

agrimer™ polyvinylpyrrolidone (PVP)

binder, dispersant rheology,
modifier, film former,
complexing agent



ashland.com / efficacy usability allure integrity profitability™

Agrimer™ polyvinylpyrrolidone (PVP)

this brochure is divided into two main segments

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These case studies highlight the uses of Agrimer™ polymers in seed coatings, granule and tablet binders and as dispersants.

general properties and uses

Agrimer™ PVP products are linear, non-ionic polymers that are soluble in water and many organic solvents. They are pH stable, and have adhesive, cohesive and binding properties. The unique ability to adsorb on a host of active ingredients makes Agrimer™ PVP homopolymers preferred co-dispersants in many formulations. Agrimer™ homopolymers have a high glass transition temperature.

Lower molecular weight (Mw) Agrimer™ polymers (Agrimer™ 15 and Agrimer™ 30) are suitable for applications where dusting is a concern, such as seed coatings and agglomeration. Higher Mw Agrimer™ polymers (Agrimer™ 90 and Agrimer™ 120) can build formulation viscosity faster and provide excellent binding and film forming properties. Higher Mw Agrimer™ polymers are also excellent carriers for pheromones and other attractants.

- linear, nonionic polymer
- high polarity/proton acceptor/ π -bonding
- amphiphilic
- physiologically inert

benefits

- compatible with a variety of active ingredients, resins and electrolytes
- enhances surface active properties of select surfactants
- forms hard glossy, transparent, oxygen permeable films
- forms films with water activity
- adhesive and cohesive properties
- crosslinkable

suggested applications

- complexing agent
- stabilizers / co-dispersants
- binders in dry / wet granulation and extrusion (dry compaction / fluidized-bed spray drying process)
- film-forming agents / binders in seed coatings, dips and pour-ons
- biological stabilization
- water binding / anti-transpiration properties
- solubility enhancers via co-precipitation or thermal extrusion
- dye-binding agent

regulatory status

The Agrimer™ PVP products listed in this brochure are exempt from the requirement of a tolerance under 40 CFR 180.960.

physical and chemical properties

The Agrimer™ polymers, a family of homopolymers of polyvinylpyrrolidone, are available in different viscosity grades, ranging from very low to very high molecular weight. This range, coupled with their solubility in aqueous and certain solvent systems and their non-toxic character, leads to their utility in a wide variety of agricultural formulations and applications. They are used, for example, as co-dispersants, as binders, for stabilizing complex organic compounds and biologicals, in film-forming, in veterinary pour-ons, as seed coating materials and as binders in conventional and extruded granules and tablets.

Agrimer™ polymers are supplied in five viscosity grades. Ashland also offers GMP grades of PVP, sold as Plasdone™ products that meet the requirements for povidone in the global pharmacopeia.

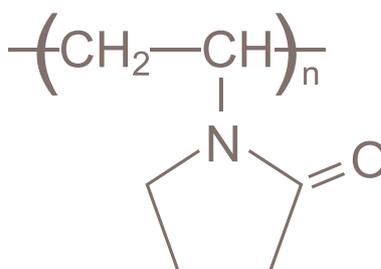


table 1: Agrimer™ PVP homopolymer solutions and powders

| property | Agrimer™ 15 | Agrimer™ 30 | Agrimer™ 60L | Agrimer™ 90 | Agrimer™ 120 |
|--|----------------------------|----------------------------|-------------------------|----------------------------|----------------------------|
| % active | 95 min. | 95 min. | 45 – 49 min. | 95 min. | 93 min. |
| at 25°C | off-white amorphous powder | off-white amorphous powder | yellow aqueous solution | off-white amorphous powder | off-white amorphous powder |
| brookfield viscosity, cps (5% solids @ 25°C) | 1 | 3 | 10 | 150 | 350 |
| bulk density, g/mL | 0.6 – 0.7 | 0.4 – 0.6 | NA | 0.3 – 0.4 | 0.2 – 0.3 |
| color (APHA) | 80 max. ^a | 80 max. ^a | 100 max. ^a | 60 max. ^a | 50 max. ^a |
| K-Value (Viscosity of 1% solution) | 13 – 19 ^a | 28 – 34 ^a | 50 – 60 ^a | 90 – 100 ^a | 108 – 130 ^a |
| % moisture | 5 max. | 5 max. | 51 – 55 | 5 max. | 7 max. |
| Mw range | 6,000 – 15,000 | 40,000 – 80,000 | 240,000 – 450,000 | 1,000,000 – 1,700,000 | 2,100,000 – 3,000,000 |
| pH (5% aqueous solution) | 3 – 7 | 3 – 7 | 3 – 7 | 3 – 7 | 4 – 8 |
| specific gravity @ 25°C | NA | NA | 1.122 | NA | NA |
| Tg (°C) | 130 | 163 | 170 (freeze-dried) | 174 | 174 |
| % nitrogen | 3.5 – 4.5 | 5.8 – 6.8 | 7.0 – 8.0 | 7.5 – 9.4 | 3.9 – 4.9 |
| saponification number (mg KOH/g) – as is | 204 | 151 | 126 | 95 | 201 |
| % solids | 48 – 52 | 48 – 52 | 48 – 52 | 48 – 52 | 48 – 52 |
| specific gravity @ 25°C | 0.0945 – 0.965 | | | | |
| Tg (°C) | 69 | 96 | 106 | 117 | 71 |

(a) 5% aqueous solution. Note: These data are typical of current production, but are not necessarily specifications.

molecular weight determination

There have been many studies on the determination of the molecular weight and Mw distribution of Agrimer™ PVP polymer and polyvinylpyrrolidone in general.

