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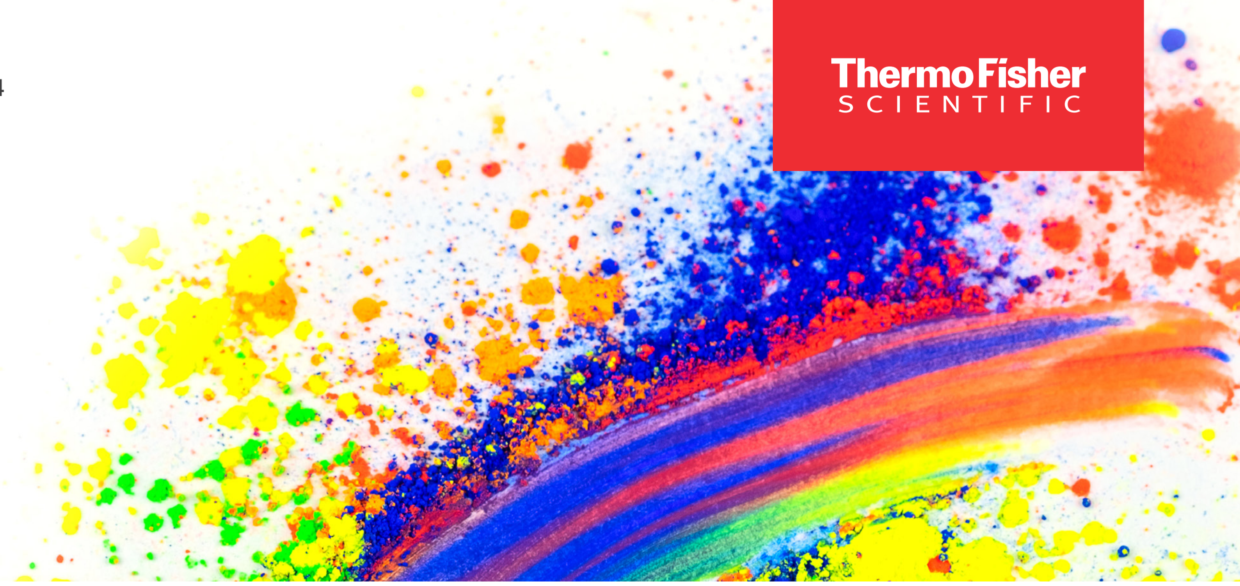

Investigating the thixotropic and shear recovery behavior of paints and coatings

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Introduction

Paints and coatings are usually highly structured fluids that consist of several different components. Colorants like pigments and dyestuffs provide color and can contribute to the final strength of the applied material. Binders are the film forming component that surrounds the pigments and prevents aggregation. They also influence the properties of the final product such as gloss, durability, flexibility and toughness. Furthermore solvents can be used as transport media which do not become part of the final paint film. Finally different kinds of additives can be added to modify the surface tension, optimize the thixotropic behavior or improve finish appearance of the paint film. All these components contribute to the flow behavior of the final paint product.

During processing, transport and application, paints and coatings are exposed to a wide range of shear rates. During processing e.g. the pumpability of a material correlates strongly

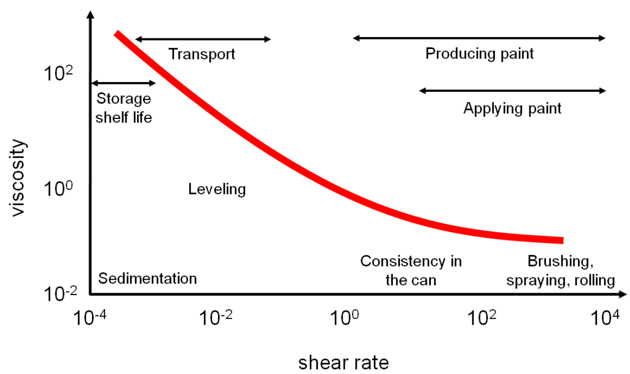

Figure 1: Shear rate depending viscosity of a coating and different applications.

