Organoclay Pregels and Quality Performance Testing

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During the 50 years since the development of organoclay rheological additives, organoclay manufacturers, the coatings industry, and other consumers of organoclays have found that measuring the rheological properties of solvent pregels does not provide an accurate assessment of the performance of formulated products. Different lots of the same type or similar grades from various producers have been subjected to various pregel viscosity measurements as incoming raw material performance tests. Organoclay pregels have also been used to assess the efficiency of an organoclay, to provide a basis for comparison with other grades, and to determine quality differences between manufacturers.

It is the objective of this article to provide practical information regarding the problems encountered by the organoclay user when attempting to measure quality by testing pregel viscosity. Using some common test criteria we also explain why the better indicator of true organoclay quality is performance of a complete paint formulation (or other product reflecting the intended final application/product evaluation).

INTRODUCTION

Many different grades of organoclays are marketed as rheological control additives for coatings, adhesives, and other applications. Bentonite and hectorite clays are carefully purified, then surface modified to make them dispersible in nonaqueous media; the resulting product is an organophilic clay (organoclay). For full development of their rheological properties in a formulated product such as a paint, organoclays must be subjected to wetting and shear to break up agglomerates of platelets. The addition of a chemical activator may be needed to ensure further separation of the clay platelets. The ultimate measure of organoclay quality is, of course, its performance in a fully formulated product; as a matter of convenience, viscosity measure-

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ments on solvent pregels have long been used as quality control tests. In the following discussion, we illustrate the potential pitfalls of this approach by examining results on two types of solvent pregels:

(1) Low level organoclay pregel (better known perhaps as 2% tol-gel[a]).

(2) Organoclay pregel concentrates (typically 8-12% by weight of organoclay additive) used to improve organoclay performance in high solids, low VOC, and poor wetting resin applications, e.g., epoxies.

Two-Percent Organolcay Gel in Toluene: This was a test developed for use as an in-plant quality control (QC) tool to determine the completion of the reaction during the manufacturing of organoclay additives. Essentially, it monitors the daily reproducibility of the clay + quaternary reaction. Plant specifications based on the 2% tol-gel viscosity were established based on historical process data from successful production runs. While these 2% tol-gel viscosity data were included on many Certificates of Analyses, they were never intended for predicting the quality or performance of the same organoclay in a finished paint. Upon review of 2% tol-gel results (*Table* 1), we see that the viscosities range from 151-253 mPa•s and do not correlate with either paint viscosity or sag control.

In this group, the lowest paint performance properties are exhibited by the organoclay (E92740, P7), which has the highest pregel viscosity.

Taking the 2% pregel one step further, two organoclay samples from different plants produced almost identical results in a paint test,[b] conducted at our European Technical Center (see *Table* 2).

However, in 2% white spirit solvent pregels,[b] the same two organoclay additives show significant viscosity variations (see *Table* 3) when prepared using different chemical activators with and without water:

Organoclay Pregel Concentrates: Use of organoclay pregel concentrates has been suggested by many to improve the solvation or wetting of the organoclay. In many applications such as high solids, there is insufficient solvent to permeate the clay structure in a uniform fashion required to initiate good dispersion and develop the proper gel structure. Therefore, if we disperse (in many cases, simply mix) the organoclay as a concentrate (8-12% by weight) into solvent alone, we can provide better solvation properties that will result in improved performance from the additive. Formulations that contain poor wetting resins will also benefit from pregel concentrates as well by improved solvation of the additive without the interference of poor wetting resins that tend to encapsulate dry powders such as organoclays.

Table 1—2% Pregel Data Compared to Viscosity and Sag Control in a Full Paint Formulation

	In Plant QC Test	*Paint Results[a]*		
Organoclay Lot#	*2% Tol Gel mPa•s*	*Stormer KU*	*Brookfield Vis. 10 rpm, mPa•s*	*Leneta Sag Mils*
C72871	223	102	4480	7.9
E92250	189	101	3640	6.5
E92270	230	101	3480	6.7
E92740, P7	253	97	3040	6.3
E92740, P10	151	99	3160	6.8

(a) Paint results from a gloss alkyd enamel, T-22907A—see Addendum B, T-22907A.

