

PVP Polyvinylpyrrolidone Polymers  
Intermediates, solvents, monomers, polymers and  
specialty chemicals

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## PVP

### (Polyvinylpyrrolidone)

- Film-former
- Protective Colloid and Suspending Agent
- Dye-Receptive Resin
- Binder and Stabilizer
- Adhesive
- Complexing Agent
- Physiologically Inert

### Commercial Types of PVP

PVP polymers are available in several viscosity grades, ranging from low to high molecular weight. This range, coupled with solubility in aqueous and organic solvent systems combined with its non-toxic character, gives PVP great flexibility. Its industrial applications include, for example, in adhesives to improve strength and toughness; in paper manufacture to increase strength and as a coating resin; and in synthetic fibers to improve dye receptivity. It is also widely employed in inks, imaging, lithography, detergents and soaps, the textile, ceramic, electrical, metallurgical industries and as a polymerization additive. PVP polymer is supplied in five viscosity grades as a powder and/or aqueous solution. Ashland also offers pharmaceutical grades of PVP; our Plasdone™ polymer and Polyplasdone™ polymer products are used in the pharmaceutical industry, and our Polyclar™ stabilizers are used in the beverage industry. Information on these polymers is available in separate brochures. Tables I and II illustrate the PVP polymers commercially available and some typical properties.

### Table I: General PVP Properties

Linear nonionic polymer

- High polarity/proton acceptor
- Amphiphilic
- Compatible with a variety of resins and electrolytes
- Soluble in water and polar solvents, insoluble in esters, ethers, ketones and hydrocarbons
- Unsuitable for thermoplastic processing
- Hard, glossy, transparent, oxygen permeable films which adhere to a variety of substrates
- Hygroscopic
- Adhesive and cohesive properties
- Cross-linkable
- Physiologically inert



**Table II: PVP Solution and Powder Products**

Property	PVP K-15		PVP K-30		PVP K-60	PVP K-90		PVP K-120	
Appearance @ 25°C	Pale yellow aqueous solution	Off-white, amorphous powder	Colorless to pale yellow aqueous solution	Off-white, amorphous powder	Yellow aqueous solution	Yellow, viscous, aqueous solution	Off-white, amorphous powder	Colorless to yellow aqueous solution	Off-white, amorphous powder
K-Value (Viscosity of 1% solution)	13-19 <sup>a</sup>	13-19 <sup>a</sup>	27-33	26-35	50-62	80-100	90-100	110-130	108-130
Color (APHA)	4 max. (VCS)	100 max. <sup>a</sup>	150 max.	80 max. <sup>a</sup>	100 max. <sup>a</sup>	40 max.	60 max. <sup>a</sup>	25 max. <sup>a</sup>	50 max. <sup>a</sup>
% Residual VP	0.1 max.	0.1 max.	.001 max.	<0.1	<0.1	<0.1	<0.1	<0.1	0.1 max.
% Active	28-32	95 min.	29-31	95 min.	45-49	20-24	95 min.	11-13	95 min.
% Moisture	68-72	5 max.	69-71	5 max.	51-55	76-80	5 max.	87-89	5 max.
% Ash (combustion)	0.012	5 max.	0.012	0.02 max.	0.044	0.016	-	0.018	-
pH (5% aqueous solution)	6-9	3-7	6-9	3-7	3-7	4-9	3-7	6-9	4-8
MW Range (measured by LALLS)	6,000-15,000		40,000-80,000		240,000-450,000	900,000-1,500,000		2,000,000-3,000,000	
Brookfield Viscosity, cps (5% solids @ 25°C)	-	1	-	3	10	-	150	-	350
Specific Gravity @ 25°C	1.061	-	1.062	-	1.122	1.051	-	1.024	-
Bulk Density (g/cc)	-	0.6-0.7	-	0.4-0.6	-	-	0.3-0.4	-	0.2-0.3
Film Density (g/cc)	1.203	-	1.207	-	-	1.216	-	-	-
Freezing Point °C	-4.1	-	-2.7	-	-2.2	-0.9	-	0.3	-
Specific Heat (cal/g/KC)	0.819	-	0.803	-	0.738	0.827	-	0.884	-
Tg (°C)	-	130	-	163	170 freeze-dried	-	174	-	176

<sup>a</sup> 5% aqueous solution

NOTE: These data are typical of current production but are not necessarily specifications.

## Physical and Chemical Properties

### Molecular Weight Determination

Polyvinylpyrrolidone can be prepared to yield products with a variety of molecular weights dependent upon the methods used to synthesize the polymer. The product so obtained has a molecular weight range from 2,500 to 2,900,000. Since the polymer consists of a series of different chain length polymers, the molecular weight is expressed as an average of the various molecular weights of the different chain length units that comprise the polymer.

There have been many studies that have been devoted to the determination of the molecular weight of PVP. The low molecular weight polymers have narrower distribution curves of molecular entities than the higher molecular weight compounds. Some of the techniques for measuring the molecular weight of various PVP products are based on measuring sedimentation, light scattering, osmometry, NMR spectroscopy, ebulliometry, and size exclusion chromatography for determining absolute molecular weight distribution. By the use of these methods, any one of three molecular weight parameters can be measured, namely the number average (Mn), viscosity average (Mv), and weight average (Mw). Each of these characteristics can yield a different answer for the same polymer as illustrated by using these measurement techniques in the analysis of the same PVP K-30 sample.

The following results were reported:

Number average (Mn) - 10,000

Viscosity average (Mv) - 40,000

Weight average (Mw) - 55,000

Therefore, in any review of the literature, one must know which molecular average is cited. Conventionally, molecular weights are expressed by their K-values, which are based on kinematic viscosity measurements.

