agrimer™ VEMA

methyl vinyl ether/ maleic anhydride copolymers

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Agrimer™ VEMA methyl vinyl ether/maleic anhydride family of copolymers

- polymeric dispersant binder
- microencapsulation
- polymeric chelants
- polymeric building block

this brochure is divided into two main segments

General properties and uses 2-9
Agricultural case studies 9-13

These case studies highlight Agrimer™ VEMA uses in problem solving commonly found issues in the agrochemical world such as crystallization inhibition and delivery of insoluble actives.

general properties and uses

Agrimer™ VEMA polymers are based on linear alternating polymers (methyl vinyl ether/maleic anhydride), which can be further modified to adjust the polymer properties.

VEMA AN grades are the anhydrous form of the polymer, which can be reacted with water to form the acid form, or reacted with alcohols to form half esters or crosslinked.

VEMA ES are the ester grades of the polymer. ES grades are water insoluble, but can be used with alcohol or similar solvent-based compositions to impart rainfastness.

VEMA H are the acid grades of the polymer. H grades are water soluble and can complex readily with metal ions (e.g., micronutrients). H grades can form stronger chelates than EDTA. The H grades have a unique fixed molecular spacing of hydrogen bonding carboxylic moieties that can be used to complex with specific active ingredients. They can provide formulation viscosity control and control release of actives.

- available in a wide range of molecular weights
- strictly alternating polymeric structure

benefits

- surface active polymers (nonionic and anionic)
- forms derivatives that can impart controlled release properties with certain actives
- polyelectrolytic properties
- have both adhesive and cohesive properties
- forms transparent films

suggested applications

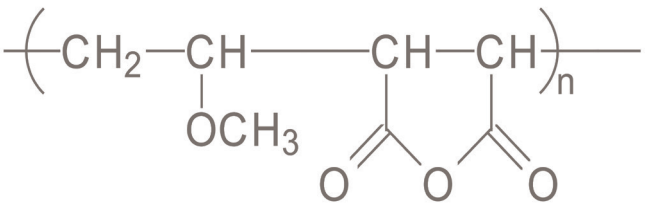
- polymeric co-dispersants
- enhance active ingredient solubility/dispersibility via co-precipitation
- binders in dry, wet granulation, hot melt extrusion
- crystal inhibition
- convert liquid actives to solids
- spreader-stickers with film forming potential
- seed and granule coatings
- microencapsulation
- soil conditioning

regulatory status

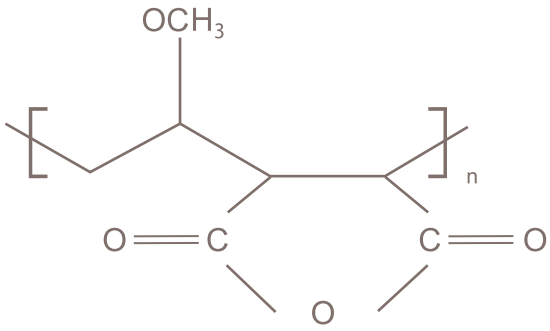
The components of Agrimer™ VEMA AN and VEMA H copolymer grades are approved for use as inerts in agricultural pesticides under 40 CFR 180.960. Agrimer™ VEMA ES grades are exempt from the requirements of a tolerance for use in food and non-food applications both pre and post harvest.

physical and chemical properties

The relationship between the different products in the VEMA family are shown below. Methyl vinyl ether is reacted with maleic anhydride to produce the strictly alternating copolymer of various molecular weights in the anhydride form. The anhydride is converted to the acid form by hydrolysis. The anhydrides can also be readily converted into half esters by reacting with alcohols. The commercially available esters are made from ethanol, isopropanol and butanol.

