Vanderbilt Minerals, LLC
A Wholly Owned Subsidiary of R.T. Vanderbilt Holding Company, Inc.
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FORMULARY
Crop Protection Pesticide
No. 921rev

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Crop Protection Pesticide Formulations No. 921

The purpose of formulating pesticide active ingredients for crop protection is to uniformly spread a small amount of an active chemical over a large area. The goal is to ensure safety in handling and during application and to optimize pesticide efficacy. This requires that the pesticide formulation be chemically stable and physically uniform under all foreseeable storage conditions so that the minimum effective amount can be accurately applied to target areas. Vanderbilt Minerals, LLC supplies a variety of minerals and chemicals to assist the pesticide formulator. These include:

Suspension Stabilizers:

Smectite Clays

VANATURAL® Bentonite
VAN GEL® Magnesium Aluminum Silicate
VEEGUM® Magnesium Aluminum Silicate

VANATURAL	Bentonite; non-irradiated
VANATURAL MC	Bentonite; low micro count
VAN GEL B	Economical grade for most suspensions
VAN GEL ES	The most electrolyte tolerant grade
VAN GEL SX	Clay/Xanthan Gum; high efficiency stabilizer
VAN GEL R	Standard grade for a wide range of applications
VAN GEL K	High acid & electrolyte compatibility
VEEGUM Pure	Non-irradiated version of VEEGUM R
VEEGUM T	The most efficient clay grade

Additional grades are available to match formulation requirements.

Xanthan Gum

VANZAN® Xanthan Gum
VANZAN D Xanthan Gum

VANZAN	General purpose grade for most applications
VANZAN D	Surface-treated to facilitate dispersion

Diluents:

CONTINENTAL® Clay
PYRAX® Pyrophyllite

CONTINENTAL	Kaolin with unusually fine particle size
PYRAX ABB	An inert diluent for pesticide powders

Dispersing Agents:

DARVAN® Dispersants

DARVAN 2	Sodium lignosulfonate
DARVAN 670[x]	Sodium polynaphthalene sulfonate

Additional grades are available to match formulation requirements.

[x]Not for agricultural applications in the USA

LIQUID CONCENTRATES

Aqueous flowables (AF) are concentrated 40% to 70% w/w suspensions of micronized active pesticide in water. Prior to spraying on target areas, aqueous flowables are diluted with water in a spray tank to achieve the minimum effective pesticide concentration. AFs must be formulated for low viscosity and good fluidity so that transfer to the spray tank is easy and complete. This requires an effective wetting agent and an efficient dispersing agent to ensure adequate dispersion of the pesticide in the water. Since the active ingredients in AFs are insoluble, good suspension stability is essential. If the suspension settles and leaves sediment at the bottom of the container, the application of the pesticide may be too weak to be effective. Also, disposal of the residue in the container becomes a problem. A combination of smectite clay (aka bentonite) and xanthan gum works synergistically to provide excellent long term suspension stability at low viscosity and at low cost.

There are three techniques commonly used to stabilize aqueous flowables:

Pre-Milled Active - When the pesticide is already milled to the desired particle size, the smectite clay and, if used, the organic gum (xanthan gum, cellulose gum) are first thoroughly hydrated before the other ingredients are added with a dispersing mixer. The formulas in Table 1 and Table 2 demonstrate the use of smectite clay suspending agent, with and without xanthan gum, to produce fluid concentrates with excellent physical stability.

Pre-Hydrated Clay/Un-milled Active - When the pesticide needs to be milled, a pre-suspension of the smectite clay can be formed as above, reserving the organic gum. This is then media milled (attritor, ball mill, sand mill) until the pesticide particles are reduced to the desired size. The organic gum is added at the end of the milling cycle, avoiding shear degradation.