### Viscosity

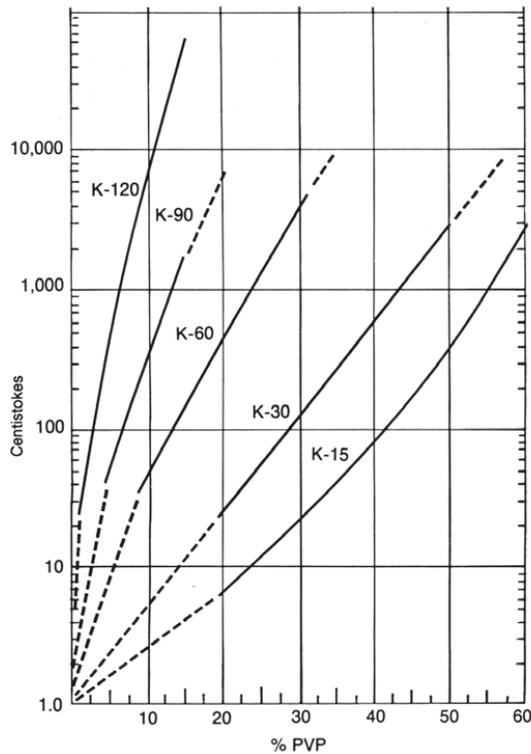
The K-values assigned to the various grades of PVP represent a function of the average molecular weight, the degree of polymerization and the intrinsic viscosity. The K-values are derived from the viscosity measurements and are calculated according to

$$\log \frac{\eta_{rel}}{c} = \frac{75K_0^2}{1 + 1.5K_0^2} + K_0$$

where c = concentration in g/100 ml solution  
 $\eta_{rel}$  = viscosity of the solution compared with solvent  
 K = 1000K<sub>0</sub>

The K-value accepted for PVP by pharmacopeias and other authoritative bodies worldwide is measured by the viscosity technique and calculated by the use of Fikenscher's equation. In aqueous solutions PVP K-15 and K-30, particularly in concentrations below 10%, have little effect on viscosity, whereas K-60 and K-90 considerably influence flow properties (Figure 1). In organic solvents the viscosity of the solution is related, of course, to that of the solvent, Table III.

**Figure 1: Effect of Concentration of Different Grades of PVP on Viscosity of Aqueous Solution at 25°C**



**Table III: Viscosities of PVP K-30 in Various Organic Solvents**

Kinematics Viscosities (in centistokes)		
Solvent	2% PVP	10% PVP
Acetic Acid (glacial)	2	12
1,4-Butanediol	101	425
Butyrolactone	2	8
Cyclohexanol	80	376
Diacetone Alcohol	5	22
Diethylene Glycol	39	165
Ethanol (absolute)	2	6
Ethyl Lactate	4	18
Ethylene Glycol	24	95
Ethylene Glycol Monoethyl Ether	3	12

Kinematics Viscosities (in centistokes)		
Solvent	2% PVP	10% PVP
Glycerin	480	2,046
Isopropanol	4	12
Methyl Cyclohexanone	3	10
N-Methyl-2-Pyrrolidone	2	8
Methylenechloride	1	3
Monoethanolamine	27	83
Nitroethane	1	3
Nonylphenol	3,300	-
Propylene Glycol	66	261
Triethanolamine	156	666

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

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

**Table IV: Effect of pH on Viscosity of 5% Aqueous PVP K-30 at 25°C**

pH	10	9	7	4	2	1	0.1	Conc. HCl
Viscosity (cp)	2.4	2.4	2.4	2.4	2.3	2.3	2.4	4.96

The densities of PVP water solutions are only slightly changed despite a significant increase in the concentration of PVP K-30, Table V.

**Table V: Effect of PVP K-30 Concentration on Density in Water**

PVP 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 on Viscosity**

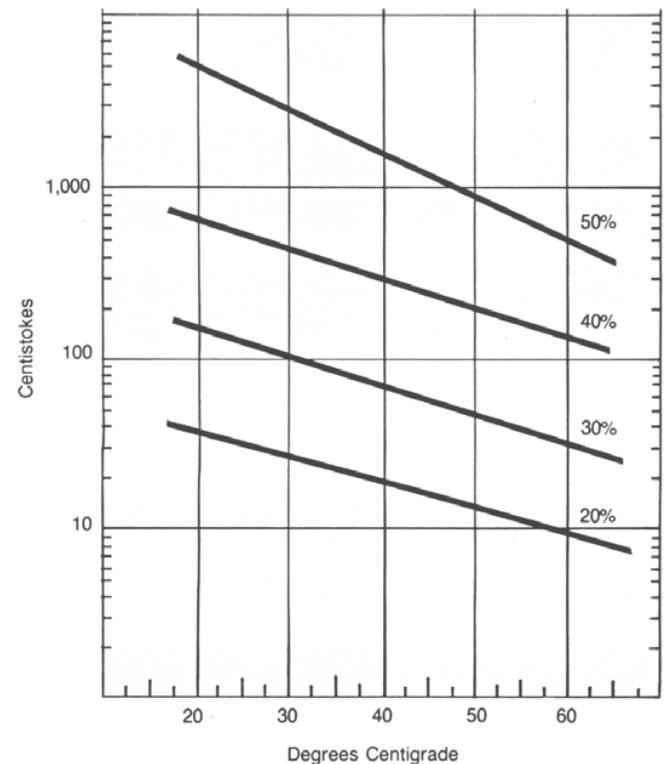
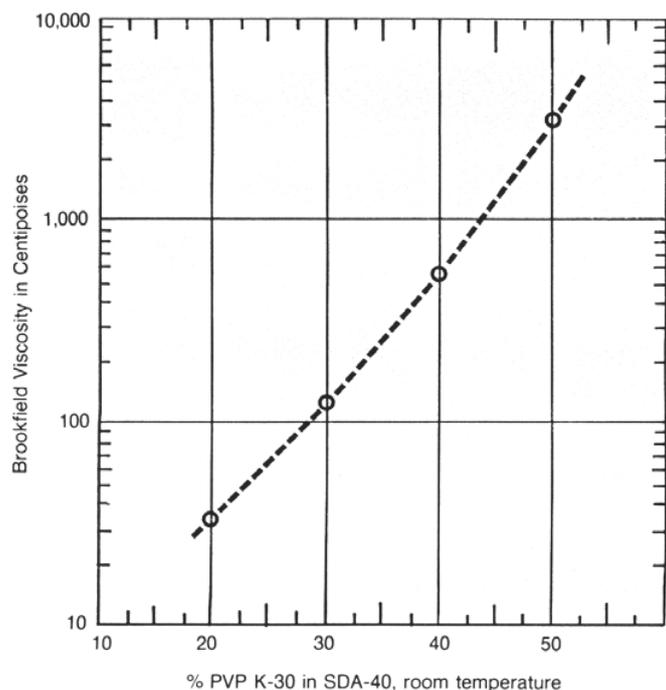


