



DuPont Specialty Chemicals

QUILON® Chrome Complex for Improved Performance of Polyvinyl Alcohol Paper Coatings, Films, and Adhesives

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INTRODUCTION

Polyvinyl alcohol PVA, is available with three major ranges of hydrolysis (99+, 96 to 98, and 86 to 89%) and also three major viscosity ranges (4 to 6, 19 to 32, and 35 to 65 centipoises). Typical uses for the various grades are shown in *Table 1*.

“Percent hydrolysis” is the percentage of the acetate groups in the starting material, polyvinyl acetate, that are hydrolyzed to alcohol groups. The desirable properties of fully hydrolyzed polyvinyl alcohol, i.e., with hydrolysis of around 98% or more, are decreased water sensitivity and increased tensile strength. Partially hydrolyzed polyvinyl alcohol, about 88% hydrolyzed, has increased water sensitivity and is a good dispersing agent.

Viscosity, which is normally cited for 4% solutions, increases with increasing molecular weight. Water sensitivity decreases and tensile strength increases with increasing viscosity or molecular weight.

A. COMPATIBILITY OF QUILON® CHROME COMPLEX WITH POLYVINYL ALCOHOL

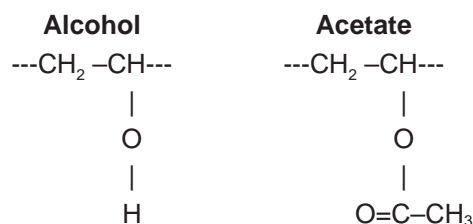
The compatibility of PVA with QUILON varies considerably with its degree of hydrolysis. In *Figure 2* the viscosity is plotted against time for aqueous solutions containing 4% QUILON S and 6% of each of Du Pont’s grades of high viscosity PVA. The mixture with fully hydrolyzed PVA (ELVANOL® HV*) gelled in less than 6 hours even

* ELVANOL® HV is Du Pont’s fully hydrolyzed polyvinyl alcohol. Its viscosity is approximately 60 centipoise. QUILON® and ELVANOL® are registered trademarks of E. I. du Pont de Nemours & Company, Incorporated.

with the addition of acetic acid, which is known to improve the stability. The solution with 98% hydrolyzed PVA was much more stable, but became quite viscous in 24 hours. With 88% hydrolyzed PVA, the viscosity was higher initially; it thickened rapidly to a peak, then decreased to a constant level. This latter solution is very stable: the viscosity remains essentially constant for over two months after the initial peak.

These differences can also be seen in *Figure 3*, where the viscosities after 2 hours are plotted against the concentration of QUILON S. As the latter increases, formulations with ELVANOL HV are less viscous, and those with 88% hydrolyzed PVA more viscous. The viscosity of a solution with 98% hydrolyzed PVA is largely independent of the QUILON S concentration.

In order to explain these gelling characteristics, it helps to compare the types of monomer units that occur in polyvinyl alcohol:



A PVA molecule contains both types of unit. In the absence of QUILON, if the polyvinyl alcohol is fully hydrolyzed, the hydroxyl groups of one chain can approximate those of adjacent chains, permitting hydrogen bonding and gellation. In the 98% hydrolyzed

TABLE 1
Uses of Polyvinyl Alcohol

Type	Typical Uses
Fully Hydrolyzed (99%) Low Viscosity	Adhesives Ceramic binder Mold-release agent
Medium Viscosity High Viscosity	Binders for pigmented paper coatings Calender stack and size-press applications Grease-resistant paper Cast films (for strength and solvent resistance) Binders for non-woven fabrics; textile sizes
Fully Hydrolyzed (96–98%)	Similar to above; gives non-gelling solutions
Partially Hydrolyzed (86–89%)	Nonionic emulsifier, protective colloid Remoistenable adhesives Cold-water-soluble films Stencil screens Textile sizes

