Journal of Materials Science and Engineering A 12 (7-9) (2022) 87-93
doi: 10.17265/2161-6213/2022.7-9.003

Critical Consideration of the Definition of Thixotropy

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Abstract: Barnes et al. defined thixotropy as "gradual decrease of viscosity under shear followed by a gradual recovery of the structure when the shear rate is removed". The investigated pigment dispersions, with a gel-sol-gel conversion, show a decrease in viscosity under shear. After the shear rate is removed, a gradual recovery of the structure occurs with the rest time. It was found that the pigment dispersions follow the thixotropy definition. The systems with shear thinning flow behavior show start-up curves with maximum in experiments with shear rates from the shear thinning region, as a characteristic for thixotropy. After cessation of the shear, a gradual recovery of the structure is not observed, or the second part of the thixotropic definition is not fulfilled. The structure of the systems with plastic flow behavior as well does not recover. We presented a new, second, definition of thixotropy for non-gel-sol-gel systems—when a constant shear deformation is applied, the shear stress or viscosity passes through a maximum and then achieves a steady state value. After the shear deformation is stopped, the stress relaxation begins. The shear stress comes to a steady state value—the residual shear stress. The structure does not recover after cessation of the shear flow.

Key words: Thixotropy, new second definition.

1. Introduction

Mewis [1] wrote: "at present, there exists a rather general agreement to call thixotropy the continuous decrease of apparent viscosity with time under shear and the subsequent recovery of viscosity when the flow is 'discontinued'."

Barnes et al. [2] defined thixotropy as "gradual decrease of viscosity under shear followed by a gradual recovery of the structure when the shear rate is removed".

The definition from IUPAC (International Union of Pure and Applied Chemistry) [3] said that the thixotropy is the "continuous decrease in viscosity with time when flow is applied to a sample that has been previously at rest, and the subsequent recovery of viscosity when flow is discontinued".

There are many reviews, such as by Mewis [1], Barnes [4], Mujumdar et al [5], Larson and Wei [6], to mention a few.

We [7] proved the existence of thixotropy in the systems with shear thinning and plastic flow behavior.

In this work we will consider the second part of the definition—"a gradual recovery ofthe structure when the shear rate is removed" [2].

2. Investigation of the Second Part of the Thixotropy Definition—"A Gradual Recovery of the Structure when the Shear Rate Is Removed"

2.1 Pigment Dispersions

The dispersions Cibanon Braun BR (experiment 3024/261) and Cibanon Yellow 3R (experiment 3051/53) [8] were investigated. These aqueous dispersions consist of water/ethylene glycol 90:10 and 18% to 20% by weight of raw pigment. Both systems are solidified gels. Through shear, the structure is destroyed, the viscosity decreases or thixotropy is observed. The system reaches the sol state. The structure rebuilds from sol to gel state after a rest time. These systems have a well reproducible gel-sol- gel conversion.

The measurements were conducted with the rotational viscometer Rheomat-30 (Contraves AG) with the DIN-45 measuring system at 25 ± 0.1 °C. The

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flow curves were recorded by switching every 15 s to the next higher shear rate.

The gel-sol conversion occurs by a defined shear for 2 min at a shear rate of 489 1/s. In the gel-sol conversion, the viscosity decreases and thixotropy is observed. To study the recovery of the structure or the sol-gel conversion, flow curves were measured immediately after the destruction of the gel structure, as well as after rest periods of varying lengths. The measurements begin after the system is completely solidified.

The flow curve of Cibanon Braun BR (experiment 3024/261), measured immediately after the shear, has shear thinning flow behavior (Fig. 1).

After 1 and 2 min of rest, we find again shear thinning flow behavior, where the first Newtonian region shows higher values. After 4-, 8-, 16-, and 32-min rest time, the values of the flow curves (Fig. 1) increase. After 8 min rest, the structure of the system is already well developed, and plastic flow behavior is observed. The flow curves after 16 and 32 min have as well plastic flow behavior, whereby the flow curves are shifted to higher shear stresses. The structure of the gel recovers successively after a rest time.

The gel shows plastic flow behavior. The structure is destroyed in the defined shear, and the sol system shows shear thinning flow behavior (Fig. 1). After cessation of the shear flow, the gel structure recovers. A longer rest causes an even better structure.