Figure 3: Viscosity of Typical PVP K-30 Ethanol Solutions



## Solubility

PVP is readily soluble in cold water and the concentration is limited only by viscosity. It is possible to prepare free-flowing solutions of PVP K-30 in concentrations up to 60% with only moderate effect on density. PVP K-60 and K-90 are available commercially as 45 and 20 percent aqueous solutions, respectively.

Roughly 0.5 mole water per monomer unit is associated with the polymer molecule in solution. This is of the same order of magnitude as the hydration reported in the literature for various proteins.

PVP K-30 is also freely soluble in many organic solvents including alcohols, some chlorinated solvents such as chloroform, methylene chloride and ethylene dichloride, nitroparaffins and amines. It is essentially insoluble in hydrocarbons, ethers, some chlorinated hydrocarbons, ketones and esters. Anhydrous PVP is soluble in  $-CHX_2$  type propellants and in several other chlorofluoralkanes if alcohol is used as a cosolvent (Table VI). Dessicated material, containing less than 0.5% water, dissolves in ketones and dioxane to give 10-50% solutions.

Dilute solutions of PVP in hydrocarbons can be prepared by the use of cosolvent, e.g., butanol, N-methyl-2-pyrrolidone, or nonylphenol. Clear 3-5% PVP solutions in aliphatic hydrocarbons may be readily prepared by adding the hydrocarbon to a butyl alcohol solution of the polymer. In oil-based products, solubilization in an alkylphenol, e.g., octyl- or nonylphenol, is useful. The alkylphenol is first heated to about 100°C and the PVP added slowly with stirring. Then the temperature may be raised to approximately 200°C to accelerate solution.

Table VI: PVP K-30 Solubility

The following representative organic solvents will dissolve 10% or more PVP at room temperature:			
<b>Alcohols</b> methanol ethanol propanol isopropanol butanol sec-butanol amyl alcohol 2-ethyl-1-hexanol cyclohexanol phenol (50°C) ethylene glycol 1,3 - butanediol 1,4 - butanediol glycerin	<b>Acids</b> formic acid acetic acid propionic acid	<b>Ketone</b> methylcyclohexanone	<b>Amines</b> butylamine cyclohexamine analine ethylenediamine pyridine morpholine 2-aminoaniline diethanolamine triethanolamine aminoethylethanolamine 2-hydroxyethylmorpholine 2-amino-2-methyl-1-propanol
<b>Ketone-Alcohol</b> diacetone alcohol	<b>Ether-Alcohols</b> glycol ethers diethylene glycol triethylene glycol hexamethylene glycol polyethylene glycol 400 2,2' - thiodiethanol	<b>Chlorinated Hydrocarbons</b> methylene chloride chloroform, ethylene dichloride	<b>Lactams</b> 2-pyrrolidone N-methyl-2-pyrrolidone N-vinyl-2-pyrrolidone
	<b>Lactone</b> γ-butyrolactone		<b>Nitroparaffins</b> nitromethane nitroethane
	<b>Ester</b> ethyl lactate		

PVP is essentially insoluble in the following solvents under the same conditions of testing:			
<b>Hydrocarbons</b> benzene toluene* xylene Tetralin** petroleum ether hexane heptane* stoddard solvent* kerosene	mineral spirits mineral oil cyclohexane methylcyclohexane turpentine	methyl ether ethyl vinyl ether isobutyl vinyl ether tetrahydrofuran	<b>Ketones</b> 1-butanone acetone cyclohexone
	<b>Ethers</b> dioxane ethylether	<b>Chlorinated Hydrocarbons</b> carbon tetrachloride chlorobenzene	<b>Esters</b> ethyl acetate sec-butyl acetate

Anhydrous PVP is directly soluble in propellants containing a  $-CHX_2$  group. It will dissolve in several other chlorofluoralkanes used in pressurized products if alcohol is used as a cosolvent.