As with any linear polymer, generally, the lower the molecular weight of the polymer the narrower its distribution curve, i.e., higher molecular weight polymers are more polydisperse.

Conventionally, molecular weights are expressed by their “K-values” that are based on kinematic viscosity measurements. The K-values of the Agrimer™ polymers are shown as suffixes, i.e., Agrimer™ 30 polymer has a K-value of 30. The K-values are a function of the average molecular weight, the degree of polymerization and the intrinsic viscosity. The K-value accepted for polyvinylpyrrolidone is measured by a viscosity technique and calculated by the use of Fikentscher's equation.

Other methods include sedimentation, light scattering, osmometry, NMR spectroscopy, ebulliometry, and size exclusion chromatography, which can provide number or weight average molecular weights (Mn or Mw

respectively). Each of these expressions of molecular weight will be a different number for the same polymer. This is illustrated below for an Agrimer™ 30 polymer that was analyzed by the three different methods.

| | |
|------------------------|--------|
| K-value | 30 |
| Number average (Mn) | 10,000 |
| Viscosity average (Mv) | 40,000 |
| Weight average (Mw) | 55,000 |

When specifying and comparing Agrimer™ PVP grades as a starting point in formulation development, the above demonstrates that it is important to know how the molecular weight is expressed in order to choose the right product for a particular application.

viscosity

In aqueous solutions, Agrimer™ 15 and 30 polymers, particularly in concentrations below 10%, have little effect on viscosity, whereas Agrimer™ 60, 90 and 120 polymers considerably influence flow properties (Figure 1). In organic solvents the viscosity of the solution is related to that of the solvent (Table 2).

figure 1: effect of concentration of Agrimer™ polymers on viscosity of aqueous solutions

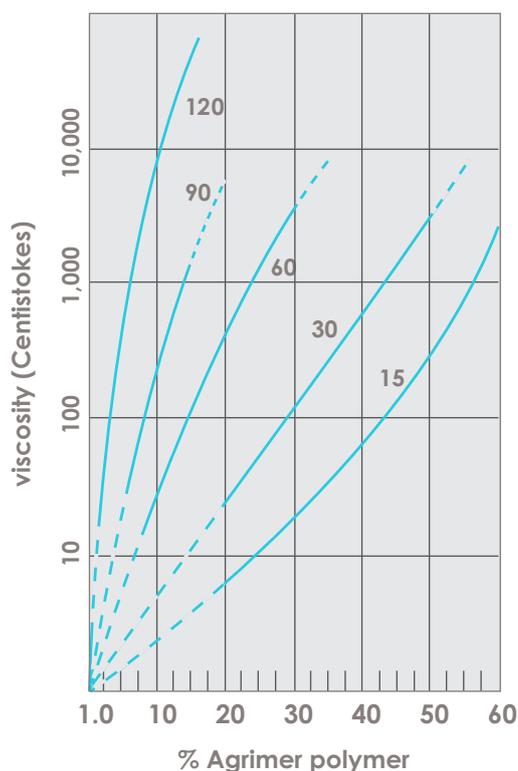


table 2: viscosities of Agrimer™ 30 polymer in various organic solvents

| kinematic viscosities (in centistokes) | | |
|--|-------|-------|
| solvent | 2% | 10% |
| 1,4 Butanediol | 101 | 425 |
| AgsoEx™ BLO | 2 | 8 |
| cyclohexanol | 80 | 376 |
| diethylene Glycol | 39 | 165 |
| ethanol (absolute) | 2 | 6 |
| ethyl lactate | 4 | 18 |
| ethylene glycol | 24 | 95 |
| glycerin | 480 | 2,046 |
| ilsopropanol | 4 | 12 |
| methyl cyclohexanone | 3 | 10 |
| monoethanolamine | 27 | 83 |
| AgsoEx 1 (NMP) | 2 | 8 |
| nonylphenol | 3,300 | - |
| propylene glycol | 66 | 261 |
| triethanolamine | 156 | 666 |
| water | 2 | 5 |

Note: Kinematic viscosity in centistokes
 = $\frac{\text{Absolute viscosity in centistokes}}{\text{Density}}$

Viscosity does not change appreciably over a wide pH range (Table 3). Strong caustic solutions precipitate the polymer, but this precipitate redissolves on dilution with water.