Figure 2: HAAKE Viscotester iQ Rheometer with Peltier temperature control unit for concentric cylinder geometries and a CC25 DIN measuring geometry.

with viscosity at medium and higher shear rates. For shelf life on the other hand the lowest shear rates and the yielding behavior are of interest. Figure 1 gives an example of the shear rate depending viscosity of a paint and the applications and processes correlating with the shear regions (1).

In order to evaluate the rheological performance of a paint usually more than just a simple single point measurement is required. In particular the investigation of application behavior requires more comprehensive test methods to simulate usage of different tools like brushes, rolls or spray guns. Measuring the change of the microstructure at high shear rates and the recovery at rest or under lower stresses and strains can be a useful tool to optimize formulations and evaluate final products.

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Materials and methods

Different kinds of commercially available paints have been tested using the Thermo Scientific™ HAAKE™ Viscotester™ iQ Rheometer in combination with a Peltier temperature control unit for concentric cylinders and a CC25 DIN measuring geometry (Figure 2). The tested materials include standard wall paint, primer paint and a lacquer for smooth surfaces. All measurements were performed at 20 °C.

A common test method for the investigation of thixotropic behavior of paints and coatings is a loop experiment including a Controlled Rate (CR) ramp from low to high high shear rates, followed by a steady shear rate element at the highest shear rate and a CR ramp back to the low shear rate (2). A typical test procedure for a thixotropy loop test in the Thermo Scientific™ HAAKE™ RheoWin™ Software is shown in Figure 3.

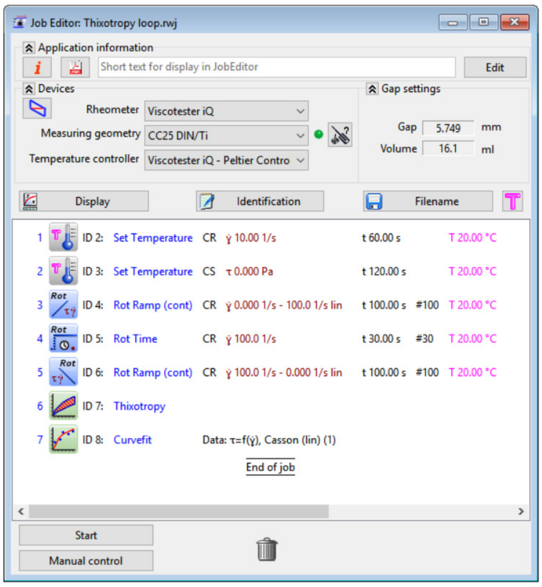

Figure 3: HAAKE RheoWin Measuring job for a thixotropy loop experiment including data evaluation.

At the beginning of the measuring procedure a pre-shear rate of 10 s^{-1} was applied for 60 s, followed by a rest period of 120 s^{-1}. This allowed the sample to equilibrate to the set temperature of 20 °C and to achieve a defined shear history prior to the actual experiment in order to optimize comparability of different samples and fillings. The following three elements belong to the actual thixotropy loop experiment. First the shear rate was ramped up from 0 to 100 s^{-1} in 100 s. Afterwards the maximum shear rate was held for another 30 s, followed by a ramp down element back to 0 s^{-1}. The last two elements are for data evaluation. First the hysteresis area between the ramp up and the ramp down curves was calculated to quantify the thixotropic behavior of the sample. A non-thixotropic material would exhibit identical viscosity curves for upward and downward ramps and therefore no hysteresis area. This kind of material recovers instantaneously from an applied stress or strain. The larger the hysteresis area on the other hand, the more a material is considered thixotropic. Since the hysteresis area depends strongly on the used experimental settings like shear rate range and shear time, the hysteresis area is not an absolute measure for thixotropy. Different materials can only be compared if the same procedure with the same settings was used for the tests. In the last element a curve fit according to the Casson model was applied to calculate the yield stress of the material. The yielding behavior is important for predicting sagging when applying paint on a vertical wall (3).

One of the major disadvantages of the thixotropy loop experiment is, that it does not provide any information about the time a material requires to recover after being exposed to a high shear rate, neither to what degree it recovers in a certain period of time. This information can be obtained from the so-called shear recovery experiments, where the change in viscosity over time is monitored after the material has been exposed to a high shear rate. However, the recovery of a material can only be measured if the applied shear stress τ or shear rate $\dot{\gamma}$ is small. In an initial step the viscosity of a material with an intact structure is measured, followed by a high shear rate period to break down the microstructure of the sample. In a third step the applied forces are reduced again to the initial value, to monitor the recovery after a high shear impact.