Directly soluble in		Soluble with cosolvent (20-30% ethanol) in	
Freon 21***	dichloromonofluoromethane	Freon 11 Genetron 11	trichlorofluoromethane
Freon 22 Genetron 14****	chlorodifluoromethane	Freon 12 Genetron 12 Freon 113 Genetron 226 Freon 114 Genetron 320 Freon 142	dichlorodifluoromethane  1,1,2-trichloro-1,2,2-trifluoroethane 1,2-dichloro-1,1,2,2-tetrafluoroethane 1-chloro-1,1-difluoroethane

\*PVP is soluble in these hydrocarbons in about 5% concentration when added to the solvent as a 25% butanol solution

\*\*Tetralin is a registered trademark of DuPont

\*\*\*Freon is a registered trademark of DuPont

\*\*\*\*Getron is a registered trademark of Allied-Signal



## Film-forming Properties

Dried unmodified films of PVP are clear, transparent, glossy and hard. Appearance does not vary when films are cast from different solvent systems, such as water, ethanol, chloroform or ethylene dichloride.

Compatible plasticizers may be added without affecting clarity or luster of the film. Moisture up take from the air by PVP can also act as a plasticizer. Among the several commercial modifiers that can be used in concentrations of 10-50% (based on PVP) to control tack and/or brittleness or to decrease hygroscopicity are:

Carboxymethylcellulose  
Cellulose acetate  
Cellulose acetate propionate  
Dibutyl tartrate  
Diethylene glycol  
Dimethyl phthalate  
Dytol B-35, J-68 and L-79\* (Aliphatic Alcohol (Mixture of C12, C14 and C16), Dodecyl Alcohol and Lauryl Alcohol)  
2-ethyl-1,3 hexanediol  
Glycerin  
Glyceryl monoricinoleate  
Hyprin GP-25\* (tris-1,2,3-hydroxypropoxypropane and bis(hydroxypropoxy)hydroxy propane)  
Igepal CO-430\* (Nonyl Phenol Ethoxylate, 4EO)  
Lorol\* (Fatty Alcohol)  
Oleyl alcohol  
Resoflex R-363\*  
Santicizer 141, B16, and E-35\*  
Santolite MHP\* (4-Toluenesulfonamideformaldehyde resin)  
Shellac  
Sorbitol

\*Trademark owned by a third party

Carboxymethylcellulose cellulose acetate, cellulose acetate propionate and shellac effectively decrease tackiness. 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% arylsulfonamide-formaldehyde resin.

In comparative tests from plasticity at 33% relative humidity, PVP films containing 10% diethylene glycol show an "elongation at break" twice that of PVP films containing 10% glycerin, polyethylene glycol 400, sorbitol, or urea, and four times that of PVP films containing 10% ethylene glycol, dimethyl phthalate, or Santicizer E-35\*. At 50% relative humidity, 10% Santicizer E-35\*, 25% glycerin, and 15% diethylene glycol are effective plasticizers. At 70% relative humidity, 25% sorbitol and 25% dimethyl phthalate may be used successfully. In PVP films used as hair fixatives, lanolin derivatives such as Acetulan and Amerchol 1-101\* (Dow), Ethoxylan 1685\* (Cognis/BASF) and Lanogel 41\* (Lubrizon), are also effective plasticizers and humidity-control agents.

## Compatibility

PVP shows a high degree of compatibility both in solution and in film form, with most inorganic salt solutions and with many natural and synthetic resins, as well as with other chemicals. (Table VII).

At 25°C the addition of 100ml of a 10% solution of:

aluminum potassium sulfate	$\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$
aluminum sulfate	$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$
ammonium chloride	$\text{NH}_4\text{Cl}$
ammonium sulfate	$(\text{NH}_4)_2\text{SO}_4$
barium chloride	$\text{BaCl}_2 \cdot \text{H}_2\text{O}$
calcium chloride	$\text{CaCl}_2$
chromium sulfate	$\text{Cr}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$
copper sulfate	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
ferric sulfate	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$
magnesium chloride	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
mercuric acetate	$\text{Hg}(\text{C}_2\text{H}_3\text{O}_2)_2$
nickel nitrate	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
lead acetate	$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$
potassium chloride	KCl
potassium sulfate	$\text{K}_2\text{SO}_4$
potassium dichromate	$\text{K}_2\text{Cr}_2\text{O}_7$
sodium bicarbonate**	$\text{NaHCO}_3$
sodium chloride	NaCl
sodium nitrate	$\text{NaNO}_3$
sodium phosphate (primary)	$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$
sodium pyrophosphate	$\text{Na}_4\text{P}_2\text{O}_7$
sodium sulfate	$\text{Na}_2\text{SO}_4$
sodium sulfite	$\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$
sodium thiosulfate	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$
silver nitrate	$\text{AgNO}_3$
zinc sulfate	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$

\*\*200 ml of a 5% solution

Any of the following salts to a 10% PVP K-30 aqueous solution (i.e., 10 parts of the test salt to 1 part of PVP) does not change the appearance of the solution.