Figure 2. Viscosity vs. Time

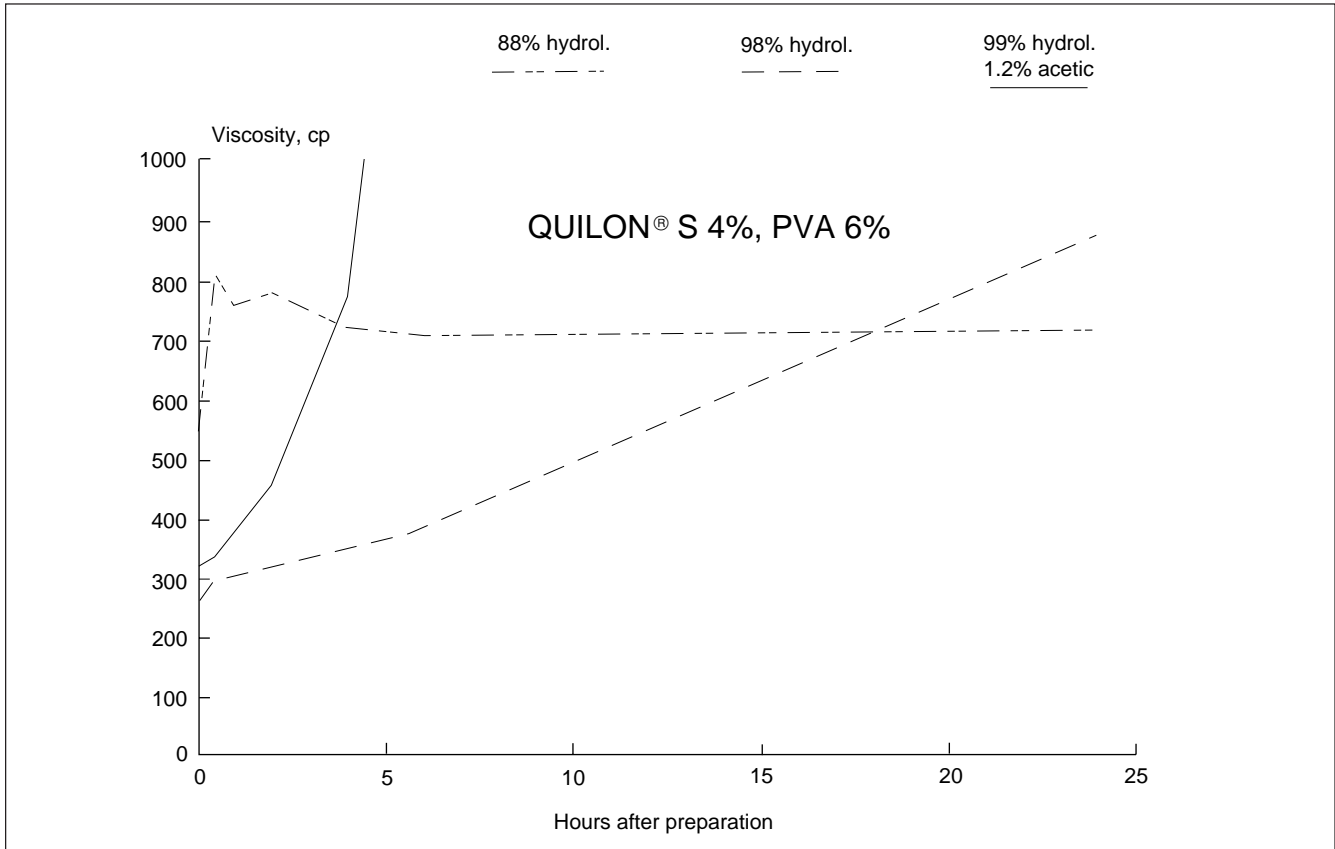
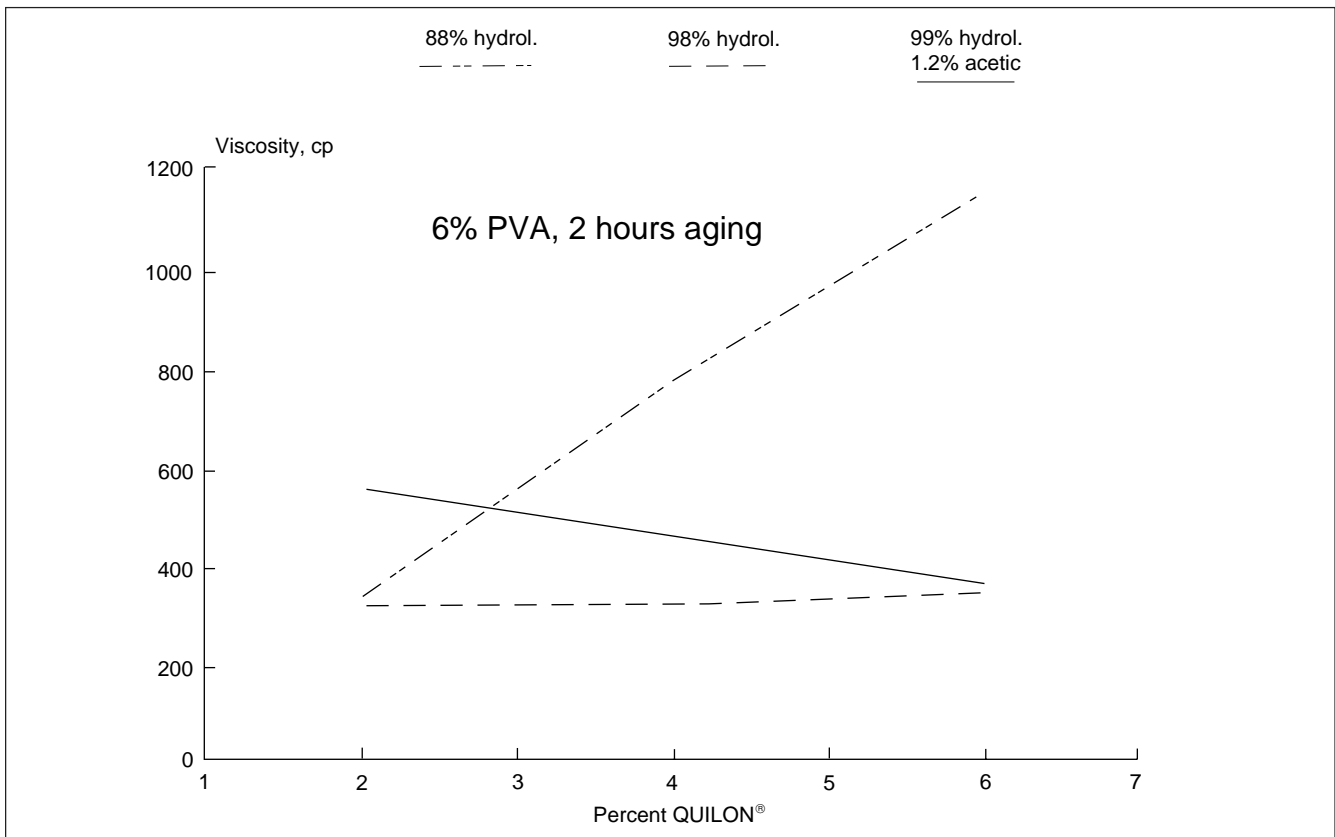


Figure 3. Viscosity vs. QUILON® Concentration



polyvinyl alcohol there are enough of the larger acetate groups to prevent this close packing, and the solutions do not gel.

QUILON[®] causes at least two effects. The viscosity decrease with fully hydrolyzed PVA, shown in *Figure 3*, suggests that it decreases the close packing of the polymer chains. The other effect is the coordination of the chrome complex with the alcohol groups. This coordination appears to be much more rapid for the partially hydrolyzed polyvinyl alcohol, as is noted from the rapid increase in viscosity in *Figure 2*.

Six percent solutions of ELVANOL[®] HV and 88% hydrolyzed PVA alone have viscosities of about 280 and 190 centipoises, respectively. The initial viscosity of the mixture of QUILON and ELVANOL HV is only slightly above the value for the PVA alone, while that for the mixture with 88% hydrolyzed PVA is considerably higher. Solutions containing 6% polyvinyl alcohol and 2, 4 and 6% QUILON have 62, 31 and 21 alcohol units per chromium atom, respectively. If each chromium atom gives a cross link between two polyvinyl alcohol chains, there are sufficient links to give a tightly bound structure.

