

Agrochemical Adjuvants Guide





Air Products provides a diverse portfolio of multifunctional surfactants that can be used in a variety of formulations as dynamic wetting agents, dispersants, emulsifiers and agricultural spray adjuvants.

Our flagship Surfynol® surfactants are especially noted for their ability to lower the dynamic surface tension of aqueous solutions and can improve the degree of surface coverage and penetration of a pesticide while providing defoaming at the same time. Our Dýnol™ and EnviroGem® superwetters can improve foliar retention and penetration or adjust the tank mix properties to improve the overall effectiveness and efficacy of the pesticide.

Air Products offers a full range of specialty surfactants for the agrochemical industry. All the surfactants that we offer to this marketplace are solvent-free and allow for safe handling in the field. **Table 1** highlights these products and the applications for which they are particularly useful.

Our offering to the agrochemical industry extends beyond the laboratory to the regulatory process. Recent successes following our involvement in the EPA joint task force and cluster support teams demonstrate our commitment and sense of responsibility to the agrochemical industry.

Features

- Nonionic surfactants based on proprietary Gemini surfactant architecture
- APE-free and HAPS-free
- Solvent-free
- pH stable from 4–11
- Broad approval under EPA 40CFR 180

Performance Advantages

- Efficient, effective and multifunctional tools
- Low use levels (0.05 wt % – 0.15 wt %)
- Adjuvants with a wide range of properties, including
 - Nonfoaming/dynamic wetting
 - Low foaming/wetting/emulsification
 - Superwetting

Table 1

Air Products Specialty Surfactants for Agrochemical Industry

Physical Property	Product Name	HLB	Wettable Powders (WP)	Emulsifiable Concentrates (EC)	Granules (GR)	Solution Concentrate—Soluble Liquids (SL)	Suspension Concentrates (SC)	Oil in Water Emulsions (EW)	Capsule Suspensions (CS)	Water-Dispersible/Water-Soluble Granules (WG/SG)	Suspo-Emulsions (SE)	Micro-Emulsions (ME)	Tank Mix Adjuvants	EPA 40 CFR 180 Listing	
Dynamic Wetting/ Defoaming  Grind Aids Wetting/ Low Foaming	Surfynol 104 ^a	4	•				•	•		•			•	Yes	
	Surfynol 420	4	•				•	•		•			•	No	
	Surfynol 82 ^a	5	•				•			•			•	Yes	
	Surfynol 440	8	•				•			•			•	Yes	
	Surfynol CT-211	9–10	•				•			•			•	Yes	
	Carbowet DC01	11	•				•			•			•	Yes	
	Surfynol CT-221	12	•				•			•			•	Yes	
	EnviroGem 2010	13–14	•	•	•	•	•	•	•	•	•	•	•	•	Yes
	Surfynol 465	13–14	•	•	•	•	•	•	•	•	•	•	•	•	Yes
	Surfynol 485 ^a	17	•	•	•	•	•	•	•	•	•	•	•	•	Yes
Superwetters	EnviroGem 360	3–4	•			•	•		•				•	No	
	Dynol 604	3–4	•			•	•		•				•	No	
	Dynol 607	8	•			•	•		•				•	No	

^aAvailable in different forms.

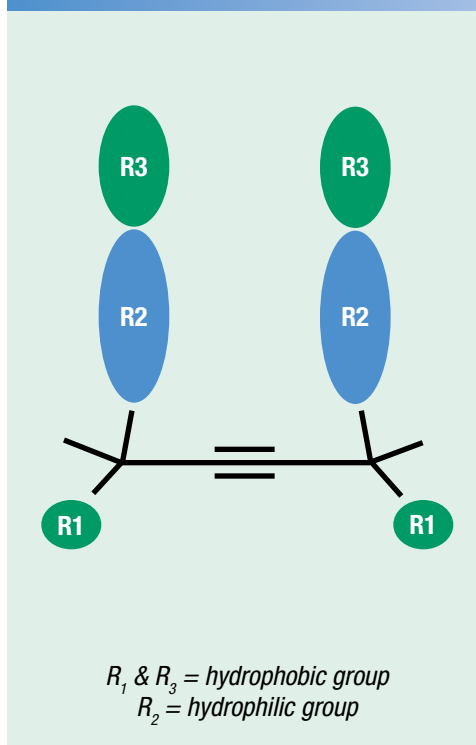
Wetting-Defoaming

Product Description

While conventional surfactants have a single, hydrophobic group (often referred to as a hydrocarbon tail) connected to a hydrophilic head, our acetylenic diol surfactants have two hydrophilic heads connected to two tails and are referred to as Gemini surfactants. The tremendous advantages seen with these additives lie in their unique chemistry. As a result of their chemical structure, our surfactants are typically more surface active than traditional hydrocarbon surfactants, making them efficient and effective for solving a variety of formulation problems in water-based systems. See **Figure 1**.

