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MODIFICATION OF RHEOLOGICAL PROPERTIES OF A SOLVENTBORNE PAINT USING ADDITIVES

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The application properties of paints such as spreading and levelling properties, film thickness, sedimentation tendency and pigment stability are determined by the paint rheological behaviour. Sufficiently shear thinning, thixotropic paints with a yield point have, as a rule, suitable application properties. If the paint does not exhibit the required properties, its rheological behaviour may be improved using a proper type of rheological additive. In this work, the rheological properties of an acrylic paint (dispersion of TiO_2 *in a solution of acrylate copolymers), which behaves as a Newtonian liquid, have been modified using three different types of commercial additives. To evaluate the influence of additive adjunction, the flow curves, yield point, oscillation tests, and creep and recovery tests have been measured for the paint samples on the dynamic rheometer RS 150 (Haake). It has been found out that the modified paints show shear thinning behaviour with a yield point and thixotropy. At the same time, they behave as viscoelastic liquids with different portion of elastic component of deformation at shear stresses in the*

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vicinity of the yield point. The additive Byk 410 has been evaluated as the most efficient type of rheological additive. Its addition to the basic paint is easy and the paint samples modified with this additive exhibit the most suitable rheological properties.

Introduction

The application properties of paints such as spreading and levelling properties, film thickness, sedimentation tendency and pigment stability are determined by the paint rheological behaviour [1–3].

For easy spraying or brushing of paints small forces are necessary. It requires significant reduction of viscosity under increasing shear stress (pseudoplasticity) and low viscosity at application conditions (at high shear rates). For good levelling properties the thixotropic behaviour and a relatively high viscosity at very low stresses are important. There is an optimum value for zero-shear viscosity η_0, at which the paint still forms a homogeneous layer and does not sag. However, not only shear dependent behaviour of the paint but also its viscoelastic properties are important.

During the storage, individual components of the paint have to be kept suspended in the paint structure so as not to produce undesirable sediment. The yield stress (point) determines a limit shear stress necessary for the destruction of this structure and its existence is needed for a good stability of the paint at the storage conditions.

Therefore, sufficiently shear thinning, thixotropic paints with yield point usually have suitable application properties. If the paint does not show the required properties, its rheological behaviour may be improved using a proper type of rheological additive. The examples of such rheology modifiers used are, for example, bentonic clays, synthetic silicas or urea derivates.

In this work, the basic acrylic paint (white email) with unsuitable rheological properties was modified using three types of commercial additives in different concentrations. The flow curves, thixotropy, yield point, and unsteady shear flow material functions of the samples tested were measured on a dynamical rheometer RS 150. The evaluation of results obtained for the individual additives used is presented.

Experimental

Paint Samples

The examined paint (white email) was a dispersion of TiO_2 (rutile type) in a solution of acrylate copolymers (68.4 % wt. of solids). The individual samples tested were prepared from the basic paint, diluted with the commercial thinner Akrylmetal LVPC 244 (SYNPO a. s.) in the weight ratio 100:14, by addition of three types of additives: urea derivate Byk 410 (A1), synthetic silica Aerosil 200 (A2), and bentonic clay Bentone SD-3 (A3).

The liquid modifier A1 was mixed by hand into the dilute basic paint in the amount giving concentrations of 0.5, 1.0, and 1.5 wt. %. The voluminous powdered additive A2 was stirred with the dilute basic paint in the amount giving concentrations of 0.5, 1.0, 1.2, 1.5, and 2.0 wt. %. using a laboratory stirrer with low rotation speed so as not to disturb the structure of the additive. For application of the powdered additive A3, the additive was first intensively stirred with the basic paint and thinner in a vertical bead mill to prepare a concentrated paste. After that, the paste was diluted with the basic paint in the amount giving the additive concentration of 1.2, 2.0, and 3.0 wt. %.

Rheological Measurements

The rheological measurements of paint samples were performed at the temperature of 23°C on the dynamical rheometer RS 150 (Haake) with coaxial cylinder sensor system Z40 DIN (R_i = 20 mm, sample volume = 65 ml) [4].