Using the HAAKE Viscotester iQ Rheometer, the shear recovery test can be performed in two different ways. The first and the third step can be performed at a low shear rate (CR) to get a baseline for the material with an intact structure and to measure the time dependent recovery. Both elements can also be performed at a low shear stress. This method simulates the effects of gravity acting on a paint, after it was applied to a surface, better than the shear rate experiment. However this test can only be conducted with a rheometer which is able to work in Controlled Stress (CS) mode. For both methods the mid part is performed in CR at an elevated shear rate. Figure 4 shows the typical test setup for a 3- step shear recovery test performed in CR-mode in the HAAKE RheoWin Software.

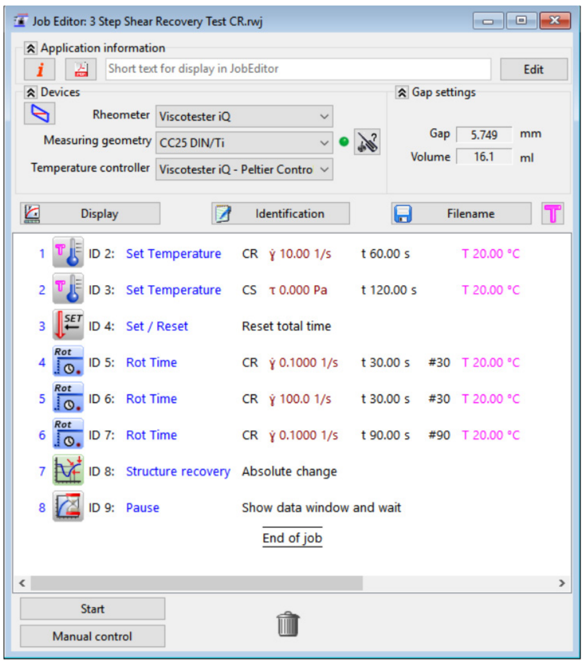

Figure 4: HAAKE RheoWin Measuring job for a 3-step shear recovery test in CR-mode including data evaluation.

Figure 5 shows the setup for the same experiment performed in CS-mode.

As for the thixotropy loop experiments, the first two elements were included for preconditioning of the material to improve comparability and reproducibility. Since the viscosity data for this type of experiment is plotted versus time, the third element resets the total experimental time t to zero and the data acquisition starts at zero seconds. The elements 3 to 6 (for the test in CR-mode) are for the actual shear recovery experiment. When performing the experiment in CS-mode, the first and the last step are conducted at a constant low shear stress. Between the constant shear and the recovery part a "Set temperature" element was included to set the rotational speed back to zero rpm. If this step is missing, undesired effects caused by the high shear rate in the second element will lead to faulty data during the beginning of recovery. The shear stresses selected for the first and the last element should correspond to a rotational speed that is within the measuring range of the rheometer. Here some pre-testing of the sample may be required. For both test methods the last element is again for data evaluation. The HAAKE RheoWin Software allows for a comprehensive data evaluation of the structure recovery test.