Utilizing our surface science expertise, we have designed a range of wetting agents with varying Hydrophilic Lipophilic Balance (HLB). The lower HLB materials exhibit a unique combination of dynamic wetting properties and defoaming. The higher HLB materials allow for a combination of wetting and emulsification performance.

Figure 1
Structure of Gemini Surfactant



Use and Applications

These products can be used as wetting agents or built-in adjuvants in agricultural formulations as well as for tank mix applications.

In agrochemical formulations, they can be used in soluble liquid (SL), suspension concentrate (SC), soluble powder (SP), soluble granule (SG) and wettable powders (WP) formulations. They allow efficacy of SL formulations, ease of addition of powders during the manufacture of SC formulations and improved dispersion in WP formulations.

As tank mix adjuvants, they can be added to a spray tank in the field to boost the functionality of pest control products. Listed below are their common functions in tank mix applications.

- Wetting Agents
- Penetrants
- Compatibility Agents

Table 2 shows Air Products' dynamic wetting agents.



Table 2

Physical Properties of Air Products Dynamic Wetting Agents

Property	Surfynol 104¹	Surfynol 420³	Surfynol 82¹	Surfynol 440²	Surfynol CT-211¹	Carbowet DC01²	Surfynol CT-221¹	EnviroGem 2010¹	Surfynol 465²	Surfynol 485²
<i>Specific Gravity (@ 21 °C)</i>	0.89	0.94	0.93	0.98	0.98	0.99	1.02	1.01	1.04	1.08
<i>Viscosity@ 20 °C, cps</i>	Solid	<250	Solid	<200	105	85	400	81	<200	<350
<i>Pour Point (ASTM D97), °C</i>	–	–25	–	–48	–10	5	0	0	7	29
<i>Flash Point (°C)</i>	>100	>110	>118	>110	>101	>110	>94	>98	>110	>110
<i>HLB</i>	4	4	5	8	9.5	11	12	13	13	17
<i>EPA Inert Ingredients Listing</i>	40 CFR 180.910, 180.920, 180.930	None	40 CFR 180.910, 180.920, 180.930							

¹ All the components of these materials are listed in the Environmental Protection Agency's regulation 40 CFR 180.910, 180.920 and 180.930. It is exempted from the requirements of tolerance when used in good agricultural practice as an inert ingredient in pesticide formulations applied to growing and harvested crops and to animals with the limitation that the concentration not exceed 2.5% of the pesticide formulation.

² All the components of these materials are listed in the Environmental Protection Agency's regulation 40 CFR 180.910, 180.920 and 180.930. It is exempted from the requirements of tolerance when used in good agricultural practice as an inert ingredient in pesticide formulations applied to growing and harvested crops and to animals with no limitation to concentration used in pesticide formulation.

³ All of the components of these materials are not listed in the Environmental Protection Agency's regulation 40 CFR 180.

Table 3**Comparison of Surface Tension and Foamability for Selected Air Products Wetting Agents and Competitive Benchmark Surfactants (0.1% Concentration)**

	<i>Surfynol 104</i>	<i>Surfynol 420</i>	<i>Surfynol 82</i>	<i>Surfynol 440</i>	<i>Surfynol CT-211</i>	<i>Carbowet DC01</i>	<i>Surfynol CT-221</i>	<i>EnviroGem 2010</i>	<i>Surfynol 465</i>	<i>Surfynol 485</i>	<i>Octylphenol + 10 EO</i>	<i>Sodium Lauryl Sulfate</i>	<i>Polyether Modified Silicone</i>	<i>Fluoro Surfactant</i>	<i>Dioctyl Sodium Sulfosuccinate</i>
<i>Equilibrium Surface Tension¹ at 0.1 wt %, (mN/m)</i>	33	32	47	34	30	34	33	30	43	51	33	44	21	21	32
<i>Dynamic Surface Tension² at 0.1 wt %, 6 b/s (mN/m)</i>	36	35	57	37	34	39	38	39	46	53	45	53	45	72	34
<i>Initial Ross-Miles Foam Height³ (cm)</i>	0	0	1	1	11	11	11	12	6	9	13	7	9	6	5
<i>Final Ross-Miles Foam Height³ at 5 minutes (cm)</i>	0	0	0	0	1	2	2	2	0	2	11	7	9	5	4

¹Measured using the Wilhelmy plate method at 25 °C. ²Measured using the maximum bubble pressure method at 25 °C. ³ASTM D 1173, 25 °C, 0.1 wt % surfactant in water.

