Solutions for High Electrolyte Systems

Specialty Phosphate Esters

Croda's Phosphate Esters are highly functional products for complex formulations used in the Agricultural Industry. Phosphate esters are among the most versatile of the surfactant classes. However, to fully utilize the advantages of this broad class of materials the formulator should have a basic understanding of the structure related performance variables associated with phosphate ester chemistry.

This brochure will highlight the Croda range of APE free, EPA cleared phosphate esters and provide important functionality criteria to aid the proper product selection for your intended application.

Performance Benefits:

- Emulsion Stability
- Electrolyte Tolerance
- Dispersion Stability
- Wetting Enhancement
- Chemical Compatibility
- Adjuvancy

Crop Care

Nature & Technology in Harmony™

CRODA

Working with Phosphate Esters

Performance Benefits

- Emulsion Stability
- Electrolyte Tolerance
- Dispersion Stability
- Wetting Enhancement
- Chemical Compatibility
- Adjuvancy

These benefits are critical to the formulation stability and performance in challenging environments such as:

- Complex tank mixtures
- Formulations applied in fertilizer containing tank mixes
- High electrolyte based adjuvant products
- Formulations containing salt based active ingredients

A few general guidelines are listed to the right to help in proper phosphate ester selection.

Carbon Chain (Hydrophobe)

- Shorter carbon chains, and those with more branching, tend to be better wetting agents
- Longer carbon chains are typically better for emulsification

Degree of Ethoxylation

- Low degree of ethoxylation provides better wetting performance
- Higher degree of ethoxylation provides better electrolyte tolerance
- Higher degree of ethoxylation results in better microemulsion performance

Mono/Di-Ester Ratio

When reacting an alcohol or alcohol ethoxylate with a phosphating compound, the result is always a mixture of mono and di-esters.

- Higher mono-ester content provides better wetting performance in concentrated electrolyte (e.g. glyphosate SL products and ammonium sulfate solutions)

Product Name	Chemical Description	EPA Status	Physical Form	Hydrophobe	Degree of Ethoxylation
Atlox™ AL-3382	PEG-5 Octyl Phosphate	920	Liquid	Octyl alcohol	5-6 moles
Atlox™ DP 13/6	PEG-6 Isotridecyl Phosphate	920	Liquid	Isotridecyl alcohol	5-7 moles
Crodafos™ CS2A	PEG-2 Cetearyl Phosphate	920	Solid	Cetearyl alcohol	2 moles
Crodafos™ D4A	PEG-4 Decyl Phosphate	920	Liquid	Decyl alcohol	5-6 moles
Crodafos™ O3A	PEG-3 Oleyl Phosphate	920	Liquid	Oleyl alcohol	3 moles
Crodafos™ O5A	PEG-5 Oleyl Phosphate	920	Liquid	Oleyl alcohol	5 moles
Crodafos™ O10A	PEG-10 Oleyl Phosphate	920	Liquid	Oleyl alcohol	9-11 moles
Crodafos™ O10D	PEG-10 Oleyl Phosphate, DEA Salt	920	Liquid	Oleyl alcohol	9-11 moles
Crodafos™ SG	PEG-10 PPG-5 Cetyl Phosphate	920	Liquid	Cetyl alcohol	8-10 moles EO 4-6 moles PO
Crodafos™ T5A	PEG-5 Tridecyl Phosphate	920	Liquid	Isotridecyl alcohol	4-6 moles
Crodafos™ T6A	PEG-6 Isotridecyl Phosphate	920	Liquid	Isotridecyl alcohol	5-7 moles
Multitrope™ 1214	PEG-4 Decyl Phosphate	920	Liquid	Decyl alcohol	4-5 moles

Table 1: Product Range

- Higher di-ester content facilitates solubility/compatibility in oil and provides improved wetting in agricultural spray mixtures (tank dilutions) containing low to moderate electrolyte concentrations
- Higher mono-ester content is better for hydrotroping and tank mix compatibilization
- Mixed ester content is frequently preferred for emulsification properties

Neutralization

Phosphate esters are typically supplied in the free acid form to provide liquid, 100% active products with maximum formulation flexibility. The phosphate ester composition (ratio of mono-ester to di-ester) determines buffering capacity and amount of neutralizing counter-ion required for a given pH level.

Figure 1 describes the neutralization behavior for a range of phosphate esters with monoethanolamine. The curves show a plateau response in the region of pKa_1 and pKa_2 for the phosphate group as neutralizing agent increases. This demonstrates the buffering effect observable in both regions.

