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Elongational flow behavior of automotive coatings and its relation to atomization and mottling

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Abstract

The elongational flow properties of waterborne and solvent borne automotive basecoats have been characterized using opposing jet and contraction flow techniques. The ratio of elongational to shear viscosity varies between less than 20 and more than 300, showing that the behavior of such fluids in complex flows (atomization, filtration, impingement of droplets on substrates) cannot be deduced from shear viscosity alone. A clear correlation is found between the elongational viscosity of the fresh material and its sprayability as well as the optical appearance of the final coating in the case of the waterborne formulations. The opposing jet technique resolves these differences much better than contraction flow experiments. No such correlation is found for the solvent borne systems presumably since their rheological properties undergo a much stronger change during application. © 2001 Published by Elsevier Science B.V.

Keywords: Elongational; Flow behavior; Automotive; Atomization; Mottling

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1. Introduction

Waterborne coatings, especially waterborne basecoats, are a core business of BASF Coatings AG. Normally the structure of modern automotive coatings is as shown in Fig. 1.

Many application properties of automotive coatings like sprayability, leveling or sagging are controlled by the rheological properties of the coating formulations. In these technical processes the coating colors are usually subject to complex flow fields (Fig. 2). In a first-order approximation such flow fields can be treated as a superposition of shear (parallel streamlines, velocity gradient perpendicular to the flow direction) and elongational or extensional flows (converging streamlines, velocity gradient lying along the flow direction) (Fig. 3).

Rheological laboratory tests are usually restricted to the simple case of laminar shear flow (parallel streamlines) and the shear viscosity is easily obtained using commercial rotational or capillary viscometers.

For Newtonian fluids the flow behavior is completely determined by the shear viscosity η and the resistance to an (uniaxial) elongational flow is given by the elongational viscosity $\eta_E = 3\eta$. For non-Newtonian (especially viscoelastic) fluids this simple relationship no longer holds and the Trouton ratio η_E/η can vary with deformation rate as well as with time and total deformation and is, in many cases, much larger than 3 [1].

In spray application droplets that have left the nozzle of a spray gun are subjected to a predominantly extensional flow. Consequently, the final droplet size distribution, e.g., of agricultural formulations [2] or of automotive coatings [3] is controlled by the elongational viscosity of the fluid.

A variety of experimental techniques have been developed in the past in order to characterize the extensional flow properties of non-Newtonian fluids [1]. The techniques available for low-viscosity liquids like automotive coatings do not provide a uniform, homogeneous extensional flow field. Therefore, only an apparent extensional viscosity η_E^{app} can de determined. Especially, it is not allowed to compare data from different instruments [4]. Nevertheless, the techniques can be used to determine differences between samples characterized under similar conditions, thus for example providing a classification or ranking of coatings with respect to their elongational flow properties.

At BASF the so-called 'opposing jet' and the 'contraction flow' techniques are available for the characterization of elongational flow properties of low-viscosity fluids. These devices are briefly described in the second part of this paper.

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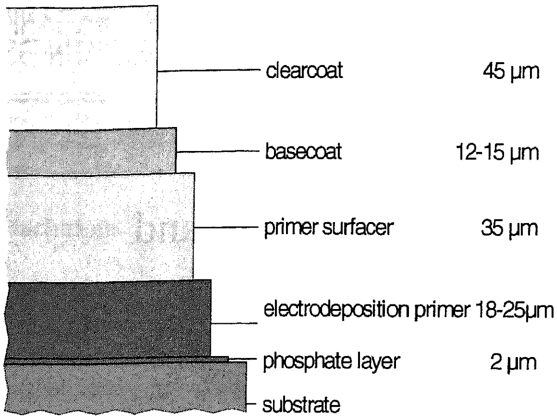

Fig. 1. Cross-section of modern automotive coatings.

In the third and fourth parts experimental elongational viscosity η_E and the shear viscosity η data for automotive coatings are presented.

The effect of various thickeners on η_E and its relation to the sprayability has been studied for a development waterborne basecoat. The relationship between mottling and elongational viscosity flow behavior has been investigated for a series of commercial solvent borne as well as waterborne automotive coatings.

