Viscosity Profiles of Solvent Based Paints:

Their Measurement and Interpretation

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A single point viscosity measurement has been proven meaningless in determining the rheological and application properties of a paint. Paints having the same "one point" viscosity can have different settling, sag, and leveling properties. These rheological differences are graphically depicted by means of viscosity profiles obtained through the use of low and high shear rate viscometers.

A method to evaluate the flow properties of paints and specifically leveling based on the rheology of sheared paint samples, as a function of time and at variable low, and ultra-low shear rates, is described.

KEY WORDS: Thixotropy; Rheological agent; Rheology; Leveling; Settling; Sagging; Rotational viscometer; Brushability.

INTRODUCTION

THE importance of viscosity as it relates to paint flow has long been recognized by the paint industry as evidenced by the extensive body of literature that has been devoted to this subject.[1-6] More recently papers have been presented dealing with newer and more sophisticated methods for evaluating paint viscosity with the objective of establishing a true and complete "viscosity profile" of a paint that can be used to replace the older incomplete and inexact methods of viscosity assessment.

A study of paint phenomena makes quite clear that a single point viscosity measurement is quite inadequate to explain all the various manifestations of paint flow (flow patterns during the preparation of the paint, settling of pigment during paint storage, viscosity behavior during paint application, and post-application flow phenomena such as sagging and leveling). Multiple-point viscosity measurements must be made. Best of all is to carry out a program of viscosity measurement to the extent that sufficient points are established to provide a continuous picture of the viscosity behavior of the paint through a broad range of shear rates. By this procedure a comprehensive "viscosity profile" is obtained that provides a sound basis for interpreting and controlling the many varied facets of paint flow.

The main purpose of the present investigation was to develop a practical method for establishing a paint viscosity profile that could be used to investigate the effect of "rheological" additives on the viscosity profile of a number of solvent based paint systems, and to devise a method for the quantitative prediction of flow behavior of the paint before and after application.

GRAPHICAL PRESENTATION OF VISCOSITY PROFILE

Pigment settling during storage, paint sagging on a vertical surface, leveling of brush marks, penetration into porous substrates and the general 'feel' or appearance of a paint are all related to specific shear stresses and shear rates and these in turn to viscosity in conformance with equation (1).

$$(\eta)\ \text{viscosity} = (\tau)\ \text{shear stress}/(D)\ \text{shear rate} \qquad (1)$$

If shear stress is measured in dyne/cm^2 and shear rate in sec^{-1}, then viscosity is expressed in poise. Since countless shear rates are possible there is also an accompanying number of possible viscosities in non-Newtonian fluids. A viscosity graph profile (viscosity vs. shear rate) provides a clear visual picture of how viscosity varies with the shear rate (a plot of log viscosity vs. log shear rate), see *Figure* 1. Logarithmic scales are employed since uniform numerical scales are completely inadequate for portraying the vast ranges of shear rates and viscosities that are involved in paint work. An alternate selection of parameters for the log scales might have been used to plot the viscosity profile, i.e., shear stress vs. shear rate. However, based on

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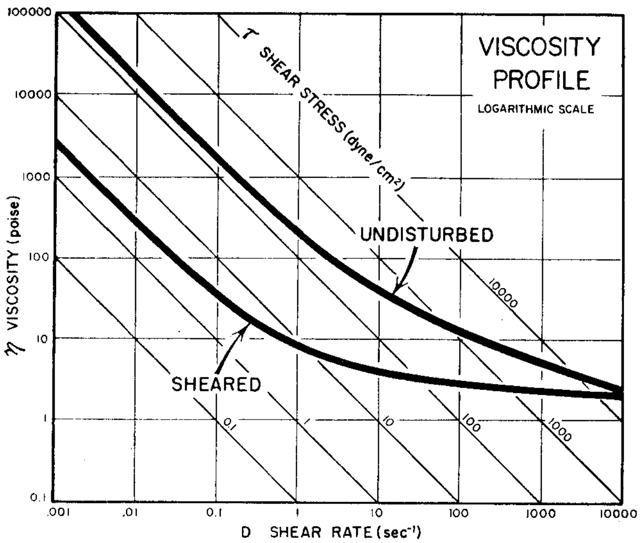

Figure 1—Viscosity profile—a typical graph of viscosity—shear rate structure relations for a thixotropic paint

considerable experimentation, the viscosity and shear rate log scales selected for this study have proven most useful in plotting the measured data and in interpreting results.

It is not the intent of this paper to review background material on various types of flow or to elucidate the mathematical derivations and equations for paint rheology phenomena. These have been adequately treated elsewhere in the recent literature.[7,8] Rather our purpose is to report on a practical procedure for establishing a viscosity profile (suitable for use in a conventional paint laboratory) that is both fundamental in nature and highly useful in practice.

In starting this investigation, three instruments, capable of supplying viscosity data at known shear rates, were compared for inter-instrument correlation and reproducibility (Weissenberg Rheogoniometer, Haake Rotovisco, and Brookfield Cone and Plate Viscometers). As shown in *Tables* 1, 2, and 3 all three were in good agreement on both the unsheared and sheared samples of paint. Differences did occur (differences that might be studied further and measured under more rigorous and comprehensive conditions for possible theoretical implications). However, these differences were not considered sufficiently significant from a practical standpoint to rate one instrument above the other. Furthermore, the dramatic variations in viscosity that resulted when shear rates were changed were of such magnitude that any minor difference due to instrumentation would have little or no effect on the significance of the total data developed. Hence, in view of relative low cost and simplicity of operation, the Brookfield Cone and Plate (C/P) Viscometer was selected for this study to develop the rheological information in medium, low, and ultra-low shear rate ranges.

Table 1—Comparison of Viscometers[a]

Shear Rate[a] (Sec⁻¹)	C/P (U)	C/P (S)	WR (U)	WR (S)
	Poise[a]			
10^{-1}	1200	180	750	180
1	130	30	110	24
10	20	8	17	6.2
100	5.8	3.8	4	3
1000	3.0	3.0	2.5	2.5

WR = Weissenberg Rheogoniometer
U = Undisturbed
S = Sheared
C/P = Brookfield Cone and Plate (RVT and 5X-HBT)

(a) Data obtained by interpolation from viscosity profiles.