To illustrate the importance of solvation and wetting with organoclays, the next set of pregel comparisons provides an excellent example of pregel viscosity versus paint performance. We have taken two lots of organoclay and prepared 9.1% pregels of each in K21 aliphatic solvent using two different disperser tip speeds: 8 m/s (1575 ft/min) and 16 m/s (3150 ft/min). The two samples of organoclay exhibit significantly different pregel viscosities (see *Table* 4). These data may have resulted from variations in % clay to organic ratios, raw material variations, or perhaps even production rate differences.

Based on the pregel viscosity data (both Brookfield and Stormer) in *Table* 4, organoclay Lot F30710 might be considered inferior to the laboratory standard. Both 8 and 16 m/s tip speeds fail to develop the pregel to an equal level matching that of the standard. However, as can be seen in *Table* 5, both organoclays are very similar in paint viscosity and equal in sag control.

From the evidence presented, it appears unlikely that organoclay pregel viscosities will provide an accurate

Table 2—Pregel Performance in Paints

	Brookfield Viscosity, 10 rpm, mPa•s	*Hegman, F.O.G.*	*Sag, Runners mm*
Organoclay Plant 1	6040	7.0A	14
Organoclay Plant 2	6480	7.0A	16
Blank — No R/A	1040	7.0A	160

(a) Two percent organoclay gel strength in toluene. See "ES Standard Method of Test X-9155" in Addendum A.
(b) Information and data from Rheox TSD Technical Newsletter "Organoclay Pregel Viscosities," May 15, 1992.

Table 3—Viscosities of Pregels Made With Different Activators With or Without Water

Chemical Activator	Organoclay Plant 1 Brookfield Viscosity, mPa•s, @ 50 rpm	Organoclay Plant 2 Brookfield Viscosity, mPa•s, @ 50 rpm
2-Propanol	180	68
2-Propanol/H_2O	300	440
Propylene carbonate	630	200
Proplylene carbonate/H_2O	820	740
Methanol	910	244
Methanol/H_2O	1360	940
Ethanol	650	416
Ethanol/H_2O	1340	1240
Blank—no activator	140	120

assessment of organoclay quality when compared to their performance in the final application. Although the organoclay samples were manufactured with the same composition, their gelling capability in the same solvent was significantly different. This holds true for not only the organoclay, but the different chemical activators as well (see comparisons in *Table* 3).

HOW DIFFERENCES RELATE TO PREGEL VISCOSITY

Efficient development of an organoclay as a pregel in a simple solvent system is virtually impossible with only propeller mixing or high-speed dispersion. A propellor simply cannot generate the necessary shear and a high-speed disperser depends on proper flow and a high particulate (pigment or extenders) level in a grind stage to develop shear. In a pregel, the particle density is not at a high enough level to provide the required shear rates to disperse all of the organoclay. Typical pregels are prepared anywhere from 5-15% concentration by weight in solvent. If we attempt to disperse TiO_2, or any pigment for that matter, at the same level as we do pregels, the results would be inconsistent and unacceptable. This is why we chose a >50% loading of TiO_2 in a pigment grind to assure high shear suitable for the required level of dispersion.

If a high density particle loading is not possible (as with organoclay pregels), the only way to obtain high viscosity in a solvent pregel is to provide high shear by mechanical force. An example of this would be putting the organoclay pregel through a colloid mill or Manton-Gaulin homogenizer as in the production of high viscosity organoclay concentrates produced for the cosmetic markets.

To further expand this explanation, we can examine the following scanning electron micrographs (SEM). Each SEM photo was taken of individually prepared 10% organoclay pregels made with different types of dispersion (mixing) equipment. The photographs illustrate various levels of pregel development viewed at 3000x magnification. The white bar in the lower right corner (10 microns in length) gives us a reference for particle measurement.

Figure 1 [SEM #1 (0074)] shows virtually no delamination of the organoclay platelet structure. The pregel was prepared using a Lightnin mixer equipped with a three-blade propellor. Dispersion energy (or shear rate) is nil and the resulting viscosity is ~1500 mPa•s. Note, however, that the resulting dispersion, if checked using a Hegman grind gauge, would indicate a reading of ~6.5 based on the size of the primary particle in the center of the photo. Using the 10 micron bar, we estimate that particle to be ~20 microns. Each Hegman unit equals 12.5 microns, thus the particle would give ~6.5 Hegman.

