



PVC

TECHNOLOGY

Fourth Edition



W.V. TITOW

ELSEVIER APPLIED SCIENCE PUBLISHERS

PVC TECHNOLOGY

Fourth Edition

聚氯乙烯技术

W. V. TITOW

M. Phil., Ph.D., C.Chem., F.R.S.C., F.P.R.I., C.Text., A.T.I.

*Formerly of the Yarsley Research Laboratories Ltd,
Ashted, Surrey, England*



ELSEVIER APPLIED SCIENCE PUBLISHERS
LONDON and NEW YORK

ELSEVIER APPLIED SCIENCE PUBLISHERS LTD
Ripple Road, Barking, Essex, England

Sole Distributor in the USA and Canada
ELSEVIER SCIENCE PUBLISHING CO., INC.
52 Vanderbilt Avenue, New York, NY 10017, USA

First edition	1962
Second edition	1966
Reprinted	1967
Third edition	1971
Fourth edition	1984

British Library Cataloguing in Publication Data

PVC technology. —4th ed.

1. Polyvinyl chloride

I. Titow, W. V.

668.4'236

TP1180.V48

ISBN 0-85334-249-0

WITH 171 TABLES AND 230 ILLUSTRATIONS

© ELSEVIER APPLIED SCIENCE PUBLISHERS LTD 1984

The selection and presentation of material and the opinions expressed in this publication are the sole responsibility of the authors concerned

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, or otherwise, without the prior written permission of the copyright owner.

Printed in Northern Ireland by The Universities Press (Belfast) Ltd.

Preface to the Fourth Edition

This book continues the tradition of the first two editions of the late W. S. Penn's original *PVC Technology*, and the extensively revised third (1971) edition prepared by myself and B. J. Lanham.

In the present edition the original general format, and the arrangement of chapters, have been largely preserved, but virtually nothing now remains of Penn's own text: a part of the contents is based on material from the 1971 Titow/Lanham version (revised, updated and mainly rewritten): the rest is new, including, *inter alia*, several chapters specially contributed by experts from the plastics industry in the UK and Europe. The section listing international (ISO) and national (BS, ASTM and DIN) standards relevant to PVC, which was first introduced (as Appendix 1) in the 1971 edition, proved a popular feature: it has now been brought up to date and considerably extended. Two further appendices provide, respectively, comprehensive unit conversion tables (with additional information on some of the most frequently encountered units, and the SI units), and a list of many properties of interest in PVC materials, with definitions, typical numerical values, and references to relevant standard test methods.

For various reasons, work on this edition involved more than the usual quota of problems: I am truly grateful to the Publisher's Acquisitions Editor, Mr G. B. Olley, for his understanding, patience, unfailing courtesy and friendly encouragement. I am also most appreciative of the helpful attitude of all other members of the Publisher's staff who were concerned with the various aspects of processing the manuscript and bringing the book out.

If my own contribution to the book has any merit, then I would like to dedicate it—respectfully and affectionately—to all my friends of the Yarsley Laboratories with whom I was privileged to share many happy years, participating in the worthwhile work of a good team.

W.V.T.

Acknowledgements

I am much indebted to Messrs W. B. Duncker, F. J. Olivier and D. J. Sieberhagen of Vynide Ltd for their most helpful comments on the draft of Chapter 18 and for the trouble they took—individually and severally—to provide the drawing for Fig. 18.3, data for Table 18.1, and a few items of information on certain practical aspects of calendering. I am also grateful to Mr J. M. Hofmeyr of Union Carbide for the information he kindly supplied on the *Ucar* range of copolymer resins, and for his permission to use it in Chapter 24.

It is a pleasure to record my thanks to Mr R. Coates of AECl/Chlor-Alkali and Plastics Ltd for a most useful discussion of the scripts of Chapters 2 and 3, for items of information I have used in Tables 2.5 and 2.6, and for arranging his Company's permission—which I very much appreciate—to reproduce from their technical literature the contents of Tables 3.4–3.7.

For the illustrations contained in the Plates my thanks are due to the companies and/or individuals identified in each caption, who kindly provided the original photographs.

A small number of graphs and drawings, and one table (Table 14.1), are straight reproductions from other publications: the copyright holders' and authors' permissions to use these items—which are mentioned in each individual case—are much appreciated.