table 3: effect of pH on viscosity of 5% aqueous Agrimer™ 30 polymers at 25°C

| pH | 10 | 9 | 7 | 4 | 2 | 1 | 0.1 |
|----------------|-----|-----|-----|-----|-----|-----|-----|
| viscosity (cp) | 2.4 | 2.4 | 2.4 | 2.4 | 2.3 | 2.3 | 2.4 |

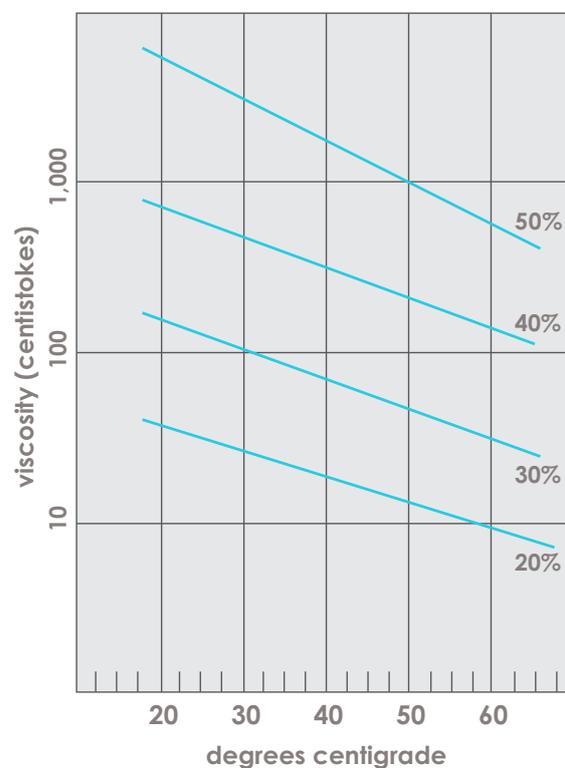
The densities of polymer-water solutions are only slightly changed despite a significant increase in the concentration of Agrimer™ 30 polymers (Table 4).

table 4: effect of Agrimer™ 30 polymers concentration on density in water

| concentration (%) | 10 | 20 | 30 | 40 | 50 |
|------------------------|------|------|------|------|------|
| density at 25°C (g/ml) | 1.02 | 1.04 | 1.07 | 1.09 | 1.12 |

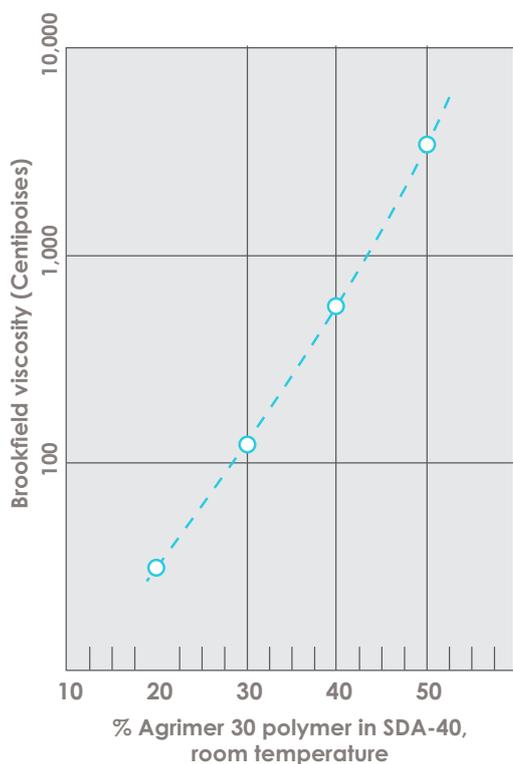
The effect of temperature on viscosity is shown in Figure 2. Any possible effect of high temperatures on finished formulations should be determined experimentally.

figure 2: effect of temperature versus viscosity at various Agrimer™ polymer concentrations



The viscosity of solutions increases with the concentration in the solvent, as illustrated in Figure 3 for Agrimer™ 30 polymers in ethanol solutions.

figure 3: viscosity of typical polymer in ethanol solutions



solubility

The Agrimer™ polymers are readily soluble in cold water with concentration limited only by viscosity. It is possible to prepare free-flowing solutions of Agrimer™ polymers in concentrations up to 60% with only moderate effect on density.

Roughly half a mole of water per monomer unit is associated with the polymer molecule in solution. This is of the same order of magnitude as the water of hydration reported in the literature for various proteins.

Agrimer™ polymers are also freely soluble in many organic solvents, including alcohols, nitroparaffins, and amines. It is essentially insoluble in hydrocarbons, ethers, some chlorinated hydrocarbons, ketones and esters. See Table 5 for solubility in different solvents.