Table 2—Comparison of Viscometers

Shear Rate (Sec⁻¹)	C/P (U)	C/P (S)	WR (U)	WR (S)
	Poise			
10^{-1}	170	100	210	110
1	38	22	35	22
10	11	7.2	11	8
100	5.0	4.4	5.2	4.5
1000	3.8		3.2	

By using the Brookfield Cone and Plate Viscometer both in a conventional manner (spring tension under constant rotational conditions) and by Patton's spring relaxation technique (no motor rotation; spring tension variable as it relaxes to minimum stress) it was possible to cover the medium, low, and ultra-low shear rate regions. Shear rate regions have been arbitrarily specified as ultra-low, less than 0.1 sec⁻¹; low, 0.1 to 10 sec⁻¹; medium, 10-1,000 sec⁻¹ and high, greater than 1,000 sec⁻¹. However, it should be understood that this is merely a general classification and other authors might select some other breakdown that would lead to overlapping. The following schedule was used in developing the viscosity data. Although previously reported in detail,[3,7] it is included here for ready reference (tests carried out at 77 F (25 C).

(1) Introduce the test sample to C/P viscometer with as little disturbance as possible and make relaxation run (undisturbed sample).

(2) Continue with an ascending series of eight rotational runs (undisturbed sample); a five-minute shearing at top shear rate (384 sec⁻¹); a descending series of eight rotational runs (sheared sample).

Table 3—Comparison of Viscometers

Shear rate (Sec⁻¹)	C/P (U)	C/P (S)	HR (U)	HR (S)
	Poise			
10	32	12	37	7.5
100	7	5	7.2	3.5
1000	3	3	3	2.7

HR = Haake Rotovisco

(3) Conclude with second relaxation run immediately after shearing for five-minutes at top shear rate of the C/P Viscometer (sheared sample).

Shearing the sample for five minutes at the maximum shear rate of the viscometer "breaks" the thixotropic structure of the paint in a manner similar to brushing. In this breakdown, the longer shearing time tends to compensate for the lower shear rate produced in the viscometer (comparison with brushing).

In the course of this investigation and using this schedule, it was noted that certain data obtained at the beginning and during the descending (undisturbed sample) runs were not always strictly reproducible. This was attributed to an inability of the operator to handle the test paints in exactly the same way (say during the introduction of the 'undisturbed' paint sample to C/P Viscometer), see *Figure* 1.

"Undisturbed" data obtained in this manner must therefore be considered as an approximation to the viscosity for the 'at rest' state as measured by this procedure. It was later found that more reproducible results for the undisturbed viscosity could be obtained if the sample were subjected to an arbitrary shear history prior to the viscosity determinations (50 mild stirs with a wooden tongue depressor on a pint sample within a one-minute period). By this conditioning step, results were found duplicable.

Results obtained after shearing at the highest shear rate (five minute working period) on the C/P Viscometer (384 sec^{-1}) were always readily reproducible (sheared sample). It is notable that samples sheared at higher shear rates (as provided by the Weissenberg Rheogoniometer) had essentially the same "sheared" viscosity profiles as those obtained with the Brookfield C/P Viscometer (with its top shear rate of 384 sec^{-1}) when taken in conjunction with a single point value obtained at the high shear rate range by a second high-shear-rate viscometer (operating at 18,500 sec^{-1}). Interpolation of data between

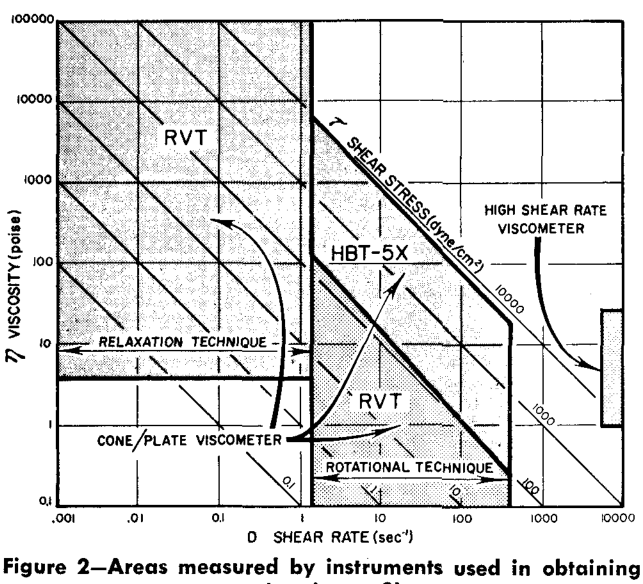

Figure 2—Areas measured by instruments used in obtaining a viscosity profile

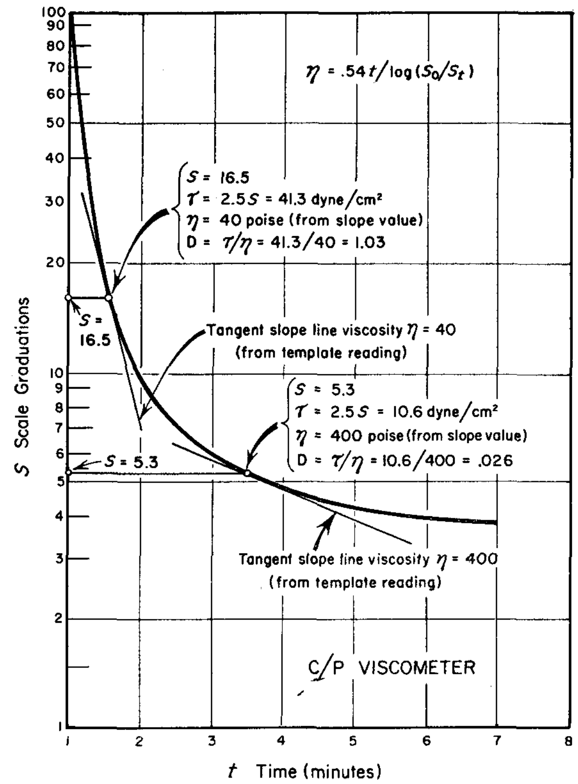

Figure 3—Graph used for obtaining data from Patton Cone and Plate Spring Relaxation Technique

the medium shear rate range and this high shear point value is valid from a practical standpoint since it has been shown that at the high shear rates, the viscosity of a paint becomes substantially constant and relatively independent of the shear rate (only nominal changes in viscosity occur through this high range).