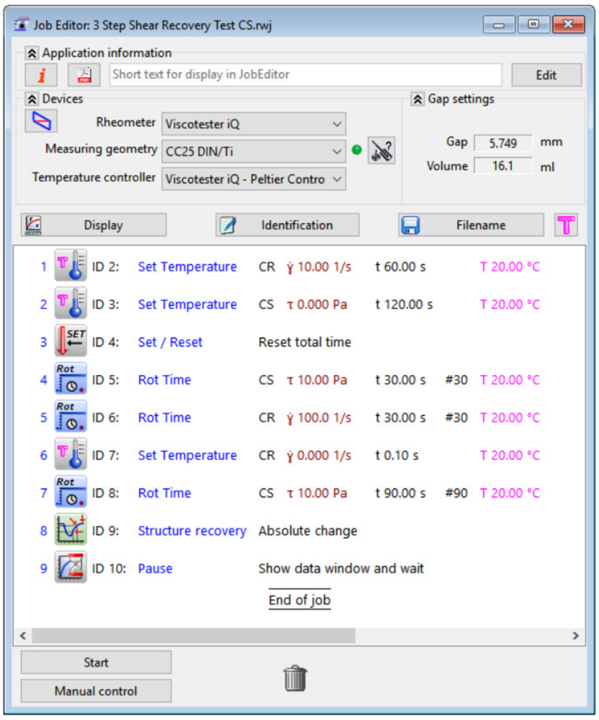

Figure 5: HAAKE RheoWin Measuring job for a 3-step shear recovery test in CS-mode including data evaluation.

Results and discussions

The results of the thixotropy loop experiment for the three paints are shown in Figure 6.

Table 1 lists the results of the data evaluation elements of the HAAKE RheoWin Measuring job as shown in Figure 3. This includes the hysteresis area between the upward and the downward curves curve of the shear stress τ and the yield stress τ_0 derived from a curve fit according to the Casson model.

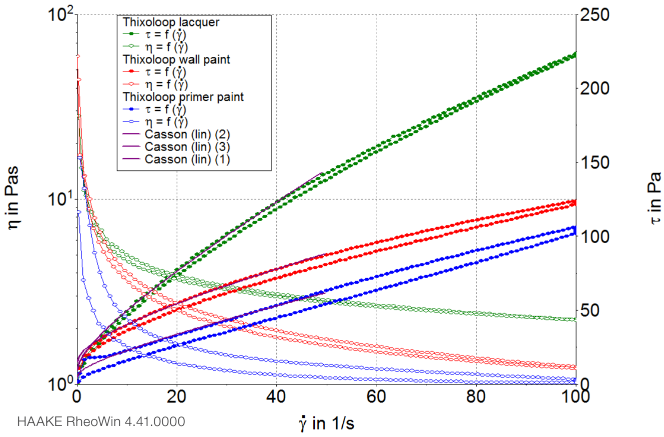

Figure 6: Results of thixotropy loop experiment for lacquer, wall paint and primer paint.

Table 1: Calculated values of hysteresis area and yield stress for lacquer, wall paint and primer paint.

Paint type	Hysteresis area in Pa/s	τ_0 in Pa according to Casson model
Lacquer	339	9.2
Wall paint	452	15.1
Primer paint	732	5.2

As it can be seen in Figure 6 and Table 1, the lacquer shows the smallest hysteresis area and therefore the least thixotropic behavior of all three samples. It can be expected that this material recovers almost instantaneously after the shear rate or shear stress is removed. This kind of behavior is of advantage to avoid sagging and the formation of droplets after a paint has been applied to a vertical wall. However the quick recovery time can also cause an uneven or structured surface when the application tool is removed. The wall paint and the primer both show a higher thixotropic behavior and a lower viscosity at elevated shear rates. One would expect better leveling behavior from these two samples compared to the primer paint.

All samples were also tested with a shear recovery experiment. As mentioned in the Materials and Methods section, there are different ways to perform this kind of test. Depending on the procedure used, one would also expect different results. Figure 7 shows the results of three tests that were performed with the wall paint. The initial and the recovery step were performed in CR-mode at a shear rate of 0.1 s^{-1} as well as in CS-mode with two different shear stresses of 8 and 10 Pa respectively.

When using the CR method, the wall paint shows the quickest recovery, but also the lowest overall viscosity in the first step. Even though the selected shear rate is low, the material cannot be considered at rest, due to the continuous shear in CR-mode. The results are therefore only partially useful.

When using the CS method, the initial viscosity signal is much higher, indicating a more intact structure. The recovery is delayed and more time-dependent. When using the lower shear stress, the viscosity in the recovery element almost reaches its initial value after 90 seconds. This correlates well with the results from the thixotropy loop performed on the same material.

