

Flow Properties at Elevated Temperatures and Clarity of HSPAN Gel–Water Dispersions

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SYNOPSIS

Dispersions of hydrolyzed-starch–polyacrylonitrile (HSPAN) gel and distilled water underwent permanent diminution of room-temperature viscosity after maintenance above a threshold temperature of 75°C for periods of several weeks. Below the threshold temperature, viscosity measured at room temperature was unaffected. Above the threshold temperature, the final room-temperature viscosity exponentially varied as the inverse absolute temperature, and the viscosity decreased with increasing temperature. The HSPAN gel–distilled water dispersions exhibited both yield stress and velocity slip at a solid boundary, but the latter was not present at low shearing stresses. The former inhibited natural convection in a vertical slot with an imposed horizontal temperature difference. Clarity of the dispersions was demonstrated by a character-visibility test. Deaerating the distilled water by boiling before mixing with HSPAN gel improved the clarity of the resulting dispersion by eliminating the formation of bubbles at elevated temperature. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Hydrolyzed-starch–polyacrylonitrile (HSPAN) gel, sometimes referred to as a slurper due to its ability to absorb up to 800 times its weight of distilled water, is a corn starch product developed in the early 1970s at the U.S. Department of Agriculture Northern Regional Research Laboratory, as described by Weaver et al.¹ In general, its development is the result of studies directed at finding nonfood uses for agricultural products, especially corn starch, as discussed by Chinnaswamy and Hanna.²

Hardin and Burmeister³ observed that gel–water dispersions formed from commercially available powder forms of HSPAN gel can exhibit both velocity slip at solid boundaries and yield stress; degeneration from a thick form as much as 20,000 times more viscous than water into a thin, watery form after lengthy maintenance at elevated temperatures was also observed. Yield stresses in similar dispersions had previously been reported by others. Bagley and Christianson⁴ observed 1000–3000 dyne/cm² yield stress in wheat starch–water dispersions

cooked at 60–75°C for 15–75 min; the yield stress increased with increasing temperature. Christianson and Bagley⁵ observed 54–250 N/m² yield stress in corn starch granule–water dispersions at 67–80°C; the yield stress increased with increasing temperature and occurred only when the volume fraction of granules exceeded 0.6. Taylor and Bagley⁶ reported 0–600 dyne/cm² yield stress for dispersions of hydrolyzed-cellulose–polyacrylonitrile graft copolymer (HCPAN) in water and NaCl solutions; the yield stress linearly increased with cQ , where c is concentration (g polymer/g suspension) and Q is swelling weight (g swollen gel/g dry polymer) in excess solvent of the same ionic strength. No yield stress was observed for $cQ < 1.7$, and the yield stress was unaffected by NaCl in the solvent.

Such behavior of an HSPAN gel–water dispersion is important to its long-term use at temperatures substantially above room temperature as might be encountered, for example, if it were subjected to a manufacturing process or used to stabilize a solar pond, inhibiting natural convection. In the following, more detailed measurements pertinent to determination of viscosity degeneration after lengthy maintenance at elevated temperatures are described. Measured values of apparent velocity slip and yield

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stress and the results of tests to demonstrate the clarity of a representative dispersion are also given.

APPARATUS AND PROCEDURE

Water Lock G-400 HSPAN gel in powder form was obtained from the Grain Processing Corporation (Muscatine, IA). Dispersions of this HSPAN gel in distilled water were prepared by slowly adding the powdered gel to a continuously stirred container of water, usually at room temperature but occasionally at about 90°C both to speed the dispersion process and to deaerate the water. To enable ready description of dispersions, a notation with three identifiers separated by dashes was devised. The first identifier indicates by *D* that distilled water was used; *T* denotes tap water. The second identifier indicates the ratio of HSPAN gel to water mass in the dispersion in hundredths of a percent. The third identifier denotes the HSPAN gel. Thus, *D-10-G400* was with distilled water with 0.1% by mass G400 (Water Lock from the Grain Processing Corporation) HSPAN gel.

Natural Convection

A natural convection test cell, shown in Figure 1, was constructed from a glass-wall aquarium tank for the purpose of ascertaining the temperature difference across a vertical slot required to initiate natural convection in a HSPAN gel-distilled water dispersion; the absence of natural convection demonstrates the existence of an effective yield stress.

Vertical slot geometry was selected because natural convection currents occur in it even with vanishingly small temperature differences for a fluid without a yield stress, according to Churchill.⁷

One side of the vertical slot consisted of an immersion heater sandwiched between an aluminum plate in contact with the test fluid and an insulated back. Styrofoam insulation of $\frac{3}{4}$ -in. thickness was affixed to all exterior surfaces of the aquarium. Three type *K* thermocouples were held with aluminized adhesive tape onto the side of the aluminum plate in contact with the test fluid. The other side of the vertical slot was a water-cooled aluminum plate to which three type *K* thermocouples were affixed to the side in contact with the test fluid.

