Low-Speed Tack Measurements of Fluids and Inks

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SYNOPSIS

Low-speed tack measurements ($\approx$ 0.1–6.0 rad/s or $\approx$ 1–57 RPM) have been determined for polymeric-based solution inks and oil-based dispersion inks, tripropylene glycol (TPG), Igepal (I-530), and N-350 (viscosity calibration standard) fluids using a metal roller/incline method. The inks and fluids were tested under "unaged" or reference conditions at 25°C. The inks were "aged" at 70°C and, subsequently, tack measurements were made at 25°C. The tack (τ_i) and angular speed (w_i) for the inks were empirically fitted as functions of incline angle (α) and "aged" time, t_{cd}. A correlation was also made for tack and percent weight change, ΔW_i. Other factors, such as viscosity, surface tension, humidity, and "aging" temperature, T_{cd}, were also found to affect the magnitude and variation of tack. Additionally, the results suggest that low-speed tack measurements are quite useful for selecting solution inks containing polymeric substances that possess the desirable spreading, mixing, and pressing properties in high-speed/high-volume printing and the component compatibility necessary for long-term performance. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The resistance of the motion of a solid surface in contact with a fluid can be defined as tack or "stickiness" of the fluid–solid interface.[1-4] This property can be measured from parallel-plate separation at a given rate or from rotational torque experiments (balls, rings, cylinders, etc.).[1,2] The forces in the rotational torque experiment can be generated by an external source (e.g., torque motors) or by gravity. In flexographic printing applications, it is often important to know the "splitting" characteristics of a fluid or ink on rotating rollers or the transfer of ink to printing surfaces at high rates of speed.[1-5] The theoretical analysis of splitting in a rigid nip by a rheological material may be described by the Navier–Stokes hydrodynamical equation.[1] Low-speed tack measurements can be used for composition differentiation of inks with desirable properties of viscosity and surface tension[1] and the mixing, spreading, and pressing characteristics of solutions containing polymeric substances and other type substances such as adhesives.[1,2]

In ink formulation, for example, fluid substances may be selected to meet the overall desired tack levels for specific purposes such as torque reduction for "data" wheel printing, the control of dust levels from paper substrates resulting from high speed and high volume printing, and long-term tack stability. For a sizable number of formulations, one would prefer that this screening process be simple and reliable. In order to address this problem, we designed a roller/incline device that could determine fluid tack over a range of relatively low rotational speeds by changing the incline angle, α. In this paper we present some of our preliminary findings[6] and show how tack influences the rotation of a moving solid surface in contact with a stationary fluid surface and how composition changes determines tack variation over time for an "aged" fluid.

EXPERIMENTAL[†]

Roller/Incline Method

Most of the data collected for our investigation was performed with a roller/incline device as shown

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[†] Certain commercial equipment, instruments, and materials are identified in this article in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by Pitney Bowes, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

schematically in Figures 1 and 2. The incline construction is of stainless steel with railings and the rollers are as designated in Table I.[6] The incline angle (α) was manually set with a screw-rod lift and the timing of the linear speed of the roller was determined with a timer accurate to 1/100 of a second. The start and stop positions were set to give a travel distance of $x = 0.373$ m. A precisely designed channel with a width approximately equal to that of the roller and a depth of 150 μm was used to control fluid thickness in the path of the roller. Each experiment was begun by applying the fluid to the channel with an aluminum knife-edge "spreader" and setting the incline angle. The angles were chosen to minimize fluid motion down the incline plane and to reduce "sliding" of the roller versus "pure" rotation of the roller.[2,7] At a preselected time, the roller was placed at the starting position with its shaft on the railing and released down the incline plane to its "stop" position; the time to travel the distance was measured and the experiment was repeated at least five times with an average error of about 5–10%.

Parallel-Plate Method

A manual parallel-plate arrangement is shown schematically in Figure 3. The force, f, necessary to separate plates of a given radius, r, is given as $f = \{3\pi\eta r^4[1/(h_0)^2 - 1/h^2)]\}/4t$ (h_0 = the initial distance between the plates; h = the separation distance at time, t; η = the viscosity of the fluid).[2] The upper plate was fixed and the bottom plate could be moved vertically downward. The maximum force, f_m, necessary to separate the plates in a time, t_m, was measured with calibrated push–pull gauges

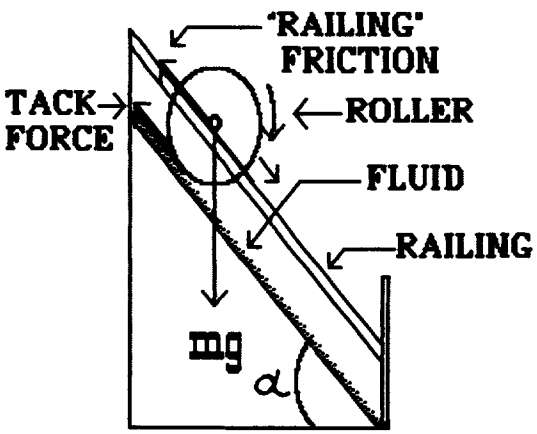

Figure 1 Schematic plane side view of roller/incline in the presence of a tack force, frictional force, and a force due to gravity; the roller rotates with an angular velocity, w, and moves with a linear velocity, v.

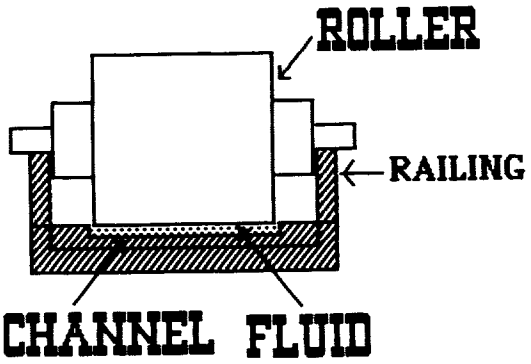

Figure 2 Schematic view of roller on railing and the fluid channel.

(ounces/gram) attached to the bottom plate. The experiment was begun by placing a given amount of fluid between the plates and pulling the gauge at an approximate constant rate for all fluids. The technique and method were tested and calibrated by using N-350 viscosity standard fluid.[6,8] The manual method also agreed rather favorably with an automated computer-based parallel-plate system used at Pitney Bowes for inks and other fluids and will be presented at a later time.[8] The automated system generates force–time graphics at controlled separation rates and has software to perform such calculations as the integral of the f–t curve and the maximum force occurring at a time, t_m.

Comparative results for the parallel-plate and roller/incline methods are presented in Table III. The ratio of the tack data of the roller, τ_R, to that of the tack of the parallel-plate, τ_P, was found to be approximately constant (5 values), i.e., $\tau_R/\tau_P = \bar{K} = 7.31 \times 10^{-3} \pm 2.91 \times 10^{-3}$ with the average variation being used as the estimate of error; this variation reflects the uncertainty in the manual force measurements. The calculated values in Table III were determined using $\bar{K}$ and seems to be in agreement with the measured values.