A few definitions and sets of numerical data have been directly quoted (with sources clearly identified) from ISO, British and ASTM Standards. Such material from ISO specifications is reproduced by permission of the British Standards Institution granted on behalf of the International Organisation for Standardisation. The extracts from Brit-

ish Standards are reproduced by permission of the British Standards Institution, 2 Park Street, London W1A 2BS, from whom complete copies of the standards concerned can be obtained. The material from ASTM Standards is copyright the American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103, and is reprinted with permission.

I am particularly grateful to Mrs Rene Chizlett—whose invaluable secretarial contribution to the previous edition was greatly missed with the present one—for timely help with last-minute verification of several items of information on suppliers of commercial PVC materials.

Mrs Connie von Gernet typed most of the manuscript—it is a pleasure to acknowledge her professional assistance. I am also most appreciative of Mrs Micky Kruger's secretarial help with two of the chapters and urgent correspondence.

No aid on the technical side could be more important than the support and patience of my wife, Margaret Ley-Titow, during the long period, not lacking in stress, when the book was being put together. For all she has done she has my truly appreciative thanks.

W.V.T.

List of Contributing Authors

W. V. TITOW

Formerly Manager (Special Projects), Yarsley Research Laboratories Ltd, Ashtead, Surrey, England

D. L. BUSZARD

Market Development and Technical Service, Plastics Chemicals, Ciba-Geigy Industrial Chemicals, Tenax Road, Trafford Park, Manchester, M17 1WT, England

P. S. COFFIN

General Manager—Technical, Rocol Ltd, Rocol House, Swillington, Leeds, LS26 2BS, England

P. FRANZ

Manager of Process R & D Department, Buss Ltd, CH-4133 Pratteln, Switzerland

W. HENSCHEL

Manager of the Design and Construction Department, Buss Ltd, CH-4133 Pratteln, Switzerland

Miss N. HERBERT

Head, Standards Information Centre, South African Bureau of Standards, Private Bag X191, Pretoria 0001, Republic of South Africa

I. D. HOUNSHAM

Sales Manager, PVC Division, Croxton and Garry Ltd, Curtis Road, Dorking, Surrey, RH4 1XA, England

B. J. LANHAM

European Marketing Manager, LNP Plastics Nederland BV., PO Box 13, Ottergeerde 24, Raamsdonksveer, The Netherlands

The late L. W. TURNER

Formerly Senior Research Associate, Yarsley Technical Centre Ltd, Redhill, Surrey, England

Contents

<i>Preface</i>	v
<i>Acknowledgements</i>	vii
<i>List of Contributing Authors</i>	xxix
 <i>Chapter 1</i>	
Introduction —W. V. TITOW	1
1.1 PVC: General Terminology and Relevant Definitions . .	1
1.2 Early History and Development of PVC	4
1.3 General Statistics	10
1.4 Outline of the PVC Sector of the Plastics Industry . .	12
1.5 Vinyl Chloride Polymers and Copolymers	13
1.5.1 PVC Homopolymers: chemical structure; mor- phology	13
1.5.2 Vinyl Chloride Copolymers	19
1.5.3 'External' Modification of PVC by Other Polym- ers	21
1.5.4 Properties of PVC Compositions	24
1.6 Chlorinated Polyvinyl Chloride (CPVC)	24
1.7 Material and Test Standards	29
References	30
 <i>Chapter 2</i>	
Commercial PVC Polymers —W. V. TITOW	37

2.1	Introduction—Production and Main Types	37
2.2	Polymer Characteristics Cardinal to Behaviour in Processing and/or Service Performance	41
2.2.1	Composition	42
2.2.2	Molecular Weight (Viscosity Number and <i>K</i> Value)	43
2.2.3	Polymer Particle Characteristics: particle size and size distribution; particle shape and morphology	46
2.2.4	Purity	48
2.3	Characterisation and Designation of Commercial PVC Polymers	49
2.4	Examples of Basic Properties of Commercial Polymers as Used for Some Major Applications	55
2.5	Commercial Sources of PVC Polymers	55
	References	57

Chapter 3

	Commercial PVC Compounds—W. V. TITOW	59
3.1	Introduction	59
3.2	Commercial Sources of PVC Compounds	60
3.3	Types and Applications of Commercial PVC Compounds	61
3.4	Properties and Designation of Commercial PVC Compounds	63
3.4.1	Designation	63
3.4.2	Properties Used in Characterisation of PVC Compounds	65
3.4.3	Some Typical Properties of Commercial PVC Compounds	65
	References	78

Chapter 4

	Elementary Principles of PVC Formulation—W. V. TITOW	79
4.1	Introduction	79
4.2	The Components, and Basic Types, of a PVC Formulation	81
4.3	Formulation Costing—Basic Points	83
4.4	Main General Considerations in the Selection of Principal Formulation Components	85

