European Coatings Tech Files

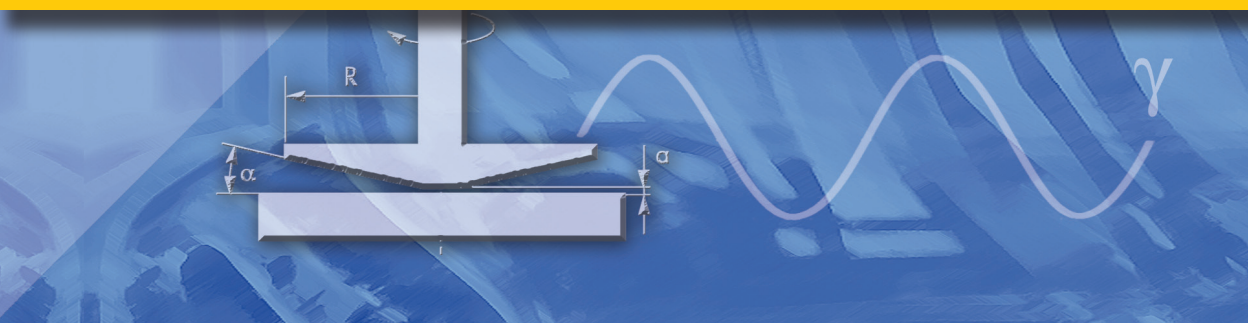
VINCENTZ

Thomas G. Mezger

The Rheology Handbook

3rd Revised Edition

eBook



Vincentz Network GmbH & Co KG

Thomas G. Mezger

The Rheology Handbook

For users of rotational and oscillatory rheometers

3rd revised edition

Thomas G. Mezger: The Rheology Handbook
© Copyright 2011 by Vincentz Network, Hanover, Germany
ISBN 978-3-86630-890-9

Cover: Wacker Chemie, Burghausen, Germany

Bibliographische Information der Deutschen Bibliothek
Die Deutsche Bibliothek verzeichnet diese Publikation in der Deutschen Nationalbibliographie; detaillierte bibliographische Daten sind im Internet über http://dnb.ddb.de abrufbar.

Mezger, Thomas G.
The Rheology Handbook, 3rd revised edition
Hanover: Vincentz Network, 2011
European Coatings Tech Files
ISBN 3-86630-890-6
ISBN 978-3-86630-890-9

© 2011 Vincentz Network GmbH & Co. KG, Hanover
Vincentz Network GmbH & Co. KG, Plathnerstr. 4c, 30175 Hanover, Germany
This work is copyrighted, including the individual contributions and figures.
Any usage outside the strict limits of copyright law without the consent of the publisher is prohibited and punishable by law. This especially pertains to reproduction, translation, microfilming and the storage and processing in electronic systems.
The information on formulations is based on testing performed to the best of our knowledge.

Please ask for our book catalogue
Vincentz Network, Plathnerstr. 4c, 30175 Hanover, Germany
T +49 511 9910-033, F +49 511 9910-029
books@european-coatings.com, www.european-coatings.com

Layout: Vincentz Network, Hanover, Germany
Printed by: Quensen Druck + Verlag GmbH & Co. KG, Hildesheim, Germany

ISBN 3-86630-890-6
ISBN 978-3-86630-890-9

European Coatings Tech Files

Thomas G. Mezger

The Rheology Handbook

For users of rotational and oscillatory rheometers

3rd revised edition

Foreword

Why was this book written?

People working in industry are often confronted with the effects of rheology, the science of deformation and flow behavior. When looking for appropriate literature, they find either short brochures which give only a few details and contain little useful information, or highly specialized books overcharged of physical formulas and mathematical theories. There is a lack of literature between these two extremes which reduces the discussion of theoretical principles to the necessary topics, providing useful instructions for experiments on material characterization. This book is intended to fill that gap.

The practical use of rheology is presented in the following areas: quality control (QC), production and application, chemical and mechanical engineering, industrial research and development, and materials science. Emphasis is placed on current test methods related to daily working practice. After reading this book, the reader should be able to perform useful tests with rotational and oscillatory rheometers, and to interpret the achieved results correctly.

How did this book come into existence?

The first computer-controlled rheometers came into use in industrial laboratories in the mid 1980s. Ever since then, test methods as well as control and analysis options have improved with breathtaking speed. In order to organize and clarify the growing mountain of information, company Anton Paar Germany – and previously Physica Messtechnik – has offered basic seminars on rheology already since 1988, focused on branch-specific industrial application. During the "European Coatings Show" in Nuremberg in April 1999, the organizer and publishing director Dr. Lothar Vincentz suggested expanding these seminar notes into a comprehensive book about applied rheology.

What is the target audience for this book? For which industrial branches will it be most interesting?

"The Rheology Handbook" is written for everyone approaching rheology without any prior knowledge, but is also useful to people wishing to update their expertise with information about recent developments. The reader can use the book as a course book and read from beginning to end or as a reference book for selected chapters. The numerous cross-references make connections clear and the detailed index helps when searching. If required, the book can be used as the first step on the ladder towards theory-orientated rheology books at university level. In order to break up the text, there are as well many figures and tables, illustrative examples and small practical experiments, as well as several exercises for calculations. The following list reflects how the contents of the book are of interest to rheology users in many industrial branches.

- **Polymers:** Solutions, melts, solids; film emulsions, cellulose solutions, latex emulsions, solid films, sheetings, laminates; natural resins, epoxies, casting resins; silicones, caoutchouc, gums, soft and hard rubbers; thermoplastics, elastomers, thermosets, blends, foamed materials; unlinked and cross-linked polymers containing or without fillers or fibers; polymeric compounds and composites; solid bars of glass-fibre, carbon-fibre and synthetic-fibre reinforced polymers (GFRP, CFRP, SFRP); polymerization, cross-linking, curing, vulcanization, melting and hardening processes

Thomas G. Mezger: The Rheology Handbook
© Copyright 2011 by Vincentz Network, Hanover, Germany
ISBN 978-3-86630-890-9

- **Adhesives and sealants:** Glues, single and multi-component adhesives, pressure sensitive adhesives (PSA), UV curing adhesives, hotmelts, plastisol pastes (e.g. for automotive underseals and seam sealings), construction adhesives, putties; uncured and cured adhesives; curing process; tack, stringiness
- **Coatings, paints, lacquers:** Spray, brush, dip coatings; solvent-borne, water-based coatings; metallic effect, textured, low solids, high solids, photo-resists, UV (ultra violet) radiation curing, powder coatings; glazes and stains for wood; coil coatings; solid coating films
- **Printing inks and varnishes:** Gravure, letterpress, flexographic, planographic, offset, screen printing inks, UV (ultra violet) radiation curing inks; ink-jet printer inks; writing inks for pens; millbase premix, color pastes, "thixo-pastes"; liquid and pasty pigment dispersions; printing process; misting; tack
- **Paper coatings:** Primers and topcoats; immobilization process
- **Foodstuffs:** Water, vegetable oils, aroma solvents, fruit juices, baby food, liquid nutrition, liqueurs, syrups, purees, thickeners an stabilizing agents, gels, pudding, jellies, ketchup, mayonnaise, mustard, dairy products (such as yogurt, cream cheese, cheese spread, soft and hard cheese, curds, butter), emulsions, chocolate (melt), soft sweets, ice cream, chewing gum, dough, whisked egg, cappuccino foam, sausage meat, sauces containing meat chunks, jam containing fruit pieces, animal feed; bio-technological fluids; gel formation of hydrocolloids (e.g. of corn starch and gelatin); interfacial rheology (e.g. for emulsions); food tribology (e.g. for creaminess); tack
- **Cosmetics, pharmaceuticals, medicaments, bio-tech products, personal care, health and beauty care products:** Cough mixtures, perfume oils, wetting agents, nose sprays, X-ray film developing baths, blood (hemo-rheology), blood-plasma substitutes, emulsions (e.g. skin care, hair-dye), lotions, nail polish, roll-on fluids (deodorants), saliva, mucus, hydrogels, shampoo, shower gels, dispersions containing viscoelastic surfactants, skin creams, peeling creams, hair gels, styling waxes, shaving creams, tooth-gels, toothpastes, makeup dispersions, lipsticks, mascara, ointments, vaseline, biological cells, tissue engineered medical products (TEMPs), natural and synthetic membranes, silicone pads and cushions, dental molding materials, tooth filling, sponges, contact lenses, medical adhesives (for skin plasters or diapers), denture fixative creams, hair, bone cement, implants, organic-inorganic compounds (hybrids); interfacial rheology (e.g. for emulsions)
- **Agrochemicals:** Plant or crop protection agents, solutions and dispersions of insecticides and pesticides, herbicides and fungicides
- **Detergents, home care products:** Household cleaning agents, liquid soap, disinfectants, surfactant solutions, washing-up liquids, dish washing agents, laundry, fabric conditioners, washing powder concentrate, fat removers; interfacial rheology
- **Surface technology:** Polishing and abrasive suspensions; cooling emulsions
- **Electrical engineering, electronics industry:** Thick film pastes, conductive, resistance, insulating, glass paste, soft solder and screen printing pastes; SMD adhesives (for surface mounted devices), insulating and protective coatings, de-greasing agents, battery fluids and pastes, coatings for electrodes
- **Petrochemicals:** Crude oils, petroleum, solvents, fuels, mineral oils, light and heavy oils, lubricating greases, paraffines, waxes, petrolatum, vaseline, natural and polymer-modified bitumen, asphalt binders, distillation residues, and from coal and wood: tar and pitch; interfacial rheology (e.g. for emulsions)
- **Ceramics and glass:** Casting slips, kaolin and porcelain suspensions, glass powder and enamel pastes, glazes, plastically deformable ceramic pastes, glass melts, aero-gels, xero-gels, sol/gel materials, composites, organo-silanes (hybrids), basalt melts
- **Construction materials:** Self-leveling cast floors, plasters, mortar, cement suspensions, tile adhesives, dispersion paints, sealants, floor sheeting, natural and polymer-modified bitumen, asphalt binders for pavements
- **Metals:** Melts of magnesium, aluminum, steel, alloys; moulding process in a semi-solid state ("thixo-forming", "thixo-casting", "thixo-forging"), ceramic fibre reinforced light-weight metals