Fluids

The fluids used for the tack measurements were commercial TPG (tripropylene glycol), commercial I-530 (Igepal), and N-350 (Cannon Instrument standard viscosity calibrating fluid; State College, PA). The solution and dispersion inks were formulated and prepared at Pitney Bowes and are designated, respectively, S and D, in which the numbers refer to specific inks with varying amounts of substances and "neat" solvents.[6] The solution inks are glycol-based (oligomeric) and contain commercially available substances such as polyethyoxylated sur-

factants, fluorescent dyes, dissolved melamine-type resins ($\bar{M}_n \approx 5000$), and other substances commonly added to inks to enhance the stability.[5] The dispersion inks are oil-based with pigments of very fine grind.[6]

Other properties of the fluids such as viscosity (Haake cone/plate viscometer and Brookfield rotational viscometer), surface tension (Fisher "ring" tensiometer), and refractive index (Abbe refractometer) are also included in Table II. The average viscosity and surface tension of the solution inks were, respectively, about 800 cP and 34.0 N/m at room temperature. The viscosities and surface tension of the dispersion inks ranged from 250 to 500 cP and about 31.0 N/m at room temperature. Included in Table II are also surface tension and refractive index results for solution ink S-285 conditioned at 70°C for 7.8 and 55.0 days.

Ink/Tack Testing

A PB 6900 printing fixture was modified to allow electronic programming of the rotation of its "data" wheels. The macro-programming controlled "firing" sequences of the "data" wheels and printout instructions for specific meter operation procedures, the state of the meter, and certain detectable failure modes. The basic steps of operation were as follows: (1) measure the initial state of the meter (voltage-level monitoring and torque measurements of the "data" wheels using push–pull gauges), (2) apply ink to "data" wheels and shaft, (3) run 20 initiation cycles of the wheels, (4) remeasure the state of the meter (including torque measurements), and (5) repeat steps a number of times for precision estimates. From the data obtained in conjunction with ink conditioning information, an assessment of the failure modes for the "data" wheels could be made. This information was also useful for estimating service life and performance of the meter.

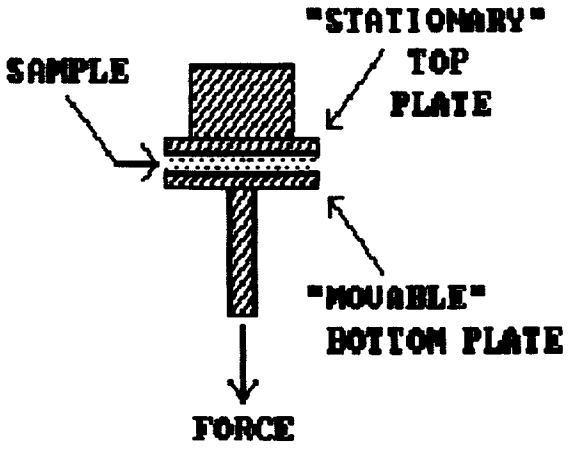

Figure 3 Schematic diagram of the parallel-plate arrangement.

ANALYSIS OF DATA

The fundamental unit of tack, τ', is force-length (torque, e.g., kg m). We have further defined this unit in force-time (e.g., kg s), τ, which is the torque unit divided by an average velocity, v_{AV}, that is, the plane motion of the rotating cyclinder down the incline plane is due to gravity (note Figs. 1 and 2). This motion can be described by the following relation:

$$\tau' = F[T'_0, T'] + G[(v_0)^2, v^2] + H(\alpha, \sigma_{Y,l}) + \Omega(\alpha) \quad (1)$$

where the function F represents the torque and the function G represents the average linear velocity of the roller, respectively, without fluid and in the presence of fluid. The function H is a correction term due to the motion of a fluid with thickness, l, and yield stress, $\sigma_{Y,l}$, on an incline of angle, α^2 and Ω is a frictional correction term for the shaft of the

Table I Some Characteristic Designations of Rollers Used in the Tack Measurements[a]

Number	Weight (kg) ($\times 10^3$)	Radius (m) R ($\times 10^2$)	Radius (m) r ($\times 10^2$)	Width (m) W_0 ($\times 10^2$)	Composition	β ($\times 10^2$)	β' ($\times 10^5$)	k_0 (rad)
1	223.08	2.534	0.249	3.83	Aluminum	6.36	237.4	14.7
2	674.40			3.83	Stainless steel			
3	821.40	2.790	0.498	3.83	Stainless steel	23.4	874.06	13.4
4	1271.70			3.83	Stainless steel			

[a] Roller #3 was used for most determinations. The constants β, β', and k_0 as defined in eqs. (8) and (9) are given for $x = 0.373$ m; R = radius of "body" of roller, r = radius of shaft of roller.

Table II Some Property Measurements for Samples Used for Tack Measurements (Unconditioned and Conditioned)

Sample[a]	Surface Tension (N/m) ($\times 10^3$)			Refractive Index		Viscosity, Pa s ($\times 10^3$)
	Uncond. (25°C)	Cond. (70°C) 7.8 days	Cond. (70°C) 55.0 days	Uncond. (25°C)	Cond. (70°C) 7.8 days	Uncond. (25°C)
TPG				1.4301 (20°C)		55
N-350[b]						778
S-664	33.1		40.0	1.5104		800
S-951	33.9		40.5	1.5095		1050
S-285	34.4	38.0	41.0	1.5093	1.5097[c] 1.5214[d]	800
D-216	31.2		37.6			425
D-172	30.9		36.3			275
D-862	32.2					

[a] Designations: S, solution; D, dispersion.
[b] Cannon Standard Viscosity Calibration Fluid.
[c] Sample closed to atmosphere.
[d] Sample open to atmosphere.

roller in contact with the surface of the railing of the fixture.[7] So,

$$T'_0 = (1/2)I_c(w_0)^2 \tag{2a}$$

$$T' = (1/2)I_c w^2 \tag{2b}$$

and

$$v_0 = w_0 R = \dot{x}_0 = x/t_0 \tag{3a}$$

$$v = wR = \dot{x} = x/t \tag{3b}$$

where I_c = the moment of inertia for the roller of mass, M, and radius, R [i.e., $I_c = (1/2)MR^2$], w_0 and t_0 and w and t are, respectively, the angular speed and travel times of the roller without fluid and in the presence of fluid; x is the linear travel distance. From eq. (3b), the hydrodynamic rate of shear is defined as

$$\text{Rate of shear} = \dot{\gamma} = v/l \tag{4}$$

where l is the thickness of the fluid.[1] Hence, eq. (1) can further be defined in terms of the measured travel times of the roller without fluid (time t_0 s) and in the presence of fluid (time t s) to yield

$$\tau' = F'[(t_0)^2, t^2] + G'[(t_0)^2, t^2] + H'(\alpha, \sigma_{Y,l}) + \Omega'(\alpha) \tag{5}$$

or

$$\tau(\text{N-s}) = \tau'(\text{N-m})/v = [\tau'(\text{N-m})/x]t \tag{6}$$

Now, neglecting H, H', Ω, and Ω' terms in eqs. (1) and (5), one may write from classical mechanics the motion of a rotating rigid body down an incline plane of angle, α, in the presence of a tack torque in N m as[7]

$$\tau' = [T' - T'_0] + \tfrac{1}{2}M[(v_0)^2 - v^2] \tag{7}$$

Substituting for torque and dividing eq. (7) by the gravitational constant, g', the tack becomes

$$\tau(\text{kg-s}) = \tau'(\text{kg-m})/v = \beta[(w_0)^2 - w^2)]t \tag{8a}$$

and

$$\tau'(\text{kg-m}) = \tau\ (\text{kg-s}) \times v = \beta'[(w_0)^2 - w^2] \tag{8b}$$

where for our setup,

$$w_0 = (x/R)/t_0 = k_0/t_0 \tag{9a}$$

$$w = (x/R)/t = k_0/t \tag{9b}$$

The constants in eq. (8) are given, respectively, for τ and τ' as $\beta = 3Mx/4g'$ (kg s^2) and $\beta' = 3Mx^2/4g'$ (kg m s^2) and in eq. (9) $k_0 = x/R$. These constants are given in Table I for two roller weights.

