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# Rheology Aspects of Leather Finishing Formulations

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*The rheological properties of leather finishing formulations were investigated. The rheological analysis was performed in a Ford cup number 4, a Brookfield viscometer, and a rheometer. The effects of the formulation parameters on the viscosity behavior showed similar trends for each technique. The tests in the rheometer showed that soft acrylic resins produced shear thinning formulations, similar to the effect of the finishing pigments. Furthermore, samples containing soft resins and polymeric pigments produced formulations with elastic properties. Finally, the Ford viscosity does not change significantly with the formulation parameters as the Brookfield viscosity does (type of pigment, resin, or resin-pigment ratio). Thus, the non-Newtonian behavior shown by the finishing samples analyzed suggests avoiding the use of the Ford cup when assessing leather finishing formulations. The Brookfield viscometer, however, would provide more reliable viscosity values when a rheometer is not at hand.*

**Keywords** Leather; Finish; Finishing formulation; Ford cup; Brookfield; Shear thinning; Rheology

## Introduction

Leather is finished to improve its characteristics of aesthetics and protection. To accomplish this primary objective, leather finishing formulations are based on different ingredients depending on the desired properties of the finish. For example, garment leather needs abrasion and water protection, automotive leather must fulfill high fog- and-heat-resistance standards, and shoe upper leather requires the ability to withstand a standard number of Bally flexes (a standard test that simulates the bending of the shoe upper while walking, DIN 53340), as well as attain specific friction (DIN 53273) and adhesion (DIN 53339) values. Therefore, each leather article must satisfy some specific properties for which the finishing formulations must be designed.

From a rheological standpoint, the finishing mixtures are formulated differently to be appropriate to the application technique being used (Adzet, 1987). A spray

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coating application requires a low viscosity fluid to facilitate flow through the nozzle. Furthermore, the high shear rates found in a spray finishing process may make it desirable to have a shear thinning fluid, i.e., a fluid whose viscosity decreases with shear, to promote an optimal fluid flow and spray application. An analogous perspective can be applied to roll coating, a finishing process whose viscosity must be controlled to prevent the formulation from sagging on the roll (Biles, 1990). Finally, the curtain coating technique needs a specific balance between surface tension and viscosity to avoid bubble formation and allow good penetration, since this coating method is primarily used in leather impregnation (Adzet, 1987).

In addition to process fluid mechanics, the rheological behavior of the finishing fluid plays a key role before and after application. During mixing, the finishing formulation is subjected to shear rates around  $100 \text{ s}^{-1}$  (Biles *et al.*, 1985), a shear level that may affect coating performance for a shear thinning formulation (Brito-de la Fuente *et al.*, 1998). After application, for example, the viscosity must be low to promote the leveling of the film by surface tension (Gurfinkel and Patera, 1997). Thus, the rheological behavior of a coating formulation influences not only application performance, but mixing characteristics and film uniformity as well.

In tanneries, the shear thinning properties of a leather finishing formulation can be used to determine its performance in the process (Biles, 1990; Biles *et al.*, 1985; Levy, 1989). The viscosity of the fluid at the shear rates of coating application can be compared to that at the shear rates of film leveling, ratio known as the rheology index (RI) factor (Biles, 1990; Biles *et al.*, 1985; Levy, 1989; Matsuda and Brendley, 1979). This index can be used to predict finish formulation performance in a roll coating operation (Matsuda and Brendley, 1979). Experiments indicate that improved flow, leveling, and base coat uniformity can be achieved by adjustments in the rheology index factor (Biles, 1990; Biles *et al.*, 1985). It has been shown that these improvements can be achieved with formulations whose rheology index ranges from 0.14 to 0.33 when used in a roll coating application of splits (Biles *et al.*, 1985). For smoothly buffed and impregnated corrected grain substrates, significantly higher RI values ( $\sim 0.6$ ) and higher high shear rate viscosities are needed to obtain an optimal uniform base coat appearance (Biles *et al.*, 1985). For topcoat applications, a RI range of 0.65 to 0.75 gives more uniform films. In a topcoat spray application, coverage and leveling reach a maximum at a shear rate ratio of 3, but beyond this value leveling decreases at the high solids range (Biles, 1990). As a result, the RI can change from 0.14 to 3, depending on the formulation, application technique, and substrate, if an adequate finish layer is desired. The relatively wide RI range shows that the RI concept is very particular for a given formulation and substrate. In addition, Levy (1989) showed that the RI factor, as defined by Matsuda and Brendley (1979), may not be universally applicable for assessing finishing formulation rheology when acrylic, butadiene, or polyurethane-based formulations are being compared. Thus, for optimum RI application, the RI should be independent of the formulation and kind of leather being treated, a subject that may be an interesting topic of future research.

Coating appearance is related not only to the rheology index but also to surface tension forces, especially in coating adhesion. Wetting, spreading, and penetration of the coating are influenced by the surface tension and the liquid-solid contact angle (Carvalho and Scriven, 1990; Coyle *et al.*, 1990). Cosolvents, surfactants, and leveling agents help decrease surface tension for water-based formulations. The capillary number involves the ratio of viscous to surface tension forces, a number that can be

used to predict formulation performance as it has been used in other coating fields (Coyle et al., 1990; Réglat and Tanguy, 1998). Thus, a further and more complete study is necessary so that the rheology index and surface tension can be related and used safely in any leather finishing formulation.

In addition, torsional modulus measurements can be used to predict finish performance. The degree of thermoplasticity can be assessed to envisage the behavior of the formulation and its response on a typical plating or embossing operation. Process conditions can range from below room temperature to beyond 110°C (Biles et al., 1987), conditions that can be simulated in the rheometer under oscillatory tests. For example, a formulation with a high torsional modulus exhibits reduced thermoplasticity and superior plating properties, results that can be improved even more by controlling the rheology index factor, i.e., reducing the steady-state shear thinning properties of the formulation (Biles et al., 1987).