2. Measurements

2.1. Opposing jet rheometer

A home-made opposing jet rheometer (Fig. 4) based on the ideas of Fuller et al. [5] and described in [6] has been used. The fluid is sucked out of a beaker through two opposing nozzles. The flow rate is controlled by the applied vacuum. The resulting flow field is schematically depicted in Fig. 4, too, but note that the true flow field is not known a priori since it depends on the rheological properties of the fluid under consideration.

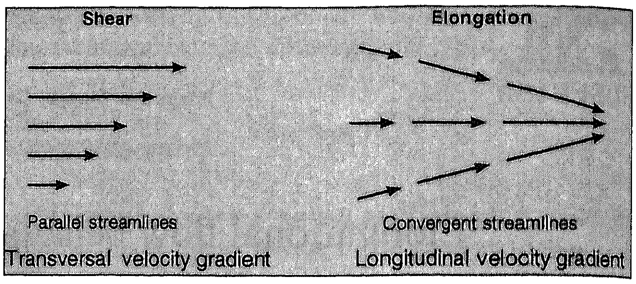

Fig. 3. Shear and elongational/converging flow fields (schematically).

Moreover the flow is neither homogeneous nor purely extensional. Nevertheless, an *apparent* average strain rate $\dot{\varepsilon}$ can be calculated from the total volumetric flow rate Q [5]

$$\dot{\varepsilon} = \frac{Q}{Ad} \tag{1}$$

where A is the area of the nozzle opening and d the distance between the two nozzles.

The *apparent* elongational viscosity η_E is then related to the force F acting on a nozzle by

$$\eta_E = \frac{Fd}{Q} \tag{2}$$

In our experiments a nozzle diameter and a gap width of 1 mm were chosen.

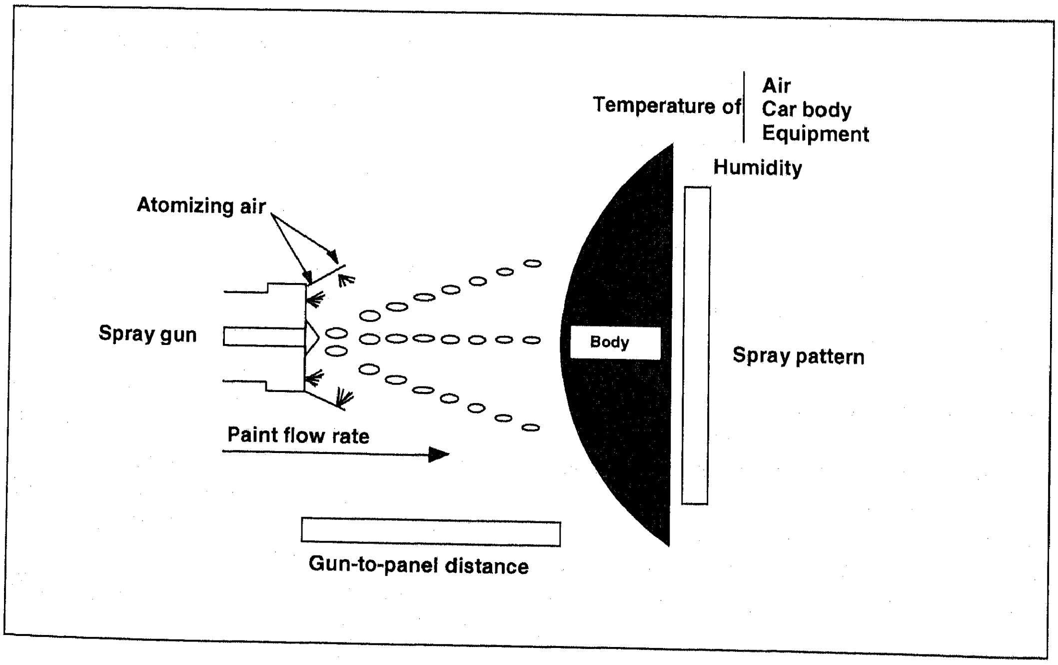

Fig. 2. Application of waterborne basecoats.