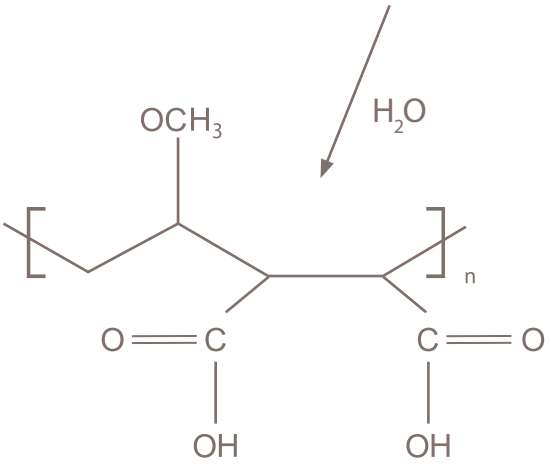


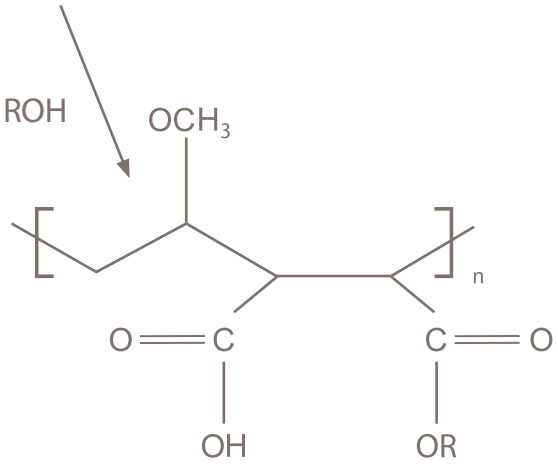
the Agrimer™ VEMA family of copolymers



Agrimer™ VEMA AN series

anhydride form	average molecular weight (Mw)
VEMA AN-216	216,000
VEMA AN-990	990,000
VEMA AN-1980	1,980,000





Agrimer™ VEMA H series

free acid form	average molecular weight (Mw)
VEMA H-240L	240,000
VEMA H-2200	2,200,000

Agrimer™ VEMA ES series

half esters	ester (R)
VEMA ES-22	ethyl
VEMA ES-33	isopropyl
VEMA ES-42	butyl
VEMA ES-43	butyl

typical physical properties of the anhydride, acid and ester forms of Agrimer™ VEMA copolymers are given in tables 1-5.

table 1: typical properties of Agrimer™ VEMA AN (anhydride) type copolymers

polymer properties	Agrimer™ VEMA AN-216	Agrimer™ VEMA AN-990	Agrimer™ VEMA AN-1980
available as	solid	solid	solid
bulk density (g/cc)	0.32	0.32	0.21
linkage	alternating	alternating	alternating
Mn (000)	216 – 230	940 – 1080	1,700 – 1,980
Mw (000)	55.5 – 79.8	153 – 311	319 – 960
physical state of solid at 25°C	white powder	white powder	white powder
relative viscosity (1% solution in MEK)	0.1 – 0.5	1.0 – 1.5	2.5 – 4.0
tap density (1000 taps, g/cc)	0.45	0.43	0.31
Tg (°C)	152	151	154

Mn = Number Average Molecular Weight Mw = Weight Average Molecular Weight Tg = Glass Transition Temperature by DSC
Properties listed are based upon 100% Polymer

table 2: typical properties of Agrimer™ VEMA H (acid) and salt type copolymers

Polymer Properties	Agrimer™ VEMA H-240L	Agrimer™ VEMA H-2200L	Agrimer™ VEMA H-815MS
available as	liquid ~ 35% in water	liquid ~ 13% in water (available as powder also)	solid
bulk density (g/cc)	NA	NA	0.60 – 0.75
linkage	alternating	alternating	alternating
Mn (000)	~ 240	~ 2,200	1,000[a]
Mw (000)	55.5 – 79.8	319 – 960	319 – 960
physical state of solid 25°C	liquid	liquid	white powder
relative viscosity (1% solution in water)	2 – 4	4 – 10	–
softening point Tg (°C)	144	144	can't be determined
specific gravity	1.0	1.0	NA
surface tension (0.1% in water, mN/m)	59.8+/-0.1	56.1+/-0.1	71.8+/-0.1
surface tension (1% in water, mN/m)	46.4+/-0.3	46.1+/-0.1	71.7+/-0.1
tap density (1000 taps, g/cc)	NA	NA	0.58
viscosity as is	100 – 200cps	~ 950cps	NA

Mn = Number Average Molecular Weight Mw = Weight Average Molecular Weight Tg = Glass Transition Temperature by DSC
[a] Base material Mw. Salt form with reversible lightly crosslinked structure.

microencapsulation and controlled release

There are a number of methods to microencapsulate products. Processes may incorporate the active into a matrix of absorbent or porous particle matrices, or form walls around the active ingredient through interfacial polymerization. Further, the release mechanism can vary from diffusion to chemical degradation of the polymeric material by heat, pH, or biodegradation. The following examples show some ways by which the Agrimer™ VEMA copolymer products can be used to encapsulate active ingredients.

- Agrimer™ VEMA copolymers have shown utility as protective colloids for active ingredients that are encapsulated by interfacial polymerization.
- some additional examples are shown below.

two methods for microencapsulating active ingredients

ion exchange

Water insoluble Agrimer™ VEMA polymer + NaOH

↓

Water soluble Agrimer™ VEMA polymer + Hydrophobic A.I. emulsified in water

+

combine and add $CaCl_2$

↓

Precipitate of A.I. in oil coated with insoluble Agrimer™ VEMA

Agrimer™ VEMA ES-22, ES-33, ES-42 or ES-43 polymers

Dissolves hydrophobic Agrimer™ VEMA ES polymer in ammonia or amines + Hydrophobic A.I. emulsified in water