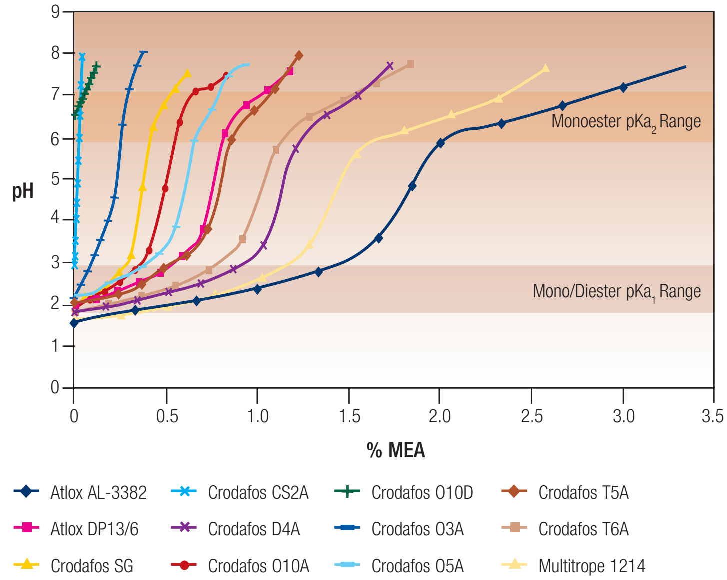

Figure 1: Neutralization curve

	Mono to Di-ester Ratio	Application				Wetting		Solubility		Viscosity Build Potential
		Emulsion	Micro-emulsion	Dispersion	Adjuvancy	Enhanced Wetting	Enhanced Wetting in Electrolytes	Increased Electrolyte Solubility	Oil Solubility/ Compatibility	
	High		■		■		■	■		Low
	Low	■				■			■	Medium
	Mixed	■		■						Very high
	Mixed		■		■			■		Medium
	Mixed	■	■		■				■	Very high
	Mixed	■	■							High
	Mixed	■	■							High
	Mixed	■	■							High
	Mixed	■	■	■	■					High
	Mixed	■	■							Medium
	Mixed	■	■			■			■	Medium
	High		■		■		■	■		Low

Formulating with Phosphate Esters

Emulsifiable Concentrates (EC)

Pairing an appropriate phosphate ester with a functional counter-ion, such as a low EO fatty amine, can result in an excellent emulsifier "pair" for ECs.

In addition to being suitable for the replacement of certain alkylbenzene sulfonates to form emulsifier systems with increased tolerance of higher hardness water, select phosphate esters have specifically been used to significant benefit as a key emulsifier type useful to stabilize emulsifiable concentrates (EC) in spray mixtures containing liquid fertilizers. While the main application for this tends to be in preemergent products for use in corn, these systems should also be highly suitable in micronutrient containing spray solutions making them an excellent choice for developing products for postemergent use over soybeans as well. Principal products for use in these applications will include solvent or oil soluble derivatives such as Crodafos T6A, Crodafos O3A, Crodafos O5A, or Atlox DP13/6 with the latter being more fully compatible in concentrates based on low polarity oils such as paraffinic or vegetable oils. Adjuvancy demonstrated by these products in field trials with herbicides like glyphosate, clethodim, and saflufencail provide an opportunity to enhance the biological performance of certain tank mixtures over mixtures of the same herbicides that may be using alkylbenzene sulfonate based emulsifier systems.

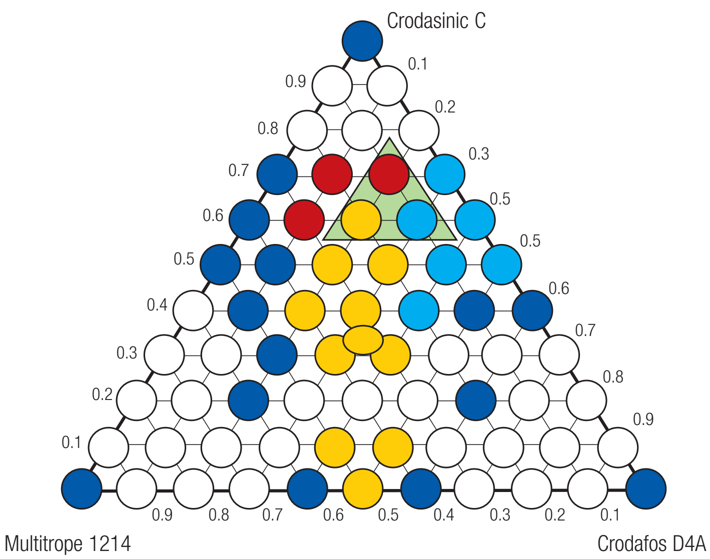

Figure 2: Experimental design triangle of a ME system focusing on varying mixtures of phosphate esters (Crodafos D4A and Multitrope 1214) and acylsarcosine (Crodasinic C).