For all samples tested, the following measurements were carried out [5]:

Flow Curves

The dependences of shear stress τ on the continuously varying shear rate $\dot{\gamma}$ (CR mode) were measured in the interval of $\dot{\gamma}$ = 0.01 - 300 s^{-1} for both increasing and decreasing shear rates (up- and down-ramp flow curves).

Yield Point

The existence of a yield point was evaluated from measurements of the dependence of deformation γ on the continuously varying shear stress τ (CS mode). Setting intervals were τ = 0.01 - 10 Pa or τ = 0.1 - 100 Pa depending on the sample viscosity.

Oscillation Tests

Oscillation tests were carried out at two distinct levels τ_1 and τ_2 of shear stress for each sample. The values of applied shear stresses were chosen in accordance with the sample viscosity function course. The value τ_1 of the shear stress corresponded to a low value of shear rate ($\dot{\gamma} \approx 0.1\ s^{-1}$), the value τ_2 to a higher value of shear rate ($\dot{\gamma} \approx 30\ s^{-1}$). Frequency sweeps were run from 0.01 to 10 Hz.

Creep and Recovery

Creep and recovery tests were also measured at the levels τ_1 and τ_2 of shear stress for each sample. Duration of the creep phase was 60 s, duration of the recovery period was 120 s.

Results and Discussion

Flow Curves and Viscosity Functions

The measurements of the flow curve and the yield point of the dilute basic paint

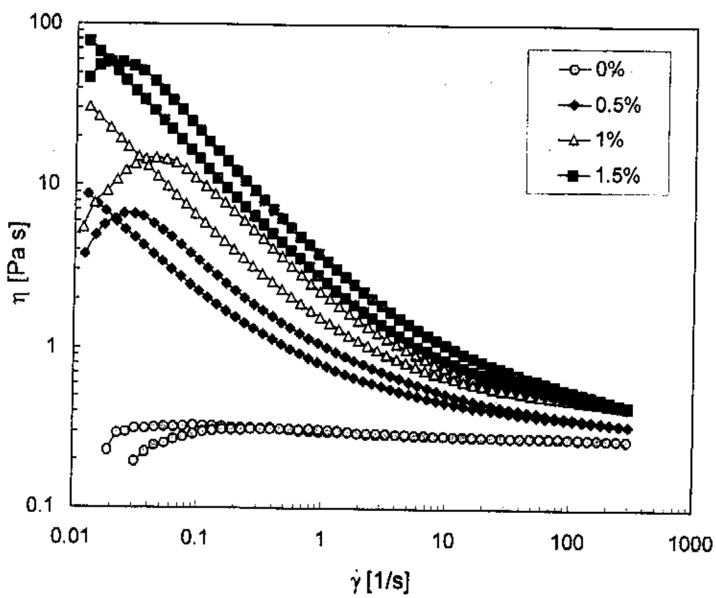

Fig. 1 Comparison of the viscosity function course for paint samples modified with additive A1 of various concentrations

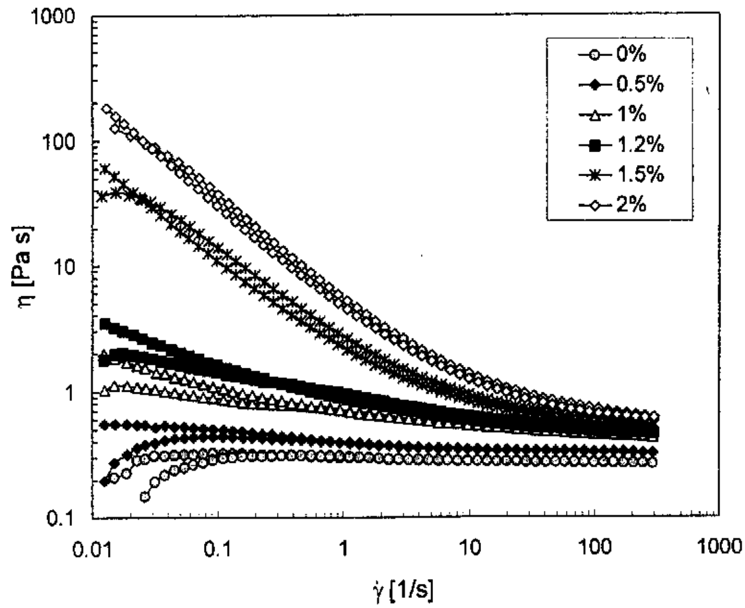

Fig. 2 Comparison of the viscosity function course for paint samples modified with additive A2 of various concentrations