- **Waste industry:** Waste water, sewage sludges, animal excrements (e.g. of fishes, poultry, cats, dogs, pigs), residues from refuse incineration plants
- **Geology, soil mechanics, mining industry:** Soil sludges, muds; river and lake sediment masses; soil deformation due to mining operations, earthwork, canal and drain constructions; drilling fluids (e.g. containing "flow improvers")
- **Disaster control:** Behavior of burning materials, soil deformation due to floods and earthquakes
- **Materials for special functions** (e.g. as "smart fluids"): Magneto-rheological fluids (MRF), electro-rheological fluids (ERF), di-electric (DE) materials, self-repairing coatings, materials showing self-organizing superstructures (e.g. surfactants), dilatant fabrics (shock-absorbing, "shot-proof"), liquid crystals (LC), ionic fluids, micro-capsule paraffin wax (e.g. as "phase-change material" PCM)

It is pleasing that the first two editions of "The Rheology Handbook", published in 2002 and 2006, sold out so unexpectedly quickly. It was positive to hear that the book met with approval, not only from laboratory technicians and practically oriented engineers, but also from teachers and professors of schools and colleges of applied sciences. Even at universities, "The Rheology Handbook" is meanwhile taken as an introductory teaching material for explaining the basics of rheology in lectures and practical courses, and as a consequence, many students worldwide are using it when writing their final paper or thesis.

Also for the third edition, further present-day examples have been added resulting as well from contacts to industrial users as well as from corporation with several working groups, e.g. for developing modern standardizing measuring methods for diverse industrial branches. Here in a nutshell, the following additional chapters of this new edition are: Types of flow in the Two-Plates-Model (Chapter 2.4), the effects of rheological additives in aqueous dispersions (Chapter 3.3.7), SAOS and LAOS tests and Lissajous diagrams (Chapter 8.3.6), nano-structures and complex rheological behavior such as shear-banding explained by using surfactant systems as an example (Chapter 9), and special measuring devices for rheo-optical systems and extensional tests (Chapter 10.8). Also the references and standards have been updated (Chapter 14). This textbook is also available in German language, and also here, three editions were published up to now, in 2000, 2006 and in July of 2010 (title: "Das Rheologie Handbuch").

I hope that "The Rheology Handbook" will prove itself a useful source of information for characterizing the above mentioned products in an application-oriented way, assuring their quality and helping to improve them wherever possible.

Acknowledgements
I would like to say a big "Thank You" to all those people without whose competent ideas and suggestions for improvement it would not have been possible to produce such a comprehensive and understandable book. The following people have been of special help to me: Heike Audehm, Monika Bernzen, Stefan Büchner, Marcel de Pender, Gerd Dornhöfer, Andreas Eich, Elke Fischle, Ingrid Funk, Patrick Heyer, Siegfried Huck, Jörg Läuger, Thomas Litters, Sabine Neuber, Matthias Prenzel, Hubert Reitberger, Michael Ringhofer, Oliver Sack, Michael Schäffler, Carmen Schönhaar, Werner Stehr, Heiko Stettin, Jürgen Utz, Detlef van Peij, Simone Will and Klaus Wollny. Sarah Knights translated the original German text into English. Besides the support of my colleagues worldwide, I would also like to mention the managers of Anton Paar GmbH in Graz, Austria, and Anton Paar Germany GmbH in Ostfildern (near Stuttgart).

Stuttgart, December 2010

Thomas G. Mezger

Technology in motion.

Anton Paar

The Modular Compact Rheometer Series offers you one thing first and foremost: An open range of possibilities.

Ask your local Anton Paar representative for a quotation or contact us directly:

Tel: +43 (0)316 257-0
E-mail: info@anton-paar.com

Find more information about the MCR series and its new features at www.anton-paar.com

Contents

1	**Introduction**	**17**
1.1	Rheology, rheometry and viscoelasticity	17
1.2	Deformation and flow behavior	18
2	**Flow behavior and viscosity**	**21**
2.1	Introduction	21
2.2	Definition of terms	21
2.2.1	Shear stress	22
2.2.2	Shear rate	22
2.2.3	Viscosity	26
2.3	Shear load-dependent flow behavior	29
2.3.1	Ideally viscous flow behavior according to Newton	29
2.4	Types of flow illustrated by the Two-Plates Model	31
3	**Rotational tests**	**33**
3.1	Introduction	33
3.2	Basic principles	33
3.2.1	Test modes controlled shear rate (CSR) and controlled shear stress (CSS), raw data and rheological parameters	33
3.3	Flow curves and viscosity functions	34
3.3.1	Description of the test	34
3.3.2	Shear-thinning flow behavior	38
3.3.2.1	Structures of polymers showing shear-thinning behavior	39
3.3.2.2	Structures of dispersions showing shear-thinning behavior	44
3.3.3	Shear-thickening flow behavior	44
3.3.3.1	Structures of polymers showing shear-thickening behavior	48
3.3.3.2	Structures of dispersions showing shear-thickening behavior	49
3.3.4	Yield point	49
3.3.4.1	Yield point determination using the flow curve diagram	50
3.3.4.2	Yield point determination using the shear stress/deformation diagram	51
3.3.4.3	Further information on yield points	53
3.3.5	Overview: Flow curves and viscosity functions	57
3.3.6	Fitting functions for flow and viscosity curves	58
3.3.6.1	Model function for ideally viscous flow behavior	59
3.3.6.2	Model functions for shear-thinning and shear-thickening flow behavior	59
3.3.6.3	Model functions for flow behavior with zero-shear and infinite-shear viscosity	60
3.3.6.4	Model functions for flow curves with a yield point	61
3.3.7	The effects of rheological additives in aqueous dispersions	64
3.4	Time-dependent flow behavior and viscosity function	68
3.4.1	Description of the test	68
3.4.2	Time-dependent flow behavior of samples showing no hardening	69
3.4.2.1	Structural decomposition and regeneration (thixotropy and rheopexy)	70

Thomas G. Mezger: The Rheology Handbook
© Copyright 2011 by Vincentz Network, Hanover, Germany
ISBN 978-3-86630-890-9

3.4.2.2 Test methods for investigating thixotropic behavior ... 72
3.4.3 Time-dependent flow behavior of samples showing hardening ... 79
3.5 Temperature-dependent flow behavior and viscosity function ... 80
3.5.1 Description of the test ... 80
3.5.2 Temperature-dependent flow behavior of samples showing no hardening ... 81
3.5.3 Temperature-dependent flow behavior of samples showing hardening ... 82
3.5.4 Fitting functions for curves of the temperature-dependent viscosity ... 83
3.6 Pressure-dependent flow behavior and viscosity function ... 85

