# agrimer™ AL

## alkylated vinyl pyrrolidone polymers

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# Agrimer™ AL alkylated vinyl pyrrolidone polymers

- binder
- dispersant
- rainfastness agent
- interfacial polymerd

**this brochure is divided into two main segments**


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| Agricultural case studies | 6-7 |


These case studies highlight the uses of Agrimer™ AL for example as a crystal inhibitor, a binder and as a dispersant agent etc.

## general properties and uses

The Agrimer™ AL family of alkylated vinyl pyrrolidone products includes surface active non-ionic polymers. The backbone includes hydrophobic and hydrophillic moieties, which drive the polymer to either the water-air or water-oil interface, providing potential emulsion stabilization and rainfastness benefits.

All grades are pH stable, with adhesive, cohesive, dispersant and emulsification properties.

- surface active polymer
- oil/water soluble depending on percent pyrrolidone and alkyl substituent chain length

## benefits

- dispersion aid for oil dispersion (OD) formulations
- adhesive properties
- spreader-sticker and anti-flocculant in one polymer
- effective in reducing oil-water interfacial tension
- not sensitive to ph or salts
- optimizes viscosity to prevent active ingredient precipitation in suspension concentrates and permitting high active ingredient loading in flowables
- foliar adhesion
- wash-off resistant interfacial films for enhanced efficacy
- optimizes biological efficacy
- antitranspirant properties

## suggested applications

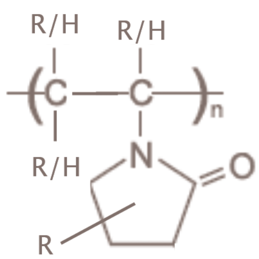
- emulsifier and anti-flocculant
- crystal inhibition
- multiple emulsions / stabilization of water-in-oil and oil-in-water emulsions
- anti-flocculants for flowables and concentrated suspensions for high active ingredient loading
- rainfastness: Form waterproof films that minimize wash-off of crop protection chemicals from foliage
- dispersion aid in oil dispersion (OD) formulations

## regulatory status

Agrimer™ AL 10LC, Agrimer™ AL 22, Agrimer™ AL 25 and Agrimer™ AL 30 are exempt from the requirement of a tolerance under 40 CFR 180.960. Agrimer™ AL 22D is approved under 40 CFR 180.920.

## physical and chemical properties

The random grafting of alpha olefins onto a vinyl pyrrolidone polymer backbone and lactam ring results in products having widely diverse properties that vary with the molecular weight of the product, the length of the alkyl group, and the degree of alkylation of the polymer. One key feature of this family is that by coupling the "pseudo-cationic" pyrrolidone with the hydrophobic alkyl groups, the polymer exhibits surfactant-like properties. The literature on formulating crop protection chemicals documents the superiority of polymeric surfactants as stabilizers of emulsions and flowable formulations, and "comb-like" polymers have been cited as being excellent stabilizers of suspension concentrates. The Agrimer™ AL graft polymers provide the formulator with a range of graft polymers having both of these desirable traits in a single molecule.



Typical physical properties of the commercially available members of the Agrimer™ AL family are given in Table 1. In addition to the products in Table 1, Agrimer™ AL-22 is available as an aqueous dispersion (Agrimer™ AL-22D) at 10% polymer content with a particle size less than one micron.

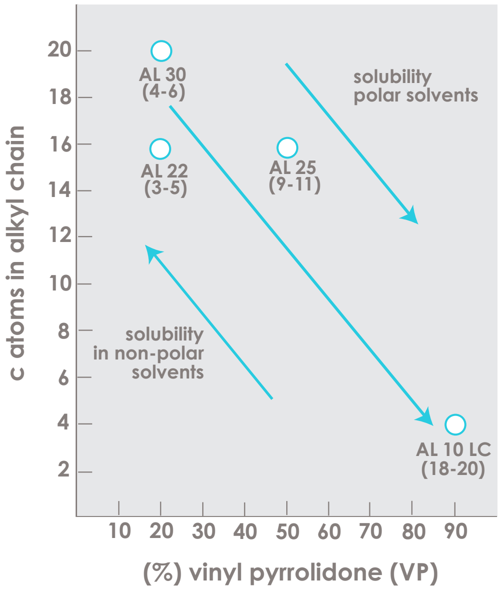
The Agrimer™ AL product line offers a broad range of hydrophilic to lipophilic balances (HLB) from 4 to 20, and the HLB is correlated with the percent alkylation, the length of the alkyl group and the molecular weight of the graft polymer. See Figure 1. These polymers vary from oil soluble to water soluble and thus find use in both organic and water-based formulations. In a oil-water system, the pyrrolidone part of the molecule assumes a pseudo-cationic charge and orients into the water phase, while the strongly hydrophobic alkyl group associates with the hydrophobic (oil) parts of the system. Therefore, the pseudo polymeric/surfactant properties of Agrimer™ AL grades can stabilize both oil-in-water and water-in-oil systems as well as dispersions of hydrophobic active ingredients.

