ammonium quaternary	540 K

Products for ODs

Denomination	Physical Form (20° C)	Viscosity (mPa.s)	Density (g/cm3)	Water Content (% Max)	Typical Dosage	Applications	Function
Alkamuls VO/2003	L	-	0.99	1	18-25	EC - OD	E for Vegetable oils
Geronol ODessa 01	VL	1000	0.95	1	20-80	one product solution for OD	
Geronol ODessa 05	VL	1300	0.91	1	20-80	one product solution for OD	
Geronol OD 21	VL	3000	0.98	< 0.5	5-25	one product solution for OD	

Categories of surfactants

Etho-propoxylated Block Copolymers

Denomination	Ionic Character	Physical Form (20° C)	Active Content (%)	HLB Value	Water Content (% Max)	Pour & Melting point (°C)	Applications	Function
Antarox B/500	Nonionic	P	100	8.9	0.5	15	EC - SC - SE	E - D
Antarox B/848	Nonionic	VL	100	9.7	0.5	15	EC - SC - ME - SE	E - D
Antarox PL/254	Nonionic	P	100		0.5	43	EC - SC	E - D
Antarox B/800	Nonionic	P	100		0,5	43	EC - SC - ME - SE	E - D
Antarox PL/104	Nonionic	P	100		0,5	44	EC - SC	E - D

Etho-propoxylated Fatty Alcohols

Denomination	Ionic Character	Physical Form (20° C)	Active Content (%)	HLB Value	Water Content (% Max)	Pour & Melting point (°C)	Applications	Function
Antarox FM/33	Nonionic	L	100	8	0.6	< 0	SC - SE	WA

Ethoxylated Fatty Alcohols

Denomination	Ionic Character	Physical Form (20° C)	EO Moles	Active Content (%)	HLB Value	Water Content (% Max)	Pour & Melting point (°C)	Applications	Function
Rhodasurf CET 5	Nonionic	L	5	100		1.5	10		
Rhodasurf ID/5	Nonionic	L	5	100	11	1	4	EC - SC - SE	WA - C - BA
Rhodasurf ID/79	Nonionic	L	7	90		10	< 0	tank mix	BA
Rhodasurf LA/30	Nonionic	L	3	100	8	1	5	Mineral Oil EC - SE	E
Rhodasurf ROX	Nonionic	L	8	85		15	< 0	EC - SC - SE	EWA
Rhodasurf 860/P	nonionic	L	6	100	12	1	3	EC - SC - SE	WA - C - BA

Ethoxylated Tristyrylphenols

Denomination	Ionic Character	Physical Form (20° C)	EO Moles	Active Content (%)	HLB Value	Water Content (% Max)	Pour & Melting point (°C)	Applications	Function
Soprophor TS/10	Nonionic	L	10	100	10	1	< 0	EC - SE - EW	E
Soprophor TS/16	Nonionic	VL	16	100	13	1	18	EC - SC- SE - EW	E - D
Soprophor BSU	Nonionic	VL	16	100	13	1	15	EC - SC - SE - EW	E - D
Soprophor CY/8	Nonionic	P	20	100	14	1	30	EC - ME - SC - SE - EW	E - D
Soprophor S/25	Nonionic	W	25	100	15	1	35	EC - ME - SC - SE - WDG	E - D
Soprophor TS/29	Nonionic	W	29	100	15	1	45	EC - ME - SC- SE - WDG	E - D
Soprophor S/40-Flakes	Nonionic	Pw	40	100	16	2	48	EC - WDG - WP	E - D - C
SoprophorTS/54	Nonionic	P	54	100	17	1	50	EC - WDG - WP	E - D

Etho-propoxylated Tristyrylphenols

Denomination	Ionic Character	Physical Form (20° C)	Active Content (%)	HLB Value	Water Content (% Max)	Pour & Melting point (°C)	Applications	Function
Soprophor 796/P	Nonionic	L	100	13.7	0.5	5	EC - SE	E
Soprophor TSP/461	Nonionic	P	100	9.2	0.5	35	EC - SC- SE	E - D
Soprophor TSP/724	Nonionic	W	100	12.3	0.5	39	EC - SC- ME	E - D

Ethoxylated Tristyrylphenols Phosphates

Denomination	Ionic Character	Physical Form (20° C)	EO Moles	Active Content (%)	HLB Value	Water Content (% Max)	Pour & Melting point (°C)	Applications	Function
Soprophor FL	Amine Salt	VL	16	98	16	2.5	5	ME - SC - SE - WDG - WP	D
Soprophor FL/60	Amine Salt	L	16	60	16	26.0	< 0	SC - SE	D
Soprophor FLK	Potassium Salt	L	16	40	16	5	< 0	SC - SE	D
Soprophor 3D33	Acid	VL	16	97.5	16	2.5	0	EC - SC - SE - WDG - WP	D

Ethoxylated Tristyrylphenols Sulphates

Denomination	Ionic Character	Physical Form (20° C)	EO Moles	Active Content (%)	Water Content (% Max)	Pour & Melting point (°C)	Applications	Function
Soprophor 4D384	Acid	VL	16	100	1	15	ME - SC - SE - WDG - WP	D

Sulphosuccinates

Denomination	Ionic Character	Physical Form (20° C)	Active Content (%)	Water Content (% Max)	Pour & Melting point (°C)	Applications	Function
Geropon DOS/PG	Sodium Salt	L	65	18.0	< 0	SC - SE - SL - WDG	WA - BA
Geropon SDS	Sodium Salt	Pw	85	2.0	-	SE - WDG - WP	WA - BA

Categories of surfactants

Polycarboxylates

Denomination	Ionic Character	Physical Form (20° C)	EO Moles	Active Content (%)	HLB Value	Water Content (% Max)	Pour & Melting point (°C)	Applications	Function
Geropon SC/213	Potassium Salt	Pw	-	90	-	10.0	-	SC - SE - WDG - WP	D - C
Geropon T/36	Sodium Salt	Pw	-	90	-	10.0	-	SC - SE - WDG - WP	D - C
Geropon TA/72	Sodium Salt	Pw	-	90	-	10.0	-	SC - SE - WDG - WP	D - C

Methyl Oleyl Laurates

Denomination	Ionic Character	Physical Form (20° C)	EO Moles	Active Content (%)	HLB Value	Water Content (% Max	Pour & Melting point (°C)	Applications	Function
Geropon T/77	Sodium Salt	Pw	-	67	-	10.0	-	SC-SE-WDG-WP	D - C

Adsorbed Surfactants

Denomination	Ionic Character	Physical Form (20° C)	Active Content (%)	Water Content (% Max)	Applications	Function
Soprophor AMC	Nonionic	Pw	60	3.0	WDG - WP	D - C
Soprophor AS/500	Nonionic	Pw	50	4.0	WDG - WP	WA - C
Soprophor K/202	Nonionic	Pw	50	4.0	WDG - WP	WA - D - C

Phenylsulphonates

Denomination	Ionic Character	Physical Form (20° C)	Active Content (%)	Water Content (% Max)	Pour & Melting point (°C)	Applications	Function
Supragil GN	Sodium Salt	Pw	70	6.0	-	SC-SE-WDG-WP	D

Alkylnaphtalene Sulphonates

Denomination	Ionic Character	Physical Form (20° C)	Active Content (%)	Water Content (% Max)	Pour & Melting point (°C)	Applications	Function
Supragil GN	Sodium Salt	Pw	70	6.0	-	SC-SE-WDG-WP	D

Condensed Alkylnaphtalene Sulphonates

Denomination	Ionic Character	Physical Form (20° C)	Active Content (%)	Water Content (% Max)	Pour & Melting point (°C)	Applications	Function
Supragil MNS/90	sodium salt	Pw	90	8.0	-	SC-SE-WDG-WP	D
Supragil RM/210-EI	sodium salt	Pw	85	8.0	-	SC-SE-WDG-WP	D
Supragil MNS/88-E	sodium salt	Pw	88	8.0	-	SC-SE-WDG-WP	D

Special Blends

Denomination	Physical Form (20° C)	Active Content (%)	HLB Value	Water Content (% Max)	Pour & Melting point (°C)	Applications	Function
Geronol FF/4	VL	68	10	1	< 0	EC - EW - SE	E
Geronol FF/4-E	VL	68	9	1	< 0	EC - EW - SE	E (high flash)
Geronol FF/6	VL	92	13	1	16	EC - EW - SE	E
Geronol FF/6-E	VL	83	13	1	15	EC - EW	E (high flash)
Geronol MS	VL	92	15	1	15	EC - EW	E
Geronol TE/250	VL	100		1	15	EC - EW - ME	E (high flash)
Geronol TE/300	P	92	14	1	35	EC - EW - ME - SE	E (high flash)
Geronol TE/777	VL	90	12	5	13	EC - EW - ME - SE	E (high flash)
Geronol TEB 25	VL	93		1	15	EC- EW - OD	E (high flash)
Geronol VB/2000	VL	93	11	1	15	EC	E (high flash)
Geronol TBE 724	P	84	10.7	1	22	EC - SE	E (high flash)
Geronol Sol 90	L	90	9.7	1	< 0	OD - EC	E (high flash)

Special Solvents

Denomination	Flash Point (°C)	Density at 20° C	Water Content (% Max)	Solubility
Rhodiasolv RPDE	100	1.09		Soluble in water
Rhodiasolv ADMA 10	> 110	0.88	0.5	
Rhodiasolv ADMA 810	> 110	0.88	0.5	
Rhodiasolv Green 21	> 65	1.02	0.5	Insoluble in water, soluble in most polar and aromatic solvents
Rhodiasolv Green 25	> 77	0.99	0.5	Insoluble in water, soluble in most polar and aromatic solvents
Rhodiasolv MATCH 111	> 61	0.99	0.2	Insoluble in water, soluble in most polar and aromatic solvents
Rhodiasolv Polarclean	> 144	1.01	0.1	Powerful polar, water soluble solvent
Rhodiasolv Li-Tec 2V	> 90	1.067	0.1	

Categories of surfactants

Tank mix adjuvants		
Denomination	**Nature**	**Actions**
Agrho Ultimate	Water based	Drift control, deposition/retention aid booster, water conditioning, wetter
Agrho WA 20	Blend of surfactant	Booster, penetrant, wetter
Agrho Starguar	Oil based	Drift control, deposition/retention aid
Rhodasurf ID/79	Surfactant	Wetter, penetrant aid, booster
Agrho FKC 1000	Surfactant	Wetter, penetrant aid,booster
Agrho Versa Twin	Emulsion	Deposition/retention aid, booster
Agrho AMSO	Oil based	Booster, water conditioning
Agrho DEP 775	Pure guar granulated ready-to-use	Anti-drift, anti-bouncing, retention aid

Rheology modifiers					
Denomination	**Physical Form (20° C)**	**Bulk Density**	**Water Content (%max)**	**Viscosity (mPas 0.3 % Brookfield)**	**Applications**
Rhodopol 23	Powder	0.8	13	2000	SC - SE - EW
Rhodopol 50 MC	Powder	0.8	13	1000	SC - SE - EW
Rhodopol G	Granules	0.7	14	2000	SC - SE - EW
Rheozan	Powder	0.8	13	4000	SC - SE - EW

Abbreviation	Stands for
BA	Biological Activator (Adjuvant)
C	Compatibility Agent
D	Dispersing Agent
E	Emulsifier
EC	Emulsifiable Concentrate
EW	Emulsion in Water
FS	Flowable concentrate for seed treatment
IPA	Isopropyl Amine
L	Liquid
K	Potassium
ME	Micro-Emulsion
OD	Oil Dispersion
P	Paste
PW	Powder
SC	Suspension Concentrate
SE	Suspo-Emulsion
VL	Viscous Liquid
WA	Wetting Agent
WDG	Water Dispersible Granule
WP	Wettable Powder

Chapter 3

Tank Mix Adjuvants

An adjuvant is any additive used with a pesticide to increase biological activity and/or to modify various physical properties of a spray solution.

The expansion of world agriculture production will be one of the most demanding challenges of the future. This will require a more intensive agriculture with a greater chemical input of crop protection products. Tank mix adjuvants will play a leading role to improve performance, effectiveness and consistency of the pesticide treatments by reducing the amount of fine spray particles that carry pesticide out of target areas.

Adjuvants

Goals of tank mix adjuvants

1. Reduction or minimization of pesticide losses
2. Enhancing or maximizing the effect of pesticideS

Categories of tank mix adjuvants

We can divide tank mix products in two main categories:

Activators
Spray adjuvants are used to enhance the biological efficacy of pesticides.

Utility / Spray modifiers
Spray adjuvants are used to modify the physical characteristics of the spray mixture.

Adjuvants actions

Wetter / Penetrator
Enhances uptake of pesticides through plant target surfaces.

Spreader / Sticker / Extender
Combines spreading and adhesive qualities to improve coverage and retention of pesticides.

Water Conditioning Agent
Reduces the antagonistic effects of impurities (Ca, Mg, Mn, Fe, etc.) found in water carrier, which results in greater pesticide efficacy.

Compatibility Agent
Improves stability and dispersion of various pesticide formulations and spray carrier mixtures.

Humectant
Increases the drying time of spray solutions which provides greater time for the pesticide to enter the targets surface. It is used during high temperature, low humidity and low spray volume situations.

Drift Agent
Reduces the amount of fine spray particles that carry pesticide out of target areas.

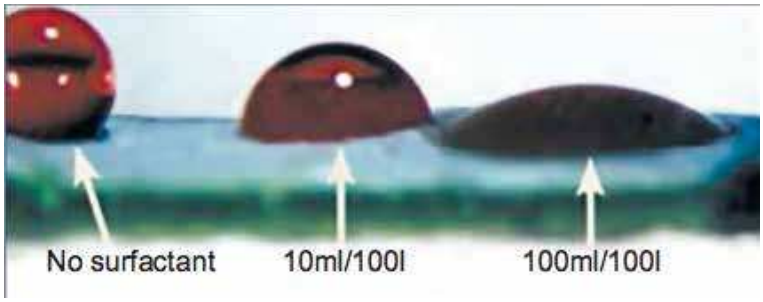
Buffer Agent / Acidifier
Generally lowers the pH of the spray solution and reduces rapid changes in pH, either higher or lower. Reduces the degradation of pesticides by chemical hydrolysis.

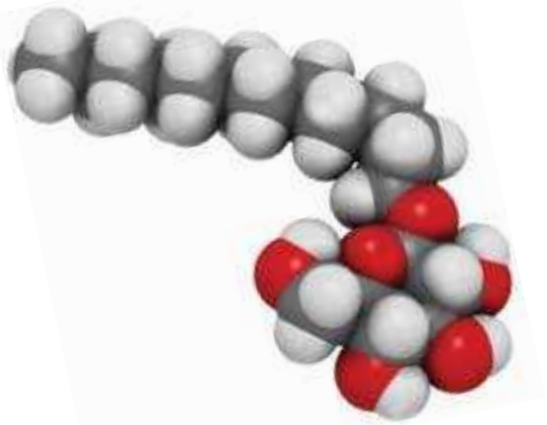
Deposition / Retention Aid
Reduces the amount of fine spray particles that carry pesticide out of target areas (Guar). Reduces evaporation of the spray droplet. It is used during high temperature, low humidity and low spray volume situations.

Nasturzio (Tropaeolum majus), garden nasturtium is an example of hard-to-wet plants.

Surfactant Adjuvants

Surfactants act as spreaders or wetting agents reducing surface tension between the spray solution droplets and the target plant, thus providing greater coverage.



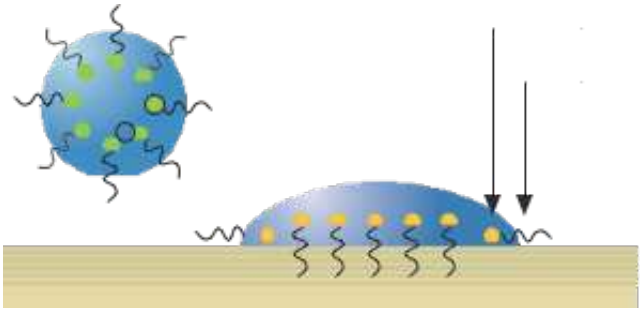


Surfactants make up by far the largest group of spray adjuvants. In agricultural applications, non-ionic (having no net electrical charge) surfactants (NIS) make up the majority of products, although a number of formulations utilize anionic surfactants to assist in dispersibility of formulations in a dry form. They are characterized by a hydrophobic tail and a hydrophilic head.

Hydrophobic Tail
Hydrophillic Head

Surfactant adjuvants are very useful because droplets with a high surface tension will be more likely to bounce off target surface, while those with a low surface tension will tend to spread on contact and be retained.

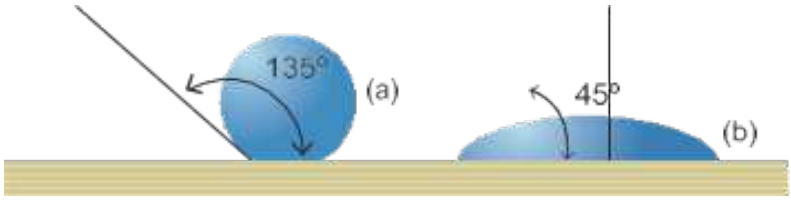
The below picture describes how surfactants reduce the surface tension and spread the droplet.



Interaction of hydrophilic and lipophilic parts of a surfactant to reduce surface tension and spread the droplet

(Source: Devine et al., 1993 adapted by Hall, 1999)

Surfactants reduce the contact angle as well. This will help difficult-to-wet leaves to have more contact with the solution of pesticide and improve its uptake.



Contact angle of droplet on a difficult-to-wet leaf surface without (a) and with (b) surfactants

Adjuvants

Rhodasurf ID/79
(Isodecyl alcohol ethoxylate 900 g/l)

A surfactant that increases the wetting and spreading properties, as well as the uptake of spray solutions on plant foliage, and enhances the activity of herbicides and insecticides. To be applied in post-emergence herbicide at a rate of 0.075 % - 0.1 %. In 100 l spray mixture dosage is 75 ml - 100 ml.

Agrho WA 20

Agrho WA 20 is a very well designed blend, consisting of:

- Sorbitan derivatives providing wetting and spreading properties, permitting a superior distribution of the spray over the plant foliage.
- An amine derivative granting an improved adhesion to leaves surface, facilitating the penetration of the pesticide into the plant through the wax and cuticle layers.
- An organic buffer improving the water quality.

The interaction of above mentioned components lead to an ultimate synergism providing outstanding results.

Application rate is 0.1 - 0.15 % for volume of water of 100-200 liter per ha for treatment with selective herbicides in cereal or rapeseed such as Sulfonylureas and Glyphosate, with contact fungicide (Chlorthalonil) and systemic fungicide (Triazoles, Morpholines, Strobis). In case of application of high volume of water (over 500 l per ha, typically in tree crops) the rate can be lower (0.025 -0.05 %). Agrho WA 20 is a low viscous product, easy to mix with water and it is particularly indicated to enhance effectiveness of crop protection products under adverse conditions (resistant weed or severe climatic conditions).

Thanks to increased penetration and faster uptake, Agrho WA 20 improves rainfastness of treatment which avoid the wash off in case of rains.

Amepon BP 27

It is an adjuvant applied with cereal herbicides containing alkylethersulfate sodium salt.

Application rate is max 1 %.

Amesurf H 77

It is a super wetter surfactant based on organomodified siloxane (trisiloxano ethoxylated) technology for pesticide spray applications. It is a highly effective, nonionic wetting agent/ spreader/ penetrant by lowering the surface tension of spray solutions. Thanks to its super spreading activity, the contact angle of spray solution is reduced, improving the spray coverage and the wetting of waxy leaves for a better penetration into the plant canopy. Therefore, it is extremely suitable to be used with all agricultural chemicals including fungicides, insecticides, miticides and foliar micro-nutrients.

The a.m. action promotes a faster uptake of the agrochemicals solution via stomatal infiltration and improves rainfastness.

Key Benefits

1. Excellent spreading characteristics
2. Pesticide uptake guarantee
3. Rainfastness Improvement

Application	Typical Application Rate
Plant growth regulators	0.025 % to 0.05 %
Herbicide	0.025 % to 0.15 %
Insecticide	0.025 % to 0.1 %
Fungicide	0.025 % to 0.05 %
Fertilisers and Micronutrients	0.025 % to 0.1 %

Product data	
General Characteristics	Value
Appearance	Clear Fluid
Viscosity, dynamic at 25° C	15 - 25 mPa.s
Density at 25 °C	1.013 - 1,027 g/cm3
Cloud point (1 % in water)	< 20° C
Flash point	105° C
Surface tension 0.1 % in H2O at 25 °C	20.5 mN/m

Alkamuls SB 10

It is a natural adjuvant for herbicide, insecticide, and fungicide. It is an oil based surfactant (soybean oil etoxylated).

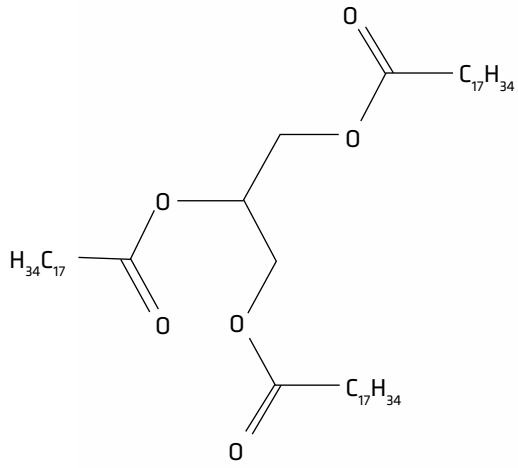
Oil Adjuvants

The main functions of oil adjuvants are:

- Enhancing the penetration of systemic pesticides into plants through the leaf cuticle and insects
- Reducing evaporation of spray droplets from the sprayer
- Increasing spray Retention/Deposition and extention of the active life of certain herbicides, insecticides and fungicides on plant surfaces.