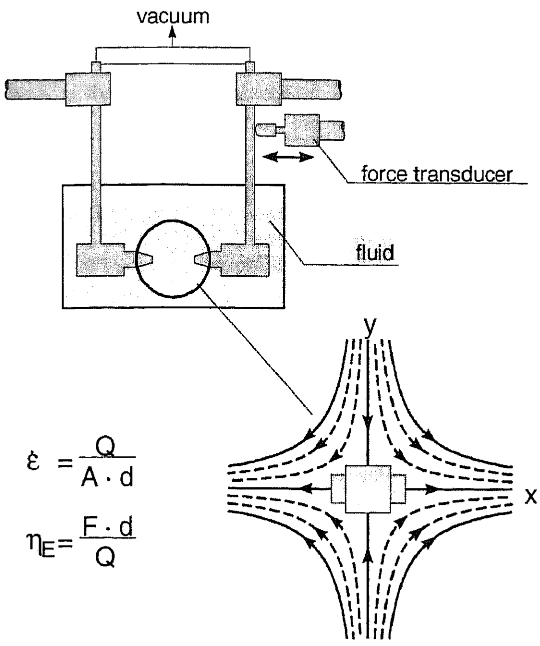

Fig. 4. Schematic drawing of the opposing jet rheometer including a sketch of a typical flow field in the gap between the nozzles.

2.2. *Contraction flow*

The flow at the die entrance in a capillary viscometer is predominantly extensional (Fig. 5) [1]. Again the true flow field is not known a priori but generally it is neither homogeneous nor purely extensional. A crude estimate based on the considerations of Metzner and Metzner [7] yields the following expressions for $\dot{\varepsilon}$ and η_{E} [1]:

$$\dot{\varepsilon} \approx \tfrac{1}{8}\dot{\gamma}_{\mathrm{a}} \tag{3}$$

$$\eta_{\mathrm{E}} = \frac{\Delta p_{\mathrm{e}}}{\dot{\varepsilon}} \tag{4}$$

where $\dot{\gamma}_{\mathrm{a}}$ is the apparent wall shear rate in the die and Δp_{e} the pressure drop at the entrance of the die. This entrance pressure drop is determined from the total pressure drop Δp experimentally according to Bagley's method [1]. For a particular sample, the extrusion pressure (at constant flow rate) has to be measured at least for two capillaries with different *L*/*R* in order to determine the pressure drop Δp $(L/R \to 0) = \Delta p_{\mathrm{e}}$ by appropriate extrapolation.

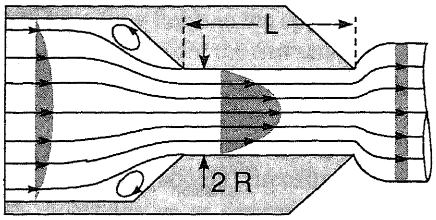

Fig. 5. Schematic flow field at the entrance of a capillary viscometer.

Measurements were performed with three dies of length 2, 8, and 15 mm, each 0.3 mm in radius.

2.3. *Steady and oscillatory shear measurements*

Flow curves were measured with a controlled stress rotational rheometer (Carri-Med CS 100) using cone&plate geometry (40 and 60 mm, 1°), oscillatory shear measurements were performed using a controlled strain rotational rheometer (Rheometrics RFS II) equipped with cone&plate geometry (50 mm, 1°).

3. Samples

Waterborne and solvent borne basecoats are complex mixtures of different components. Fig. 6 shows the differences in solid content, pigmentation, resin amount and solvents between solvent- and waterborne coatings.

This different agents provide certain properties in the basecoat system. Fig. 7 gives an overview over all components and their function in the coating. Without rheological additive a typical waterborne basecoat formulation is a

