Encyclopedia of Fluid Mechanics

VOLUME 7

Rheology and Non-Newtonian Flows

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in collaboration with

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Library of Congress Cataloging-in-Publication Data

(Revised for vol. 7)

Encyclopedia of fluid mechanics.

Includes bibliographies and indexes.
Contents: v. 1. Flow phenomena and measurement—
v. 2. Dynamics of single-fluid flows and mixing—[etc.]
— v. 7. Rheology and non-Newtonian flow.
1. Fluid mechanics—Dictionaries. I. Cheremisinoff, Nicholas P.
TA357.E53 1986 620.1'06 85-9742

Series ISBN 0-87201-492-4

ISBN 0-87201-540-8

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in memory

A final acknowledgment belongs to my beloved mother, Louise, whose efforts in no small way contributed to this entire series. Beyond the typing services provided for many of the contributors and meticulous effort of volume indexing, she was and still remains the Editor's major source of inspiration.

PREFACE

This volume of the Encyclopedia is devoted to the subjects of rheology and flow dynamics of non-Newtonian fluids. Although related topics are treated in previous volumes, prior subject coverage was specific to the generic flow topics of those volumes. This work attempts to provide a unified treatment of practical rheology and industrial handling/processing of rheologically complex fluids.

Non-Newtonian behavior is encountered in an overwhelming number of situations throughout nature and in commercial operations. Examples where such behavior occurs are industrial waste flows; process slurry operations; the manufacture of dies, inks, pigments, and paints; polymer and plastics synthesis and fabrication; preparation of cosmetics and health care products; food processing; and even biological phenomena such as blood flow and coagulation. In fact, nature, along with mankind's capitalization of nature in industry, offers many more examples of rheologically complex materials than those described by rigorous Newtonian mechanics. Despite this over-abundance of encounters, our theoretical foundations and process design methodology are largely empirical, and often drawn by analogy from specific fluid studies.

The present work attempts to provide a unified treatment of the subjects starting from an advanced entry level. Fundamental concepts and properties of viscous flow behavior are presented in Volumes 1, 2, 5, and 6 of this series. This volume provides only an overview of basic principles and directs detailed attention to state-of-the-art topics in handling/processing viscous materials. The work is organized into three sections. Section I contains twelve chapters aimed at phenomenological description and establishing theoretical development of non-Newtonian flow behavior. Discussions and modeling of flow regimes in symmetric and non-symmetric flow systems are discussed. The relations between viscous behavior and transport properties are presented. Section II contains five chapters addressing the topics of slippage and drag phenomena. These behaviors are major properties but are often least understood in practical process operations. The final section contains eighteen chapters on characterization, behavior, and processing of polymers and elastomeric materials. Polymer technology is perhaps the most advanced in terms of our understanding of viscous flow properties, and although principles discussed evolved from the study of these materials, concepts and design methodology are general. There are three main themes in this section, namely (1) the relationships between the molecular structure of the fluid and its deformation properties, (2) industrial handling operations, including design methodology, and (3) techniques for assessing and predicting the behavior of viscous materials in industrial processing equipment.

This work represents the efforts of 44 researchers/practitioners from around the world. In addition, it reflects the opinions of scores of colleagues who provided invaluable suggestions and critiques. Deepest gratitude is extended to the contributors and to Gulf Publishing Company whose efforts are presented herein.

Nicholas P. Cheremisinoff

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CHAPTER 1

CHARACTERIZATION OF THIXOTROPIC FLUIDS

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INTRODUCTION

Rheological Classification of Fluid Behavior

Rheology is the science of deformation and flow of materials in response to stress. A rheological equation describes or relates stress or deformation to flow variables of materials such as strain, shear rate, and time. Fluids can be conveniently classified based on their rheological properties as follows [1, 2]: (a) Newtonian fluids follow the simplest rheological equation of Newton's law of viscosity, the stress being proportional to the shear rate. The flow curve (shear stress vs. shear rate) shows a linear relationship and passes through the origin. (b) Time-independent non-Newtonian fluid exhibits a non-linear relationship between the shear stress and the shear rate, or its flow curve exhibits a yield stress (not passing through the origin), provided its viscosity is not time dependent. Time-independent non-Newtonian fluids have attracted more attention by rheologists than others. More than fifteen rheological equations or models have been proposed to represent the time-independent relation as summarized by Skelland [2]. These equations employ two to five parameters to describe the pseudoplastic (shear thinning) or the dilatant (shear thickening) properties of time-independent non-Newtonian fluids with or without a yield stress. (c) Time-dependent non-