Add acid H_3PO_4 or HCl

↓

Precipitate is formed with the Agrimer™ VEMA ES polymer coating the perimeter of the oil droplet containing the A.I.

table 3: typical properties of Agrimer™ VEMA ES (esterified) type copolymers

polymer properties	Agrimer™ VEMA ES-22M	Agrimer™ VEMA ES-22	Agrimer™ VEMA ES-33	Agrimer™ VEMA ES-42	Agrimer™ VEMA ES-43
available as	50% in EtOH	50% in EtOH	50% in IPA	50% in EtOH	50% in IPA
bulk density (g/cc)	0.32	0.32	0.32	0.24	0.21
description	half ethyl ester	half ethyl ester	half isopropyl ester	half butoyl ester	half ethyl ester
linkage	alternating	alternating	alternating	alternating	alternating
Mw (000)	22 – 40	30 – 46	12 – 13.7	~ 50	~ 50
Mn (000)	60 – 100	100 – 150	44.5 – 50	125 – 150	125 – 150
relative viscosity (1% in solvent)	1.30 – 1.35 (EtOH)	1.36 – 1.45 (EtOH)	1.2 (IPA)	1.43 – 1.50 (EtOH)	1.3 (EtOH)
specific gravity	0.99	0.98	0.96	0.98	0.96
surface tension (0.1% in water, mN/m)	insoluble	insoluble	insoluble	insoluble	insoluble
Tg (°C)	101	92	94	70	70
viscosity as is	11,400	18,600	31,200	10,500	85,000

EtOH = Ethanol IPA = Isopropyl alcohol Mn = Number Average Molecular Weight Mw = Weight Average Molecular Weight Tg = Glass Transition Temperature by DSC
Properties listed are based upon 100% Polymer

table 4: solubility of Agrimer™ VEMA AN type polymers (% by weight) in various solutions1

solvent	Agrimer™ VEMA AN-216	Agrimer™ VEMA AN-990	Agrimer™ VEMA AN-1980
AgsolEx™ 8	< 1	< 1	< 1
AgsolEx 1	< 40	< 40	< 30
AgsolEx BLO	< 40	< 40	< 30
Aromatic 150	< 1	< 1	< 1
Aromatic 200	< 1	< 1	< 1
ethanol	esterifies	esterifies	esterifies
mineral oil	< 1	< 1	< 1
soybean oil	< 1	< 1	< 1
water	hydrolyzes	hydrolyzes	hydrolyzes

[1] Properties listed are based on 100% Agrimer™ VEMA copolymer.

table 5: solubility of Agrimer™ VEMA H type polymers (% by weight) in various solvents[1]

solvent	Agrimer™ VEMA H-240L	Agrimer™ VEMA H-2200	Agrimer™ VEMA H-2200L	Agrimer™ VEMA H-815MS
AgsolEx 8	< 1	< 1	< 1	< 1
AgsolEx 1	40 – 50	40 – 50	40 – 50	< 1
AgsolEx BLO	50	40	40	< 1
Aromatic 150	< 1	< 1	< 1	< 1
Aromatic 200	< 1	< 1	< 1	< 1
ethanol	50	40	40	< 1
mineral oil	< 1	< 1	< 1	< 1
soybean oil	< 1	< 1	< 1	< 1
water	50	50	50	50 slowly

[1] Properties listed are based on 100% Agrimer™ VEMA H copolymer. Water solubility and ease of dissolution are pH dependent. Agrimer™ VEMA H-815MS copolymer will ion exchange to slowly dissolve (pH dependent).

customization

As shown on page 7, the Agrimer™ VEMA family is modified into a number of commercial families having quite different properties. There are a number of other reactions which allow for the preparation of ingredients that can be tailored to specific active ingredients and/or applications. Page 8 shows a variety of reactions that are commonly used to obtain specific performance characteristics.

surface activity

The Agrimer™ VEMA family are surface active polymers that reduce the surface tension of water from about 72.8 mN/m (dynes/cm) to about 45 mN/m @ 2% copolymer addition (2% is analogous to the critical micelle concentration for the VEMA family). Generally, the surface tension reduction is inversely related to concentration, although the lower molecular weight copolymers are slightly more effective in reducing surface tension. Note that the anhydride form converts to the acid form in water and that the reduction in surface tension is mostly due to the hydrolyzed species (Figure 1).