B. FORMULATIONS OF QUILON S AND PARTIALLY HYDROLYZED POLYVINYL ALCOHOL

The following sections give the viscosities and stabilities of the solutions over a range of QUILON and PVA concentrations. These data allow a choice of solution viscosity, and predict how it will change with time.

The viscosity-time curves (not shown) for solutions of QUILON S with partially hydrolyzed PVA all essentially follow the curve given for 88% hydrolyzed PVA in *Figure 2*. The viscosity of the mixture rapidly increases in the first hour after preparation, peaks in one to two hours, and then slowly decreases to an essentially constant value within about 4 hours. It then changes very little, even in two months or more.

In *Figure 4*, the PVA concentration is constant at 6%, and the viscosity is plotted against the QUILON concentration. The curves show the original viscosities and those after two hours and 24 hours. The viscosity at 2 hours is always higher than that at 24 hours, as described above. There is also a fairly uniform increase in viscosity as the QUILON concentration is increased.

In *Figure 5*, the QUILON concentration is constant at 4%, and concentration of 88% hydrolyzed PVA varies. As expected, the viscosity increases with PVA concentration.

Figure 4. Viscosity vs. QUILON[®] Concentration

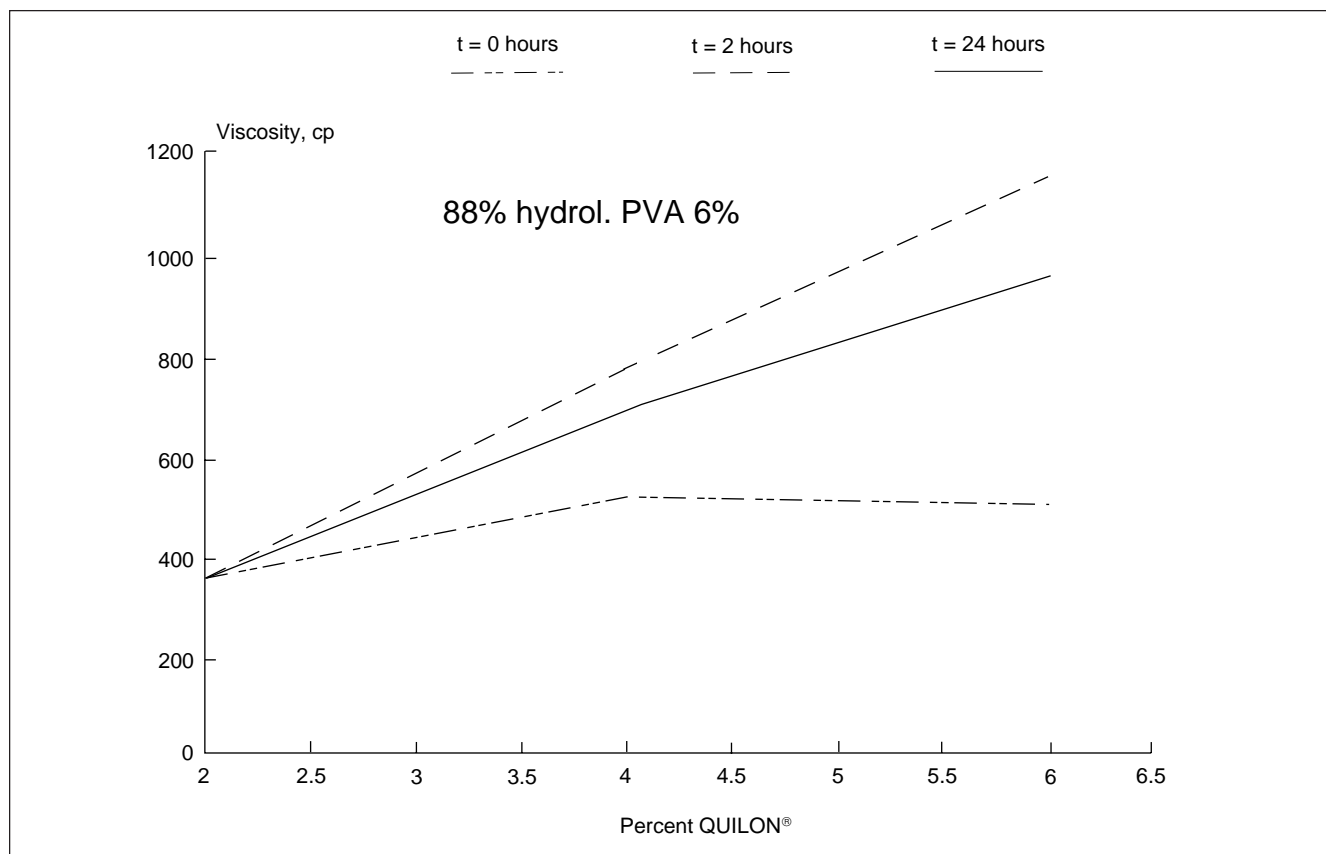
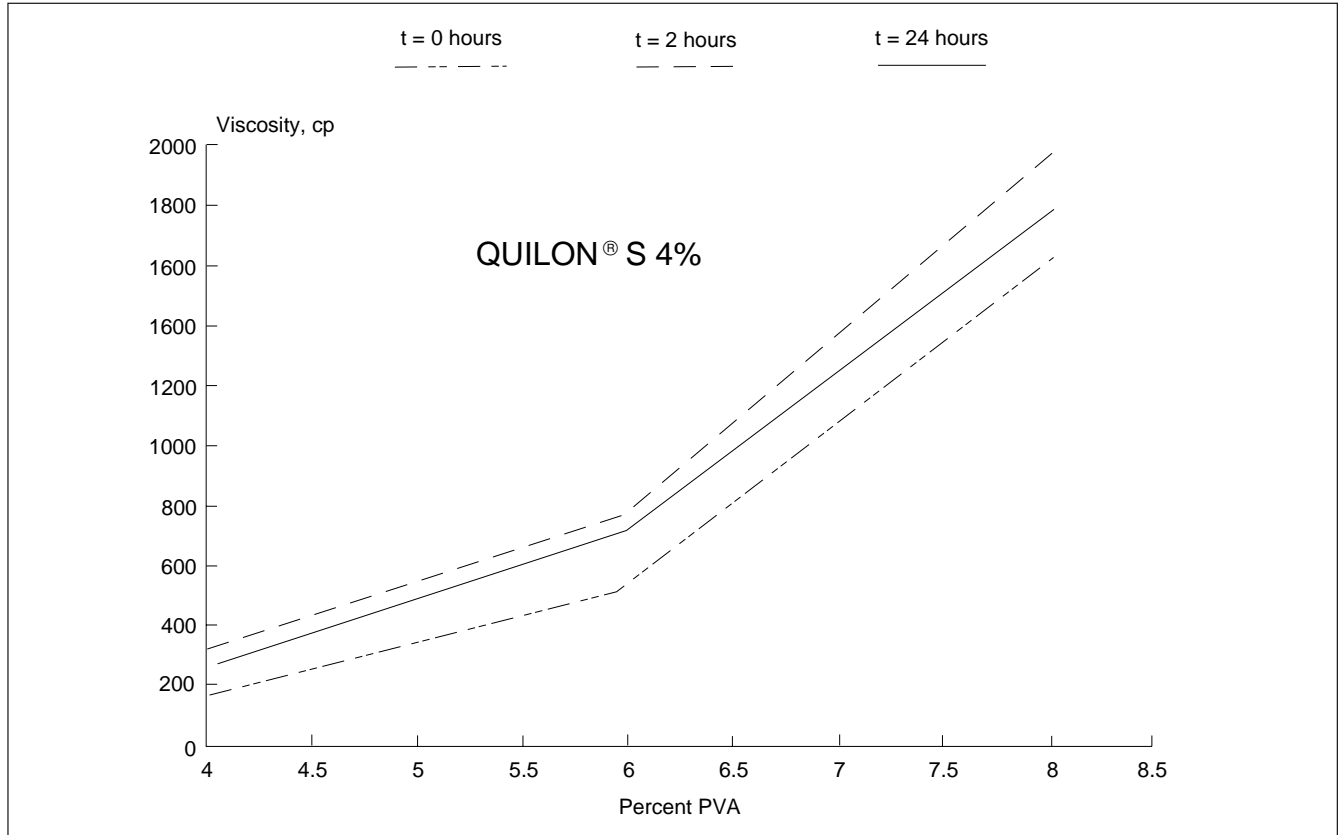