Newtonian fluids display time-dependent behavior in the flow curve in addition to the shear-rate dependency. Therefore, the viscosity of time-dependent non-Newtonian fluids is a function of both the shear rate and the time of shearing. They are usually subdivided into two groups, thixotropic fluids and rheopectic fluids. The former are shear-thickening time-dependent fluids. (4) Viscoelastic fluids possess the viscous property of a liquid and the elastic property of a solid. Thus the rheological properties of viscoelastic fluids are inadequately described by relationships between the shear stress and the shear rate unless the elastic properties of the stress and the strain are included. The simplest rheological equation for viscoelastic fluid is the Maxwell model, which includes two rheological parameters – the viscosity and the rigidity modulus. Various theories of viscoelasticity have resulted in many differential or integral constitutive equations relating the shear stress with shear rate, strain, and time.

History of Thixotropy

"Thixotropy" was introduced by Freundlich in 1928 [3]. He and his co-workers observed that many colloidal solutions show a decreased resistance to flow upon being stirred or shaken and revert to their original resistance after being allowed to stand still [4]. He suggested that this phenomenon was due to the structural change of the colloidal particles – a reversible, isothermal gel-sol transition through mechanical disturbance. This reversible, isothermal, viscosity decrease phenomenon was called thixotropy.

The term "thixotropy" has been in continuous use to the present time by many investigators. However, Freundlich's original definition was not uniformly adhered to. It was sometimes interpreted as pseudoplastic or shear-thinning property without considering the time-dependent behavior. Others used it to represent the non-linear viscoelasticity of fluids, failing to recognize the inelastic property of thixotropic fluids.

Experimental Measurements of Thixotropy

The qualitative detection of thixotropy can be achieved experimentally. Capillary viscometers are not suitable for the study of shear rate and time dependencies of viscosity of thixotropic fluids due to the varying shear rate in the flowing system. Both cone-and-plate type and Couette-type viscometers are commonly used. Common proposed experiments are as follows:

The hysteresis loop. Shear stress is monitored in response to shear-rate variation. The shear rate is linearly increased from zero to a maximum value and then decreased from this maximum value to zero. This experiment, originally employed by Green and Weltman [5], generates a hysteresis loop on the flow curve. The hysteresis loop has been used ever since as one of the characteristic curves for the identification of a thixotropic fluid. This experiment is modified into three other experiments: (a) A multiple hysteresis loop is obtained from the continuation of cycles of the shear-rate increase and decrease [6]. The progressive breakdown of gel-structure of the fluid induced by shear can be observed by the gradual reduction of the area enclosed in hysteresis loops. The enclosed area eventually becomes zero and the flow curve of the fluid behaves as a pseudoplastic fluid. (b) A multiple hysteresis is measured with a finite period of pause between cycles. The pause between cycles will establish the necessary rest time required by the fluid to regain its gel-sol equilibrium condition. (c) Another modified hysteresis loop is obtained. When the shear-rate half cycle reaches the maximum value, it is held at this rate for a period of time before returning to zero.

The stress-decay curve. The time-dependent effect on shear stress at constant shear rate is measured, until a steady-state shear stress is reached. This experiment, first designed by Pryce-Jones with a Couette viscometer, demonstrates the time-dependency of viscosity of various thixotropic fluids [7]. This experimentally observed curve is referred to as the stress-decay curve or the torque-decay curve, and is another characteristic curve of thixotropy fluid. This experiment with a step function of shear rate can be replaced by an alternate experiment with a multiple-step function of shear rates from high to low values. It results in a series of stress-decay curves while shear rates