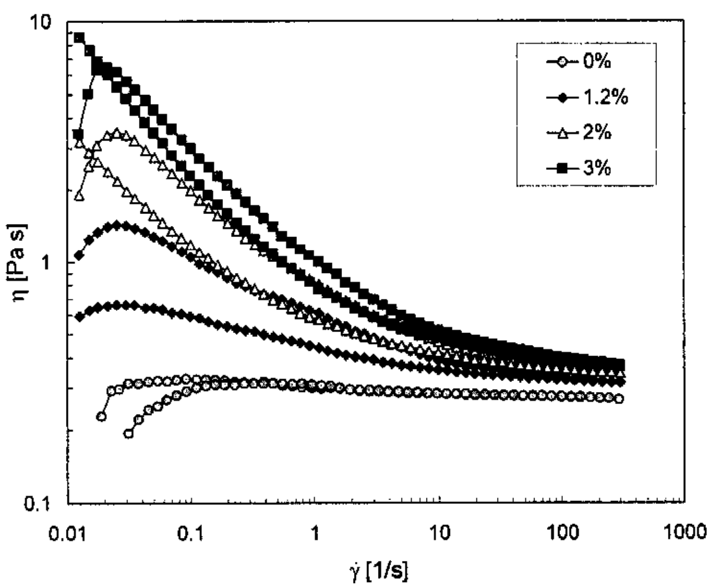

Fig. 3 Comparison of the viscosity function course for paint samples modified with additive A3 of various concentrations

showed that its rheological behaviour was nearly Newtonian (μ = 0.29 Pa s), i.e. without any thixotropy and yield point. Therefore, the paint rheological properties were modified using the above-mentioned additives and the resulting changes were examined.

The courses of experimental viscosity functions obtained for the dilute basic paint (0 % of additive) and paint samples with different content of the additives are compared in Figs 1 – 3. It is evident that the addition of any type of modifier improved rheological behaviour of the basic paint. The modified paints show shear thinning and thixotropic behaviour. At the same time, the measure of shear thinning increases with the rising concentration of the additive. The viscosity of the paint increases fastest by adjunction of the additive A1. Concerning the others, an expressive increase of the paint viscosity appears when the content of the additives A 2 and A3 is 1.5 % and 2.0 %, respectively. At the same time, an overshoot of viscosity at the beginning of measurements was observed namely for paints modified with additives A1 and A3 (Figs 1 and 3). Such behaviour can be ascribed to a structural breakdown of the paint.

Thixotropy

The hysteresis loops of the up- and down-flow curves document a thixotropic behaviour of the modified paint samples in contrast to the basic paint for which no thixotropy was marked.

The measure Δ of the thixotropy, which is given by hysteresis area (proportional to the energy required to change the dispersion structure), is summarized for all the samples tested in Table I. For the additives A1 and A2, the

Table I Measure of thixotropy for $\dot{\gamma}$ from 0.1 s^{-1} to 300 s^{-1} and yield stress

Sample	Δ Pa s^{-1}	τ_0 Pa
BP - basic paint	0	0
BP + 0.5 % A1	270	0.373
BP + 1.0 % A1	275	0.665
BP + 1.5 % A1	1097	1.492
BP + 0.5 % A2	0	0
BP + 1.0 % A2	140	0
BP + 1.2 % A2	558	0
BP + 1.5 % A2	860	1.36
BP + 2.0 % A2	1326	2.36
BP + 1.2 % A3	202	0.06
BP + 2.0 % A3	255	0.193
BP + 3.0 % A3	308	0.186

level of thixotropy markedly increases with the rising concentration of the additive. On the other hand, only weak increase in the thixotropy level was observed with the rising concentration of the additive A3.