Emulsifiable Crop Oil Concentrates (COC)

A combination of vegetable oil and surfactants/ emulsifiers acting as penetrants, stickers, humectants, etc.



Triglyceride ester oleic acid

Main characteristics

1. Non-phytotoxic oils + surfactants
2. Generally 80-95% oiland5-20% surfactants
3. Boost of spreading/ wetting function, thanks to the surfuctant component
4. Increase in spray Retention/Deposition
5. Increase in penetration through the leaf cuticle
6. Generally more effective than nonionic adjuvants in low humidity, on drought- stressed and/or larger weeds

Emulsifiable Methylated Crop Oil Concentrates (MOC)

An emulsifiable methylated seed oil + surfactants, acting as penetrants, sticker and humectants.

Main characteristics

1. Methylated seed oils + surfactants
2. Boost of spreading/ wetting function, thanks to the surfuctant component
3. Better effect than crop oil concentrates
4. Very low evaporation rate, enhances spray retention and uptake
5. Easer penetrates to plant cuticle
6. Protection against UV degradation
7. The most active chemical structure in adjuvants
8. Good performance under dry stressed conditions

Amesolv CME Plus

it is methylated canola oil based adjuvant with a very well designed emulsifier system to form a stable emulsion in water.

Main actions

1. It forms a consistent spray by reducing the number of very fine droplets (< 100 mi- cron).
2. It improves spreading of the solution to the leaf, due to reduction of surface tension.
3. It accelerates the penetration of the active ingredient into the leaves, limiting evaporation of the spray solution.

Guar Based Adjuvants

What is Guar Polymer?

Guar gum is an important component of another type of tank mix adjuvants. It comes from guar plant, also known as cluster plant. This plant grows mostly in Pakistan and north India. Guar Gum modified polymers (galactomannan polysaccharide) is extracted from the seed of guar plant. This polymer is widely used in personal care as well as hair conditioners.

Main actions

1. Drift control of the spray
2. Maximization of deposition retention aid (anti-bouncing)

The drift control is directly related to the spray droplet distribution: drift is minimized when drops below 150 µm are reduced.

The coverage is maximized when the greatest amount of spray atomized is between 150 and 400 µm.

As a final result, tank mix adjuvants containing guar gum reduce the amount of fine spray particles that carry pesticide out of target areas.

DRIFT, How far will particles go?			
Droplet	Diameter (in µm)	Time to f all 3 m	Travel distance in 5 km/h wind
Fog	5	66 min	4.8 km
Very Fine	20	4.2 min	340 m
Fine	100	10 sec	13 m
Medium	240	6 sec	8 m
Guar Zone	400	2 sec	2.5 m
Fine Rain	1,000	1 sec	1.5 m

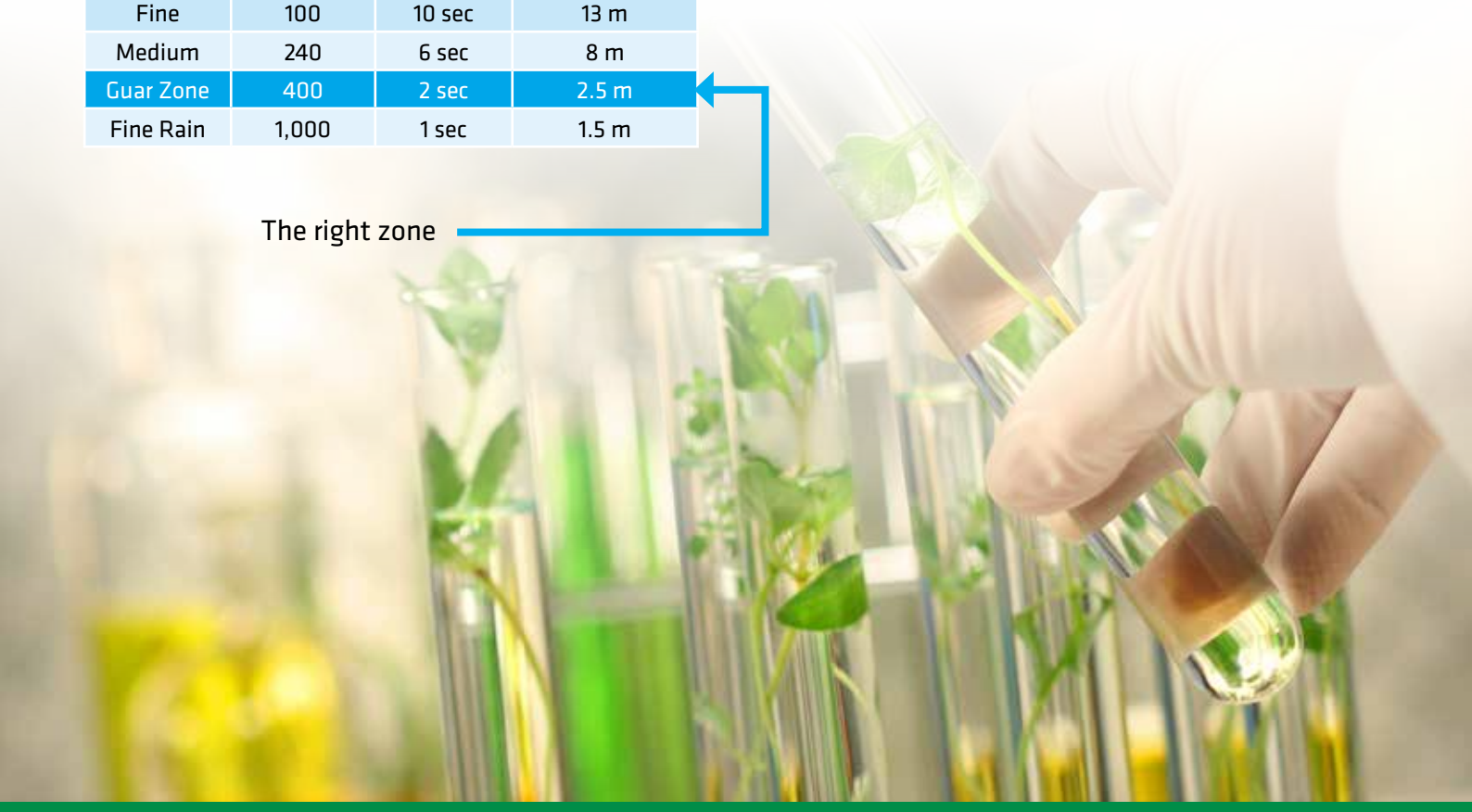
The right zone

Users visually notice a remarkable difference

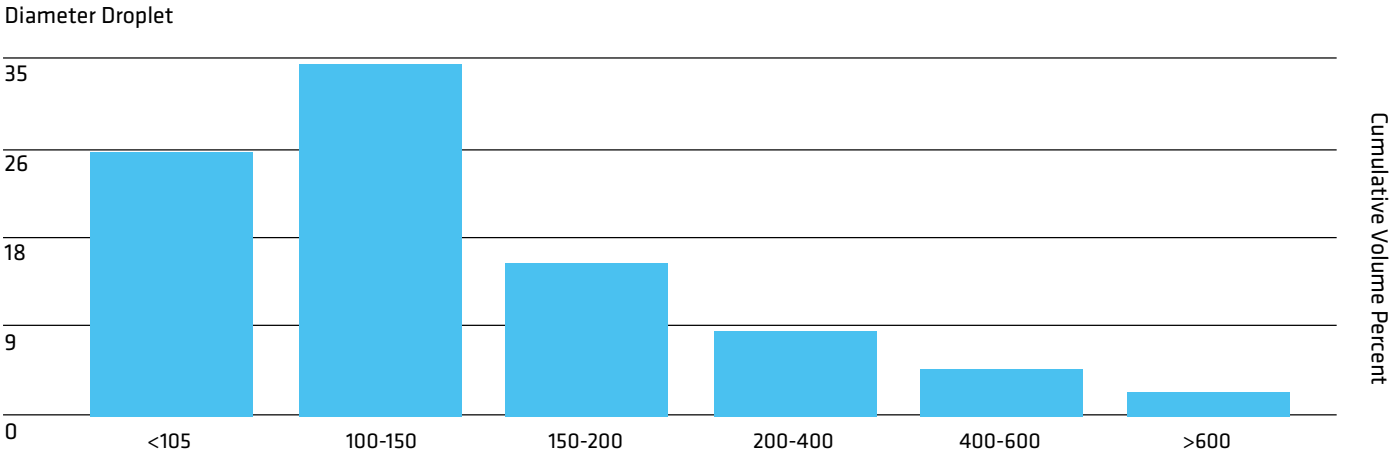
Without Guar

With Guar

Pesticide drift (source: www.epa.gov)
The physical movement of pesticide droplets or particles through the air from the target site to any non-target site Droplets sensitive to drift: < 150 microns

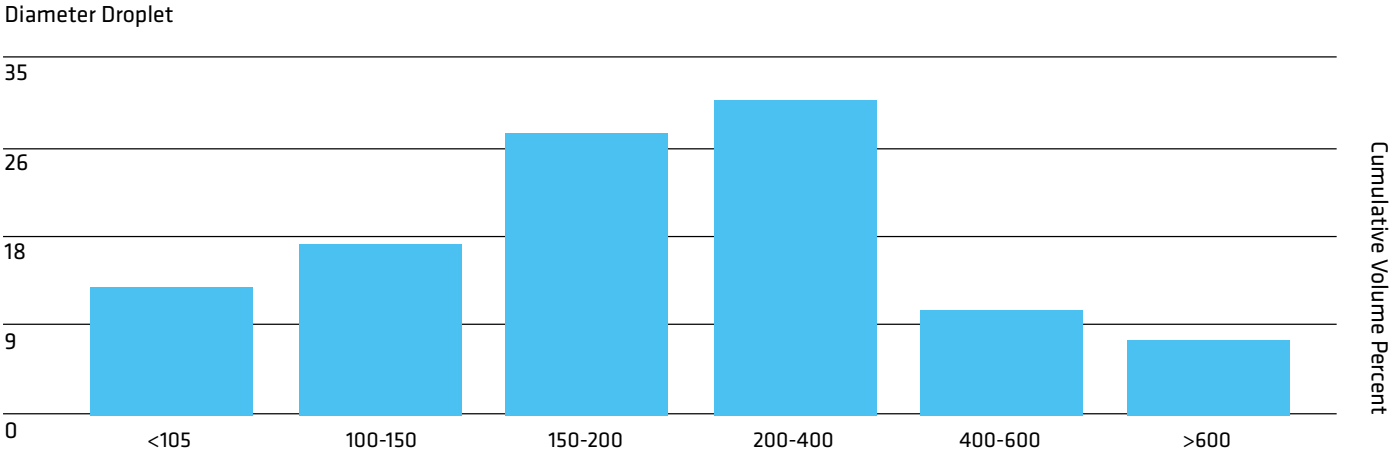


Distribution of droplets size in a standard pesticide solution



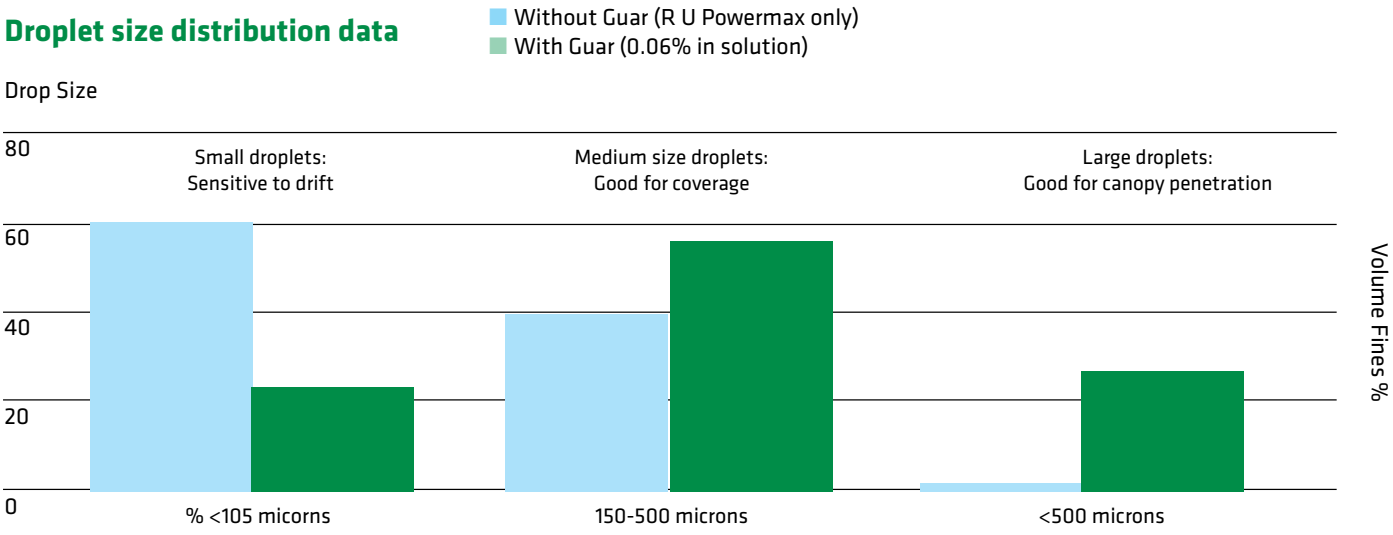
Over 60 % of the droplets are bellow 150 micron = Droplet sensitive to drift

Distribution of droplets size in a pesticide solution with Guar



1. reduction of fines
2. move to bigger droplet

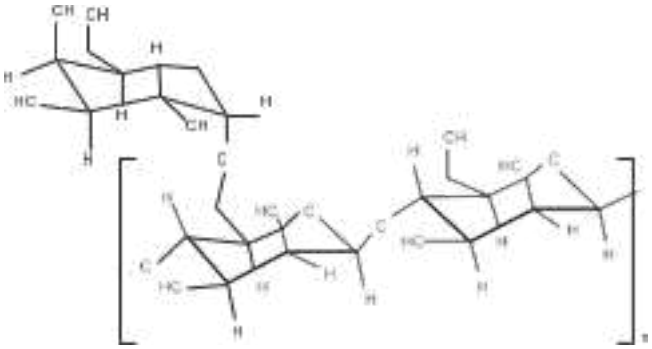
Droplet size distribution data



Adjuvants

Guar controlling droplet

Controlling the impact of drops onto solid surface is important for the treatment of herbicide and pesticides for a precise targeting.



The oiler wax-like layer of leaves is a non -wetting substrate that causes sprayed droplet to rebound; often less than 50 % of the initial spray is retained by the plant. By adding a flexible polymer such as guar gum to the aqueous phase, we can inhibit droplet rebound in a hydrophobic surface and improve deposition without altering the shear viscosity of the solutions.

Anti-bouncing action of Guar gum derivatives

WIthout Polymer

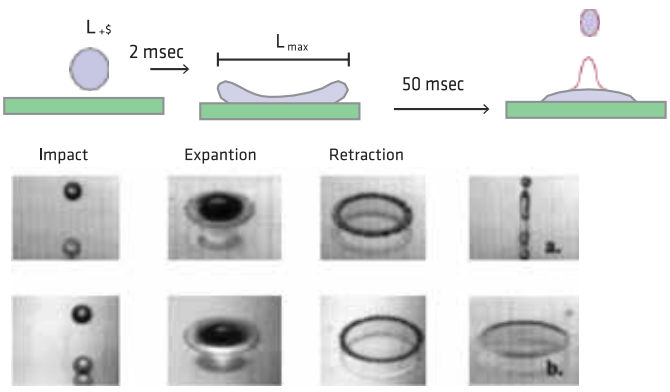
WIth Polymer

Picture 1 shows how spray behavior changes by using two tank mix adjuvants containing guar: high velocity drops impact in foliar surface, expand and subsequently retract and drop rebounds off the surface.

A droplet rebound from foliar surface can be markedly suppressed by small amount of a guar polymer contained in our tank mix adjuvants.

		Oil based: Agrho Starguar	Water based: Agrho Ultimate
	Water	Oil-Guar	AQ-Guar
t = 0 ms			
t = 2.6 ms			
t = 9.3 ms			
t = 29.3 ms			
t = 56 ms			
t = 96 ms			

High speed photography (picture 2) reveals similar impact and expansion stage of both pure water and spray containing our guar based tank mix adjuvant, Agrho Starguar. By contrast, the retraction phase is very different for the pure water: the drop retracts violently, leading to ejection of part of the droplet from the surface, normally referred as drop rebound. With Agrho Starguar the drop retracts much more slowly and remains deposited on the surface.



picture 2: behavior of spray

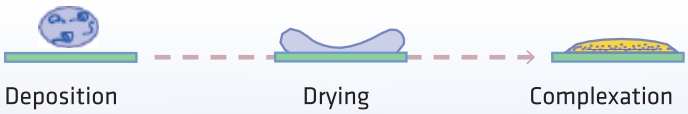
Straight Guar derivatives

Agrho DEP-775

it is 100 % guar polymer formulated in a ready to use extruded granules easily dispersible in water at a rate of 60 g/100 litres of water. The polymer is activated when hydrated and is highly compatible with all the formulations and crop protection products. Major advantages of Agrho DEP-775:

- Control of 2 antagonistic effects, Drift and retention, resulting to an improved delivery
- Control of the Retention/Adhesion by film- formation
- Stable effectiveness vs. shear (when pumping, mixing, spraying, impacting)
- Versatile solvent-free formulations
- Rainfastness with an improved resistance to wash-off

Once the droplet has reached the target (after drift control and rebound), and the droplet deposit covers the leaves, Agrho DEP-775 additive can form a film by producing a complex when drying.



Multi-functional tank mix adjuvants

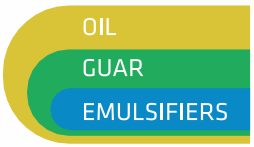
Thanks to its formulation know-how, Solvay has developed a new generation of multi- purpose tank mix adjuvants by combining few components in a single product and bringing innovative features in all-in-one solution.

The basic concept is to take advantage of specific drift control technologies and combine them in formulated liquid tank mix adjuvants, exhibiting multifunctional benefits.

Oil based multifunctional adjuvants

Rather difficult formulation challenges have been overcome by combining vegetable oil or its esters with guar derivatives showing symbiotic effects and resulting in outstanding performance in the field.

Agrho Starguar



This adjuvant is based on oil carrier with a specific surfactant system and a stabilized anti-drift/ anti-rebound polymer.

It is an ideal adjuvant to maximize performance of post-emergence herbicide requiring oil-based enhancer such as Clethodim, Quizalofop, Mesosulfuron, Indo-sulfuron methyl and Pyroxsulam.

Recommended application rate: 0.5 - 0.75 %

Starguar™

Advantages

- Enhanced penetration
- Efficacy booster
- Deposition retention aid
- Anti-bouncing
- Drift control
- Reducing fines
- Right to the target product

Agrho AMSO

This product is an oil based multi-functional tank mix adjuvant with the following main components:

- An oil carrier
- Designed surfactant system
- Humectant and water conditioning agent

This is ideal for Clethodim. Reduction in efficacy of Clethodim by sodium bicarbonate in spray solution is effectively overcome by addition of a crop oil concentrate to ammonium sulphate.

Agrho Versa Twin

Homogeneous liquid oil based adjuvant, with a sophisticated surfactant system, oil and antidrifting agent.

Main actions:

- Coverage
- Efficacy booster
- Deposition/retention aid

Recommended application rate: 0.3 - 0.5 %.

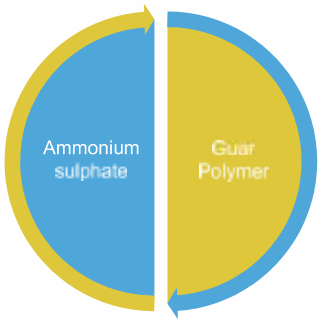
Water based multifunctional adjuvants

Agrho Ultimate

It is a water based adjuvant with specific wetting and penetrating effects containing a stabilized anti-drift/ anti-rebound polymer, water conditioner and humectant.

Agrho 460

It is an ammonium sulphate and guar polymer stabilized in water.



Main actions:

- Humectant and water conditioner
- Deposition /retention aid
- Antidrifting

Coverage Efficacy booster

Deposition/retention aid Recommended application rate: 0.3 - 0.5 %.