Figure 2 graphically indicates the standard regions and procedures finally adopted for this investigation. The shaded areas depict the viscosity ranges that can be measured with the noted instrumentations. In part of the low to medium shear rate range (1 to 384 sec^{-1}) two Brookfield C/P Viscometers of different "spring capacities" (RVT:7,187 dynes/cm; 5X-HBT: 287,480 dynes/cm) were employed to cover the viscosity ranges encountered. This was necessary since in many cases the viscosity exhibited by the solvent based paints exceeded the range of the RVT model viscometer but fell within the range of the Brookfield 5X-HBT model.

In developing the data in the low and ultra-low shear rate ranges by the C/P Spring Relaxation technique, it should be stressed that the procedure measures viscosity as it moves from higher to lower shear rates (*Figure* 3). Hence, the data developed during this test procedure are not only measuring the viscosity at a different shear rate but also at a different time in its stage of "viscosity recovery" after being subjected to a prior stressing history. This method of measurement approaches the behavior of a paint that has been brushed on a vertical surface with regard to its flow conditions. Initially a high shear rate is applied to the paint, by means of the brush (simulated by five minutes shear at the highest shear rate in the viscometer). Removal of the brush immediately reduces the shear stress acting upon the paint to a very much lower value. The shear stress now acting on the paint film is produced only by the action of surface tension forces and the force of gravity (in our viscometer model these forces are simulated by the tension of the spring). As the viscosity "recovers" the shear rate decreases and the applied film approaches a condition of complete immobility (no sag). This condition is simulated by the spring relaxation technique when the viscosity approaches infinity (spring relaxes to a velocity approaching zero).

Using this evaluation technique the experimental results revealed that the effects of brushing on a vertical surface can be closely reproduced and assessed when the spring relaxation technique is applied to the sheared paint (see Appendix I). Also, it should be observed that the film flow after brushing and the ability of the paint to level out with controlled sag are phenomena that occur at a decreasing shear rate. This condition of decreasing shear rate is simulated by the spring relaxation viscosity measurement.

EVALUATION AND INTERPRETATION

A series of paints (see Appendix II for formulations) was prepared in which the only variable was the type and/or amount of rheological agent used in the system (alkyd gloss enamel). Also included was an enamel based on a commercial thixotropic alkyd resin, and a chlorinated rubber paint. In the alkyd gloss enamel formulation, sufficient amounts of rheological additive were introduced to give equivalent Stormer viscosities (KU value). In the case of the alkyd gloss control (no rheological additive), the solids concentration was increased to the point to where the Stormer KU value reached the same standard value as for the other paints. Leneta sag readings[9] were routinely made on all paints (*Tables* 4, 5, 6).

Alkyd Gloss Enamel

Table 4 gives the data on four gloss paints: a modified control, two prepared with different organic rheological additives, and a fourth made with an inorganic gellant.

From an inspection of these paint data, it becomes readily apparent that no relationship exists at all between Stormer viscosity (KU value) and resistance to sagging. Visual examination of the undisturbed cans of paint showed that the two paints modified with the two organic agents had more consistency (apparent body) than the other two. Brushout samples of all four systems failed to reveal substantial differences in visual leveling but some "brush drag" was noted for the control paint on a manual brushout.

Comparison of the viscosity profiles shown in *Figures* 4-7 indicates that at the ultra-low shear rates (less than 0.1 sec^{-1}), the two paints modified with the organic rheological agents* possess much higher viscosities in the "unsheared" or "undisturbed" state. This explains their much more "bodied" appearance. The higher viscosity of the control at high shear rates (ca $10{,}000^{-1}$) explains the brush drag.

Previous investigators[8] have related sag control to the flow behavior of paints in the low and ultra-low shear rate regions (0.1 to 0.01 sec^{-1}). A comparison of the viscosity data in this region (for both the unsheared and sheared states) shows higher viscosities for the two paints modified with the organic rheological agents and accordingly both provided excellent sag control. The inorganic gellant also provided sag control but the control with no additive sagged excessively.

All four paints leveled equally well on brushing.

It has been accepted[5,8] that the ability of a paint (containing a thixotropic additive) to level well after application is related to its viscosity recovery rate in

* Rheox 1 and Rheox 53 registered trademark of Baker Castor Oil Co.

Table 4—Alkyd Gloss Enamel

	Viscosity (Krebs Units)	Leneta Sag Rating
Rheox 53[a] (10 PHG)	86	25 (Best)
Rheox 1[a] (8 PHG)	85	20
Inorganic gellant	87	8
Control[b]	86	3 (Fail)

(a) Organic thixotropic agents supplied by the Baker Castor Oil Co.
(b) KU value brought to 86 by solvent adjustment.

Table 5—Thixotropic Alkyd

	Viscosity (Krebs Units)	Leneta Sag Rating	Brushout	
			Leveling	Sqg Rating
Control	85	12+ (Most)	Excellent	Runs (Most sag)
Inorganic Gellant	100	35 (Least)	Brushmarks	Excellent (Least sag)
Rheox 53	97	35 (Intermediate)	Good	Good (Medium sag)

Table 6—Chlorinated Rubber Based Paint

	Viscosity		Leneta Sag Rating
	Krebs Units	Brushometer (Poise)	
Thixatrol ST[a] (14 PHG)	105	3.3	60+ (Best)
Inorganic gellant (16 PHG)	118	3.6	16+

(a) Organic thixotropic additive, Baker Castor Oil Co.