**Table VII: Compatibility of PVP in Solutions and Films**

Class	Compound Tested	Solvent	% TTL Solids	Solution or Melt Appearance	Film Compatibility
Ether-Alcohols	Polyethylene glycol	ethanol	5	S clear, colorless	C
	Ucon Oil® 50-HB 5100*	ethanol	5	S clear, colorless	IN
	Ucon Oil® 75-HB 90,000*	ethanol	5	S clear, colorless	H
Gums	arabic	water	5	PS cloudy, heterogeneous	C
	karaya	water	4	I two-phase	H
	tragacanth	water	4	PS white, homogeneous	H
	sodium alginate	water		S	C
Glycerides	olive oil	chloroform	5	S clear, light yellow	IN
	castor oil	ethanol	5	S clear, colorless	IN
	lanolin	chloroform	6	S clear, light yellow	H
	lecithin	water	1	I opaque homogeneous	IN (1:3) H (1:1,3:1)
Esters	beeswax	chloroform	5	S clear, colorless	H
	diethylene glycol stearate	propargyl alcohol	3	S clear, yellow	IN
	Flexo® 300* (triethylene glycol bis-alpha-ethylecaproate)	ethanol	5	S clear, colorless	IN
	cellulose acetate propionate	chloroform	4	S clear, colorless	C
	cellulose acetate	1:4 ethanol/ethylene dichloride	4	S clear, light 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	
Misc. Resins	shellac	ethanol	5	S clear, colorless	C
	ethylcellulose	ethanol	4	PS cloudy, homogeneous	C
	methylcellulose	water		S	C
	carboxymethylcellulose (low viscosity grade)	water	1	S clear, colorless	C
	corn dextrin***	water		S	C
Synthetic Polymers	Saran® B-1155* (vinylidene chloride polymer)	N-methyl-2-pyrrolidone	3	S yellow	IN
	PVI-C poly (vinyl isobutyl ether)		4	I two liquid phases	IN
	PVM poly (vinyl methyl ether)	chloroform		S	C
	polystyrene	hot melt		S clear, colorless	IN
	polyvinyl alcohol	chloroform		S	C
Surfactants	Alipal® CO-436* (ammonium salt of sulfated nonylphenoxypoly (ethyleneoxy) ethanol)	water	3	S clear, colorless	C
	Duponol® (sodium lauryl sulfate)	water	5	S clear, colorless	
	Nekal® BX-78* (sodium alkylnaphthalene sulfonate)	water	3	S hazy, light yellow	IN
Quaternary Ammonium Compounds	Hyamine® 2389*	water	2	S clear, colorless	
	Tetrosar®	water	10	S clear, colorless	
	BTC® (alkylidimethylbenzyl ammonium chloride)	water	10	S clear, colorless	
	Isothar® (lauryl isoquinolinium bromide)	water	10	S clear, colorless	
	cetylpyridinium chloride	water	10	S clear, colorless	

\*Trademark owned by a third party

\*\*Ratio of PVP to compound 1:3, 1:1, 3:1

\*\*\*Ratio of PVP to compound 1:19

Abbreviations:

S - Soluble

I - Insoluble

IN - Incompatible

H - Homogeneous

C - Compatible

PS - Partially soluble

Colloidal suspensions are formed by 10% solutions of the following salts when added to 10% aqueous PVP solutions in the amounts shown:

Class	Compound Tested	Ratio Test Salt: PVP
Sodium Carbonate	Na <sub>2</sub> CO <sub>3</sub>	1.85:1
Sodium Phosphate, Dibasic	Na <sub>2</sub> HPO <sub>4</sub> ·7H <sub>2</sub> O	3.7:1
Sodium Phosphate, Tribasic	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	1.28:1
Sodium Metasilicate	Na <sub>2</sub> SiO <sub>3</sub> ·5H <sub>2</sub> O	3:1

When reviewing Table VII, one should note the general procedure followed in determining compatibility was to dissolve PVP K-30 and the test material separately in a mutual solvent. After mixing the two solutions, appearance was observed. The solution was then cast onto a glass plate and the resulting film examined after evaporation of the solvent.

## Protective-Colloid Action

Small amounts of PVP effectively stabilize emulsions, dispersions and suspensions. Even lyophobic colloids, which exist without significant affinity for the medium, can be protected by PVP. Apparently, the polymer is absorbed in a thin molecular layer on the surface of the individual colloidal particles to prevent contact and overcome any tendency to form a continuous solid phase.

The best viscosity grade to use depends, of course, on the application, in some cases, the lower molecular weight polymers, PVP K-15 or PVP K-30, are more efficient than the higher molecular weight material. For example PVP K-15 is particularly effective as a dispersant for carbon black and low-bulk-density solids in aqueous media. It is used in detergent formulations to prevent soil redeposition on synthetic fibers and as a protective colloid for pigments in cosmetics. In viscous systems, on the other hand, PVP K-90 is most suitable, e.g., as a dispersant for titanium-dioxide or organic pigments or latex polymers in emulsion paints. Also in the suspension polymerization of styrene, PVP K-90 is preferred as the protective colloid because lower molecular weight polymer produces too fine a bead.

## Complex Formation and Crosslinking

PVP forms molecular adducts with many other substances. This can result in a solubilizing action in some cases or in precipitation in others. Physiological effects, such as toxicity, may be modified and in the case of certain antibiotics, anesthetics, and other drugs, pharmacological action may be enhanced and duration of effect prolonged.

PVP crosslinks with polyacids like polyacrylic or tannic acid to form complexes which are insoluble in water or alcohol but dissolve in dilute alkali. Gantrez™ AN copolymer (Ashland), methyl vinyl ether/maleic anhydride copolymer, will also insolubilize PVP when aqueous solutions of polymers are mixed in approximately equal parts at low pH. An increase in pH will solubilize the complex.

Ammonium persulfate will gel PVP in 30 minutes at about 90°C. These gels are not thermoreversible and are substantially insoluble in large amounts of water or salt solution. The more alkaline sodium phosphates will have the same effect. When dried under mild conditions, PVP gels retain their uniform structure and capacity to swell again by absorption of large amounts of water.

Resorcinol and pyrogallol also precipitate PVP from aqueous solution, but these complexes redissolve in additional water. In alcoholic solution, no precipitation takes place.