A similar picture is observed after the defined shear of Cibanon Yellow 3R (experiment 3051/53) (Fig. 2).

The recovery of the gel structure occurs in this dispersion (Fig. 2) faster than Cibanon Braun (Fig. 1). The plastic flow behavior is achieved after 4 min of rest time.

The investigated pigment dispersions obviously follow the second part of the definitionof thixotropy—"a gradual recovery of the structure when the shear rate is removed" [2].

2.2 Systems with Shear Thinning and Plastic Flow Behavior

The systems with shear thinning flow behavior have a first Newtonian region and a shear thinning region. In start-up experiments with shear rates from the first Newtonian region, a steep increase in shear stress begins up to the steady state value (Fig. 3A).

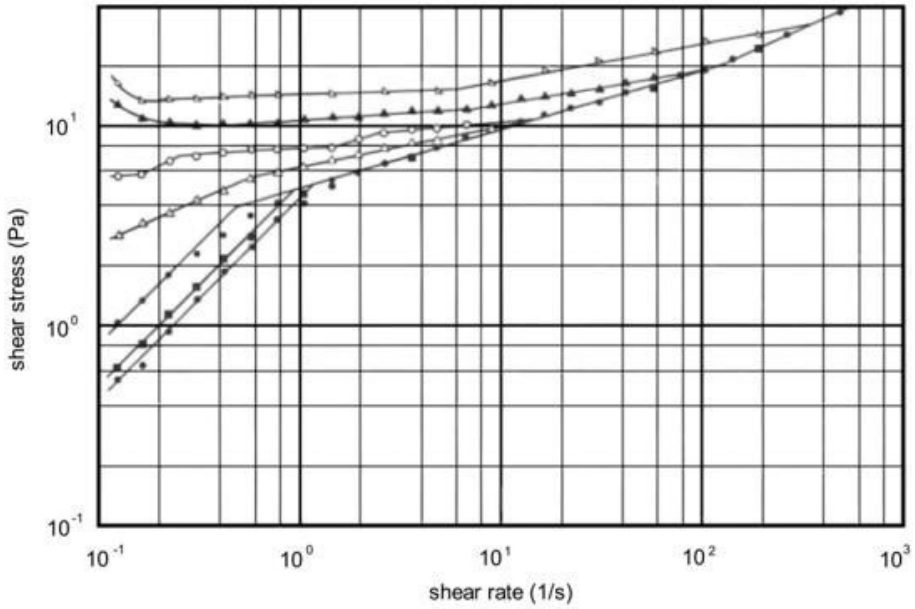

Fig. 1 Flow curves of Cibanon Braun BR (experiment 3024/261).

• immediately after shear, ■ after 1 min rest, ● after 2 min, Δ after 4 min, ○ after 8 min, ▲ after 16 min, ◦ after 32 min rest time.

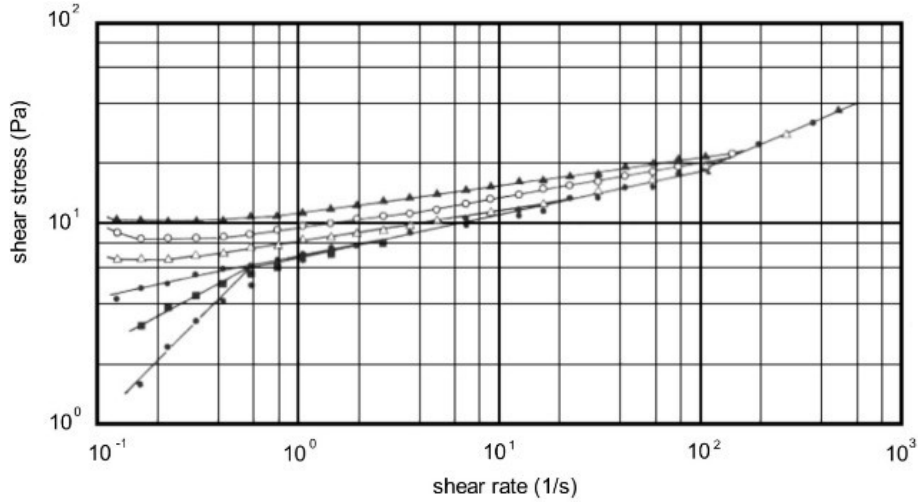

Fig. 2 Flow curves of Cibanon Yellow 3R (experiment 3051/53).
• immediately after shear, ■ after 1 min rest, ● after 2 min, Δ after 4 min, ○ after 8 min, ▲ after 16 min rest time.

