

What follows are three inventions concerning,

**The Reactions of PVP with Strong Bases**

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**1. Alkaline Associative thickener waxes based on PVP and Sodium Laurate.**

Gels/waxes based on the associate thickener reaction of stearate salts and PVP are known(USP 3,576,776; Muszik and Dierichs, Apr. 27, 1971; USP 3,964,632; Cohen and Lennon, June 22, 1976 ). This is not unexpected because a positive charge on PVP can be generated by large anions which attracts the stearate chains which can then form virtual cross-links. PVP is water soluble because of charge separation with a partial positive charge on nitrogen and a corresponding negative charge on oxygen of the pendant lactams. However as a large anion (stearate) approaches the polymer, it adheres because of the growing positive charge as the lactam oxygen picks up a proton. However, I have found that sodium salts do form extensive virtual cross-links while potassium salts of fatty acids do not form tight virtual cross-links. This is contrary to the claims of the prior art where no distinction is claimed for all alkali salts of fatty acids from C8 to C22!

I have discovered that if the soap is sodium laurate (but not potassium laurate) for example, an associative thickener wax is formed even in the

presence of high pH solutions. This is unexpected, novel and useful. Such waxes can be liquified with modest heat and reform on cooling. Such waxes have significant uses such as hair relaxers, depilatories, make-up removers, protective coatings and such. The advantage being the ability of PVP to protect the skin. The waxes form even under very alkaline pH's and can be hard to soft depending on the ratio of PVP to sodium laurate. Said waxes can be painted on a surface when in liquid form. Such adhering coatings can protect metals from acidic corrosion and the skin from corrosive caustic. Such coatings when no longer needed can be washed off with hot water. Alternatively, when potassium laurate is added to PVP aqueous concentrates at a variety of levels and even in the presence of excess alkali, will not form a wax but the composition remains liquified and can form a stringy gel after standing for several days at room temperature.

Sodium stearate forms non-flowing waxes in the presence of excess caustic but under the same conditions potassium stearate forms lightly cross-linked, flowing gels or liquids with PVP K-30. When optimized according to the prior art, hard waxes can be obtained with fatty acid sodium salt but the prior art did not understand that when potassium is substituted for sodium, hard waxes are not formed. Indeed, in the case of laurate salts, potassium results in clear liquids which can gel after standing for several days.

Since my invention is to produce wax soap/PVP formulations that tolerate

high pH's, hydrolytic stability is important. PVP is supposedly very difficult to hydrolyze or to be covalently attacked? Therefore, it would seem that said formulations are stable over time having long shelf lives. Sodium laurate based melt-able waxes can be melted numerous times returning to the solid form upon cooling. However the recent patent to Beisang et. al. (USP 7,988,986; Aug. 2, 2011) is of great interest. It claims that when PVP is concentrated in water to say 60-80% solids in the presence of 0.1% NaOH, it will form stable gels even when eventually neutralized and diluted with equilibrium absorbed water. This can only happen if the cross-links are covalently bonded. I have tried their claim with 2% NaOH and KOH in 50% PVP and obtained gels within a few hours.

This cross-linking situation should not occur in the case of my associative thickener waxes because I employ mild more dilute conditions vs Beisang and no wax or gels are formed without sodium laurate. However, KOH under the same procedure as employed with NaOH and lauric acid, can result in stringy gels. This might suggest that KOH is a more effective cross-linker than NaOH and does not require concentrated PVP solutions as suggested by Beisang et. al.?