Conclusion 1—This 10% pregel appears to be well dispersed but produces very little viscosity development. Therefore, Hegman grind readings taken on organoclay pregels may not be indicative of platelet delamination. Taking this observation one step further, if Hegman grind were used in a final paint to determine the degree of activation, we may be misled into thinking that we had effectively dispersed the rheological additive. Upon testing in the QC laboratory, one would then find a low viscosity and feel that a post correction is necessary. Through the addition of possibly more thixotrope, a very significant and undesirable viscosity rise may occur with aging due to continued development of the underactivated organoclay as viewed in *Figure* 1.

Figure 2 [SEM #2 (0100)] is a photo of a typical pregel prepared by a Cowles-type, high-speed dispersator. This type of equipment can produce >10K sec^{-1} of shear.

Table 4—Pregel Concentrate Test Data[a]

	Brookfield Viscosities [mPa•s] at 10 rpm	20 rpm	50 rpm	100 rpm	Krebs Stormer Units
Sample A (based on K21 pre-gel 8 m/s					
Organoclay Lot F30710	3320	1940	940	556	58
Organoclay Std.	12140	6970	3136	1700	90
Sample B (based on K21 pre-gel 16 m/s)					
Organoclay Lot F30710	5520	3030	1374	774	66
Organoclay Std.	11200	6330	2900	1580	85

(a) Elementis Specialties internal project report LK-TC-03-016 issued August 2003. Formulation and procedures are attached as Addenda B, C.

Considerable development of the organoclay can now be observed by the many thin platelets being separated (delaminated) from large original particles as previously seen in *Figure* 1. Depending on the nature of the solvent and chemical activator, the 10% pregel represented by *Figure* 2 may range from ~25K to 100K mPa•s or more. The degree of development can vary even more by variations in procedure, tip speed, and condition of the blade along with duration of mixing. However, it is still very obvious that much of the organoclay structure remains underdeveloped by the remaining amount of agglomerated organoclay. For this reason, it would be highly recommended that this pregel be added to the pigmented grind phase of the paint production for further and more complete dispersion.

Table 5—Paint Performance Results[a]

	Brookfield Viscosities [mPa•s] at				Sag Control, Microns
	10 rpm	20 rpm	50 rpm	100 rpm	
Sample A (based on K21 pre-gel 8 m/s)					
Organoclay Lot F30710	2240	1950	1592	1432	210
Organoclay Std.	2400	2030	1644	1454	210
Sample B (based on K21 pre-gel 16 m/s)					
Organoclay Lot F30710	2020	1780	1500	1362	210
Organoclay Std.	2180	1910	1592	1428	210

(a) Elementis Specialties internal project report LK-TC-03-016 issued August 2003. Formulation and procedures are attached as Addenda B, C.

Conclusion 2—While considerably more viscosity has been developed in this example, only a fraction of the 10% organoclay pregel has been delaminated and made available for producing the hydrogen bonded platelet network that provides the viscosity. Therefore, when organoclays dispersed in solvent pregels create such a wide range of viscosity development with only partial development, it is now becomes more apparent why pregels are misleading performance indicators.

In *Figure* 3 [SEM #3 (0048)], the final SEM, we can complete the pregel story. The structure seen is of a pregel prepared using a Manton-Gaulin homogenizer capable of producing shear rates in excess of 300K sec^{-1}. Examining SEM #3, virtually 100% development or delamination of the organoclay down to its basic individual platelet structure can be seen. The viscosity developed from complete platelet separation due to high shearing force can be >1.5 to 2 million mPa•s. While no one typically advocates the use of 10% organoclay in a final product, this final SEM demonstrates the capacity of this type of rheological additive to provide tremendous viscosity.

In addition, as observed earlier in the chemical activator comparison in *Table* 3, their efficiency will vary with the solvent being used. If those pregel mixtures were dispersed under high shear, as in *Figure* 3, much higher viscosities would also be developed and the differences would be diminished.