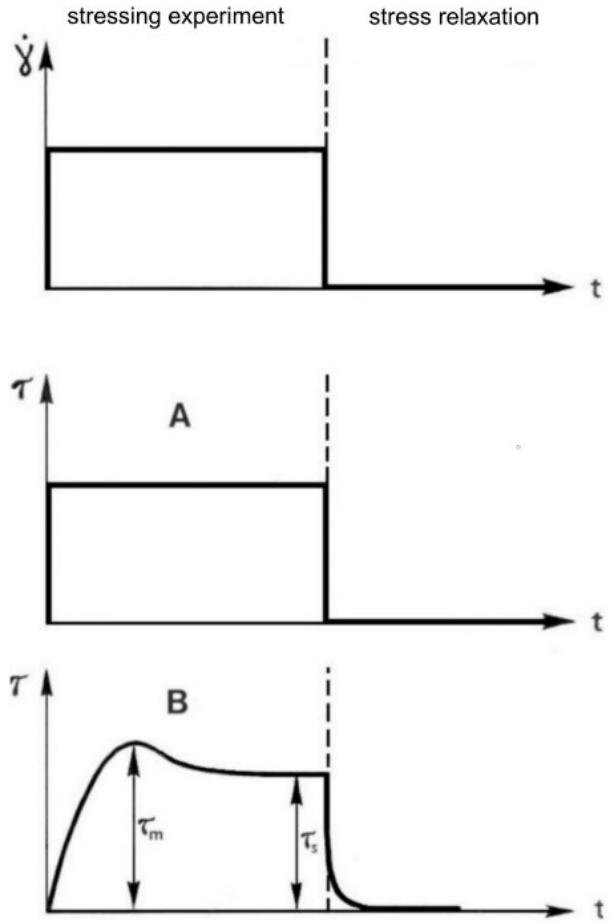

Fig. 3 Start-up experiments with shear rates from the first Newtonian region (3A) and shear rates from the shear thinning region (3B).

In start-up experiments with shear rates from the shear thinning region, the start-up curve undergoes an overshoot τ_m, after that the shear stress begins to decrease (Fig. 3B). The shear rate at onset of shear thinning [9] is the shear rate at which the start-up curve shows the first sign of an overshoot. This is the first sign of thixotropy. The decrease in shear stress or viscosity occurs up to a steady state shear stress τ_S.

The shear thinning systems have thixotropic properties in the shear thinning region [7]. The stress relaxation begins after cessation of the shear. In both cases, no residual shear stress τ_R is observed (Fig. 3).

The formulation Araldite XB3008A, Op14/79 was investigated. The system consists of the epoxy resin Araldite GY260 and various fillers and thixotropic agents. Fig. 4 shows the flow curve of the formulation.

This system shows shear thinning flow behavior. The shear thinning region begins or the shear rate at onset of shear thinning appears at 0.28 1/s (Fig. 4).

Fig. 5 shows a start-up test with a shear rate of 2.8 1/s from the shear thinning region, followed by a stress relaxation. As expected, the start-up curve shows a maximum or thixotropy.

After reaching the steady state shear stress, the shear deformation is stopped, and the stress relaxation begins. The residual shear stress is zero.

We waited 4 min to see if a “gradual recovery of the structure when the shear rate is removed” occurs, as is to be expected according to the definition of thixotropy.