Figure 5. Viscosity vs. Percent PVA (88% hydrol.)



Similar data have been obtained for solutions containing PVA from other manufacturers. The curves were essentially the same as in Figures 4 and 5, except that at high ratios of QUILON® to PVA, some viscosities were slightly higher after 26 hours aging.

An outstanding feature of these solutions is that high viscosity can be combined with good stability. The viscosity can be increased by increasing the concentration of either the QUILON or the polyvinyl alcohol.

C. FORMULATIONS OF QUILON S AND FULLY HYDROLYZED POLYVINYL ALCOHOL

Solutions of QUILON S and fully hydrolyzed polyvinyl alcohol continuously thicken and eventually gel. As noted previously, increasing the concentration of QUILON increases the stability. The stability of the mixture can also be increased by first reducing the pH of the PVA into the 3–4 range. Although hydrochloric acid can be used for this purpose, the best paper-treatment properties are obtained with acetic acid, preferably added while the PVA is solubilized by heating. The best results are obtained with an amount of acetic acid corresponding to 95% hydrolysis of the polyvinyl alcohol. The PVA is then solubilized by the usual procedure of heating at 195 to 205 F for 10 to 30 minutes.

Figures 6 and 7 give viscosities of 4% and 6% solutions of ELVANOL® HV (99% hydrolyzed, with acid added as described above) as functions of the QUILON concentration. The viscosity decreases as the QUILON becomes more concentrated. Solutions with low ratios of QUILON to polyvinyl alcohol thicken and gel readily while those with ratios of 1:1 and 1.5:1 are usable for about 6 hours. Solutions with the higher QUILON:PVA ratios show moderate viscosity increases of about 25% in 24 hours.

The viscosities of solutions of QUILON S and 98% hydrolyzed PVA are relatively independent of QUILON content. With time, however, solutions with QUILON:PVA ratios of 1:1 increase about 70% in viscosity; most of this increase takes place in the first 2 hours or less. Here again, the stability is improved at higher QUILON ratios. It may be practicable to age a solution in the preparation room, so that the viscosity does not significantly increase during an 8-hour shift on a treatment line.

In a few high-spot experiments, additives such as plasticizers, have been found to improve the stability of some of the formulations. When these formulations were used to coat paper, however, the resistance to grease and water were decreased.