The literature concerning PVP is quite vast and mostly concerns the use and formulation of the polymers. References concerning the post polymerization derivative chemistry are relatively few as are those that reveal how to form

useful PVP gels. The first question about such chemistry is the hydrolytic stability of the polymer. Apparently it is quite difficult to hydrolyze the lactam groups even in basic or acidic solutions. If only a few pendent amino acid groups are desired then this is possible (Lorenz and Lee, USP 6,379,702; Apr. 30, 2002). The exact location of such groups on the polymer chain is obviously impossible to determine, but those most sterically available are at or near the polymers terminals. Such amino acid containing polymers have found use as gelling agents with appropriate cross-linkers. Amino acid pendant groups could possibly cross condense forming cross-links by themselves? The carboxylic acid groups of said pendant amino acids would be expected to be in the unreactive carboxylate form; however when pendant to polymer backbones, carboxylic acid pKa's rise and are more difficult to neutralize.

#### Other Approaches to PVP Gel Compositions:

Excellent reviews of the polymerization of vp have appeared (Login, Vol. 24, pp1069-1099; Kirk-Othmer Encyclopedia of Chemical Technology, 4<sup>th</sup> ed, 1997). It points out that polymerization of vp in water with hydrogen peroxide produces polymers with hydroxyls on one end with a hydrogen on the other. Minor amounts of polymers with hydroxyl on both ends result from two active chains terminating by reacting together. Functional groups such as hydroxyls are required if further covalent chemistry with PVP such as cross-

linking is the goal. Early patents to Staub et. al. USP 4,254,239; Mar. 3, 1981 and USP 4,350,791; Sep. 21, 1982, claim that adding reducing agents to aqueous PVP result in new hydroxyl groups. Later references realized that the reducing agent reacts with pendant pyrrolidone groups (Arnold et. al. USP 7,473,738; Jan. 6, 2009). The actual structure is not revealed but must be a hydroxyl containing moiety as the hydroxyl number was found to increase with increasing reducing agent. Reduction of the lactam to hydroxycycloalkylamine or all the way to the amine pendant group seems to be the result of this reduction (Cohen and Minsk, JOC v.24, 1404, 1959). Such reduced OH containing PVP are used to form cross-linked gels by reaction of said hydroxyl groups.

PVP can be attacked with free radical sources such as ammonium persulfate, electron beams and other actinic radiation resulting in cross-linked polymers. PVP can also react with hypochloride. The goal of the above PVP chemistry is to form gels. However, my approach is to form alkaline waxes and not gels and is simple, very cost effective and totally non-toxic. Such meltable wax chemistry is highly desired and of great utility especially when stable high pH formulations are desired.

### **Description of Invention**

I have discovered that PVP grades such as K-12 and K-30 will form waxes when mixed with lauric acid at pH's of 8 and above, when the base is sodium

hydroxide and not with potassium hydroxide. The interesting observation is that even at extreme alkaline conditions PVP will still form waxes and remain stable. Such waxes are reversible with heat to the clear liquid form. The actual reason for the difference between sodium and potassium is not entirely clear but not to be limited by speculation, I suggest that potassium salts are more water soluble and hence coordinate more water molecules around the fatty carboxylate interfering with the approach of said large anion to the polymer backbone. KOH is free to attack the PVP. The gels generated with KOH/potassium laurate, are not reversible. This may be identical to previously mentioned reaction of NaOH with concentrated PVP, Beisang et. al. (USP 7,988,986; Aug. 2, 2011). Because of PVP's resistance to hydrolysis, the actual chemistry behind gelation in strong alkalis such as excess KOH remains unexplained. My speculations concerning the cross-link chemistry centers on the growing literature concerning the ability of PVP to absorb oxygen to form hydroperoxides, possibly in alkaline solution oxygen is absorbed at a greater rate. Its decomposition to free radicals whether absorbed or already present, accounts for gelation?

#### General Procedure for Preparing Said Waxes:

PVP K-30 powder is mixed with distilled water to prepare a 50% clear solution. Powdered or flake lauric acid (1-4% by weight of PVP) is mixed with the PVP solution warmed to 50-90C. To this mixture is added 1N NaOH in aliquots to dissolve the lauric acid and produce the desired final pH. Upon

cooling, the clear mixture solidifies to form a wax.