Although both viscosity and surface tension are very important in coating performance, apparently little scientific work has been published concerning the leather finishing process. Just a few references can be found, especially those regarding the concept of the rheology index factor. Still, the RI's applicability may be questioned, since it must be evaluated and monitored for each single formulation and application process. As a consequence, knowledge about the role of the rheology of the finishing formulations on application performance may be better understood. From a rheological standpoint, our objective is to analyze the rheological properties of some finishing formulations for leather in regard to the film properties of the finished leather.

## Experimental

The finishing formulations used in this investigation contained an acrylic resin in aqueous emulsion form and a pigment aqueous suspension. The ingredients were purchased from Stahl (Peabody, Mass.) and used as received; some of their physical properties are shown in Table I. Different resin-pigment ratios (dry basis) were tested (Table II). The formulations were always made in the same manner and with the same mixing system to avoid differences in the preparation procedure.

**Table I.** Selected properties of the components of the finishing formulations

Product	Base	ID (Stahl)	pH	Glass transition temp. ( $T_g$ , °C)	Mean diameter (nm)	Solids %
Impregnation resin	Acrylic	RI-1199	9.0	-22.5	68.45	35
Soft resin	Acrylic	RA-17	9.0	-34	107.15	35
Hard resin	Acrylic	RA-36	7.5	8	134.37	39
Black pigment	Black carbon	PP-8315	9.0	—	—	24
Brown pigment	Iron oxide	PP-3085	8.5	—	—	27
White pigment	Titanium dioxide	PP-11-183	8.5	—	—	61

Information provided by Stahl.

**Table II.** Selected finishing formulations analyzed in the rotational rheometer

Formulation	Dry basis (gr)				Water (gr)	Solids %
	Resin		Pigment <sup>a</sup>			
1	RA-17	40	Bl	20	240	20
2	RA-17	45	Bl	15	240	20
3	RA-17	45	W	15	240	20
4	RA-17	40	Br	20	240	20
5	RA-17	45	Br	15	240	20
6	RA-36	45	Bl	15	240	20
7	RA-36	45	W	15	240	20
8	RA-36	45	Br	15	240	20

<sup>a</sup>Pigment color: Bl = black, Br = brown, W = white.

All fluid samples were taken to the Brookfield viscometer (spindle #2 at 60 rpm) and the Ford cup (No. 4) for the viscosity determination. Both spindle number and speed were chosen in such a manner that the readings for most of the leather finishing formulations were in the middle of the Brookfield measurement range for the spindle. The Ford cup is shown in Figure 1 for those who are not familiar with it. The Ford cup No. 4 estimates the viscosity through gravity by emptying a cup with a bottom hole of 4 mm diameter. The Brookfield viscometer measures the viscosity in an infinite medium with different spindles, depending on the viscosity of the sample.

**Figure 1.** The Ford cup No. 4.

Regarding the rotational rheometer (Haake CV 20 N and a Couette geometry), the tests were performed at steady state and with a temperature control bath (Haake F3T) at shear rates ranging from 50 to 300 s<sup>-1</sup>. The viscoelastic properties were determined through small amplitude oscillation shear flow experiments performed in the linear viscoelastic region. The linear region was predetermined by a strain amplitude sweep at a constant frequency. The frequency of the tests ranged from 1 to 50 s<sup>-1</sup> and matched an oscillatory shear range from 10 to 780 s<sup>-1</sup>. All the reported values are the mean of at least two replicates.

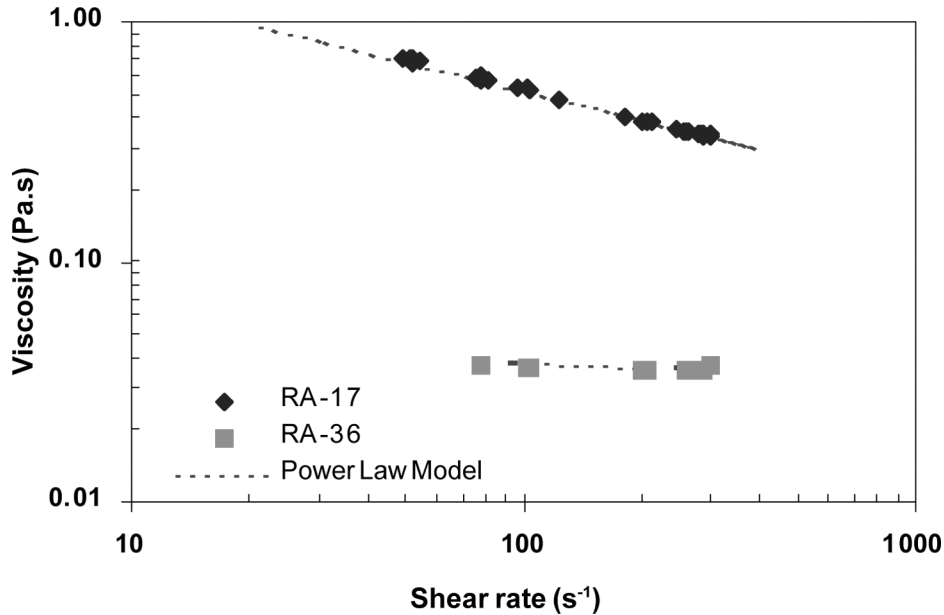
All the samples were made using a Cowles mixer to improve homogenization. The resin was added to the water, and then the pigment. No precipitation of the components was observed in any case. The Brookfield and Ford viscosities were determined after the finish preparation procedure, and then the samples were taken to the rheometer.