## table 1: typical properties of Agrimer™ AL graft polymers

| property | Agrimer™ AL 10LC | Agrimer™ AL 22 | Agrimer™ AL 25 | Agrimer™ AL 30 |
|---|---|---|---|---|
| appearance @ 25°C | off-white powder | yellow viscous liquid | pale-yellow clear isopropanol solution | off-white yellow waxy mass |
| alkylation group | butane ($C_4$) | hexadecene ($C_{16}$) | hexadecene ($C_{16}$) | eicosene ($C_{20}$) |
| % ash | < 0.1 | < 0.5 | < 0.1 | < 0.1 |
| VP/Alkylation ratio | 90/10 | 20/80 | 50/50 | 30/70 |
| % bromine number | 20 max. | 15 max. | – | 8 max. |
| Brookfield viscosity @ 25°C | – | 2500 max.[b] | 300 max. | 20,000 max.[c] |
| color (VCS) | not applicable | 1 max.[a] | 2 max. | 2 max.[a] |
| density (g/ml) | 0.258g/ml (tap) | 0.90 | 0.88 | 0.95 |
| film adhesivity[g] | – | 151.9 | 370.5 | 217.5 |
| Film pencil hardness (20% conc.) | – | 4B | 4B | 4B |
| flashpoint °F (°C) | none | none | 62 (16.7) | none |
| HLB estimated[f] | 18 – 20 | 3 – 5 | 9 – 11 | 4 – 6 |
| melting point (°C) | Tg=155 (as is) | 8.5 | Tg=150[e] | 35 – 40 |
| % moisture | 5.0 max. | – | – | – |
| % nitrogen (as is) | 10.0 – 12.0 | 2.0 – 3.0 | 2.5 – 3.5 | 2.9 – 3.6 |
| Mw (GPC-relative to PEO standards) | 12-22,000 | 11,000 – 17,000 | – | 14,000 – 20,000 |
| polydispersity (Mw/Mn) | 1.3 – 1.4 | 2.0 – 4.0 | – | 2.0 – 4.0 |
| Relative viscosity (1% toluene)[d] | – | 1.03 – 1.05 | – | 1.17 – 1.20 |
| % solids | 95 min. | 95 min. | 45-55 | 96 min. |

(a) 50% Toluene (b) Determined at 50°C (c) Determined at 80°C (d) Cannon-Fenske #100 @ 25°C (e) Freeze-Dried (f) Calculated: HLB=20 (H/ H+L); H=Hydrophilic(pyrrolidone) portion, L=Hydrophobic(alkyl) portion (g) IMASS Slip/Peel Tester - Force (g) to separate from parafilm
NOTE: These data are typical of current production, but are not specifications.

## figure 1: calculated HLBs of Agrimer™ AL family




The surfactant-like properties result in products that:

- reduce oil-water interfacial tensions to 1 to 2 dynes/cm at concentrations as low as 0.001%
- are strong emulsifiers, for example completely emulsifying octanol-water
- reduce aqueous surface tension to 30 dynes/cm at 1.0% (Agrimer™ AL 10LC polymer)