Another method of making customized polymeric surfactants is by reacting Agrimer™ VEMA AN with nonionic surfactants resulting in a half ester conjugate of the polymer and the surfactant which form flexible clear films on drying.

viscosity

As with the reduction in surface tension, the anhydrides are hydrolyzed in aqueous solutions resulting in a concentration dependent increase in viscosity (Figure 2).

figure 1: viscosity as a function of copolymer concentration

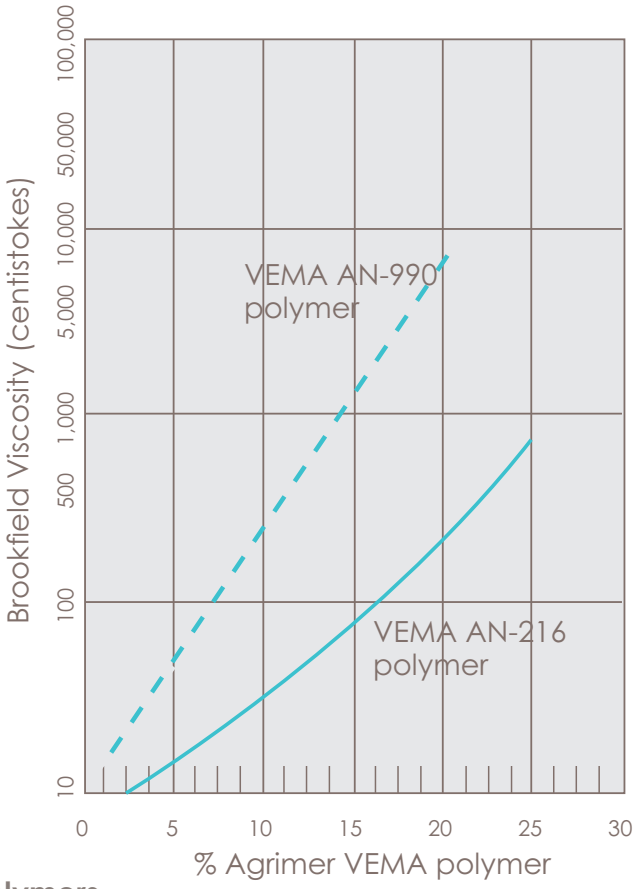
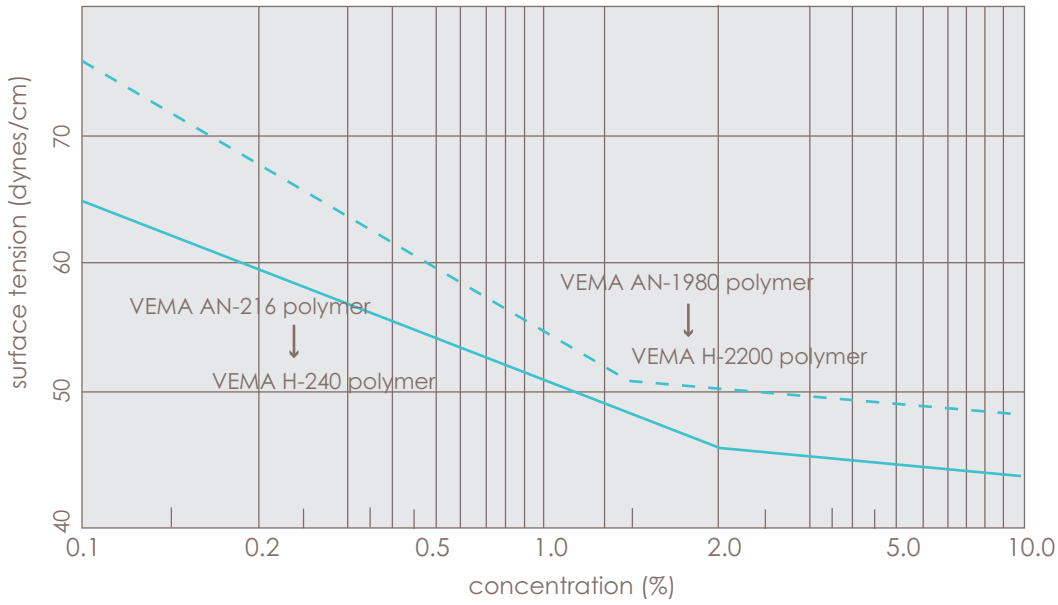
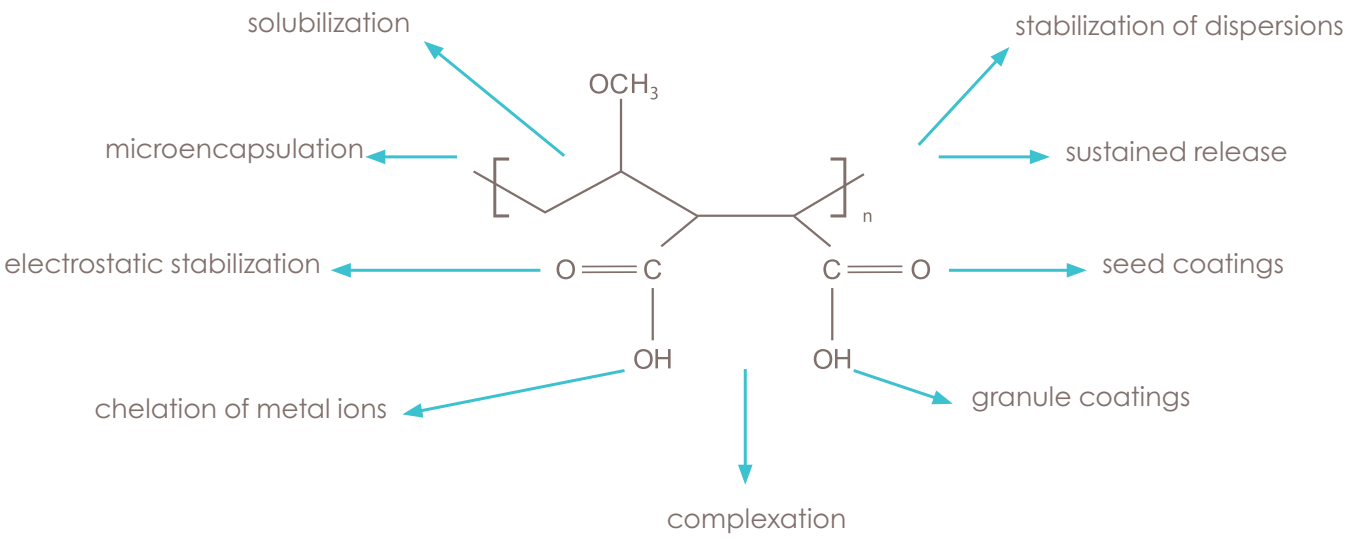