Conclusion 3—By determining the extent of viscosity development upon complete dispersion, we should have a better understanding of organoclay additives and organoclays in general. The structure seen in *Figure* 3 exhibits the basic configuration of an organoclay in its final application (albeit at significantly lower loadings ~0.5-1.0%) and will be quite reproducible while providing stable viscosity and sag control.

SUMMARY

- If we attempt to develop and use test methods to measure a property (organoclay pregel viscosity in this

Figure 1—Pregel prepared by a mixer equipped with three-blade propellor.

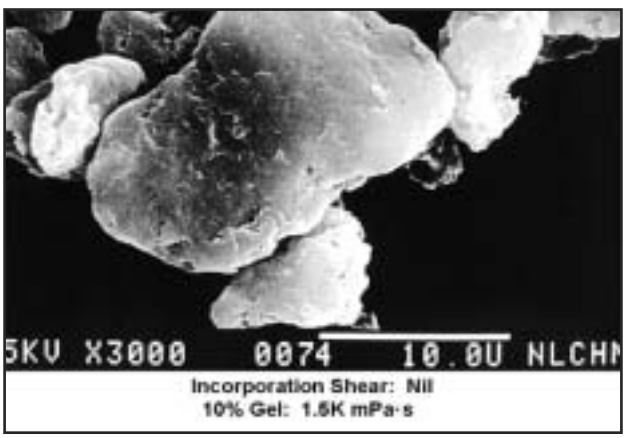
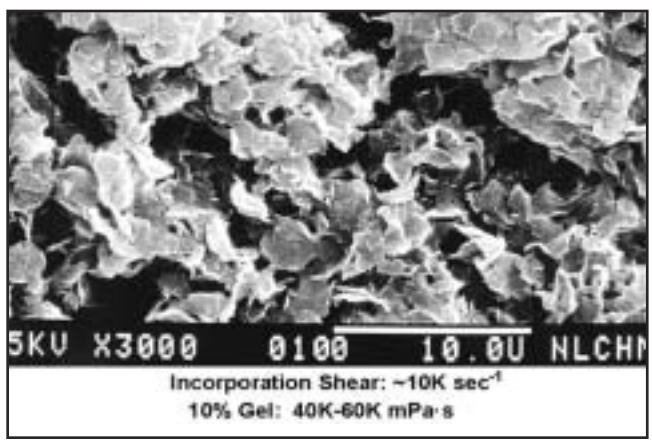


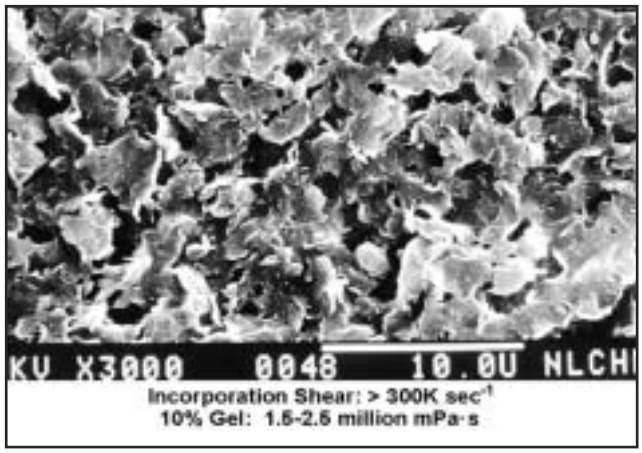
Figure 2—Typical pregel prepared by Cowles-type, high-speed dispersator.



study) of a product that is only marginally developed (~1.0-5.0% in this case, and perhaps more or less depending on conditions) the test method may be neither reproducible nor credible.

- With even less reliability and meaningful results, the pregel comparisons between similar or different grades of competitive organoclay producers fail to provide an accurate picture of their potential.
- In addition, it has been seen that solvent pregels exhibit inconclusive data when used as a predictor of organoclay quality and how it will behave in its final application.
- Rather than utilizing a pregel test to determine the efficacy of an organoclay, it is indicated by the supporting data that an internal paint formulation be utilized that is representative of end-use applications.

Figure 3—Pregel prepared by Manton-Gaulin homogenizer.