Yield Point

The existence of yield point was determined from the dependence $\gamma - \tau$ of deformation on the shear stress. If the substance shows a yield stress, the obtained dependence can be approximated in a log-log plot by two straight line segments. The slope of the bottom one is theoretically equal to 1 and corresponds to the deformation of a solid, the slope of the upper one corresponds to a liquid deformation (flow) and is evidently greater than 1. The value τ_0 of the yield point is given by the intersection of these two segments. A typical course of the dependence $\gamma - \tau$ is shown in Fig. 4.

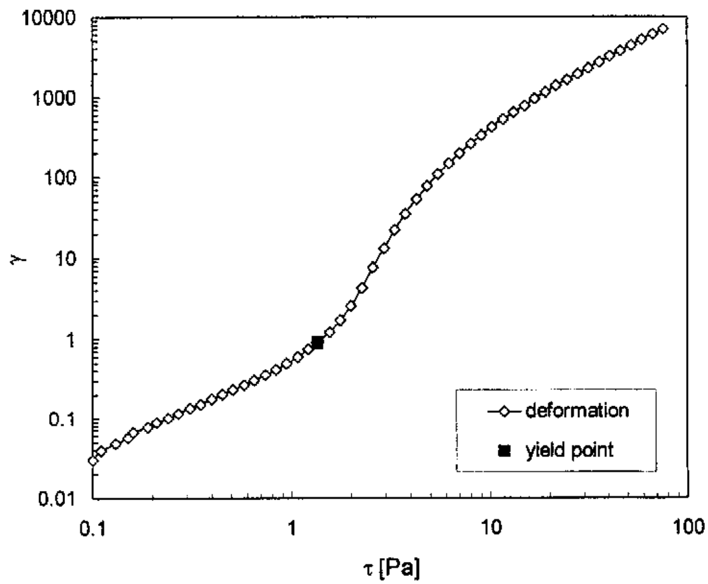

Fig. 4 Dependence of deformation γ on shear stress τ for the paint sample modified with additive A2 with concentration of 1.5 %

The evaluation the experimental dependences of deformation γ on the shear stress τ, showed that the samples of the basic paint and paints modified with the additive A2 at low concentrations do not exhibit any yield point. The experimental values of the yield stress τ_0 are summarized in Table I.

Flow Models

The up-flow curve of all paint samples can for $\dot{\gamma} > 0.05\ \mathrm{s^{-1}}$ be approximated using the four-parameter Carreau flow model

$$\tau = \left\{ \eta_\infty + \frac{\eta_0 - \eta_\infty}{\left[1 + (\lambda\dot{\gamma})^2\right]^{\frac{1-m}{2}}} \right\} \dot{\gamma} \tag{1}$$

Table II Parameters of the Carreau viscosity model

Sample	η_0 Pa s	η_∞ Pa s	λ s	m
BP - basic paint	0.32	0.263	3.9	0.709
BP + 0.5 % A1	7.18	0.327	40	0.397
BP + 1.0 % A1	31.9	0.438	43.8	0.24
BP + 1.5 % A1	69.3	0.471	47.3	0.21
BP + 0.5 % A2	0.445	0.318	4.7	0.62
BP + 1.0 % A2	0.926	0.333	10	0.78
BP + 1.2 % A2	1.7	0.369	18	0.694
BP + 1.5 % A2	38	0.548	35.7	0.211
BP + 2.0 % A2	148	0.631	52.9	0.149
BP + 1.2 % A3	1.59	0.287	33	0.579
BP + 2.0 % A3	3.68	0.328	35	0.456
BP + 3.0 % A3	6.37	0.357	38	0.392