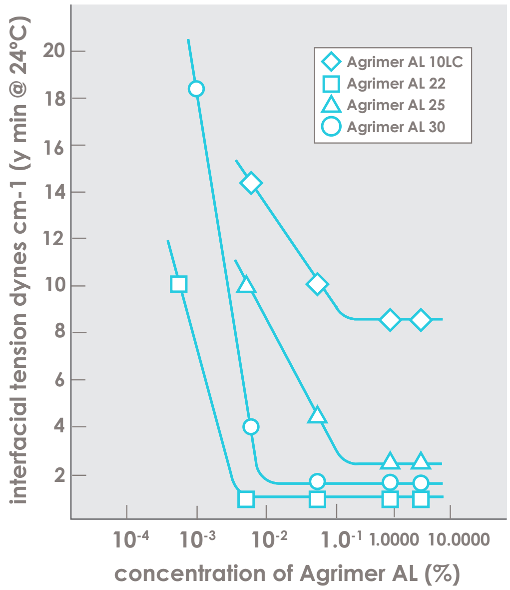
1% Agrimer™ Al 22, AL 25 and AL 30 in Aromatic 150 did not reduce surface tension below 31 dynes/cm as the polymers are in complete solution and do not accumulate at the solvent/air interface. However, addition of water produces accumulation on the interface causing considerable reduction of the interfacial tension. See Figure 2.

HLB value and solubility are directly related. A high HLB is indicative of solubility in polar solvents, while a low HLB suggests solubility in oils or non-polar solvents. As predicted by HLB's, Table 2 shows that the Agrimer™ AL line varies in solubility from very hydrophobic (Agrimer™ AL 30 polymer) to hydrophilic (Agrimer™ AL 10LC polymer).

The combination of a long alkyl group and a high percentage of alkylation results in a hydrophobic polymer such as Agrimer™ AL 30 polymer. Its films are very water resistant and less likely to be washed off by rain or irrigation water.

At the other end of the spectrum is the hydrophilic Agrimer™ AL 10LC graft polymer that has a moderate degree of adhesiveness coupled with water solubility. This makes it excellent as an anti-flocculant in concentrated dispersions, as a stabilizer of oil-in-water emulsions, in microencapsulation using interfacial polymerization and as a binder in granules and tablets.

## figure 2: interfacial tension of water and Aromatic 150 in the presence of Agrimer™ AL graft polymers




## table 2: solubilities** of Agrimer™ AL graft polymers (%) in various solvents

| solvent | Agrimer™ AL 10LC | Agrimer™ AL 22 | Agrimer™ AL 25 | Agrimer™ AL 30 |
|---|---|---|---|---|
| aromatic 150 | <1 | >50 | >50 | >50 |
| aromatic 200 | <1 | >50 | >50 | 30-40 |
| AgsolEx™ 8 | 2-5 (3 days) | <1 | >50 | <1 |
| AgsolEx™ 1 | 48 | <1 | >50 | <1 |
| AgsolEx™ BLO | >50 | <1 | >50 | <1 |
| ethanol | >50 | <1 | >50 | <1 |
| mineral oil | <1 | >50 | <1 | <1 |
| soybean oil | <1 | >50 | <1 | <1 |
| water | 12 | <1 | <1 | <1 |

** When solubility ≥ 10%, solubility was measured by dissolving an appropriate quantity of polymer in 10g solvent and stirring solvent in an orbital shaker for four hours. When solubility ≥ 5%, solubility was measured by mixing appropriate quantities in rotating wheel for four hours.

The solubility of Agrimer™ AL 30 polymer is limited to petroleum hydrocarbons, while Agrimer™ AL 22 polymer is slightly more soluble and can be used not only in hydrocarbon solvents but also in mineral and vegetable oils. On the other end of the spectrum is Agrimer™ AL 10LC polymer which is soluble in polar solvents including water.

Partition coefficient, surface tension reduction and oil-water interfacial tension are key parameters in the selection of anti-flocculants for concentrated emulsions and oil and water-based suspension concentrates.

As shown in Table 3, the Agrimer™ AL polymers are excellent emulsifiers. They are so active in emulsifying octanol and water that no partition coefficients could be determined, and even at 0.1% they reduced water-oil interfacial tension from 37 dynes cm-1 down to less than 2 dynes cm-1 a 95% reduction in interfacial tension.