Electrical energy was supplied to the heater at a rate determined by measuring the voltage difference, controlled by a Variac, imposed across the heater and the current that flowed through the heater; the product of voltage drop and current equaled the heat flow. The heat transfer rate between the heated and cooled vertical plates equaled the measured electrical input to the heated vertical plate minus the heat loss QL estimated from the relationship

$$QL = UL(T_b - T_r)$$

where T_b is the temperature at the back of the heated vertical plate, T_r is the temperature of the room air, and UL is a heat loss coefficient determined by calibration as described by Hardin and Burmeister.³

Verification that the natural convection test cell can provide accurate measurements was obtained

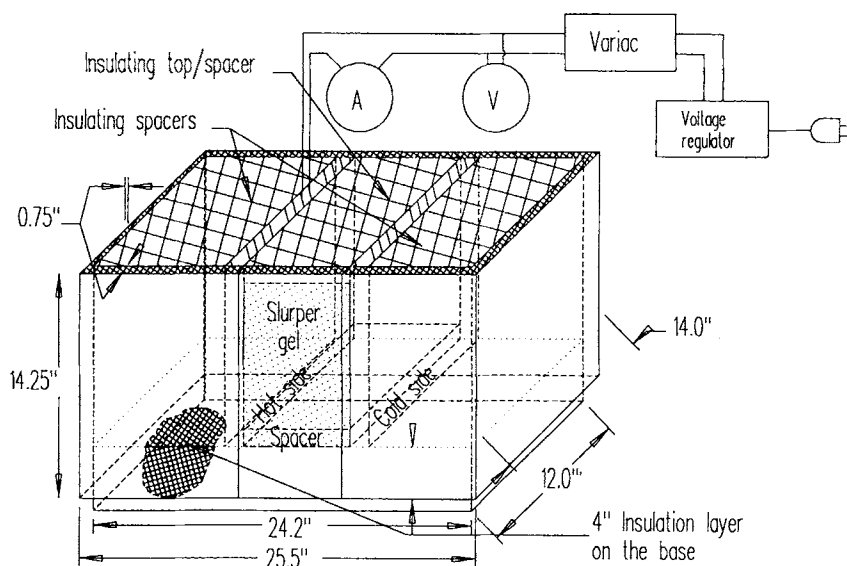


Figure 1 Natural convection test cell.

by comparing measurements for distilled water and air with two accepted correlations for the Nusselt number. One, due to MacGregor and Emery,⁸ is

$$Nu = 0.42 Ra^{0.25} Pr^{0.012} \left(\frac{l}{x}\right)^{-0.3} \quad (1)$$

for $10^4 < Ra < 10^7$, $1 < Pr < 2 \times 10^4$, and $10 < l/x < 40$, where $Nu = hx/k$ is the Nusselt number, $Ra = g\beta\Delta T x^3/\nu\alpha$ is the Rayleigh number, $Pr = \nu/\alpha$ is the Prandtl number, l/x is the aspect ratio, h is the natural convection heat transfer coefficient, x is the vertical slot spacing, l is the slot height, k is the fluid thermal conductivity, g is the local acceleration of gravity, β is the fluid coefficient of thermal expansion, ΔT is the temperature difference between the heated and cooled plates, ν is the fluid kinematic viscosity, and α is the fluid thermal diffusivity. The other, due to Catton,⁹ is

$$Nu = 0.22 \left(Ra \frac{Pr}{Pr + 0.2}\right)^{0.28} \left(\frac{l}{x}\right)^{-0.25} \quad (2)$$

for $Ra < 10^{10}$, $Pr < 10^5$, and $2 < l/x < 10$. For distilled water, the heat loss correction was 7–25% of the input to the electric resistance heater. The corrected input into the resistance heater was within 20% of the calorimetric heat flow rate given by the product of the mass flow rate, specific heat, and temperature rise of cooling water through the cooled plate. Linear departure from the pure conduction regime at vanishingly small Ra was observed, as reported by Churchill,⁷ from the finding of Batchelor¹⁰ that

$$Nu = 1 + \frac{Ra}{720} \left(\frac{x}{l}\right) \quad (3)$$

Makeup distilled water was added periodically, about 0.5 liter/week, to the HSPAN gel-distilled water dispersion at the top of the vertical slot to compensate for evaporation. The makeup distilled water was not stirred into the dispersion. Sufficient time (2–3 days depending on the amount of dispersion in the cell) was allowed to elapse after any change for steady state to ensue before measurements were recorded.

Viscosity

A Brookfield linear-variable differential transformer (LVDT) rotating-spindle viscometer with cylindrical spindles was used to measure viscosity of HSPAN gel-distilled water dispersions. All viscosity mea-

surements were made at room temperature with the fluid in an 800-mL beaker of 10.4 cm diameter filled 10.2 cm deep. The initial level of the dispersion in the beaker was marked on the outside of the beaker; because dispersion viscosity is dependent on the fraction of water, makeup distilled water was added whenever the elapsed testing time (often several hours) allowed appreciable evaporation to occur.

A strip-chart recorder was used to obtain continuous traces of the viscometer torque to assist in ascertaining that steady conditions had been achieved. For example, even at the lowest viscometer rotational speed of 0.3 rpm, as many as 4 hours were required before quasi-steady conditions were achieved. The viscometer output often fluctuated by 1–10%, probably due to periodic buildup and breakdown of a structure in the dispersion. The accuracy of the viscometer was established by comparing measured glycerin and water viscosities with values reported in the literature.

HSPAN gel-distilled water dispersions were maintained at elevated temperature for periods of up to a month in glass beakers placed atop temperature-controlled electrical heaters. Usually, the heater temperature was controlled by the output from a proportional temperature controller whose input was from a thermocouple immersed in the dispersion and with insulating styrofoam jackets on the sides of the beakers. In some tests, however, the temperature level of the heater was set and the un-insulated beaker rested on the heater surface; then temperature sometimes varied throughout the dispersion by as much as 20°C, but usually only by 5–10°C. In all cases, the tops of the beakers were sealed with a plastic wrap to retard water evaporation. Makeup distilled water was stirred into a dispersion after it had been removed from the heater and had cooled to room temperature.

A Corning Model 610A pH meter was used to monitor the pH of the HSPAN gel-distilled water dispersions. The pH was measured before each viscosity measurement, at the beginning and end of the time that a dispersion was maintained at elevated temperature, and at intervals during the time that a dispersion was in the natural convection test cell.