Table III Parameters of the Herschel-Bulkley model

Sample	τ_0 Pa	K Pa s^n	n
BP - basic paint	0	0.299	0.981
BP + 0.5 % A1	0.15	0.611	0.879
BP + 1.0 % A1	0.54	0.884	0.861
BP + 1.5 % A1	1.37	1.101	0.819
BP + 0.5 % A2	0.009	0.378	0.971
BP + 1.0 % A2	0.028	0.658	0.917
BP + 1.2 % A2	0.056	0.804	0.882
BP + 1.5 % A2	1.02	1.09	0.848
BP + 2.0 % A2	3	1.508	0.809
BP + 1.2 % A3	0.01	0.424	0.937
BP + 2.0 % A3	0.057	0.514	0.916
BP + 3.0 % A3	0.16	0.608	0.895

The values of the Carreau model parameters of the paint samples tested are given in Table II.

The data given in Table II document a distinct increase in the zero-shear rate viscosity η_0 of the modified paint and a weak increase of the infinity shear rate

Table IV Oscillation tests measured at low values τ_1 of shear stresses for f = 0.1 Hz

Sample	δ °	G' Pa	G'' Pa	τ Pa
BP - basic paint	88.1	0.008	0.217	0.04
BP + 0.5 % A1	68.1	0.256	0.635	0.3
BP + 1.0 % A1	53.2	1.496	2.002	2.5
BP + 1.5 % A1	31.5	9.716	5.952	3
BP + 0.5 % A2	82.3	0.039	0.287	0.05
BP + 1.0 % A2	75.2	0.111	0.419	0.1
BP + 1.2 % A2	70.2	0.262	0.728	0.1
BP + 1.5 % A2	66.2	1.008	2.287	1.3
BP + 2.0 % A2	66	2.305	5.169	3
BP + 1.2 % A3	74.1	0.117	0.409	0.05
BP + 2.0 % A3	71.9	0.187	0.571	0.05
BP + 3.0 % A3	67.2	0.237	0.563	0.05

Table V Oscillation tests measured at higher values τ_2 of shear stresses for f = 0.03 Hz

Sample	δ °	$G' \times 10^2$ Pa	$G'' \times 10^2$ Pa	τ Pa
BP - basic paint	89.8	0.019	4.9	10
BP + 0.5 % A1	89.8	0.027	7.5	10
BP + 1.0 % A1	89.4	0.114	10.3	30
BP + 1.5 % A1	89.4	0.183	16	30
BP + 0.5 % A2	89.8	0.018	6	10
BP + 1.0 % A2	89.9	0.024	8.9	10
BP + 1.2 % A2	89.6	0.072	10.5	10
BP + 1.5 % A2	88.8	0.329	15.4	10
BP + 2.0 % A2	88.5	0.934	35.5	10
BP + 1.2 % A3	89.8	0.023	6.2	10
BP + 2.0 % A3	89.7	0.033	7.1	10
BP + 3.0 % A3	89.7	0.04	8.2	10

viscosity η_∞ with the rising concentration of the additives. The observed increase of difference $\eta_0 - \eta_\infty$ corresponds to the increasing intensity of paint shear thinning.

The courses of down-flow curves can for $\dot{\gamma} > 0.05 \ s^{-1}$ be approximated by the Herschel-Bulkley model

$$\tau = \tau_0 + K\dot{\gamma}^n \quad (2)$$

whose parameters are given in Table III. At the same time, the values of parameter τ_0 of the Herschel-Bulkley model are comparable with those of the yield point (Table I).

Oscillation Tests

From the oscillation measurements, the values of storage modulus G', loss modulus G'', dynamic viscosity η', dynamic rigidity η'' and loss angle $\delta = arctg G''/G' = arctg \eta'/\eta''$ were determined at two distinct levels τ_1 and τ_2 of the shear stress as functions of the frequency f. Examples of the results obtained for the low shear stresses τ_1 and frequency $f = 0.1$ Hz are given for all paint samples tested in Table IV and for the higher shear stresses τ_2 and frequency $f = 0.03$ Hz in Table V. The example of the course of dependences of material functions G', G'', and δ on the frequency f at $\tau_1 = 3$ Pa is shown in Fig. 5 for the paint with additive A1 concentration of 1.5 %.