4 Elastic behavior and shear modulus ... 89
4.1 Introduction ... 89
4.2 Definition of terms ... 89
4.2.1 Deformation and strain ... 89
4.2.2 Shear modulus ... 90
4.3 Shear load-dependent deformation behavior ... 93
4.3.1 Ideally elastic deformation behavior according to Hooke ... 93

5 Viscoelastic behavior ... 97
5.1 Introduction ... 97
5.2 Basic principles ... 97
5.2.1 Viscoelastic liquids according to Maxwell ... 97
5.2.1.1 Maxwell model ... 97
5.2.1.2 Examples of the behavior of VE liquids in practice ... 99
5.2.2 Viscoelastic solids according to Kelvin/Voigt ... 102
5.2.2.1 Kelvin/Voigt model ... 102
5.2.2.2 Examples of the behavior of VE solids in practice ... 104
5.3 Normal stresses ... 106

6 Creep tests ... 109
6.1 Introduction ... 109
6.2 Basic principles ... 109
6.2.1 Description of the test ... 109
6.2.2 Ideally elastic behavior ... 110
6.2.3 Ideally viscous behavior ... 111
6.2.4 Viscoelastic behavior ... 111
6.3 Analysis ... 112
6.3.1 Behavior of the molecules ... 112
6.3.2 Burgers model ... 112
6.3.3 Curve discussion ... 113
6.3.4 Definition of terms ... 116
6.3.4.1 Zero-shear viscosity ... 116
6.3.4.2 Creep compliance, and creep recovery compliance ... 117
6.3.4.3 Retardation time ... 118
6.3.4.4 Retardation time spectrum ... 119
6.3.5 Data conversion ... 121
6.3.6 Determination of the molar mass distribution ... 122

7 Relaxation tests ... 123
7.1 Introduction ... 123
7.2 Basic principles ... 123
7.2.1 Description of the test ... 123

7.2.2 Ideally elastic behavior ... 124
7.2.3 Ideally viscous behavior ... 125
7.2.4 Viscoelastic behavior ... 125
7.3 Analysis ... 126
7.3.1 Behavior of the molecules ... 126
7.3.2 Curve discussion ... 127
7.3.3 Definition of terms ... 128
7.3.3.1 Relaxation modulus ... 128
7.3.3.2 Relaxation time ... 129
7.3.3.3 Relaxation time spectrum ... 130
7.3.4 Data conversion ... 132
7.3.5 Determination of the molar mass distribution ... 134

8 Oscillatory tests ... 135
8.1 Introduction ... 135
8.2 Basic principles ... 135
8.2.1 Ideally elastic behavior ... 136
8.2.2 Ideally viscous behavior ... 138
8.2.3 Viscoelastic behavior ... 138
8.2.4 Definition of terms ... 139
8.2.5 The test modes controlled shear strain and controlled shear stress, raw data and rheological parameters ... 144
8.3 Amplitude sweeps ... 146
8.3.1 Description of the test ... 146
8.3.2 Structural character of a sample ... 146
8.3.3 Limiting value of the LVE range ... 148
8.3.3.1 Limiting value of the LVE range in terms of the shear strain ... 148
8.3.3.2 Limiting value of the LVE range in terms of the shear stress ... 151
8.3.4 Determination of the yield point and the flow point by amplitude sweeps ... 151
8.3.4.1 Yield point or yield stress τ_y ... 151
8.3.4.2 Flow point or flow stress τ_f ... 152
8.3.4.3 Yield zone between yield point and flow point ... 152
8.3.4.4 Evaluation of the two terms yield point and flow point ... 153
8.3.4.5 Measuring programs in combination with amplitude sweeps ... 153
8.3.5 Frequency-dependence of amplitude sweeps ... 154
8.3.6 SAOS and LAOS tests, and Lissajous diagrams ... 155
8.4 Frequency sweeps ... 159
8.4.1 Description of the test ... 160
8.4.2 Behavior of unlinked polymers (solutions and melts) ... 161
8.4.2.1 Single Maxwell model for unlinked polymers showing a narrow MMD ... 161
8.4.2.2 Generalized Maxwell model for unlinked polymers showing a wide MMD ... 165
8.4.3 Behavior of cross-linked polymers ... 168
8.4.4 Behavior of dispersions and gels ... 171
8.4.5 Comparison of superstructures using frequency sweeps ... 174
8.4.6 Multiwave test ... 174
8.4.7 Data conversion ... 176
8.5 Time-dependent behavior at constant dynamic-mechanical and isothermal conditions ... 176
8.5.1 Description of the test ... 176
8.5.2 Time-dependent behavior of samples showing no hardening ... 177
8.5.2.1 Structural decomposition and regeneration (thixotropy and rheopexy) ... 178

8.5.2.2 Test methods for investigating thixotropic behavior ... 179
8.5.3 Time-dependent behavior of samples showing hardening ... 185
8.6 Temperature-dependent behavior at constant dynamic mechanical conditions ... 188
8.6.1 Description of the test ... 189
8.6.2 Temperature-dependent behavior of samples showing no hardening ... 190
8.6.2.1 Temperature curves and structures of polymers ... 190
8.6.2.2 Temperature-curves of dispersions and gels ... 197
8.6.3 Temperature-dependent behavior of samples showing hardening ... 200
8.6.4 Thermoanalysis (TA) ... 202
8.7 Time/temperature shift ... 203
8.7.1 Temperature shift factor according to the WLF method ... 204
8.8 The Cox/Merz relation ... 209
8.9 Combined rotational and oscillatory tests ... 210
8.9.1 Presetting rotation and oscillation in series ... 210
8.9.2 Superposition of oscillation and rotation ... 210

9 Complex behavior, surfactant systems ... 213
9.1 Surfactant systems ... 213
9.1.1 Surfactant structures and micelles ... 213
9.1.2 Emulsions ... 222
9.1.3 Mixtures of surfactants and polymers, surfactant-like polymers ... 223
9.1.4 Applications of surfactant systems ... 225
9.2 Rheological behavior of surfactant systems ... 226
9.2.1 Typical shear behavior ... 226
9.2.2 Shear-induced effects, shear-banding and “rheo chaos” ... 229

10 Measuring systems ... 233
10.1 Introduction ... 233
10.2 Concentric cylinder measuring systems (CC MS) ... 233
10.2.1 Cylinder measuring systems in general ... 233
10.2.1.1 Geometry of cylinder measuring systems showing a large gap ... 233
10.2.1.2 Operating methods ... 233
10.2.1.3 Calculations ... 234
10.2.2 Narrow-gap concentric cylinder measuring systems according to ISO 3219 ... 235
10.2.2.1 Geometry of ISO cylinder systems ... 235
10.2.2.2 Calculations ... 237
10.2.2.3 Conversion between raw data and rheological parameters ... 238
10.2.2.4 Flow instabilities and secondary flow effects in cylinder measuring systems ... 238
10.2.2.5 Advantages and disadvantages of cylinder measuring systems ... 240
10.2.3 Double-gap measuring systems (DG MS) ... 241
10.2.4 High-shear cylinder measuring systems (HS MS) ... 241
10.3 Cone-and-plate measuring systems (CP MS) ... 242
10.3.1 Geometry of cone-and-plate systems ... 242
10.3.2 Calculations ... 242
10.3.3 Conversion between raw data and rheological parameters ... 244
10.3.4 Flow instabilities and secondary flow effects in CP systems ... 244
10.3.5 Cone truncation and gap setting ... 244
10.3.6 Maximum particle size ... 245
10.3.7 Filling of the cone-and-plate measuring system ... 246
10.3.8 Advantages and disadvantages of cone-and-plate measuring systems ... 246