Application of water based multifunctional adjuvants
Water based multifunctional adjuvants are ideal to maximize performance of following herbicides where antagonism from mineral salts in the water can affect their performance:

- Roundup, Cornerstone, etc. (Glyphosate)
- Liberty, Liberty ATZ (Glufosinate)
- Banvel, Clarity, Distinct, Sterling (Dicamba)
- 2-4-D amine
- MCPA amine
- Imazethapir
- Clopyralid
- Dichlorprop
- Picloram
- Mecoprop
- Bentazone
- Pyrasulfotole

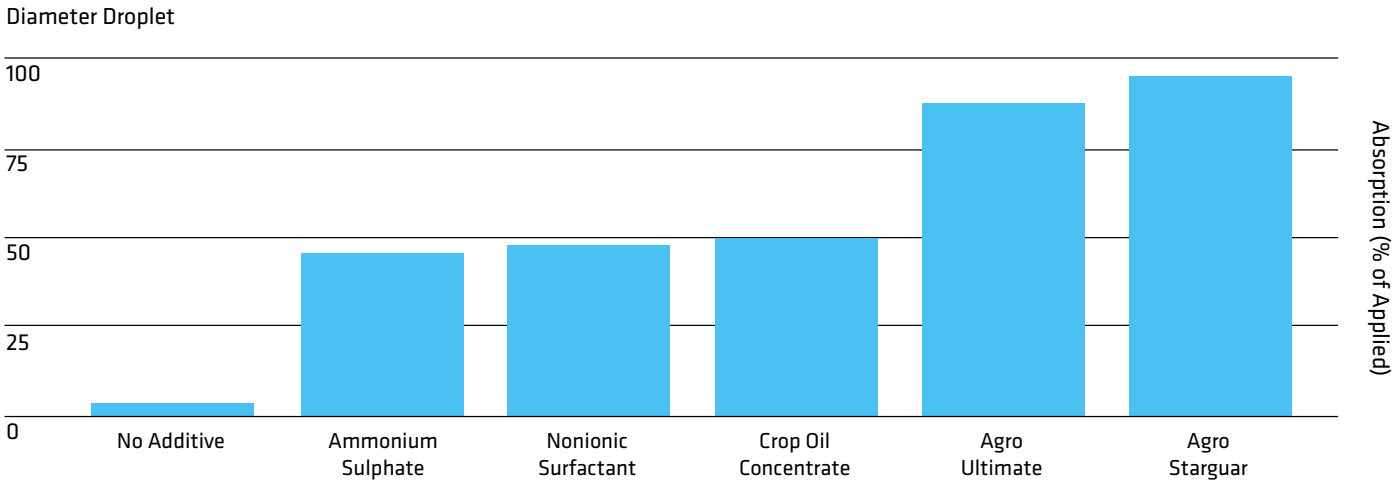
Recommended dose rate: 0.5 - 0.75 %

Importance of spray additives

As it is clearly shown in the diagram below, tank mix adjuvants have a great impact on pesticide effectiveness. Solvay has moved a step ahead with multifunctional additives by adding Guar polymer to traditional and standard tank mix adjuvants components. The result is “all- in-one” new generation activator products with outstanding properties and improved effectiveness and performance in the field.

Non-ionic surfactants provide better crop tolerance during high humidity conditions comparing to oil based adjuvants. Meanwhile, methylated seed oil based adjuvants provide better control during very dry conditions compared to nonionic surfactants or conventional crop oil concentrates. Nonionic surfactants work well with Roundup while oil based surfactants inhibit its performance.

Foliar absorption of pursuit (Imazethapyr) and surfactants



Chapter 4

Emulsifiable Concentrates - EC

Due to the operator exposure concerns and solvent VOC emissions, ECs are less and less used. But the use of "new green solvents and emulsifiers" has recently given new opportunities to EC formulations.

Emulsifiable Concentrates (EC), despite the evolution of other up-to-date formulations, are still used worldwide due to their simple manufacturing process and lower costs. For application in the field, such formulations are diluted in water, forming oil-in-water emulsion which allows a homogeneous distribution of active ingredients on crops. Emulsifiable concentrates have some advantages when compared to other formulations:

- Low cost of production
- Very simple technology
- Often better biological activity

Despite some disadvantages such as:

- High amount of solvents
- Often low flash point
- High dermal toxicity
- Packaging disposal

These disadvantages can be partially overcome by choosing high flash point solvents and a new packaging technology such as "gel-in-water soluble bags". However, the formulations will always contain solvents.

Emulsifiable Concentrates

Formulations

Emulsifiable Concentrates generally contain:
Active Ingredients

- Solvents / Co-solvents
- Emulsifiers
- Stabilizers, stickers, antifoam.

Active ingredients (A.I.)

Active ingredients have to be chemically stable and soluble in the solvents to obtain a suitable active content.

Solvents / Co-solvents

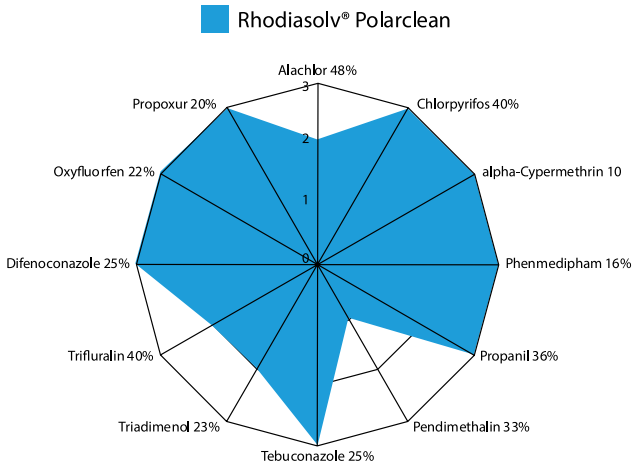
Aromatic and paraffinic solvents such as Xylene and Solvesso are still widely used in EC. To ease the storage, handling and transportation, high flash point solvents such as Solvesso 150 and Solvesso 200 are used along with new solvents with a more favorable eco-toxicological profile.

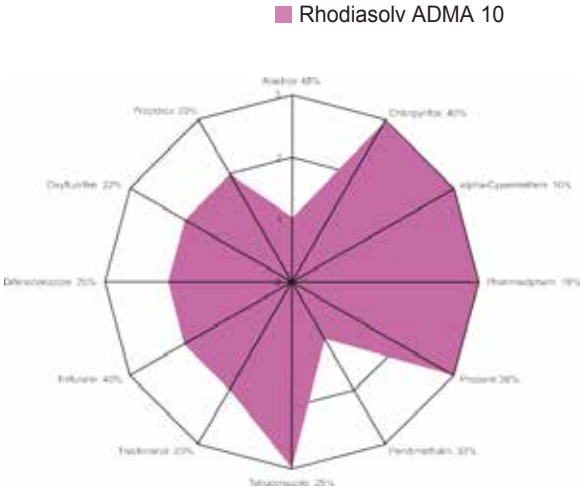
When the solubility of A.I. in aromatic solvents is not sufficient to obtain a suitable active content, it is necessary to add a polar solvent. In the past the most common co-solvents used were Cyclohexanone, Isophoron and N-methylpyrrolidone. Nowadays they have been replaced by a new generation of solvents with better eco-toxicological properties.

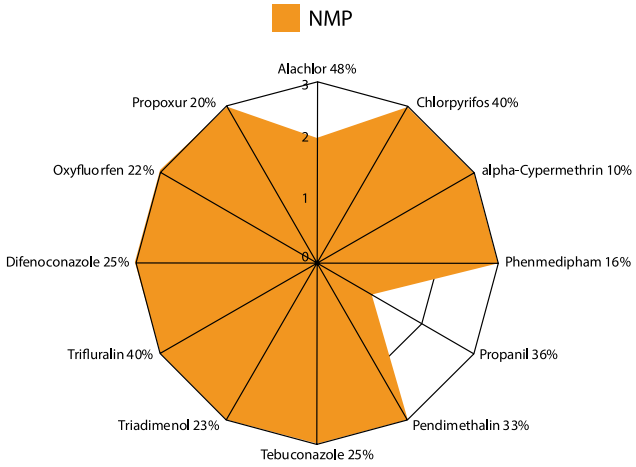
Rhodiasolv Polarclean

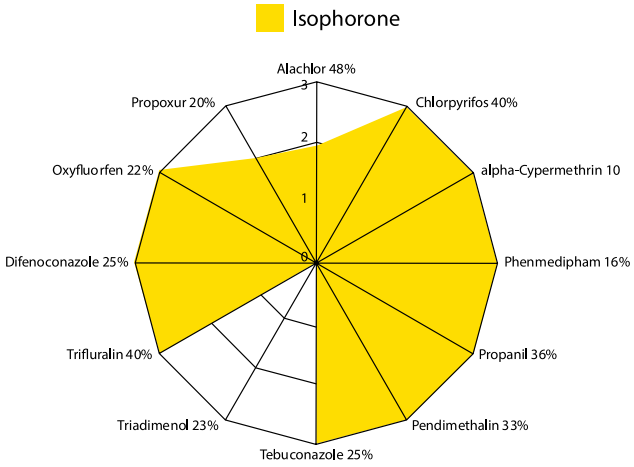
Solvay has recently developed a new solvent, Rhodiasolv Polarclean. It is a powerful ester amide polar water soluble solvent with outstanding properties. The following diagrams show the solubility of various agricultural A.I. in Rhodiasolv Polarclean compared to other solvents:

a. Harmful but effective agrochemical solvent such as N-M Pyrrolidone
b. Other amides commonly used in agrochemicals (Rhodiasolv ADMA 10 and ADMA 810)
c. Other esters such as 2 ethyl hexyl lactate









Application test on market products:
1. not soluble
2. stable 7 day at room temperature
3. stable 7 day at 0° C
4. stable 7 day at 0° C with seeding

Emulsifiable Concentrates

By using the method of solubility parameters, it is possible to choose the solvent system more quickly and with better accuracy.

For the "solubility test" we use the following solvents:

- Solvesso 150-ND
- Xylene
- Amesolv CME (methyl ester of canola oil)
- Rhodiasolv Polarclean
- Rhodiasolv Green 21 & 25 (blended)
- Rhodiasolv RPDE & IRIS (diester)
- Rhodiasolv Match 111 (blended)
- Rhodiasolv ADMA 10 (decanamide)
- Rhodiasolv ADMA 810 (octa/decanamide)
- Cyclohexyl acetate
- 2,Ethyl Hexyl acetate

If soluble, we perform a cold stability test: solution is stored for 1 week at 0° C with seeding.

Rhodiasolv MATCH 111

It is particularly suitable to replace dangerous solvents such as Isophoron , Cyclohexanone and in some cases N-Methyl Pyrrolidon providing a safer and more favorable eco-toxological formulation.

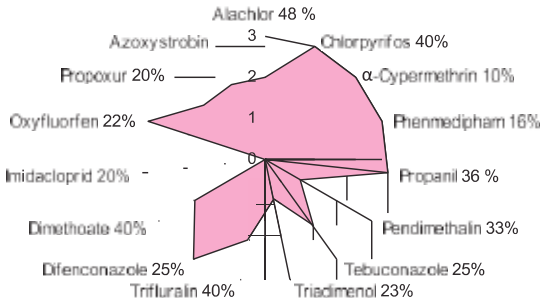
Characteristics of Rhodiasolv MATCH 111	
Appearance	Clear liquid
Flash point	> 61°C
Pour point	< - 5°C
Density (20° C)	0.99
Water content	0.2%

Solubility: Dispersible in water and soluble in most polar and aromatic solvents

Hansen Parameters of Match 111			
G	D	P	H
20.4	16.3	8.5	8.6

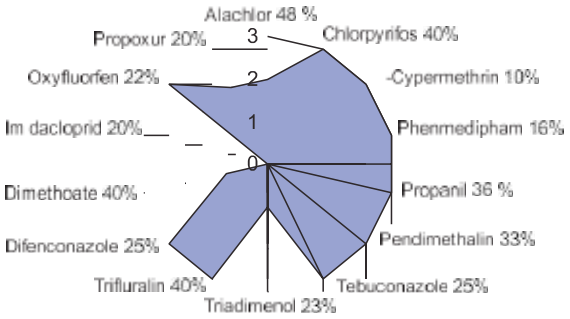
Solubility tests in few formulations

Match 111 - solubility test



Solubility diagram of Isophoron is very close to Match111

Isophoron - solubility test



Emulsifiers

One or more hydrophilic nonionics surfactants will have to be balanced with a lipophilic anionic one in the formulation.

Screening of the suitable emulsifiers

According to a very well-known method, two solutions should be prepared:

Solution A: a solution of active ingredients, solvents and stabilizer emulsified by 5 % of a Straight Emulsifier, or by a Blended Emulsifier with low HLB value.

Solution B: a solution of active ingredients, solvents and stabilizer emulsified by 5 % of a Straight Emulsifier, or by a Blended Emulsifier with high HLB value.

The two solutions are mixed at different ratio, as shown in the following scheme, to find the best balance. The best ratio showing a good blooming and emulsion stability should be chosen, for instance 40:60.

% Solution A	90	80	70	60	50	40	30	20	10
% Solution B	10	20	30	40	50	60	70	80	90

Finally, it is fine tuned by reducing the range of control to 5% (e.g. 35:65 - 55:45 - 65:35 and so on) to guarantee the best possible emulsion stability. If none of ratios are satisfactory, the test should be repeated with another nonionic surfactant until a suitable pair is found.

In some cases , it may be necessary to use more than 5% of emulsifiers to obtain the requested performances. A higher emulsifier content provides a better resistance to aging and broader range of activity.

Straight Emulsifiers are single surfactants of Hydrophilic (nonionic) or Lipophylic (anionic) activity to be balanced in the formulation to achieve suitable HLB and optimum emulsifiability. Their balancing is sometimes critical and the proper ratio of emulsifiers must be strictly applied.

Blended Emulsifiers are blends of anionic and nonionic surfactants used as pairs. Due to, their compositions the balance can be easier and consequently they offer a wider range of application, thus reducing the number of emulsifiers required. Normally formulations are less sensitive to variations in water temperature and hardness. Blended emulsifiers are also used for some specific formulations which could be difficult to achieve with straight emulsifiers.

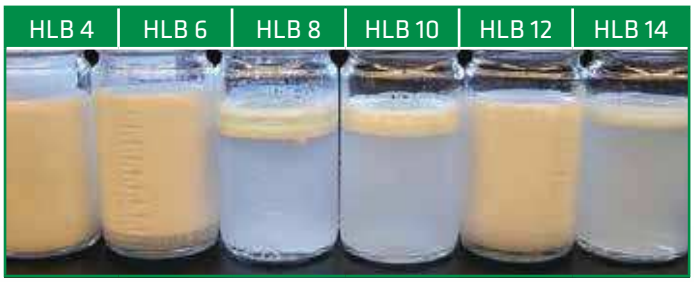
Emulsifiers screening scheme	
Blended emulsifiers	
Surfactants with low HLB (lipophilic activity)	Surfactants with high HLB (hydrophilic activity)

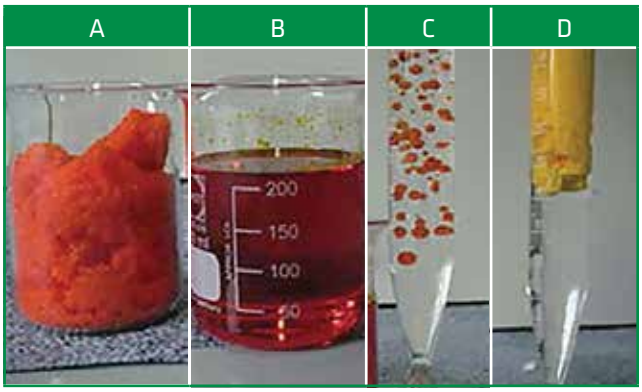
Control methods

There are different control methods referred to by large manufacturers and countries, in compliance with the particular environmental and legislation requirements.

According to CIPAC control methods, the qualitative specifications of EC formulations can be summarized and simplified as follows:

1. Limpid solution without suspended matter, sediment or crystals
2. Active ingredient content
3. Emulsion stability and re-emulsion (CIPAC 1-MT 36).
4. pH (CIPAC 1-MT 75).
5. Storage: low temperature stability (CIPAC 1-MT 39).
6. Storage: high temperature stability





In above picture:

a. Technical active ingredients
b. Final EC formulation
c. Solution of active ingredient and solvent without emulsifiers
d. Perfect blooming in EC formulation with emulsifiers

Examples of recipes

Betanal with standard solvent

Ethofumesate 60 - DMP 60 - PMP 60 g/l EC	
Desmedipham tech. 97%	61.9 g/l
Ethofumesate tech. 98%	61.2
Phenmedipham tech. 97%	61.9
Geronol VB/2000	160
Isophoron	up to 1 Liter

Ethofumesate 112 - PMP 91 - DMP 71 g/l EC	
Ethofumesate tech. 97.3%	115 g/l
PMP tech. 97%	94
DMP tech. 97%	74
Isophoron	562
Geronol TBE/724	180

Desmedipham 160 - Penmedipham 160 g/l EC	
DMP tech. 97%	165 g/l
PMP tech. 97%	165
Isophoron	548
Geronol TBE/724	150

Ethofumesate 60 - DMP 60 - PMP 60 g/l EC	
Desmedipham tech. 97%	61.9 g/l
Ethofumesate tech. 98%	61.2
Phenmedipham tech. 97%	61.9
Isophoron	711
Geronol TBE/724	100

Betanal with no dangerous solvents

Ethofumesate 112 - PMP 91 - DMP 71 g/l EC	
Ethofumesate tech. 98%	114.3 g/l
Phenmedipham tech. 97%	93.8
Desmedipham tech. 97%	73.2
Geronol TBE/724	150
Rhodiasolv ADMA 10	557.7

Desmedipham 160 - Phenmedipham 160 g/l EC	
Desmedipham tech. 97%	165 g/l
Phenmedipham tech. 97%	165
Geronol TBE/724	150
Rhodiasolv ADMA 10	522

Ethofumesate 112 - PMP 91 - DMP 71 g/l EC	
Ethofumesate tech. 98%	114.3 g/l
Phenmedipham tech. 97%	93.8
Desmedipham tech. 97%	73.2
Geronol TBE/724	150
Rhodiasolv ADMA 810	557.7

Ethofumesate 112 - PMP 91 - DMP 71 g/l EC *(Oily Formulation)*	
Ethofumesate tech. 98%	114.3 g/l
Phenmedipham tech. 97%	93.8
Desmedipham tech. 97%	73.2
Geronol TBE/724	150
Canola oil	100

Geronol VB/2000 is a blended emulsifier with a built-in adjuvant.

Geronol TEB/724 is a versatile emulsifier suitable bothfor isophoron and N,N Decanamide solvents.