Cowhide leather was used in the finishing tests. The leather sections were taken from the center (croupon) to minimize the effects of the differences in the leather structure with respect to position. To reproduce the common process of finishing corrected grain, the crust leather was buffed with sandpaper #380 to eliminate the surface defects and then impregnated with the acrylic resin RA-1199 (Table I) to seal the grain porous structure. After application by spraying, the leather samples were plated with an 80°C hot grabbed plate at 10 Kg/cm<sup>2</sup>. The physical tests carried out on the finish were: Bally flexes, a test that simulates the bending of the shoe while walking and evaluates the cracking of the film at the bending region (DIN 53340); adhesion, a test that assesses the adhesion of the finish film to the leather (DIN 53339); and friction, a test that measures the resistance of the film to a moving felt when the felt is dry or wet, and when the leather is wet (DIN 53273). The leather used was chrome-tanned and contained 56.2% humidity, 4.7% chrome oxide, and a pH of 3.1, and was 1.8–2.0 mm in thickness. All the reported values are the mean of two replicates.

The basis of the experimental design was 54 experiments, expressed as 3<sup>3</sup> · 2<sup>1</sup>, but only eight samples were analyzed in the rheometer. The three-level factors included the solids content (20, 25, and 30%), resin emulsions (three), and pigment suspensions (three). The two-level fourth main factor was the resin-pigment ratio (2:1 and 3:1). The eight selected formulations considered two resins, three pigments, and two resin-pigment ratios. Hence, only the main effects were obtained from the fractional experimental set.

## Results and Discussion

In order to better understand the rheological behavior of the formulations, the two resins and the three pigments were analyzed one by one in the rheometer. The rheograms for the two resins are shown in Figure 2. RA-17, the soft one, presents a definite shear thinning behavior with a flow index of  $n = 0.6$  of the power law rheological model ( $\mu = K\dot{\gamma}^n$ , where the index  $n$  controls the rate of change of viscosity with shear rate and the consistency index  $K$  shifts up or down the curve). RA-36, the hard one, is mostly Newtonian ( $n = 0.94$ , being  $n = 1$  for a Newtonian fluid) with a viscosity lower than that of RA-17 (Table III). Thus, the differences in the characteristics of the resins will significantly affect the rheological behavior of the finishing formulations in which they are used. Although it is known that the RA-17 behavior may be due to the deformation of the emulsion droplets under

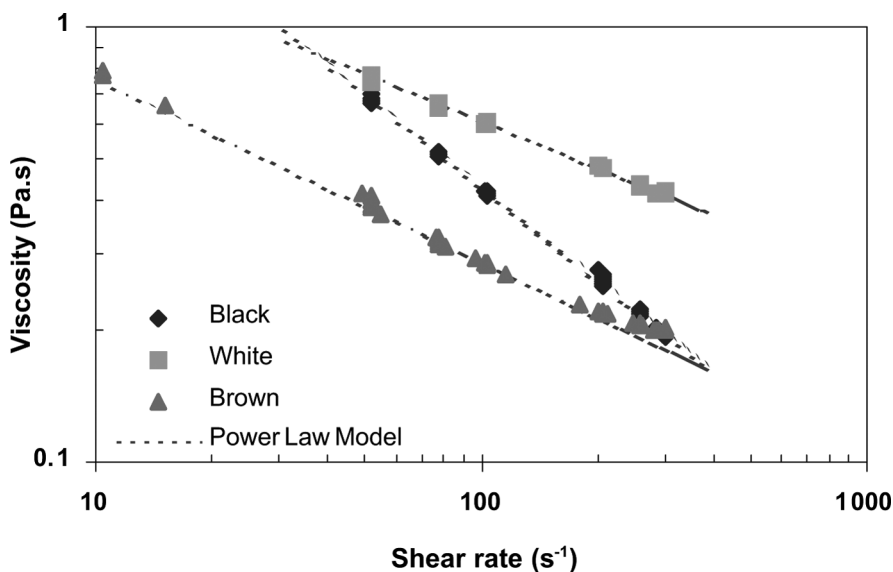


**Figure 2.** Flow curves for the acrylic resins and fitting to the power law model.

shear (Schramm, 1994; Macosko, 1994), the fact that RA-17 is more prone than RA-36 to deformation is not clearly understood. A soft resin may contain either a low molecular weight distribution or a short polymer backbone (in reference to the glass transition temperature), hence soft resin drops may be easier to deform than hard ones. That would partially explain the lower  $n$  value for RA-17. However, the interfacial tension and the amount of plasticizer (if it was used) included in the resin formulation would certainly affect the shear required to deform the drop. The information provided by Stahl (mean particle diameter, glass temperature, and solids content) was not sufficient to understand the observed behavior. The clarification may require manufacturer's proprietary information such as the stabilizer used, interfacial tension, ratio of the viscosity of the droplet liquid to that of the water, amount and type of plasticizer used, etc. (Mascoko, 1994).