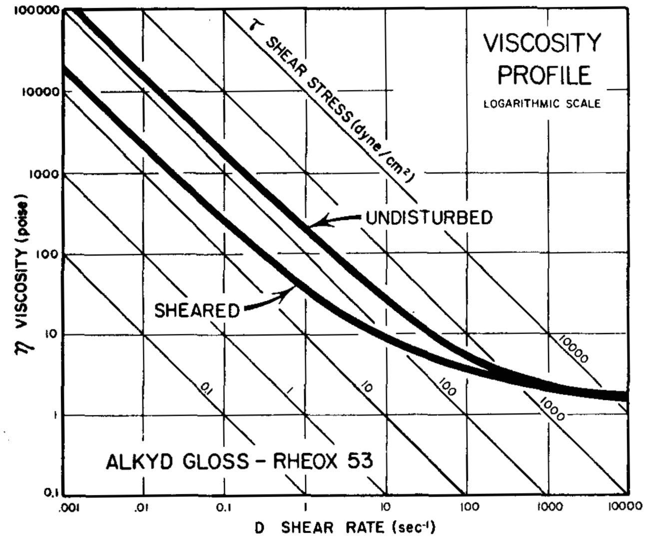

Figure 4—Viscosity profile of alkyd gloss paint prepared with organic thixotropic additive (Rheox 53)

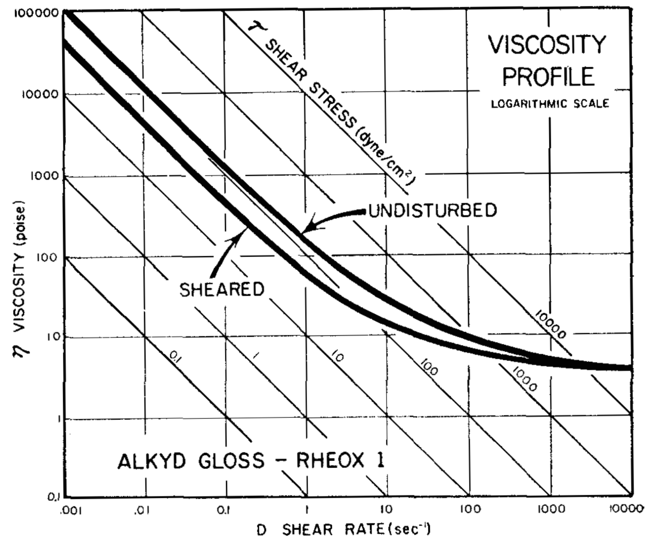

Figure 5—Viscosity profile of alkyd gloss paint prepared with organic thixotropic additive (Rheox 1)

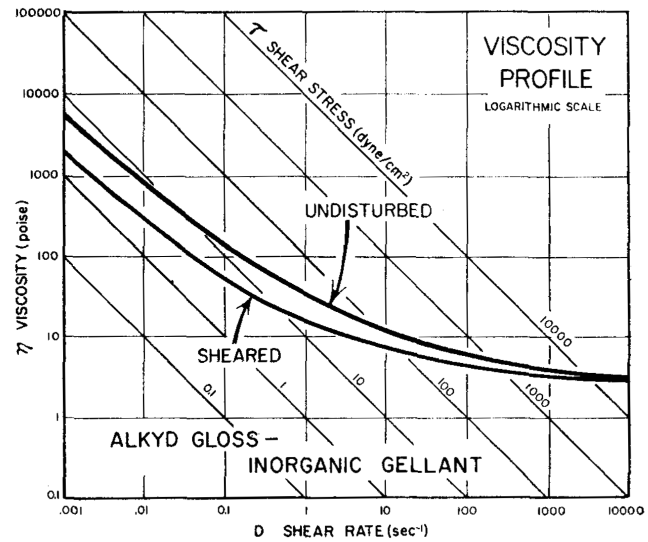

Figure 6—Viscosity profile of alkyd gloss paint prepared with inorganic gellant

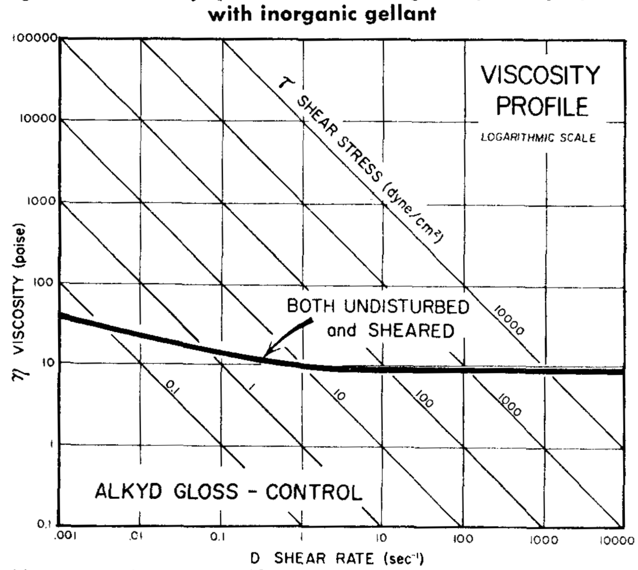

Figure 7—Viscosity profile of modified (higher solids) control

the low and ultra-low shear rate regions. An examination of typical viscosity profiles points up some of the trouble that has been encountered in the past with regard to semantics when discussing such terms as 'thixotropic paint' and 'recovery' in the literature. Inspection of the submitted viscosity profiles shows quite clearly the differences that exist between the sheared and undisturbed states of a thixotropic system. Depending on the applied shear rate and its duration it is possible to pass through any number of intermediate viscosities between the depicted upper and lower limits at some given time.

It is possible that the recovery of a paint with a near-pseudoplastic rheological behavior at a given shear rate may be so rapid or immediate that it becomes substantially unmeasurable by conventional instrumentation. Hence, it becomes necessary for one thing to widen the range of shear rate considered and, from a practical standpoint, to also assess a paint in terms of its actual application behavior.

In our evaluation of paint behavior (as based on the viscosity profiles) it has generally been found that the 'undisturbed viscosity profile' can be directly related to the appearance of the undisturbed paint in the can, to pigment settling, and to the ability of the brush to pick up paint for application without dripping. The sheared viscosity profile (and its recovery rate) can be directly related to brush drag, leveling, sag control, and paint penetration into porous substrates (*Figure* 1)

A further contributing factor that should be considered in interpreting the sheared viscosity profile is loss of solvent during and after application (neglected in the present investigation). Work is underway on this aspect of the problem wherein changes are being made in the solvent content to simulate solvent evaporation to the environment following paint application.