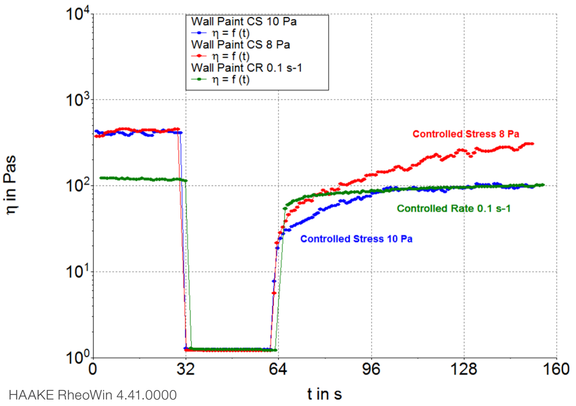

Figure 7: Results of 3-step shear recovery test for wall paint using different settings.

Figure 8 shows the comparison of all three coatings using the CS method with a shear stress of 8 Pa in the initial and the recovery element. The wall paint shows the highest initial viscosity and also the most significant drop at the beginning of the high shear step. The recovery within 90 s is 68 %. A high viscosity at rest (or at low stresses) usually slows down effects like phase separation and sedimentation (see Figure 1) and therefore improves the shelf life of a formulation. A low viscosity in the medium to high shear rate range is preferred for an easy application with low effort (e.g. with a brush). A delayed recovery improves the leveling behavior of a coating.

Brush or roller marks are avoided when the viscosity is not recovering instantaneously, but allows for the formation of an even surface. However, if the recovery is too slow the material may tend to sag and form droplets, especially when applied on a horizontal surface. Finding the right balance between too slow and too fast recovery after structural breakdown is a crucial point in the development of new paint formulations.

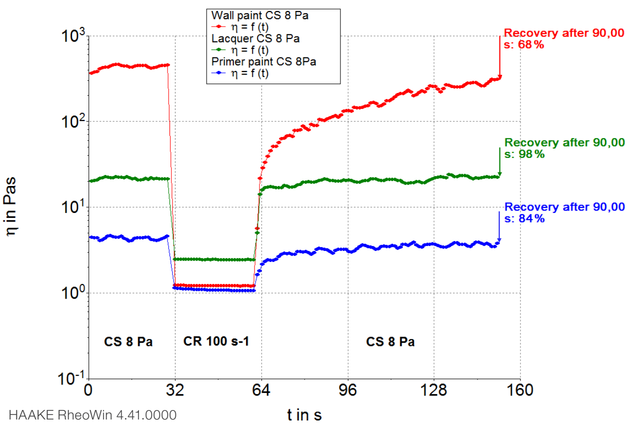

Figure 8: Results of 3-step shear recovery test for wall paint (red), laquer (green) and primer paint (blue) using the CS method.

The lacquer shows an almost instantaneous recovery in this experiment. After a few seconds the viscosity is almost constant and nearly at the same level as in the first element. These results correlate well with data obtained from the thixotropy loop experiment, where the lacquer showed the smallest hysteresis area of all three samples. Compared to the other two samples, the value of the lacquer viscosity at high shear rate is about twice as high (2 Pa·s). The primer paint shows the lowest overall viscosity (at low stress and at high shear rate). As expected from the results obtained with thixotropy loop experiment, the recovery of the material is delayed. After 90 s the viscosity reaches 84 % of its initial value. The numerical values of initial and high shear viscosity as well the as the final degree of recovery are summarized in Table 2.

Table 2: Initial and high shear viscosity as well as the final degree of recovery for laquer, wall paint and primer paint.

Paint type	Initial viscosity at 8 Pa in Pa·s	Equilibrium viscosity at 100 s^{-1} in Pa·s	Recovery after 90 s in %
Lacquer	21.5	2.4	98
Wall paint	431	1.2	68
Primer paint	4.3	1.1	84

Conclusions

Measuring the thixotropic behavior is an important method to evaluate the performance and applicability of paints and coatings. The HAAKE Viscotester iQ Rheometer is a modern Quality Control rheometer that goes beyond the capabilities of standard viscometers. In addition to common thixotropy loop experiments, the HAAKE Viscotester iQ Rheometer with its ability of conducting measurements in Controlled Stress (CS) mode, allows for a more accurate and comprehensive material characterization. This includes shear recovery experiments to investigate the application and processing behavior of complex paint formulations.

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