Un-Milled Active/In-Situ Clay Hydration - All ingredients except the organic gum are added directly to the media mill without pre-dispersion. The smectite clay hydrates as the pesticide particles are milled. Generally, smectite clay is best delaminated when it is pre-hydrated, but the high shear imparted by the mill is usually sufficient. The organic gum, typically xanthan gum, is added and dissolved as the last step; it interacts with the clay to form the colloidal structure that keeps the pesticide particles uniformly dispersed and suspended during storage. The formulas in Table 3 demonstrate the use of the **VAN GEL B/VANZAN** suspending agent combination to produce low viscosity fluid concentrates with excellent physical stability. These formulas were prepared in 2 kg batches in a laboratory impact mill. All ingredients were charged to the mill except the xanthan gum. Milling proceeded until the average particle size of the active was reduced to less than 5 micrometers. The xanthan gum was then added and milling was continued only long enough to allow the gum to dissolve.

Emulsifiable Concentrates (EC) are blends of pesticide, emulsifiers and adjuvants dissolved in a volatile oil. Low melting point or liquid pesticide actives have traditionally been formulated into EC's. When the EC is added to water in the spray tank, it forms a stable dilute emulsion. ECs are a convenient means of using water as a vehicle for oil-soluble pesticides. However, their oily solvent base creates several hazards: ECs can be absorbed through the skin, burn foliage, and attack the rubber and plastic parts of spray equipment.

Concentrated emulsions (EW) contain up to 50% w/w of oil-soluble pesticide. EWs minimize the disadvantages of emulsifiable concentrates by minimizing the level of solvent needed to dissolve the pesticide, and then emulsifying this solution in water. The concentrated emulsion is simply diluted in the spray tank for application. The combination of smectite clay and xanthan gum stabilizes the concentrated emulsion against separation in the same way that it stabilizes concentrated AF suspensions. To prepare the concentrated emulsion, the smectite clay is hydrated in the water phase before the emulsion is formed. The xanthan gum can be dissolved in the water either before or after emulsification.

Suspo-emulsions (SE) are produced by combining an aqueous flowable with a concentrated emulsion. The need to ensure long-term fluidity and physical stability requires that particular care be taken in the selection of proper wetting agents and emulsifiers. The smectite clay/xanthan gum combination ensures the stability of the dispersed oil phase against coalescence and prevents the agglomeration of pesticide particles. **DARVAN** dispersants are useful in promoting the optimum dispersion of the pesticide particles.

Wettable Powders

Wettable powders (WP) are dry concentrates containing 50% or more of micronized active pesticide blended with a wetting agent, a dispersing agent and a finely ground diluent. Prior to spraying on target areas, wettable powders are dispersed into water in a spray tank to achieve the minimum effective pesticide concentration. The active may be a crystalline solid or a liquid or low melting point compound absorbed onto a carrier. The wetting agent ensures easy dispersion of the active in water, and the dispersing agent, such as a **DARVAN** Dispersant, inhibits the agglomeration of pesticide particles. **CONTINENTAL** Clay is widely used as the solid diluent in wettable powders because of its naturally fine particle size, its broad compatibility with pesticide actives and its ability to inhibit the settling of pesticide particles in the spray tank. Typical formulations are shown in Table 4.

Because wettable powders are applied as dilute aqueous suspensions, drift into non-target areas is more easily controlled than with dusts, but exposure to respirable pesticide powder remains a concern.

Water Dispersible Granules

Water dispersible granules (WDG), or **dry flowables (DF)**, are wettable powders that have been aggregated into uniform granules for easier handling and to eliminate respirable particles. They are dispersed in the spray tank and applied as dilute suspensions in the same way as wettable powders. WDGs incorporate the same ingredients as wettable powders, including **DARVAN** dispersants and **CONTINENTAL** clay, although generally with a higher level of active and less diluent. The granules must be strong enough to resist crumbling into powder, yet still readily and completely disintegrate and disperse in the spray tank. This avoids nozzle clogging and ensures the finest particle size of the active ingredient for optimum efficacy.

Several methods are used to form granules from the starting powder blend. These include pan granulation, fluid bed granulation, spray drying, high speed mixer agglomeration and extrusion granulation. Extrusion granulation is generally preferred on the basis of safety, versatility and economy.

Dusts

Dusts (D) are formulated as ready-to-use pesticides, with no dilution required. The active is either a crystalline solid ground to 1-10 micrometers, or a liquid or waxy compound absorbed onto an inert mineral carrier. The concentration of active is typically less than 10% by weight, with a finely ground mineral diluent making up the balance. Aerial application of dusts was once commonly practiced, but this has all but been abandoned due to inhalation hazards and the tendency of dusts to drift into non-target areas. Today dusts are used for small area treatment such as gardens, for seed treatments and for the control of parasites on pets and livestock.