Microemulsions (ME)

Phosphate esters can be excellent, low toxicity microemulsifiers for a number of applications such as manufacturing concentrates or ready to use (RTU) products. When combined with other surfactants, such as amphoterics or sarcosinates, they can provide stable microemulsion systems in electrolytes such as 40% (w/w) ammonium sulfate (AMS).

Microemulsions formed in high electrolyte concentrations rely on a few classes of surfactants that present very high electrolyte tolerance within their chemical structure. Among the classes of chemistry suitable for producing these systems, phosphate esters provide a broad range of flexibility in terms of their composition and related performance. To produce stable microemulsions in high electrolyte concentrations, phosphate esters should be selected from groups presenting (1) a high degree of direct solubility in the target electrolyte as well as from a type presenting (2) high solubility in the target oil system along with the desired electrolyte tolerance provided from the ether-phosphate structure of these materials. Drawing from a material in both classes, a combination of phosphate esters can be used alone or combined with other functional materials to modify performance and produce a stable system. (This approach is outlined in Croda's patent application on the use of these materials to form stable microemulsions in high electrolyte).

Ingredient	Weight (%)
Crodasinic C Crodafos D4A Multitrope 1214	15.0
MSO	15.0
AMS (40% active)	62.5
Monoethanolamine	4-5 (to pH 7.0-7.5)
Water	q.s. to 100%

Unstable samples

Stable samples

Stable samples at both room temperature and 54°C, but unstable at 4°C

Stable at both room temperature and 4°C, but unstable at 54°C

Phosphate Esters in Adjuvants

Phosphate esters can be effective adjuvants on their own in addition to their formulation attributes.

Treatment	SEFTA 21-DA-A	ABUTH 21-DA-A	AMATA 21-DA-A	IPOHE 21-DA-A
Glyphosate + AMS + NIS	95	84	90	40
Glyphosate + AMS + TAE* @ 0.25%	96	85	94	47
Glyphosate + AMS + Multitrope 1214 @ 0.25%	97	89	94	47
Glyphosate + AMS + Crodafos D4A @ 0.25%	98	95	95	50
Glyphosate + AMS + Crodafos O3A @ 0.25%	94	88	96	45
Glyphosate + AMS + Atlox AL-3382 @ 0.25%	96	85	90	46
Glyphosate + AMS + Crodafos SG @ 0.25%	96	90	95	46
LSD (P= 0.05)	2.8	4.2	5.4	9

*TAE = Tallow alkylamine ethoxylate

SEFTA= Giant Foxtail ABUTH= Velvetleaf AMATA= Common Waterhemp IPOHE= Ivyleaf Morningglory

Standard Treatment as Control Statistically Lower Statistically Equal Statistically Greater

Table 2: Adjuvancy screen. Phosphate esters compared to standard NIS adjuvant.

When used as part of a microemulsifier system for adjuvant oils, a multifunctional and efficacious "all-in-one" adjuvant product can be produced which provides a complete adjuvant solution for glyphosate tank mixtures where an oil-loving herbicide is also present. This approach has the added benefit of minimizing the oil antagonism to glyphosate often found when adding more traditional MSO and COC type adjuvants.

Glyphosate, Microemulsions, and Tembotrione

Treatment	AMATA 7 DA-A	AMATA 14 DA-A	AMATA 21 DA-A	IPOSS 7 DA-A	IPOSS 14 DA-A	IPOSS 21 DA-A	ABUTH 7 DA-A	ABUTH 14 DA-A	ABUTH 21 DA-A
Glyphosate + 0.42% AMS + 0.25% NIS	83	89	88	42	52	53	50	70	74
Tembotrione + 0.42% AMS + 1% MSO	57	95	96	49	52	57	71	93	96
Glyphosate + Tembotrione + 1% MSO + 0.25% NIS + 0.42% AMS	73	94	96	48	57	67	66	91	98
Glyphosate + Tembotrione + 1.0% ME-7*	89	95	97	50	64	68	68	90	98
Glyphosate + Tembotrione + 1.5% ME-7*	94	97	98	52	57	67	64	88	98
Glyphosate + Tembotrione + 2.0% ME-7*	94	96	99	48	55	68	62	96	97
LSD (P=.05)	6.6	4.5	3.7	5.8	9	5.4	4.2	5.2	3.9

* ME-7 = 20% (w/w) MSO in AMS adjuvant blend made with Atlox AL-3382

AMATA= Common Waterhemp IPOSS= Morningglory ABUTH= Velvetleaf

Standard Treatment as Control Statistically Lower Statistically Equal Statistically Greater

Table 3: Glyphosate and Tembotrione tank mix screen. Lower MSO use rate all-in-one adjuvants provided equivalent weed control at 21 days after treatment vs. standard rate MSO and NIS tank added components.