Claims:

1. An aqueous associative alkaline wax with a pH of from 8 to 12 prepared with 10-60% PVP, fatty acids(1-4% based on PVP charge) and sodium hydroxide sufficient to adjust the formulation to the desired pH.
2. The associative alkaline wax of claim 1 wherein the PVP is selected from K-12 to K-90 molecular weights and the fatty acid is lauric acid.
3. An alkaline wax hair relaxer or depilatory or make-up remover or protective coating formulation comprising 10-60% aqueous PVP selected from K-12 to K-90 molecular weights, lauric acid and sodium hydroxide sufficient to adjust the pH of said formulation to somewhere in 8 to 12 range.

## **2. Hydroxide chain extension conversion of low MW PVP to Higher MW Mixtures.**

PVP is manufactured in several MW grades from a few thousand to 1.2 million daltons( also referred to as K12 through K120). This requires individual polymerization reactions for each grade. This is equipment intense as the large commercial volumes required can keep separate manufacturing equipment busy for each grade. A simpler approach to manufacture various MW mixed grades is to start with one lower MW grade ( Staub et. al., USP 4,330,451; May 18, 1982) and perform hydroxide cross-linking or more accurately chain extension. My method is both simple and cost effective, resulting in mixtures that contain no peroxide or cross-linker residues. Such residues can effect the safety and pharmaceutical applications of free radical cross-linking methods such as the previously mentioned Staub patent.

The prior art clearly reveals that hydroxide will gel PVP. This is presented as a warning

that it will cross-link and gel in the presence of strong alkali (Drug Delivery Technology, June 2008, vol 8, No6). No one to my knowledge has claimed that such cross-linking can be controlled and stopped by simply neutralizing the base. I have found that acetic acid is acceptable and has the advantage of being non-corrosive. The resulting acetate salt is innocuous.

I have found that PVP K-30 (44,000 to 54,000 daltons) is a good grade to start with. It can be dissolved in water as a 50% solution for example and activated with aqueous KOH until pH above 9-10. The mixture can then be heated in a water bath until the desired thickening is achieved at which point the cross-linking reaction is extinguished with HOAc. Various mixed grades of PVP can be produced by this method because partial amounts of a large master batch can be removed and neutralized as the viscosity of the master batch rises. As long as the remaining mixture does not gel, multiple MW PVP mixtures can be produced from the same batch. Alternatively, individual mixtures can be produced. The viscosity of the reaction mixture must be continuously monitored so that the desired mixture can be obtained avoiding gelation. Gelation is not reversible but the gelled mixture is initially flow-able and can be removed easily from a reactor, but if left to continue to react without neutralization, will continue to form tighter if not ringing gels. When the mixture of hydroxide and K-30 is at the desired viscosity, it must be neutralized with HOAc for example. This requires adequate mixing to make sure the pH uniformly drops into a safe neutral pH. The hydroxide employed must not be too concentrated because if concentrated, a gel coat will form around the base before it can dissolve in the aqueous PVP concentrate. This will result in gel clumps that can be removed by dilution of the mixture and filtration through a bag filter. I have found that a 10% NaOH or KOH does not form gel coats but dissolves uniformly.

The drawback to this approach is that you end up with a mixture of MW fractions. For; example in one experiment, doubling or tripling the MW of PVP K-30 results in a

mixture of 60-70% K-30, 20-25% K-60 and 5-15% K-90 for example. In another experiment, nearly a 50/50 mixture of K-30 and K-60 formed (as determined by GPC chromatography). Conditions of dilution, hydroxide concentration, pH, temperature and mixing all effect the ratio of the MW fractions and optimization can certainly be performed. Someone of ordinary skill would be able to conduct experiments designed with the above in mind, to prepare a desired mixture of MWs.

The actual mechanism of the cross-link chemistry is not known; however, not to be constrained by any theory, I suggest that the cross-link chemistry centers on the growing literature concerning the ability of PVP to absorb oxygen to form hydroperoxides, possibly in alkaline solution oxygen is absorbed at a greater rate. Its decomposition to free radicals wether absorbed or already present, accounts for gelation?