The white-light clarity of a dispersion relative to distilled water was qualitatively demonstrated by making use of a technique described by Craig et al.¹¹ A 35-mm camera mounted on a tripod was positioned in front of a fluid-filled 300-mL beaker that had the word “CLARITY” taped onto the back outside. A slide projector positioned behind and slightly to the side of the camera illuminated the beaker;

light from the projector was transmitted through the fluid, reflected from the word, and transmitted through the fluid, finally being recorded by the camera.

RESULTS AND DISCUSSION

Natural Convection

Steady-state measurements with G400 HSPAN gel-distilled water dispersion in the natural convection test cell gave the results shown in Figure 2. To form the Nusselt and Rayleigh numbers, properties of distilled water were used for all fluid properties except that the effective viscosity of the HSPAN gel-distilled water dispersion measured in the Brookfield viscometer at 0.3 rpm was used. The pH of the dispersion did not vary with time and ranged from 7.09 to 7.15, normal for distilled water.

As seen in Figure 2, for the "D-10-G400, aspect ratio = 1.7" data, the Nusselt number is unchanging at only slightly greater than unity, indicating that heat flowed between the vertical heated and cooled

plates by conduction alone. Observations of particles in the dispersion through the viewing window confirmed that there were no convection currents. The temperature of the heated plate ranged from 23°C to 87°C and the temperature of the cooled plate ranged from 15°C to 21°C. Even though the 87°C temperature is above the threshold temperature of 75°C discussed later, at which the dispersion begins to degenerate after lengthy exposure, no change in dispersion properties was discerned.

The aforementioned comments apply to the "D-10-G400, aspect ratio = 2.6" data as well. Since the dispersion is the same for these two sets of data, the Rayleigh number/aspect ratio combined range, 2×10^2 – 2×10^5 , is large enough to support the interpretation that there is no tendency to natural convection, and the combined data lie only a few percent above unity and well below both Eq. (3) for vanishingly small Ra and Eq. (1) for large Ra .

The "D-20-G400, aspect ratio = 4.2 and = 12" data lie in the Rayleigh number/aspect ratio range of 4.5×10^0 – 1.5×10^3 . As for the D-10-G400 dispersion, these data lie below both Eq. (3) and Eq. (1). The temperature of the heated plate ranged from 22°C to 57°C.

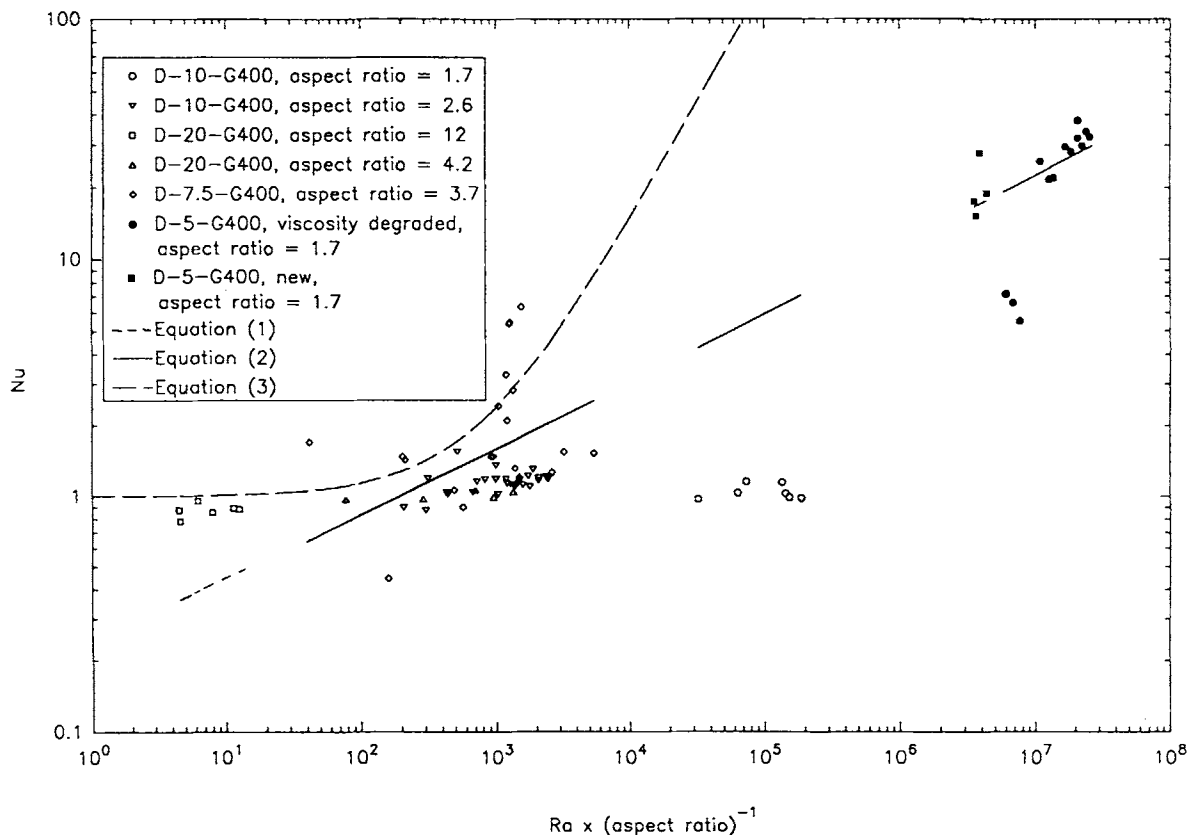


Figure 2 Nusselt number versus Rayleigh number–inverse aspect ratio product for D-10-G400 HSPAN gel–distilled water dispersion.