Under the influence of actinic light, diazo compounds and oxidizing agents, such as dichromate, render PVP insoluble.

Heating in air to 150°C will crosslink PVP and strong alkali at 100°C will permanently insolubilize the polymer.

**Detoxifying Properties.** PVP offers a novel approach to the reduction of toxicity and sensitivity problems inherent in many compounds. It binds various toxins, dyes, drugs and other chemicals.

This complexing action may be specific rather than general, but tests on many different materials indicate that the toxic and irritant properties of the majority are tempered by PVP. The accumulated evidence indicates that even in relatively low concentrations, PVP may permit the use of certain materials which would otherwise be too toxic, irritating, or skin fatiguing for many purposes.

The case of iodine is illustrative. Feeding aqueous PVP-iodine solutions containing 2.5% available iodine to rats significantly reduced the oral toxicity (LD) of iodine. The LD<sub>50</sub> in Lugol's solution (an aqueous iodine solution) was 400 mg/kg in rats, whereas for the PVP-iodine solution the comparable value was 1400 mg/kg in rats. In a 1% PVP solution, solubility of the halogen is increased 17-fold over that in water.

Moreover, this PVP-iodine complex retains the full germicidal properties of elemental iodine while oral toxicity to mammals is drastically reduced.

Other germicidal products, such as chlorinated phenols and bisphenols, in combination with PVP, exhibit reduced toxicity and lowered incidence or intensity of skin reactions while maintaining good germicidal properties. Applying a sanitizer-cleaner solution with the potential to irritate the subject's skin, the addition of PVP at 0.1 concentration levels between 0.1% to 5.0% markedly reduced the irritation to the skin in proportion to the increase in the levels of PVP added to the formula. For example, with the addition of only 0.25% of PVP to this sanitizer-cleaner solution, the irritation results at the primary application level was reduced to zero in 50 subjects from a level of 7 from the same product that does not contain PVP. In the case of the challenge application, the irritation level of the product containing no PVP was 11 subjects, whereas at the 0.25% PVP concentration in the otherwise identical sanitizer-cleaner the challenge application level that showed irritation was only 4. Similarly, tests on the effect of PVP on the irritating properties of high-foaming detergents (sodium alkyl sulfates) indicate the intensity and incidence of skin irritation can be reduced by incorporation of as little as 1% PVP into formulations for shampoos, bubble baths, toothpastes, etc.

Other chemicals which show reduced oral toxicity in PVP solution include potassium cyanide, nicotine and formamide.

## Stability

PVP powder 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. Bulk polymer is supplied in tied polyethylene bags enclosed in fiber packs. When not in use, the polyethylene bag should be kept closed at all times in the covered container.

On PVP films, moisture acts as a plasticizer. These films are otherwise chemically stable.

The equilibrium water content of PVP solid or films varies in a linear fashion with relative humidity and is equal to approximately one-third the relative humidity. Samples of dried, powdered PVP, subjected to 20, 52 and 80 percent relative humidity until equilibrium is reached, show a 10, 19 and 31 percent moisture weight gain, respectively.

Exposure to extreme elevated temperatures should be avoided, though PVP powder is quite stable to heat. Some darkening in color and decreased water solubility are evident on heating in air at 150°C. However, PVP appears to be quite stable when heated repeatedly at 110-130°C for relatively short intervals.

Aqueous PVP is stable for extended periods if protected from molds. The usual preservatives-benzoic acid, dichlorophene, hexachlorophene, sorbic acid, esters of p-hydroxybenzoic acid are quite effective. However, appropriate tests should be made with finished products containing PVP before deciding on a preservative. Steam sterilization (15 lb. pressure for 15 min.) can also be used and this treatment does not appear to change the properties of the solutions.

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 100ml of 3.5% PVP K-30 solution is raised from pH 4 to pH 7 by the addition of 1-2ml 0.1 N sodium hydroxide.

## Industrial Applications of Polyvinylpyrrolidone

Polyvinylpyrrolidone is widely used in a broad variety of industries. This is due to its unique physical and chemical properties, particularly because of its good solubility in both water and many organic solvents, its chemical stability, its affinity to complex both hydrophobic and hydrophilic substances and its nontoxic character. Several hundreds of papers have been published describing the advantages of using PVP in formulas for the following product areas.