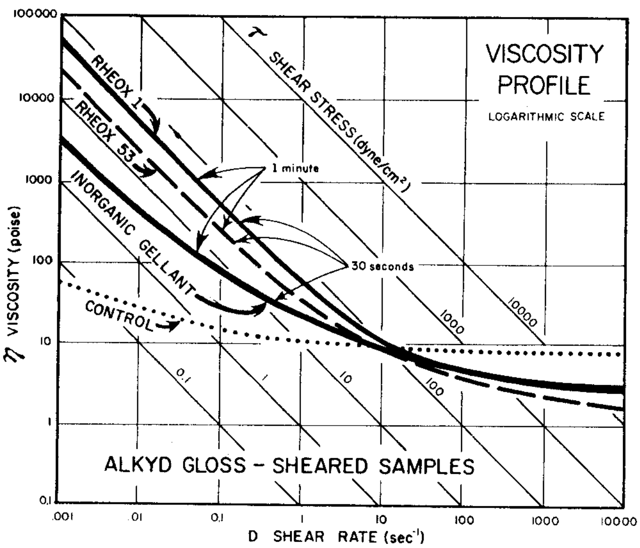

Figure 8—Comparison of "sheared" viscosity profiles of alkyd gloss paints—organic thixotropic additives (Rheox 1 and Rheox 53); inorganic gellant and control (modified, no additive). Viscosity-shear rate data at different time intervals indicated

Neglecting the undisturbed viscosity profile of the four paints and considering only the sheared viscosity profiles (*Figure* 8), the reason for higher sag ratings of the two organic thixotropic-containing-paints becomes obvious. They not only have higher viscosity at low shear rates (.01 sec^{-1}), but they attain these higher viscosities much sooner (see 30 sec. and 1 min. readings). The higher brush drag of the control paint on brushing is evidenced by this higher viscosity at high shear rates (ca 10,000 sec^{-1}).

Since all paints appeared to level well despite significant differences in viscosity among them at low shear rates, it was decided to determine if the measured viscosities at low shear rates could be used to explain these results.

By using equation (2) (for the time for leveling as given by Patton[3])

$$t = \frac{.0044\eta\ \lambda^4 \log\ (Zo/Zt)}{\gamma\ X^3} \qquad (2)$$

and by inserting suitable values as proposed by him for a typical situation (see Nomenclature section for values used), it is revealed that even at the highest viscosity after one minute for the organic thixotropic agent,* the time required for leveling of a three mil thick coating is only 43.3 seconds.

With regard to Stormer viscosity, note that at only one point on these several curves is the viscosity the same (shear rate of about 20-50 sec^{-1}). Our work indicates that the Krebs-Stormer viscosity measurement normally correlates with viscosities obtained in the shear rate range of 20-125 sec^{-1}. The data reveal that a one point viscosity, as obtained with the Stormer paddle viscometer, fails to provide information that can be related to application properties.

Since all four paints leveled well in spite of significant differences in low shear rate viscosity, it is suggested that differences in low shear rate viscosities alone are not controlling and that viscosity recovery rates must be taken into consideration.

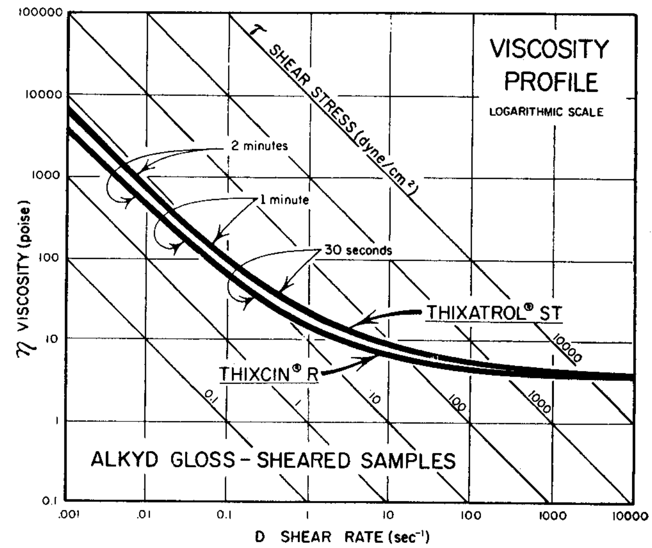

Figure 9—Comparison of "sheared" viscosity profiles of alkyd gloss paints prepared with two organic thixotropic additives (Thixcin R and Thixatrol ST). Viscosity-shear rate data obtained at different time intervals indicated

Similar results were obtained in the evaluation of paints containing two other organic thixotropic agents† as shown in *Figure* 9.

Thixotropic Alkyds

A commercial thixotropic alkyd resin was obtained and formulated into an enamel per the resin supplier's suggested formula (a rheological additive

* Rheox 1.

† Thixcin R and Thixatrol ST registered trademarks of Baker Castor Oil Co.