**Table III.** Rheological parameters for the ingredients of the finishing formulations

Rheology	Viscosity power law model $\mu = K\dot{\gamma}^n$		Modulus range (Pa)	
	K	n	Elastic	Viscous
Resin emulsions				
RA-36	0.05	0.94	0.02–0.1	1.2–7.5
RA-17	3.26	0.60	0.02–2.0	0.1–0.3
Pigment suspensions				
Black	11.2	0.29		
Brown	2.0	0.64		
White	3.2	0.66		

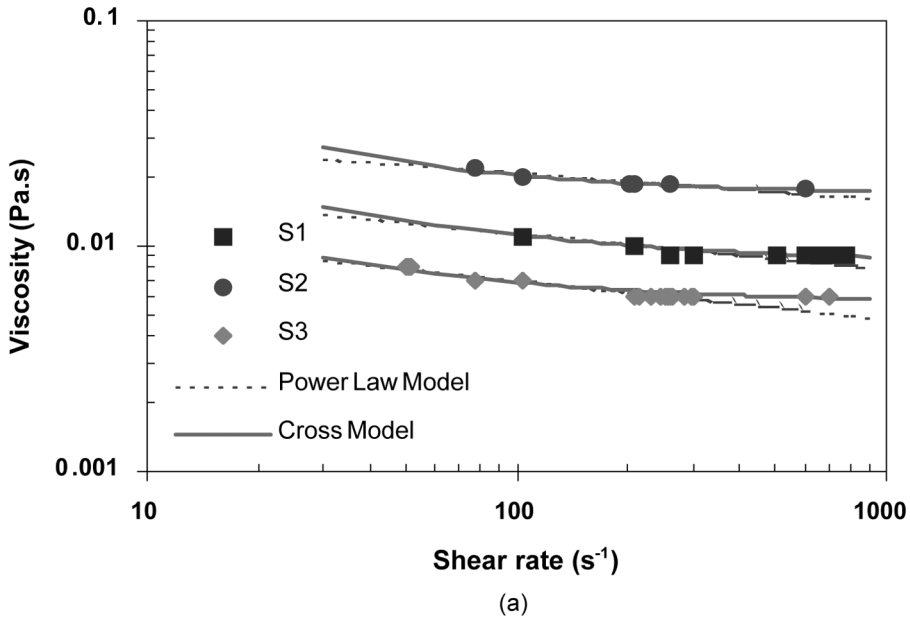


**Figure 3.** Flow curves for the pigment suspensions and fitting to the power law model.

Generally speaking about pigment suspensions, typical rheological behavior depends on the sort of pigment, the particle size, and the particle shape (Roper and Attal, 1993; Bousfield, 1993; Nott et al., 1989). The three pigment suspensions used here were of different types, but all of them were found to be shear thinning. Figure 3 shows that the black pigment exhibits the strongest shear thinning behavior (lower  $n$  value). The black pigment suspension contains polymer particles, and its rheological behavior fits the common rheology for polymers (Mascosko, 1994). Both brown and white pigment suspensions are made of minerals, namely iron oxide and titanium dioxide, respectively. Both colors present a common flow curve for mineral suspensions: shear thinning; however, the brown pigment suspension shows an increasing power index  $n$  at moderate shear rates, as seen from the divergence from the power law model. The fitting of the Cross model (Hjelm, 2000) to the rheological behavior of the brown suspension confirms it ( $\mu = \mu_{\infty} + (\mu_0 - \mu_{\infty}) / [1 + (t\dot{\gamma})^p]$ , where  $\mu_0$  controls the viscosity plateau at low shear rates,  $p$  is the shear thinning index,  $t$  controls the shear rate at which the shear thinning region starts, and  $\mu_{\infty}$  is the viscosity plateau at high shear rates). The power law model may predict the rheological behavior of the black and white pigment suspensions and the two resin emulsions with the parameters shown in Table III.

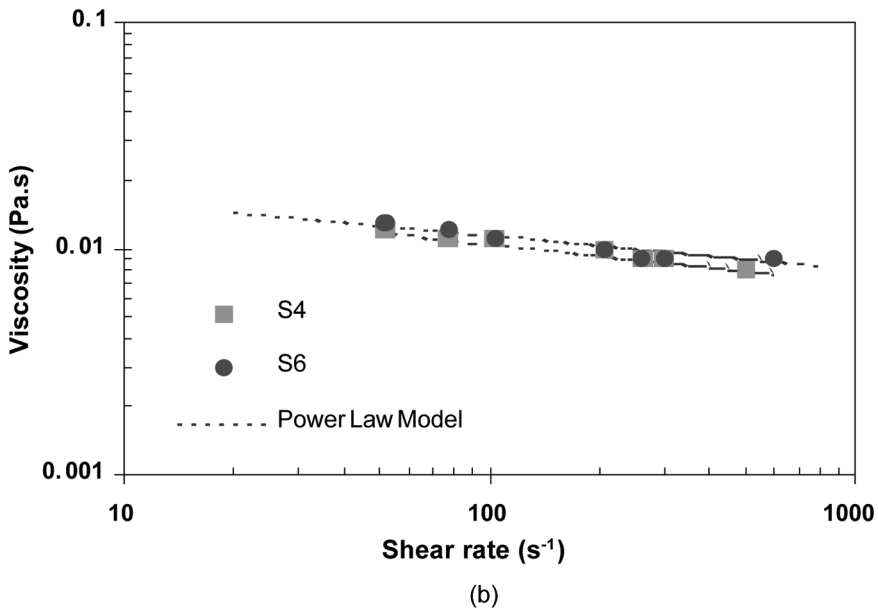
From a statistical point of view, eight different finishing formulations were investigated. First, we present the rheological behavior of the samples under pure shear (Figures 4(a), 4(b), 4(c)). The effect of the resin on the rheological behavior of the samples is illustrated by the sample pairs 2–6, 3–7, and 5–8. Sample 2 (RA-17) presents a slightly higher viscosity than sample 6 (RA-36). Sample 2 also shows a trend towards Newtonian behavior at high shear rates, as observed from the comparison of the Cross and power law models (Figure 4(a)). Although sample 6 definitely follows the power law behavior, both samples show very similar shear thinning indexes  $n$ . Samples 3 and 5, containing RA-17, are also more viscous than





**Figure 4.** (a) Flow curves for samples 1, 2, and 3 and fitting to the power law and cross models; (b) flow curves for samples 4 and 6 and fitting to the power law model; (c) flow curves for samples 5, 7, and 8 and fitting to the power law and Carreau models.

their respective counterparts containing RA-36, samples 7 and 8 (Figures 4(a), 4(c)). Thus, RA-17 will enhance the viscosity of the formulations. Since RA-36 is nearly Newtonian, the shear thinning behavior of formulations containing RA-36 will surely come from the pigment, as observed in samples 6, 7, and 8 (Figures 4(b), 4(c)).