Area of Use	Advantages of PVP
<b>Adhesives</b> ...pressure-sensitive and water-remoistenable types...food packaging (indirect food contact)...metal adhesives...abrasives...sandcore binder...rubber to metal adhesives.	<ul style="list-style-type: none"> <li>• Specific adhesive for glass, metals, plastics. Imparts high initial tack, strength, hardness.</li> <li>• Particularly suitable for hot-melt and remoistenable adhesive applications.</li> <li>• Forms grease-resistant films.</li> <li>• Films can be cast from water or organic solvents. Modifies viscosity of polymer-based adhesives. Raises cold-flow temperature.</li> <li>• Raises softening point of thermoplastics.</li> <li>• On paper, improves gloss, printability and grease resistance.</li> <li>• Skin products film-former and an enhancer of denture adhesives effectiveness.</li> </ul>
<b>Ceramics</b> ...binder in high temperature fire prepared products such as clay, pottery, porcelain, brick products...dispersant for ceramic media slurries...and viscosity modifier.	<ul style="list-style-type: none"> <li>• Binder is completely combustible in the firing process and therefore exerts no influence on the ceramic end product and in addition, is compatible with inorganic materials.</li> </ul>
<b>Glass and Glass Fibers</b> ...acts as a binder, lubricant and coating agent.	<ul style="list-style-type: none"> <li>• Aids in processing and helps to prevent abrasion of glass.</li> </ul>
<b>Coatings/Inks</b> ...ball-point inks...protective colloid and leveling agent for emulsion polymers/coatings/printing inks...pigment dispersant...water-colors for commercial art...temporary protective coatings...paper coatings...waxes and polishes.	<ul style="list-style-type: none"> <li>• Suspending agent, flow promoter in inks.</li> <li>• Non-thixotropic.</li> <li>• Promotes better gloss, high tinctorial strength, more uniform shades.</li> <li>• Antiblock agent.</li> <li>• Grease resistant.</li> </ul>
<b>Personal Care</b> ...hair-grooming products, shampoos, tints, creams...shave and after-shave preparations...eye make-up...face powders...deodorants...bath preparations...lipsticks...leg-care products...other skin products...dentifrices...fragrance binders.	<ul style="list-style-type: none"> <li>• Adhesive quality provides use as thickeners, dispersing agents and binders.</li> <li>• Contributes to hair management, luster, smoothness.</li> <li>• Forms controlled rewettable, transparent films.</li> <li>• Emulsion stabilizer in creams and lotions.</li> <li>• Particularly suitable as an adjuvant in skin cleansing and skin protection type products.</li> <li>• Protects skin from shampoo and household detergents.</li> <li>• Aids in reduction of toxicity and sensitivity problems.</li> <li>• Promotes emolliency, lubricity, and a natural moisture balance in skin preparations.</li> <li>• Improves consistency of shampoos and hair colorant products.</li> <li>• Promotes leveling and aids retention of color in hair dyes.</li> </ul>

Area of Use	Advantages of PVP
<p><b>HI &amp; I...</b>dye transfer inhibitor...liquid laundry products...detergent briquettes and bars...detergent encapsulating agent...soap sheets...waterless hand cleaners...industrial sanitizers...auto cleaning solutions...grease remover...stain (urine) remover...foam stabilizer for bubble baths...dirt deposition inhibitor for synthetic fibers and resin-treated fabrics...binder for tablet formulations.</p>	<ul style="list-style-type: none"> <li>• Compatible in clear liquid, heavy-duty detergents.</li> <li>• Loose-color scavenger during laundering.</li> <li>• Improves emollient action and detergent storage stability.</li> <li>• Stabilizes foam.</li> <li>• Reduces irritation.</li> <li>• In enzyme containing products used to coat and bind the enzyme thereby minimizing dusting.</li> </ul>
<p><b>Electrical Applications...</b>storage batteries...printed circuits...TV picture tubes...binder for metal salts or amalgams in batteries...gold, nickel, copper and zinc plating...a thickener for solar gel ponds and as an adhesive to prevent leakage of batteries...serves as an expander in cadmium-type electrodes...binder in sintered-nickel powder plates.</p>	<ul style="list-style-type: none"> <li>• Hydrophilic material in electrode separators of microporous film type.</li> <li>• Compatible dispersant in printed circuits to improve uniformity.</li> <li>• Shadow masks and protects light sensitive materials in TV picture tubes.</li> <li>• Compatible dispersant for solar collection heat transfer liquids, for gold, nickel, copper and zinc plating baths and cathode ray tubes.</li> </ul>
<p><b>Lithography and Photography...</b>foil emulsions...etch coatings...plate storage...gumming of lithographic plates...dampener roll solutions...photo and laser imaging processes... microencapsulation...thermal recording... carrier, finisher preserver of lithographic plates... thermal transfer recording ribbons and optical recording discs.</p>	<ul style="list-style-type: none"> <li>• Light-hardenable, water-soluble colloid for diazo, dichromate, or silver emulsion layers.</li> <li>• Obviates deep-etching of metal plates.</li> <li>• Offers uniform viscosity, temperature stability.</li> <li>• Nonthixotropic. Defogant.</li> <li>• Adheres tightly to plates in non-image areas.</li> <li>• Grease-proof and water receptive.</li> <li>• Chemically inert to ink ingredients.</li> <li>• Binder, dispersant carrier and improves adhesion for light absorber dyes and anti-stick agent.</li> <li>• Increases covering power density and contrast as well as speed of emulsions used in photography.</li> </ul>
<p><b>Fibers and Textiles...</b>synthetic fibers...dyeing and printing...fugitive tinting...dye stripping and dispersant... scouring...delustering...sizing and finishing...grease-proofing aid...soil release agent. Widely used as dye dispersant and to disperse titanium dioxide.</p>	<ul style="list-style-type: none"> <li>• Backbone for grafting monomers.</li> <li>• Improves dye receptivity of such hydrophobic fibers as polyolefins, viscoses, rubber latices, polyacrylonitriles and acrylics.</li> <li>• Restores the color to faded textiles.</li> <li>• Dye fixation improver and dye vehicle in wool transfer printing. Thickener for heat activated textile adhesives, textile finishes and print parts for various types of fabrics.</li> <li>• Acts as a dye scavenger in print washing.</li> <li>• Solubilizer for dyes.</li> <li>• Contributes enhanced adhesives to glass-fiber sizes.</li> </ul>
<p><b>Membranes...</b>macroporous, multiporous, desalination, gas separating, liquid ultrafiltration, hemodialysis, selective permeability types of membranes.</p>	<ul style="list-style-type: none"> <li>• Good compatibility and crosslinking properties.</li> <li>• Ability to complex with a broad variety of compounds.</li> <li>• Strong polar character and hydrophilicity improves selective material separation properties.</li> </ul>
<p><b>Metallurgy...</b>processing for both ferrous and nonferrous metals...coating ingredient to aid or remove material from metal surfaces such as copper, nickel, zinc and aluminum.</p>	<ul style="list-style-type: none"> <li>• Corrosion inhibitor in quenching baths.</li> <li>• Coating to facilitate the cold forming of metals.</li> <li>• Binder for casting molds and cores.</li> <li>• Thickener, viscosity controlling agent, adhesion improver, water soluble flux.</li> </ul>
<p><b>Paper...</b>inorganic papers, cellulose papers, rag stock...rag stripping...coloring and beating operations...copying paper, printing paper and electric insulating papers... paper adhesives.</p>	<ul style="list-style-type: none"> <li>• Improves strength and stability.</li> <li>• Prevents sliding.</li> <li>• Improves luster, binding, absorbency, whitening and gloss.</li> <li>• Solubilizes dyes for coloring, dye stripping.</li> <li>• Fiber and pigment dispersant.</li> <li>• Helps in preventing deposition of pitch.</li> <li>• Complexing agent for modifying resins.</li> <li>• Binder for inorganic flakes and fibers.</li> </ul>
<p><b>Polymerizations...</b>acrylic monomers...unsaturated polyesters...olefins, including PVC...styrene beads... substrate for graft polymerization...template in acrylic polymerization.</p>	<ul style="list-style-type: none"> <li>• Acts as particle-size regulator, suspending agent and viscosity modifier of emulsion polymers. In polymerization products, improves strength, clarity, color receptivity.</li> <li>• Post-polymerization additive to improve dyeability and stability of latices.</li> <li>• Pigment dispersant.</li> </ul>