Figure 2 and Table 3 offer formulators a wide selection of superior anti-flocculants for oil and water-based suspension concentrates and flowable systems (SC and FS). These polymers also have utility in stabilizing emulsifiable concentrates and microemulsions. Agrimer™ AL 10LC polymer is the anti-flocculant of choice in water-based suspension concentrates and for stabilizing oil-in-water emulsions. Agrimer™ AL 25 polymer can be microemulsified together with hydrophobic active ingredients into water-based systems. Agrimer™ AL 25 and Agrimer™ 22 polymer are the anti-flocculants of choice for oil-based concentrated suspensions and for stabilizing water-in-oil emulsions.

The significant oil-water interfacial tension reduction given by the Agrimer™ AL graft polymers is accompanied by a significant reduction of the surface tension of aqueous solutions (Figure 3). This combination of properties makes the Agrimer™ AL polymers both excellent system stabilizers and very effective spreaders of aqueous spray solutions on waxy surfaces.

Ashland has formulated both pendimethalin and Thidiazuron into emulsion concentrates containing either 5.0% of a phosphate ester or ones having the phosphate ester totally replaced by Agrimer™ AL 25 polymer in the solvent system. Formulations containing the Agrimer™ AL line were equivalent to the conventional surfactant-containing formulations, as measured by the stability of the emulsion upon dilution and crystallization. However, the polymeric surfactants provide better spread on waxy surfaces, and they provide the additional advantage of adhering the active ingredient to the leaf surface and wash off resistance.

## comparative adhesiveness

While adhesiveness is an important attribute to consider when selecting a sticker, secondary attributes, such as resistance to washoff, must also be kept in mind. Screening tests of many polymers and copolymers revealed that the adhesiveness of the Agrimer™ AL family of graft polymers was up to five times greater than that of any other product tested.

While the low water solubility of most of the Agrimer™ AL polymers results in some use limitations, Ashland has developed new technology which allows the hydrophobic Agrimer™ AL 25 polymer to be used in aqueous systems for superior performance.

### table 3: partition coefficients and surface tensions for Agrimer™ AL graft polymers

| polymer properties | Agrimer™ AL 10LC | Agrimer™ AL 22 | Agrimer™ AL 25 | Agrimer ™AL 30 |
|---|---|---|---|---|
| octagol/ $H_2O$ partition coefficient | all polymers produced an emulsion at 10% level | | | |
| **surface tension in Aromatic 150, dynes cm$^{-1}$ @ 21°C | | 31.2 ± 0.2 (Conc. = 1.0%) | | |
| surface tension in water, dynes cm$^{-1}$ min, @ 21°C | 33.7 ± 0.04 (Conc. = 1.0%) See Fig. 2 | | | |

** No reduction in the surface tension because the polymers are in complete solution and no accumulation is observed on the solvent-air interface. However, addition of water produces accumulation on the interface, causing considerable reduction in the interfacial tension.