10.4 Parallel-plate measuring systems (PP MS) ... 248
10.4.1 Geometry of parallel-plate systems ... 248
10.4.2 Calculations ... 249
10.4.3 Conversion between raw data and rheological parameters ... 250
10.4.4 Flow instabilities and secondary flow effects in a PP system ... 251
10.4.5 Recommendations for gap setting ... 251
10.4.6 Automatic gap setting and automatic gap control using the normal force control option ... 251
10.4.7 Determination of the temperature gradient in the sample ... 252
10.4.8 Advantages and disadvantages of parallel-plate measuring systems ... 252
10.5 Mooney/Ewart measuring systems (ME MS) ... 254
10.6 Relative measuring systems ... 255
10.6.1 Measuring systems with sandblasted, profiled or serrated surfaces ... 255
10.6.2 Spindles in the form of disks, pins, and spheres ... 256
10.6.3 Krebs spindles or paddles ... 259
10.6.4 Paste spindles and rotors showing pins and vanes ... 260
10.6.5 Ball measuring systems, performing rotation on a circular line ... 261
10.6.6 Further relative measuring systems ... 262
10.7 Measuring systems for solid torsion bars ... 262
10.7.1 Bars showing a rectangular cross section ... 263
10.7.2 Bars showing a circular cross section ... 265
10.7.3 Composite materials ... 266
10.8 Special measuring devices ... 267
10.8.1 Special measuring conditions which influence rheology ... 267
10.8.1.1 Magnetic fields for magneto-rheological fluids ... 267
10.8.1.2 Electrical fields for electro-rheological fluids ... 268
10.8.1.3 Immobilization of suspensions by extraction of fluid ... 268
10.8.1.4 UV light for UV-curing materials ... 269
10.8.2 Rheo-optical measuring devices ... 269
10.8.2.1 Terms from optics ... 270
10.8.2.2 Microscopy ... 274
10.8.2.3 Devices for measuring anisotropy in terms of optical rotation and birefringence ... 275
10.8.2.4 SALS for diffracted light quanta ... 275
10.8.2.5 SAXS for diffracted X-rays ... 276
10.8.2.6 SANS for scattered neutrons ... 277
10.8.2.7 Velocity profile of flow fields ... 278
10.8.3 Other special measuring devices ... 278
10.8.3.1 Interfacial rheology on two-dimensional liquid films ... 278
10.8.3.2 Dielectric analysis, and DE conductivity of materials showing electric dipoles ... 278
10.8.3.3 NMR, and resonance of magnetically active atomic nuclei ... 280
10.8.4 Other kinds of testings besides shear tests ... 280
10.8.4.1 Tensile tests, extensional viscosity, and extensional rheology ... 280
10.8.4.2 Tack test, stickiness and tackiness ... 284
10.8.4.3 Tribology ... 287

11 Instruments ... 291
11.1 Introduction ... 291
11.2 Short overview: methods for testing viscosity and elasticity ... 291
11.2.1 Very simple determinations ... 291

11.2.2 Flow on a horizontal plane ... 292
11.2.3 Spreading or slump on a horizontal plane after lifting a container ... 293
11.2.4 Flow on an inclined plane ... 294
11.2.5 Flow on a vertical plane or over a special tool ... 294
11.2.6 Flow in a channel, trough or bowl ... 295
11.2.7 Flow cups and other pressureless capillary viscometers ... 296
11.2.8 Devices showing rising, sinking, falling and rolling elements ... 296
11.2.9 Penetrometers, consistometers and texture analyzers ... 298
11.2.10 Pressurized cylinder and capillary devices ... 300
11.2.11 Simple rotational viscometer tests ... 301
11.2.12 Devices with vibrating or oscillating elements ... 304
11.2.13 Rotational and oscillatory curemeters (for rubber testing) ... 305
11.2.14 Tension testers ... 307
11.2.15 Compression testers ... 308
11.2.16 Linear shear testers ... 308
11.2.17 Bending or flexure testers ... 308
11.2.18 Torsion testers ... 309
11.3 Flow cups ... 310
11.3.1 ISO cup ... 311
11.3.1.1 Capillary length ... 311
11.3.1.2 Calculations ... 312
11.3.1.3 Flow instabilities, secondary flow effects, turbulent flow conditions in flow cups ... 313
11.3.2 Other types of flow cups ... 314
11.4 Capillary viscometers ... 315
11.4.1 Glass capillary viscometers ... 315
11.4.1.1 Calculations ... 317
11.4.1.2 Determination of the molar mass of polymers using diluted polymer solutions ... 319
11.4.1.3 Determination of the viscosity index VI of petrochemicals ... 323
11.4.2 Pressurized capillary viscometers ... 324
11.4.2.1 MFR and MVR testers driven by a weight (“low-pressure capillary viscometers”) ... 324
11.4.2.2 High-pressure capillary viscometers driven by an electric drive, for testing highly viscous and paste-like materials ... 329
11.4.2.3 High-pressure capillary viscometers driven by gas pressure, for testing liquids ... 332
11.5 Falling-ball viscometers ... 334
11.6 Rotational and oscillatory rheometers ... 335
11.6.1 Rheometer set-ups ... 337
11.6.2 Control loops ... 338
11.6.3 Devices to measure torques ... 341
11.6.4 Devices to measure deflection angles and rotational speeds ... 342
11.6.5 Bearings ... 343
11.6.6 Temperature control systems ... 344

12 Guideline for rheological tests ... 349
12.1 Selection of the measuring system ... 349
12.2 Rotational tests ... 349
12.2.1 Flow and viscosity curves ... 349
12.2.2 Time-dependent flow behavior (rotation) ... 350

12.2.3 Step tests (rotation): structural decomposition and regeneration ("thixotropy") ... 350
12.2.4 Temperature-dependent flow behavior (rotation) ... 351
12.3 Oscillatory tests ... 351
12.3.1 Amplitude sweeps ... 351
12.3.2 Frequency sweeps ... 351
12.3.3 Time-dependent viscoelastic behavior (oscillation) ... 352
12.3.4 Step tests (oscillation): structural decomposition and regeneration ("thixotropy") ... 352
12.3.5 Temperature-dependent viscoelastic behavior (oscillation) ... 353
12.4 Selection of the test type ... 354
12.4.1 Behavior at rest ... 354
12.4.2 Flow behavior ... 355
12.4.3 Structural decomposition and regeneration ("thixotropic behavior", e.g. of coatings) ... 355

13 Rheologists and the historical development of rheology ... 357
13.1 Development until the 19th century ... 357
13.2 Development between 1800 and 1900 ... 360
13.3 Development between 1900 and 1949 ... 367
13.4 Development between 1950 and 1979 ... 376
13.5 Development since 1980 ... 379

14 Appendix ... 383
14.1 Symbols, signs and abbreviations used ... 383
14.2 The Greek alphabet ... 391
14.3 Conversion table for units ... 391

15 References ... 395
15.1 Publications and books ... 395
15.2 ISO standards ... 407
15.3 ASTM standards ... 409
15.4 DIN, DIN EN, DIN EN ISO and EN standards ... 414
15.5 Important standards for users of rotational rheometers ... 417

Author ... 418

Index ... 419

1 Introduction

1.1 Rheology, rheometry and viscoelasticity

a) Rheology

Rheology is the science of deformation and flow. It is a branch of physics and physical chemistry since the most important variables come from the field of mechanics: forces, deflections and velocities. The term "rheology" originates from the Greek: "rhein" meaning "to flow". Thus, rheology is literally "flow science". However, rheological experiments do not merely reveal information about **flow behavior of liquids** but also about **deformation behavior of solids**. The connection here is that a large deformation produced by shear forces causes many materials to flow.

All kinds of shear behavior, which can be described rheologically in a scientific way, can be viewed as being in between two extremes: flow of ideally viscous liquids on the one hand and deformation of ideally elastic solids on the other. Two illustrative examples for the extremes of ideal behavior are low-viscosity mineral oils and rigid steel balls. Flow **behavior of ideally viscous fluids** is explained in Chapter 2. **Ideally elastic deformation** behavior is described in Chapter 4.

Behavior of all real materials is based on the combination of both a viscous and an elastic portion and therefore, it is called viscoelastic. Wallpaper paste is a viscoelastic liquid, for example, and a gum eraser is a viscoelastic solid. Information on **viscoelastic behavior** can be found in Chapter 5. **Complex and extraordinary rheological behavior** is presented in Chapter 9 using the example of surfactant systems.

Table 1.1 shows the most important terms, all of which will be covered in this book. This chart can also be found at the beginning of Chapters 2 to 8, with those terms given in bold print being discussed in the chapter in hand.

Table 1.1: Overview on different kinds of rheological behavior

Liquids		**Solids**	
(ideal-) viscous flow behavior Newton's law	viscoelastic flow behavior Maxwell's law	viscoelastic deformation behavior Kelvin/Voigt's law	(ideal-) elastic deformation behavior Hooke's law
flow/viscosity curves	creep tests, relaxation tests, oscillatory tests		

Rheology was first seen as a science in its own right not before the beginning of the 20th century. However, scientists and practical users have long before been interested in the behavior of liquids and solids, although some of their methods have not always been very scientific. A list of important facts of the historical development in rheology is given in Chapter 13. Of special interest are here the various attempts to classify all kinds of different rheological behavior, such as the classification of Markus Reiner in 1931 and 1960, and of George W. Scott Blair in 1942. The aim of the rheologists' is to measure deformation and flow behavior of a great variety of matters, to present the obtained results clearly and to explain it.