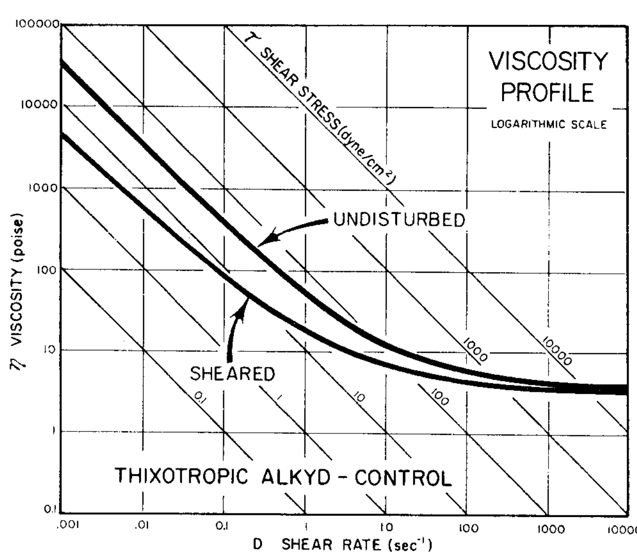

Figure 10—Viscosity profile of control paint based on thixotropic alkyd resin

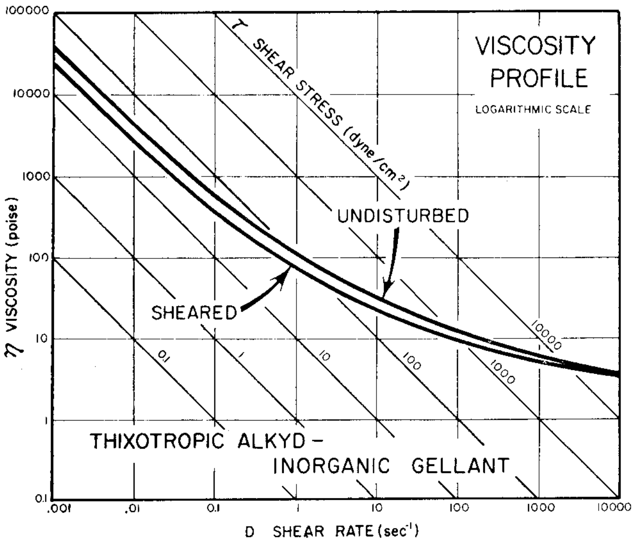

Figure 11—Viscosity profile of paint based on thixotropic alkyd resin modified by inorganic gellant

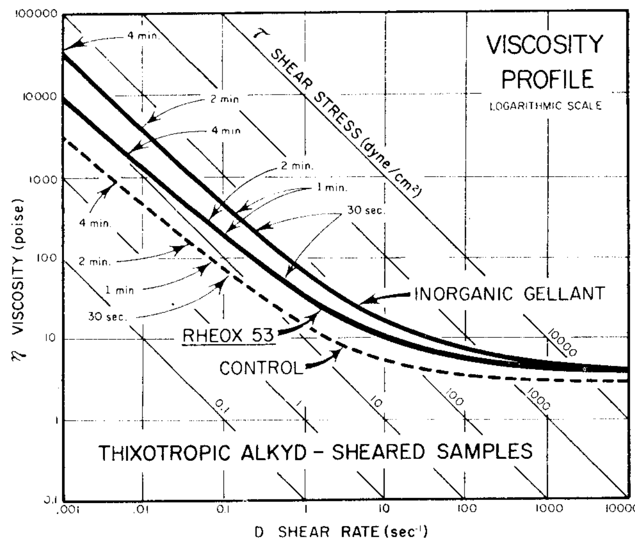

Figure 13—Comparison of "sheared" viscosity profiles of paints based on a thixotropic alkyd resin modified with an inorganic gellant; organic thixotropic additive (Rheox 53); and unmodified control. Viscosity-shear rate data obtained at different time intervals indicated

in the formulation was recommended). The paint was initially prepared without the addition of the rheological additive suggested by the supplier and the Stormer viscosity and Leneta sag rating determined. The values obtained indicated that the paint should be satisfactory. However, an actual brushout of the paint showed this not to be the case since, although the paint leveled well, it sagged quite badly (*Table* 5). On the other hand, the viscosity profile (*Figure* 10) indicated that this poor result might have been expected since although the paint is thixotropic (indicated by the major differences between the unsheared and sheared viscosity profiles) the profile for the sheared paint showed the viscosities at the low shear rates to be too low to prevent sagging.

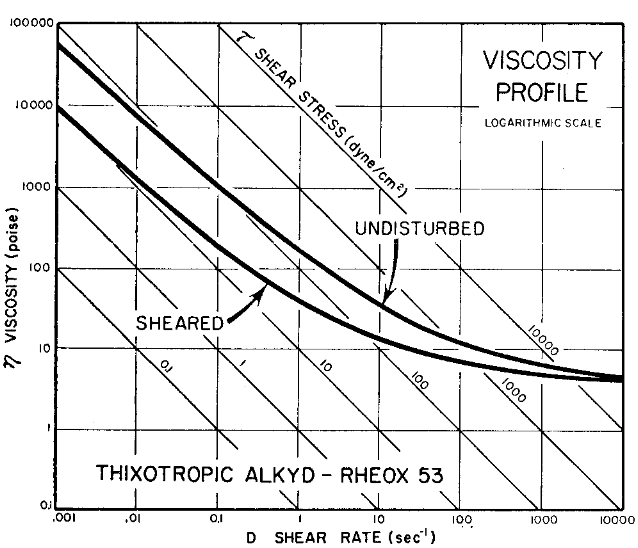

Figure 12—Viscosity profile of paint based on thixotropic alkyd resin modified by organic thixotropic additive (Rheox 53)

Two further thixotropic alkyd samples were prepared, one with an organic thixotropic additive and one with an inorganic gellant. The viscosity profiles for these paints (*Figures* 11, 12) indicated that although both paints should have good sag control they might not level too well. As shown in *Table* 5, it was found that the paint prepared with the inorganic gellant had excellent sag control but exhibited brush marks. The paint prepared with the organic thixotropic additive also had good control and its leveling, although not as good as the control, was satisfactory.

The sheared viscosity profiles of the three paints were reevaluated, but this time the interpretation took into consideration the time data applicable to the situation. Results on this basis became more easily explained (*Figure* 13). Note that even after four minutes, the control viscosity failed to build up to even 1000 poise. The viscosity range of the paint prepared with the organic thixotropic additive for the first two minutes (though higher) is not too significantly greater. Thereafter its viscosity became two to three times higher. In the case of the inorganic gellant the viscosity builds much faster than for either of the other two systems during the first 30 seconds and at the end of two minutes was almost 100 times greater. The results obtained by the brushouts of the samples are thus readily explained.

Chlorinated Rubber Based Paints

Two chlorinated rubber based paints were prepared, one containing a modified organic based rheological agent and one inorganic gellant.