The "D-7.5-G400, aspect ratio = 3.7" data lie in the Rayleigh number/aspect ratio range of 1.5×10^2 – 1.5×10^3 . The data begin substantially to rise above a unity Nusselt number at a Ra /aspect ratio of 10^3 , suggesting that natural convection begins to be important then. This is consistent with Eq. (3), as seen in Figure 2. The data even lie above Eq. (1) for a Newtonian fluid. After approximately 2 weeks in the natural convection cell, it was observed that the HSPAN material settled to the bottom of the slot with clearer water at the top. The HSPAN fraction might have been below the level for a saturated dispersion, as discussed by Taylor and Bagley¹²; the dispersion was initially saturated, however.

The "D-5-G400, new, aspect ratio = 1.7" data suggest Newtonian behavior, lying close to the Newtonian correlation. The viscosity-degraded group of these data was obtained after it was observed that there had been a change in the consistency of the dispersion and that settling had occurred. The viscosity of the degenerated dispersion was measured to be one fifth of its initial value. The temperature of the heated plate ranged from 22°C to 31°C.

Slip and Yield Stress

In the development of the relationships reported by Hardin and Burmeister³ to relate Brookfield viscometer torque to HSPAN gel-distilled water dispersion velocity slip and yield stress, it is assumed that there is purely circumferential velocity in the region between the rotating spindle and the beaker wall. To test the accuracy of this assumption, flow was visualized about a rotating 1 spindle in a D-10-G400 dispersion that had been heated 2 days at 80°C.

Fluorescent pigment, first dusted onto a razor blade that was subsequently thrust into the dispersion at a right angle to the surface, was formed into a sheet along a radial line from the center of the beaker. Then the cylindrical spindle was inserted into the center of the beaker. Upon illumination by ultraviolet light, the pigment showed the region in which dispersion motion had occurred several hours after initiation of spindle rotation, as illustrated in Figure 3. The region in which the dispersion flows includes a region at the air-dispersion interface, as assumed. But this region is shallow, and most of the spindle is enveloped by a thin shell of circulating dispersion that extends only about a third of the way to the beaker wall. Hence, the measurements of displacement of a radial line drawn on the dispersion at the air-dispersion interface, the procedure devised by Hardin and Burmeister³ and described

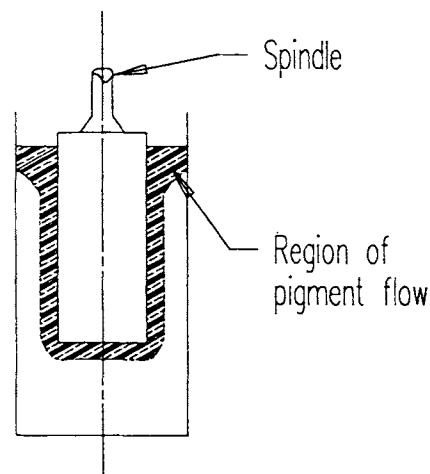


Figure 3 Sketch of D-10-G400 HSPAN gel-distilled water dispersion flow about a rotating Brookfield viscometer spindle in a beaker.

later in this article, might give results for velocity slip and yield stress that are not properties of the fluid alone.

The results of the velocity slip and yield stress measurements are in Table I. Blanks in the table indicate that the phenomenon described by the parameter was not observed. The velocity slip coefficient B is related to shear stress τ by the relationship

$$v_{\text{slip}} = B\tau$$

in which v_{slip} is the relative tangential velocity between the fluid and the solid surface on which the shear stress acts. In terms of the radius r_o of the beaker in which measurements are made, the shear stress τ_i acting on the viscometer spindle, and the angular velocity ω_c at which the outer annulus of dispersion is in flywheel motion, the slip coefficient is given by

$$B = r_o^3 \omega_c / \tau_i r_i^2$$

The yield stress is found from additional observation of the inner radius r_c at which the outer annulus of dispersion is in flywheel motion as

$$\tau_c = \tau_i r_i^2 / r_c^2$$

The G400 HSPAN gel in this study was from a batch different from the G400 HSPAN gel previously used by Hardin and Burmeister,³ partially explaining differences with their results; however, the yield stress of the dispersion is of the same magnitude as that, 0.32–1.35 N/m², previously

Table I Slip Coefficients and Yield Stresses for HSPAN Gel–Water Dispersions

Sample	Spindle No.	Spindle Speed, (rev/min)	Slip Coefficient, (m ³ /N s)	Yield Stress, (N/m ²)
From the present study				
D-7.5-G400	1	0.3		0.99
D-7.5-G400	1	1.5		1.04
D-7.5-G400	1	3.0		0.32
D-10-G400	1	0.3	7.36×10^{-5}	0.99
D-10-G400	2L	0.3	0.37×10^{-5}	1.35
D-10-G400	2L	0.3	0.12×10^{-5}	1.34
D-10-G400	2L	1.5	0.20×10^{-5}	
D-10-G400	2L	0.6	0.23×10^{-5}	
From Hardin and Burmeister ³				
T-50-G400 ground	1	12.0	0.0251	1.549
T-50-1-G400	1	30.0	0.0185	2.424
T-25-1-G400	1	0.6	0.0208	0.917
T-25-1-G400	1	1.5	0.0403	1.438
D-25-1, 4-G400	1	60.0	0.0145	1.566
T-20-1-G400	1	1.5	0.0264	1.33
D-10-1-G400	1	6.0	0.3502	0.04

found. These values are considerably below the yield stresses (100–300 N/m²) reported by Bagley and Christianson⁴ for a wheat starch–water dispersion and those (54–250 N/m²) reported by Christianson and Bagley⁵ for a corn starch granule–water dispersion. However, they are in the range (0–60 N/m²) reported by Taylor and Bagley⁶ for HCPAN–water dispersions. The possibility that the cQ value for the HSPAN gel–water dispersions of the present study was near the lowest value for which yield stress occurs was not tested. Also, De Kee et al.¹³ point out that yield stresses determined from a flow situation, as in a viscometer, sometimes differ from those determined from a static situation.