The preferred diluent for pesticide dusts is **PYRAX ABB** Pyrophyllite. This finely ground pyrophyllite is an inert, non-hygroscopic, neutral pH mineral which provides optimal compatibility with pesticide actives and is safe for plants and animals. **PYRAX ABB** has a relatively high bulk density, resulting in “heavy” dusts that drift less on application to plants, and that enable animal dusts to penetrate fur for good skin contact.

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Table 1. Sulfur Flowable Concentrate (6 lbs/gal) from Pre-Milled Active

			For Organic Farming	
		No. 616 Wt.%	No. 621 Wt.%	No. 622 Wt.%
A	**VAN GEL® SX** Magnesium Aluminum Silicate	0.30	--	--
	VEEGUM® Pure Magnesium Aluminum Silicate	--	1.00	0.24
	VANZAN® Xanthan Gum	--	--	0.06
	Water	28.70	27.10	27.80
B	Sodium Polynaphthalene Sulfonate	2.50	2.50	2.50
	Propylene Glycol	9.50	9.50	9.50
	Carbowet®GA211[1]	0.10	--	--
	Tween® 80-NV-LQ-(AP)[2]	--	1.00	1.00
	Preservative	q.s.	q.s.	q.s.
C	Yellow Jacket® Wettable Sulfur, 90.0% min.[3]	58.90	58.90	58.90
Viscosity, cps[A]				
1 Day		1290	1040	1520
1 Month		1390	1540	1560
3 Months		2050	1350	2150
Stability, 3 months				
Gelation, 5/20/50°C		none	none	none
Bleed[B], 5/20/50°C		vsl/vsl/tr	sl/sl/vsl	vsl/sl/sl
Packing, 5/20/50°C		none	none	none
Freeze/Thaw, 3 cycles		passed	passed	passed
Bloom		passed	passed	passed
pH		6.7	7.2	7.6
Density, lbs/gal		11.9	12.0	11.9

Note: Use an appropriate mixing blade and speed to prevent excessive air entrapment.

Procedure: For the respective formulas, sift the **VAN® GEL SX, VEEGUM® Pure** or the combination of **VEEGUM Pure** and **VANZAN®** (sequentially or as a dry blend) into an established vortex in the water. Mix until fully hydrated. Please review our Preparation of Dispersions guidance*. Add the sodium polynaphthalene sulfonate and mix until thoroughly dissolved. Then, add the rest of Part B ingredients and mix completely after each. Avoid air entrapment. Slowly add the sulfur, Part C, increasing the mixer speed as needed. Mix until thoroughly dispersed.

[A]20°C samples, Brookfield at 60 rpm

[B]tr: trace, vsl: very slight, sl: slight

[1]Air Products and Chemicals, Inc., Allentown, PA
[2]Croda, Edison, NJ
[3]Georgia Gulf Sulfur Corporation, Valdosta, Georgia

*http://www.vanderbiltminerals.com/ee_content/Documents/Technical/Preparation_of_Dispersions_Trifold_Web.pdf

*Please see user advisory on page 1

Table 2. Thiram Seed Treatment No. 624 (1.75 lb/gal) from Pre-Milled Active

		Wt.%
A	**VAN GEL® SX** Magnesium Aluminum Silicate	0.70
	Water	36.90
B	Sodium Polynaphthalene Sulfonate	2.50
	Propylene Glycol	9.50
	Carbowet® GA211Surfactant[1]	0.10
	Kathon® CG/ICP II [2]	0.15
	Carbowax® PEG 400 IND[2]	19.25
	Sunsperse® Red 48:2 (Code: RPD-0048)[3]	11.6
C	Thiram P®[4] (Thiram Technical, 99%) (EPA Reg. No. 45728-1)	19.3
D	Triethanolamine, 99%	q.s

Viscosity, cps*	
1 Day	630
1 Month	950
3 Months	800
Bleed, 3 months 5/20/45°C	trace/very slight/very slight
Freeze/Thaw, 3 cycles	passed
pH, 24 hrs	8.3
Density, lbs/gal	9.1