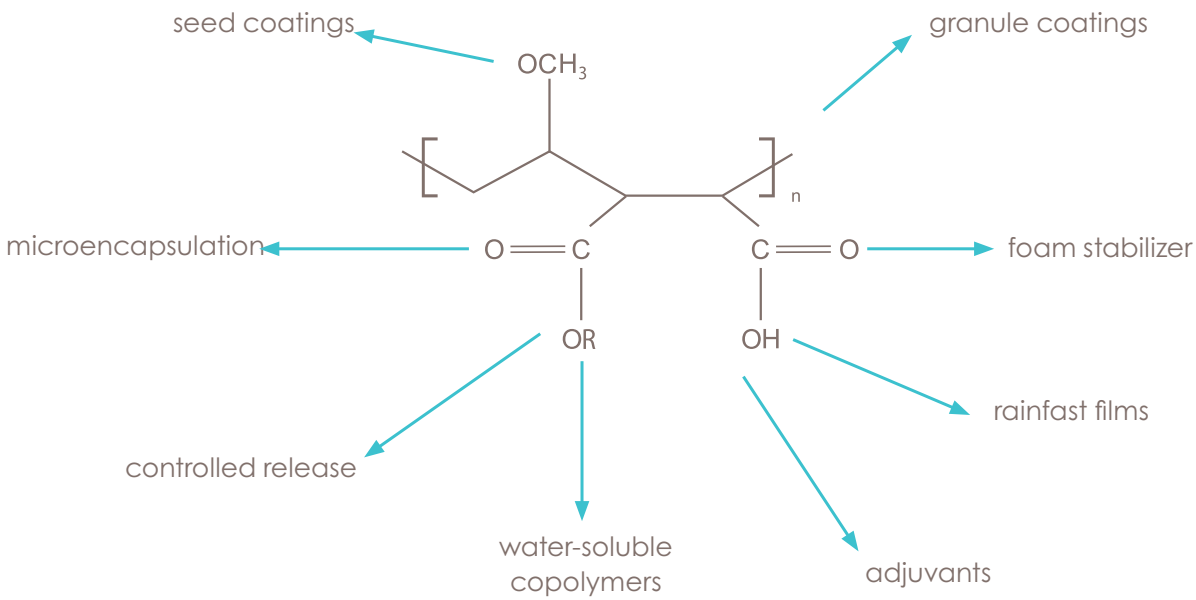
figure 2: surface tension reduction by VEMA copolymers