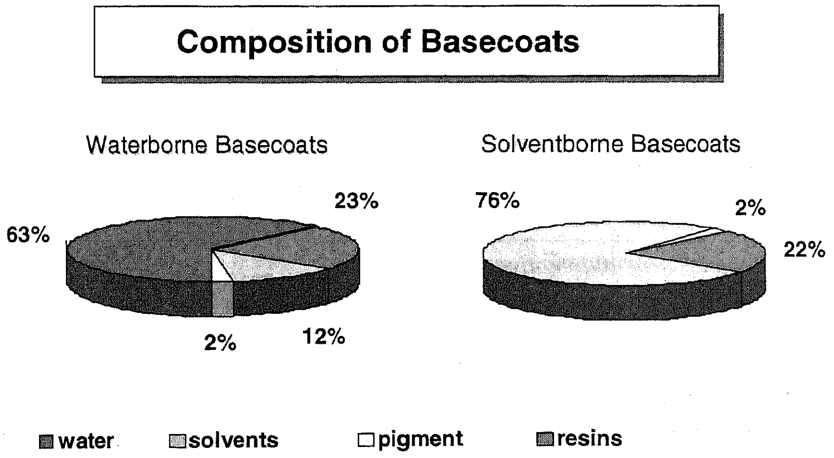

Fig. 6. Composition of basecoats.

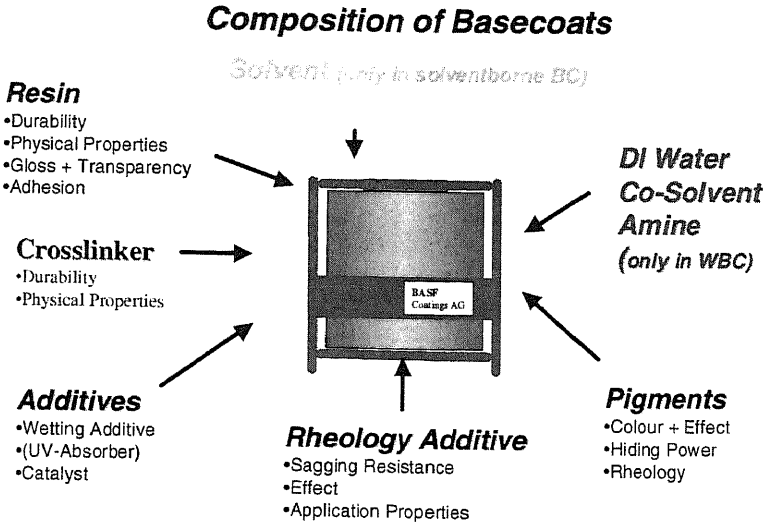

Fig. 7. Composition of basecoats.

low-viscosity Newtonian fluid. The rheology control agents introduce shear thinning and in some cases thixotropic behavior and thus provide the desired leveling and sagging resistance as well as good application properties (pumpability and sprayability) and thus also influence the appearance of the final coating film (gloss, metallic effect, etc.). Therefore, phenomena like atomization and mottling are strongly influenced by the thickeners of these basecoats.

Good mottling behavior means that there are no optical defects (macroscopic light and dark shades) in a metallic coating. A good atomization ranking here means that the droplet size after application on the substrate is very small.

3.1. Development waterborne basecoat — elongational viscosity and atomization

Six formulations of a development waterborne basecoat with different thickeners were investigated. Solids content and amount of thickener were adjusted to yield the same shear viscosity function (flow curves) for all samples (see Fig. 8). Three samples were made up with organic thickeners only (commercial acrylate-based thickener, slightly cross-linked).

The second set of samples was made up with a mixture of an synthetic clay mineral and the commercial acrylate-based thickener (see Section 4, Table 2).

3.2. Development solvent- and waterborne automotive coatings with different mottling properties

Different development waterborne and solvent borne basecoat systems were tested with respect to their mottling behavior and their elongational viscosity. Sample labels, amount and composition of thickener are given in Table 1. The mottling behavior is characterized according to the test