Figure 6. Viscosity vs. QUILON® Concentration

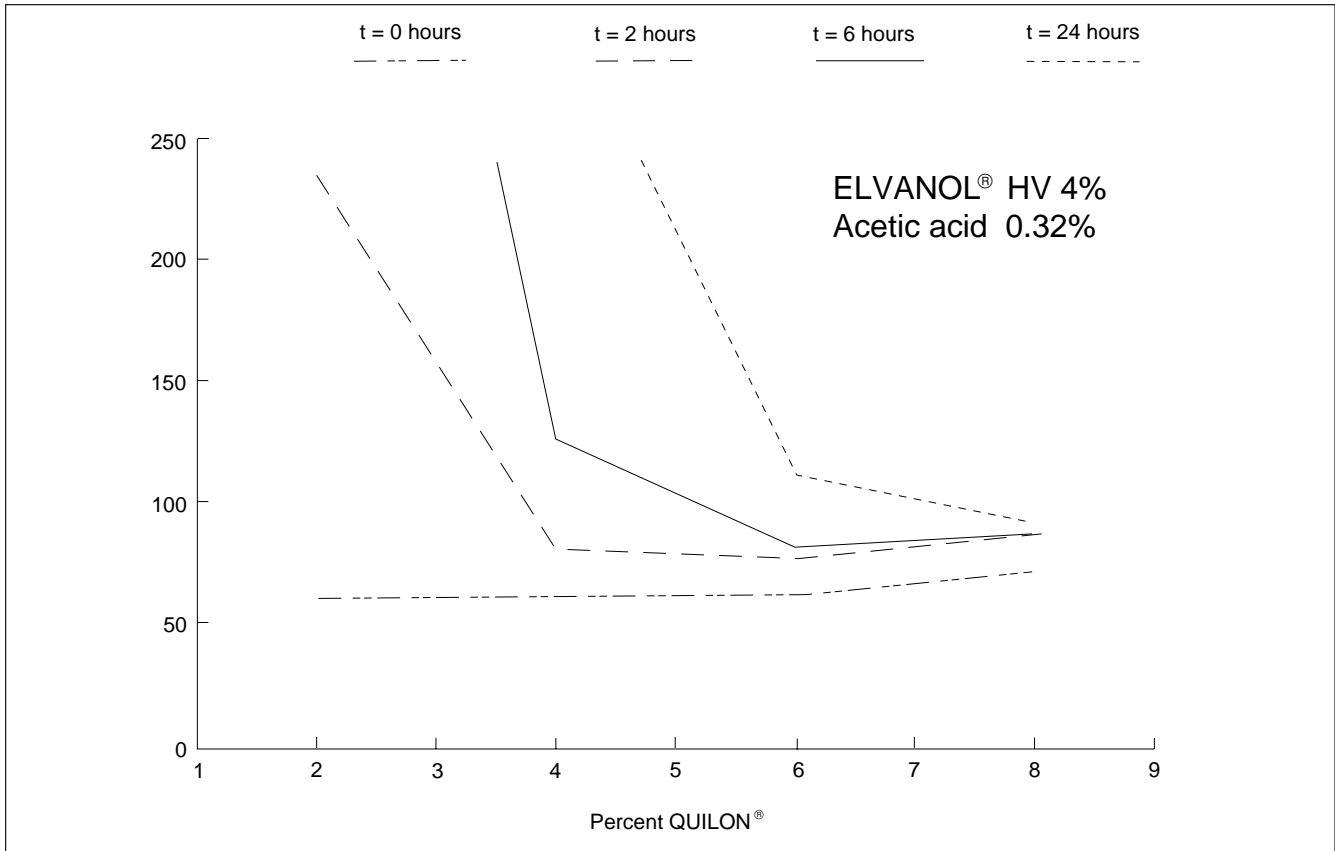
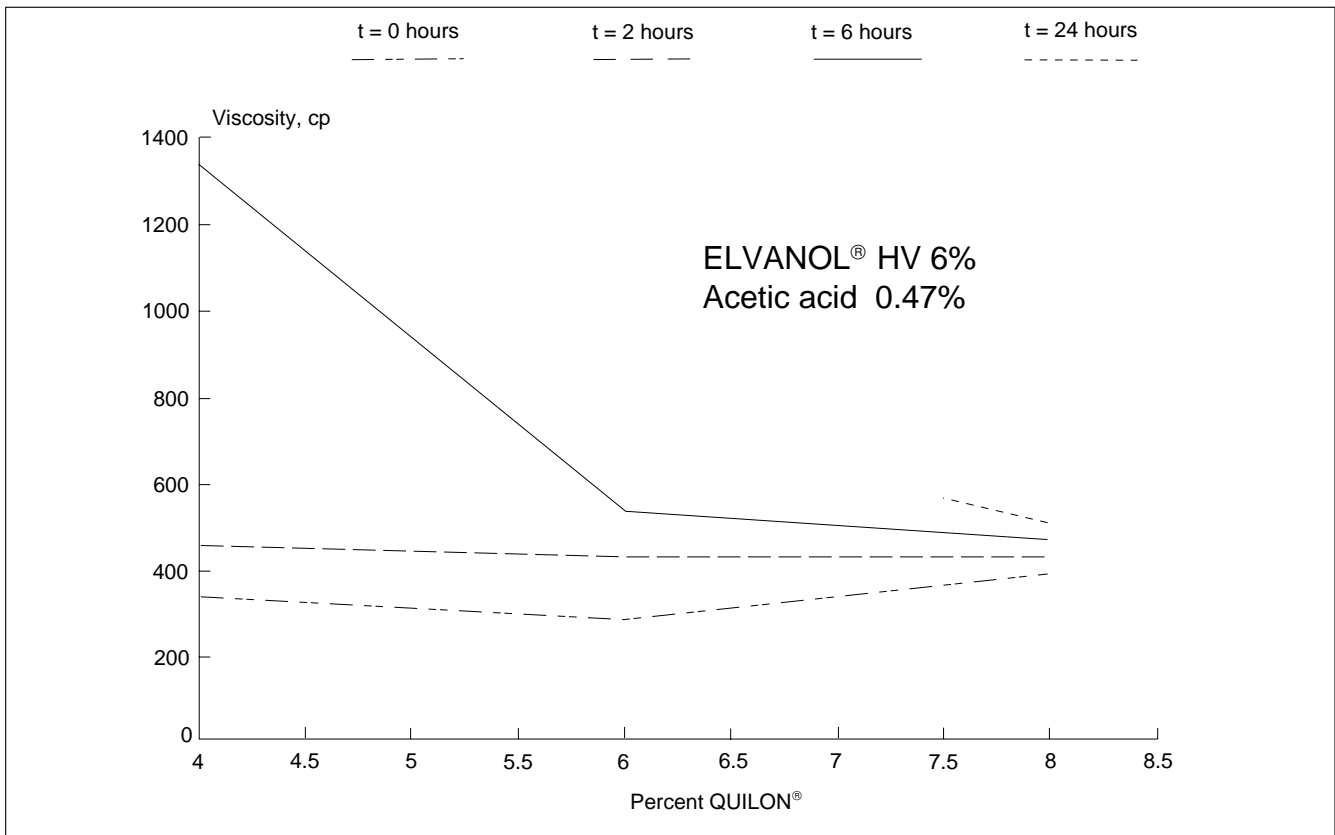


Figure 7. Viscosity vs. QUILON® Concentration



D. LOW VISCOSITY POLYVINYL ALCOHOL

The work described above was done with high-viscosity polyvinyl alcohols, which are desirable in paper coatings. Although only a few checks have been made, products of the types shown in *Figure 1* would probably give essentially the same results as the ones exhaustively tested. In addition, the low-viscosity, medium-viscosity and high-viscosity materials probably have the same viscosity characteristics at any given hydrolysis; slower gelling should be obtained, however, if the original viscosities are lower.