Agrimer™ VEMA H applications

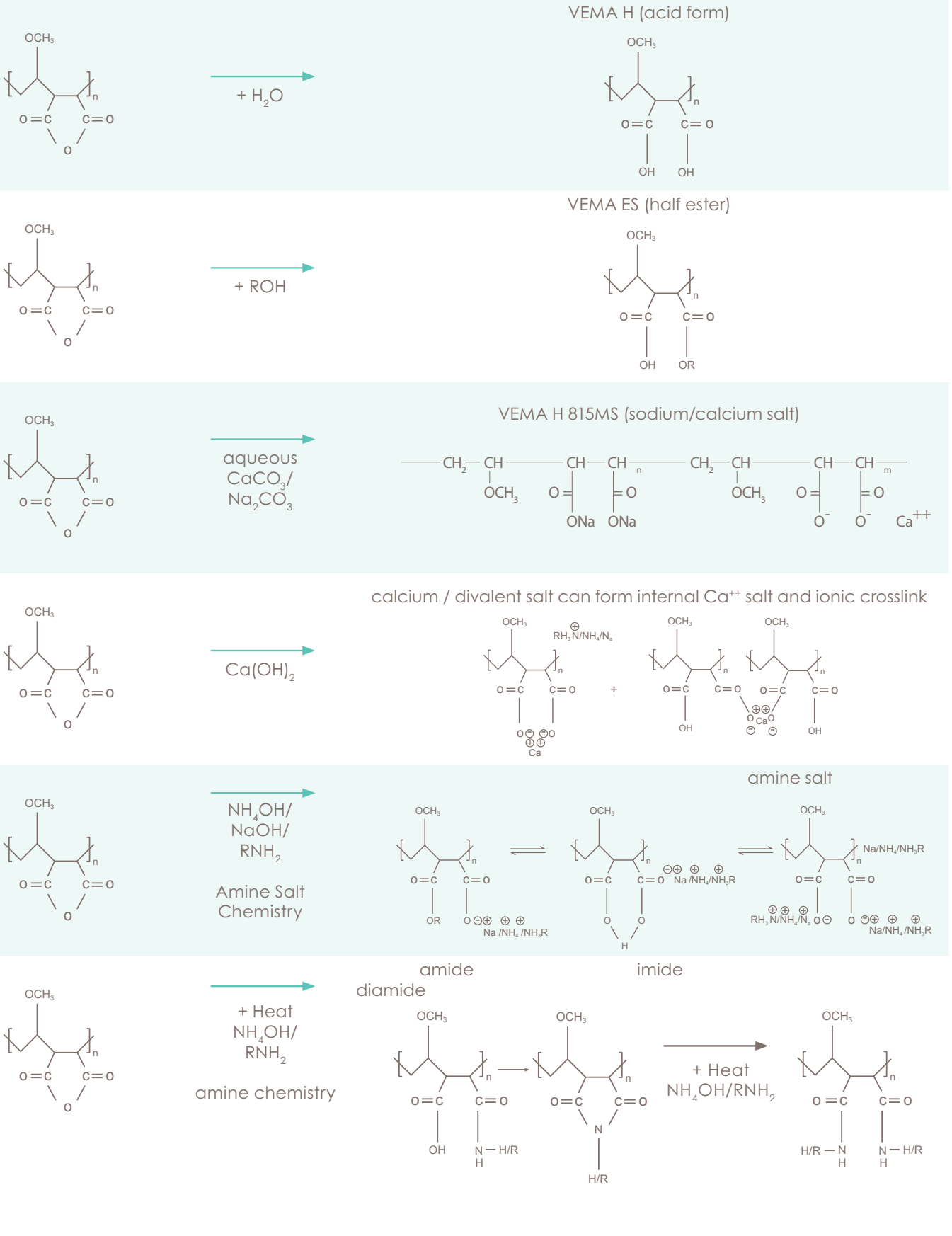


Agrimer™ VEMA ES applications



Agrimer™ VEMA polymer products and examples of simple derivatives for agchem applications

VEMA AN



Viscosity shows a bimodal increase when titrated with a base (Figure 3). The first maximum is due to the neutralization of the first acid moiety of the diacid form, which gives the polymer an overall negative charge. Further viscosity increases will occur upon the addition of more base neutralizing the second acid moiety. If the base is a strong base, such as sodium hydroxide, the viscosity increase is more prominent at the second neutralization point.

agricultural case studies

granules and tablets

Agrimer™ VEMA-H series are good binders which disperse quickly if used in conjunction with certain surfactants and active ingredients. The ES series also has potential utility in this application if neutralized with a base to increase water solubility. The copolymers have certain dispersants or pairs of dispersants that are superior to other potential combinations. Table 6 shows polymer-dispersant combinations that Ashland has found to perform best with its VEMA copolymers.