EMPIRICAL RELATIONS

The roller angular speed, $(w_u)_i$, for the unconditioned ("unaged") inks and fluids, i, were fitted as a function of incline angle, α, to yield

$$(w_u)_i = (k_i)_{AV}\alpha^{3/2} \tag{10}$$

where $(w_u)_i$ was found to be proportional to the incline angle, α, raised to the $\frac{3}{2}$ power. From eq. (10) and the conditioning time, t_{cd}, the roller angular speed, w_i, for the conditioned ("aged") fluids was determined as follows:

$$w_i = (w_u)_i/[1 + C_i(w_u)_i(t_{cd})^{\delta}] \tag{11}$$

where $\delta = \delta_i$ is the exponent and C_i is a constant. In a similar fashion, the tack (kg s) was fitted as a function of α and w_i to give

$$\tau_i = (K_i)_{AV}\alpha/w_i \tag{12}$$

or, by combining eqs. (11) and (12), the tack becomes

$$\tau_i = \{[(K_i)_{AV}/(k_i)_{AV}]\alpha^{-1/2}\} \times \{1 + C_i(k_i)_{AV}\alpha^{3/2}(t_{cd})^{\delta}\} \tag{13}$$

Further simplification of eq. (13) leads to the following incline angular dependency at constant t_{cd} for the "aged" fluid, i.e.,

$$\tau_i = A_i/\sqrt{\alpha} + B_i\alpha \tag{14}$$

where

$$A_i = (K_i)_{AV}/(k_i)_{AV} \tag{15a}$$

$$B_i = (K_i)_{AV}C_i(t_{cd})^{\delta} \tag{15b}$$

Equation (14) implies that at a given α, tack (kg s) is made up of two terms, namely

$$\tau_i = \sum_1 + \sum_2 \tag{16}$$

where $\sum_1 = A_i/\sqrt{\alpha}$ is the "unaged" component and $\sum_2 = B_i\alpha$ is the "aged" component. A critical angle, α_c, may be defined for $\sum_1 = \sum_2$, i.e.,

$$\alpha_c = (A_i/B_i)^{2/3} \tag{17}$$

Likewise, from eqs. (14), (16), and (17), the critical tack may be defined as

$$(\tau_i)_c = 2A_i/\sqrt{\alpha_c} = 2B_i\alpha_c = 2(A_i)^{2/3}(B_i)^{1/3} \tag{18}$$

For a given fluid, the critical parameters in eqs. (17) and (18) are assumed to describe the conditions at which the "aged" fluid is equivalent to the "unaged" fluid for a critical angle, α_c. The constants $(k_i)_{av}$, C_i, δ, $(K_i)_{AV}$ and the critical parameters are summarized in Table VIII. When $t_{cd} = 0$, $\sum_2 = 0$ and τ_i in eq. (16) describes the tack of the unconditioned or "unaged" fluid at the reference temperature, T_u.

RESULTS

Tack measurements for this study are presented in Tables III–V, VII, IX, and X, and Figures 4–7. Percent weight changes for the inks are shown in Table VI and Figures 8 and 9. The sensitivity of the tack measurements depend on the chosen unit and the region of the roller angular speed, w_i, e.g., τ' (kg m) is most sensitive at higher speeds as shown in Figure 4 and τ(kg s) is more sensitive at lower speeds as shown in Figure 5. It is also apparent that tack is strongly dependent on the type of fluid and the conditioning temperature and time as exhibited by Figures 6 and 7.

Tables V and VI and Figures 8 and 9 show humidity and temperature effects over time that may dramatically affect tack properties. At room temperature, for example, absorption of water vapor becomes an overriding factor for tack variation for the inks. Above some higher transition temperature (e.g., $\approx$ 28.0, 27.4, 30.0, and 25.2°C, respectively, for S-664, S-951, S-285, and D-862), the lost of solvent components becomes a controlling factor in tack changes. The humidity effect is most observable for the water-sensitive glycol-based solution inks as opposed to the oil-based dispersion inks.

The tack of polymeric and dispersed solutions that may exhibit, respectively, viscoelastic and thixotropic properties are more complex and may not be adequately described by the hydrodynamic rate of shear expressed by eq. (4).[1,2,9] In such systems in which there is a time/rate of shear dependence of the stress $[\sigma(t, \dot{\gamma})]$ and viscosity $[\eta(t, \dot{\gamma})]$, the rate of shear is more correctly expressed as the ratio of stress to viscosity [i.e., $\dot{\gamma} = \sigma(t, \dot{\gamma})/\eta(t, \dot{\gamma})$].[10–12] The viscosity of polymeric and dispersed solutions may be highly dependent on the concentration of its components, c_i, e.g., $\eta = b_0'(c_i)^n$ where n may be 2 or greater.[2,11,12] The behavior of the dispersion inks

Table III Tack Measurements for Unconditioned Fluids Determined from Parallel Plate and Dynamic (Roller) Methods at 25°C[a]

	Tack				
	Static: Parallel Plates[c]	Dynamic: Roller			
Sample[b]	τ (kg s)	w (rad/s)	$v \times 10^2$ (m/s)	Rate of Shear (s^{-1})	$\tau \times 10^3$ (kg s)
TPG	0.0263[d]	6.0	16.7	1113	0.192
Igepal-530[e,f]	1.50[d]	1.38	3.85	257	11.0
N-350[e,g]	7.51[d]	0.58	1.62	108	54.9
S-664	2.65	2.8	7.81	521	18.3
S-951	3.10	1.6	4.46	297	37.7
S-285	3.81	3.1	8.65	577	15.4
S-285[h]	13.2				96.5[d]
S-285[i]	9.40				68.7[d]
S-272	5.41	1.7	4.74	316	35.0
D-216	1.35				9.87[d]
D-172	0.73	4.8	13.4	893	5.15
D-862	1.35				9.87[d]

[a] w, roller angular speed (rad/s) at an incline angle of 0.29 radians; v, roller angular velocity; l, fluid thickness = 1.5×10^2 μm; roller weight = 8.214×10^{-1} kg; r, roller radius = 0.0279 m.

[b] Designations: S, solution; D, dispersion.