E. PREPARATION OF QUILON®-POLYVINYL ALCOHOL FORMULATIONS

The polyvinyl alcohol solutions were prepared by heating at 8 to 10% solids, adding the acetic acid before heating when necessary. The solutions were prepared in four-liter resin kettles heated with steam; the temperature was held at about 90 C (195 F) or higher for 30 minutes to ensure solubilization.

The QUILON®-PVA solutions were prepared by first adding the necessary water to the concentrated polyvinyl alcohol solution, mixing, and then adding the QUILON with further mixing. This procedure appeared to give better paper performance than adding the QUILON to the water first and then adding the polyvinyl alcohol. Adding the QUILON before heating to solubilize the

polyvinyl alcohol gave poor paper-coating results.

In the absence of PVA, QUILON solutions are usually neutralized (pH -4) before application to paper. With PVA this may or may not be advisable. Neutralization causes more rapid gellation and is inimical to grease and water repellency. It does, however, improve release. Neutralizer is always added last.

F. PAPER COATING PROPERTIES

Unneutralized formulations with QUILON:PVA ratios of 1:1 to 1.5:1 gave the best coatings on paper. A 1:1 ratio is best economically, and increasing to the 1.5:1 ratio does not change the properties appreciably. The higher ratio would be advantageous for other reasons, however; e.g., if a more stable formulation is desired with a fully hydrolyzed polyvinyl alcohol, or a higher viscosity is desired with a partially hydrolyzed polyvinyl alcohol as discussed previously.

Table 2 summarizes the properties of the most favorable coatings. As stated above, no one coating gives the best results in all tests. A coating recommendation must therefore take into consideration the concentration and viscosity requirements along with the intended use for the end product; it will be necessary to select a formulation based on *Table 2* in conjunction with the viscosity-concentration data presented in the previous sections.

The first formulation in *Table 2*, which contains 4%

Figure 8. Viscosity vs. QUILON® Concentration

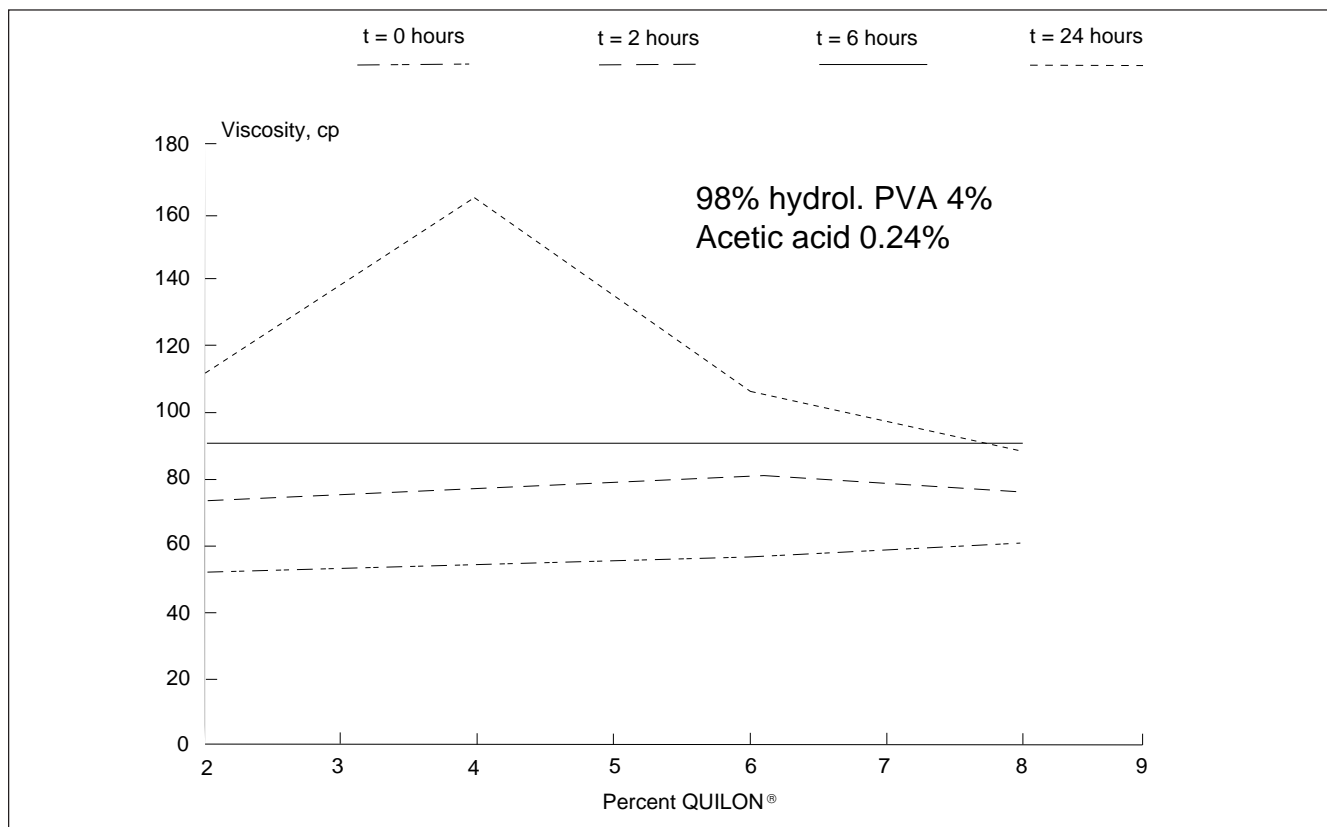
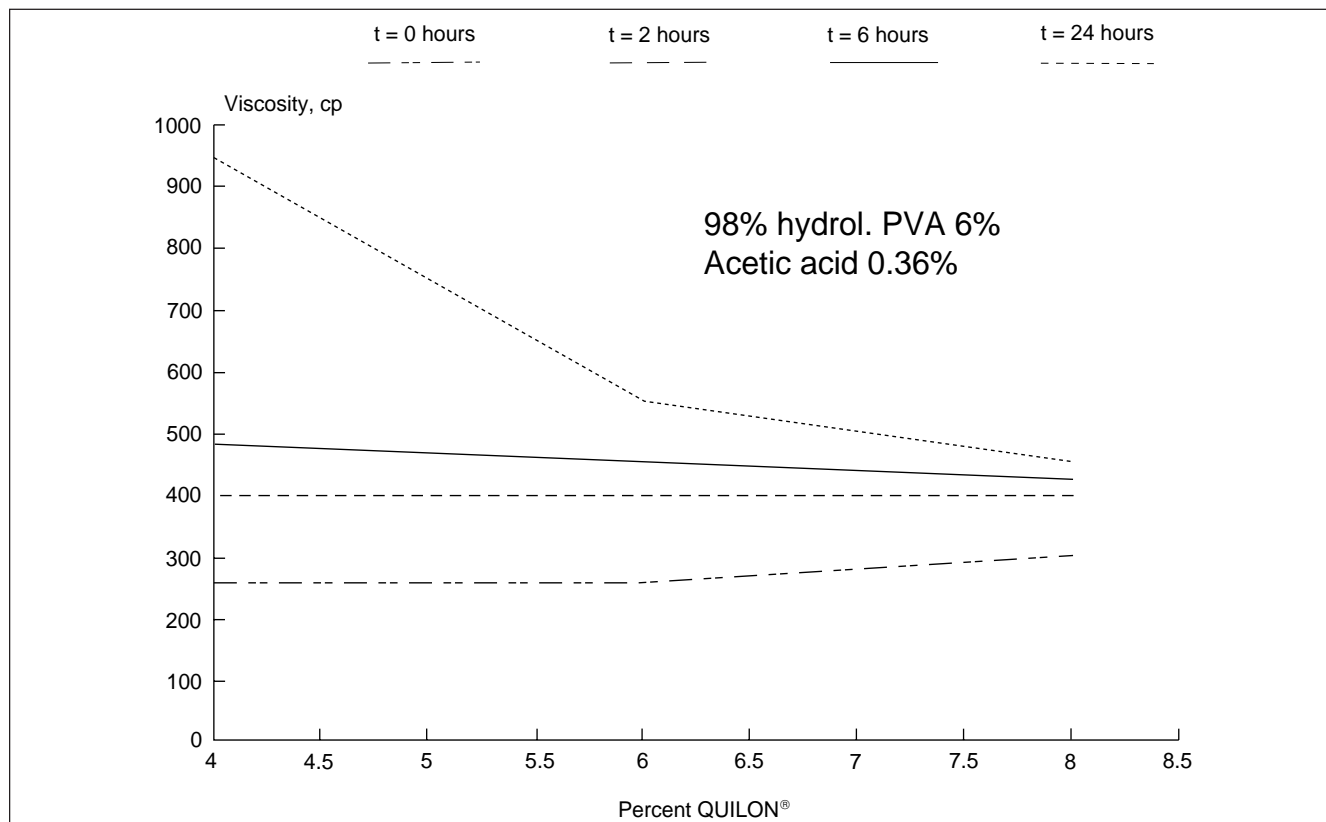