The slip coefficient values in this second phase are nearly four orders of magnitude smaller than those previously measured; this might be because the present measurements were made at smaller spindle rotational speeds than those of the previous study. Graham et al.¹⁴ report that the microstructure of a concentrated suspension can be affected by a viscometer since particles migrate to the low shear-rate regions of the flow field. Because of this, it is possible that both the yield stress and velocity slip values are somewhat dependent on the measurement conditions. It appears that both the D-10-G400 and D-7.5-G400 dispersions have about the same yield stress. The D-7.5-G400 dispersions has no velocity slip, however. Wall slip recently has been studied by others. Mannheimer¹⁵ pointed out that wall slip

is usually the consequence of a thin film of liquid that is between the solidlike particles of a dispersion and a solid surface; in this film there is a steep velocity gradient, giving the appearance of a wall slip and leading to the apparent-wall-slip term. According to Yoshimura and Prud'homme,¹⁶ it is only for polymer melts (see also Stewart¹⁷) that slip truly occurs at a solid wall. Buscall et al.¹⁸ explain that wall slip depends on the shearing stress level at the solid surface and the length of time it has acted. With delay times on the order of hours, wall slip is not observed until a critical shearing stress value is exceeded, typically about 1 N/m², about the stress level shown in Table I. With delay times on the order of minutes, wall slip can be observed at all levels of shearing stress. The apparent wall slip is said by Wein and Tovchigrechko¹⁹ usually to be a second-order effect, contributing 1–10% to viscometer torques; its neglect can result in a misinterpretation of primary viscometric measurements. Kee and Fong²⁰ point out that some experiments in some fluids conclusively show no flow at low shearing stress values, while other experiments show that flow is merely very slow at low shearing stress values. On the basis of a mathematical representation of molecular-level processes for formation of molecular binding points, they show that if the applied shearing stress is greater than the yield stress, a minimum time lapse must occur before enough of the molecular binding points are destroyed for flow to occur.

Viscosity Degradation

The viscosity of HSPAN gel–distilled water dispersions substantially decreased after being maintained at temperatures considerably above room temperature for periods of several weeks, as observed earlier by Hardin and Burmeister.³ To quantify the viscosity degradation, dispersions were maintained at set temperatures for times of up to 3 weeks with viscosity measurements made at intervals. Dimensionless apparent viscosity versus time is shown in Figure 4. The dimensionless apparent viscosity $\mu' = \mu/\mu_0$ is the ratio of the apparent viscosity μ to the initial apparent viscosity μ_0 (see Table II) immediately after achieving this temperature.

The “D-30-G400 with 0.1% NaHCO₃: 83–92°C” data were taken to ascertain whether or not acidic attack is the phenomenon responsible for viscosity degradation. For that case, 0.1% mass fraction of sodium bicarbonate NaHCO₃, a base, was mixed into the dispersion to counteract the effect of any acid. The data in Figure 4 show that viscosity degradation occurred with neither diminution nor augmentation, suggesting that neither acidic nor basic attack played a direct role in these results. A 0.3% mass fraction G400 HSPAN gel was used so that the initial viscosity would be equivalent to that of the 0.1% dispersions used for most of the other data sets. Un-tested was the possibility that the threshold temperature for long-term degradation of dispersion viscosity is affected by the same phenomena that determine the gelatinization which might have been affected by the NaHCO₃; as shown by Jane,²¹ for example, sodium sulfate Na₂SO₄ in distilled water can linearly increase the initiation of corn starch gelatinization from 63°C to 112°C.

Dispersions maintained at 90°C or above show a continual drop in apparent viscosity from the beginning. Samples maintained between 76°C and 80°C show an increase in apparent viscosity for the first few days but then a continual decrease. In each case, the apparent viscosity appears asymptotically to reach a steady-state value below the initial one. However, for dispersions maintained at less than 60°C, the apparent viscosity decrease was small, about 10% over 22 days for Sample B. It was observed during the natural convection testing that dispersions did not break down over a period of several weeks when maintained at temperature of 50°C or less. The peaking behavior shown in Figure 4 is similar to the effect of crosslinking on waxy corn starch viscosity versus temperature, discussed by Wurzburg.²² The data in Figure 4 appear to be described by the equation

$$\mu' = \exp(-t/\tau) + \mu'_\infty[1 - \exp(-t/\tau)]$$

in which τ is the time constant for the viscosity degradation, the initial viscosity μ_0 is the peak viscosity, and t is the time lapse since achievement of the peak viscosity. The values of τ and μ'_∞ determined by a nonlinear-least-squares technique are shown in Table III. Because of the large values of τ , a test only a few hours long would be too short to reveal the long-term effects of elevated temperature on viscosity. The earlier statement of Gugliemelli et al.²³ that viscosity is unaffected by temperature near 100°C was based on tests of a few hours duration.

A plot of the dimensionless asymptotic viscosity μ'_∞ versus absolute temperature of heating is shown in Figure 5. There it is seen that above 75°C, the dimensionless asymptotic viscosity μ'_∞ monotonically decreases with increasing temperature as

$$\mu'_\infty = \begin{cases} 1, & T < 348\text{K} \\ \exp\left(\frac{21,670}{T} - 62.28\right), & T \geq 348\text{K} \end{cases} \quad (4)$$

If the data at the two lowest temperatures were excluded (because μ'_∞ must approach unity at room temperature), the breakpoint would have been in the range of gelatinization temperatures, 62–72°C. The linearity of the plot above the threshold temperature of 348 K in Figure 5 suggests the essential accuracy of the data inasmuch as properties that vary with temperature as a consequence of groups attaining a specified energy level (Burmeister²⁴) follow Boltzmann's law. These results are based on measurements that extend through only about 20 days and still might not represent the viscosity after months at elevated temperature.