**Figure 4.** Continued.

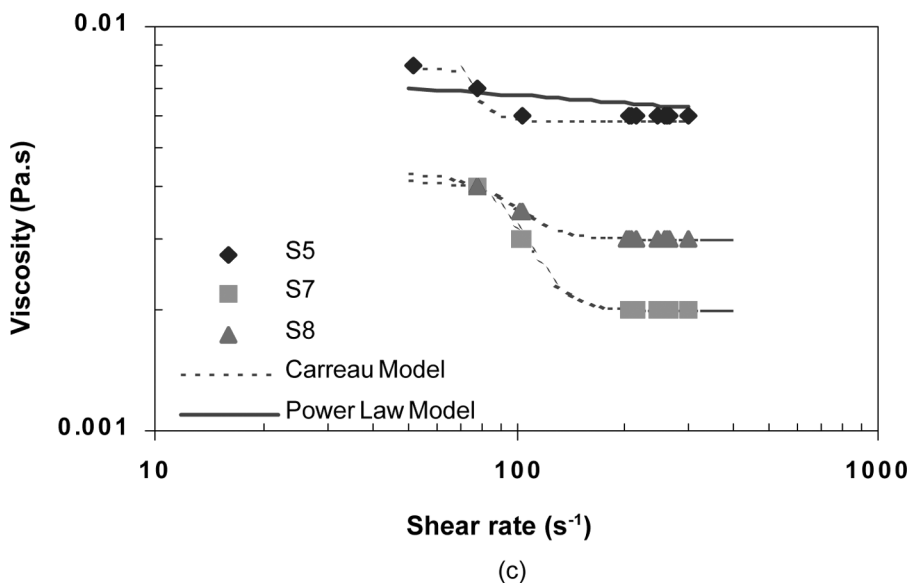


Figure 4. Continued.

To evaluate the effect of the pigment, samples 2, 3, and 5 can be compared (Figures 4(a), 4(c)). The rheological behavior will depend on the sort of pigment used since these formulations containing RA-17 show different rheological behaviors. Similar results are observed when samples 6, 7, and 8, containing RA-36, are compared (Figures 4(b), 4(c)). The black pigment containing formulations present the highest viscosity. This may be due to the agglomerates that that pigment tends to form, as explained in Hjelm et al. 2000. The brown and white RA-17 containing formulations present comparable viscosities but different rheological behaviors that may be due to the different nature of both pigments (particle size, stabilizer used, additives added to the pigment suspension, etc). For the RA-36 at low shear rates, the viscosity level for both white and brown formulations is similar and Newtonian. At high shear rates, however, the viscosity level is higher for the brown pigment containing formulation. Again, the nature and properties of the pigment suspension makes the difference. Samples 5, 7, and 8 (Figure 4(c)) follow the Carreau rheological model (Macosko, 1994) with two Newtonian plateaus at low and high shear rates ( $\mu = \mu_{\infty} + (\mu_0 - \mu_{\infty})[1 + (\lambda\dot{\gamma}^2)]^{-p}$ , where  $\mu_0$ ,  $\mu_{\infty}$ , and  $\lambda$  have similar meanings as in the Cross model, and  $p$  is the shear thinning index). From the literature, one may infer that, at low shear rates, when the orientation fields are sufficiently apart, a Newtonian viscosity is to be observed (Roper and Attal, 1993). At high shear rates, the fields change to fit the lowest resistance to flow, generating the second Newtonian plateau. However, from the tests performed on the ingredients alone (Figure 3) and the information provided by Stahl we cannot fully explain the behavior of samples 5, 7, and 8 (Figure 4(c)).

Increasing the resin-pigment ratio enhances the viscosity of the samples (sample pairs 1-2 and 4-5). Samples 1 and 2 (Figure 4(a)) show both shear thinning and Newtonian behavior, depending on the shear rates, as seen from the fitting of the Cross and power law models. Samples 2 and 5 show a consistently high viscosity that

is imparted by the high resin/pigment ratio, independently from the pseudoplastic and Newtonian character of each formulation. Thus, a higher resistance to flow takes place when the concentration of the resin increases.

From the Ford and Brookfield viscosities, the effect of the resin is similar to what was observed in the rheometer. RA-17 enhances the viscosity of the formulation. The trends regarding the effect of the pigment are different. In respect to the Ford and Brookfield viscosities and RA-36, the black pigment is the one that increases viscosity the most. However, the formulations with RA-36 and the brown pigment possess the highest Brookfield viscosity. In addition, the resin-pigment ratio does not show a similar trend with either viscometer. Thus, the viscosity from both viscometers is different. The superior viscometer would be the one that better distinguishes the differences in the formulations.