Emulsifiable Concentrates

Tebuconazole 250 g/l EC	
Tebuconazole tech. 97.3%	257 g/l
Rhodiasolv ADMA 10	571
Geronol TEB-25	150

Tebuconazole 250 g/l EC	
Tebuconazole tech. 97.3%	257 g/l
Geronol TE/300	150
Rhodiasolv Green 25	up to 1000

Oxyfluorfen tech. 97.5%	23.6 %
Rhodiasolv ADMA 10	41.4
Polarclean	25
Rhodacal 60/BE	3
Antarox B/848	7

Acetochlor 900 g/l EC	
Acetochlor tech. 95%	947.4 g/l
Amesolv CME	49.6
Rhodacal 60/BE	50
Soprophor CY/8	50

Clethodim 240 g/l EC	
Clethodim tech. 85 %	282,4 g/l
Rhodasurf 860/P	100
Alkamuls OR/36	100
Amepon SB/65 (stabiliser)	15
Amesolv CME (Methyl ester)	up to 100

Cypermethrin 10 % EC	
Cypermethrin tech. 93%	10.6 %
Solvesso 150-ND	82.4
Geronol FF/4	4.5
Geronol MS	2.5

Cypermethrin 10 % EC (with green solvent)	
Cypermethrin tech. 93 %	10.6 %
Rhodacal 60/BE	3
Alkamuls T/85 -V	7
Amepon SB/65 (stabiliser)	2
Amesolv CME (Methyl ester)	up to 100

Triadimenol 22 % EC	
Triadimenol tech. 95 %	23.2 %
Rhodiasolv Green 21	49.8
Rhodiasolv ADMA 10	17
Antarox B/848	10

Abamectin 18 g/l EC (with green solvent)	
Abamectin tech. 99%	19 g/l
Rhodiasolv Match 111	840
Geronol TE/777	150

Dimethoate 40 % EC	
Dimethoate pure tech.95%	42 %
Antarox SC/138	4
Cyclohexanone	42
Solvesso 150-ND	up to 100

Emulsifiable Concentrates

Deltamethrin 2.5 % EC	
Deltamethrin tech. 98%	2.6 %
Solvesso 150-ND	90.4
Geronol FF/4	4,2
Geronol FF/6	2.8

Propiconazole 250 g/l EC	
Propiconazole tech. 96.2 %	260 g/l
Solvesso 150-ND	550
Polarclean	100
Rhodacal 70	24
Geronol MS	56

Lambda-cyhalothrin 100 g/l E	
Lambda-cyhalothrin tech. 97%	103 g/l
Geronol FF/4	46
Geronol MS	34
Solvesso 150-ND	up to 1000

Quizalofop-P-ethyl 5 % EC	
Quizalofop-P-ethyl tech. 95 %	5.3 %
Rhodiasolv RPDE	79.7
Geronol TE/777	15

Pendimethalin 330 g/l EC	
Pendimethalin tech.94%	351 g/l
Rhodacal 60B/BE	38
Soprophor 796/P	32
Solvesso 150-ND	up to 1000

Permethrin 10 % EC	
Permethrin tech. 93%	10.8 %
Solvesso 150-ND	82.2
Geronol FF/4	3.0
Geronol MS	4.0

Propiconazole 200 g/l EC	
Propiconazole tech. 96.2 %	208 g/l
Match 111	747
Geronol TE/250	100

Quizalofop-P-tefuryl 4 % EC	
Quizalofop-P-tefuryl tech. 97 %	4.1 %
Amesolv CME (methyl ester)	84.4
Amepon SB/65 (stabilizer)	1.5
Geronol FF/4	4.5
Geronol MS	5.5

Examples with Rhodiasolv MATCH 111

Abamectin 1.8 % EC	
Abamectin tech. 99%	1.9 %
Rhodiasolv Match 111	84
Geronol TE/777	15

Bromoxynil 35 % EC	
Bromoxynil tech. 95%	36.9 %
Rhodiasolv Match 111	65.1
Geronol TE/777	10

Bifenthrin 15 - Cyhalothrin 5 % EC	
Bifenthrin tech. 95%	15.8 %
Cyhalothrin tech. 97%	5.2
Rhodiasolv Match 111	73.3
Geronol TE/250	10

Cyfluthrin 10 % EC	
Cyfluthrin tech. 98.5%	10.2 %
Rhodiasolv Match 111	85.2
Geronol TE/777	10

Cyproconazole 10 % EC	
Cyproconazole tech. 98%	10.2 %
Rhodiasolv Match 111	79.8
Geronol TE/250	10

Deltamethrin 10 % EC	
Deltamethrin tech. 98%	10.2 %
Rhodiasolv Match 111	84.7
Geronol TE/777	10

Difenconazole 25 % EC	
Difenconazole tech. 95%	26.32 %
Rhodiasolv Match 111	71.38
Geronol TE/250	10

Esfenvalerate 5 % EC	
Esfenvalerate tech. 85%	5.9 %
Rhodiasolv Match 111	85.4
Geronol TE/777	10

Etofenprox 30 % EC	
Etofenprox tech. 97%	30.9 %
Rhodiasolv Match 111	63.1
Geronol TE/777	6

Ethofumesate 11 - PMP 9 - D7 % EC	
Ethofumesate tech. 95%	11.6 %
Phenmedipham tech. 95%	9.5
Desmedipham tech. 95%	7.4
Rhodiasolv Match 111	62.7
Geronol TE/777	15

Fipronil 20 % EC	
Fipronil tech. 97%	20.6 %
Rhodiasolv Match 111	69.4
Geronol TE/777	10

Flubendiamide 10 % EC	
Flubendiamide tech. 97.2%	10.3 %
Rhodiasolv Match 111	83.9
Geronol TE/777	10

Flufenoxuron 10 % EC	
Etofenprox tech. 98%	10.2 %
Rhodiasolv Match 111	83.6

Fluroxypyr-meptyl 20 %	
Fluroxypyr-meptyl tech. 97	20.62 %
Rhodiasolv Match 111	73.88
Geronol TE/777	9

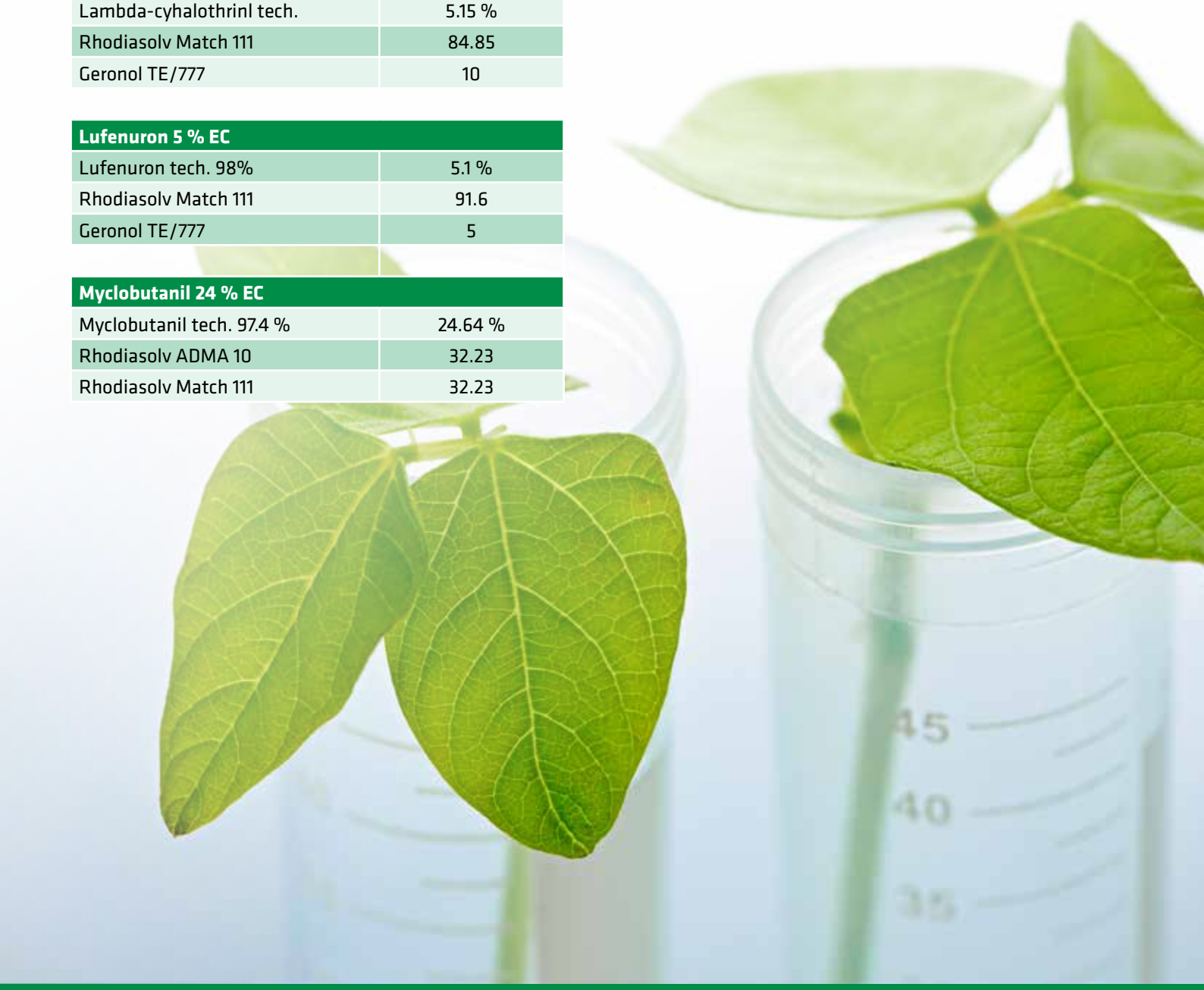
Haloxyfop-methyl 10.8 % EC	
Haloxyfop-methyl tech. 96	11.2 %
Rhodiasolv Match 111	82.4
Geronol TE/250	10

Hexythiazox 3.1 % - Abamectin 2 % EC	
Hexythiazox tech. 98%	3.16 %
Abamectin tech. 98%	2.04
Rhodiasolv Match 111	84.8
Geronol TE/777	10

Lambda-cyhalothrin 5 % EC	
Lambda-cyhalothrinl tech.	5.15 %
Rhodiasolv Match 111	84.85
Geronol TE/777	10

Lufenuron 5 % EC	
Lufenuron tech. 98%	5.1 %
Rhodiasolv Match 111	91.6
Geronol TE/777	5

Myclobutanil 24 % EC	
Myclobutanil tech. 97.4 %	24.64 %
Rhodiasolv ADMA 10	32.23
Rhodiasolv Match 111	32.23



Chapter 5

Soluble Liquid SL

- Easy to make and use
- Cost-effective
- Infinitely dilutable, No flash point
- Physically stable below saturation concentration

Soluble Liquids are water soluble formulations of active ingredients in water or in polar solvents. The active ingredients must be absolutely chemically stable in water or in the selected solvents.

Formulation

The typical composition of SL usually contains:

Active ingredient(s)	100 to 600 g/l
Surfactants	50 to 200 g/l
Buffers, sequestering agent	0 to 30 g/l
Water (or polar solvents)	up to 1000 ml

In many cases actives ingredients are solution of alkaline salts. Thus, sequestering agents are necessary to avoid flocculation of salts in field- rate dilution water.

Often the biological activity of SL is linked to the presence of a biological activator or wetter to improve the penetration of the active ingredient into the cuticular layer.

Characteristics

The formulation must be chemically and physically stable and also clear at the usual storage temperatures.

For application in the field, soluble liquids must be obviously soluble in water of various hardness and temperatures.

Surfactant selection

Soluble liquids have a strong hydrophilic character and have difficulties in wetting and penetrating the lipophilic barrier of the foliage.

Surfactants used can be divided in two groups: wetting agents and biological activators, even if it is often difficult to differentiate the two properties. Most surfactants show both activities in a single compound.

Glyphosate formulations

Glyphosate formulation is the most common formulation produced worldwide. For this formulation a built-in adjuvants is a key aspect to consider. Adjuvants improve the biological activity of an active ingredient, providing a constant activity in various climatic or application conditions. They can affect droplet deposit, rainfastness, translocation through cuticular layer, etc., and by this way modify the activity of plant protection active ingredients.

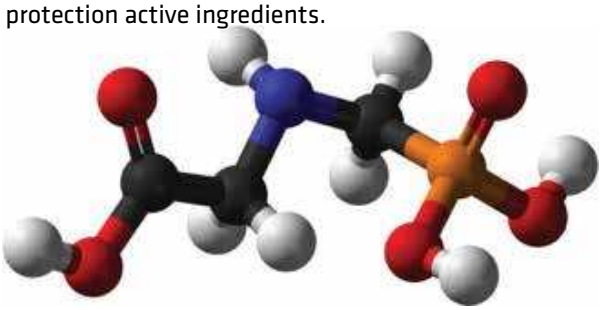


Fig: Glyphosate 3D molecule

As a result of regulations and environmental concerns, producers of plant protection compounds are looking for surfactants with low toxicity and low impact on the environment.

Solvay has a very wide range of proposals of adjuvants to better suit the needs and expectations of the customers:

- excellent cost-performance profile
- best Glyphosate efficacy
- safe and environmental friendly
- not toxic, not eye irritating
- not eco-toxic, readily biodegradable
- compatible with various salts and loads
- good properties in formulation: low foam, low viscosity

Here you find the different proposals, highlighting the main characteristics of the proposed solutions:

Glyphosate IPA salts

Glyphosate 360 SL	
Glyphosate IPA salt (46 % ac.)	780 g/l
Water	280
Geronol CF/AS 30	120

Advantages of using Geronol CF/AS 30

- As efficient as tallow amine in Glyphosate formulations
- Easy to mix, no gel formation Low viscosity
- Low foam
- Cheaper than tallow amine Fully re-assessed for EPA APVMA frog friendly
- No known tank-mix incompatibility

Soluble Liquid SL

High load Glyphosate IPA

Starting from glyphosate IPA salt:

Glyphosate 500 g as acid equivalent	
Glyphosate IPA salt	1088 g/l
Geronol CF/AS 30 HL	120

Starting from glyphosate acid:

Glyphosate 540 g as acid equivalent	
Glyphosate acid tech. 95%	568 g/l
IPA (99%)	190*
Agrho FKC 1000	140
Water	341

* It might require additional quantity of IPA to compensate for some losses in the process. This depends on the efficiency of the plant equipment and range of weed species.

Advantages of using Agrho FKC 1000

- Non-skin sensitization, low eye and skin irritation vs. market TAE benchmarks.
- Fully re-assessed for EPA Globally available.
- Low viscosity Glyphosate concentrates yield in cold temperature conditions, better off- loading from reactor, tank trucks, rails cars, outdoor storage tanks, customer packaging vs. TAE and other Glyphosate surfactants.
- Lower viscosity in cold conditions (0° C), allowing higher loading of Gly-IPA above 510 g/L. TAE formulations limit IPA loading, due to its poor solubility in concentrated formulations.
- Lower surface tension (32 dynes/cm at 20° C) vs. TAE (39.5 dynes/cm at 20° C), super wetting performance.
- Colorless low viscosity liquid, able to add dyes if desired.
- No Warning or Danger labels needed.

Glyphosate K salts

Glyphosate 360 g/l K salt	
Glyphosate acid tech. 98%	368 g/l
KOH 50%	320
Geronol CF/82 CC	120
Water	432

Glyphosate 450 g/l K salt	
Glyphosate acid tech. 96%	469 g/l
KOH 50%	352
Geronol CF/82 CC	130
Water	379

Glyphosate 540 g/l K salt	
Glyphosate acid tech. 96%	563 g/l
KOH 50%	422
Geronol CF/82 CC	160
Water	215

Advantages

Lower cost thanks to the following factors:

- Less neutralization cost
- Less raw Material
- Lower price of KOH compared to IPA
- Less packaging cost , less transport cost

Processing

- No loss due to high volatility of IPA
- Less temperature constraints
- Higher concentration/density
- Easier application of K2CO3

Examples of recipes

Ethephon 48 % SL	
Ethephon tech. 85%	56.5 %
Water	60.5
Rhodafac ARB/70	10

Mepiquat-Chloride 30.5 - Ethephon 15.5 % SL	
Mepiquat-chloride tech. 98.8%	31.12 %
Ethephon tech. 70%	22.14
Water	47.54
Rhodafac ARB/70	10

Clopyralid 30 % SL	
Clopyralid tech. 95%	31.6 %
Monoetanolamine	10.2
Geronol CF/AS 30	15
Water	58.2

Imidaclorprid 20 % SL	
Imidacloprid tech. 95%	21 %
N,MP	75
Purasolv NPL	10
Alkamuls OR/36	4

Paraquat 20 % SL (high viscosity)	
Paraquat tech. 42 %	43.5 %
Geronol MP 966W	10
Water	up to 100

The dosage in 200 g/L SL is normally 8 to 10%, pH is normally controlled at 4.0 to 6.0. Viscosity of the final formulation can be from 100 to 300cps depending on the Paraquat source and pH.

Imazethapyr 10.6 % SL	
Imazethapyr tech. 90%	11.8 %
Geronol CF/AS 30	10
Ammonia(NH3)	5
Water	73.2

Imazamox 4 % SL	
Imazamox tech. 95%	4.2 %
Methanolamine	0.06
Rhodiasolv Polarclean	40
Geronol CF/AS 30	10
Water	45.84

2,4D 48 – Dicamba 7 % SL	
2,4D acid tech. 98%	49.5 %
Dicamba tech. 95%	7.4
Dymethylamina 33% (neutralizing agent)	35
Geronol CF/AR-E	10
Water	17.1

Dicamba 48 % SL	
Dicamba tech. 98%	49 %
Dymethylamina 33%	29.5
Geronol CF/AR-E	10
Water	28.7

Bentazone 48 % SL	
Bentazone tech. 95%	50.5 %
Sodium hydroxide 50%	16.5
Geropon T/36-DF	10
Water	up to 100

2,4D 48 – Dicamba 7 % SL	
2,4 D acid tech. 97.2 %	33.33 %
MCPA tech. 92 %	30.84
DMA tech. 33	43.8
Water	0.5
Geronol CF/AR-E	10

Glufosinate 28 % SL	
Glufosinate tech. 95%	29.5 %
Water	50.95
Antifoam 8610	0.05
1-metoxy-2-propanol	1

Chapter 6

Suspension Concentrates SC

- Aqueous based
- No flash point
- Low skin penetration
- Possibility to reach higher A.I. Concentrations

The suspension concentrates (SC), also known as “flowables”, consist of insoluble solid active ingredients dispersed (normally at high concentration) in water. Suspension concentrates have recently shown a rapid development, mainly due to their several benefits when compared to other formulations:

- No dust
- No problem of toxicity or flammability due to solvents
- Good efficiency due to the smaller particle size
- Low packaging volume

The following properties can be highlighted in this type of formulation:

- Long term storage stability (no settlement, stable rheological behavior, etc.)
- Fairly low viscosity (easily pourable and readily dispersible in water)
- Good stability of the diluted dispersion at the application rate

The choice of surfactants (wetting, dispersing, compatibility agents) is essential to meet above properties.

The typical composition of SC usually contains:

Active ingredient(s)	400 to 800 g/l
Wetting agents	5 to 15 g/l
Dispersing agents	20 to 50 g/l
Antifreeze	20 to 80 g/l
Antifoam and stabilizer	1 to 5 g/l
Thickener	1 to 4 g/l
Preservative	0.1-0.5
Water	up to 1000 ml

General method of preparation

Definition of suitable active ingredients:

Formulation of solid active ingredients in a SC form needs the following characteristics:

- Very low solubility in water (crystal growth can occur especially at high temperature)
- Excellent chemical stability against hydrolysis. Stabilizers, buffers, reducing agents, etc., can be added when necessary to improve the chemical stability of active ingredients.
- Melting point higher than 50° C, in order to allow easy wet grinding and storage stability.

Effects of surfactants

Surfactants are basic components in suspension concentrates. They play several key roles in the physical-chemical characteristics and properties of such water based formulations:

- Wetting of the solid particles of active ingredients
- Wet milling aid
- Dispersing properties of the solid particles in the continuous phase
- Long term stabilization of the micronized particles
- Stability of the micronized particles at a diluted state during field application

Stabilization

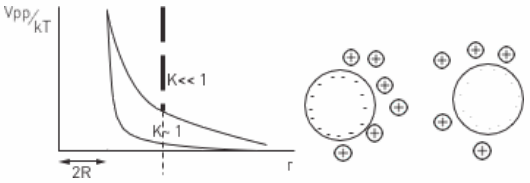
After milling, the dispersed particles have an inherent tendency to flocculate irreversibly as a result of the attractive forces, namely "Van der Waals forces", depending on the active ingredient and its particle size distribution. The adsorption of a surfactant onto the solid particles generates repulsive forces which contrast with the attractive ones.

These repulsive forces are of two types which can be involved either singularly or in combination:

1. Electrostatic repulsion

The electric charge given by ionic surfactants (anionic, cationic or zwitterionic) adsorbed onto particles, causes electrostatic repulsion between the dispersed particles. The strength of these repulsions is given by the following equation (Debye-Hukel approximation):

D: particles size
r: distance between two particles
K: ionic strength



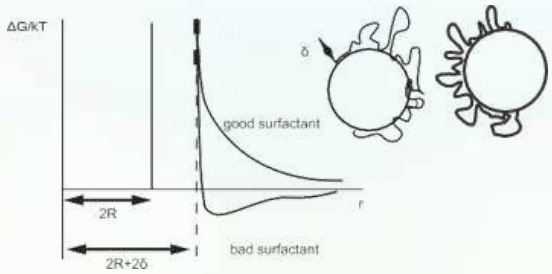
The strength of this force depends on:

- the dielectric constant and the chemical composition of the continuous phase
- the particle size
- the electrolyte concentration

If the ionic strength (K) of the continuous phase increases, the electrostatic strength decreases, thus, flocculation becomes possible (suspensions lose their stability). The strength of the electrostatic force can be evaluated by Zeta potential measurement vs. pH, ionic strength or temperature.

2. Steric repulsion

This type of stabilization is obtained by using a non-ionic surfactant which has a long hydrophilic chain adsorbed onto solid particles. When two particles approach, the chains interact, providing a repulsion force.



The strength of this force depends on:

- the quantity of surfactant adsorbed onto the particles
- the interaction between
- the hydrophilic chains of the surfactant and the continuous phase (solubility, compatibility vs. temperature, etc.)
- the length of the chains
- the temperature

Steric repulsion is a strong force, but sensitive to temperature (for ethoxylated surfactants: the higher the temperature, the weaker the force). The strength of this force can be evaluated by measuring the quantity of surfactant adsorbed onto the particles.

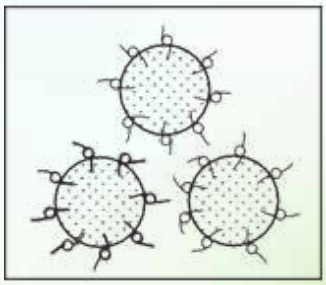
Choosing a surfactant is difficult and is the key step in the development of a SC formulation. An optimum choice can only be made by experimentation in order to find surfactants strongly adsorbed onto the formulated active ingredients, and able to generate the highest repulsive forces between the solid particles in the chosen continuous phase.

Furthermore, to obtain a long term stability of suspension concentrates in various climatic conditions, it is recommended to use the two types of stabilization (electrostatic and steric) combined with a gravitational stabilization given by thickeners.

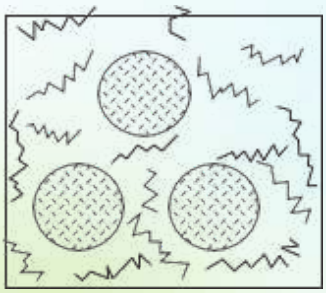
Gravitational stabilization

Besides the stabilization of the dispersed solid active ingredient by modifying the interfaces (with surfactants or polymers), the use of a thickener (xanthan gum, guar gum, bentonites, etc.) is necessary to obtain a good long term stability and to avoid settlement in various climatic conditions.

In the case of **Rhodopol** (xanthan gum), a pseudo- cross-linked structure is obtained in water, due to the "rod-like" form of xanthan macromolecule and reversible interactions between these molecules even at low concentration. This phenomenon, called gravitational stabilization by continuous phase structuration, should avoid sedimentation and caking during long term storage of suspension concentrates.