[c] Area of plates = $A_0 = 8.55 \times 10^{-4}$ m^2; initial plate separation = $h_0 = 3.3 \times 10^2$ μm (the pulling rate of the push-pull gauges were kept approximately constant).

[d] These values were determined from $\tau_R = \bar{K} \times \tau_p$ where $\bar{K} = 7.31 \times 10^{-3} \pm 2.91 \times 10^{-3}$ (using five values).

[e] Incline angle $\alpha = 0.11$ rad.

[f] Using roller #1 in Table I, the tack was found to be 0.0157 kg-s.

[g] Cannon Standard Viscosity Calibration Fluid.

[h] Sample conditioned for 7.8 days at 70°C ("open" environment).

[i] Sample conditioned for 7.8 days at 70°C ("closed" environment).

Table IV Tack Measurements for Conditioned Inks Determined from Dynamic (Roller) Method at 25°C[a]

	Tack							
	Conditioned: 70°C				Conditioned: 70°C			
	7.8 days (α = 0.29 rad)				55.0 days (α = 0.11 rad)			
Sample[b]	w (rad/s)	$v \times 10^2$ (m/s)	Rate of Shear (s^{-1})	$\tau \times 10^3$ (kg-s)	w (rad/s)	$v \times 10^2$ (m/s)	Rate of Shear (s^{-1})	$\tau \times 10^3$ (kg s)
S-664	0.98	2.73	182	64.5	0.096	0.268	17.9	190.2
S-951	0.54	1.51	101	118.5	0.10	0.279	18.6	182.8
S-285	0.96	2.68	179	65.7	0.18	0.502	33.5	101.6
D-216	3.7	10.3	687	11.0	1.1	3.07	205	14.7
D-172	3.6	10.0	667	11.7	0.92	2.57	171	18.3
D-862	6.4	17.9	1193	4.6	2.5	6.98	465	2.86

[a] w, roller angular speed at the indicated incline angles; v, roller angular velocity; l, fluid thickness = 1.5×10^2 μm; roller weight = 8.214×10^{-1} kg; r, roller radius = 0.0279 m.

[b] Designations: S, solution; D, dispersion.

Table V Tack Measurements for Conditioned (Vacuum: Δp = 0.84 Torr) Ink S-664 Determined from Dynamic (Roller) Method[a]

Time (days)	w (rad/s)	$v \times 10^2$ (m/s)	Rate of Shear (s^{-1})	$\tau \times 10^3$ (kg-s)
0.0	2.8	7.81	521	18.3
0.79	2.8	7.81	521	18.3
4.9	1.9	10.1	673	16.1
7.8	1.3	3.63	242	47.4

[a] w, roller angular speed and incline angle α = 0.29 rad; v, roller angular velocity; l, sample thickness = 1.5×10^2 μm; roller weight = 8.214×10^{-1} kg at 25°C.

are also dependent on the interaction and size distribution of the pigment particles.[1,2] In our case, the pigments are fine grind and rather homogeneous. The tack results in Tables III and IV tend to support the fact that the "aged" dispersion inks are more stable in composition over time than the solution inks. The solution inks may become unstable at low temperatures (below about 10°C) due to changing solubility of fluids which may result in phase separations.[10] These results also seem to indicate that long-term "aging" tests (e.g., 55 days) will better differentiate the solution inks as to tack behavior. In systems showing such dependencies of composition and time, tack will be quite sensitive to small changes in concentration as evidenced by percent weight changes of the fluid.[6] Other mechanical properties of inks and fluids such as modulus and normal stress may also be quite significant in printing processes at high rates of speed (rollers and ink transfer/impact) and should be taken into consideration when evaluating the performance and service life of a given printing system.[1,3-5,13]

PERCENT WEIGHT CHANGE

At a given temperature, T, and time, t, the percent weight change, $\Delta W_i(t, T)$, in an open system reflects the net change in water vapor absorption (hygroscopicity) or lost of liquid substances for fluid, i, and may be empirically represented by the following:[14]

$$\Delta W_i(t, T) = (C_0)_i\{1 - \exp[-f_i(T)t']\} \quad (19)$$

where $(C_0)_i$ is a limiting constant for a given fluid, i, $f_i(T)$ is a function of temperature, T, and $t' = t - t'_0$ *where* t and t'_0 are, respectively, the time and transition time for $\Delta W_i(t, T)$. The sign of the percent weight change at a given t and T depends on the loss of solvent components or the gain of water vapor. The function, $f_i(T)$, was found to be adequately represented by[6]

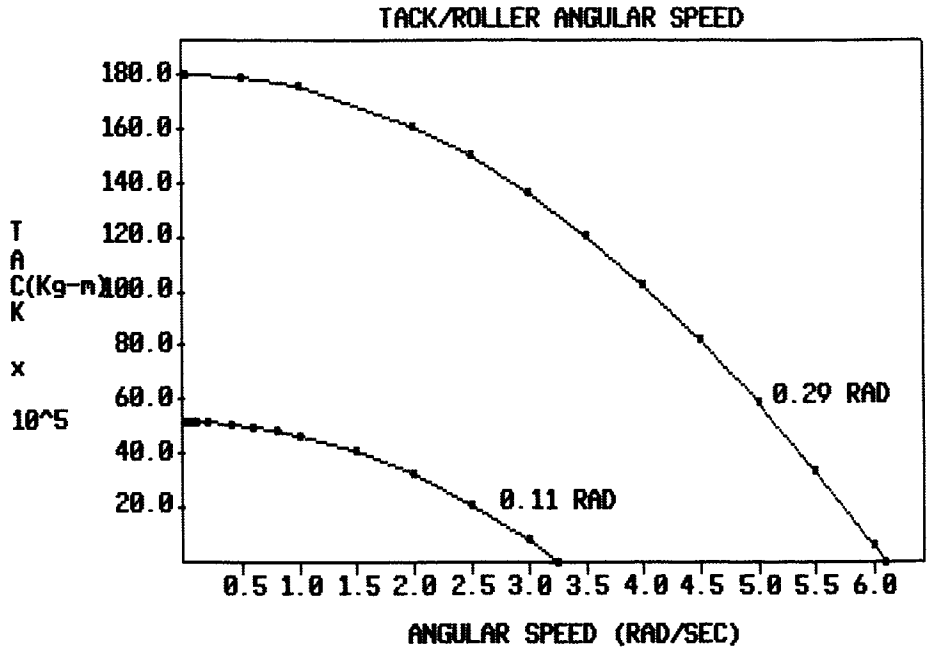

Figure 4 Tack (kg-m) versus roller angular speed at α = 0.11 rad and α = 0.29 rad; calculations were based on eq. (8b).