As seen from Table IV, the viscosity values obtained from the viscometers and rheometer are different. In fact, with regard to the shear rates of the application process of about  $40,000 \text{ s}^{-1}$  (Biles et al., 1985), it may be very difficult to distinguish the formulations if we rely only on the Ford viscosity. The Brookfield viscometer amplifies the differences among the viscosity values of the samples since it relies on the torque measured on the rotating spindle at higher shear rates (at least near the spindle) than those of the Ford cup. The torque spindle measurement principle is widely used in modern rheometers to obtain absolute viscosity values with known gap. This principle permits the Brookfield viscometer, with different spindles and speeds, to

**Table IV.** Rheological parameters for the leather finishing formulations

Sample	Power law model $\mu = K\dot{\gamma}^n$		Viscosity (mPa.s)	
	K	n	Ford	Brookfield
1	0.024	0.84	21.8	10.5
2	0.037	0.88	23.4	15.0
3	0.015	0.83	21.4	7.5
4	0.024	0.83	93.6	191
5	0.091	0.93	22.3	8.0
6	0.023	0.85	21.1	5.0
7	—	—	20.4	5.0
8	—	—	20.4	8.0
Cross model $\frac{\mu - \mu_\infty}{\mu_0 - \mu_\infty} = \frac{1}{1 + (t\dot{\gamma})^p}$				
Brown pigment	$\mu_0 = 2.4$	$\mu_\infty = 0.103$	$t = 1$	$p = 0.66$
1	$\mu_0 = 0.0084$	$\mu_\infty = 0.1$	$t = 1$	$p = 0.75$
2	$\mu_0 = 0.017$	$\mu_\infty = 0.22$	$t = 0.9$	$p = 0.89$
3	$\mu_0 = 0.0056$	$\mu_\infty = 0.06$	$t = 1$	$p = 0.8$
Carreau model $\frac{\mu - \mu_\infty}{\mu_0 - \mu_\infty} = [1 + (\lambda\dot{\gamma}^2)]^p$				
5	$\mu_0 = 0.008$	$\mu_\infty = 0.006$	$\lambda = 0.013$	$p = 21.6$
7	$\mu_0 = 0.004$	$\mu_\infty = 0.002$	$\lambda = 0.01$	$p = 7.185$
8	$\mu_0 = 0.004$	$\mu_\infty = 0.003$	$\lambda = 0.01$	$p = 7.06$

obtain more realistic viscosity values than those from the Ford cup, whose readings also depend on gravity but lack steady state. In both instruments, it is very difficult to assess the real shear rate of the experiment, so shear thinning effects may affect the readings, specially if the tests are performed at different shear rates. This possibility may affect the comparison of the results between the Ford and Brookfield viscosities.

The different behavior at low and high shear rates has been already observed in the literature (Biles, 1990; Biles et al., 1985; Levy, 1989; Matsuda and Brendley, 1979) and used to define the rheology index factor. Surprisingly, the Ford cup is still used as the only source of viscosity measurement by many leather finishers to control the viscosity of the finishing formulation. Although the rheometer is the only instrument that gives reliable results, the Brookfield viscometer would certainly provide viscosity values closer to the real ones than the Ford cup and should be better used in tanneries when access to a rheometer is not available.

### Oscillatory Tests

Figure 5 shows the results for the viscoelastic properties from the oscillatory tests performed on the resins. Both present a predominant viscous behavior with a complex viscosity almost constant. For RA-36, the viscous component  $\eta'$ , the dynamic viscosity, of the complex viscosity  $\eta^*$  decreases slightly with frequency, showing that some deformation is occurring as in the rheological behavior of polymers (Schramm, 1994; Macosko, 1994).

Samples 1 and 2 were found mostly elastic (Figure 6(a)), elasticity defined as when the elastic modulus,  $G'$ , is greater than the viscous modulus,  $G''$ . In that situation, the phase angle  $\alpha$ , defined as  $\tan \alpha = G''/G'$ , is lower than  $45^\circ$ . The two finishing samples contain RA-17 and the black pigment, components that play a dominant

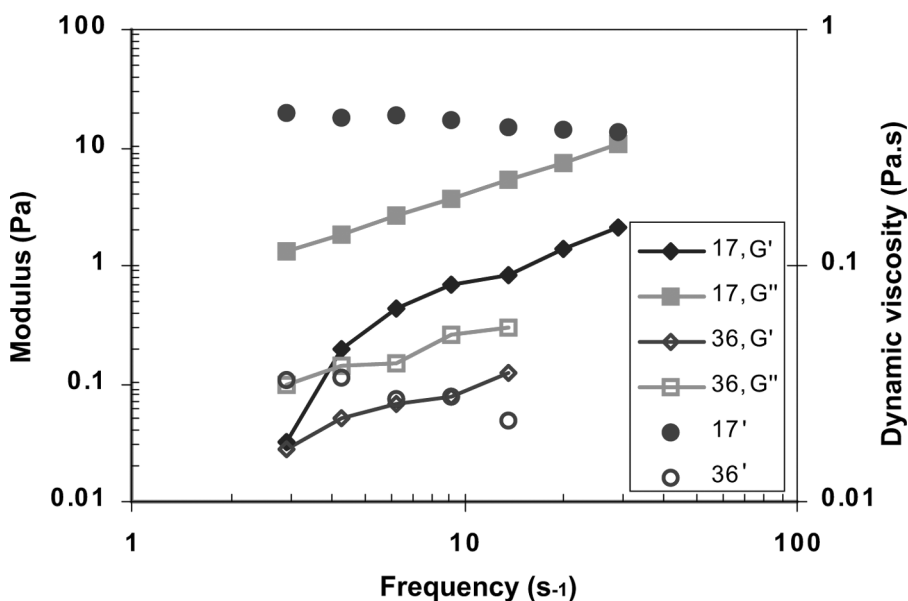


Figure 5. Oscillatory tests for the resins.