Because of the valuable uses of PVP, an inexpensive mixture of MW's is a valuable and useful technology. In fact I would guess that certain applications of PVP actually require MW mixtures.

Example:

To a seal-able glass jar, 23.95g of a 50% aqueous Kollidon K-30(BASF) is added. This is followed by 0.35g of 50% aqueous KOH. After vigorous mixing, the jar is placed in a heated water bath at 60-90C until visibly thick at which point HOAc is added drop wise until the mixture is neutralized. Analysis by GPC (Biorad column, HP-1037A RI detector and MeOH/H<sub>2</sub>O 20% mixture) indicates roughly a 50/50 mixture of "K-60" and K-30 PVP type MW grades.

I Claim:

A method of producing mixtures of PVP MW grades comprising the reaction of group 1 hydroxides, and other bases that can adjust aqueous solutions of 30-75% PVP selected from K-17 to K-90 to pH's greater than 9 or so by mixing said bases with said lower MW PVP and holding said mixtures at a temperature at which cross-linking occurs at such a rate that the thickening mixture can be neutralized to afford the desired higher MW mixture without gelation.

### **3. Stable PVP/NaOH Powder that gel when heated**

PVP is known to react with hydroxides such as NaOH to form gels. These gels are insoluble in water. Depending on which grade of PVP is used and the nature and amount of base, loose to hard gels can be prepared. The mechanism of this gelation reaction is currently unexplained.

PVP can be gelled with free radical sources such as persulfates and heat or actinic radiation such as e-beams. Functional groups can be built into the polymer so that post cross-linking can be performed. There is a significant literature around PVP gels. Such gels are referred to as hydrogels and have several applications such as oxygen permeable contact lenses ( Login, Kirk-Othmer Encyclopedia of Chemical Technology, Vol 24, 1997), and the delivery of pharmaceuticals. In hydrogel form, PVP has many valuable features such as being nonirritating, innocuous to body tissues, hydrolytic stability, not effected by enzymes, non-degradable, environmentally safe.

I have discovered that PVP such as K-30 can be dispersed in solvents such as toluene and the treated with aqueous base for example NaOH. The dispersed PVP absorbs the aqueous NaOH but does not gel and can be filtered and dried to a powder. If this powder is heated, it then cross-links forming gels. This discovery is unexpected because when PVP concentrates are exposed to the same caustic levels, they immediately gel to a

difficult to handle mess. The variables for said invention are the amount of PVP vs solvent and the levels and type of base. A preferred solvent is toluene and the preferred base is NaOH. The resulting heated and cured powder can be dispersed in water and the base washed out or neutralized with acid. The resulting gel can be recovered and dried. It can then be formulated with various actives such as medicinals. The resulting formulation can deliver said actives.

Example:

A flask is charged with 29.8g of Kollidon K-30 powder. To this is added 79g of toluene and the mixture is vigorously shaken to disperse the insoluble PVP. NaOH 50% is dissolve in 10.1g distilled water and this solution is quickly added to the PVP/toluene slurry and vigorous shaken for one hour. The resulting mixture is vacuum filtered and air dried to a friable powder. The powder remains unchanged for several days and shows no sign of instability; however, if the powder is compressed into a disc and heated to 40-90C, the lower temperature preferred, it gels into and insoluble disc. Said disc can be washed free of residual NaOH or the NaOH can be neutralized with acids such as HCL. The neutralized disc can be vacuum oven dried.

I claim:

1 Stable alkaline base containing PVP powders comprising the addition of aqueous alkaline base to a slurry of PVP in a non-reactive solvent in which the PVP is not soluble.

2. A process of preparing the alkaline base containing PVP powders comprising adding PVP to a base non-reactive solvent to form a slurry and adding aqueous alkaline to said slurry and eventually filtering and collecting and drying said powders.