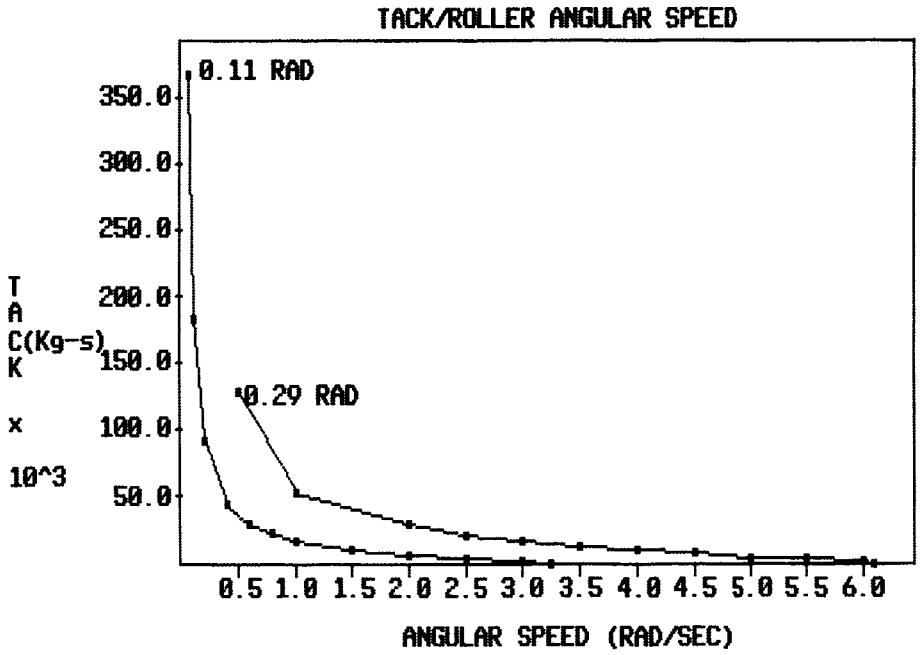

Figure 5 Tack (kg-s) versus roller angular speed at $\alpha = 0.11$ rad and $\alpha = 0.29$ rad; calculations were based on eq. (8a).

$$f_i(T) = E_i(T)/T \tag{20}$$

$$-\ln[D_i(t, T)] = f_i(T)t' = [E_i(T)/T]t' \tag{21}$$

where $E_i(T)$ is a function of temperature, T. From eq. (19), one may define:

where $D_i(t, T) = \{1 - [\Delta W_i(t, T)/(C_0)_i]\}$. Over a narrow temperature range $E_i(T)$ is approximately

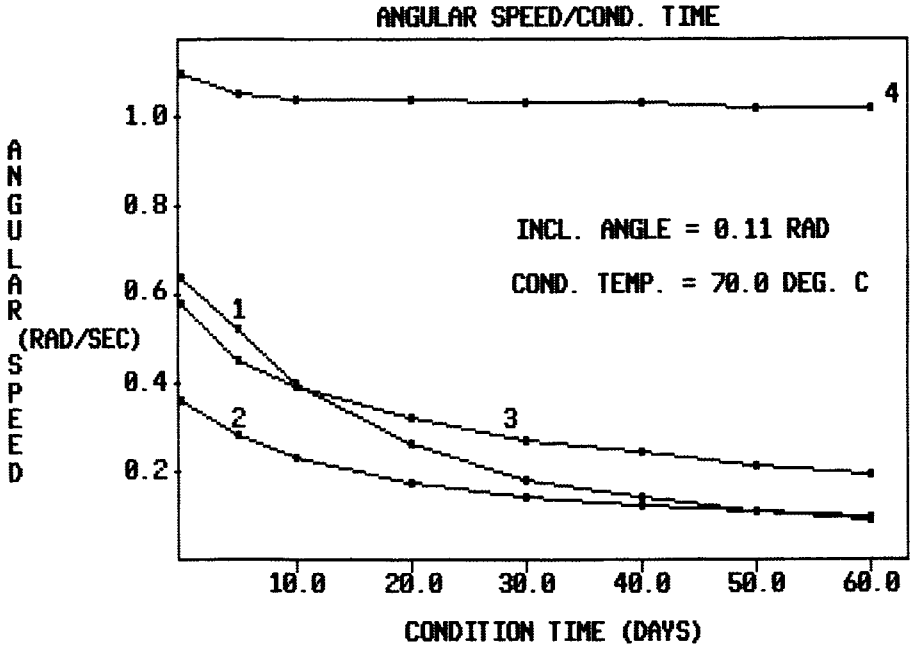

Figure 6 Roller angular speed (rad/s) versus condition time (t_{cd}) (at 70°C) for (1) S-664, (2) S-951, (3) S-285, (4) D-172.

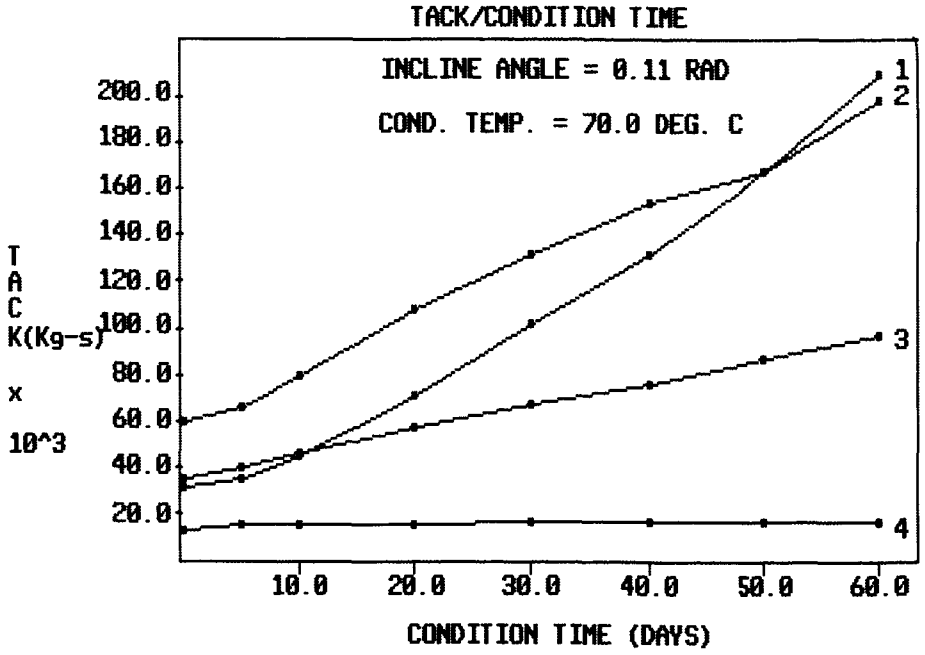

Figure 7 Tack (kg-s) versus condition time (t_{cd}) (at 70°C) for (1) S-664, (2) S-951, (3) S-285, (4) D-172.

constant and exhibits characteristics of an activation energy for vaporization.[14]

The "aging" or conditioning data in Table VI was used to determine the functions in eqs. (20) and (21) at t_{cd} and T_{cd} as follows: $-\ln[D_i(t_{cd}, T_{cd}]$ was plotted versus t_{cd}. From the slope of the line, $f_i(T_{cd})$ was determined; and, from the slope, $E_i(T_{cd}) = f_i(T_{cd}) \times T_{cd}$. In a similar fashion, the data in Table VI were used to determine $f_i(T_u)$ and $E_i(T_u)$ at the reference or unconditioned temperature, T_u. For example, for ink S-664 at T_{cd} = 346°K and T_u = 298°K, respectively, $f_i(T_{cd}) = -0.034$ and $f_i(T_u) = -0.010$ (within $\approx \pm 20\%$). The constant $(C_0)_i$ was also estimated from the unconditioned or ref-