Stabilization by interfaces properties changes: Surfactants and Polymers ELECTROSTATICAL or STERICAL STABILIZATION



With Rhodopol there is a structuration of the continuous phase GRAVITATION STABILIZATION

Selection of components

Wetting agents

Most of the dispersing agents themselves show wetting properties. Thus, for some active ingredients which are easy to wet, it is not necessary to add a specific wetting agent, while for the others the addition of a wetting agent is a must.

Dispersing agents

For the majority of the active ingredients, phosphoric esters and sulphated derivatives of ethoxylated additives give the best results, due to the ethoxylated chain and its anionic termination which generates both steric and electrostatic repulsion.

In some cases it may be necessary to use only nonionic surfactants for compatibility problems or non-ethoxylated surfactants for specific formulations, crystal growth problems, etc.

Antifreeze

Monopropylene glycol is the most common antifreeze agent used. The recommended rate is around 10% of the total water content in the formulation.

Thickeners

The main role of this ingredient is to keep active materials in suspension and to prevent sedimentation during long term storage. It must, therefore, have a very strong suspending capability even at low concentration.

Moreover, it must have good chemical compatibility with the active materials, good chemical stability and should cause the minimum increase in dynamic viscosity.

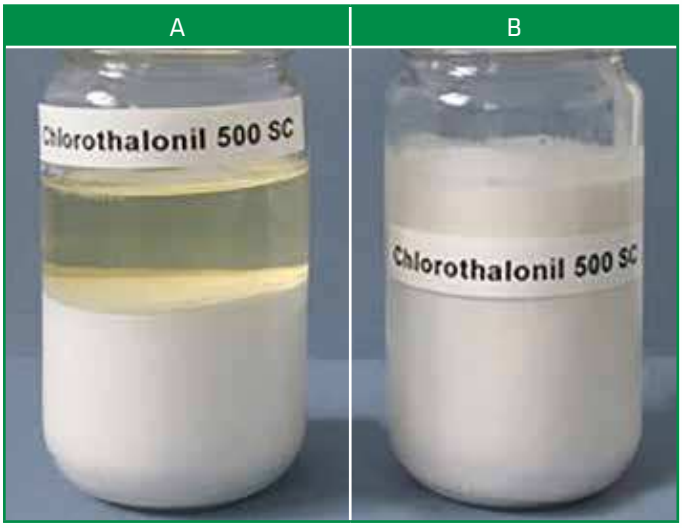
Rhodopol (xanthan gum) range of thickener is suitable to provide long term storage stability in the majority of cases.

Rheozan, a non-ionic thickener, having similar rheological properties as Rhodopol, shall be used in acidic formulations at pH lower than 5.0.

Suspension Concentrates SC

Antifoam

The role of this additive is to avoid foam forming during preparation of the suspension and also during water dilution and field application. It must be chemically inert and efficient, even at low concentration. Non-ionic silicone antifoams fulfill perfectly such specifications, being efficient at low concentration at any pH.



Sample A without thickener, Sample B with thickener

Preservative

Many different bactericides may be used to protect the products against bacteria.

Control methods

Dispersibility: the blooming effect

Blooming effect is checked by pouring a few ml of the suspension concentrate with a pipette into a test tube containing 250 ml of standard hardness water (CIPAC) at room temperature. Simply by inverting the test-tube, the formulation should disperse.

Suspensibility

The CIPAC test referred to wettable powders should be applied. Generally the suspensibility will exceed 85% in various conditions (temperature, water hardness and concentration).

Fineness

Several types of equipment can be used: optical microscope particle size analyzer

The average particle size should be about 4 µm, with a maximum of 5% over 10 µm for active materials with density lower than 1.5. For active ingredients with higher density, it is preferable to go down to 3 µm with a maximum of 5% between 5 and 8 µm. It is also important to bear in mind that for certain active ingredients, an excessive fineness (< 1.5 µm) can greatly increase phytotoxicity and crystal growth.
For some active ingredients this fineness can improve the biological efficacy. This must be checked in any case.

Viscosity and rheological behavior

The correlation between rheological parameters and different quality criteria, such as physical stability, flowability or suspensibility, will help the formulator to choose the right ingredients and check precisely the long term stability of suspension concentrates.

Different types of equipment can be used to measure viscosity or to evaluate the rheological behavior of suspension concentrates:

- Ford cup or equivalent
- Brookfield (RVT or LVT)
- Rheometers
- Dynamical rheometers

They can be used either singularly or in combination.
For example a Ford cup or a Brookfield is convenient for control measurement. More sophisticated rheometers during formulation development are necessary to have a better prediction of the long term stability of the formulation.
Content of active materials

This needs to be checked with appropriate methods for each active ingredient. The concentration is usually expressed in g/l.

Storage stability

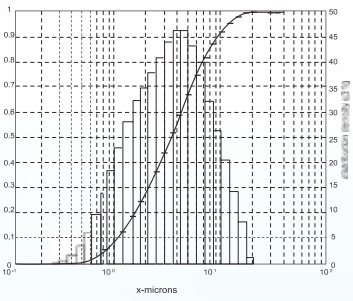
Commercial formulations should be stable for at least 2 years, without any significant change of viscosity and without sedimentation of the active ingredients.

However, the presence of a supernatant water layer on the top (which can limit the formation of a film or crust on the surface) is acceptable, provided that only a slight agitation is needed for the mixture to re-disperse. Some accelerated aging tests give an accurate indication of the long term stability of SC formulations:

- Tropical test: 2 weeks at +54° C (CIPAC 1-MT 46.1.3)
- Cold stability test: 1 week at 0° C (CIPAC 1-MT 39)
- Stability at “high” temperature for two months at +45° C
- Stability to thermal shock: samples in sealed opaque glass bottles are submitted to temperature cycles (24 hours at -5° C and 24 hours at +45° C) for a one or two months period.

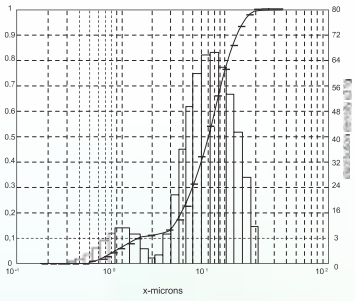
Tests can either be carried out alone or in combination according to the long term stability requirements. Aged samples have to be checked: no sedimentation (soft cake or claying of active ingredient at the bottom of the bottle) and no chemical degradation of active ingredients should occur. It is also important to check that viscosity has not changed by more than 10% compared to the initial value. Particle size must also be checked to ensure that no crystal growth or flocculation occurred during aging tests, especially in high or cyclic temperature tests.

Distribution on volume



Typical particle size distribution of a SC formulation

Distribution on volume



Particle size distribution showing crystal growth

Industrial production

On an industrial scale, it is possible to make suspension concentrates by using:

- either pre-milled powdered active material (down to 100 µm)
- or the still damp filter-cake of the A.I. directly from the last step of the synthesis.

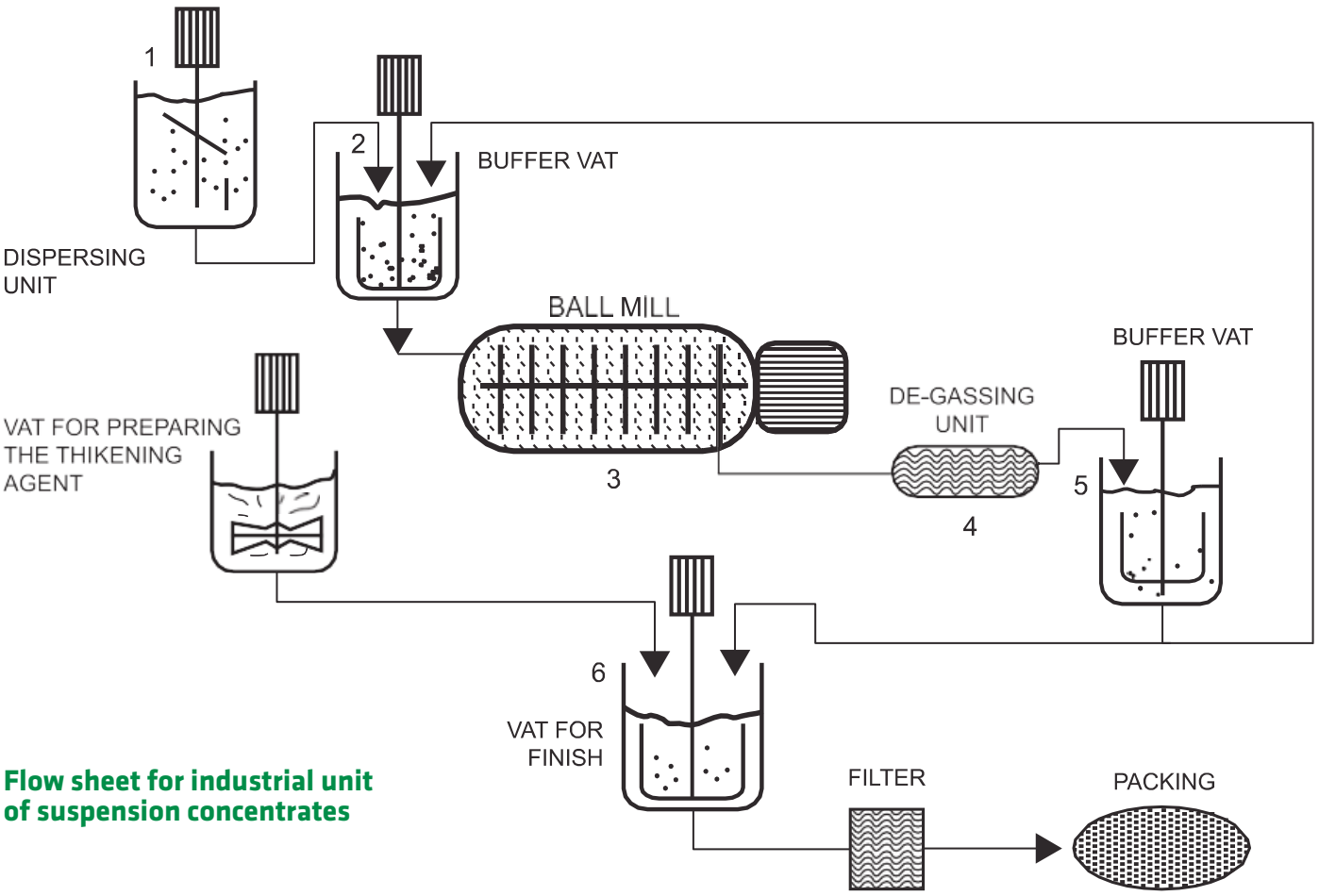
This second method is much superior from both economical and technical points of view:

- gains in energy (drying and pre-milling are avoided)
- easier grinding: the active materials are not caked as they are after drying
- less foam formation: there is no incorporation of air, as is the case when powders are used.

Note: In order to be able to use this second method, it is necessary to have a filter-cake with an active material content at least 15% higher than the desired final concentration. We have found that adding 0.1 to 0.2% of dispersing agents to the slurry prior to filtration facilitates this operation and increases the content of active materials in the cake by 15 to 20%.

Moreover, the presence of dispersing agents facilitates subsequent re-dispersion.

The following is a generic flow-sheet for an industrial unit:



Flow sheet for industrial unit of suspension concentrates

Examples of S.C. recipes

Azoxystrobin 20 - Cyproconazole 8 %	
Azoxystrobin tech. 95%	20.7 %
Cyproconazole tech. 95%	8.5
Glycol	5
Silcolapse 426-R	0.2
Rhodasurf 860/P	1
Soprophor TSP/461	3
Rhodopol 23 (3% sol.)	12
Water	up to 100

Flutriafol 125 g/l	
Flutriafol tech. 97.2%	129 g/l
Propylen Glycol	60
Silcolapse 426-R	2
Rhodasurf 860/P	10
Soprophor TSP/461	30
Rhodopol 23 (2% sol.)	210
Water	up to 1000

Sulfur 720 g/l	
Sulfur tech. 99%	728 g/l
Glycol	40
Silcolapse 426-R	1
Supragil MNS/90	15
Supragil GN	25
Calcium Carbonate	15
Rhodopol 23 (3% sol.)	60
Water	up to 1000

Metamitron 400 - Ethofumesate 100 g/l	
Metamitron tech. 98%	409 g
Ethofumesate tech. 98,5%	102
Glycol	50
Silcolapse 426-R	2
Rhodasurf 860/P	10
Soprophor 4D384	45
Rhodopol 23 (2% sol.)	100
Water	up to 1000

Carbendazim 500 g/l	
Carbendazim tech. 98%	510 g/l
Glycol	50
Silcolapse 426-R	2
Soprophor TSP/461	30
Rhodasurf 860/P	10
Rhodopol 23 (2% sol.)	80
Water	up to 1000

Imidacloprid 600 g/l	
Imidacloprid tech. 97%	619 g/l
Glycol	40
Silcolapse 426-R	2
Rhodasurf 860/P	10
Geropon DA 1349	30
Rhodopol 23 (3% sol.)	50
Water	up to 1000

Prochloraz-Zn 450 g/l	
Prochloraz-Zn tech. 96.77%	550 g/l
Silcolapse 426-R	2
Rhodasurf 860/P	10
Antarox PLG/254	60
Rhodopol 23 (3% sol.)	80
Water	up to 1000

Metamitron 700 g/l	
Metamitron tech. 98%	715 g/l
Glycol	25
Silcolapse 426-R	2
Soprophor 4D 384	60
Rhodasurf 860/P	5
Rhodopol 23 (2% sol.)	50
Water	to 1000

Suspension Concentrates SC

Folpet 500 g/l	
Folpet tech. 94%	532 g/l
Glycol	50
Silcolapse 426-R	2
Soprophor TSP/461	30
Rhodasurf 860/P	10
Rheozan (2% sol.)	90
Water	up to 1000

Chlorothalonil 500 g/l	
Chlorothalonil tech. 97.4%	516 g/l
Glycol	50
Silcolapse 426-R	2
Soprophor TSP/461	30
Rhodasurf 860/P	10
Rhodopol 23 (2% sol.)	120
Water	up to 1000

Tebuthiuron 500 g/l	
Tebuthiuron tech. 95%	526 g/l
Monopropylen glycol	40
Silcolapse 426-R	2
Rhodasurf 860/P	10
Antarox B/848	30
Rhodopol 23 (2% sol.)	50
Water	up to 1000

Metribuzin 600 g/l	
Metribuzin tech. 97.4%	616 g/l
Glycol	40
Silcolapse 426-R	1
Soprophor 4D 384	15
Supragil MNS/90	15
Rhodasurf 860/P	5
Rhodopol 23 (2% sol.)	80
Water	up to 1000

Notes
Amecoat HCA 83 : sticker
Red 2G/AC : pigment
Red 48:2 : pigment
Agrimer 30 : dispersing, crystal growth inhibitor

Examples of F.S. recipes

Difenoconazole 3 %	
Difenoconazole tech. 95%	3.2 %
Propylen Glycol	10
Silcolapse 426-R	0.1
Rhodasurf 860/P	0.5
Soprophor FL	3
Amecoat HCA 83	8
Rhodopol 23 (2% sol.)	20
Red 2G/AC	6
Water	up to 100

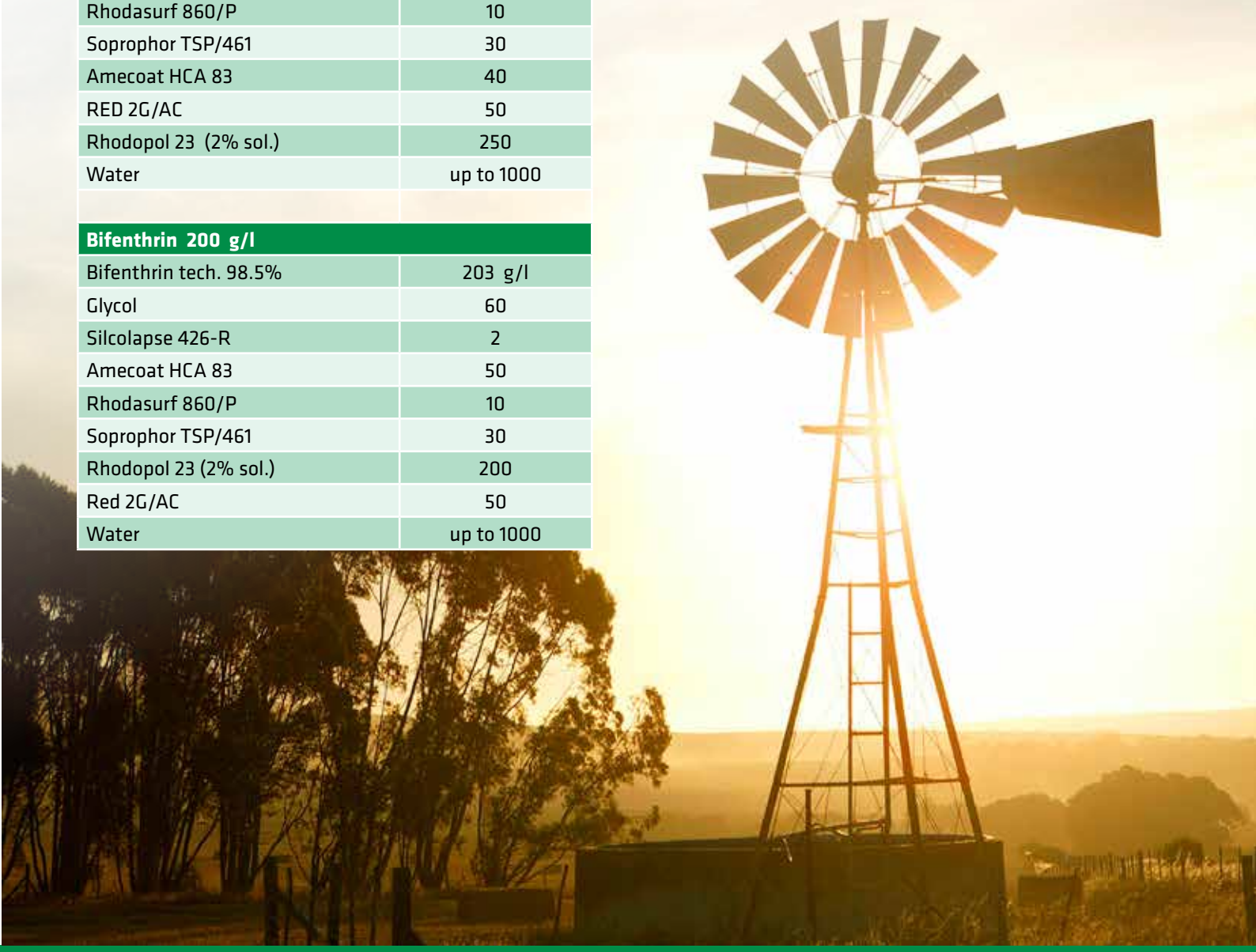
Tebuconazole 60 g/l	
Tebuconazole tech. 97%	62 g/l
Propylen Glycol	60
Silcolapse 426-R	5
Rhodasurf 860/P	10
Soprophor TSP/461	30
Amecoat HCA 83	40
RED 2G/AC	50
Rhodopol 23 (2% sol.)	250
Water	up to 1000

Bifenthrin 200 g/l	
Bifenthrin tech. 98.5%	203 g/l
Glycol	60
Silcolapse 426-R	2
Amecoat HCA 83	50
Rhodasurf 860/P	10
Soprophor TSP/461	30
Rhodopol 23 (2% sol.)	200
Red 2G/AC	50
Water	up to 1000

Imidacloprid 600 g/l	
Imidacloprid tech. 96%	625 g/l
Glycol	30
Silcolapse 426-R	1
Rhodasurf 860/P	5
Geropon DA 1349	30
Rhodopol 23 (3% sol.)	60
Amecoat HCA 83	40
Red 2G/AC	50
Water	up to 1000

Notes

Amecoat HCA 83 : sticker
Red 2G/AC : pigment
Red 48:2 : pigment
Agrimer 30 : dispersing, crystal growth inhibitor



Chapter 7

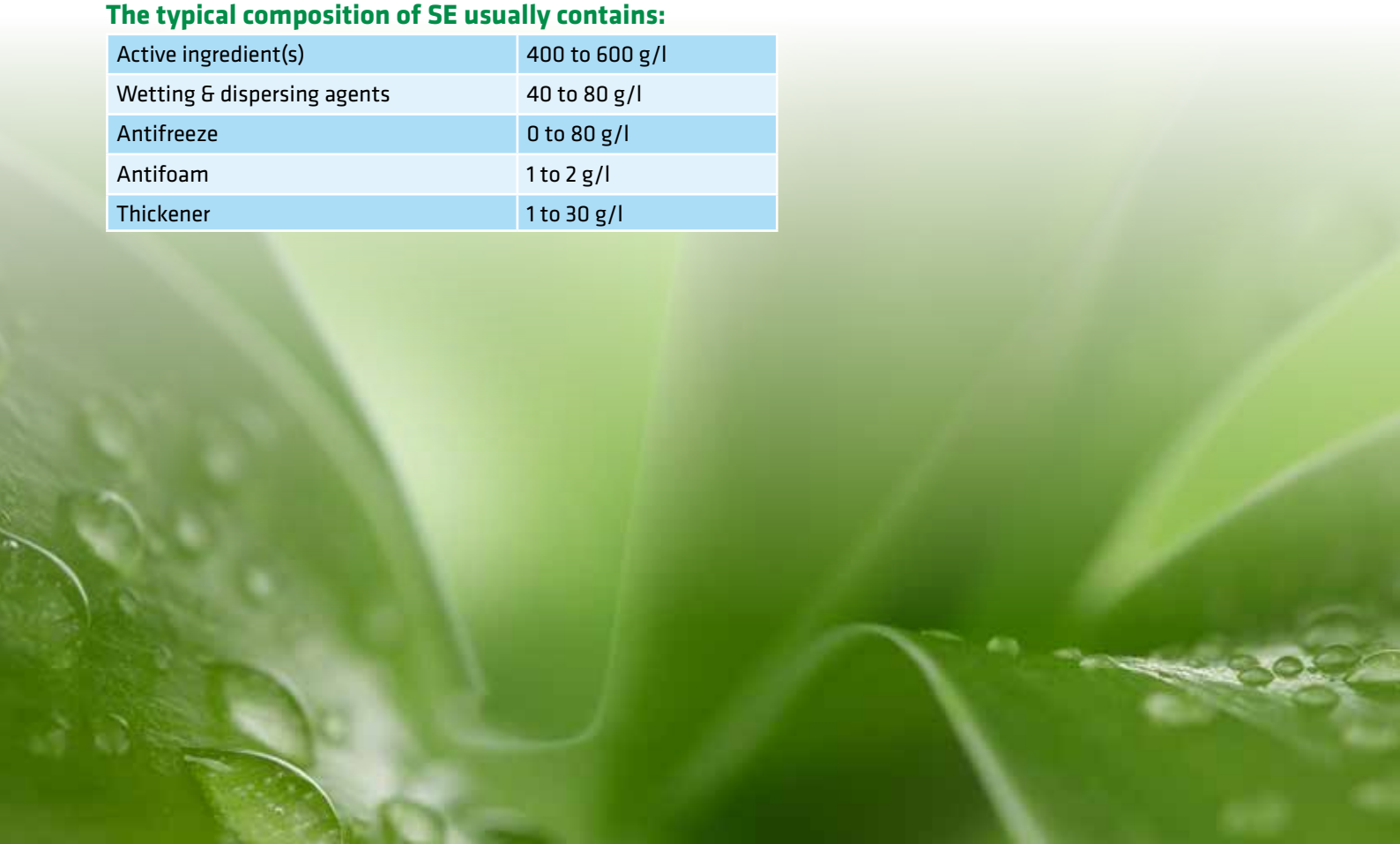
Suspo-Emulsion SE

- Mixtures of A.I.'s of widely different properties
- No flash point
- Reduced solvent concentration

A suspo-emulsion (SE) is aformulation containing both solid and liquid (or low melting point solid + solvent) active ingredients, dispersed in an aqueous phase. It is possible to using this method to put together different active ingredients with different physical-chemical characteristics, in the same water based formulation.