Glyphosate, Microemulsions, and Clethodim

Treatment	ZEAMX 14 DA-A	ZEAMX 28 DA-A	BRAPP 14 DA-A	BRAPP 28 DA-A	IPOSS 14 DA-A	IPOSS 28 DA-A
Clethodim + 1% COC + 0.42% AMS	86	95	93	92	0	0
Glyphosate + Clethodim + 1% COC + 0.25% NIS + 0.42% AMS	85	83	97	93	43	45
Glyphosate + Clethodim + 1.0% ME-7*	86	94	94	90	43	58
Glyphosate + Clethodim + 1.5% ME-7*	88	94	96	92	48	63
Glyphosate + Clethodim + 2.0% ME-7*	89	92	97	96	43	52
LSD (P=.05)	2.8	5.9	4.4	10.4	8.4	8.9

* ME-7 = 20% (w/w) MSO in AMS adjuvant blend made with Atlox AL-3382

ZEAMX= Corn, volunteer BRAPP= Broadleaf signalgrass IPOSS= Morningglory

Standard Treatment as Control | Statistically Lower | Statistically Equal | Statistically Greater

Table 4: Glyphosate and Clethodim tank mix screen. Lower MSO use rate all-in-one adjuvants provided equal or better weed control at 28 days after treatment vs. standard rate MSO and NIS tank added components.

Glyphosate, Microemulsions, and Saflufenacil (Glyphosate resistant weeds)

Treatment	ERICA-HR 5 DA-A	ERICA-HR 10 DA-A	AMATA-HR 20 DA-A	AMATA-HR 5 DA-A	AMATA-HR 10 DA-A	AMATA-HR 20 DA-A
Glyphosate + 0.42% AMS + 0.25% NIS	12	42	42	33	37	45
Saflufenacil + AMS + 1% MSO	70	86	75	79	95	92
Glyphosate + Saflufenacil + 0.42% AMS + 1% MSO + 0.25% NIS	70	89	81	83	96	96
Glyphosate + Saflufenacil + 1.0% ME-7*	61	85	69	63	89	94
Glyphosate + Saflufenacil + 1.5% ME-7*	61	84	71	67	90	96
Glyphosate + Saflufenacil + 2.0% ME-7*	65	89	74	70	95	97
LSD (P=.05)	5.4	8.8	11.9	7.3	8	10.1

* ME-7 = 20% (w/w) MSO in AMS adjuvant blend made with Atlox AL-3382

ERICA-HR= Herbicide-resistant Marestail (glyphosate) AMATA-HR= Herbicide-resistant Common waterhemp (glyphosate)

Standard Treatment as Control | Statistically Lower | Statistically Equal | Statistically Greater

Table 5: Glyphosate and Saflufenacil tank mix screen. Lower MSO use rate all-in-one adjuvants used at 1.5% and 2.0% provided equivalent weed control at 20 days after treatment vs. standard rate MSO and NIS tank added components.

Glyphosate, Microemulsions, and Saflufenacil

Treatment	AMATA 7 DA-A	AMATA 14 DA-A	AMATA 28 DA-A	PANDI 7 DA-A	PANDI 14 DA-A	PANDI 28 DA-A
Glyphosate + 0.25% NIS + 0.42% AMS	50	62	58	28	63	71
Saflufenacil + MSO @ 1% + 0.42% AMS	87	77	58	13	12	8
Glyphosate + Saflufenacil + 0.25% NIS + 1.0% MSO + 0.42% AMS	93	92	81	50	67	67
Glyphosate + Saflufenacil + 1.0% ME-7*	94	95	93	50	67	64
Glyphosate + Saflufenacil + 1.5% ME-7*	94	95	92	55	72	66
Glyphosate + Saflufenacil + 2.0% ME-7*	96	96	95	57	77	72
LSD (P=.05)	5.9	6.1	7.5	8.8	5.5	9.7

* ME-7 = 20% (w/w) MSO in AMS adjuvant blend made with Atlox AL-3382

AMATA= Common waterhemp   PANDI= Fall panicum

Standard Treatment as Control   Statistically Lower   Statistically Equal   Statistically Greater

Table 6: Glyphosate and Saflufenacil tank mix screen. Lower MSO use rate all-in-one adjuvants provided equal or better weed control at 28 days after treatment vs. standard rate MSO and NIS tank added components.

Further information

Croda sales and distribution are coordinated through an extensive worldwide network of associates and agents.
If you would like product samples, formulation advice, or technical assistance, please contact your nearest Croda regional office.

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Europe, Middle East & Africa cropcare@croda.com
North America marketing-usa@croda.com
Latin America cropcare.latam@croda.com
Asia Pacific cropcare.apac@croda.com

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