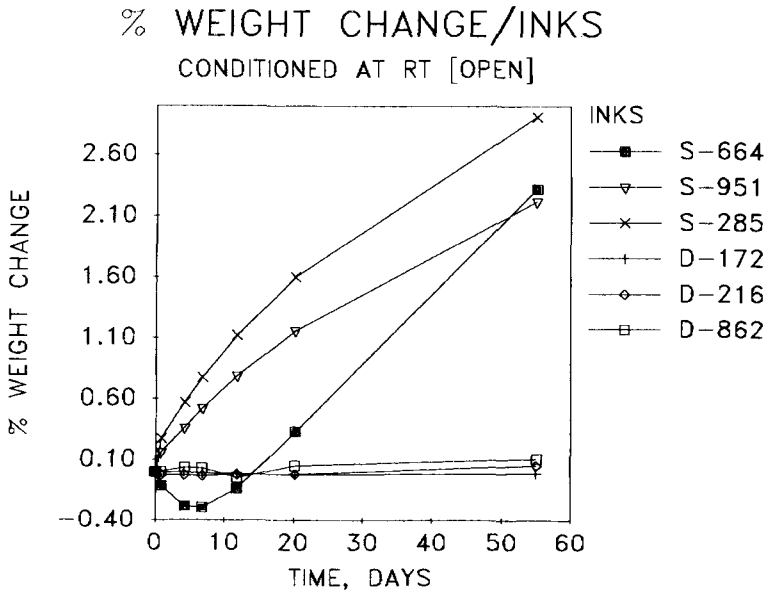

Figure 8 Percent weight changes versus time (days) at room temperature (under "open" conditions).

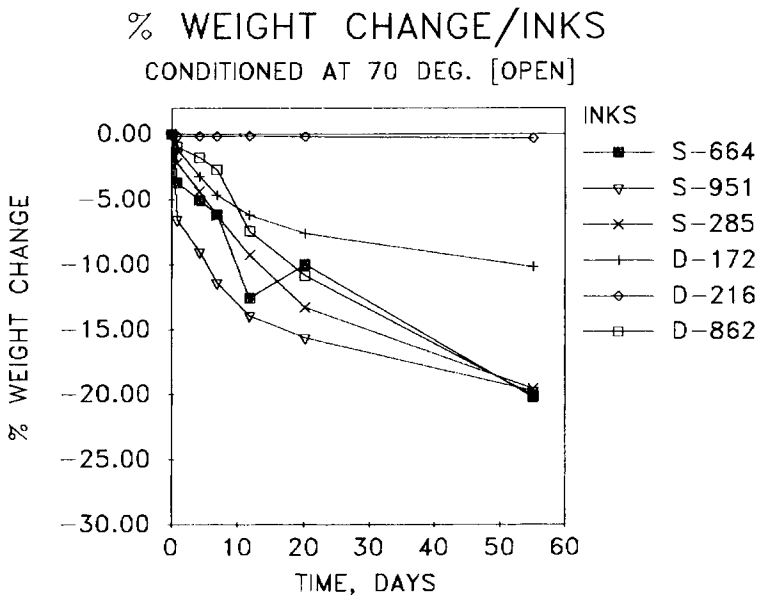

Figure 9 Percent weight changes versus time (days) at 70°C (under "open" conditions).

erence data and the "aging" data in Table VI by plotting $\Delta W_i(t, T_u)$ versus $1/t^n$ or $\Delta W_i(t_{cd}, T_{cd})$ versus $(1/t_{cd})^n$ for each fluid, i, where $n = \frac{1}{2}$ reasonably represented the data.

In an open system, eq. (19) represents the net effect of components lost and components gained by the fluid as indicated in Figures 8 and 9. If the loss rate of solvent vehicles is greater than the sorp-

Table VI Percent Weight Changes for Unconditioned (25°C) and Conditioned (70°C) Inks under "Open" Atmospheric Conditions

Time (days)	% Weight Change[a]					
	S-664	S-951	S-285	D-216	D-172	D-862
0.86						
Uncond.	−0.11	0.16	0.27	−0.024	0.004	0.002
Cond.	−3.69	−6.53	−2.21	−0.16	−1.14	−0.98
4.3						
Uncond.	−0.28	0.36	0.57	−0.024	0.0005	0.035
Cond.	−5.05	−9.00	−4.39	−0.17	−3.23	−1.78
6.8						
Uncond.	−0.29	0.52	0.77	−0.032	−0.012	0.031
Cond.	−6.14	−11.36	−6.21	−0.17	−4.66	−2.69
7.8						
Uncond.	−0.25	0.56	0.86	−0.021	−0.013	0.031
Cond.	−6.86	−12.40	−6.91	−0.19	−5.10	−2.90
11.8						
Uncond.	−0.14	0.79	1.12	−0.021	−0.015	−0.048
Cond.	−12.56	−13.92	−9.22	−0.15	−6.18	−7.38
20.2						
Uncond.	0.33	1.16	1.60	−0.019	−0.022	0.051
Cond.	−9.96	−15.62	−13.28	−0.18	−7.58	−10.84
55.0						
Uncond.	2.32	2.22	2.91	0.053	−0.012	0.11
Cond.	−20.21	−19.72	−19.56	−0.31	−10.17	−20.07

[a] Designations: S, solution; D, dispersion.

Table VII The Effect of Incline Angle (α) on the Tack of Unconditioned TPG and Inks (25°C) and Conditioned Ink S-285[a] (55 days at 70°C)[a]

	Incline angle (rad)							
	0.11		0.18		0.22		0.29	
Sample	w (rad/s)	$\tau \times 10^3$ (kg s)	w (rad/s)	$\tau \times 10^3$ (kg s)	w (rad/s)	$\tau \times 10^3$ (kg s)	w (rad/s)	$\tau \times 10^3$ (kg s)
TPG	3.2	0.217					6.0	0.194
S-664[b]	0.64	27.6					2.8	18.3
S-951[b]	0.36	50.9					1.6	37.6
S-285[b]	0.44	41.4					3.1	15.4
S-285[c]	0.18	102.2	0.20	114.0	0.44	73.2		

[a] w, roller angular speed; v, roller angular velocity; l, sample thickness = 1.5×10^2 μm; roller weight = 8.214×10^{-1} kg.
[b] Designation: S, solution.
[c] Conditioned sample.

tion rate of water vapor, then above a critical temperature, T_0, ΔW_i is negative over such a range. But, competition between these rates may lead to the behavior as observed for liquid S-664 in Figure 8 at the reference temperature ($\approx$ 298°K) which is below the critical temperature. In this case, ΔW_i is negative up to a transition time, t'_0, and is positive for $t > t'_0$. This behavior indicates that $D_i(t, T)$ in eq. (21) is greater than 1.0 for $t < t'_0$ and smaller than 1.0 for $t > t'_0$.