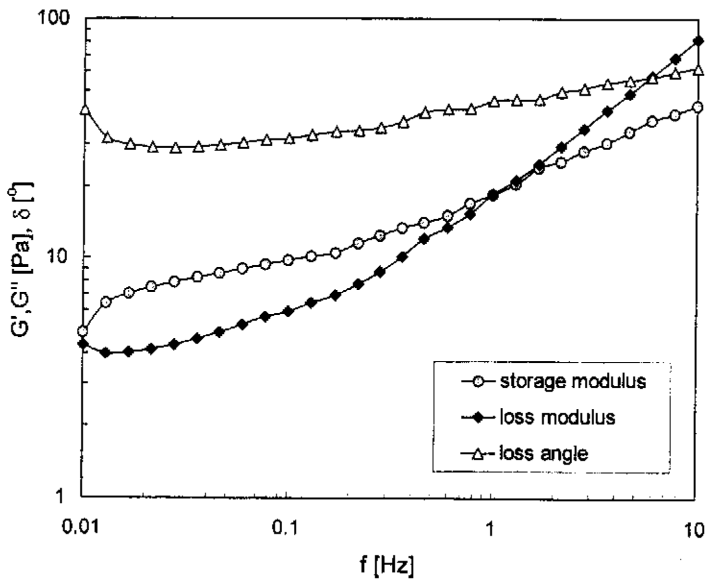

Fig. 5 Oscillation tests for the paint sample modified with additive A1 with concentration of 1.5 % ($\tau_1 = 3$ Pa)

In contrast to the Newtonian behaviour of the basic paint, all modified paint samples behave as viscoelastic substances with more or less obvious amount of elastic component at the low values τ_l of shear stress (in the vicinity of the yield point). The addition of A1 caused the biggest growth of the elasticity of samples. It is evident from Table V that by the influence of the increasing shear stress, the inner structure of a dispersion changes and the paint behaves as a purely viscous liquid ($\delta \approx 90°$).

Creep and Recovery

The results of creep and recovery tests are in a qualitative agreement with those of oscillation tests. The measurements show that all the samples with additives behave as viscoelastic liquids at low shear stress values τ_l, contrary to the Newtonian behaviour of the basic paint. The deformation γ increases nonlinearly with the increasing time in the creep phase, and in the recovery phase it decreases to a finite residual value. The example of the corresponding course of dependences of deformation γ on the time t is shown in Fig. 6 for paint samples modified with additive A1.

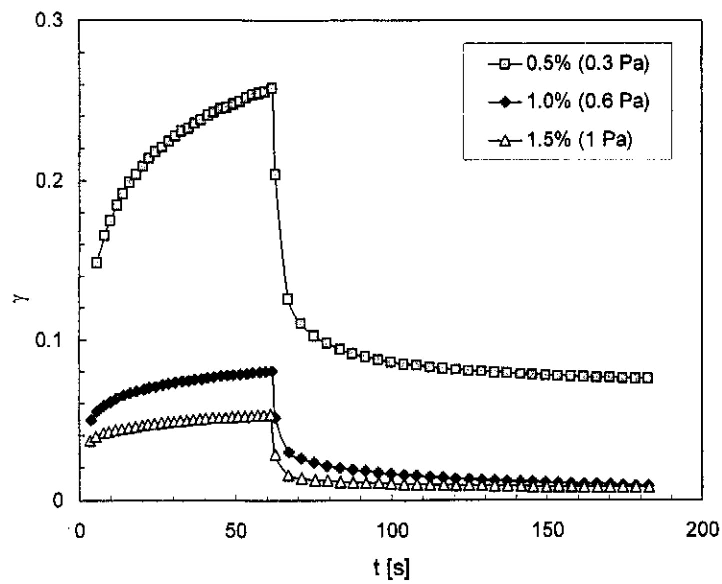

Fig. 6 Creep and recovery tests performed at the shear stresses τ_l for the paint samples modified with additive A1

At the level τ_2 of shear stress, all samples behave as purely viscous liquids. The increase in γ with increasing time is nearly linear in the creep phase, and in the recovery phase the value of deformation γ is constant. This is documented in Fig. 7 where the course of dependences of the deformation γ on the time t at τ_2 = 10 Pa is shown for paint samples modified with additive A2.