Dilute solutions of Agrimer™ PVP polymer in hydrocarbons may be prepared by the use of a cosolvent, e.g., butanol, AgsolEx™ 1 solvent, or nonylphenol. Clear 3-5% Agrimer™ PVP polymer solutions in aliphatic hydrocarbons may be readily prepared by adding the hydrocarbon to a butyl alcohol solution of the polymer. In some oil-based products the solubilization in an alkylphenol, e.g., octyl- or nonylphenol, is useful. The alkylphenol is first heated to about 100°C and the polymer is added slowly with stirring. The temperature may then be raised to approximately 200°C to accelerate dissolution.

table 5: Agrimer™ 30 polymer solubility

The following representative organic solvents will dissolve 10% or more polymer at room temperature:

| | | | |
|--|--|---|--|
| <p>acids</p> <ul style="list-style-type: none"> acetic acid formic acid propionic acid | <p>amines</p> <ul style="list-style-type: none"> aminoethylethanolamine 2-aminoethanol 2-amino-2-methyl-1-propanol aniline butylamine cyclohexylamine diethanolamine ethylenediamine 2-hydroxyethylmorpholine morpholine pyridine triethanolamine | <p>ester</p> <ul style="list-style-type: none"> ethyl lactate <p>ether alcohols</p> <ul style="list-style-type: none"> diethylene glycol glycol ethers hexamethylene glycol polyethylene glycol 400 (PEG 400) 2,2-thiodiethanol triethylene glycol | <p>lactams</p> <ul style="list-style-type: none"> AgsolEx 1 solvent N-vinyl-2-pyrrolidone 2-pyrrolidone |
| <p>alcohols</p> <ul style="list-style-type: none"> amyl alcohol butanol cyclohexanol ethanol ethylene glycol glycerin methanol N-ethyl-1-hexanol phenol (50°C) propanol isopropanol sec-butanol 1,3-butanediol 1,4-butanediol | <p>chlorinated hydrocarbons</p> <ul style="list-style-type: none"> chloroform ethylene dichloride methylene dichloride | <p>ketone</p> <ul style="list-style-type: none"> methyl cyclohexanone <p>ketone Alcohol</p> <ul style="list-style-type: none"> diacetone alcohol | <p>lactone</p> <ul style="list-style-type: none"> AgsolEx BLO <p>nitroparaffins</p> <ul style="list-style-type: none"> nitroethane nitromethane |

Agrimer™ 30 polymer is essentially insoluble in the following solvents under the same conditions of testing:

| chlorinated hydrocarbons | ethers | hydrocarbons | | ketones |
|---|--|---|---|--|
| <ul style="list-style-type: none"> ○ carbon tetrachloride ○ chlorobenzene | <ul style="list-style-type: none"> ○ dioxane ○ ethyl ether ○ ethyl vinyl ether ○ isobutyl vinyl ether ○ methyl ether ○ tetrahydrofuran | <ul style="list-style-type: none"> ○ benzene ○ cyclohexane ○ heptane ○ hexane ○ kerosene ○ methylcyclohexane ○ mineral oil | <ul style="list-style-type: none"> ○ mineral spirits ○ petroleum ether ○ stoddard solvent ○ toluene ○ turpentine ○ xylene | <ul style="list-style-type: none"> ○ acetone ○ 2-butanone ○ cyclohexanone |
| esters | | | | |
| <ul style="list-style-type: none"> ○ ethyl acetate ○ sec-butyl acetate | | | | |

Compatible plasticizers may be added to modify Agrimer™ homopolymer films, and moisture taken up from the air can also act as a plasticizer. The following commercial modifiers may be used to control film tack, brittleness or water management properties.

- Agrimax™ C-500 series
- cellulose acetate
- cellulose acetate propionate
- dibutyl tartrate
- diethylene glycol
- dimethyl phthalate
- 2-ethylhexanediol-1,3
- glycerin
- glycerylmonoricinoleate
- Igepal® CO-430 (Solvay)
- oleyl alcohol

Agrimax C series, cellulose acetate, cellulose propionate, and shellac effectively decrease the tackiness of the films. Dimethyl phthalate is less effective, whereas glycerin, diethylene glycol, and sorbitol increase tackiness. Films essentially tack-free over all ranges of relative humidity may be obtained with 10% ethyl-sulfonamide-formaldehyde resin.

In comparative tests for plasticity (33% relative humidity), Agrimer™ 30 polymer films containing 10% diethylene glycol show an “elongation at break” twice that of homopolymer films containing 10% glycerin, polyethylene glycol 400, sorbitol, or urea, and four times that of Agrimer™ 30 polymeric films containing 10% ethylene glycol or dimethyl phthalate. At 50% relative humidity, 25% glycerin, and 25% diethylene glycol are effective plasticizers. At 70% relative humidity, 25% sorbitol and 25% dimethyl phthalate may be used successfully.

compatibility

The Agrimer™ polymers are compatible with most inorganic salt solutions and with many natural and synthetic resins, as well as with other chemicals (Tables 6

and 7).

table 6: inorganic salt compatibility

| | |
|--------------------|---|
| Ammonium chloride | NH ₄ Cl |
| Ammonium sulphate | (NH ₄) ₂ SO ₄ |
| Calcium chloride | CaCl ₂ |
| Copper sulphate | CuSO ₄ ·5H ₂ O |
| Ferric chloride | FeCl ₃ ·6H ₂ O |
| Magnesium chloride | MgCl ₂ ·6H ₂ O |
| Potassium chloride | KCl |
| Potassium sulphate | K ₂ SO ₄ |
| Zinc sulphate | ZnSO ₄ ·7H ₂ O |