The relationship of tack, τ_i, to the percent weight change, ΔW_i, as functions of t_{cd} and T_{cd} may be shown by utilizing the results of eqs. (11), (12), and (19). These manipulations lead to the following result:[6]

$$\tau_i(t_{cd}, T_{cd}) = C_1 + [C_2 \times Q(t_{cd}, T_{cd})] \quad (22)$$

where $C_1 = [(K_i)_{AV}/(k_i)_{AV}]/\sqrt{\alpha}$, $C_2 = C_i(K_i)_{AV}\alpha$ and $Q(t_{cd}, T_{cd}) = \{\ln[1 - \Delta W_i(t_{cd}, T_{cd})/(C_0)_i]/f_i(T_{cd})\}^{\delta}$; eq. (22) is also consistent with the results of eqs. (14),

Table VIII Parameters for the Calculation of Tack [$\tau_i = (K_i)_{AV}\alpha/W_i$], Conditioned Roller Angular Speed [$W_i = (W_u)_i/[1 + C_i(W_u)_i(t_{cd})^{\delta}]$], and Unconditioned Roller Angular Speed [$(W_u)_i = (k_i)_{AV}\alpha^{3/2}$]

							t_{cd} = 7.8 d[d]		t_{cd} = 55 d[d]	
Sample[a]	$(k_i)_{AV}$ (rad$^{-1/2}$/s)	#Vals[b]	C_i (s/rad-days$^{\delta}$)	δ_i	$(K_i)_{AV}$ ($\times 10^3$) (kg)	#Vals[c]	α_c (rad)	$(\tau_i)^c$ ($\times 10^3$) (kg s)	α_c (rad)	$(\tau_i)^c$ ($\times 10^3$) (kg s)
TPG	63.0 ± 24.0	2			5.2 ± 1.2	2				
I530	37.8	1			138					
S-664	17.7 ± 0.2	2	0.044	1.32	180 ± 18	4	0.19	46.0	0.035	109.3
S-951	10.0 ± 0.2	2	0.20	0.90	190 ± 4	4	0.18	88.2	0.057	159.4
S-285	15.9 ± 3.8	2	0.14	0.78	178 ± 20	4	0.20	49.8	0.073	82.9
S-272	10.9	1			205	1				
D-216					144 ± 4	2				
D-172	30.7	1	0.030	0.21	128 ± 28	3	0.79	9.35	0.60	10.8
D-862					84 ± 18	2				

[a] The error estimate for $(k_i)_{AV}$ and $(K_i)_{AV}$ is given as an average.
[b] The two (2) values were determined, respectively, at α = 0.11 rad and α = 0.29 rad; the one (1) values for I-530 and (S-272, D-172) were determined, respectively at α = 0.11 rad and α = 0.29 rad.
[c] The values represent unconditioned samples at 70.0°C (α = 0.11 rad and/or α = 0.29 rad) and the conditioned samples at 70.0°C [t = 7.8 days (α = 0.29 rad); t = 55.0 days (α = 0.11 rad)]: 4 values [uncond. (α = 0.11 and 0.29 rad) and cond.]; 3 values [uncond. (α = 0.29 rad) and cond.]; 2 values [cond. only]; and 1 value [uncond. (I-530: α = 0.11 rad; S-272: α = 0.29 rad)].
[d] Critical parameters as determined from eqs. (17) and (18); the conditioning or "aging" temperature was 70°C; the angle and tack values are averaged, respectively, from (A_i and B_i) and (Σ_1 and Σ_2).

Table IX Calculation of Tack, τ_i, and Roller Angular Speed, $(W_u)_i$, for Unconditioned Fluid/Inks at 25°C Using the Paremeters in Table VIII[a]

Inclined Angle[b] (rad)	Sample	Angular Speed, $(W_u)_i$ (rad/s)		Tack, $\tau_i \times 10^3$ (kg s)	
0.11	TPG	Exptl:	3.2	Exptl:	0.22
		Calcd:	2.3	Calcd:	0.25
		% dev:	28.1	% dev:	−13.6
	S-664	Exptl:	0.64	Exptl:	27.6
		Calcd:	0.65	Calcd:	30.5
		% dev:	−1.6	% dev:	−10.5
	S-951	Exptl:	0.36	Exptl:	50.9
		Calcd:	0.36	Calcd:	58.1
		% dev:	0.0	% dev:	17.6
	S-285	Exptl:	0.44	Exptl:	41.0
		Calcd:	0.58	Calcd:	33.8
		% dev:	−31.8	% dev:	17.6
0.29	TPG	Exptl:	6.0	Exptl:	0.19
		Calcd:	9.8	Calcd:	0.15
		% dev:	−63.3	% dev:	21.0
	S-664	Exptl:	2.8	Exptl:	18.3
		Calcd:	2.8	Calcd:	18.6
		% dev:	0.0	% dev:	−1.6
	S-951	Exptl:	1.6	Exptl:	37.7
		Calcd:	1.6	Calcd:	34.4
		% dev:	0.0	% dev:	8.8
	S-285	Exptl:	3.1	Exptl:	15.4
		Calcd:	2.5	Calcd:	20.6
		% dev:	19.4	% dev:	−33.8
	S-272	Exptl:	1.7	Exptl:	34.2
		Calcd:	1.7	Calcd:	30.4
		% dev:	0.0	% dev:	11.1
	D-172	Exptl:	4.8	Exptl:	5.2
		Calcd:	4.8	Calcd:	7.7
		% dev:	0.0	% dev:	−48.1

[a] Roller weight = 8.214×10^{-1} kg; roller radius = 0.0279 m.
[b] Average % deviations: $\alpha = 0.11$ [$(W_u)_i$, ±15.3; τ, ±14.8]; $\alpha = 0.29$ [$(W_u)_i$, ±13.8; τ, ±20.7].

(15a), and (15b). By determining the parameters for eq. (19) and using the results in Table VIII, $\tau_i(t_{cd}, T_{cd})$ may be calculated from eq. (22). Calculations for S-664 and D-172 agree within the average deviations as given in Table X. By comparing Tables VI and X with Figures 8 and 9, the results show quite clearly that tack is affected by the weight changes in its composition. Other parameters such as heats of vaporization,[15] heat capacity,[16] and density[17] may be useful as a basis for defining the thermodynamic nature of tack for an open system in which vapor pressure and composition change with temperature and time.