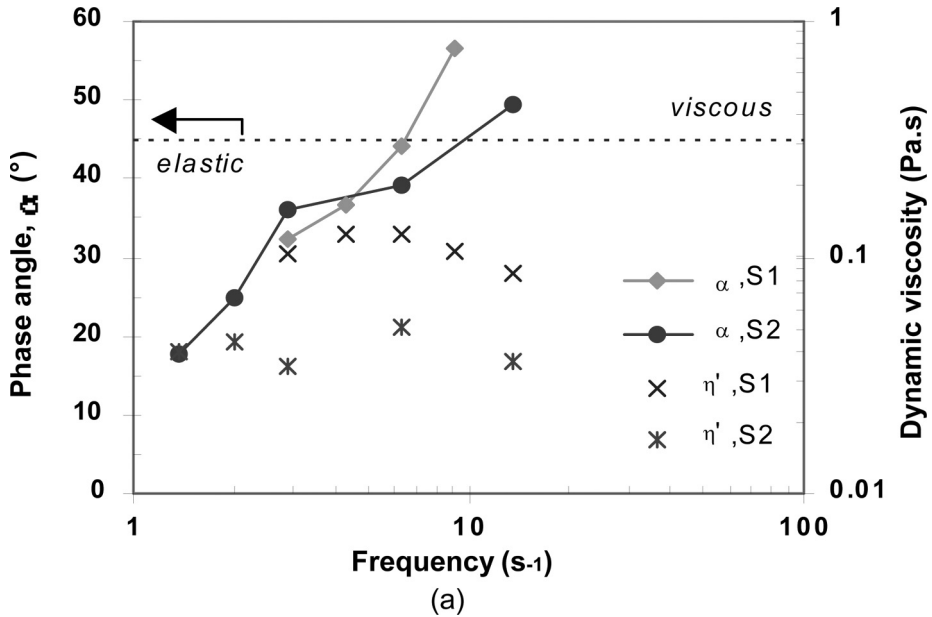


Figure 6. Oscillatory tests for (a) samples 1 and 2, (b) samples 4 and 7, and (c) samples 3, 5, 6, and 8.

role in developing a structure. In most of the samples, there appears to be a crossover of moduli (see Table V). This may indicate that a macromolecular network with important elastic properties is formed when  $G' > G''$ . The kind of interactions