The causes of this degradation are not known, especially since the pH values always were within the range for distilled water, arguing against the possibility of the acidic attack to which starches are susceptible (Wurzburg²⁵). Katritzky et al.^{26,27} in pursuit of the origin of petroleum state that above 200°C, organic materials in water can undergo purely thermal reactions, but most are acid–base, oxidation–reduction, condensation, and disproportionation reactions that require water as a reagent or catalyst. Something of this sort might apply to HSPAN gel–distilled water dispersions even though the viscosity degradation seems to become important at a temperature (75°C) substantially below the 200–400°C level at which Katritzky et al. worked.

Alternatively, the mechanism of the degradation might be related to the gelatinization phenomenon

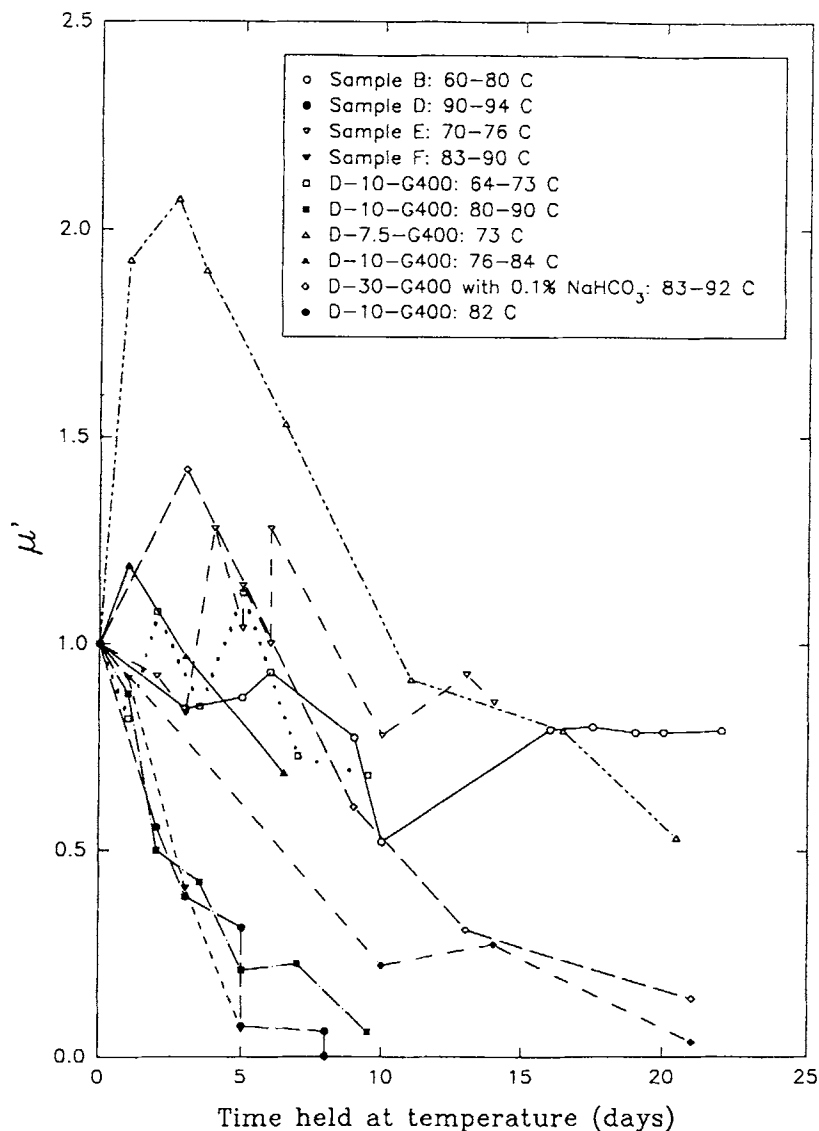


Figure 4 Dimensionless apparent viscosity versus time at elevated temperature for D-10-G400 HSPAN gel-distilled water dispersion, including samples B, D, E, and F.

described by Wurzburg.²⁸ When a slurry of starch in water is heated above a critical temperature, the hydrogen bonds responsible for the structural integrity of the granule weaken. As this occurs, the molecules start to form helices or coils, and the granules imbibe water and swell. After further heating to higher temperature, the granules rupture, releasing the polymeric molecules and aggregates. In distilled water, corn starch gelatinization begins at a temperature of 62°C and is completed at 72°C; during gelatinization, the viscosity of the slurry rises to a peak at which the granules have achieved their maximum hydration, after which the viscosity drops. The effects of acidity and so forth on gelatinization temperature are discussed by Zobel²⁸ and Snyder.²⁹

The manner in which gelatinization is modified when the starch is crosslinked, reinforcing the hydrogen bonds responsible for the granule integrity, is described by Wurzburg.²⁵

As seen in Figure 4, behavior similar to that described earlier for gelatinization was observed for D-10-G400 HSPAN gel-distilled water dispersions maintained at elevated temperature. Although it might be fortuitous, the threshold temperature of approximately 75°C for degradation of D-10-G400 dispersion viscosity is slightly above that, 72°C, at which gelatinization is complete. As noted by Zobel,²⁹ the gelatinization temperature determined as that at which viscosity begins to increase is generally higher than the gelatinization temperature deter-

Table II Initial Apparent Viscosity for Figure 3 HSPAN Gel–Water Dispersions

Sample	Initial Viscosity (cP)
Sample B (D-10-G400): 60–80°C; #2L spindle (#1 for last 6 points) at 0.3 rpm	22,000
Sample D (D-10-G400): 90–94°C	27,000
Sample E (D-10-G400): 70–76°C	27,000
Sample F (D-10-G400): 83–90°C	22,000
D-10-G400: 64–73°C; #2L spindle at 1.5 rpm	6,600
D-10-G400: 80–90°C; #2L spindle at 1.5 rpm	6,600
D-7.5-G400: 73°C; #1 spindle at 0.3 rpm	8,100
D-10-G400: 76–84°C; #2L spindle at 0.3 rpm	16,000
D-30-G400 with 0.1% NaHCO ₃ : 83–92°C; #1 spindle at 0.3 rpm	16,200
D-10-G400: 82°C; #1 spindle at 0.3 rpm	17,900

mined by loss of birefringence, as those values previously mentioned here were. Additionally, as pointed out by Snyder,³⁰ the temperature (termed the pasting temperature) at which a starch slurry begins to show an increase in viscosity is usually several degrees higher than the endpoint of the gelatinization range.