At 25°C the addition of 100 ml of a 10% solution of the above fertilizer salts to 10% Agrimer™ 30 polymer aqueous solution (i.e., 10 parts of the fertilizer to 1 part of Agrimer™ 30 polymers) did not change the appearance of the solution.

protective-colloid action

Small amounts of Agrimer™ polymers effectively stabilize emulsions, dispersions, and suspensions. Even hydrophobic colloids, which exist without significant affinity for the medium, can be protected by Agrimer™ polymers. One explanation would be that the polymer is adsorbed in a thin molecular layer on the surface of the individual colloidal particles resulting in a steric hindrance that prevents coalescence.

The best viscosity grade to use depends on the application. Most suspension concentrate formulations employ the lower molecular weight Agrimer™ 15 or Agrimer™ 30 polymers to enhance the stability of the formulation. Agrimer™ 15 polymer is particularly effective as a co-dispersant for a large number of hydrophobic active ingredients in aqueous media. If, however, the stabilizing effect relies on both the steric hindrance mechanism and stabilization due to increased viscosity, the higher molecular weight products like Agrimer™ 90 or Agrimer™ 120 polymer may be more suitable.

table 7: compatibility of Agrimer™ 30 polymers with various resins, gums and surfactants for forming film

| Class | Compound tested | Solvent | % | Solution or melt appearance | Film compatibility |
|------------------------------|--|-------------------------------------|----|-----------------------------|-------------------------|
| esters | beeswax | chloroform | 5 | S clear, colorless | H |
| | cellulose acetate | 1:4 ethanol/ ethylene dichloride | 4 | S clear, light yellow | C |
| | cellulose acetate propionate | chloroform | 4 | S clear, colorless | C |
| | diethylene glycol stearate | propargyl alcohol | 3 | S clear, yellow | IN |
| ether alcohols | polyethylene alcohol Ucon Oil* SD-HB 5100 (polyethylene glycol, Union Carbide) | ethanol | 5 | S clear, colorless | C |
| | ucon oil* 75-HB 90,000 (Union Carbide) | ethanol | 5 | S clear, colorless | H |
| glycerides | castor oil | ethanol | 5 | S clear, colorless | IN |
| | olive oil | chloroform | 5 | S clear, light yellow | IN |
| | lanolin | chloroform | 6 | S clear, light yellow | H |
| | lecithin | water | 1 | I opaque, homogeneous | IN (1:3) H (1:1,1:3) |
| gums | Acacia | water | 5 | PS cloudy | H |
| | karaya | water | 4 | I two-phase | H |
| | sodium alginate | water | | S | C |
| | tragacanth | water | 4 | PS white, homogeneous | H |
| misc. resins | ethylcellulose | ethanol | 4 | PS cloudy, homogeneous | C |
| | Agrimax™ C-500 series (low viscosity grade) | | 1 | S clear, colorless | C |
| | corn dextrina | water | | S | C |
| | Agrimax C-300 series | water | | S | C |
| | shellac | ethanol | 5 | S clear, yellow | C |
| phenols | 2,2 thiobis-(4-6-dichlorophenol) | ethanol | 6 | S clear, colorless | |
| | hexachlorophene [2,2'-methylene-bis (3,4,6 -trichlorophenol)] | ethanol | 6 | S clear, colorless | |
| quarterly ammonium compounds | BTC* (alkyldimethylbenzyl ammonium chloride, Stepan) | water | 10 | S clear, colorless | |
| | cetylpyridinium chloride | water | 10 | S clear, colorless | |
| | Hyamine* 2389 (Dow) | water | 2 | S clear, colorless | |
| | Isothar* (Lauryl isoquinolinium bromide, Stepan) | water | 10 | S clear, colorless | |
| | Tetrosar* (Stepan) | water | 10 | S clear, colorless | |
| surfactants | Alipal* CO-436 (ammonium salt of sulfated nonylphenoxypoly (ethylenoxy) ethanol, (Solvay)) | water | 3 | S clear, colorless | C |
| | DuPont* (sodium lauryl sulphate, DuPont) | water | 5 | S clear, colorless | |
| | Nekal* BX-78 (sodium alkyl naphthalene sulphate, Solvay) | water | 3 | S hazy, light yellow | IN |
| synthetic | polyvinyl alcohol | | | S | C |
| | Polystyrene | chloroform | | S clear, colorless | IN |
| | | chloroform | 4 | I two liquid phases | IN |
| | | hot melt | | S | C |
| | Saran* B-1155 (vinylidene chloride polymer, Dow) | AgosolEx™ 1 solvent | 3 | S yellow | IN |

* Ratio of Agrimer™ polymers to compound 1:19

Abbreviations:

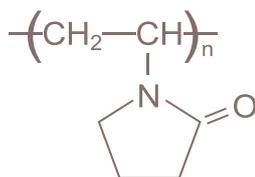
S = Soluble PS = Partially Soluble I = Insoluble IN = Incompatible

H = Homogeneous C = Compatible

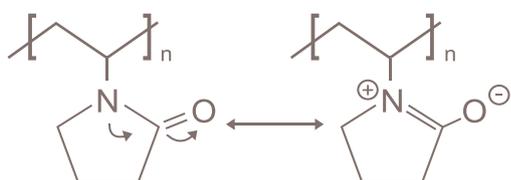
Compatibilities (Table 7) were determined by separately dissolving Agrimer™ 30 polymer and the test material in mutual solvents. The clarity of the solution was noted. The admixture was then cast upon a glass plate and the resulting film examined after evaporation of the solvent.

complex formation and crosslinking

Agrimer™ PVP polymers contain a pendent lactam ring which is part of the monomeric repeat unit structure, shown below.



Methylene groups in the ring and a linear aliphatic backbone contribute to the hydrophobic nature of the polymer. The dipole moment of the ring is close to that of AgsolEx™ solvent (NMP)(4.07D).¹ The high polarity of the ring can be attributed to strong resonance stabilization, shown below, facilitated by a near planar ring geometry. Electron delocalization stabilizes overlap of π orbitals.



Because of their unique structure of hydrophobic and hydrophilic segments, Agrimer™ PVP polymers can form complexes with a variety of compounds. The pyrrolidone binding mechanisms can include one or more of the following types of interactions: hydrogen bonding; polar or hydrophobic attractive forces, and stabilization from π -bond overlap. In addition, the ability of the polymer to form tertiary complexes with compounds can increase the potential for complexation. Hydrogen bonding is one force by which they form complexes with polymethacrylic acid and tannin.² This could help delivery of similar complex materials in an aqueous medium.

Agrimer™ polymers can also form complexes with phenols, such as resorcinol and pyrogallol, as a result of hydrophobic bonding and an exothermic interaction between the lactam ring and the electron system of the aromatic molecule.³ Further, they form non-covalent complexes with many hydrophobic active ingredients leading to increased water solubility. Ashland has shown that the coprecipitation of Agrimer™ 30 polymer with such active ingredients as a fluorosubstituted aniline herbicide, a substituted pyridine carboxylate herbicide, and a highly hydrophobic chloro-fluoroalkyl substituted biphenyl urea type insecticide, resulted in more than a 100 fold increase in the water solubility/dispersibility of these active ingredients.

Agrimer™ homopolymers crosslink with polyacids like polyacrylic or tannic acid to form complexes that are insoluble in water or alcohol but dissolve in dilute alkali. Agrimer™ VEMA H polymer series (Ashland's methyl vinyl ether/maleic acid copolymer), will also precipitate the polymers when aqueous solutions of the two polymers are mixed in approximately equal parts at low pH; this complex can be solubilized by increasing the pH.

Ammonium persulfate and alkaline sodium phosphates will gel Agrimer™ 30 polymer in 30 minutes at 90°C. These gels are practically insoluble in water or salt solutions. When dried under mild conditions, the Agrimer™ polymer gels retain their uniform structure and capacity to swell again by absorption of large amounts of water. Also, heating in air to 150°C will crosslink the Agrimer™ polymers, and strong alkali at 100°C will permanently insolubilize the polymer.

stability

Agrimer™ PVP polymer powders can be stored under ordinary conditions without undergoing decomposition or degradation. However, since the powder is hygroscopic, suitable precautions should be taken to prevent excessive moisture pickup. The equilibrium water content of Agrimer™ PVP polymer solids or films varies in a linear fashion with relative humidity and is equal to approximately one-third the relative humidity. Samples of dried, powdered Agrimer™ 30 polymer, subjected to 20%, 52%, and 80% relative humidity until equilibrium is reached, showed a 10%, 19%, and 31% moisture weight gain, respectively.

Exposure to extreme elevated temperatures should be avoided, though Agrimer™ PVP polymer powder is quite stable to heat. Some darkening in color and decreased water solubility are evident on heating in air at 150°C. However, the polymers are quite stable when heated repeatedly at 110-130°C for relatively short intervals, and can be safely extruded as a hot melt with many active ingredients.

Aqueous Agrimer™ PVP polymer solutions are stable for extended periods if protected from mold. However, appropriate tests should be made on the finished products before deciding on a preservative. The polymer has no buffering power, and large changes in the pH of solutions are observed upon addition of small amounts of acids or bases. For example, the pH of 100 ml of 3.5% Agrimer™ 30 polymer solution is raised from pH 4 to pH 7 by the addition of 1-2 ml 0.1 N sodium hydroxide.

agricultural case studies

granule and tablet binders

One of the largest uses of the Agrimer™ PVP polymers is as binders in solid formulations such as granules, WP, WDG, WSG and tablets, especially those employing wet granulation methods like pan, extrusion, fluid bed and spray drying processes. Agrimer™ 30 polymer is used most often, although lesser amounts of Agrimer™ 90 polymer have been used with a careful selection of the appropriate dispersants. The keys to a successful product are low granulation moisture (reducing drying costs), low friability (reducing dustiness), a hard product that is resistant to breakage while still being readily dispersed, and a high powder to granule conversion rate (yield). The Agrimer™ PVP polymers have shown consistent performance advantages in these key parameters.