Stormer viscosity and Leneta sag rating were measured (*Table* 6). A brushout of the samples re-

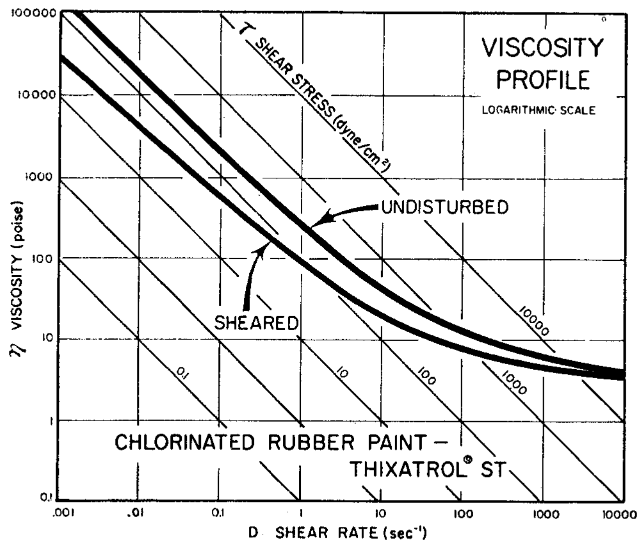

Figure 14—Viscosity profile of chlorinated rubber based paint containing an organic thixotropic additive (Thixatrol ST)

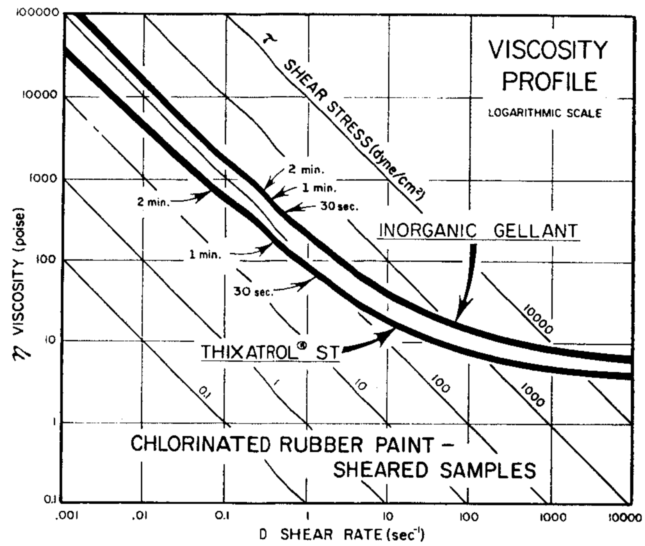

Figure 16—Comparison of "sheared" viscosity profiles of paints based on chlorinated rubber modified with an inorganic gellant and an organic thixotropic additive (Thixatrol ST). Viscosity-shear rate data obtained at different time intervals indicated

vealed an improper leveling of the inorganic gellant sample but the paint did exhibit good sag control. Examination of the viscosity profiles of the two systems, *Figures* 14 and 15, suggest that the sample prepared with the modified organic based rheological agent should be thixotropic (and should have good sag control and leveling); that the inorganic gellant should be near-pseudoplastic in nature and should also have excellent sag control. In further evaluating the viscosity profiles of the two paints, but using time/viscosity data, *Figure* 16, it also becomes apparent that the sample based on the inorganic gellant builds viscosity initially at a much faster rate (compared to the modified organic based thixotrope) thus explaining the difference noted in leveling.

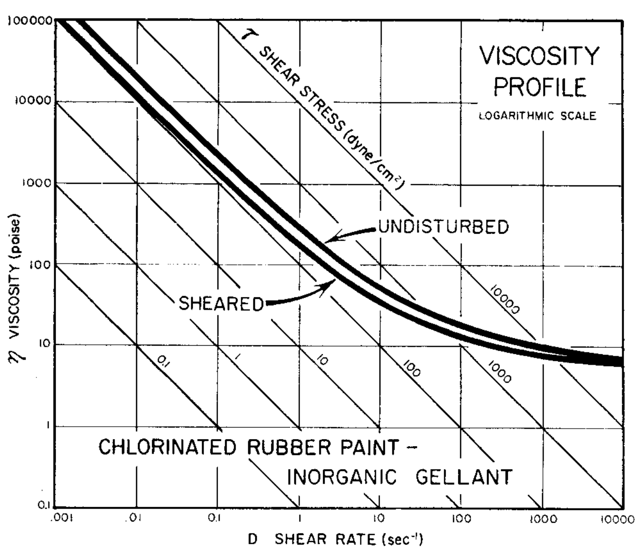

Figure 15—Viscosity profile of chlorinated rubbed based paint containing an inorganic gellant

SUMMARY AND CONCLUSIONS

A method based on low cost instrumentation has been provided to establish the viscosity profile of paints. As opposed to single point viscosity measurements, the viscosity profile supplies overall basic viscosity information that can be readily related to rheological performance. In the present paper viscosity profiles have been used to compare the effect of different rheological agents on flow behavior. A single point measurement is virtually meaningless for paint work (except for plant control) since it does not relate to the many different shear rates involved in paint technology (from manufacturing to film curing). On the other hand, the information provided by the paint viscosity profiles can be related to practical paint flow performance.

The use of the C/P spring relaxation technique yields data relative to viscosity recovery (after severe stressing) that correlates well with leveling and sag behavior after paint application. A fairly low viscosity within the first few seconds or minutes assures brush mark leveling whereas sag control is attained through a subsequent viscosity recovery. Paints without a rheological additive exhibit little or no thixotropic behavior and negligible thixotropic recovery. Hence leveling occurs but the paint sags excessively.

Certain flow additives cause too fast a viscosity recovery, and although sag control is obtained, satisfactory leveling is absent. Other flow additives provide a slower viscosity recovery that achieves a delicate balance between permissible sag and satisfactory leveling.

The advantages provided by the C/P relaxation technique are basic in that: (1) the viscosities are

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measured in the low and ultra-low shear rate regions that apply to leveling and sagging phenomena and (2) the viscosities are measured at decreasing shear rates that tend to correlate with actual post-application conditions. Laboratory experimental data have been submitted to substantiate these claims. ♦

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Nomenclature

λ	= Brush mark wavelength (cm)	(.1 cm)
Z_o	= Wave amplitude ($t = 0$) (cm)	(.0025 cm (1 mil))
Z_t	= Wave amplitude ($t = t$) (cm)	(.0001 cm)
η	= Viscosity (poise)	(1,000 poise)
γ	= Surface tension (dyne/cm)	(32 dyne/cm^2)
X	= Thickness (cm)	(.0076 cm (3 mil))
t	= Time (sec)	
v_o	= Velocity of flow at wet film surface (cm/sec)	
ρ	= Density of applied paint (g/cm^3)	
g	= Acceleration of gravity (980 cm/sec^2)	
τ	= Shear stress (dyne/cm^2)	
D	= Shear rate (sec^{-1})	

APPENDIX I

Flow in a paint film immediately after application to a vertical surface is characterized by drastic decrease in shear stress and a corresponding sudden change in the shear rate and viscosity. An explanation is offered to indicate why the C/P spring relaxation technique (for measuring viscosity) is so suitable for establishing the flow conditions that apply to the post-application conditions of leveling and sagging.