ADDENDUM A—Standard Method of Test No. X-9155

MATERIAL: Organoclay 27, Organoclay 34, and Organoclay 38

DETERMINATIONS: High Shear Gel Strength, 2% organoclay gellant in toluene (by weight)

EQUIPMENT:

1. Waring Blender EP-1 with EPS-2 switch (Explosion Proof), Waring Products, New Hartford, CT Waring-Eberbach 8520 container and cover,[a] 8672 Blending Assembly. (Use 8752 teflon gasket set and 8680 replacement blades—Waring-Eberbach, Ann Arbor, MI)[a]
2. Powerstat, variable transformer type 116B, Superior Electric Company, Bristol, CT (or equivalent)
3. Solid state voltage regulator
4. Timer
5. Metal or plastic funnel, 3/4" O.D. narrowest diameter
6. 5 ml pipette, 0.1 graduations, or 5 ml Syringe or similarly precise measuring device (for Polar Additive)
7. 16-oz glass jar.[b]
8. Thermometer: 20°-120°F. (1°F divisions)
9. Analytical balance
10. Brookfield Viscometer, Model RVF-100 with spindle No. 2, Brookfield Viscometer Co., Stoughton, MA
11. Stormer Viscometer, paddle type (ASTM, D-562-55). (Optional)

(a) An 8560 aluminum container and 8670 Blending Assembly are acceptable if only used for gellants and noncorrosive materials. Check for corrosion frequently and remove as necessary.

(b) The soldered seams in some paint cans have been known to cause viscosity differences.

REAGENTS:

1. Amsco toluene (or similar 3E distillation range toluene).
2. Polar additive, 95 parts of commercial pure methanol (99% plus grade) and 5 parts distilled water by weight.

PROCEDURE:

The Waring Blender is connected to the Powerstat, then to the voltage regulator which in turn is connected to the timer. The timer is connected to the power line. Timer setting (see below) automatically starts blender.

Be certain the Waring Blender has no moisture in container prior to usage. Toluene and polar additive should be at room temperature (75°-85°F.) prior to addition to sample.

Add 170 ml of toluene to Waring Blender and *slowly* add exactly 6.0 grams of the organoclay product under test into toluene (170 ml of toluene weighs 145 grams at 77°F.) Addition to be made with Powerstat setting at lowest rpm to aid in proper dispersion of organoclay product. Addition of organoclay should require approximately 15 sec.

Screw on lid with sampling plug removed. Operate blender at a speed of 10,800 rpm. Set timer immediately for 2 min. Place funnel in sampling plug space. Funnel remains in place until blender contents are transferred to a glass jar.

After 2 min, add 170 ml of toluene through funnel before the blender stops. Reset blender to achieve 14,700 rpm. Set timer immediately for 2 min.

After 2 min, add 4.0 ml of polar additive through funnel before the blender stops. Reset blender to achieve 15,700 rpm. Set timer immediately for 2 min.

After blender stops, transfer contents to 16-oz glass jar. Transfer slowly to aid in eliminating air bubbles. Use spatula to remove remainder. Remove *all* excess material from container.

Measure temperature of sample. If in excess of 90°F, place in circulating water bath and bring to 77°F + 1°F. Gellant temperature reduction is to be achieved within 1.5 hr from removal from Waring Blender and reaching required temperature.

Do not unnecessarily disturb gel.

BROOKFIELD VISCOSITY MEASUREMENT[a]:

Measurements with the Brookfield Viscometer should be made at 77°F ± 1°F. Viscosity measurements must be taken immediately after determination of content's temperature.

Lower the No. 2 spindle (properly affixed to the viscometer) slowly and slightly to one side of the center of the surface of the material until it is immersed to the proper depth (scribe line on spindle). Then move the container slowly in a horizontal plane until the spindle is located in approximately the center of the container so that the test will be run in a region undisturbed by the lowering of the spindle.

Set viscometer for 10 rpm. Turn on ON-OFF control switch. Set timer immediately for one minute. Depress clutch at one min. Record scale reading or make mental note of scale reading and record later (clutch is still depressed).

Reset viscometer for 20 rpm. Release clutch. Set timer immediately for 30 sec. Depress clutch at 30 sec. Record, as indicated above.