The typical composition of SE usually contains:

Active ingredient(s)	400 to 600 g/l
Wetting & dispersing agents	40 to 80 g/l
Antifreeze	0 to 80 g/l
Antifoam	1 to 2 g/l
Thickener	1 to 30 g/l



General method of preparation

Definition of suitable active ingredients

For the development of such formulations, the solid and liquid ingredients must be insoluble in the aqueous phase.

Effects of emulsifiers

One of the best methods to obtain good suspo-emulsions, is to prepare separately a suspension concentrate with the solid A.I. as well as a concentrate emulsion with the liquid or low melting point A.I. (EW/EC). Then, these two formulations are mixed together under normal agitation. In this way, the characteristics of the formulation are controlled very well. It is also important to avoid wet-milling of the mixture of solid and liquid A.I.s for three main reasons:

- the liquid A.I. could act as a lubricant and could disturb the milling process.
- usually the solid A.I. content is too low for a good wet-milling. It is better to mill the solid alone at the highest possible concentration.
- the emulsifiers ratio and the grade of obtained emulsifiability could be disturbed (wider particle size distribution, etc.) by the components used for SC.

Surfactants (emulsifiers, dispersing and wetting agents) are the basic components in water based suspo-emulsions. They play several roles in the development, the properties and the long term stability of these formulations.

Emulsifiers, dispersing and wetting agents provide:

- wetting and dispersion of the solid particles of the A.I. into the water continuous phase, by reduction of the Oil/ Water interfacial tension

- steric and/or electrostatic stabilization of the micronized droplets, to avoid flocculation, aggregation or coalescence
- wet milling aid
- long term stabilization of micronized particles.
- improvement of the suspension compatibility with the emulsion at a concentrated or diluted state.

Surfactants also serve to avoid flocculation or aggregation between solid dispersed particles and liquid active droplets. They can have the double role of dispersing agent and emulsifier.

Selection of components

Dispersing agents and emulsifiers

Surfactants have to be chosen taking into account the fact that the two formulations will be mixed together. In this case, the compatibility between the different components is important.

Antifreeze

Monopropylene glycol or glycerine, used at approx. 10% on total water volume in the formulation, are the most common antifreezes. The dose sharing can be done between suspension and emulsion during their preparation.

Thickeners

Rhodopol (xanthan gum) range of thickeners is perfectly suited to provide long term storage stability in the vast majority of cases. It needs to be added (2% water solution) in the blending phase of the two pre-mixes.

Rheozan, a non-ionic thickening agent having rheological property similar to Rheozan, shall be used when formulations have a pH lower than 5.0.

Antifoam

The role of this additive is to avoid foam forming during the preparation of the formulation but also during water dilution and field application. It must be chemically inert and efficient, even at low concentrations.

Laboratory formulation

First, prepare the suspension and the emulsion.

Mix together by stirring the two formulations normally, so as to obtain a homogeneous suspo- emulsion. An antifoam can be used during the process.

At this stage, the viscosity should be between 300 to 500 mPa.s (Brookfield 20 rpm).

If necessary, add **Rhodopol** or **Rheozan** (2% water solution) slowly to increase viscosity, and eventually add water to adjust the active concentration.

The final viscosity should be between 750 to 1500 mPa.s (Brookfield 20 rpm)

Control methods

Dispersibility: blooming effect

Blooming effect is checked by adding a few ml of the flowable formulation, using a pipette into a test tube containing 250 ml of water of standard hardness (CIPAC) at room temperature. Simply by inverting the test-tube, the suspo-emulsion should disperse.

Suspensibility

Due to the nature of the formulation, the suspensibility will exceed 85% in various conditions (temperature, water hardness and concentration). However, it is necessary to check if the formulation is stable when diluted, and more specifically that no phase separation or hetero-flocculation occur.

Fineness

Several types of equipment can be used:

- optical microscope to obtain a general idea of the particle size and particle size distribution.
- particle size analyzer laser, Counter Coulter, when accurate information on particle size and particle size distribution is needed.

The average fineness should vary between 2 to 8 µm, depending on the physical characteristics of the active ingredient. With a specific gravity of a solid A.I. higher than 1.5 kg/l, it is best to go down to 3 µm.

We recommend to measure the particle size of SC and EW first, and then the particle size of the suspo-emulsion. This provides a lot of information on the compatibility and potential long term stability of this type of formulation. It is also important to bear in mind that for certain active ingredients, an excessive fineness (< 1.5 µm) can greatly increase phytotoxicity, crystal growth or Laplace ripening.

Rheological measurement

The correlation between rheological parameters and different quality criteria such as physical stability, flowability, suspensibility or long term stability will help the formulator to choose the right ingredients and check the long term stability of suspo-emulsions precisely.

In order to evaluate the rheological behavior of suspo-emulsion, different types of equipment can be used to measure the viscosity:

- Brookfield (RVT or LVT)
- Rheometers such as Rheomoat 115 (Contraves) or equivalent
- Dynamical rheometers (such as Carimed or RFS types)

They can be used either singularly or in combination. Sophisticated rheometers provide a lot of information on the characteristics and on the long term stability of suspo-emulsions.

Example of dispersion in water of S.E.

The rheological measurements for suspo-emulsions are the same as those for suspension concentrates or emulsions in water.

Dynamic rheological studies (visco-elastic behavior) can also be carried out to obtain further information concerning the stability and general properties of suspo-emulsions.

Active ingredients content

To avoid the crystal growth and insure long term stability, active ingredients must be water insoluble. As appropriate to each product, the concentration is usually expressed in g/l of the different active ingredients.

Storage stability

The commercial formulation should be stable for at least 2 years, without any significant change of viscosity, phase separation or agglomeration between droplets and solid particles. The presence of a supernatant water layer on the surface is acceptable provided that only slight agitation is needed for the re-homogenization.

Some accelerated aging tests give a clear indication of the long term stability:

- tropical test: 2 weeks at +54° C (CIPAC 1-MT 46.1.3)
- cold stability test: 1 week at 0° C (CIPAC 1-MT 39)
- stability at “high” temperature for two months at +45° C
- stability to thermal shocks: samples in sealed opaque glass bottles are submitted to temperature cycles (24 hours at -5° C and 24 hours at +45° C) for one or two month period.

Aged samples have to be checked: no sedimentation (soft cake or caking of active ingredient at the bottom of the bottle) and no chemical degradation of active ingredients should occur. It is also important to check that viscosity has not changed by more than 10% compared to the initial value. Particle size must also be checked to ensure that no crystal growth, flocculation, or droplet size increase occurred during aging tests especially at hot and cyclic temperature and cycle.

Suspo-Emulsion SE

Examples of recipes

Diuron 32 - Glyphosate 18 - Oxyfluorfen 14.4 % SE	
Diuron tech. 98 %	32.6 %
Glyphosate-IPA salt (46% a	39.1
Oxyfluorfen tech. 97%	14.9
Monopropylen glycol	3.3
Amersil B/30	0.1
Antarox B/848	2
Rhodasurf 860/P	0.3
Geronol CF/AR-E	5
Rheozan (2% sol.)	5.6
Water	up to 100

Ethofumesate 12 - DMP 12 - PMP 12 - 26 % SE	
Phenmedipham tech. 97 %	12.4 g/l
Desmedipham tech. 98%	12.3
Ethofumesate tech. 97%	12.4
Soya oil	26
Monopropylen glycol	3.35
Amersil B/100	0.07
Soprophor 3D33	3.01
Rhodasurf ROX	0.99
Rheozan (3% sol.)	2
Water	up to 100

Metolachlor 37.5 - Terbutylazine 12.5 - Mesotrione 3.75 %	
Mesotrione 3.75 % SE	39.1 %
Metolachlor tech. 96%	12.9
Terbutylazine tech. 97%	3.96
Mesotrione tech. 95%	1.6
Monopropylen glycol	0.01
Amersil B/30	1.2
Soprophor TSP/461	0.02
Rhodasurf 860/P	0
Soprophor TS/10	2.8
Rheozan (2% sol.)	up to 100
Water	

Tebuconazole 16.8 - Azoxystrobin 8.4 % SE	
Tebuconazole tech. 97%	17.325 %
Azoxystrobin tech. 98.5%	8.526
Rapeseed oil	21.6
Propylen Glycol	3.5
DV8610 (antifoam)	0.14
Soprophor TSP/461	2.1
Rhodasurf 860/P	0.89
Rhodopol 23 (3% sol.)	6
Water	up to 100

Metolachlor 30 - Metazachlor 25 % SE	
Metolachlor tech. 97%	31 %
Metazachlor tech. 98%	25.6
Monopropylen glycol	4
Amersil B/30	0.01
Soprophor TSP/461	1.5
Rhodasurf 860/P	0.25
Soprophor BSU	8
Rheozan (3% sol.)	9
Water	up to 100

Chapter 8

Oil Dispersions OD

- Formulation of A.I.s with low solubility in solvents
- No flash point
- Built-in adjuvant
- Formulation of water sensitive A.I.s

OD is a non aqueous suspension concentrate. It combines very good biological efficacy with an environmental friendly formulation. The active ingredient is dispersed in oils, or methylated crop oils.

Main features are:

- No Aromatic Solvent
- Non-aqueous formulation
- Non-flammable & low volatility Higher efficiency
- No safety labeling issue

Oil Dispersions OD

Typical composition

The typical composition of OD usually contains:

Active Ingredient	40 – 200 g/l
Emulsifier	100 – 200 g/l
Dispersant	50 – 100 g/l
Rheology Modifier	50 – 100 g/l
Stabilizer	1 - 10 g/l
Oil or Methyl Ester	up to 1 Liter

Particle size	2 – 4 µm
Viscosity (Brookfield, #2, 20 rpm)	1000-1500 cPs
Emulsion stability	Excellent
Suspensibility	> 90 %
Efficacy	Similar to EC

Production process is similar to SC, but water is replaced by oil media.

Why ODs have a bright future?

ODs have several advantages vs. standard formulations:

OD as a replacement of EC

Nowadays ECs are under strong regulatory pressure to replace toxic and flammable solvents for less toxic and non-flammable solutions. OD meets these requirements: the oil content gives a favorable eco-toxicological profile, guaranteeing a very high biological efficacy.

- No toxic and no flammable formulations
- Very high biological efficacy

OD as a replacement of SC

Suspension concentrates are very safe formulations but the aqueous media is not normally ideal to boost pesticides' biological efficacy. Growers, as a standard practice, add tank mix adjuvants to guarantee a higher performance of SC formulations. Whilst, OD, with its oil content, guarantees the highest biological results. For water sensitive active ingredients, OD represents the sole technical solution to liquid formulations.

- Very safe formulation along with high biological performance
- Ideal for active ingredients not stable in water

OD as an alternative to WDG

Water dispersible granules are very safe, but are quite expensive. Optimal biological efficacy requires adjuvants. OD with its oil content and better particle size distribution combines high efficacy with lower cost.

- Better efficacy at lower cost

Formulation challenges in ODs

OD formulation presents several challenges in production. To obtain a good and stable formulation over the time, in addition to optimum process, optimal formulation additives are also required. A particular attention must be given to the rheological agents whose dispersion and activation are key to the long term stability of the formulation.

Important requirements for additives:

Perfectly dispersible in oil

- No phase separation
- Easy milling
- No agglomeration

Excellent oil emulsification

- Stable dilution
- Good Coverage and Penetration

Rheological agent is the key factor of the formulation. It should meet the following properties:

- Provision of right yield value
- Provision of right viscosity
- Homogeneous dispersion and activation in the formulation

Production process must ensure:

- Total activation of the Rheological agent
- Even distribution of the whole formulation

Solvay's solution for ODs

Alkamuls VO/2003

Emulsifier specifically designed for vegetable oil formulations:

Nicosulfuron 40 g/l OD

Nicosulfuron tech. 97 %	41.2 g/l
Rapeseed oil (canola oil)	668.8
Alkamuls VO/2003	200
Tixosil 365	40

Geronol ODessa

Geronol ODessa represents all in one solution to formulate ODs. It has several functions at the same time:

- Emulsifying agent
- Dispersing agent
- Rheological additive
- Built-in Activator

Advantages:

Main specifications of Geronol ODessa 01	
Physical form (20° C)	liquid
Viscosity (mPa.s)	1000
Density	0.95
Water content (% max)	< 1

Simplicity with Geronol ODessa 01

Production of ODs is quiet simple with Geronol ODessa.
Only 3 simple steps:

- ODessa, Vegetable oil and technical active ingredients
- Mill to reach the the right particle
- Size Pack it

Solvay has designed 2 versions:
Geronol ODessa 01: for oil based solution
Geronol ODessa 05: for methylated canola oil

- Excellent performance
- No need of extra step or equipment
- Suitable for vegetable oils & for methyl ester of vegetable oils

Highlights of Geronol Odessa 01:

- Ready and easy to use solution for stable ODs
- Robust technology suitable for various A.I.s and contents
- Containing rheology modifier, emulsifier and oil
- Liquid concentrate specially designed for vegetable oils

Geronol ODessa is also suitable for methyl esters. In this case, Geronol ODessa 05 is recommended.

Example of recipes in rapeseed oil (with Geronol ODessa 01)

Herbicides

Nicosulfuron 4 % OD	
Nicosulfuron tech. 97%	4.2 %
Geronol ODessa 01	45
Rapeseed oil	46.2

DMP 10 - PMP 10 % OD	
DMP tech. 96%	10 .5 %
PMP tech. 96%	10.5
Geronol ODessa 01	45
Geronol TEB-25	15
Rapeseed oil	18.5

Ethofumesate 11.2 - PMP 9.1 - DMP 7.1 % OD (Betanal Progress 27.4 %)	
Ethofumesate tech. 97%	11.5 %
PMP tech. 97%	9.4
DMP tech. 97%	7.3
Geronol ODessa 01	43
Geronol TEB-25	15
Rapeseed oil	15.1

Isoproturon 20 % OD	
Isoproturon tech. 95%	26.1 %
Geronol ODessa 01	20
Geronol SOL-90	20
Rapeseed oil	41

Metamitron 30 % OD	
Metamitron tech. 98%	31 %
Geronol ODessa 01	29
Geronol SOL-90	20
Rapeseed oil	20

Rimsulfuron 25 % OD	
Rimsulfuron tech. 95%	26.3%
Geronol ODessa 01	43.7
Geronol SOL-90	20
Rapeseed oil	10

Fungicides

Copper Hydroxide 25 % OD	
Copper Hydroxide tech. 62%	40.3 %
Geronol ODessa 01	40
Geronol SOL-90	20
Rapeseed oil	23.8

Copper Oxychloride 20 % OD	
Copper Oxychloride tech. 57%	35.1 %
Geronol ODessa 01	39.9
Geronol SOL-90	15

Azoxystrobin 20 % - Cyproconazole 8 % OD	
Azoxystrobin tech. 98 %	20.4 %
Cyproconazole tech. 98 %	8.2
Geronol ODessa 01	7
Geronol SOL-90	15
Soprophor CY/8	5
Rapeseed oil	46

Mancozeb 35 % OD	
Mancozeb tech. 85%	41.2 %
Geronol ODessa 01	10
Geronol SOL-90	20
Rapeseed oil	42.8

Thiabendazole 25 % OD	
Thiabendazole tech. 95%	26.3 %
Geronol ODessa 01	25
Geronol SOL-90	20
Rapeseed oil	32.2

Insecticide

Imidacloprid 20 % OD	
Imidacloprid tech. 95%	21.1 %
Geronol ODessa 01	58.9
Geronol SOL-90	20

Flufenoxuron 5 % OD	
Flufenoxuron tech. 98%	5.1 %
Geronol ODessa 01	43
Rapeseed oil	up to 100

Abamectin 8.4 % OD	
Abamectin tech. 95%	9 %
Geronol ODessa 01	50
Rapeseed oil	41

Atrazine 19.6 % OD

Good Storage Stability

Room Temperature

After 54° C storage

Nicosulfuron 4 % OD

Good Storage Stability

Room Temperature

After 54° C storage

Thiabendazole 7 % OD

Good Storage Stability

Room Temperature

After 54° C storage

Example of recipes in methyl ester (with Geronol ODessa 05)

Herbicides

Nicosulfuron 16 % OD	
Nicosulfuron tech. 95%	16.9 %
Geronol ODessa 05	82.1

Fenoxaprop-ethyl 6.4 - Iodosulfuron 0.8 % OD	
Fenoxaprop-ethyl tech. 98%	6.6 %
Iodosulfuron tech. 88%	0.9
Geronol ODessa 05	87.9

Ethofumesate 11.2 – PMP 9.1 – DMP 7.1 % OD (Betanal Progress 27.4 %)	
Ethofumesate tech. 98.5 %	11.37 %
Phenmedipham tech. 97 %	9.38
Desmedipham tech. 97 %	7.32
Geronol ODessa 05	58.23
Alkamuls OL 40	15

Oxyfluorfen 20 % OD	
Oxyfluorfen tech. 97%	21 %
Geronol ODessa 05	79

Tebuconazole 25 % OD	
Tebuconazole tech. 98.2%	25.8 %
Geronol ODessa 05	42
Alkamuls T/85 -V	25
Amesolv CME	5

Chapter 9
Water Dispersible Granules WDG

- No flash point, No solvents
- Easy packaging
- High A.I. content, if feasible
- Good stability of the formulation

Water Dispersible Granules (WDG) are obtained by blending and agglomerating a ground solid active ingredient together with surfactants and other formulation ingredients, using water (or water plus surfactants) as agglomerating agent. A drying step is necessary to reduce moisture to 1 to 2% range.

The shape, size and performance of the granules vary, according to manufacturing process.

The typical composition of WDG usually contains:

Active ingredient(s)	50 to 90 %
Dispersing/Binding agents	5 to 20
Wetting agents	1 to 4
Antifoam, stabilizer, buffer	0 to 4
Fillers, disintegrating agents	up to 100

Water Dispersible Granules WDG

Method of preparation

Requirements for the active ingredient

Solid actives are more suitable for granulation. Nevertheless, it is possible to formulate liquid A.I.s as water dispersible granules, by adsorbing them onto an inert support, usually micronized silica such as **Tixosil.**

A high melting point of active ingredient(s) is required, particularly for spray-dried granules (MP > 150° C) and also to reach a proper storage stability at 50° C.

Concerning spray-dried granules, it is especially important to check the thermal stability of the active ingredient as pure material and also in the slurry (chemical stability, risk of explosion, determination of optimum spray drying conditions, etc.).

Final suspension values of WDG, depend on their fineness. To obtain optimum results, the particle size must be between 1 to 10 µm.

A milling process is necessary in order to get the right particle size of A.I.s. Wet-milling is generally used for spray-dried formulations. Dry milling (by jet-mill) is generally carried out on the active ingredients mixed with the other ingredients, and inerts are needed for the granulation processes.