ACCELERATED TESTING

In many cases of long-term use of inks and fluids, it is desirable to know the useful range of service life. Often it is not feasible to examine such substances over extended time periods. To circumvent such inconveniences, accelerated testing may be used to simulate such time periods.[10,14,18] These tests may take the form of mechanical[10,18] and/or thermal modes.[14] In this investigation, the thermal mode was used. In some instances heat may cause chemical reactions or degradation of certain substances of a given fluid. To augment the thermal mode of accelerated testing, an experiment was performed using vacuum as shown in Table V for the solution ink S-664. By comparing the tack results in Table V with the results in Table X at $t = 7.8$ days, there appears to be reasonable agreement if one takes into consideration thermal testing at 70°C versus vacuum testing at room temperature. By calibrating such systems, a vacuum pressure may be found to compliment a given temperature.[6]

Table X Calculation of Tack, τ_i, and Roller Angular Speed, W_i, for Conditioned Inks at 70°C Using the Parameters in Table VIII[a]

Condition Time[b] (Days)	Sample	Angular Speed, W_i (rad/s)		Tack, $\tau_i \times 10^3$ (kg s)	
7.8					
(α = 0.29 rad)	S-664	Exptl:	0.98	Exptl:	64.5
		Calcd:	0.98	Calcd:	53.2
		% dev:	0.0	% dev:	17.5
	S-951	Exptl:	0.54	Exptl:	118.5
		Calcd:	0.53	Calcd:	104.0
		% dev:	1.8	% dev:	12.2
	S-285	Exptl:	0.96	Exptl:	65.7
		Calcd:	0.91	Calcd:	56.7
		% dev:	5.2	% dev:	13.7
	D-172	Exptl:	3.6	Exptl:	11.7
		Calcd:	3.9	Calcd:	9.5
		% dev:	−8.3	% dev:	18.8
55.0					
(α = 0.11 rad)	S-664	Exptl:	0.096	Exptl:	190.2
		Calcd:	0.097	Calcd:	204.1
		% dev:	−1.0	% dev:	−7.3
	S-951	Exptl:	0.10	Exptl:	182.8
		Calcd:	0.099	Calcd:	211.1
		% dev:	1.0	% dev:	−15.5
	S-285	Exptl:	0.18	Exptl:	101.6
		Calcd:	0.20	Calcd:	97.9
		% dev:	−11.1	% dev:	3.6

[a] Roller weight = 8.214×10^3 kg; roller radius = 0.0279 m.
[b] Average % deviations: t = 7.8 days (w_i, ±3.8; τ, ±15.6); t = 55.0 days (w_i, ±4.4; τ, ±8.8).

To illustrate the thermal accelerated testing procedure, eq. (19) can be defined for the "aging" test at temperature, T_{cd}, and time, t_{cd}. At temperature, T_a, a time, t_a, may be determined from the following:[14]

$$\ln\{1 - [\Delta W_i(t_{cd}, T_{cd})/(C_0)_i]\} = -\ln[D_i(t_{cd}, T_{cd})] = -\ln[D_i(t_a, T_a)] \quad (23)$$

i.e., by setting the expression in eq. (23) equal to $f_i(T_{cd})t_{cd} = \{E_i(T_{cd})/T_{cd}\} = f_i(T_a)t_a = \{E_i(T_a)/T_a\}t_a$ and solving for t_a, one obtains

$$t_a = t_{cd} \times \{[E_i(T_{cd})/E_i(T_a)]\} \times [T_a/T_{cd}] \quad (24)$$

Equation (24) is useful as a guide for estimating the time, t_a, at temperature, T_a; the time, t_a, is equivalent to the time, t_{cd}, at temperature, T_{cd}; but, the exact interpretations may be difficult due to extrapolation uncertainties.[14] As an example, for t_{cd} = 55 days and T_{cd} = 343°K and T_a = 298°K, t_a for S-664 and D-172 was found to be, respectively, 200 days ($\approx$ 0.60 years) and 670 days ($\approx$ 1.8 years). From these results, a 55-day "aging" test at 70°C predicts that it would take the dispersion ink approximately three times as long to reach an equivalent tack value of the solution ink at 25°C. This calculation also suggests an enhanced service life and performance for meter components such as "data" wheels in the presence of this dispersion ink versus the solution ink. As discussed earlier, humidity and temperature changes may dramatically affect the uncertainty of these calculations.

CONCLUSION

Preliminary results suggest that tack is a function of viscosity, surface tension, roller angular speed, conditioning or "aging" temperature, time, humidity, and fluid composition. These measurements express surface and bulk properties of fluids, which can be obtained from dynamic and static testing. The magnitude and contribution of the forces to each property depend on the measurement geometries (e.g., shearing, extensional, compressional,

and/or some combination) and may be analyzed from a theoretical and experimental basis. The incline method used in this investigation was found to be simple and sensitive to the tack variability of different types of fluids at low rotational speeds and the results agree rather favorably with manual and automated parallel-plate testing. The tack information obtained was used to help select fluid substances of the proper viscosity, surface tension, and long-term stability for solution inks containing certain polymeric substances. The information was further used to maximize print performance and the service life of certain printing components in contact with such fluids by simulating conditions that contributes to mechanical failures of these components in actual use.

NOMENCLATURE

A_i	empirical constant = $(K_i)_{AV}/(k_i)_{AV}$
B_i	empirical constant = $(K_i)_{AV} C_i (t_{cd})^{\delta}$
α	incline angle
α_c	critical incline angle for "unaged" and "aged" fluid
β	constant for τ_i
β'	constant for $(\tau_i)'$
$(C_0)_i$	limiting constant for ΔW_i
C_1	empirical constant for ΔW_i
C_2	empirical constant for ΔW_i
C_i	empirical constant for w_i
$D_i(t, T)$	empirical function of time, t, and temperature, T, for ΔW_i
δ	δ_i = empirical exponent for t_{cd} for fluid, i
ΔW_i	weight change (loss or gain) of fluid, i
$E_i(T)$	empirical function of temperature, T, for fluid, i, for ΔW_i
$E_i(T_{cd})$	empirical function of "aging" temperature, T_{cd}, for fluid, i, for ΔW_i
$f_i(T)$	empirical function of temperature, T for ΔW_i
$f_i(T_{cd})$	empirical function of "aging" temperature, T_{cd}, for fluid, i, for ΔW_i
g'	gravitational constant
I_c	moment of inertia
k_0	constant for roller angular speed and travel times, t_0 and t
$(k_i)_{AV}$	empirical constant for $(w_u)_i$
$(K_i)_{AV}$	empirical constant for τ_i
M	mass of roller
$Q_i(t_{cd}, T_{cd})$	empirical function of "aging" time, t_{cd}, and "aging" temperature, T_{cd}, for ΔW_i
R	radius of roller
T	temperature (°K)
T_a	temperature (°K) chosen to evaluate the time, t_a, for the accelerated test at T_c and t_{cd}
T_c	conditioning or "aging" temperature (°K)
T'_0	torque of roller without fluid/ink
T'	torque of roller in presence of fluid/ink
t_0	travel time of roller without fluid/ink
t'_0	transition time for ΔW_i
t	time
t'	$t - t'_0$
t_{cd}	condition time for w_i
τ_i	tack (kg-s)
τ'_i	τ' = tack (kg-cm)
$(\tau_i)_c$	critical tack (kg-s) for the critical incline angle, α_c
$(v_{AV})_0$	$v_0 = x/t_0$ = average velocity of roller without fluid/ink
$(v_{AV})_i$	$v = x/t$ = average velocity of roller in presence of fluid/ink
w_0	roller angular speed (rad/s) without fluid/ink
$(w_u)_i$	roller angular speed (rad/s) of unconditioned or "unaged" fluid/ink
w_i	roller angular speed (rad/s) of conditioned or "aged" fluid/ink
x	linear travel distance of roller

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