Additionally, the Boltzmann form of Eq. (4) yields an energy $-\Delta E$ that is in qualitative agreement with the enthalpy of gelatinization $-\Delta H_G = 4.1\text{--}4.6$ cal/g reported by Zobel.²⁹ The exponent of Eq. (4) is

$$-\Delta E/RT = 21,670 K/T$$

where the universal gas constant $R = 1.986$ cal/mol K. From this it is found that $-\Delta E = 43,037$ cal/mol. A typical corn starch–acrylonitrile gel molecular weight is 37,000, according to Fanta and Doane,³¹ and has about one third corn starch by mass. Thus $-\Delta E = (43,037 \text{ cal/mol}_{\text{dispersion}}) (3 \text{ g}_{\text{dispersion}}/\text{g}_{\text{starch}})/(37,000 \text{ g}_{\text{dispersion}}/\text{mol}_{\text{dispersion}}) = 3.5 \text{ cal/g}_{\text{starch}}$.

Clarity

The clarities of some D-10-G400 HSPAN gel–distilled water dispersions relative to distilled water are shown in Figure 6. In general, clarity diminishes with increasing HSPAN mass fraction. In Figure 7 the bubbles in the beaker on the left are believed to be a consequence of dissolution of air from the dispersion at elevated temperature. The population of bubbles formed during about 10 h of heating and changed little after that, with the bubbles being stationary. Deaerating the distilled water by boiling prior to mixing with HSPAN gel resulted in the dispersion in the beaker on the right with fewer and smaller bubbles when maintained at an elevated temperature.

It was observed that if the G400 HSPAN gel was mixed into boiling deaerated distilled water, the dispersion formed more quickly and homogeneously and with less mixing than was the case with aerated distilled water at room temperature. In the former

Table III HSPAN Gel–Water Dispersion Time Constant and Asymptotic Apparent Viscosity

Sample	Time Const. (τ , Day)	Asymptotic Apparent Viscosity (μ'_{∞} , cP)
Sample B (D-10-G400): 60–80°C; #2L (#1 for last 6 points) at 0.3 rpm	9.4 ± 5	16,780 ± 1500
Sample D (D-10-G400): 90–94°C	2 ± 0.5	7002 ± 3500
Sample E (D-10-G400): 70–76°C	No estimates made	
Sample F (D-10-G400): 83–90°C	3.2	0 + 1500
D-10-G400: 64°C; #2L spindle at 1.5 rpm	2.5 ± 1	4651 ± 250
D-10-G400: 80–90°C; #2L spindle at 1.5 rpm	2.7 ± 1	770 ± 150
D-7.5-G400: 73°C; #1 spindle at 0.3 rpm	6 ± 1	2600 ± 800
D-10-G400: 76–84°C; #2L spindle at 0.3 rpm	2.2 ± 1	13,470 ± 2250
D-30-G400 with 0.1% NaHCO ₃ : 83–92°C; #1 spindle at 0.3 rpm	5 ± 1	2279 ± 600
D-10-G400: 82°C; #1 spindle at 0.3 rpm	5 ± 1	400 ± 350

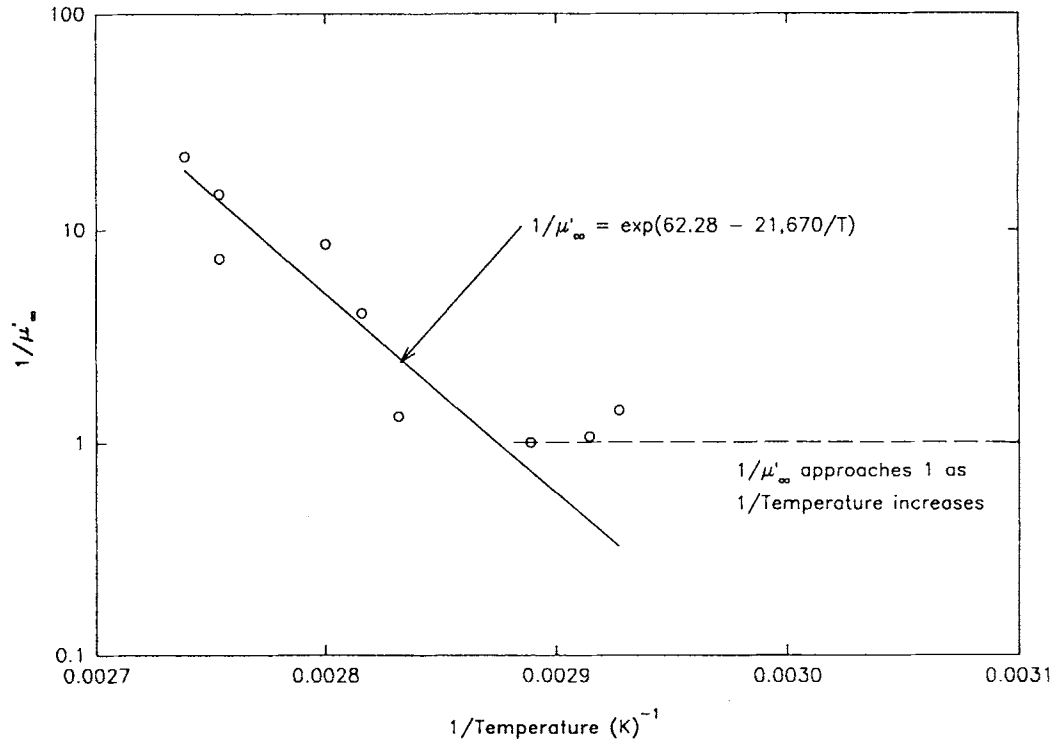


Figure 5 Asymptotic apparent dimensionless viscosity versus heating temperature for D-10-G400 HSPAN gel-distilled water dispersion.