Thomas G. Mezger: The Rheology Handbook
© Copyright 2011 by Vincentz Network, Hanover, Germany
ISBN 978-3-86630-890-9

b) Rheometry

Rheometry is the measuring technology used to determine rheological data. The emphasis here is on **measuring systems, instruments,** and **test** and **analysis methods**. Both, liquids and solids can be investigated using rotational and oscillatory rheometers. **Rotational tests** which are performed to characterize viscous behavior are presented in Chapter 3. In order to evaluate viscoelastic behavior, **creep tests** (Chapter 6), **relaxation tests** (Chapter 7) and **oscillatory tests** (Chapter 8) are performed. Chapter 10 contains information on **measuring systems** and **special measuring devices**, and Chapter 11 gives an overview on diverse **instruments** used.

Analog programmers and on-line recorders for plotting flow curves have been on the market since around 1970. Around 1980, digitally controlled instruments appeared which made it possible to store measuring data and to use a variety of analysis methods, including also complex ones. Developments in measuring technology are constantly pushing back the limits. At the same time, thanks to standardized measuring systems and procedures, measuring results can be compared world-wide today. Meanwhile, several rheometer manufacturers can offer test conditions to customers in many industrial branches which come very close to simulate even complex process conditions in practice.

A short **guideline for rheological measurements** is presented in Chapter 12 in order to facilitate the daily laboratory work for practical users.

Chapter 14 (Appendix) shows all the used **signs, symbols and abbreviations** with their units. The **Greek alphabet** and a **conversion table for units** (SI and cgs system) can also be found there.

References are listed in Chapter 15. The publications and books can be identified by the number in brackets (e.g. as [123]). Here, also more than 400 **standards** are listed (**ISO, ASTM, EN and DIN**).

c) Information for "Mr. and Ms. Cleverly"
Throughout this textbook, the reader will find sections for "Mr. and Ms. Cleverly" which are marked with a symbol showing glasses: 👓

These sections are written for those readers who wish to go deeper into the theoretical side and who are not afraid of a little extra mathematics and fundamentals in physics. However, these "Cleverly" explanations are not required to understand the information given in the normal text of later chapters, since this textbook is also written for beginners in the field of rheology. Therefore, for those readers who are above all interested in the practical side of rheology, the "Cleverly" sections can simply be ignored.

1.2 Deformation and flow behavior

We are confronted with rheological phenomena every single day. Some experiments are listed below to demonstrate this point. The examples given will be discussed in detail in the chapters mentioned in brackets.

Experiment 1.1: Behavior of mineral oil, plasticine, and steel
Completely different types of behavior can be seen when the following three subjects hit the floor (see Figure 1.1):
a) The **mineral oil** is flowing and spreading until it shows a very thin layer finally (**ideally viscous flow behavior**: see Chapter 2.3.1)

b) The **plasticine** will be deformed when it hits the floor, and afterwards, it remains deformed permanently (inhomogeneous **plastic behavior** outside the linear viscoelastic deformation range: see Chapter 3.3.4.3d)
c) The **steel ball** bounces back, and exhibits afterwards no deformation at all (**ideally elastic behavior**: see Chapter 4.3.1)

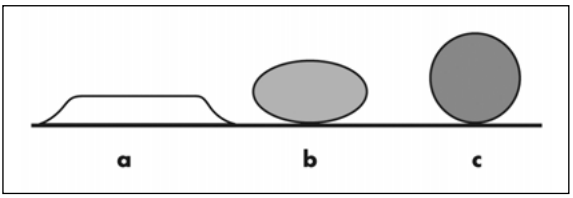


Figure 1.1: Deformation behavior after hitting the floor: a) mineral oil, b) plasticine, c) steel ball

Experiment 1.2: Playing with "bouncing putty" (some call it "Silly Putty")
The **silicone polymer** (unlinked PDMS) displays different **rheological behaviors depending on the period of time under stress** (viscoelastic behavior of polymers: see Chapter 8.4, frequency sweep):
a) **When stressed briefly and quickly**, the putty behaves like a rigid and elastic **solid**: If you mold a piece of it to the shape of a ball and throw it on the floor, it is bouncing back.
b) **When stressed slowly at a constantly low force** over a longer period of time, the putty shows the behavior of a flexible and yielding, highly viscous **liquid**: If it is in the state of rest, thus, if you leave it untouched for a certain period of time, it is spreading very slowly under its own weight due to gravity to show an even layer with a homogeneous thickness finally.

Experiment 1.3: Do the rods remain in the position standing up straight?
Three wooden rods are put into three glasses containing different materials and left for gravity to do its work.
a) In the glass of **water**, the rod changes its position immediately and falls to the side of the glass (**ideally viscous flow behavior**: see Chapter 2.3.1).
Additional observation: All the air bubbles which were brought into the water when immersing the rod are rising quickly within seconds.
b) In the glass containing a **silicone polymer** (unlinked PDMS), the rod moves very, very slowly, reaching the side of the glass after around 10 minutes (polymers showing **zero-shear viscosity**: see Chapters 3.3.2.1a, 6.3.4.1 and 8.4.2.1a).
Additional observation concerning the air bubbles which were brought into the polymer sample by the rod: Large bubbles are rising within a few minutes, but the smaller ones seem to remain suspended without visible motion. However, after several hours even the smallest bubble has reached the surface. Therefore, indeed long-term but complete de-aeration of the silicone occurs finally.
c) In the glass containing a **hand cream**, the rod still remains standing straight in the initial position even after some hours (**yield point**: see Chapters 3.3.4 and 8.3.4.1; and **structure strength at rest of dispersions**: see Chapter 8.4.4a).
Additional observation concerning the air bubbles: All bubbles, independent of their size, remain suspended, and therefore here, no de-aeration takes place at all.

Summary
Rheological behavior depends on many influences. Above all, the following test conditions are important:
- Type of loading (preset of deformation, velocity or force; or shear strain, shear rate or shear stress, respectively)
- Degree of loading (low-shear or high-shear conditions)
- Duration of loading (the periods of time under load and at rest)
- Temperature (see Chapters 3.5 and 8.6)

Further important parameters are, for example:

- Concentration (of solid particles in a suspension: see Chapter 3.3.3; of polymer molecules in a solution: see Chapter 3.3.2.1a; of surfactants in a dispersion: see Chapter 9). Using an "Immobilization Cell," the amount of liquid can be reduced under controlled conditions (e.g. when testing dispersions such as paper coatings: see Chapter 10.8.1.3).
- Ambient pressure (see Chapter 3.6)
- pH value (e.g. of surfactant systems: see Chapter 9).
- Strength of a magnetic or an electric field when investigating magneto-rheological fluids MRF or electro-rheological fluids ERF, respectively (see Chapters 10.8.1.1 and 2).
- UV radiation curing (e.g. of resins, adhesives and inks: see Chapter 10.8.1.4).

2 Flow behavior and viscosity

In this chapter are explained the following terms given in bold:

Liquids		Solids	
(ideal-) viscous flow behavior Newton's law	viscoelastic flow behavior Maxwell's law	viscoelastic deformation behavior Kelvin/Voigt's law	(ideal-) elastic deformation behavior Hooke's law
flow/viscosity curves	creep tests, relaxation tests, oscillatory tests		

2.1 Introduction

Before 1980 in industrial practice, rheological experiments on pure liquids and dispersions were carried out almost exclusively in the form of rotational tests which enabled the characterization of flow behavior at medium and high flow velocities. Meanwhile since measurement technology has developed, many users have expanded their investigations on deformation and flow behavior performing measurements which cover also the low-shear range.

2.2 Definition of terms

The **Two-Plates-Model** is used to define fundamental rheological parameters (see Figure 2.1). The upper plate with the (shear) area A is set in motion by the (shear) force F and the resulting velocity v is measured. The lower plate is stationary (v = 0). Between the plates there is the distance h, and the sample is sheared in this shear gap. It is assumed that the following **shear conditions** are occurring:

1) The sample shows **adhesion** to both plates **without any wall-slip effects**.
2) There are **laminar flow conditions**, i.e. flow can be imagined in the form of layers. Therefore, there is **no turbulent flow**, i.e. no vortices are appearing.