Figure 9. Viscosity vs. QUILON® Concentration



QUILON S, 4% ELVANOL® HV and acetic acid, shows the best combination of coating properties: the water and grease resistance are outstanding and release is good. It also uses the lowest cost polyvinyl alcohol. The main drawback of this system is poor stability: viscosity increases rapidly, and the formulation would have to be used within 8 hours. This will not be too important if the rate of usage is high.

The formulation with the best release is essentially the one discussed in the paragraph above, with the addition of Standard Neutralizer.* This decreases the water and grease-resistance slightly and further decreases stability.

The stability can be improved by using a polyvinyl alcohol with a lower degree of hydrolysis, but the water and grease resistance are slightly decreased. The release is still good, but the Keil test value is considerably above the values obtained with the formulations above.

The best grease resistance is obtained with an 88% hydrolyzed polyvinyl alcohol, which also gives a stable solution. The water resistance is not as good as before, however, but is better than that from ELVANOL® HV alone, which is the most water-resistant type of polyvinyl alcohol. The release was good, but the Keil test values were again higher than the best obtained.

Laboratory equipment was used in all this work. Im-

proved results can probably be obtained with regular plant equipment used continuously.

The concentration of ELVANOL HV in the control in this work was 7% since this was approximately equivalent to the QUILON S formulations in cost and it was desired to keep the solution viscosity close to those of the formulations. A higher concentration would have increased the viscosity considerably and would give too heavy a coating.

Viscosities and pH of the solutions when prepared and when used to treat the paper are given in *Table 2*, along with the elapsed time between solution preparation and paper treatment.

This work used unbleached, Kraft flour-bag paper on a laboratory coater, essentially a doctor blade with an adjustable gap. The coated paper was air-dried to near dryness and then drum dried at 245 F. This procedure had some possible drawbacks. Air bubbles occasionally remaining on the surface of the paper could be a source of pinholes in the coating. Furthermore, the drying procedure is not typical of a commercial treatment. A plant operation in which the paper is passed between heated rollers would cause the coating to flow slightly and would also produce a slight calendering effect which would improve the coating.

With one exception, the basic weights of the treated

* A formate-urea buffer. See the brochure "QUILON® Chrome Complexes for Release and Surface Treatment; Properties, Uses, Storage and Handling."