Performance Benefits**Dynamic Surface Tension Reduction**

Surface tension reduction through the use of a surfactant allows a liquid solution to wet a low surface energy substrate. Reduction in static (equilibrium) surface tension can give an indication of a surfactant's performance, but many agrochemical applications never reach equilibrium. Consequently, in systems where surfaces are quickly generated, such as spraying, the surfactants must rapidly migrate to the interface to wet difficult-to-wet foliar substrates. As shown in **Table 3**, Surfynol surfactants can effectively lower surface tension under conditions of rapid surface formation (increased bubble rate) due to their ability to quickly migrate to newly formed surfaces. Therefore, under dynamic conditions, these products can outperform a wide variety of conventional surfactants such as octylphenol ethoxylates, sodium lauryl sulfate, polyether silicones and fluoro surfactants.

Unique Combination of Defoaming and Wetting

Water-based systems have surface tensions that are too high to permit adequate coverage of many low-energy substrates. As a result, surfactants that function as wetting agents are required. However, most surfactants cause foam, and the subsequent use of defoamers can result in sub-optimal performance. The Surfynol series of surfactants can eliminate this problem by providing the necessary coverage with nonfoaming wetting agents such as Surfynol 104, 420, SE, 82, and 440 surfactants, or with low foaming products such as Carbowet DC01; Surfynol CT-211, CT-221, 465 and 485; and EnviroGem 2010 surfactants (**Table 3**).

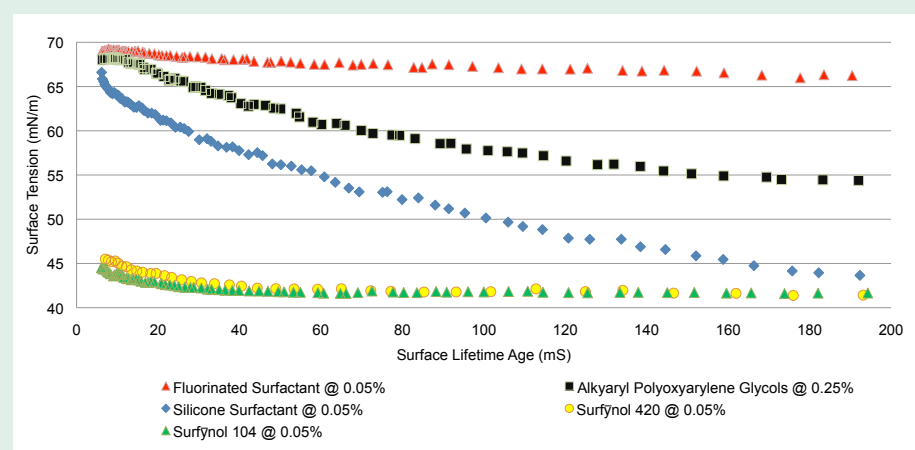
In glyphosate formulations, Surfynol 104 and Surfynol 420 surfactants are particularly useful since they can provide excellent defoaming while being homogeneously distributed in the formulation; in contrast, typical silicone based defoamers are insoluble and phase separate over time.ⁱ



Modeling of the spray process has shown that the surface age of the droplets at leaf impact can be as little as 60 mS.ⁱⁱ A lower surface tension at this very fast time scale is an indicator of how well the droplet will wet and adhere to leaf surfaces; this is expected to translate into improved plant uptake. **Figure 2** shows the comparison of dynamic surface tension profiles of selected Air Products wetting agents, Surfynol 104 and Surfynol 420 surfactants, with commercial benchmarks. This demonstrates that Surfynol 104 and Surfynol 420 surfactants can have the fastest dynamic wetting rates, even at 0.05% concentration, as compared to the commercial benchmark surfactants. In the case of alkylaryl polyoxyarylene glycols, the wetting performance is still not comparable, even at higher concentrations of 0.25%.

Figure 2

Comparison of Dynamic Surface Tension Profiles of Surfynol 104, Surfynol 420 and Commercial Benchmark Surfactants



Air Products Grind Aids Offering

There are three stage involved in particle dispersion, 1) Wetting of Agglomerates: this step is critical in aqueous media because of high cohesive energy of water, 2) Reduction to Aggregates or Primary Particles: this is usually achieved by milling/grinding as a way to input energy and 3) Dispersion and Stabilization: once particle size is reduced, pigment particles must remain separated and suspended to prevent flocculation.