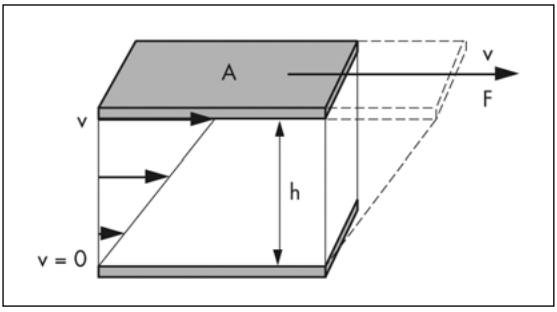


Figure 2.1: The Two-Plates-Model for shear tests to illustrate the velocity distribution of a flowing fluid in the shear gap

Accurate calculation of the rheological parameters is only possible if both conditions are met.

Experiment 2.1: The stack of beer mats

Each one of the individual beer mats represents an individual flowing layer. The beer mats are showing a laminar

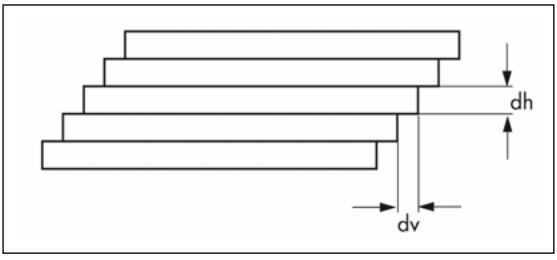


Figure 2.2: Laminar flow in the form of planar fluid layers

Thomas G. Mezger: The Rheology Handbook
© Copyright 2011 by Vincentz Network, Hanover, Germany
ISBN 978-3-86630-890-9

shape, and therefore, they are able to move in the form of layers along one another (see Figure 2.2). Of course, this process takes place without vortices, thus without showing any turbulent behavior.

The real geometric conditions in rheometer measuring systems are not as simple as in the Two-Plates-Model. However, if a shear gap is narrow enough, the necessary requirements are largely met and the definitions of the following rheological parameters can be used.

2.2.1 Shear stress

Definition of the shear stress:

Equation 2.1: $\tau = F/A$

τ (pronounced: "tou"); with the shear force F [N] and the shear area A [m^2], see Figure 2.1. The following holds: $1N = 1kg \cdot m/s^2$

The unit of the shear stress is [Pa], ("pascal").
Blaise Pascal (1623 to 1662 [278]) was a mathematician, physicist, and philosopher.
For conversions: $1Pa = 1N/m^2 = 1kg/m \cdot s^2$
A previously used unit was [dyne/cm^2]; with: $1dyne/cm^2 = 0.1Pa$

Note: [Pa] is also the unit of pressure
100Pa = 1hPa (= 1mbar); or 100,000Pa = 10^5Pa = 0.1MPa (= 1bar)
Example: In a weather forecast, the air pressure is given as 1070hPa (hectopascal; = 107kPa).

Some authors take the symbol σ for the shear stress (pronounced: "sigma") [18, 215]. However, this symbol is usually used for the tensile stress (see Chapters 4.2.2 and 10.8.4.1). To avoid confusion and in agreement with the majority of current specialized literature and standards, here, the symbol τ will be used to represent the shear stress (see e.g. ASTM D4092 and DIN 1342-1).

2.2.2 Shear rate

Definition of the shear rate:

Equation 2.2: $\dot{\gamma} = v/h$

$\dot{\gamma}$ (pronounced: "gamma-dot"); with the velocity v [m/s] and the distance h [m] between the plates, see Figure 2.1.
The unit of the shear rate is [1/s] or [s^{-1}], called "reciprocal seconds".

Sometimes, the following terms are used as synonyms: **shear gradient, velocity gradient, strain rate,** and **rate of deformation**.

Previously, the symbol D was often taken instead of $\dot{\gamma}$. Nowadays, almost all current standards are recommending the use of $\dot{\gamma}$ (see e.g. ASTM D4092). Table 2.1 presents typical shear rate values occurring in industrial practice.

For "Mr. and Ms. Cleverly"

a) Definition of the shear rate using differential variables

Equation 2.3: $\dot{\gamma} = dv/dh$

with the "infinitely" (differentially) small velocity difference dv between two neighboring flowing layers, and the "infinitely" (differentially) small thickness dh of a single flowing layer (see Figure 2.2).

Table 2.1: Typical shear rates of technical processes

Process	Shear rates $\dot{\gamma}$ (s^{-1})	Practical examples
Physical aging, long-term creep within days and up to several years	10^{-8} ... 10^{-5}	Polymers, asphalt
Cold flow	10^{-8} ... 0.01	Rubber mixtures, elastomers
Sedimentation of particles	≤ 0.001 0.01	Emulsion paints, ceramic suspensions, fruit juices
Surface leveling of coatings	0.01 ... 0.1	Coatings, paints, printing inks
Sagging of coatings, dripping, flow under gravity	0.01 ... 1	Emulsion paints, plasters, chocolate coatings (couvertures)
Self-leveling at low-shear conditions in the range of the zero-shear viscosity	≤ 0.1	Silicone polymers (PDMS)
Dip coating	1 ... 100	Dip coatings, candy masses
Applicator roller, at the coating head	1 ... 100	Paper coatings
Thermoforming	1 ... 100	Polymers
Mixing, kneading	1 ... 100	Rubber mixtures, elastomers
Chewing, swallowing	10 ... 100	Jelly babies, yogurt, cheese
Spreading	10 ... 1,000	Butter, toothpastes
Extrusion	10 ... 1,000	Polymer melts, dough, ceramic pastes, tooth paste
Pipe flow, capillary flow	10 ... 10^4	Crude oils, paints, juices, blood
Mixing, stirring	10 ... 10^4	Emulsions, plastisols, polymer blends
Injection moulding	100 ... 10^4	Polymer melts, ceramic suspensions
Coating, painting, brushing, rolling, blade coating (manually)	100 ... 10^4	Brush coatings, emulsion paints, wall paper paste, plasters
Spraying	1,000 ... 10^4	Spray coatings, fuels, nose spray aerosols, adhesives
Impact	1,000 ... 10^5	Solid polymers
Milling pigments in fluid bases	1,000 ... 10^5	Pigment pastes for paints and printing inks
Rubbing	1,000 ... 10^5	Skin creams, lotions, ointments
Spinning process	1,000 ... 10^5	Polymer melts, polymer fibers
Blade coating (by machine), high-speed coating	1,000 ... 10^7	Paper coatings, adhesive dispersions
Lubrication of engine parts	1,000 ... 10^7	Mineral oils, lubricating greases

There is a **linear velocity distribution** between the plates, since the velocity v decreases linearly in the shear gap. Thus, for laminar and ideally viscous flow, the velocity difference between all neighboring layers are showing the same value: dv = const. All the layers are assumed to have the same thickness: dh = const. Therefore, the shear rate is showing a constant value everywhere between the plates of the Two-Plates-Model since

$\dot{\gamma}$ = dv/dh = const/const = const (see Figure 2.3).

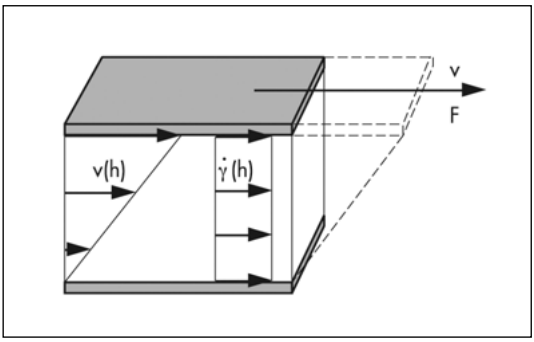


Figure 2.3: Velocity distribution and shear rate in the shear gap of the Two-Plates-Model

Both $\dot{\gamma}$ and v provide information about the velocity of a flowing fluid. The advantage of selecting the shear rate is that it shows a constant value throughout the whole shear gap. Therefore, the shear rate is independent of the position of any flowing layer in the shear gap. Of course, this applies only if the shear conditions are met as mentioned in the beginning of Chapter 2.2. However, this does not apply to the velocity v which decreases from the maximum value v_{max} on the upper, movable plate to the minimum value $v_{min} = 0$ on the lower, immovable plate. Therefore when testing pure liquids, sometimes as a synonym for shear rate the term **velocity gradient** is used (e.g. in ASTM D4092).

b) Calculation of shear rates occurring in technical processes
The shear rate values which are given below are calculated using the mentioned formulas and should only be seen as rough estimations. The main aim of these calculations is to get merely an idea of the dimension of the relevant shear rate range.