Prototype atrazine granules were prepared by pan granulation to give a final composition of 92.3% atrazine, 0.2% defoamer, 1.5% wetting agent, 3% dispersant, and 3% binder. A comparison of Agrimer™ 30 polymer and lignosulfonate is shown in Table 8.

Table 8: Comparative binding properties of Agrimer™ 30 polymer and lingosulfonate

| Binder | Suspensibility | Granulation moisture % | Foam index | Granule to powder conversion % |
|---------------------|----------------|------------------------|------------|--------------------------------|
| Agrimer™ 30 polymer | 88 | 8 | 44 | 75 |
| Lignosulfonate | 78 | 15 | 57 | 60 |

When Agrimer™ 30 polymer is used as a binder, it takes less moisture to prepare a WDG which gives a higher yield to granule formation, greater suspensibility and hardness, and lower foaming. A pyrimidine-based substituted phenylsulfonamide (a systemic herbicide) has also been successfully granulated, but in this case Agrimer™ 15 polymer was the preferred binder. Lignosulfonate and Agrimer™ 30 polymer have been shown to work synergistically in these types of formulations and this is commercially practiced using the pan granulation process.

dispersants

A substituted thiazolyl pyridine carboxylate rice herbicide was granulated with Agrimer™ 30 polymer as the preferred binder. The active was co-precipitated with 50% Agrimer™ 30 polymer from ethanol followed by drying. The granule, without additional surfactant, produced stable dispersions on dilution in water. The biological activity of the granule was equal to or better than the corresponding EC formulation. Agrimer™ 30 polymer is also used in aqueous flowables of chlorothalonil to increase its long term stability (anti-flocculant) and to improve the dispersion of the active after dilution in the spray tank. Agrimer™ PVP polymers enhance the suspensibility when used with standard polymeric dispersants.⁴

binder/disintegrant system

Abisulfate salt of a substituted imidazolidone derivative, a selective post-emergent herbicide, has been successfully formulated as a water soluble granule using Agrimer™ ATF polymer as a disintegrant and Agrimer™ 30 and 90 polymers as binders. Agrimer™ ATF polymer has also been used as a disintegrant for a selective post-emergent herbicide, thifensulfuron methyl, in a readily dispersible tablet formulation.

seed coatings

Agrimer™ 30 polymer has been used to coat sugar beet seeds, giving up to 10% improvement in germination and emergence as compared to the uncoated seeds. The 10% Agrimer™ 30 polymer solutions were applied to the seeds at a volume of 0.1 to 1 liter of solution per 100 kg of seeds. In another example, legume seeds were coated with a rhizobia-Agrimer™ 30 polymer slurry. The survival rate of the rhizobia in the slurry was several orders of magnitude greater than the seeds treated with the rhizobia alone.

Biological stabilization

The use of Agrimer™ 30 polymer to increase the yield of fermented yeast has been reported. The Agrimer™ polymer has been shown to detoxify the fermentation media, perhaps by complexing with the phenolic-type, self-limiting toxins in the media.

dips and pour-ons

A topical formulation for direct application to the skin has been described using up to 20% Agrimer™ 30 polymer and avermectin in an aqueous/ethanol medium for effective treatment of ecto- and endo-parasitic infestations.⁵

process examples co-precipitation

Agrimer™ 30 polymer can be co-precipitated with active ingredients to improve their solubility or dispersability. Both the polymer and active are dissolved in a common solvent. As the solvent is removed, the polymer and active form an amorphous glassy matrix that is less toxic to humans, frequently with enhanced pesticidal activity.

- Seven parts Agrimer™ 30 polymer and 3 parts fenbutatin oxide are dissolved in methylene chloride. The solvent is evaporated to yield a solid which can be easily ground to a consistent powder size.
- A 30-fold increase in the dispersion of prodiamine can be accomplished when a solid is made from a co-precipitate of the active with Agrimer™ 30 polymer.
- Cypermethrin was made into a high melting solid using Agrimer™ 30 polymer. Nine parts polymer and one part active are made into a co-precipitate using ethanol. The resulting solid softens at 121°C (Tg). The dissolution rate of the co-precipitate can be further improved by the incorporation of citric acid (48% Agrimer™ 30 polymer, 42% citric acid and 10% cypermethrin). The addition of the citric acid and the polymeric binder prior to the granulation process increases granule hardness while maintaining excellent dissolution.

co-melting and extrusion

Co-melting of low melting actives and certain polymers is a tool for making water dispersible granules of hydrophobic actives that may be liquids at room temperature. The active ingredient, the Agrimer™ polymer and an additional plasticizer (to reduce the glass transition temperature of the mixture for easier extrusion), are co-extruded with the correct dispersants.⁶