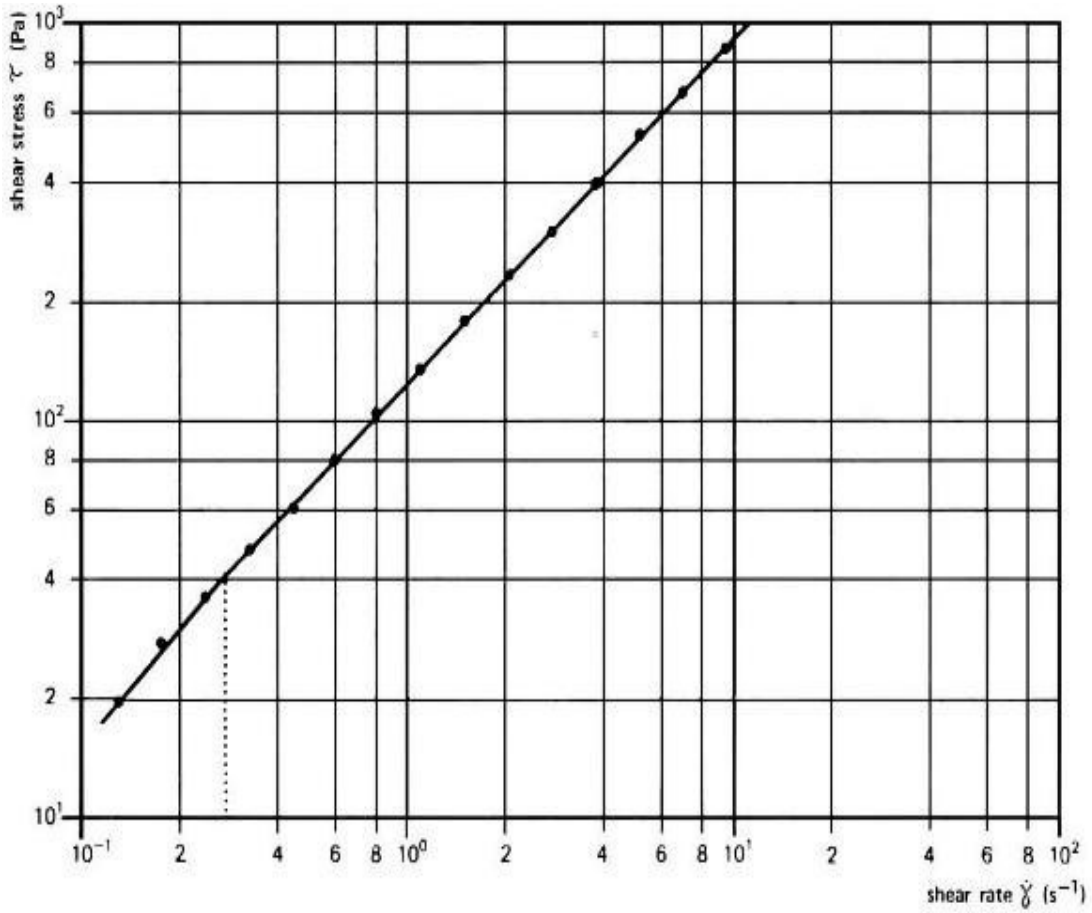

Fig. 4 Flow curve of XB3008A, Op.14/79 (Rheomat-30, cone-plate 2, 25 ± 0.1 °C).