table 6: copolymer-dispersant pairs

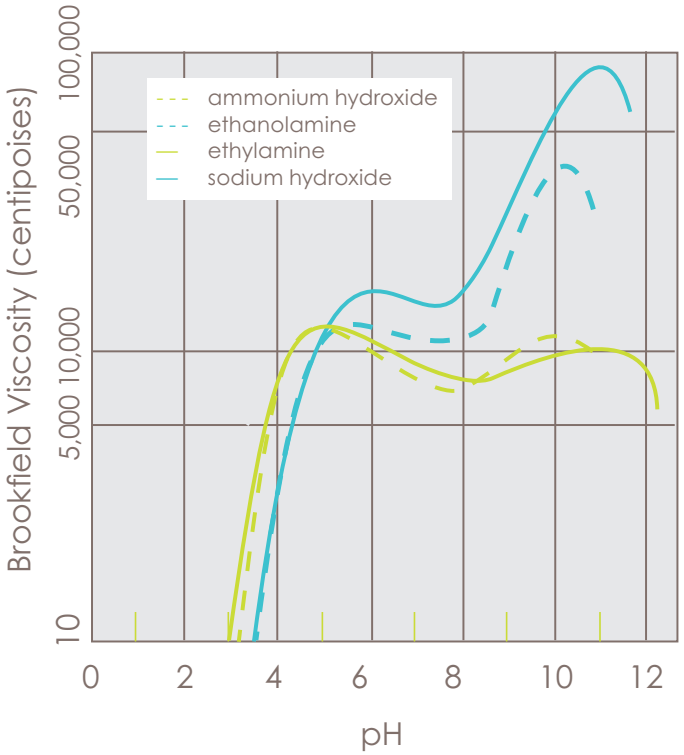
copolymer	dispersant
Agrimer™ H Series	castor oil ethoxylates, phosphate esters, sodium dodecyl benzene sulfonate, sodium dodecyl sulfate
Agrimer™ ES Series	ethoxylated (30 EO) glyceryl mono isostearate (Tagat 1)

Low levels of Ashland's AgsolEx™ 8 and AgsolEx 12 solvents (octyl- and dodecyl-pyrrolidones), have been incorporated into granules and tablets to help wet them and aid in disintegration/solubilization of the A.I. Superwetters such as AgsolEx 8 solvent or Ashland's Agrimer™ Easy-Wet™ 20 wetting agent can provide an additional benefit by aiding the wetting and spreading of postemergence foliar penetration of actives on leaf surfaces.

crystallization prevention

Agrimer™ VEMA ES-22 @ 30%, neutralized with 1-5% amino methyl propanol (AMP), in 65-70% propylene glycol along with AgsolEx 8 solvent has been shown to prevent crystallization of a variety of hydrophobic active ingredients when diluted to spray concentrations.

figure 3: viscosity increases with increasing pH



delivery of insoluble actives

Ashland has developed a formulation in which an insoluble active can be microdispersed or microemulsified in a system that also contains a hydrophobic polymer to assist in adhesion and preventing washoff. This system is multi-functional in that many hydrophobic active ingredients and UV absorbers can be microdispersed for preventing UV degradation, for making veterinary pour-ons, and for formulating stable micro-dispersions for horticultural and agricultural sprays or aerosols. Table 7 shows a typical formulation into which a variety of hydrophobic active ingredients can be loaded at 1-4% in the fully diluted spray.

table 7: typical microemulsion matrix

Ingredients	WT%
Agrimer™ VEMA ES-42	4.00
alkylphenol ethoxylate (Igepal CO 630)	3-8
amino methyl propanol (AMP) for partially neutralizing the VEMA ES-42	0.18
ethanol	30-50
tagat 1	1-4
UV stabilizer or active ingredient	1-20
water	40-45

properties of the above system

appearance	45 °C = clear 21 °C = clear 3 °C = cloudy
dynamic surface tension	3 mN/m @ 2-10 bubbles/sec.
particle size 0.007-0.03 microns	fully reverts with warming
static surface tension	undiluted = 26.7 mN/m dilution 1:10 = 7.5 mN/m
wetting time	undiluted = 1 sec. dilution 1:10 = 7.4 secs.

converting liquid actives to solids

Co-precipitation procedures can also be used for converting liquid products into dry granules. For example, Ashland has demonstrated the conversion of liquid chloracetanilides such as metolachlor-granules by co-precipitating them by freeze drying or spray drying with an equivalent amount of Agrimer™ VEMA H-240L polymer. The resulting granules have excellent physical properties while being instantly dispersible in water even though no surfactants are used.

This solid metolachlor as prepared above (1:1 polymer to A.I.), at 1-2% in water, instantly produced a dispersion that was stable for > 24 hours and showed 100% recovery on standing over a period of 24 hours. This simple technique also has several formulation variables that can be manipulated, such as:

- hydrophilic-hydrophobic balance
- counter ions
- pH
- crosslinking of the polymer
- the use of additional dispersing agents

A hypothesis is that the unique VEMA backbone-spacing is a requirement for the polymer active complex and its capacity to instantly disperse in water.

stickers

Agrimer™ VEMA ES-22 and ES-42 copolymers can be made in water as a submicron size clear composition, typically as a microemulsion. These compositions can be used as additives in formulations to provide hydrophobic film coatings.

veterinary pour-ons and UV stabilizer/ sticker/adjuvants

The microemulsion shown in Table 7 can also accommodate many pyrethroids used in animal pour-on formulations. Not only does the formulation and its variants have low surface tension, resulting in spreading over the animal's back, but the presence of the Agrimer™ VEMA ES-42 polymer acts as a waterproof film to reduce subsequent rain washoff. UV absorbers can be incorporated if the active ingredient is unstable to UV radiation and the viscosity of the product can also be modified with such thickeners as Agrimax™ C200 series of hydroxy propyl cellulose.

dispersion stabilizers

At certain levels of neutralization these copolymers will produce negatively charged polyelectrolytes that can stabilize dispersions. The introduction of counter ions leading to enhanced viscosity will further potentiate the stabilizing effects.