- Granules made by hot melt extrusion of alpha cypermethrin at 33.3% contained Agrimer™ 30 polymer (66.2%) as the binder together with toluene sulfonic acid at 0.5%. The resulting granules have excellent physical properties and biological performance. The biological performance enhancement was shown to be related to the fact that the cypermethrin granules formed very efficacious pseudo-microemulsions upon dilution.

fluidized bed drying

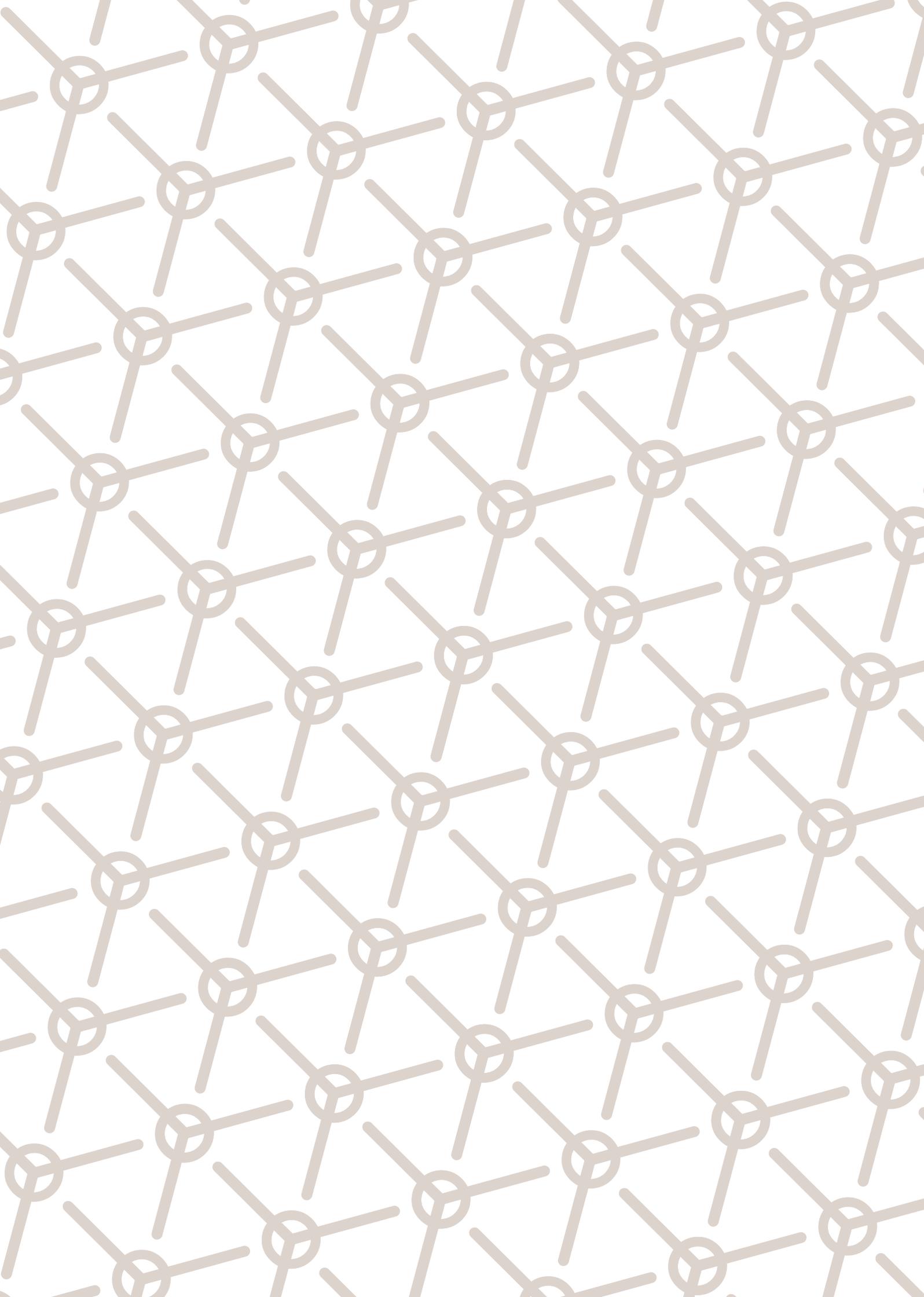
Agrimer™ 30 polymer has been used to enhance the granule strength of a solid suspoemulsion that employs the use of both spray drying and fluid bed granulation. First, a stable emulsion of both isoproturon and fluoroglycofen was developed. The isoproturon emulsion was then spray-dried resulting in a granule nucleus containing one of the ingredients. The fluoroglycofen was then layered upon the solid granule using fluid bed granulation.

spray drying

Agrimer™ 30 polymer is co-processed with trifluraline to produce an active ingredient embedded in a polymer matrix/coating. An aqueous solution of 10% Agrimer™ 30 polymer and 0.5% sodium dodecyl benzene sulfonate, is slurried with melted trifluralin and subsequently spray-dried.

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