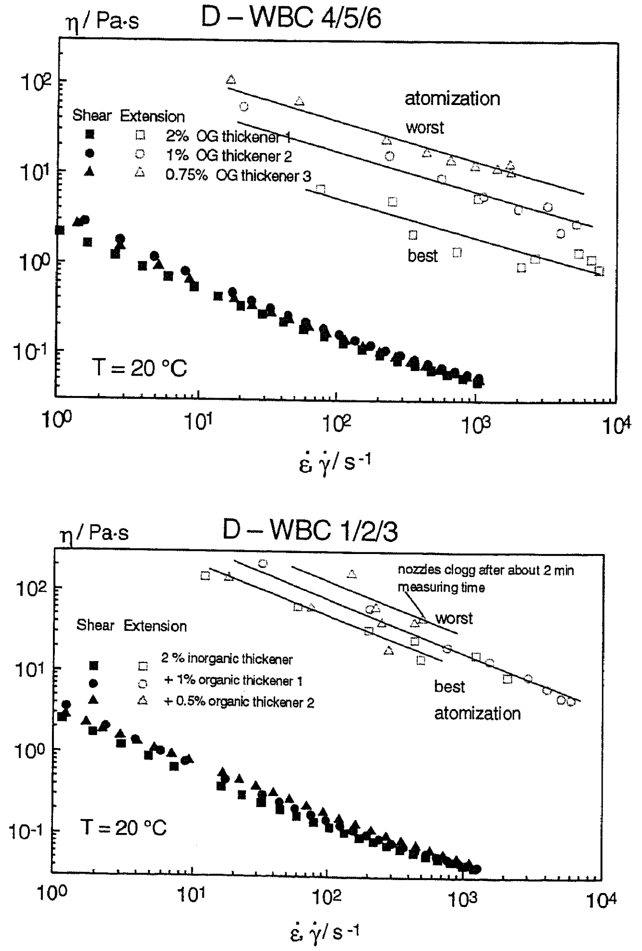

Fig. 8. Shear and elongational viscosity vs. shear/apparent elongation rate for D-WBC formulations with different thickeners, elongational viscosity data as obtained from opposing jet rheometry.

Table 1
Different development waterborne and solvent borne basecoat systems

Sample	System characterization	Mottling results
Waterborne BC		
D-WBC/A	1.0% acrylate thickener, solvents optimized	1
D-WBC/B	1.0% acrylate thickener, standard solvent	2
D-WBC/C	1.0% acrylate thickener, standard solvent	3
D-WBC/D	0.9% acrylate thickener, standard solvent	4
Solvent borne BC		
D-SBC A	MD 1 standard version	3
D-SBC B	MD 1 plus additive	5
D-SBC C	MD 1 different resin system	2

method “mottling behavior of basecoat systems” developed by BASF Coatings.

In a first series variations of the waterborne basecoat system D-WBC-A/D with different thickener amounts and different mixtures of solvents but the same resin system were tested. The different mixtures of solvents lead to significant changes in the mottling behavior.

The second series included solvent borne basecoats because these systems show pronounced mottling.

4. Results and discussion

4.1. *Atomization and elongational viscosity*

The results of the elongational viscosity measurements performed with the opposing jet rheometer are summarized and compared to the corresponding shear viscosity data in Table 2 and Fig. 8. A Trouton ratio of about 300 is found for these coating formulations which is far from the value of 3 which holds for Newtonian fluids. Furthermore, the Trouton ratio is almost independent of the shear/elongation rate. Although the shear viscosities are essentially the same for all samples, significant differences are observed with respect to the elongational viscosity, leading to the conclusion, that the flow behavior of such automotive coating formulations in complex flow fields cannot be deduced from shear viscosity measurements alone. Since the samples containing an inorganic thickener are thixotropic and shear thinning, while the samples with pure organic thickeners are only shear thinning, the true flow fields in the opposing jet device may be substantially different for the two sets of samples. Therefore, it does not make sense to compare data between these two types of formulations. Within each set of samples there is a clear correlation between the sprayability/atomization ranking and the elongational viscosity. Atomization gets worse with increasing η_E as determined from opposing jet rheometry.

Entrance pressure loss data from capillary contraction flow experiments are also given in Table 1. Elongation rates and viscosities are estimated from the measured entrance pressure data and apparent shear rates according to Eqs. (3) and (4). The order of magnitude of the η_E values are similar to those obtained from opposing jet rheometry. However, this comparison should not be taken too seriously. Though predominantly elongational, the flow fields, especially the total deformations that are seen by the fluid elements, are different in the two experimental devices. Nevertheless, these data again support our finding that atomization gets worse with increasing elongational viscosity. But the opposing jet technique is much more sensitive to changes in the elongational flow behavior of such coating formulations than the entrance pressure loss measurements. Within the set of samples made up with organic thickener only the elongational viscosity as revealed by opposing jet rheometry changes by a factor of 6, while the entrance pressure loss changes only by a factor of 2.

Moreover, it should be noted that our opposing jet device provides data in the elongation rate ranges from 10 to $10^4\,s^{-1}$, while the entrance pressure loss measurements yield reliable data for nominal elongation rates greater than $10^5\,s^{-1}$.