Chlorothalonil and carbaryl suspension concentrates were prepared by wet milling together with a thickener, an antifreeze, a biocide, a defoamer and different types and ratios of dispersants (Table 8). The principal dispersants were Agrimer™ 30 PVP polymer and Agrimer™ ES-42 polymer (40% neutralized with NaOH), as compared with commercial formulations containing an EO/PO block copolymer plus napthalene sulfonate formaldehyde condensate.

table 8: increased dispersion stabilities using Agrimer™ PVP and Agrimer™ VEMA polymers as dispersants

	dispersants	% suspended (4 hrs.)	inversions for redispersion
commercial chlorothalonil	B[1]	33	32
experimental chlorothalonil	A[2]	93	7
commercial carbaryl	B	59	-
experimental carbaryl	A	99	2

[1] B = Pluronic P104 @ 3.0% & VEMA ES-42 @ 6.5%
[2] A = Agrimer™ 30 @ 2.6% & Agrimer™ VEMA ES-42 @ 0-5% (40°C neutralized with NaOH)

The Agrimer™-containing concentrates (Table 8), after 2 weeks storage at 52°C, were comparable to the commercial formulations with regard to typical stability parameters. However, the Agrimer™-containing suspensions, after dilution to use rates, were 2-3 times more stable than the commercial formulations and were more easily resuspended.

hot melts

Hot melt extrusion is used with active ingredients that have low melting points. Choosing the appropriate binder requires a match between the extruder head temperature and the glass transition temperature (Tg) of the polymer. Table 9 shows the Tg for some of Ashland's polymers as well as their thermal decomposition temperatures (Td).

The copolymers shown in Table 9 have melting temperatures that allow them to be milled or converted into granules by extrusion. Usually, the melting point of the active ingredient and a polymer will fall between the two. For example, metalochlor, which is a liquid at room temperature, can be converted into a granule with a Tg of 380°C by coprecipitating it with an equivalent amount of the solid version of Agrimer™ VEMA H-240L polymer.

table 9: glass transitions (Tg) & decomposition (Td) temperatures

copolymer	Tg (°C)	Td (°C)
Agrimer™ VEMA H-240L	~ 144	> 300
Agrimer™ VEMA H-2200	~ 144	> 300
Agrimer™ VEMA AN-216	~ 152	> 300
Agrimer™ VEMA AN-1980	~ 154	> 300

soil conditioners

Experimental work on soil aggregation has shown that Agrimer™ VEMA H-2200 polymer at 0.075% in a silty clay loam, increased the percent of soil aggregates that were greater than 0.50 mm by 150%. Increased aggregation leads to increased water penetration, better tilth and reduced wind erosion. Applications range from turf to horticultural mixtures and potting media.

feed supplement gels

Agrimer™ VEMA AN copolymers have been used to produce thixotropic gels of vitamin and mineral feed supplements for ruminant animals. Further, Agrimer™ VEMA ES42 polymer has shown utility as a rumen bypass. It has been used to form low-pH-stable encapsulated drugs that are stable in the gut, which are released in the high pH environment of the intestine.

seed coatings

Most processes can be adapted for the application of a final "flash" coat to either decrease friability, dusting or increase hardness from soil-applied granules.

For seed treatments, the coatings must adhere to the seed, give even coverage at low treatment volumes, be easy to apply, and provide for optimum biological performance. Many of Ashland's water soluble polymers and copolymers are used to coat seeds. The recommended VEMA copolymers are Agrimer™ VEMA AN-216 and Agrimer™ VEMA H-2200 polymers. By neutralization of any of the Agrimer™ VEMA AN series polymers with, for instance, ammonium or sodium hydroxide, a water soluble polymer is formed that can be used for coating. A combination of Agrimer™ PVP or Agrimer™ VA polymers series along with Agrimer™ VEMA H polymer series applied one after the other has shown to produce sustained release in seed coatings via a hydrogen bonding mechanism.

Many seed coatings are applied in an organic medium which includes AgsolEx™ 1 solvent for solubilizing the active ingredient and AgsolEx 8 solvent as a super wetter. In these systems it is possible to use water insoluble polymers that form even harder films. Examples include the Agrimer™ VEMA ES polymer series of half esters.

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