The sag velocity at the surface of a paint film applied to a vertical substrate is given by equation (3)

$$v_o = \rho X^2 g / 2\eta \qquad (3)$$

During the downward paint flow, the value of the numerator of equation (3) remains substantially unchanged since the changes occurring in g, and X are minor (assumes that the paint does not sag excessively). It is recognized that immediately after the brush or roller coater is removed after application, the viscosity is generally subject to a large increase (over several decades). Therefore, v_o in equation (3) decreases with time as a consequence of the viscosity increase.

Experience has shown that a limited amount of paint flow is required to achieve leveling (induced by surface tension forces). Hence, only a small amount of paint flow within a brief period is required to obscure brush marks. After leveling is obtained the viscosity must rise sufficiently to render v_o negligible. Otherwise intolerable sagging occurs.

The maximum shear stresses acting on a paint film after application are given by equations (4) and (5).

$$\text{Sagging } \tau = X\rho g \text{ (due to gravity)} \qquad (4)$$

$$\text{Leveling } \tau = 248\ XZ\gamma/\lambda^3 \text{ (due to surface tension)} \qquad (5)$$

Just after the application process itself is terminated, the viscosity is at its lowest point, at which stage viscosity recovery begins. The shear stress due to sagging is essentially constant at this point (a valid assumption for practical purposes) whereas η is an increasing variable. Then based on the fundamental flow equation (equation (6)) the shear rate (sec^{-1}) must be accordingly decreasing.

$$D = \frac{\tau}{\eta} \qquad (6)$$

Thus, shear rate is a decreasing variable during the post-application period for both leveling and sagging conditions. In line with this reasoning it is proposed that instrumentation for measuring paint flow should be adapted to conditions that reproduce as closely as possible this decreasing shear rate variation that is actually taking place.

Viscosity recovery rate is the controlling variable in the rheology of a paint film during the leveling and sag period. The nature of the flow that occurs after application is characterized by a viscosity profile that rises rapidly within a brief period (seconds) and then tapers off at a gradually diminishing rate. The shear rate correspondingly decreases rapidly at first and then more slowly with time. This type of flow sequence is simulated in a semi-quantitative fashion by the use of the C/P viscometer using the spring relaxation technique.

Laboratory findings based on this procedure indicate that the bulk of the thixotropic change that takes place in paint flow after application probably occurs within the first few seconds or minutes.

APPENDIX II

Alkyd Gloss Enamel—Modified Control

Formulation	Pounds
Alkyd (TT-R-266a, Type I, 70%)	60
Mineral spirits (K.B. 38, 320-385 F (160-196 C))	45
Titanium calcium, 30% TiO_2 (MIL-T-15195)[a]	220
Rutile titanium dioxide (TT-P-4426 Type III)	220
Disperse for 15 minutes or until the desired fineness is obtained, at a speed of 5400 rpm, then add the letdown as follows:	
Alkyd (TT-R-266a, Type I, 70%)	414
Mineral Spirits (K.B. 38, 320-385 F)	50
24% Lead naphthenate	3.5
6% Cobalt naphthenate	2.5
Anti-skinning agent (methyl ethyl ketoxime)	1.0

(a) This pigment is no longer being offered commercially.

Thixotropic Alkyd Enamel

Formulation	Pounds
Thixotropic alkyd resin, 65% Solids	115
Mineral spirits (K.B. 38, 320-385 F)	40
Soya lecithin	4
Zirconium octoate 6%	7
Thixotrope	As indicated
Mix the above 5 minutes on Cowles, at low speed, then add:	
Rutile titanium dioxide (TT-P-4426 Type III)	300
Zinc oxide (TT-P-463a, Type I, Grade A)	25
Calcium carbonate (ASTM-1199-66T Type GC)	60
Disperse for a minimum of 15 minutes or until the desired temperature and fineness are obtained, at high speed, then add the letdown as follows:	
Thixotropic alkyd resin, 65% Solids	359
24% Lead naphthenate	4
6% Cobalt naphthenate	2.5
Anti-skinning agent (methyl ethyl ketoxime)	2
Mineral spirits (K.B. 38, 320-385 F)	111

Alkyd Gloss Enamel

Formulation	Pounds
Alkyd (TT-R-266a, Type I, 70%)	60
Mineral spirits (K.B. 38, 320-385 F)	45
Thixotrope	As indicated
Mix the above for 5 minutes on the Cowles, at low speed. Then add:	
Titanium calcium, 30% TiO_2 (MIL-T-15195)	220
Rutile titanium dioxide (TT-P-4426 Type III)	220
Disperse for 15 minutes or until the desired temperature and fineness are obtained, at high speed, then add the letdown as follows:	
Alkyd (TT-R-266a, Type I, 70%)	414
Mineral spirits (K.B. 38, 320-385 F)	100
24% Lead naphthenate	3.5
6% Cobalt naphthenate	2.5
Anti-skinning agent (methyl ethyl ketoxime)	1.0

High Build Chlorinated Rubber Paint

Formulation	Pounds
Chlorinated rubber, 10 cps	176
Chlorinated paraffin (40% Cl, 25-40 poises)	71
Chlorinated polyphenyl, solid	43
Dioctyl sebacate	14
Thixotrope	As indicated
Titanium rutile (TT-P-4426 Type III)	204
Barytes (ASTM-D604-42)	43
Talc (TT-P-403A)	111
Xylene	340
Aromatic solvent (370-410 F (188-210 C), 90 K.B.)	85
Epichlorohydrin	0.8
Epoxy resin liquid (11,000-13,500 cps 189 - 195 epoxide equivalent)	5

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