Effects of surfactants

Surfactants play several roles during the preparation of the formulation and determine the final performances of the granules:

- help the milling of A.I. by adsorption onto the solid particles (for spray-dried formulation)
- help the blending and the extrusion by reducing the friction forces (binding and lubricant effect)
- provide wettability to the particles of the active ingredient
- provide stabilization by giving cohesion to the system

Wetting agent

Wetting agents decrease the interfacial tension between the solid active ingredient (which is mostly hydrophobe) and water. The choice of a wetting agent has to be made taking into account the hydrophobic character of the A.I., as well as the type of dispersing agent used in the formulation. This is the wetting/dispersing system which gives the performance properties to the granules. it has to be optimized for each formulation according to granulation process.

Dispersing agent

Dispersing agents change the potential of interactions by adsorption on the surface of the active ingredient particle, avoiding reagglomeration or flocculation (steric and electrostatic stabilization). The lipophilic part is adsorbed onto the organic particles and the hydrophilic part provides to the particles with a good affinity for the aqueous medium.

Binding agent

The binding agent must have a long polymeric chain in order to create cohesive forces between solid particles. Polymeric dispersing agents also act as binding agents in general.

Disintegrating agent

This type of additive can be sometimes useful for improvement of dispersibility. Clays are generally selected for this purpose.

Fillers

Sometimes to respect a specific active content, a certain quantity of an inert charge can be used to adjust the composition and to improve its performances. Fillers can be water soluble (for extrusion, pan granulation, fluid bed) or not water soluble (all processes) and can be used alone or in combination to meet the formulation requirements.

Selection of components

Dispersing and binding agents
The most efficient dispersing agents are synthetic polymers. These products act also as binding agents.

Wetting agents
The most effective surfactants to use as wetting agents in WDG are anionic, while nonionics are rarely used.

Compatibility agents
When the WDG formulation has to be mixed together with some other formulations like EC, or when tank mix compatibility is needed between two active ingredients, we recommend to incorporate a compatibility agent into the WDG formulation. These products are also efficient to improve the dispersibility of the granules.

Disintegrating agents and fillers
Inert mineral compound such as clays, bentonites, diatomaceous, colloidal silica, kaolin, etc., which swell by water absorption, improve WDG's dispersibility in many cases. Starch (corn, potatoes, etc.) can be very efficient, especially because they have aqueous swelling properties and also binding capabilities. These inerts can also be used as fillers in order to adjust the active content in the formulation. In some cases water soluble salts, such as potassium phosphate, sodium and ammonium sulphates, sodium citrate or urea can be used. These fillers are susceptible to help dispersibility by creating porosity in the granules. They are mainly recommended for extrusion, pan granulation and fluid bed granulation.

Antifoams
The choice of an antifoam depends on the process used. It can be used to limit foam during the process (spray drying technique) and also to limit foam during dilution in the tank or application on crops.

Manufacturing process of WDG

Advantages and disadvantages

Process	Advantages	Disadvantages
Spray drying	Good dispersibility, No tendency to dust, Free flowing	Low density, Medium resistance to attrition
Extrusion	High density, Good resistance to attrition	Poor spontaneity to disperse
Fluid bed granulation	Good dispersibility, Good resistance to attrition	Quite dusty

Spray drying

The working process has three steps: preparation of a slurry spray-drying of the slurry drying of the granules

General composition

Active ingredient(s)	40 to 80 %
Dispersing agent	4 to 10
Wetting agent	2 to 4
Lignosulfonate salt	0 to 10
Antifoam, stabilizer	0 to 10
Water	up to 100

Preparation of the slurry
The slurry is prepared by blending active ingredient(s), wetting and dispersing agents and the other components with water. Then it should be homogenized by strong suitable mechanical stirring or high shear mixer. If necessary, such dispersion shall be adjusted with water and milled in wet equipment in order to obtain a slurry with the following properties:

i. Dry extract of the slurry: between 50 and 65%
ii. Average particle size: 1 to 5 µm (particles should not exceed 10 µm)
iii. Viscosity (Brookfield 20 rpm, at 25° C): less than 1000 mPa.s
iv. Dynamic rheology of the slurry: Pseudo- plastic behavior

Spray drying procedure
The slurry is sprayed through a nozzle (bi-fluid nozzle or pressure nozzle) in large droplets (100 to 500 µm). The conditions for the spray drying (inlet temperature, slurry flow rate, inlet air flow rate, nozzle type etc.) must be adjusted depending on the equipment, in order to get the right residential time of the particles inside the spray drier. Spray dried granules are perfectly spherical (sizes range between 150 and 400 µm) and hollow (see picture).

This hollow shape is the result of a migration of the different components of the formulation during water evaporation. Granules have a relatively poor resistance to attrition because of their structures. The moisture after spray drying normally varies between 8 to 12%.

A discontinuous or continuous drying is necessary in order to get a residual moisture between 0.5 to 2%, depending on the influence it has on the suspension behavior of granules (an optimum residual moisture has to be determined). Fluid beds are very suitable to obtain homogeneous final drying of the granules.

Extrusion

Granules are directly obtained from the ground dry mixture of the A.I., binding/dispersing agent, wetting agent, fillers and other additives mixed with water. Two types of equipment are generally used to wet the ground powder: a low shear, kneading type mixer, or a high shear, high intensity mixer. The water content has to be adjusted in order to obtain the right rheology of the mixture. Generally this amount of water should be between 10 to 20%. The amount of water is the critical factor: if the paste is too dry, it will not extrude, but simply pour through the screen holes as a wet powder. Too much water will give a sticky paste which is difficult to extrude. The dried granules will, in this case, have impaired dispersibility. With even more liquid, the extruded strands stick together, forming clumps. These clumps do not break apart in the dryer, causing a loss of yield of on- size product. This point is more or less critical, depending on the dispersing/wetting agent. The paste is then pressed through a drilled screen by an extruder.

Photo of extruder

The available extruder types are:
- basket
- roller
- radial

Radial extruders are well adapted to this formulation because the pressure is low. In fact, the compaction of the mixture should not be too high in order to obtain good dispersibility of the granules. At a laboratory scale, the basket extruder is the most suitable type.

A critical process parameter to adjust, is the thickness of the extrusion plate, which is typically 0.8 to 1.2 mm. This is necessary to minimize the pressure developed during extrusion which may affect granule dispersibility. The extrude, coming from the screen, form comparatively long strands before they break. These extrudes then drop into the dryer where they break up into short cylinders, typically with length 3 to 5 times the cylinder diameter.

A discontinuous or continuous drying is necessary in order to get a residual moisture between 0.5 to 2% (an optimum residual moisture has to be determined). Fluid beds are very suitable to obtain homogeneous drying of the granules.

Extrusion is quite versatile and well adapted to different sizes of production.

Fluid bed

An aqueous solution of the wetting agent is sprayed directly onto a fluidized bed of the blended and milled formulation powder. Hot air is used to fluidize the bed, so that the granules are being dried as they agglomerate. The amount of water, the flow rate of the spraying and the air temperature should be adjusted to obtain the optimum performance.

The granules are irregular in shape and in size (between 0.5 to 2 mm).

This process is more suitable for small scale productions.

Examples of recipes

Carbendazim 80 % WDG	
Carbendazim tech. 98%	82 %
Tixosil 38 A	2
Bevaloid 6352 DD	1
Geropon T/77	2
Supragil WP	3
Supragil MNS/90	6
Bretax S*	2
Kaolin	2

Rimsulfuron 25 % WDG	
Rimsulfuron tech. 95%	27 %
Sodium Sulphate	54
Soprophor SDS	3
Geropon SC/213	8
Ca lignosulphonate	5
Hexametaphosphate (stabilizing agent)	3

Pymetrozine 50 % WDG	
Pymetrozine tech. 95%	52.7 %
Tixosil 38 A	2
Supragil WP	2
Geropon SC/213	10
Bretax S R02	13
Kaolin	20.3

Mancozeb 75 % WDG	
Mancozeb tech. 85%	89 %
Bretax S*	4
Supragil MNS/90	4
Geropon SDS	3

Tribenuron-methyl 75 % WDG	
Tribenuron-methyl tech. 95%	79 %
Geropon SDS	2
Geropon T/36	10
Bretax S*	4
Ammonium sulphate	3
Tixosil 38 A	2

Bordeaux Mixture 20 % WDG	
Bordeaux Mixture tech. 26%	77 %
Tixosil 38 A	3
Supragil WP	1
Geropon T/77	1
Supragil RM/210-EI	7
Bretax S*	7
Calcium carbonate	4

Tebuconazole 45 % WDG	
Tebuconazole tech. 98%	46
Tixosil 38 A	5
Kaolin	27
Supragil WP	2
Geropon T/36	20

Diuron 46.8 % - Hexazinone 13.2% WDG	
Diuron tech. 98%	48.1 %
Hexazinone tech. 97%	13.6
Tixosil 38 A	3
Supragil WP	2
Geropon T/36	12
Kaolin	21.3

** Bretax S: Sodium lignosulphonate*

Chapter 10

Microemulsions ME

- Very stable and easy to produce
- Water based
- No flash point
- Clear solution
- Very good compatibility

Microemulsions are especially well suited to active ingredients used at low application rates, low active content formulations, wood treatment or when a clear solution is required at the application rate.

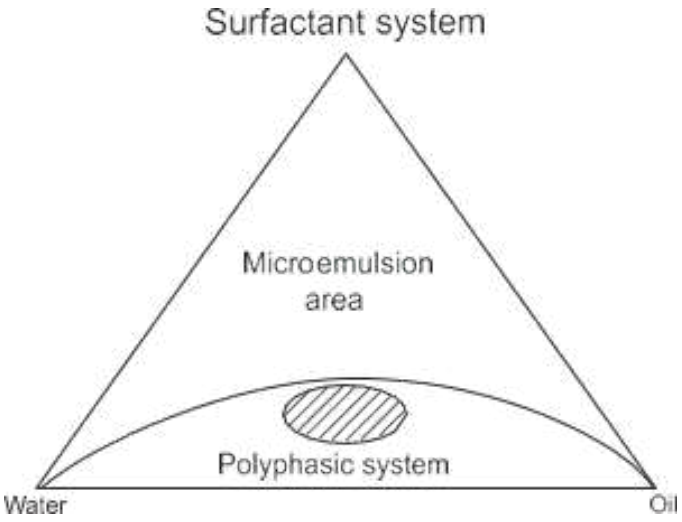
A microemulsion is a clear, thermodynamically stable mixture of at least three components:

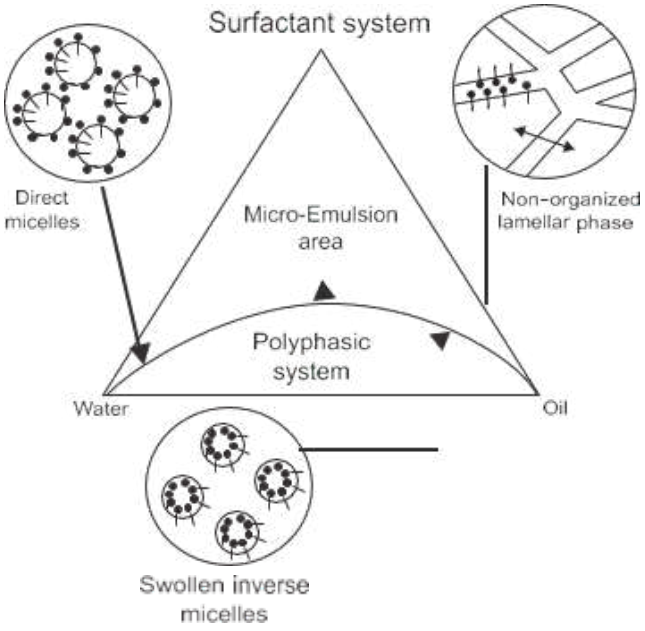
- a hydrophobic component (non water- soluble oil) which could be a liquid, a low melting solid (less than +50° C), or a solid dissolved in an organic solvent.
- a surfactant system
- water

A co-solvent is often added to the mixture to increase the solubilizing power of the surfactant system. Different substances can be used as co- solvents, alcohols, amines or etheralcohols.

Different from an emulsion, the characteristic size of the hydrophobic or the hydrophilic domains is typically 10 nm. In fact, microemulsions are a particular type of colloidal system. The typical dimension of the local structure explains why microemulsions are transparent.

Phase diagrams are very useful to describe such systems. This simplified ternary representation describes the different phases obtained when





Each corner of the phase diagram represents a pure compound. Each side represents the different compositions of a blend of two components, and a point inside the diagram represents the composition of a blend of the three components. These diagrams are often complex.

When the water content of a microemulsion is low (near the oil corner of the phase diagram), the local structure consists of swollen inverse micelles. The oil phase is continuous and water micellar droplets are the dispersed phase. Surfactant and co-surfactant molecules are disposed on the interface between water and the hydrophobic phase (oil). As the water content increases, the shape and the volume of the hydrophilic core of inverse micelles expands. At a given water content, a continuous water path exists; so the water phase becomes continuous. The water and the oil phases make an interpenetrated bi-continuous network. Near the water comer, the oil content is low and then the microemulsion looks like a direct micellar solution. The structure of these different systems can be studied or characterized by low angle X-rays of neutron scattering, rheological or conductivity measurements.

Method of preparation

The typical composition of ME usually contains:

Active ingredient	50 to 300 g/l
Surfactants	100 to 400
Solvents/co-solvents	0 to 300
Antifoam	0 to 10
Antifreeze or buffer	0 to 100
Water	up to 1 L

Definition of a suitable active ingredient

Microemulsions are suitable for liquid active ingredients. A low melting point or solid active ingredient has to be solubilized in an appropriate solvent first. Active ingredients should be chemically stable in water.

The criteria for the choice of a solvent are the following:

- high flash point and non-toxic
- high solubilizing properties for the active ingredient to avoid crystallizations during storage

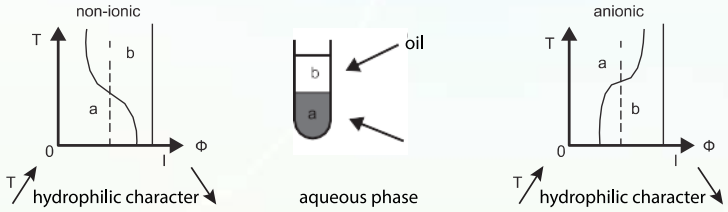
Microemulsions ME

Effect of surfactants

The process to obtain microemulsions (ME) is simpler than those used to prepare emulsions in water (EW). Since a microemulsion is a thermodynamically stable phase, the result is absolutely independent of the way of preparation. Microemulsification is spontaneous. Water in oil (w/o) microemulsions, (near the oil- surfactant border of the phase diagram) are easier to formulate than oil in water (o/w) microemulsions. This difference arises from the energy difference between solubilizing water in oil and solubilizing oil in water. The water in oil process is thermodynamically more favorable.

Surfactants are basic components in microemulsions. Nevertheless, it is somehow difficult to find the appropriate surfactants and co-surfactants (surfactant system) to obtain stable formulations over a large temperature range (-10° C to +54° C). Microemulsions require quite high concentrations of surfactants (typically 2% to 30%). This high amount is due to the small size of the oil and water domains, thus, due to the large area of the interface. Nevertheless, this amount can be reduced by optimizing the choice of the surfactant and co-surfactant. There are no real definitive guide rules that one may use, but we recommend to use a blend of nonionic and anionic surfactants to guarantee the physical stability vs. temperature. This effect is illustrated by the following diagram. It represents the affinity of a surfactant (nonionic or anionic) with oil or water at different temperatures.

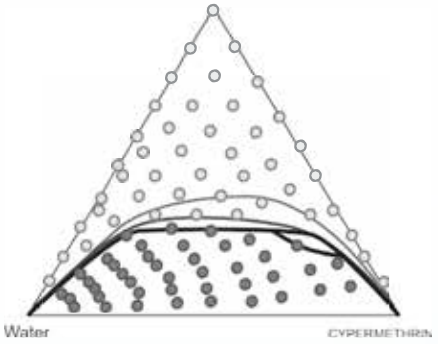
Φ: Volumic fraction of oil / water



For example at high temperature, a nonionic surfactant has a better affinity with oil (area b), while at a lower temperature it has a better affinity with water (area a). It is the contrary for an anionic surfactant.

By blending nonionic and anionic surfactants it is possible to combine these effects and obtain a microemulsion stable over a large range of temperatures. The ratio between these emulsifiers must be optimized in order to obtain the best thermal stability. The phase diagram below shows the influence of temperature on an optimized surfactant system for Cypermethrin.

Surfactant Sysyem



Microemulsion

Lamellar Phase

Polyphasic System

Limits of the microemulsion area
/ -5°C / 30°C / 45°C

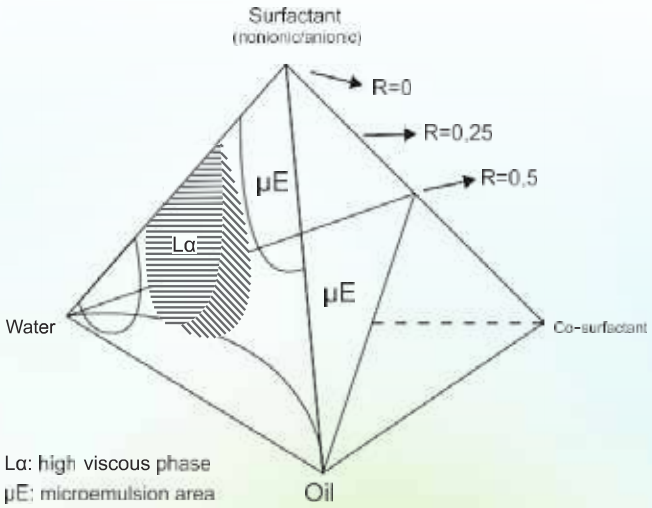
Choosing surfactants to make a microemulsion, depends on the nature of the active ingredients.

Selection of a co-solvents

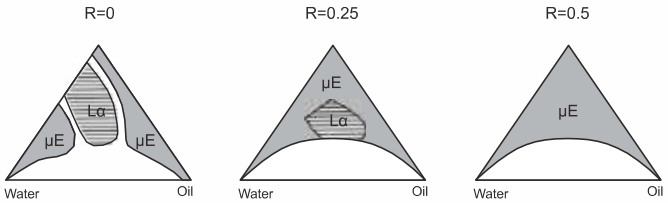
A co-solvent is often added to the mixture to increase the solubilizing power of the surfactant system. Generally speaking, the best co-solvents are small molecules which have a great affinity for the oil/water interface. They have to be chosen according to the nature of surfactants and to the nature of the oil to be microemulsioned. They can also prevent the formation of a viscous phase (lamellar phase etc.).

The ratio R=Co-solvent/Surfactants, normally varies from 0.3 to 0.8. This ratio and the nature of the co-solvents have to be optimized in order to lower the surfactants content, to obtain the best thermal stability and to avoid forming viscous phases.

This representation of a quaternary water-oil- alcohol-surfactants system in a tetrahedral phase diagram, illustrates the influence of the co-solvents on the nature of the different phases. The ratio R=0.5 could be considered as the optimum ratio for this system.



The following diagrams are the two-dimensional representation of ternary water-oil-surfactants systems for ratios R of 0.25 and 0.5.



Different molecules (alcohols, amines, ether alcohols, etc.) can be used as co-solvents. Light alcohols like isobutanol, propanol and butanol are suitable for micro-emulsions. However, their flash points are too low to be used in plant protection formulations.

Laboratory formulation and industrial production

Microemulsions are thermodynamically stable formulations and the result is independent from the way of preparation. This point makes microemulsions very attractive from a manufacturing point of view.

However, we recommend to blend the organic phase (active ingredient with solvent, if necessary) with surfactants and co-surfactant and then to add water and mix slowly.

Control methods

Storage stability

The commercial formulations should be stable for at least 2 years. Microemulsions are thermodynamically stable which means that in a determinate range of temperature, their physical stability is not affected by time, if no chemical degradation occurs. Some accelerated aging tests give an indication of the long term stability:

- tropical test: 2 weeks at +54° C (CIPAC 1-MT 46.1.3)
- cold stability test: 1 week at 0° C (CIPAC 1-MT 39)

M.E.	E.W.

ME (microemuslion)

Appearance: Clear, light passes through
Droplet size: around 10-50 nanometer, nanosize oil-droplets

- requires high level of surfactants input
- thermodynamically stable
- very safe and user-friendly
- good efficacy thanks to high surfactant content
- stability at "high" temperature for two months at +45° C
- stability to thermal shocks: samples in sealed opaque glass bottles are submitted to temperature cycles (24 hours at -5° C and 24 hours at +45° C) for one or two month period.

Microemulsions should remain clear. Chemical degradation of the active ingredient should be evaluated, especially for low active content formulations.