Air Products Grind Aids, Surfynol CT 211, Carbowet DC01, Surfynol CT-221 and EnviroGem 2010 can provide dynamic stabilization by enhanced wetting at faster time scales leading to faster milling with low foam. This can translate to ease of addition of powders in the manufacture of SC Formulations as well as improve dispersion in WP and WG/SG formulations.

Superwetters

Product Description

Superwetters are surfactants with structures that allow them to efficiently adsorb and pack at interfaces, resulting in extremely low equilibrium surface tensions, fast wetting times and low contact angles on low surface energy substrates like foliar surfaces. Dýnol 604, Dýnol 607 and EnviroGem 360 superwetting surfactants are low-VOC, low-foam, nonionic wetting agents

Table 4

Physical Properties of Air Products Superwetters

Material/Property	Dýnol 604^a	Dýnol 607^a	EnviroGem 360^a
<i>Appearance</i>	<i>Amber Liquid</i>	<i>Amber Liquid</i>	<i>Clear Liquid</i>
<i>Specific Gravity @ 25 °C</i>	<i>0.97</i>	<i>~1</i>	<i>1.01</i>
<i>Flash Point, °C</i>	<i>164</i>	<i>100</i>	<i>175</i>
<i>Activity %</i>	<i>100</i>	<i>100</i>	<i>100</i>
<i>Calculated HLB (Water dispersibility)</i>	<i>3–4</i>	<i>8</i>	<i>3–4</i>
<i>EPA Inert Ingredient Listing</i>	<i>None</i>	<i>None</i>	<i>None</i>

^aAll of the components of these materials are not listed in the Environmental Protection Agency's regulation 40 CFR 180.

ideal for high performance waterborne agro-chemical applications. These wetting agents have the ability to reduce both equilibrium and dynamic surface tension to a degree not found with other surfactants. This excellent balance of properties, generally not possible with fluoro or silicone surfactants, makes them excellent alternatives for difficult-to-wet substrates requiring good flow and leveling under diverse application conditions. Also, compared to many fluoro and silicone surfactants, the use of these Gemini surfactants reduces or eliminates issues such as increased foaminess or water sensitivity, often associated with traditional surfactants. Physical properties of our super-wetters are shown in **Table 4**.

These surfactants promote substrate wetting of waterborne systems by effectively lowering both the equilibrium (static) and the dynamic surface tension of aqueous systems. This is demonstrated by the very low surface tension values of a 0.1 wt % solution in water.

The values in **Table 5** represent greatly improved surface tension reducing capabilities compared to those available in traditional surfactants. In a formulated system, these surfactants will rapidly migrate to the interface, providing excellent coverage over low-energy foliar surfaces. In addition, these surfactants, which have a Gemini structure, will have little or no impact on water sensitivity. These surfactants

are also ideally suited for very low VOC applications. This combination of performance benefits makes these surfactants a suitable alternative to fluoro and silicone surfactants. However, compared to fluoro or silicone surfactants, these surfactants will typically not impart excessive foaming, nor are they likely to cause incompatibilities in agrochemical formulations.

As mentioned earlier, the calculated surface age of the droplets at leaf impact can be as little as 60 mS.ⁱⁱ A lower surface tension at this very fast time scale is an indicator of how well the droplet will wet and adhere to leaf surfaces and is expected to translate into improved plant uptake. **Figure 3** shows the comparison of dynamic surface tension profiles of Air Products' superwetters with commercial benchmarks. Dýnol 604, followed by Dýnol 607 and EnviroGem 360 surfactants, even at 0.05% concentration, has significantly faster dynamic wetting rates as compared to the commercial benchmark surfactants. In the case of alkylaryl polyoxyethylene glycols, the wetting performance is still typically not comparable, even at higher concentrations of 0.25%.

Figure 4 depicts the very low contact angles achieved with a 0.1 wt % solution of EnviroGem 360 surfactant compared to a typical conventional surfactant. On a low-energy substrate, the EnviroGem 360 surfactant provides a lower contact angle and superior wetting. The ability of EnviroGem 360 surfactant to provide low contact angles allows formulators to develop formulations that effectively wet out the most difficult-to-wet foliar substrates.