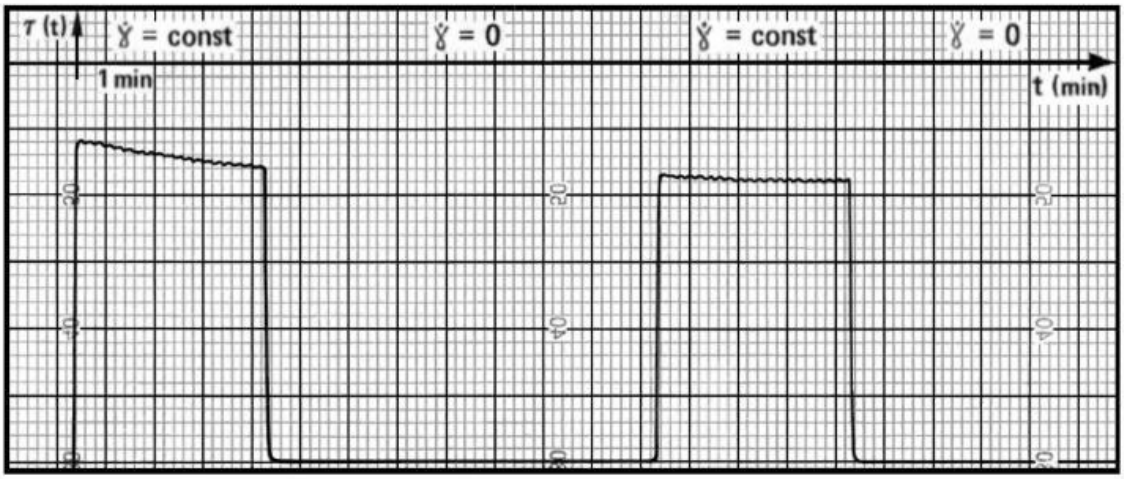

Fig. 5 Start-up test with 2.8 1/s—stress relaxation—of the system XB3008B (Rheomat-30, cone-plate 2, 25 ± 0.2 °C).

But the shear stress or the structure does not recover, and consequently does not follow the second part of the definition. A new start-up experiment leads to a similar start-up curve.

The systems with plastic flow behavior have one or more yield stress regions [10]. The flow curve of the system CW214, Exp.534, 6 months after production (Fig. 6) shows two yield stress regions.