TABLE 2
QUILON® S-Polyvinyl Alcohol Formulations on Kraft Paper

Formulation	Formulation Properties					Water Resistance			
	Original Viscosity, ¹ cp	pH	Treating Viscosity, ¹ cp	pH	Elapsed Time, hr	Basis Weight, lb/3000 ft ² (g/m ²)	Drop Roll-off ³	IP ⁴ Test, sec	Cobb ⁵ Size, mg/m ²
4% QUIILON 4% ELVANOL HV ²	75	2.60	103	2.05	3.0	41.2 (67)	5	41	19.20
4% QUIILON 4% ELVANOL HV 4% Standard Neutralizer	75	3.40	200	2.85	2.0	41.8 (68)	2	3	20.42
4% QUIILON 4% 98% Hydrolyzed PVA	73	2.95	80	2.25	1.1	41.6 (67)	3	6	21.07
4% QUIILON 4% 98% Hydrolyzed PVA 4% Standard Neutralizer	55	3.50	83	2.55	4.0	42.7 (69)	0	<2	23.31
4% QUIILON 4% 88% Hydrolyzed PVA	200	2.75	285	2.15	4.0	41.3 (67)	0	<2	22.55
7% ELVANOL HV	—	—	585	7.05	—	— 41.4 (67)	0	<1	23.46
None (Untreated Paper)	—	—	—	—	—	— 37.5 (61)	0	<1	30.82

¹ Brookfield

² Acetic acid added before heating; equivalent to 95% hydrolysis

³ 0–5 scale, 5 best

⁴ International Paper water repellency test

⁵ 120 seconds

TABLE 2 (continued)
QUILON® S-Polyvinyl Alcohol Formulations on Kraft Paper

Grease Resistance			Release			
Turpentine		Olive Oil		Keil Test, ⁷ g	Scotch Tape Test, g pounds	Mullen Burst
Penetration, sec	Diameter, in	Penetration, sec	Diameter, in			
1800+	5/8	600+	3/4	487	306	35.2
1800+ ⁶	11/16	600+ ⁶	3/4	456	192	37.4
1800+	5/8	600+	1	664	277	40.0
1800+ ⁶	3/4	600+	15/16	718	—	41.0
1800+	1/2	600+	1-1/8	736	—	40.2
<1	2-1/2	10	2-1/8	—	416	39.0
<1	2-3/4	<1	3-1/2	Tore	Tore	35.0

⁶ One test sample developed a single pinhole

⁷ Tappi Release Test RC-283

paper fell in a fairly narrow range. The coating weight was about 4 pounds per ream.

Water resistance was evaluated by three methods: The first is the standard 0–5 drop roll-off method, a rating of 5 indicating perfect roll-off. Water repellency was also evaluated using the International Paper test. These values on the whole were quite poor. The single treatment drop roll-off of 5 had an I.P. test time of 41 seconds, compared to a value of thousands of seconds commonly obtained with QUILON® alone on paper. The third method was the Cobb Size test, which measures the amount of water absorbed in 120 seconds' contact. The Cobb size values correlated fairly well with the other test values, and were better than either polyvinyl alcohol by itself or untreated paper.

Grease resistance was measured by two tests, using turpentine and olive oil. In the turpentine test, 5 drops of turpentine dyed with red oil is placed on a piece of test paper and time necessary for penetration is measured. If the turpentine does not penetrate in 30 minutes, the test is stopped. The diameter of the spot is measured after 30 minutes. The olive oil test is similar, except that 10 drops are used, with a test time of 10 minutes. With both materials it was found that, if the grease did not penetrate in the test time, it would not penetrate at all. These tests give an indication of resistance to penetration and also a measure of the grease crawl. As noted in *Table 2*, some treatments prevented spreading even with a pinhole in one of the samples.

Release was measured using two tests. In the Keil test, Tappi Routine Control Test #283, a 6-inch piece of one-inch wide adhesive tape is placed on the test paper, rolled, and then heated at 70 C for 20 hours with a weight of 1/4 psi on the tape. The force to pull off the tape is then measured. In the Scotch® tape test, one-inch Scotch tape is applied to the paper and the sandwich is passed through a wringer with full pressure. The sample is allowed to condition overnight at room temperature before the stripping force is measured.

The strength of the paper was measured using the Mullen Burst test. All the coated papers were stronger

than the untreated paper. The strength did not correlate well with either solution pH or coating weight.

G. FILM PROPERTIES

The addition of QUILON to polyvinyl alcohol changes the properties of films formed from the solution. The adhesion of the film is increased and the grease and water resistance are improved. The adhesion to glass and metal is so good that we were unable to isolate films cast on these substrates.

Air-dried films of two formulations and the polyvinyl alcohols alone were formed on MYLAR® polyester film to enable the continuous film to be peeled off. The formulations and film properties are shown in *Table 3*. Grease resistance was measured by clamping the film in a frame, inclining it at 30 degrees, and adding drops of turpentine and olive oil. The drops did not spread and did not wet the QUILON-ELVANOL® HV film. They wetted the film from QUILON and 88% hydrolyzed PVA, but did not spread. The drops did spread on both polyvinyl alcohol films with no added QUILON.

Water resistance of the films was measured by placing the film in a frame on top of a beaker and dropping water from a burette held one inch above the film at a rate of about one milliliter per minute. The films stretched and finally broke as the water was added. The time and volume of water held by the film were recorded. The two QUILON formulations retained the water far longer than the control films.

The water resistance of the same four films was also measured on glass. The glass plates were placed in a Gardner washability machine, covered with water and stroked with the one-pound brush; the number of strokes needed to penetrate the film and to remove the film across the full width were recorded. Here again, QUILON improves the water resistance.

H. OTHER POSSIBLE USES OF QUILON–POLYVINYL ALCOHOL FORMULATIONS

The former discussion has mainly concerned the use of QUILON–polyvinyl alcohol formulations in paper coating and films. *Table 1* suggests other possible uses. For example, QUILON should improve the water and solvent-resistance of adhesives, ceramic binders, textile sizes and mold-release agents.

TABLE 3
QUILON® S-Polyvinyl Alcohol Films

Formulation	Film Thickness 10 ⁻² in	Grease Resistance ¹		Water Retention ¹ Seconds	Water Retention ¹ Volume, mL	Water Resistance of Films on Glass ¹	
		Turpentine	Olive Oil			Strokes to First Hole	Strokes to Remove Full Width
% QUIILON % ELVANOL HV ²	0.5	Very Good No Spread	Very Good No Spread	2502	42.4	7,000	13,600
% QUIILON % 80% Hydrolyzed PVA	0.5	Good No Spread	Good No Spread	414	7.0	400	1,400
% ELVANOL HV	0.5	Spreads	Spreads	41	0.7	20	50
% 88% Hydrolyzed PVA	0.5	Spreads	Spreads	5	0.2	10	16

¹ Description of test in text.

² Acetic acid added before heating, equivalent to 95% hydrolysis.