1) Coating processes: painting, brushing, rolling or blade-coating
$\dot{\gamma} = v/h$, with the coating velocity v [m/s] and the wet layer thickness h [m]

Examples:
1a) **Painting with a brush:**
With v = 0.1m/s and h = 100μm = 0.1mm = 10^{-4}m; result: $\dot{\gamma} = 1000s^{-1}$

1b) **Buttering bread:**
With v = 0.1m/s and h = 1mm = 10^{-3}m; result: $\dot{\gamma} = 100s^{-1}$

1c) **Applying emulsion paint with a roller**
With v = 0.2m/s (or 5s per m), and h = 100μm = 0.1mm = 10^{-4}m; result: $\dot{\gamma} = 2000s^{-1}$

1d) **Blade-coating of adhesive emulsions** (e.g. for pressure-sensitive adhesives PSA):
with the application rate AR (i.e. mass per coating area) m/A [g/m²]; for the coating volume V [m³] applies, with the mass m [kg] and the density ρ [1g/cm³ = 1000kg/m³]: V = m/ρ
Calulation: h = V/A = (m/ρ)/A = (m/A)/ρ = AR/ρ; with AR = 1g/m² = 10^{-3}kg/m² holds: h =10^{-6}m = 1μm; and then: $\dot{\gamma} = v/h$. See Table 2.2 for shear rates occurring in various kinds of blade-coating processes [14, 76].

Table 2.2: Shear rates of various kinds of blade-coating processes for adhesive emulsions

Coating process	Application rate AR [g/m²]	Coating velocity v [m/min]	Coating velocity v [m/s]	Layer thickness h [μm]	Approx. shear rate range $\dot{\gamma}$ [s⁻¹]
Metering blade	2 to 50	up to 250	up to 4.2	2 to 50	80,000 to 2 mio.
Roller blade	15 to 100	up to 100	up to 1.7	15 to 100	10,000 to 100,000
Lip-type blade	20 to 100	20 to 50	0.33 to 0.83	20 to 100	3,000 to 50,000
Present maximum	2 to 100	700	12	2 to 100	120,000 to 6 mio.
Future plans		up to 1,500	up to 25		250,000 to 12.5 mio.

2) Flow in pipelines, tubes and capillaries
Assumptions: horizontal pipe, steady-state and laminar flow conditions (for information on laminar and turbulent flow see Chapter 3.3.3), ideally viscous flow, incompressible liquid. According to the **Hagen/Poiseuille relation**, the following holds for the maximum shear stress τ_w and the maximum shear rate $\dot{\gamma}_w$ in a pipeline (index "w" for "at the wall"):

Equation 2.4 $\tau_w = (R \cdot \Delta p)/(2 \cdot L)$

Equation 2.5 $\dot{\gamma}_w = (4 \cdot \dot{V})/(\pi \cdot R^3)$

with the pipe radius R [m]; the pressure difference Δp [Pa] between inlet and outlet of the pipe or along the length L [m] of the measuring section, respectively (Δp must be compensated by the pump pressure); and the volume flow rate $\dot{V}$ [m^3/s]. This relation was named in honor to *Gotthilf Heinrich Ludwig Hagen* (1797 to 1848) [172] and *Jean Louis Marie Poiseuille* (1799 to 1869) [291].

Examples:
2a) **Pipeline transport of automotive coatings** [105], [350]
For a closed circular pipeline with the diameter DN 26 (approx. R = 13mm = $1.3 \cdot 10^{-2}$m), and the volume flow rate $\dot{V}$ = 1.5 to 12L/min = $2.51 \cdot 10^{-5}$ to $2.00 \cdot 10^{-4}m^3/s$; results: $\dot{\gamma}_w$ = 14.6 to $116s^{-1}$ = approx. 15 to $120s^{-1}$. For a pipeline branch with DN 8 (approx. R = 4mm = $4 \cdot 10^{-3}$m), and $\dot{V}$ = 0.03 to 1L/min = $5.06 \cdot 10^{-7}$ to $1.67 \cdot 10^{-5}m^3/s$; results: $\dot{\gamma}_w$ = 10.1 to $332s^{-1}$ = approx. 10 to $350s^{-1}$

2b) **Drinking water supply, transport in pipelines** [61]
For a pipeline with the diameter DN 1300 (approx. R = 650mm = 0.65m), and a volume flow rate of max. $\dot{V}$ = 3300L/s = $3.30m^3/s$; and for a second pipeline with DN 1600 (approx. R = 800mm = 0.80m) with max. $\dot{V}$ = 4700L/s = $4.70m^3/s$; results: max. $\dot{\gamma}_w$ = 15.3 and $11.7s^{-1}$, respectively.

2c) **Filling bottles using a filling machine** (e.g. drinks in food industry):
Filling volume per bottle: V = 1L = $0.001m^3$; filling time per bottle: t = 5s, then:
$\dot{V} = V/t = 2 \cdot 10^{-4}m^3/s$; diameter of the circular geometry of the injection nozzle: d = 2R = 10mm; result: $\dot{\gamma}_w = 2037s^{-1}$ = approx. $2000s^{-1}$

2d) **Squeezing an ointment out of a tube** (e.g. pharmaceuticals):
Pressed out volume: V = $1cm^3 = 10^{-6}m^3$; time to squeeze out: t = 1s; then: $\dot{V} = V/t = 10^{-6}m^3/s$; diameter of the tube nozzle: d = 2R = 6mm; result: $\dot{\gamma}_w = 47.2s^{-1}$ = approx. $50s^{-1}$

2e) **Filling ointment into tubes using a filling machine** (e.g. medicine):
Filling volume per tube: V = $100ml = 10^{-4}m^3$; filling time per tube (at 80 work-cycles per minute, where 50% is filling time): t = (60s/2)/80 = 0.375s; then: $\dot{V} = V/t = 2.67 \cdot 10^{-4}m^3/s$, using an injection nozzle with an annular geometry and a cross sectional area of $A = 24 \cdot 10^{-6}m^2$, which for a rough estimation, corresponds to a circular area showing $R = 2.76 \cdot 10^{-3}$m (since $A = \pi \cdot R^2$); result: $\dot{\gamma}_w = 16{,}200s^{-1}$

3) Sedimentation of particles in suspensions
Assumptions: fluid in a state-at-rest; the particles are almost suspended and therefore they are sinking very, very slowly in a steady-state process (laminar flow, at a Reynolds number $Re \leq 1$; more about Re numbers: see Chapter 10.2.2.4b); spherical particles; the values of the weight force F_G [N] and the flow resistance force F_R [N] of a particle are approximately equal in size.

According to **Stokes' law** (*Georges Gabriel Stokes*, 1819 to 1903 [348]):

Equation 2.6: $F_G = \Delta m \cdot g = F_R = 3 \cdot \pi \cdot d_p \cdot \eta \cdot v$

with the mass difference Δm [kg] between a particle and the surrounding fluid, the gravitation constant $g = 9.81m/s^2$, the mean particle diameter d_p [m], the shear viscosity of the dispersion fluid η [Pas], and the particles' settling velocity v [m/s].

The following applies: $\Delta m = V_p \cdot \Delta\rho$, with the volume V_p [m^3] of a particle, and the density difference $\Delta\rho$ [kg/m^3] = (ρ_p - ρ_{fl}) between the particles and the dispersion fluid; particle density ρ_p [kg/m^3] and fluid density ρ_{fl} [kg/m^3].

The following applies for spheres: $V_p = (\pi \cdot d_p^3)/6$; and therefore, for the settling velocity

Equation 2.7:
$$v = \frac{\Delta m \cdot g}{3 \cdot \pi \cdot d_p \cdot \eta} = \frac{V_p \cdot \Delta\rho \cdot g}{3 \cdot \pi \cdot d_p \cdot \eta} = \frac{\pi \cdot d_p^3 \cdot \Delta\rho \cdot g}{6 \cdot 3 \cdot \pi \cdot d_p \cdot \eta} = \frac{d_p^2 \cdot g}{18 \cdot \eta} \cdot (\rho_p - \rho_{fl})$$

Assumption for the shear rate: $\dot{\gamma} = v/h$
with the thickness h of the boundary layer on a particle surface, which is sheared when in motion against the surrounding liquid (the shear rate occurs on both sides of the particle). This equation is valid only if there are neither interactions between the particles, nor between the particles and the surrounding dispersion fluid.
Assuming simply, that $h = 0.1 \cdot d$, then: $\dot{\gamma} = (10 \cdot v)/d$

Examples: Sedimentation of sand particles in water
3a) With $d_p = 10\mu m = 10^{-5}m$, $\eta = 1mPas = 10^{-3}Pas$, and $\rho_p = 1.5g/cm^3 = 1500kg/m^3$ (e.g. quartz silica sand), and $\rho_{fl} = 1g/cm^3 = 1000kg/m^3$ (pure water); results: v = approx. $2.7 \cdot 10^{-5}m/s$
Such a particle is sinking a maximum path of approx. 10cm in 1h (or approx. 2.3m per day).
With $h = 1\mu m$ results: $\dot{\gamma} = v/h$ = approx. $27s^{-1}$
3b) With $d_p = 1\mu m = 10^{-6}m$, and $\eta = 100mPas$ (e.g. water containing a thickener, measured at $\dot{\gamma} = 0.01s^{-1}$), and with the same values for ρ_p and ρ_{fl} as above in Example (3a), results: v = approx. $2.7 \cdot 10^{-9}m/s$ (or v = 0.23mm per day). With $h = 0.1\mu m$ results: $\dot{\gamma} = 0.03s^{-1}$ approximately.