Figure 3

Comparison of Dynamic Surface Tension Profiles of Air Products Superwetters and Commercial Benchmark Surfactants

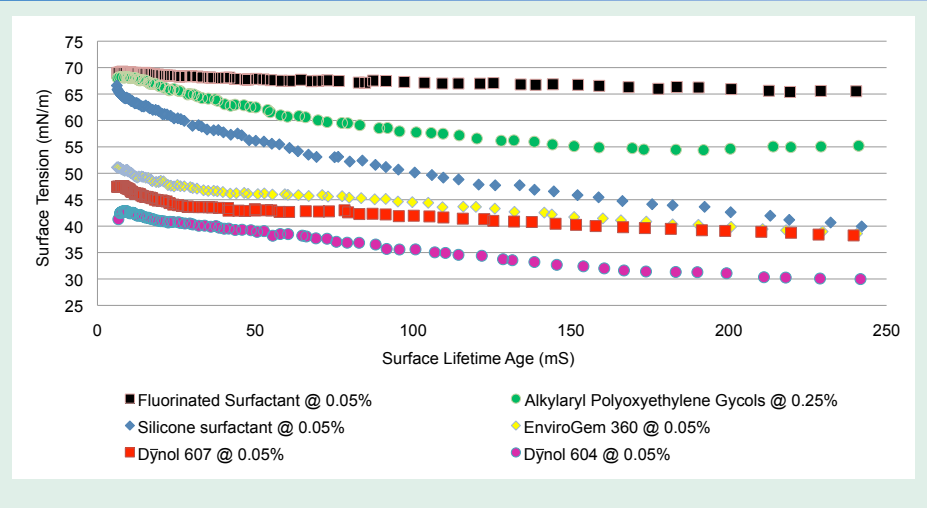
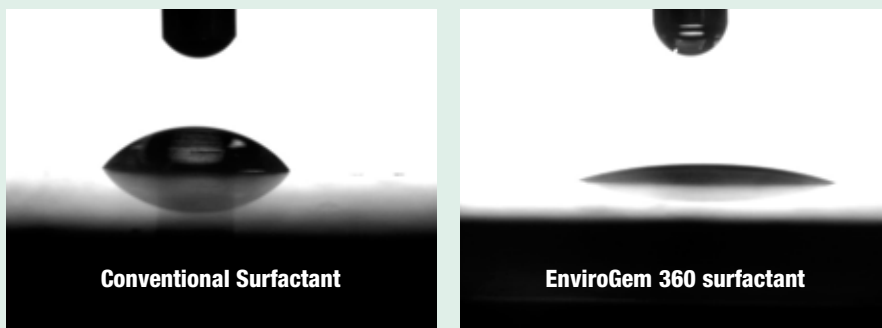


Figure 4

Contact Angle

0.1 wt % aqueous surfactant solution, oily metal surface, 10 second wetting time, 23 °C



A 0.1 wt % aqueous solution of EnviroGem 360 surfactant gives a 36° contact angle on Parafilm and a 40° contact angle on untreated polyethylene

Table 5

Surface Tension and Foam Properties of Air Products Superwetters Compared to Competitive Benchmark Surfactants

Material/Property	Dýnol 604	Dýnol 607	EnviroGem 360	Octylphenol + 10 EO	Sodium Lauryl Sulfate	Polyether Modified Silicone	Fluoro Surfactant	Diocetyl Sodium Sulfosuccinate
Equilibrium Surface Tension ¹ at 0.1 wt %, (mN/m)	26	26	28	33	44	21	21	32
Dynamic Surface Tension ² at 0.1 wt %, 6 b/s (mN/m)	28	27	35	45	53	45	72	34
Initial Ross-Miles Foam Height ³ (cm)	2.5	9	1	13	7	9	6	5
Final Ross-Miles Foam Height ³ at 5 minutes (cm)	0	1	0	11	7	9	5	4

¹Measured using the Wilhelmy plate method at 25 °C. ²Measured using the maximum bubble pressure method at 25 °C. ³ASTM D 1173, 25 °C, 0.1 wt % surfactant in water.

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¹ J.W. Kassebaum, "Surfynol Surfactants as Defoamers in Glyphosate Formulations," *Pesticide formulations and application systems*: 13th volume, Issue 1183, by Paul D. Berger, Bala N. Devisetty, Franklin R. Hall, ASTM, Philadelphia, 1993.

² Peter J. G. Stevens et al., "Adhesion of Spray Droplets to Foliage: The Role of Dynamic Surface Tension," *Pestic. Sci.* 1993, 38, 237-245.

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