Make observations in the same manner for 50 rpm (25 sec) and 100 rpm (12 sec).[a]

Convert the Brookfield scale readings to millipascal•seconds (mPa•s). Conversion factors for a No. 2 spindle on a scale of 0-100 are 40 (10 rpm), 20 (20 rpm), 8 (50 rpm) and 4 (100 rpm). To determine millipascal•seconds (mPa•s) value, multiply the scale reading by the factor for each rpm setting. The reading at 50 rpm is the specification reading.

CHECKS:

Observation should be made of the 10 rpm and 100 rpm readings. In these toluene gels, there is usually a relationship in which the 20 rpm result is about one-half, and the 100 rpm result about one-tenth of the 10 rpm reading. Where this is not the case, it most often reflects excessive agitation of the gel prior to the 10 rpm Brookfield reading. If the Brookfield data for all four speeds does not have a reasonable correlation along these lines, the data is faulty due to disturbing the gel or an error in measurement and the complete gel test should be repeated.

(a) Brookfield measurements will precede Stormer determinations when both tests are run.

CALIBRATION:

1. Waring Blender, Powerstat and Voltage Regulator should be operated as a single unit. Use Stroboscope, to insure that Powerstat settings are known for the speeds required: low (10,800 rpm), medium (14,700 rpm) and high (15,700 rpm). Internal calibration every three months.

2. Brookfield Viscometer. Use Brookfield viscosity standards to calibrate every three months.

ADDENDUM B—Aliphatic Alkyd Gloss Enamel 0.97% Rheological Additive T-22907A

Raw Material	Pounds	Gallons
Long oil soya alkyd, 70% NV	150.0	18.75
Mineral spirits 66/3	76.0	11.60
Organoclay 34 rheological additive	10.0	0.71
Mix 3 min @ 3000 RPM then:		
MeOH/H_2O (95/5)	3.0	0.45
Mix 1 min @ 3000 RPM then:		
Kronos 2090 TiO_2	325.0	9.53
Disperse at high speed for 15 min.		
Letdown:		
Long oil soya alkyd, 70% NV	401.7	50.21
Mineral spirits 66/3	49.3	7.53
6% Zirconium drier	10.3	1.43
6% Cobalt drier	3.4	0.46
Exkin #2	2.0	0.25
Total	1030.7	100.92

Formula Constants	Physical Characteristics
Total solids (vol) . . . 53.41	Gloss . . . . . 82 @ 60°
Total solids (wt) 70.05	Fineness 7.5A
% PVC. 19.00	Viscosity . . . . 97 KU
Lb per gal 10.21	Sag, mils 6.0

ADDENDUM C—LK-TC-03-016

Formulation Part 1:

Pregel Preparation				
Organoclay 34 Lot #	**F30710**	**Std.**	**F30710**	**Std.**
K21 solvent . . . . . (%)	87.5	87.5	87.5	87.5
Organoclay 34 . . . . . (%)	9.1	9.1	9.1	9.1
Dispersing for 15 min at . . . . . m/s	8	8	16	16
Anti-Terra U . . . . . (%)	1.46	1.46	1.46	1.46
Propylene carbonate . . . . . (%)	1.89	1.89	1.89	1.89
Water . . . . . (%)	0.15	0.15	0.15	0.15
Methanol/water (90:10) . . . (%)	—	—	—	—
	100	100	100	100
Paint Preparation				
Conventional alkyd . . . . . (%)	90	90	90	90
Pregel . . . . . (%)	10	10	10	10

ADDENDUM D—LK-TC-03-016

Formulation Part A-F: Air Dry Alkyd

Raw Material	**Function**	**Supplier**	**Weight %**
Woreekyd B870 75% in white spirit	Resin	Worlee Chemie GmbH	15.6
Kronos 2310	Pigment	Kronos Titan GmbH	30.4
Disperse for 20 min at 16 m/s with 4 cm toothed blade			
Woreekyd B870 75% in white spirit	Resin	Worlee Chemie GmbH	41.2
Durham VX88	Drier	Elementis Specialties Inc.	1.4
Durham CA 111	Anti-skin agent	Elementis Pigments Ltd.	1.4
			90.0
Mix at 10 m/s for 15 min			
10% organoclay 34 pregel		Elementis Specialties Inc.	10.0
			100.0

Solids: 74%
PVC: 17%

CT