EW (emulsion in water)

Appearance: Milky, light does not pass through
Droplet size: around 2- 4 Micron, oil droplets dispersed in water

- requires high energy input (high shear mixing)
- not thermodynamically stable
- it needs suitable emulsifier system for long-term stability
- reduced solvent amount vs. EC safer and user-friendly vs. EC
- not flammable

Examples of recipes

Cypermethrin 10 % ME	
Cypermethrin tech. 93%	10.8 %
Butyl glycol	20
Soprophor TSP/724	20
Water	49.2

Deltamethrin 10 % ME	
Deltamethrin tech. 98.5%	10.2 %
Cyclohexanon	40
Soprophor TSP/724	25
Water	24.8

Permethrin 10% ME	
Permethrin tech. 93%	10.8 %
Butyl Glycol	25
Soprophor TSP/724	20
Water	44.2

Tetramethrin 10 % ME	
Tetramethrin tech. 92%	11 %
Cyclohexanone	30
Soprophor TSP/724	25
Water	34

Cypermethrin 10 % - tetramethrin 2.28 % - PBO 11.28 % ME	
Cypermethrin tech.95%	10.53 %
Tetramethin tech 95 %	2.4
PBO tech. 95 %	12.63
Dipropylene glycol methyl ether	8
Alkamuls 14/R	30
Water	16.44

Pyrethrin 1.5 % + PBO 11.5 ME	
Pyrethrin pale 50%	1.5 %
PBO tech. 95 %	12.2
Dipropylene glycol methyl ether	0
Antarox B/848	20
Water	26.3

Chapter 11

Emulsion in Water EW

- Formulation of A.I.s with low solubility insolvents
- Aqueous based , no flash point
- Low content of solvent
- Good eco-toxicity profile

Emulsion in water (EW), results from the dispersion of a liquid or a low melting point active ingredient in a water continuous phase. The size of the dispersed droplets generally varies from 0.5 to 2 µm.

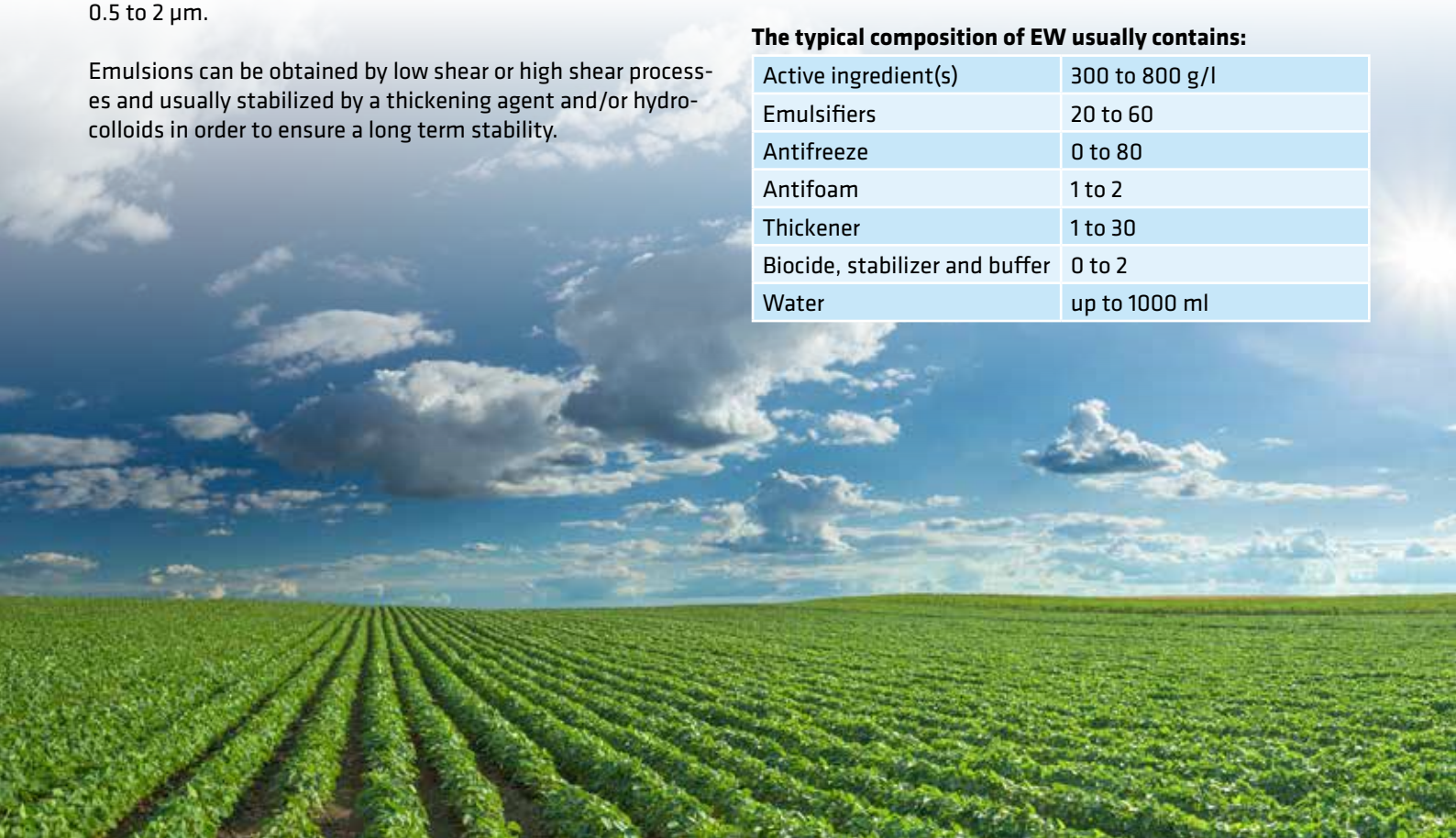
Emulsions can be obtained by low shear or high shear processes and usually stabilized by a thickening agent and/or hydrocolloids in order to ensure a long term stability.

EW formulations, in comparison to EC formulations, offer:

- reduction of the phytotoxicity, eco-toxicity and dermal toxicity
- higher flash point and therefore safer in transport and storage
- compatibility with water-based Suspension Concentrates (SC)
- concentrated base inwaterforSuspoemulsions (SE) formulations

The typical composition of EW usually contains:

Active ingredient(s)	300 to 800 g/l
Emulsifiers	20 to 60
Antifreeze	0 to 80
Antifoam	1 to 2
Thickener	1 to 30
Biocide, stabilizer and buffer	0 to 2
Water	up to 1000 ml



Method of preparation

Definition of suitable active ingredients

Emulsions in water are suitable for liquid active ingredients and also for low melting point A.I.s which cannot be formulated under a Suspension Concentrate (SC) form.

Active ingredients need to have a good chemical stability in water.

Small amount of solvent can be added to obtain a solution of the active ingredient.

Stabilizing agent or buffer can be added when necessary.

Manufacture description and structures of emulsions.

Preparation

Different parameters are involved in the preparation of an emulsion. The energy input, the temperature, the way of introduction of different ingredients and the rheology are important factors in obtaining a long term stable emulsion.

Emulsifiers can be added to water or to A.I.s and components should be mixed by a suitable blender (high speed mixing agitation) to achieve an average size of approx 1 µm.

The use of an antifoam during the process is highly recommended to avoid the increase of viscosity due to air entrapment.

The final viscosity, after degassing, vary considerably depending on the components and the working process. It should be between 1000 and 2500 mPa.s (Brookfield 20 rpm) to perform a long term stability.

If necessary, the viscosity value can be adjusted by adding a 2% water solution of **Rhodopol 23.**

Roles of emulsifiers

Emulsifiers are basic components in water based concentrated emulsions. They should be used in the emulsion:

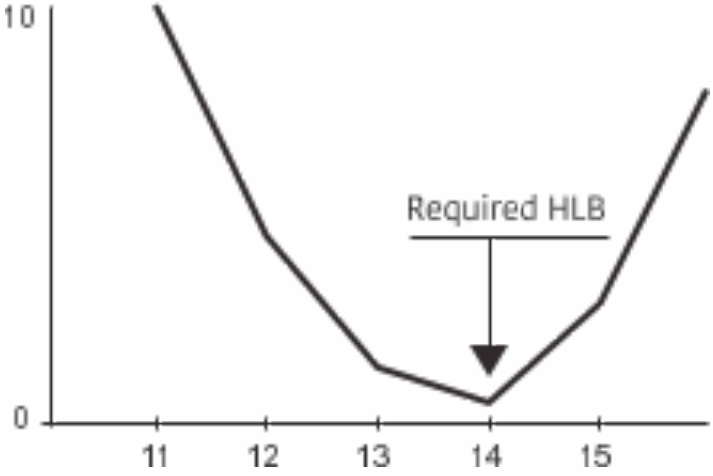
- to allow the wetting and dispersion of the organic phase into the aqueous phase by reducing the oil/water interfacial tension during mixing.
- to provide steric and electrostatic stabilization to the micronized droplets against flocculation, aggregation or coalescence in a concentrated state, and to guarantee the long term stability of emulsions in various storage conditions.
- to facilitate dispersion of the formulation during water dilution and stabilize the micronized droplets of active ingredient in the diluted state.
- to improve compatibility with other formulations in a diluted state at the application rate.

Selection of components

Emulsifiers

To be efficient, surfactants need to be strongly adsorbed or solubilized at the oil/water interface. They assure the fluidity of the emulsion by developing strong repulsive forces hindering aggregation, flocculation or coalescence. After emulsification, the dispersed droplets have an inherent tendency to flocculate as the result of the attractive Van der Waals and electrostatic forces. The strong adsorption of well chosen surfactants at the oil/water interface of the droplets, generates repulsive forces (steric and/ or electrostatic) in order to balance the attractive ones positively. The choice of a surfactant system depends on the polarity of the oil to be emulsified, the interactions between the oil phase and the surfactant system and the nature of the continuous phase.

Emulsion in Water



The required HLB to emulsify this active ingredient (example) is about 14 (it corresponds to the emulsion with the smallest particle size). According to the chemical nature of the active ingredient, the chemical nature of the hydrophobic part of the emulsifier has to be optimized at around the same required HLB value, in order to generate the strongest affinity with the liquid to be emulsified.

Antifreezes

Monopropylene Glycol or Glycerine are the most commonly used antifreezes in the range of 50 to 80 g/l.

Thickeners

Rhodopol, should be added after the mixing step, to provide a perfect long term storage stability in most cases.

Antifoams

The role of this additive is to avoid formation of foam during preparation, water dilution and field application.

Control methods

Storage stability

The commercial formulations should be stable for at least 2 years without any significant change of viscosity and without sedimentation or phase separation. However, the presence of a supernatant water layer on the surface is acceptable, providing only a slight agitation needed for the mixture to redisperse.

Some accelerated aging tests give a fast indication of the long term stability:

- tropical test: 2 weeks at +54° C (CIPAC 1-MT 46.1.3)
- cold stability test: 1 week at 0° C (CIPAC 1-MT 39)
- stability at “high” temperature for two months at +45° C
- stability to thermal shocks: samples in sealed opaque glass bottles are submitted to temperature cycles (24 hours at -5° C and 24 hours at +45° C) for one or two month period.

Examples of recipes

Tebuconazole 25 % EW	
Tebuconazole tech. 97.3%	25.7 %
Rhodiasolv ADMA 10	56.1
Geronol TEB-25	15
Water	1

Cypermethrin 10 % - Tetrametrhin 2 % - PBO 5 % EW	
Cypermethrin tech. 93%	10.8 %
Tetramethrin tech. 95%	2.1
PBO tech. 95%	5.3
Water	51.8
Rheozan	10
Alkamuls OR/36	20

Cypermethrin 10 % EW	
Cypermethrin tech. 93%	10.8 %
Propylen glycol	5
Alkamuls OR/36	7
Soprophor TS/10	3
Rheozan (2% sol.)	20
Water	54.2

Deltamethrin 5 % EW	
Deltamethrin tech. 98%	5.1 %
Cychlohexanone	20
Alkamuls 14/R	5
Rhodopol 23 (2% sol.)	20
Water	49.9

Lambda - cyhalothrin 5 % EW	
Lambda-cyhalothrin tech. 98%	5.3 %
Amesolv CME (methyl ester canola oil)	10
Alkamuls RC	10
Water	74.7

Ethofenprox 5 % EW	
Ethofenprox tech. 98%	5.2 %
Amesolv CME (methyl ester canola oil)	30.5
Alkamuls OR/36	10.2
Water	54.1

Permethrin 10 % EW	
Permethrin tech. 92%	10.9 %
Methyl ester	15
Alkamuls OR/36	7
Soprophor TS/10	3
Water	64.1

Cyfluthrin 5 % EW	
Cyfluthrin tech. 92%	5.4 %
Rhodiasolv ADMA 10	5
Alkamuls OR/36	4.2
Soprophor TS/10	1.8
Water	83.6

Penconazole 20 % EW	
Penconazole tech. 95%	21.1 %
Solvesso 150-ND	30
Water	32.9
Rhodopol 23 (2% sol.)	6

Chapter 12

Wettable Powders WP

- Dust hazard
- Bulky products
- Difficult to handle and measure
- Formulation replaced by WDG

Production of Wettable Powders (WP) is relatively simple with moderate costs.

Physical-chemical characteristics

According to international specifications, the physical-chemical characteristics of WP, have to comply with the following requirements:

- Quick wetting
- Complete dispersibility
- Suspension stability
- Low foaming
- No caking during storage

Formulation

WP can differ remarkably according to active ingredient content, required performances, application rates, etc. The typical composition of WP usually contains:

Components	Solid A.I.	Liquid or waxy A.I.
Active ingredient(s)	up to 90 %	up to 50 %
Wetting agent	1 to 5 %	1 to 5 %
Dispersing agent	3 to 10 %	3 to 10 %
Stabilizer, compatibility agent	0 to 5 %	0 to 5 %
Colloidal silica	up to 15 %	up to 40 %
Fillers	up to 100 %	up to 100 %

Selection of components

Active Ingredients

Each A.I. has particular physical-chemical characteristics. Therefore, to choose the additives and inerts it is necessary to take into account several elements, partially listed in this section. The basic differences affecting the choice of additives are primarily the physical state (solid or liquid), the chemical stability at environmental conditions, pH, etc.

Absorbing anticaking fillers

The absorbing filler is usually a precipitated silica with a high absorptive power. Milled silica is preferable for formulations of absorbed A.I. which only need homogenization. Either diatomite or calcium silicate may also be used. The percentage of absorbent filler must be sufficient to lead to a dry, free-flowing powder, before and after tropical tests.

Fillers

There is a wide range of fillers to choose. Either natural mineral products such as kaolin, attapulgite, calcite, diatomite, etc. The choice must be made according to the physical- chemical characteristics with consideration to the following properties:

Fineness: particle size needs to be as low as possible, in order to obtain a suitable suspensibility.

pH and pK: need to be chosen according to the chemical properties of the active ingredients, in order to ensure the storage stability.

Free moisture: usually should be as low as possible to avoid degradation of the A.I.

Impurities: can increase the risk of degradation of A.I. and must be as low as possible.

Crystalline silicas: are often present in a filler with natural origin, and their level should be as low as possible to avoid undue wear on the equipment.

Anticaking property: is an especially important characteristic for the wettable powders of high A.I. content, or when the A.I. has a low melting point, in order to insure suitable free flowing.

Wettable Powders

Wetting agent
As the majority of active ingredients have a hydrophobic nature, the surfactants are needed to provide rapid wetting and dispersion. The wetting agent should not create stable foam to avoid problems during the field treatment.

Dispersing agent
Our dispersing agents are synthetically produced and show very high efficiency at low concentration. They also act as chelating and sequestering agents.

Sometimes they are used in small amounts (0.5 to 1%) to improve activity of lignosulfonate salts.

Compatibility agent
Some flocculation may occur when WP with EC is mixed in the tank. In order to make them compatible, a designed polymeric component shall be used, normally at 1 to 3% to provide the correct characteristics.

Antifoam
Solvay has especially designed an antifoam to solve the foaming problems of WP, to be blended after grinding or in the spraying tank. This antifoam is based on a silicone compound micro-encapsulated in a soluble filler, which releases the antifoam's active component when it is dispersed in water.

Examples of recipes

Captan 80 % WP	
Captan pure tech.	80 %
Supragil WP	2
Supragil MNS/90	3
Inerts	up to 100

Copper Oxychloride 40 % - Cymoxanil 4 % WP	
Copper Oxychloride tech. 57%	70 %
Cymoxanil tech. 96%	4.2
Kaolin	22.8
Supragil MNS/90	2
Supragil WP	1

Atrazine 80 % WP	
Atrazine tech. 96%	84 %
Kaolin	8
Tixosil 38 A	4
Supragil WP	2
Geropon T/36	2

Benomyl 50 % WP	
Benomyl tech. 95%	52.6 %
Kaolin	42.4
Geropon SDS	2
Supragil MNS/90	3

Carbendazim 50 % WP	
Carbendazim tech. 96%	51 %
Kaolin	46
Supragil WP	2
Supragil MNS/90	1

Carboxim 75 % WP	
Carboxim tech. 98%	77 %
Kaolin	18
Supragil WP	2
Supragil MNS/90	3

Mancozeb 80 % WP	
Mancozeb tech. 90%	88.9 %
Kaolin	6.1
Supragil WP	2
Supragil MNS/90	3

Mancozeb 64 % - Metalaxyl 8 % WP	
Mancozeb tech. 90%	71.2 %
Metalaxyl tech. 95%	8.4
Kaolin	15.9
Supragil WP	1.5
Supragil MNS/90	3

Metribuzin 70 % WP	
Metribuzin tech. 95%	74 %
Kaolin	22
Supragil WP	2
Geropon T/36	2

Pirimicarb 50 % WP	
Pirimicarb tech. 95%	53 %
Kaolin	44
Supragil WP	2
Geropon T/36	1

Thiobendazole 60 % WP	
Thiobendazole tech. 95%	64 %
Kaolin	31
Supragil WP	2

Metribuzin 70 % WP	
Metribuzin tech. 95%	73.6 %
Kaolin	16.4
Supragil WP	2
Soprophor AMC	8

Acetamiprid 20 % WSP	
Acetamiprid tech. 95%	21 %
Sugar	67
Sodium Benzoate	10
Supragil WP	1
Supragil GN	1

Benomyl 50 % WP	
Benomyl tech. 95%	52.6 %
Sugar	42.4
Geropon SDS	2
Supragil MNS/90	3
or	
Benomyl tech. 95%	52.6 %
Supragil MNS/90	3
Geropon SDS	2
kaolin	up to 100

Mancozeb 80 % WP	
Mancozeb tech. 85% (by Duslo)	94 %
Tixosil 38 A	2
Supragil WP	1

Abbreviations

Abbreviation	Stands for
AI	Active Ingredient
APVMA	Australian Pesticide and Veterinary Medicine Authority
BA	Biological Activator (Adjuvant)
C	Compatibility Agent
CIPAC	Collaborative International Pesticides Analytical Council
D	Dispersing Agent
E	Emulsifier
EC	Emulsifiable Concentrate
EPA	Environmental Protection Agency
EW	Emulsion in Water
FS	Flowable concentrate for seed treatment
IPA	Isopropyl Amine
L	Liquid
K	Potassium
ME	Micro-Emulsion
N,MP	N-Methyl-2-pyrrolidone
OD	Oil Dispersion
P	Paste
Pw	Powder
R&I	Research and Innovation
RFS	Rheometrics Fluids Spectrometer
SC	Suspension Concentrate
SE	Suspo-Emulsion
VL	Viscous Liquid
WA	Wetting Agent
WDG	Water Dispersible Granule
WP	Wettable Powder
WSP	Water Soluble Powder

SOLVAY Way

The way we do business

Solvay puts into practice a sustainable development policy called Solvay Way because we are convinced our future is dependent upon the responsible way in which we conduct our current activities — a way that reflects our commitments to each of our stakeholders. Solvay Way encompasses three interlinked, equally important spheres: the Environment Sphere, the People Sphere and the Economic Sphere. Based on a framework of responsibilities, Solvay Way allows Solvay sites and businesses to conduct self-assessments of their practices and establish action plans that promote continuous progress. At Solvay, the way we do business creates sustainable value for all of our stakeholders through our innovation and partnerships.

> Responsible Care is the chemical industry's voluntary continuous improvement initiative to promote safe handling of products. (1987)

> The United Nations Global Compact aims to ensure that heads of companies promote and uphold 10 universal principles concerning human rights, working conditions, respect for the environment and anti-corruption. (2003)

> The International Federation of Chemical, Energy, Mine and general workers' unions. (2005)

> Solvay Novecare has achieved worldwide ISO-9001 Quality Management System Multi-Site Certification. (2008)

SOLVAY
asking more from chemistry®

North America
Solvay Novecare – 504 Carnegie Center – Princeton, NJ 08540 – USA
Phone: +1-800-973-7873 – Fax: +1-609-860-0463 – NovecareCC@solvay.com

Europe
Solvay Novecare – 40, rue de la Haie-Coq – F-93306 Aubervilliers Cedex – France
Phone: +33 (0) 1 53 56 50 00 – Fax: +33 (0) 1 53 56 53 90 – NovecareCC@solvay.com

Asia Pacific
Solvay Novecare – 1, Biopolis Drive – #05-01/06 AMNIOS – Singapore 138 622
Phone: +65 - 6291 1921 – Fax: +65 - 6394 3376 – NovecareCC@solvay.com

Latin America
Solvay Novecare – Centro Empresarial – Avenida Maria Coelho Aguiar, 215, Bloco B-1° Andar
Cep: 05804-902 – São Paulo-SP Brazil
Phone: +55 11 3747-7637 – Fax: +55 11 3741-8378 – NovecareCC@solvay.com

www.solvay.com

WW | EU | JUNE | 2016 | SOLVAY NOVECARE - Dileo Graphic Design, mariadileo@comcast.net