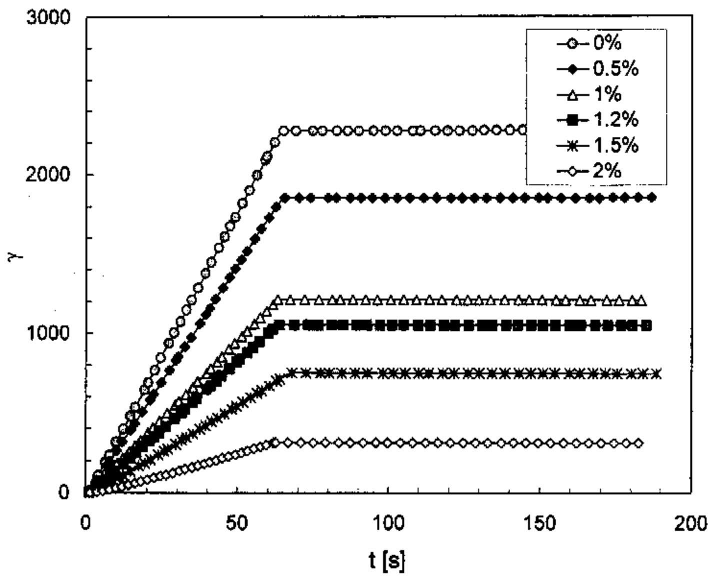

Fig. 7 Creep and recovery tests performed at the shear stresses τ_2 with the paint samples modified with additive A2

Conclusion

Using dynamic rheometer RS 150 (Haake), the flow curves, yield point, oscillation tests, and creep and recovery tests have been measured for a sample of the basic acrylic paint and for eleven samples of paints modified with an addition of three types of additives.

The rheological measurements have proved that the basic paint behaves as a Newtonian liquid. The addition of the each type of additive used improved its unsuitable rheological behaviour. The modified paints show shear thinning behaviour with yield point and thixotropy. At the same time, the extent of shear thinning increases with increasing concentration of the additive. The viscosity of the paint increases to the highest degree by addition of the additive A1.

The up-flow curve can be approximated for all paint samples using the four-parameter Carreau model. At the same time, the Herschel-Bulkley model approximates the courses of down-flow curves.

At low values τ_1 of shear stress, all modified paint samples behave as viscoelastic liquids with different portions of elastic component of deformation. Under the influence of increasing shear stress, inner structure of dispersions is breaking and their behaviour approaches that of a purely viscous liquid.

The additive A1 has been evaluated as the most efficient type of rheological additive. Its addition to the basic paint is easy and the paint samples modified using the additive A1 have the most useful rheological properties. Therefore, the additive A1 has been selected for practical testing the application properties of acrylic paints.

Symbols

f	frequency, Hz
G'	storage modulus, Pa
G''	loss modulus, Pa
K	parameter of Herschel-Bulkley viscosity model, Pa s^n
m	parameter of Carreau viscosity model
n	parameter of Herschel-Bulkley viscosity model
R_i	radius interior cylinder, m
t	time, s
γ	deformation
$\dot{\gamma}$	shear rate, s^{-1}
Δ	thixotropy measure, Pa s^{-1}
δ	loss tangent angle, °
η	non-Newtonian viscosity, Pa s
η_0	zero shear rate viscosity, Pa s
η_∞	infinity shear rate viscosity, Pa s
η'	dynamic viscosity, Pa s
η''	dynamic rigidity, Pa s
λ	time parameter of Carreau viscosity model, s
μ	viscosity, Pa s
τ	shear stress, Pa
τ_0	yields stress or parameter of Herschel-Bulkley viscosity model, Pa

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