### figure 3: surface tension of aqueous solutions of Agrimer™ AL 10LC polymer vs concentration

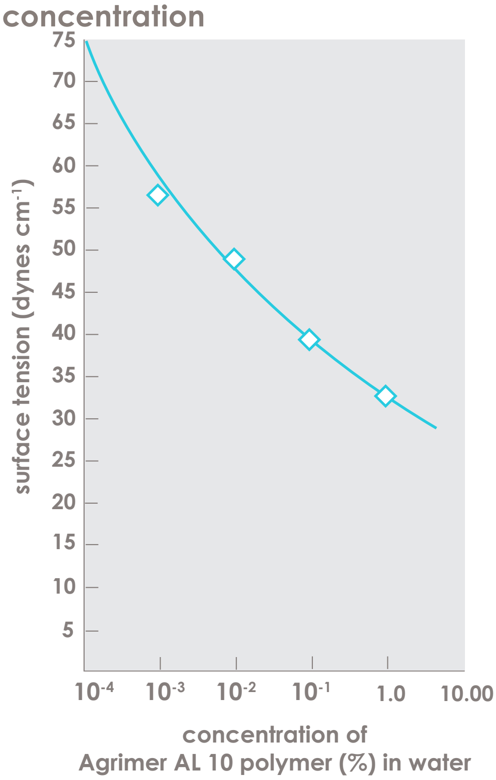


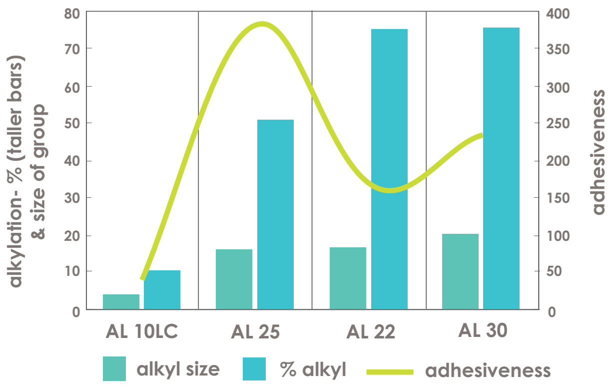
Figure 4 shows the complex correlation between adhesiveness and the degree of alkylation in the Agrimer™ AL polymer family. This data indicates that:

1. adhesiveness is maximized when the polymer contains about 50% of the more hydrophilic pyrrolidone moiety, and
2. a longer alkyl group provides more adhesiveness than a shorter one for a given percentage of alkylation.

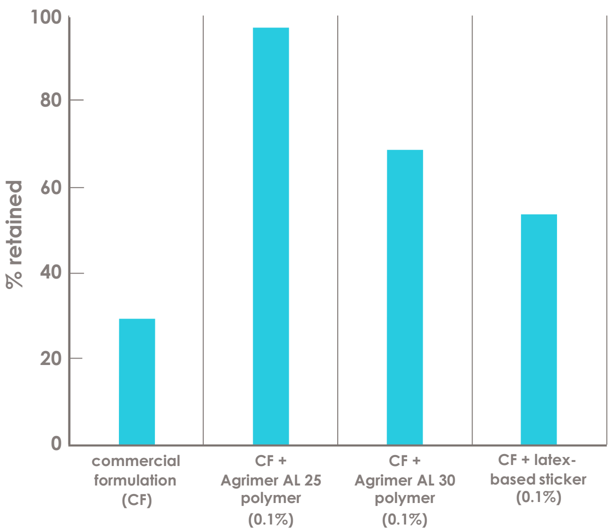
As shown, Agrimer™ AL 25 polymer, having 50% pyrrolidone and an alkyl group of C16, is the best commercially available adhesive in the family.

Adhesiveness is related to rainfastness – a primary consideration in sticker adjuvants. Figure 5 shows that rainfastness (1.0 inches of simulated rain) can be more than doubled by the simple addition of Agrimer™ AL 25 or AL 30 polymers to the commercial formulation of pendimethalin.

### figure 4: the adhesiveness of Agrimer™ AL polymer products as influenced by alkyl chain length & % alkylation




### figure 5: enhanced rainfastness of pendimethalin




## agricultural case studies

### dispersion/solubility enhancement

A co-precipitate of Agrimer™ AL 10LC polymer and a highly hydrophobic insecticide, a fluorinated phenyl urea, was 30 times more dispersible in water than was the insecticide alone. The apparent solubility of the insecticide was also enhanced by about 10 fold.

### flowables using Agrimer™ AL 10LC polymer

Carbaryl and chlorothalonil formulations, both containing the dispersants Pluronic* P104 (3%) and Morwet* D-425 (0-5%), were 41% and 56% flocculated at 4 hours after dilution to spray concentrations. New formulations were developed by adding Agrimer™ AL 10LC polymer at 2.6% and Easy-Sperse™ P-20 dispersant (Ashland) at 0.5% to the commercial formulation. The amount of carbaryl flocculated after 4 hours improved from 41% in the non-Agrimer™ AL-containing formulation to 9% in the improved formulation. Similarly, chlorothalonil improved from 56% flocculated to 14% in the reformulation containing the Agrimer™ polymer.

Agrimer™ AL 10LC polymer is used to prevent agglomeration. A highly hydrophobic active ingredient, in a suitable water miscible solvent, produced a highly agglomerated system upon dilution in the spray tank leading to precipitation and nozzle clogging. When Agrimer™ AL 10LC polymer was added to the solvent-active ingredient solution it prevented agglomeration. The active ingredient formed a highly stable and effective dispersion consisting of very fine particles.