Figure 6 Clarity comparison of distilled water with D-10-G400 HSPAN gel-distilled water dispersion. Left to right: distilled water, new dispersion, dispersion heated at 60°C, dispersion heated at 73°C, and dispersion heated at 70-78°C.

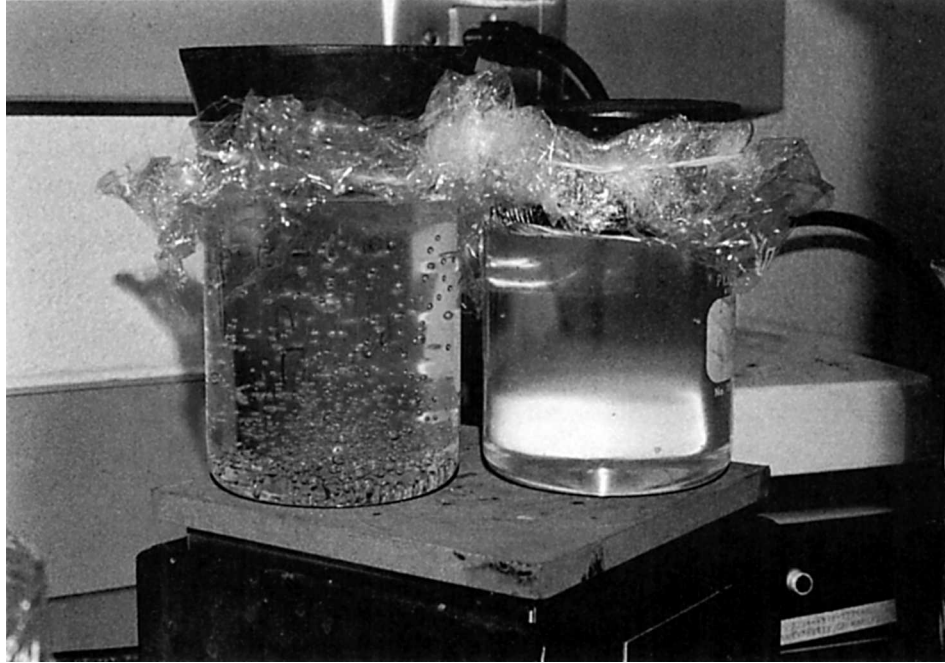


Figure 7 Bubbles in D-10-G400 HSPAN gel–distilled water dispersion made with aerated (left) and deaerated (right) distilled water after 2 days at elevated temperature.

case, there were none of the initial clumps that are common at room temperature.

Craig et al.,¹¹ in their discussion of the effect of starch granule size on clarity, noted that starch granule–distilled water dispersions increased in clarity with decreasing granule size. Jane et al.³² and Lim and Jane³³ considered the effect of different size starch granules on the transparency and tensile strength of starch–polyethylene blown films. It is possible that finer HSPAN gel particles than those used in the present study would result in greater clarity, too.

A more detailed discussion of this method is available (Hardin and Burmeister³⁴).

Partial support of R. Hardin by the Kansas Corn Commission, Contract No. 1044, is acknowledged.

NOMENCLATURE

B	Slip coefficient ($\text{m}^3/\text{N s}$)
E	Energy (J/mol)
g	Gravitational acceleration (m/s^2)
H_G	Enthalpy of gelatinization (J/kg)
h	Heat transfer coefficient ($\text{W/m}^2 \text{K}$)
l	Natural convection cell height (m)
Nu	Nusselt number, $Nu = hx/k$ (dimensionless)
Pr	Prandtl number, $Pr = \nu/\alpha$ (dimensionless)

R	Universal gas constant (J/mol K)
Ra	Rayleigh number, $Ra = g\beta\Delta T x^3/\nu\alpha$ (dimensionless)
r_c	Radius at which flywheel flow begins (m)
r_i	Viscometer spindle radius (m)
r_o	Beaker radius (m)
QL	Heat loss (W)
T_b	Temperature at heater back (K)
T_r	Temperature of room air (K)
t	Elapsed time (s)
ΔT	Temperature difference between heated and cooled plates (K)
UL	Heat loss coefficient (W/K)
v_{slip}	Slip velocity (m/s)
x	Natural convection cell width (m)

Greek Symbols

α	Fluid thermal diffusivity (m^2/s)
β	Fluid coefficient of thermal expansion (K^{-1})
μ	Viscosity (N s/m^2)
μ_o	Initial viscosity (N s/m^2)
μ_∞	Final viscosity (N s/m^2)
μ'	Dimensionless viscosity, $\mu' = \mu/\mu_o$
μ'_∞	Dimensionless final viscosity, $\mu'_\infty = \mu_\infty/\mu_o$
ν	fluid kinematic viscosity (m^2/s)
τ_c	Yield stress (N/m^2)

- τ Time constant (s)
 τ_l Shear stress on the viscometer spindle (N/m²)
 ω_c Angular speed of flywheel flow (rad/s)

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Received August 26, 1994

Accepted January 10, 1995