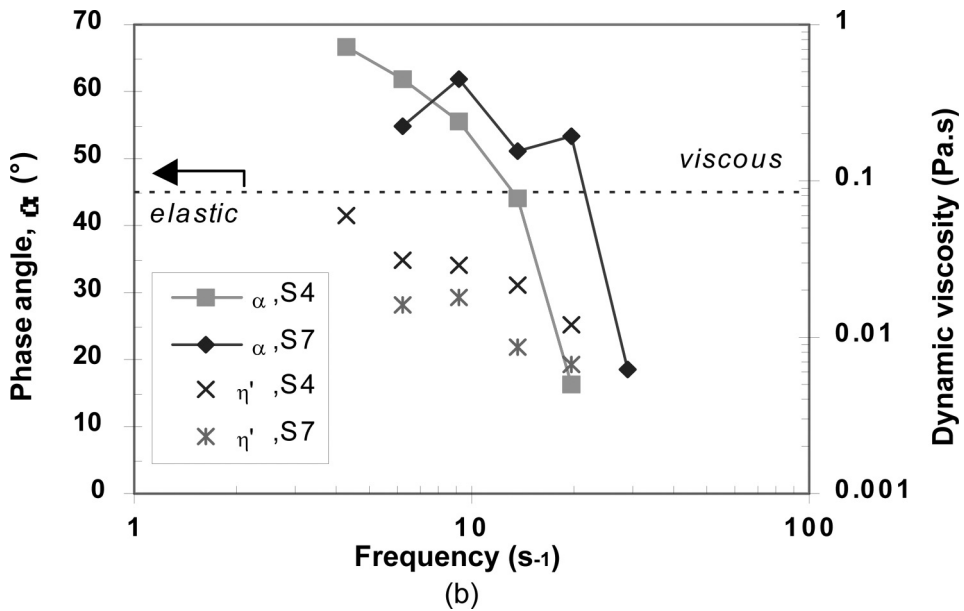


Figure 6. Continued

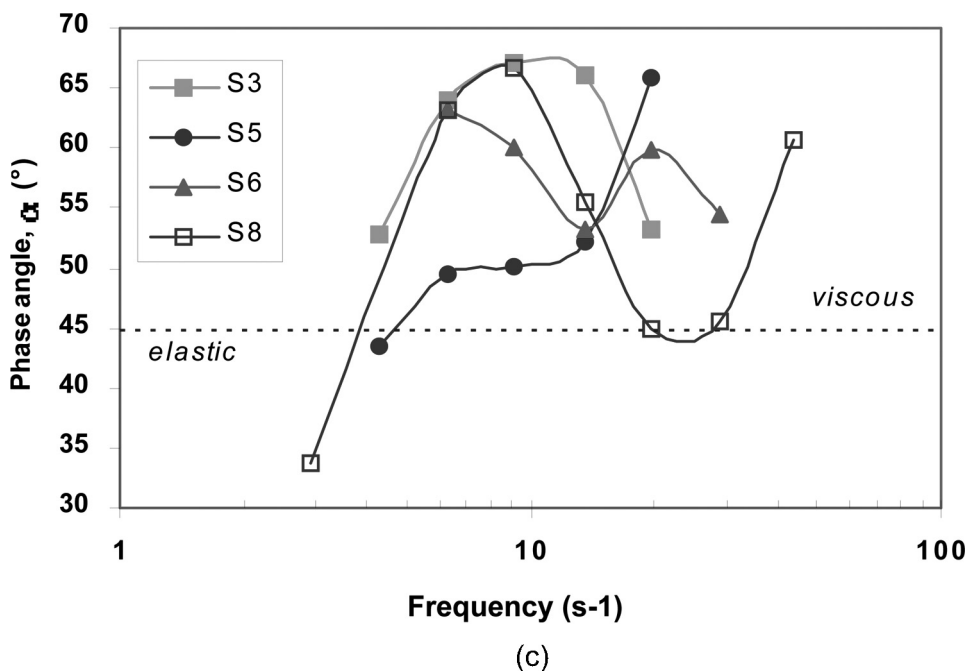


Figure 6. Continued

presented in the carbon black/polymer is difficult to assess since they depend on the carbon black used (Lignin Institute, 2003). Carbon blacks with a low level of structure have few primary particles in compact structures. Carbon blacks with a high level of structure have many primary particles fused into long, complex chains (Lignin Institute, 2003). The agglomerates are formed predominantly by end-on associations of the rod-like aggregates, and the surface structure of the carbon black appears smooth over length scales of about 1 nm (Hjelm et al., 2000). Further studies on production suggest that a shell-like aggregate structure is present in commercial

**Table V.** Elastic and viscous modulus for the leather finishing formulations

Sample	Modulus (Pa)	
	Elastic	Viscous
1	0.5	0.3–1.05
2	2.5–8	1.15–9
3	0.2–0.7	0.05–0.75
4	0.1–0.2	0.12–0.18
5	0.1–0.9	0.15–0.14
6	0.4–2.4	0.5–2
7	0.08–0.15	0.07–0.2
8	0.12–0.16	0.15–0.18

carbon blacks (Hjelm et al., 2000). Thus, the combination of dispersant, particle size, structure, and surface oxidation determines the properties of the carbon black suspension such as its conductivity (Hjelm et al., 2000). The dispersant is adsorbed onto the black's surface and imparts stability by steric and electrostatic mechanisms (Lignin Institute, 2003). Thus, the kind of interactions that may take place between the resin and the carbon black come from the charges induced in the carbon particles (or clusters) and the charges available in the polymer, mainly those coming from the  $-\text{COO}$  acrylic functional group.

In Figure 6(b), samples 4 and 7 develop elasticity with increasing frequency, thus those samples tend to behave like solids at relatively high frequencies (oscillatory shear). Samples 3, 5, 6, and 8 (Figure 6(c)) are predominantly viscous and present  $G'' > G'$  in most of the frequency range tested; thus, the interactions that produce elasticity (for the iron and titanium oxides) may be minimal when compared to those produced by the carbon black pigment. Although these samples have in common the same solids content, they cover the three pigments and the two resin-pigment ratios. This parameter variation makes very it difficult to interpret these results.

### *Leather Finish Properties*

Table VI shows the corresponding results obtained from the rheometer with respect to selected physical properties of the leather samples when changing the formulation parameters. The main result that can be inferred from the table is that the resin hardness increases the resistance under the web felt and web leather friction tests but decreases the viscosity of the formulation. Thus, it will be more difficult to damage a hard film by friction, as one may expect, although coming from a relatively low viscous formulation. Furthermore, formulations containing the hard resin present lower adhesion values (lower viscosity) than those containing the soft resin. One may expect the opposite since lower viscosities promote a better flowing inside the substrate to produce better adhesion. To better understand that phenomenon, we

**Table VI.** Response of physical properties of leather samples to change in formulation parameters

Sample	Bally flexes (cycles)	Friction (cycles)		Adhesion (gr/cm)
		Wet felt	Wet leather	
STD DIN	50000	25	25	600
1	36000	10	25 <sup>a</sup>	760.4
2	50000 <sup>a</sup>	15	10	743.4
3	50000 <sup>a</sup>	20	25 <sup>a</sup>	1397.7
4	50000 <sup>a</sup>	8	6	938.8
5	12000	6	16	967.4
6	50000 <sup>a</sup>	16	24	422.1
7	50000 <sup>a</sup>	25 <sup>a</sup>	25 <sup>a</sup>	1392.2
8	50000 <sup>a</sup>	24	10	315.9

<sup>a</sup>These results overcome the limit stated in the standard DIN procedure. The tests were not continued further.

need to assess both viscosity and surface tension of the finish just immediately after application (Alonso et al., 2001), since they both govern the application performance just after application. In regard to viscoelasticity, the formulations with the soft resin have both viscous and elastic modulus higher than those containing the hard resin, results that may also be linked to what was mentioned above in regard to the hardness of the resin. Hence, at least with the formulations tested here, the characteristics of the resin strongly govern the rheological behavior of the formulation and the dry film properties on the leather. A central concern about these results is that the natural nonuniformity of the leather may have affected the finish performance.

## Conclusions

The rheological properties of leather finishing formulations were investigated. The viscosity in both Ford cup and the Brookfield viscometers and in the rheometer was studied. From the results, the soft resins produce shear thinning formulations, in a manner similar to the finishing pigments. The black polymeric pigment seems to develop the highest level of flowing resistance since it provides the highest viscosity among the samples. In addition, the resin-pigment ratio enhances the viscosity of the formulation. The samples involving a soft resin and a polymeric pigment produce shear thinning formulations with viscoelastic properties. Furthermore, the Ford viscosity does not change significantly with the formulation parameters (type of pigment, resin, or resin-pigment ratio), a fact that suggests avoiding its use to assess the quality of a leather finishing formulation. The Brookfield viscometer, however, would provide more reliable viscosity values when a rheometer is not at hand. In regard to the finished leather, the resin hardness increases resistance to the felt friction tests but decreases the viscosity and viscoelasticity of the formulations, as well as the adhesion values of the finished film.

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