Area of Use	Advantages of PVP
<b>Water and Waste Treatment, and Hygiene</b> ...scale inhibitor, prevention of corrosion in water transfer systems, clogging of reverse osmosis membranes, water treatment in fish hatchery ponds...removal of oil, dyes from waste water and as an oil-ball forming agent in oil spill removal...floculant in waste water treatment... waste water clarifier in papermaking...in deodorants for neutralization of irritant and poisonous gas, in air conditioning filters.	<ul style="list-style-type: none"> <li>• Complexes and gels in water to react with undesired water products.</li> </ul>
<b>Oil/Gas</b> ...additive to cement used in the oil industry... viscosity modifier.	<ul style="list-style-type: none"> <li>• Cement set-time retarder, reduces speed of fluid loss and improves the sealant properties of the well casing.</li> <li>• Used as a viscosity modifier in drilling muds.</li> </ul>

## Physiological Properties

### PVP Is Safe

In the half century since the invention of PVP, a very extensive body of toxicological data in animal and man has been developed. It is perhaps the most extensive body of toxicological information available on any pharmaceutical excipient or food additive in use today.

The data supports the conclusions reached by individual workers, as well as numerous regulatory bodies, that PVP is safe.

Contributing to this favorable safety profile are the following:

**Biological Activity:** Because of its unique chemical nature, PVP would be expected to be biologically inert apart from exerting osmotic activity. A large number of animal and human studies support the metabolic inertness of this polymer and hence, the safety of PVP.

**Absorption:** The absorption of PVP from the gastro-intestinal tract is very limited and proceeds primarily by fluid-phase pinocytosis.

**Metabolism:** PVP is not metabolized.

**Pharmacological Effects:** With normal use, PVP does not modify physiological activity.

### More Specifically:

**Acute Toxicity:** Studies in rodents, dogs and primates have shown that PVP is a substance with a very low acute toxicity. It is essentially impossible to kill animals by administration of PVP except by gross osmotic imbalance. Thus, the LD<sub>50</sub> of PVP orally is reported to exceed 100g/kg and be over 10g/kg intravenously or intra-peritoneally.

**Sub-chronic Toxicity:** Repeat dose oral studies in rodents and dogs have shown apart from loose stool at high doses, which is related to the bulk purgative actions of PVP, there is no evidence of any toxicity as judged by clinical chemistry, hematology and histopathology. The no-adverse effect level (NOEL) in sub-chronic studies in rodents and dogs exceeds 5g/kg/day.

**Chronic Toxicity:** In two well conducted chronic studies using PVP K-25 and PVP K-90 in the diet at dose levels as high as 10% and 5% respectively, over a two-year period, there was no evidence of any substance-related toxicity in clinical chemistry, hematology, urine analysis and histopathology review. There was no evidence of any carcinogenic effect or evidence of PVP storage in any organ. There was no evidence of any cumulative damage over the two-year studies.

**Teratology:** Teratogenicity studies on PVP given orally, intravenously and intra-aminotically in rats and/or rabbits have shown no evidence of embryotoxicity or teratogenicity.

**Mutagenicity:** *In vitro* and *in vivo* mutagenicity studies have shown that PVP does not have any genotoxic or clastogenic activity.

## In Summary

An extensive body of toxicological data in animals supports the biological inertness of PVP. The acute, sub-chronic and chronic toxicity of orally administered PVP is extremely low. It is not a sensitizer or irritant. There are no reported adverse effects following oral administration in humans. The currently permitted United Nations' World Health Organization's Food and Agriculture Organizations joint expert committee on food additives established an allowable daily intake of 50mg/kg/day for food use provides an adequate margin of safety. There would appear to be no reason to restrict its oral pharmaceutical use in any way. There have been no reports of adverse effects following its use intravenously as a plasma expander, even after the administration of very large amounts.

Based on the available data, PVP should prove safe in normal industrial applications.

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