### crystal inhibition

Hydrophobic members of the Agrimer™ AL polymer family have also been shown to prevent crystal formation after dilution as both liquid concentrate and tank mix additives.

An emulsion concentrate of tebufenpyrad was mostly precipitated (crystallized) within 1 hour after dilution in the spray tank. The addition of 2-5% Agrimer™ AL 25 polymer to the concentrate resulted in negligible crystal formation from 8-20 hours, depending upon the amount of dilution.

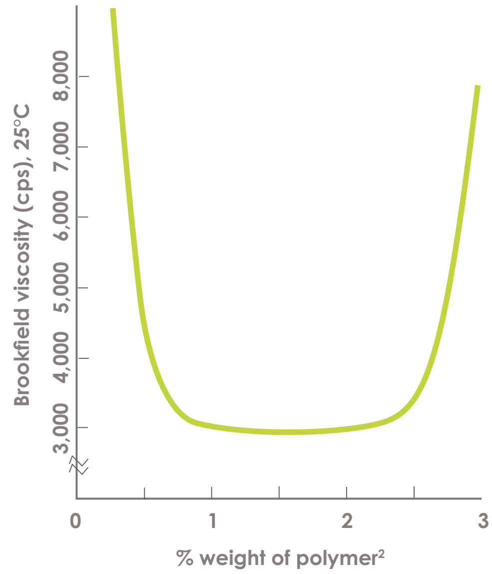
A highly hydrophobic pesticide was formulated as an emulsion concentrate using AgsolEx™ 8 as the primary co-solvent. However, the active ingredient crystallized out of solution within 1 hour after dilution. A premix was developed that contained Agrimer™ AL 22 polymer, an anionic surfactant, and AgsolEx 12 (a solvent/surfactant). The addition of the premix at 0.1% to the spray tank completely prevented crystal formation for 48 hours.

## seed coatings

Seed coatings containing pesticides and fertilizers to maximize seedling emergence and vigor are becoming increasingly important with the development of high value, genetically engineered seeds. Coatings containing Agrimer™ VA or Agrimer™ AL polymer have been shown to offer higher survival of rhizobia bacteria on inoculated legume seeds. Biological pesticides, both organisms and extracted actives like proteins and polypeptides, have also been shown to be stabilized by Agrimer™, Agrimer™ VA or Agrimer™ AL polymer products.

Agrimer™ AL polymers are excellent in seed coatings, possibly as a result of ionic and hydrophobic interactions as well as hydrogen bonding. Furthermore, as shown in Figure 6, Agrimer™ AL 25 polymer is an excellent dispersant that also reduces viscosity. This allows for high loading of hydrophobic dyes and active ingredients into sprayable organic coating systems.

## figure 6: typical critical viscosity/concentration curve for Agrimer™ AL 25 polymer in a commercial pigmented coating formulation[1]




1 7% Silica pigment in a 100% solids coating
2 Based on total formulation

## binders

The polymeric alloy made by using a combination of Agrimer™ VA 6 (PVP-vinyl acetate copolymer) and Agrimer™ AL 10LC polymer was a superior binder in almost all measured parameters as compared to any of the other binders used alone (Table 4).

## table 4: binder effect on yield and suspendability of Atrazine

| binder | granulation moisture % | powder granule conversion % | filter sed. susp. % | cone sed. index |
|---|---|---|---|---|
| Agrimer™ 30 polymer | 8 | 75 | 88 | 8.0 |
| Agrimer™ VA 6 polymer | 10 | 84 | 95 | 8.0 |
| Agrimer™ AL 10LC polymer | 8 | 88 | 85 | 6.7 |
| Agrimer™ AL 10LC + VA6 polymer | 8 | 86 | 86 | 6.0 |
| Lingosulfonate | 15 | 60 | 78 | 13.0 |

## enhancing dissolution

Some excellent binders for granules and tablets may show unacceptably slow disintegration in the spray tank with some active ingredients. A co-precipitate (co-spray or freeze-dried) of Agrimer™ AL 10LC polymer and citric acid (1:1) resulted in a three-fold increase in the copolymer's dissolution rate.

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