Procedure: Using a Cowles Disperser or equivalent mixer, sift the **VAN® GEL SX** into an established vortex in the water. Mix until fully hydrated. Please review our Preparations of Dispersions guidance**. Slowly add the sodium polynaphthalene sulfonate and mix until thoroughly dissolved. Then, add the rest of Part B ingredients and mix completely after each. Slowly add the Thiram, Part C, increasing the mixer speed as needed. Mix until thoroughly dispersed. Decrease the mixing speed and adjust the pH to 8.8 as necessary with triethanolamine.

*20°C samples, Brookfield at 60 rpm

[1]Air Products and Chemicals, Inc., Allentown, PA
[2]Dow Chemical, Midland, MI
[3]Sun Chemical Corporation, Cincinnati, OH
[4]Taminco US Inc./ A subsidiary of Eastman Chemical Company, Allentown, PA

**http://www.vanderbiltminerals.com/ee_content/Documents/Technical/Preparation_of_Dispersions_Trifold_Web.pdf

*Please see user advisory on page 1

Table 3. Flowable Concentrates from Un-Milled Active / In-Situ Clay Hydration

	No. 388 Carbaryl 4 lbs/gal	No. 386 Carbaryl 5 lbs/gal	No. 387 Atrazine 4 lbs/gal	No. 389 Sulfur 6 lbs/gal
VAN GEL® B Magnesium Aluminum Silicate	0.40%	0.40%	0.40%	0.50%
Sodium Lignosulfonate	2.00	3.50	--	--
Sodium Polynaphthalene Sulfonate	--	--	2.00	2.50
Water	41.24	25.78	41.42	34.09
Propylene Glycol	10.00	15.00	7.50	9.50
Carbowet® GA211[1]	0.10	0.10	--	0.10
Surfynol® 104H[1]	--	--	0.50	--
Atlox® 4896[2]	--	--	2.00	--
Triton® X114[3]	--	--	--	0.15
Citric acid	0.08	0.08	--	--
Triethanolamine	--	--	qs, pH 7	--
Preservative	0.10	0.10	0.10	0.10
Carbaryl, 99% Tech.	46.00	55.00	--	--
Atrazine, 98% Tech.	--	--	46.00	--
Flour Sulfur	--	--	--	53.00
VANZAN® Xanthan Gum	0.08	0.04	0.08	0.06
Viscosity, cps[A]				
1 Day	480	900	420	800
1 Month	460	880	420	780
3 Months	460	870	410	760
Stability, 3 months				
Gelation, 4/20/50°C	none	none	none	none
Bleed[B], 4/20/50°C	0/tr/vsl	tr/tr/vsl	0/0/tr	0/sl/tr
Packing, 4/20/50°C	none	none	none	none
Freeze/Thaw, 5 cycle	passed	passed	passed	passed
Bloom	passed	passed	passed	passed
Avg particle size, µm[C]	3.1	4.5	2.7	2.7
pH	5.5	5.5	7.0	7.3
Density, lbs/gal	9.2	9.4	9.1	11.6

[A]Brookfield, 60 rpm

[B]tr:trace, vsl: very slight, sl: slight

[C]Coulter

[1]Air Products and Chemicals, Inc., Allentown, PA
[2]ICI Americas, Inc., Bridgewater, NJ
[3]Union Carbide Chemicals & Plastics Technology Corporation, Danbury, CT

*Please see user advisory on page 1

Table 4. Typical Wettable Powder Formulations

Atrazine	50%	--	--	--	--
Carbaryl	--	75%	--	--	--
Diuron	--	--	80%	--	--
Mancozeb	--	--	--	75%	--
Sulfur	--	--	--	--	80%
Morwet EFW*	4-6	4-6	4-6	4-6	4-6
Sodium Lignosulfonate	--	4-6	--	--	--
Sodium Polynaphthalene Sulfonate	3-4	--	4-6	4-6	4-6
CONTINENTAL® Clay	qs to 100%				

*Akzo Nobel Surfactants, Chicago, IL

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*Please see user advisory on page 1

NOTES

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