The strong sprayability differences observed between the formulations differing only with respect to the organic thickener used are at first surprising, since these products are very similar in their chemical composition. But on the other hand, from polymer melt rheology it is well known [1] that slight differences in longchain-branching or cross-linking change the elongational flow properties drastically. Presumably, this is the key to controlling the elongational flow and hence the sprayability of such HASE-type organic thickeners. Further studies using thickeners with systematically varying cross-linking characteristics are necessary to answer this open question experimentally.

Table 2
Development waterborne basecoat (D-WBC) — shear and elongational viscosity for samples with different amount and composition of thickener[a]

Sample	Shear η (mPa s) $\dot{\gamma}_a = 10^3\,s^{-1}$	Opposing jet η_e (mPa s) $\dot{\varepsilon} = 10^3\,s^{-1}$	Contraction Δp_e (bar) $\dot{\gamma}_a = 3\times10^5\,s^{-1}$	Flow η_e (mPa s) $\dot{\varepsilon} = 4\times10^4\,s^{-1}$	Atomization ranking (1 = best)
D-WBC 1 (2% IO thickener)	43	15500	6.5	17 300	1
D-WBC 2 (2% IO + 1% OG thickener 1)	44	17500	6.2	16 500	2
D-WBC 3 (2% IO + 0.5% OG thickener 2)	50	≈21500	7.3	19 500	3
D-WBC 4 (2% OG thickener 1)	50	2150	6.0	16 000	4
D-WBC 5 (1% OG thickener 2)	54	6600	8.3	22 100	5
D-WBC 6 (0.75% OG thickener 3)	52	12900	13.3	35 500	6

[a] IO: inorganic thickener, OG: organic thickener.

Table 3
Shear and elongational viscosity of various development solvent- and waterborne automotive basecoats

Sample	η (mPa s) at $\dot{\gamma}_a = 1000\,\mathrm{s}^{-1}$	$\eta_E{}^a$ (mPa s) at $\dot{\varepsilon} = 1000\,\mathrm{s}^{-1}$	Trouton ratio	G' (Pa) at $\omega = 1\,\mathrm{s}^{-1}$	G'/G'' at $\omega = 1\,\mathrm{s}^{-1}$	Mottling result
D-WBC/A	40	1500	38	5.3	3.0	1
D-WBC/B	70	8000	114	19.2	2.6	2
D-WBC/C	55	6000	109	14.6	3.8	3
D-WBC/D	40	8950	224			4
D-SBC A	24	580	24			3
D-SBC B	28	470	17			5
D-SBC C	22	640	29			2

[a] From opposing jet rheometry.

4.2. Mottling and elongational viscosity

In Table 3 steady shear and elongational viscosities of the basecoats listed in Table 2 are compared. For some of the formulations the storage and loss moduli G' and G'' have been determined from oscillatory shear experiments. The values for G' and the ratio G'/G'' determined at an angular frequency $\omega = 1\,\mathrm{s}^{-1}$ are also listed in Table 3.

The shear viscosities at $1000\,\mathrm{s}^{-1}$ are around 25 mPa s for the solvent borne systems and vary from 40 to 70 mPa s for the waterborne systems. The Trouton ratios vary from about 20 to more than 300. So again it must be concluded that the flow behavior in elongational or converging/diverging flow fields of such automotive coating formulations cannot be deduced from shear viscosity measurements.

For development waterborne coatings we find a good correlation between elongational viscosity and mottling, the latter getting worse with increasing Trouton ratio. But there seems to be no correlation between mottling and linear viscoelastic properties like G' or the ratio G'/G''.

On the other hand, no correlation between mottling and elongational viscosity is found for the development solvent borne basecoats. These formulations show very low elongational viscosities and although their mottling behavior strongly differs, the measured Trouton ratios are quite similar.

Solvent borne coatings undergo a much stronger change with respect to their rheological behavior due to the loss of solvent during spraying than waterborne formulations. This might be the reason why no correlation between mottling and the flow behavior of the fresh material is found in that case. Therefore, a rheological characterization of the coatings after application is recommended in order to get further insight into that important topic.

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