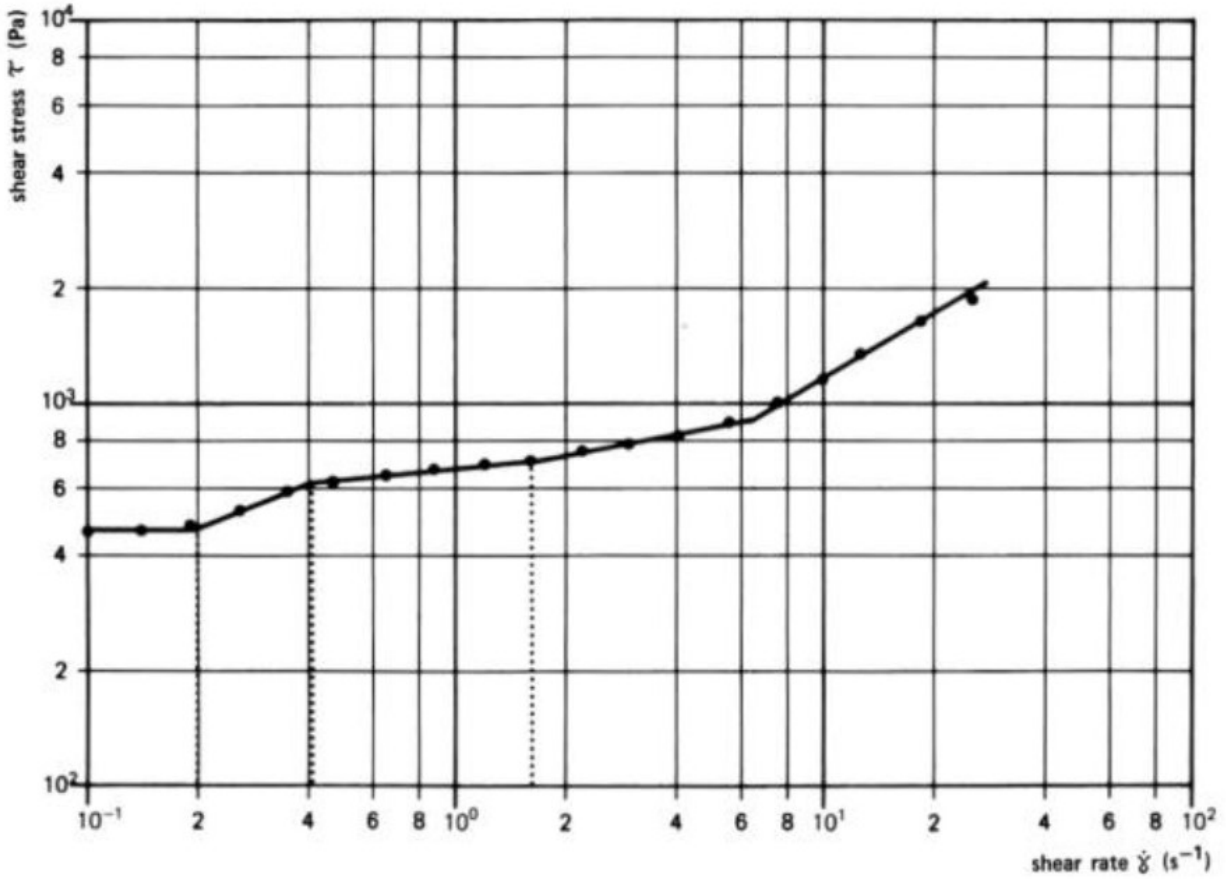

Fig. 6 Flow curve of the system CW214, Exp.534, 6 months after production (Rheomat-30, cone-plate 4, 25 ± 0.2 °C).

Fig. 7 Start-up test with 0.13 1/s—stress relaxation of the system CW214, Exp.534, 6 months after production (Rheomat-30, cone-plate 4, 25 ± 0.2 °C).

The start-up curve with a shear rate from the first yield stress region (Fig. 7) exhibits an overshoot or thixotropic behavior.

A residual shear stress is observed in the stress relaxation—about 29% of the structure is still in order after the shear. The residual shear stress increases precious little after 6 min, up to the steady state values. Although part of the structure is still in order after the shear, the structure does not recover.

The systems with shear thinning and plastic flow behavior, obviously do not follow the second part of the thixotropy definition—"a gradual recovery of the structure when theshear rate is removed" [2].

A new (second) definition must be introduced for the systems with shear thinning and plastic flow behavior, as non-gel-sol-gel systems. This new or second definition for thixotropy can be described as follows—a start-up curve increases in the shear stress, goes through a maximum, which is characteristic for the thixotropy. It follows a decrease in the shear stress up to a steady state value. After cessation of the shear flow, begins the stress relaxation. From the residual shear stress, one can draw conclusions about the structure, remaining after the shear. The structure does not recover after cessation of the shear flow.

3. Summary

The aim of this work was to investigate the second part of the thixotropy definition "a gradual recovery of the structure when the shear rate is removed" [2]. For this purpose, pigment dispersions and systems with shear thinning and plastic flow behavior were investigated.

The pigment dispersions are solidified gels. Through defined shear, the structure is destroyed, and a gel-sol conversion takes place. These dispersions obviously have thixotropic properties. Immediately after cessation of the shear, the recovery of the structure begins. The recovery of the structure from sol to gel was studied by recording of flow curves after a rest period of varying lengths. With the rest period, a better gel structure is created—from shear thinning to plastic flow behavior. One can assume the plastic flow behavior as a feature of the gel structure. It was found that the pigment dispersions meet the definition—"gradual decrease of viscosity under shear followed by a gradual recovery of the structure when the shear rate is removed" [2].

For the systems with shear thinning and plastic flow behavior, the well-known working method with start-up experiments were applied. The start-up curves with shear rates from the shear thinning region of the shear thinning systems show a maximum or thixotropic properties. We consider the maximum of a start-up curve as an indication of thixotropic properties. After cessation of the shear flow, the stress relaxation begins. The residual shear stress of the systems with shear thinning flow behavior is zero. It is to be expected, according to definition, "a gradual recovery of the structure when the shear rate is removed", but nothing happened. The systems with shear thinning flow behavior do not follow the second part of the thixotropic definition.

The start-up experiments of the systems with plastic flow behavior show an overshoot or thixotropy. After cessation of the shear, about 29% of the structure is still in order. The residual shear stress increases precious little, but the structure does not recover.

The systems with plastic flow behavior do not meet the second part of the thixotropicdefinition.

A second definition is obviously needed for the non-gel-sol-gel systems.

We can now postulate:

- The valid today definition, especially the second part, "gradual recovery of the structure when the shear rate is removed" is valid only to systems with a gel-sol-gel conversion.
- For the remaining systems, which do not have a gel-sol-gel conversion, a new definition needs to be introduced. Thixotropy can now be defined as follows: when a constant shear deformation is applied, the shear stress or viscosity passes through a maximum and then

achieves a steady state value. After removing the shear deformation, the stress relaxation begins. The shear stress comes to a steady state value—the residual shear stress. The shear stress or the structure does not rebuild after cessation of the shear flow.

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