Note 1: Calculation of a too high settling velocity if interactions are ignored
Stokes' sedimentation formula only considers a single particle sinking, undisturbed on a straight path. Therefore, relatively high shear rate values are calculated. These values do not mirror the real behavior of most dispersions, since usually interactions are occurring. The layer thickness h is hardly determinable. We know from colloid science: It depends on the strength of the ionic charge on the particle surface, and on the ionic concentration of the dispersion fluid (interaction potential). Due to ionic adsorption, a diffuse double layer of ions can be found on the particle surface. For this reason, in reality the result is usually a considerably lower settling velocity. Therefore, and since the shear rate within the sheared layer is not constant: **It is difficult to estimate the corresponding shear rate values occurring with sedimentation processes.**

Note 2: Particle size of colloid dispersions
Colloid particles are showing diameters in the range of 10^{-9} to $10^{-7}m$ (or 1 to 100nm) [397], or from 10^{-9} to $10^{-6}m$ (or 1nm to 1μm) [128]. Due to Brownian motion, the particles usually are remaining in a suspended state and do not tend to sedimentation. Above all, the limiting value of the settling particle size depends on the density difference of particles and dispersing fluid.

End of the Cleverly section

2.2.3 Viscosity

For all flowing fluids, the molecules are showing relative motion between one another, and this process is always combined with internal frictional forces. Therefore for all fluids in motion, a certain flow resistance occurs which may be determined in terms of the viscosity. All materials which clearly show flow behavior are referred to as **fluids** (thus: **liquids and gases**).

a) Shear viscosity
For ideally viscous fluids measured at a constant temperature, the value of the ratio of shear stress τ and corresponding shear rate $\dot{\gamma}$ is a material constant. Definition of the shear viscosity:

Equation 2.8: $\eta = \tau/\dot{\gamma}$

η (eta, pronounced: "etah" or "atah"), **the unit of shear viscosity is [Pas], ("pascal-seconds")**.

The following holds: $1Pas = 1N \cdot s/m^2 = 1kg/s \cdot m$

For low-viscosity liquids, the following unit is usually used:
1mPas ("milli-pascal-seconds") = 10^{-3}Pas
Sometimes, for highly viscous samples the following units are used:
1kPas ("kilo-pascal-seconds") = 1000Pas = 10^3Pas, or even
1MPas ("mega-pascal-seconds") = 1,000kPas = 1,000,000Pas = 10^6Pas
A previously used unit was [P], ("poise"; at best pronounced in French); and: 1P = 100cP; however, this is not an SI unit [59]. This unit was named in honor to the doctor and physicist *Jean L.M. Poiseuille* (1799 to 1869) [291].
The following holds: 1cP ("centi-poise") = 1mPas, and 1P = 0.1Pas = 100mPas

Sometimes, the term **"dynamic viscosity"** is used for η (as in DIN 1342-1). However, some people use the same term to describe either the complex viscosity determined by oscillatory tests, or to mean just the real part of the complex viscosity (the two terms are explained in Chapter 8.2.4b). To avoid confusion and in agreement with the majority of current international authors, here, the term "viscosity" or "shear viscosity" will be used for η. Table 2.3 lists viscosity values of various materials.

The inverse value of viscosity is referred to as **fluidity** φ (phi, pronounced: "fee" or "fi") [303]. However today, this parameter is rarely used. The following holds:

Equation 2.9: $\varphi = 1/\eta$ with the unit $[1/Pas] = [Pas^{-1}]$

For "Mr. and Ms. Cleverly"

Note 1: Usually, samples are viscoelastic when showing high viscosity values.
Many rheological investigations showed that at values of $\eta > 10$kPas, the elastic portion should no longer be ignored. These kinds of samples should no longer be considered simply viscous only, but visco-elastic (see also Chapter 5).

Note 2: Shear viscosity η and extensional viscosity η_E
For ideally viscous fluids under uniaxial tension the following applies for the values of the extensional viscosity (in Pas) and shear viscosity η (also in Pas): $\eta_E(\dot{\varepsilon}) = 3 \cdot \eta(\dot{\gamma})$, if the values of the extensional strain rate $\dot{\varepsilon}$ $[s^{-1}]$ and shear rate $\dot{\gamma}$ $[s^{-1}]$ are equal in size (see also Chapter 10.8.4.1: Trouton relation).

End of the Cleverly section

b) Kinematic viscosity
Definition of the kinematic viscosity:

Equation 2.10: $\nu = \eta/\rho$

ν (ny, pronounced: "nu" or "new"), with the density ρ $[kg/m^3]$, (rho, pronounced: "ro").
For the unit of density holds: $1g/cm^3 = 1000kg/m^3$
The unit of kinematic viscosity is $[mm^2/s]$; and: $1mm^2/s = 10^{-6}m^2/s$

Table 2.3: Viscosity values, at T = +20°C when without further specification; own data and from [18, 215, 276]

Material	Viscosity η [mPas]
Gases/air	0.01 to 0.02 / 0.018
Pentane/acetone/gasoline, petrol (octane)/ethanol	0.230 / 0.316 / 0.538 / 1.20
Water at 0 / +10 / +20 / +30 / +40 / +50 / +60 / + 70 / +80 / +90 / +100°C	1.79 / 1.31 / 1.00 / 0.798 / 0.653 / 0.547 / 0.467 / 0.404 / 0.354 / 0.315 / 0.282
Mercury	1.55
Blood plasma at +20 / +37°C	1.7 / 1.2
Wine, fruit juices (undiluted)	2 to 5
Milk, coffee cream	2 to 10
Blood (from a healthy body) at +20 / +37°C	5 to 120 / 4 to 15 (at $\dot{\gamma}$ = 0.01 to 1000s^{-1})
Light oils	10
Glycol	20
Sulphuric acid	25
Sugar solutions (60%)	57
Motor oils SAE 10W-30, at +23 / +50 / +100°C	50 to 1000 175 / 52 / 20
Olive oils	Approx. 100
Gear oils	300 to 800
Glycerine	1480
Honey, concentrated syrups	Approx. 10Pas
Polymer melts (at processing conditions, e.g. between T = + 150 and 300°C, and at $\dot{\gamma}$ = 10 bis 1000s^{-1})	10 to 10,000Pas
Polymer melts: zero-shear viscosity at $\dot{\gamma} \leq 0.1s^{-1}$ and at T = +150 to 300°C	1kPas to 1MPas
Silicone (PDMS, unlinked, zero-shear viscosity)	10 to 100kPas
Hotmelts (maximum processing viscosity for melt extruders)	100kPas
Bitumen (example): at T = +80 / +60 / +40 / +20°C and at T = 0°C	200Pas / 1kPas / 20kPas / 0.5MPas and 1MPas, i.e., then almost like a viscoelastic solid

A previously used unit was [St] ("stokes"); with: 1St = 100cSt. This unit was named in honor to the mathematician and physicist *George G. Stokes* (1819 to 1903) [348]. The following holds: 1cSt ("centi-stokes") = 1mm^2/s.

Example: Conversion of the values of kinematic viscosity and shear viscosity
Preset: A liquid shows $\nu = 60mm^2/s = 60 \cdot 10^{-6}m^2/s$, and $\rho = 1.1g/cm^3 = 1100kg/m^3$
Calculation: $\eta = \nu \cdot \rho = 60 \cdot 10^{-6} \cdot 1100\ (m^2/s) \cdot (kg/m^3) = 66 \cdot 10^{-3}kg/(s \cdot m) = 66mPas$

Usually, kinematic viscosity values are measured by use of flow cups, capillary viscometers, falling-ball viscometers or Stabinger viscometers (see Chapters 11.2.11L and 11.3 to 11.5).