4.4.1	Nature and Characteristics of Individual Components of a Formulation: PVC polymer; heat stabilisers; plasticisers; lubricants; polymeric modifiers; fillers; colourants	86
4.4.2	Interactions and Mutual Effects of Formulation Components: compatibility effects; synergism; other mutual effects	103
4.4.3	Side Effects of Formulation Components: 'secondary functionality' effects; undesirable side-effects	105
4.5	Some Special End-use Requirements	106
4.5.1	Food-contact Applications	106
4.5.2	Resistance to Weathering	107
4.5.3	Electrical Insulation	107
4.6	Examples of Basic Formulations	107
4.6.1	Film and Sheetting	107
4.6.2	Calendered Plasticised Vinyl/Asbestos Flooring (Tiles)	109
4.6.3	Pipe and Tubing	110
4.6.4	Cable Covering and Insulation	111
4.6.5	Gramophone Records	112
4.6.6	Blow-moulded Bottles	112
4.6.7	Injection Mouldings	113
4.6.8	Extruded Profile	114
4.6.9	Paste Formulations	114

Chapter 5

Theoretical Aspects of Plasticisation—D. L. BUSZARD	117
5.1 General Introduction	117
5.2 Definition of Plasticisers and Plasticisation	117
5.3 Chemical Nature of Plasticisers	119
5.4 Theories of Plasticisation	120
5.5 Stages of Plasticiser Interaction with PVC Polymer	122
5.6 Requirements for PVC Plasticisers	124
5.6.1 Compatibility and Miscibility: the μ value; solubility parameter δ ; clear point temperature; Flory-Huggins interaction parameter χ ; A_p/P_0 ratio; loop or roll compatibility tests; maximum torque temperature	125

5.6.2	Effectivity of Plasticisers	132
5.6.3	Permanence of Plasticisers	134
5.7	General Relationships between the Structure of Plasticisers and their Behaviour in PVC	136
5.8	Ageing of Plasticised PVC	138
5.9	Antiplasticisation	142
	References	143

Chapter 6

Commercial Plasticisers—D. L. BUSZARD	147
6.1 Introduction	147
6.2 Classification of Commercially Available Plasticisers	147
6.3 Group Characteristics of Major Plasticiser Classes	148
6.4 Synonyms and Abbreviations	148
6.5 Group 1 Plasticisers—Phthalates	152
6.5.1 Lower Phthalates	152
6.5.2 General-purpose Phthalates	153
6.5.3 Linear Phthalates	153
6.5.4 Higher Phthalates	156
6.5.5 Miscellaneous Phthalates	158
6.6 Group 2 Plasticisers—Phosphates	159
6.6.1 Triaryl Phosphates	159
6.6.2 Trialkyl Phosphates	160
6.6.3 Mixed Alkyl Aryl Phosphates	161
6.6.4 Halogenated Alkyl Phosphates	163
6.7 Group 3 Plasticisers—Trimellitates	163
6.8 Group 4 Plasticisers—Aliphatic Diesters	163
6.9 Group 5 Plasticisers—Polymeric Plasticisers	165
6.10 Group 6 Plasticisers—Miscellaneous Plasticisers	170
6.10.1 Epoxy Plasticisers	170
6.10.2 Chlorinated Paraffins	171
6.10.3 Monoesters	173
6.10.4 Glycol Esters	173
6.10.5 Hydrocarbon Extenders	174
6.10.6 Other Miscellaneous Plasticisers	174
6.11 Storage and Handling of Plasticisers	175
6.12 Plasticiser Manufacturers	180
References	180

Chapter 7

Properties of Plasticised PVC—D. L. BUSZARD	181
7.1 Introduction	181
7.2 Formulation of a Plasticised PVC Compound	181
7.2.1 The 'Desirability Function'	183
7.2.2 Computer-assisted Formulating	183
7.3 Softness and Tensile Properties	184
7.3.1 Effect of Plasticiser	185
7.3.2 Compounding at Equal Efficiency	185
7.4 Low-temperature Properties	192
7.5 Permanence Properties	195
7.5.1 Extraction Resistance	196
7.5.2 Migration Resistance	199
7.5.3 Volatile Loss	200
7.5.4 Automotive Fogging	202
7.5.5 High-humidity Compatibility	204
7.6 Flame-retardant Properties	204
7.7 Electrical Properties	206
7.8 Weathering and Light Stability	206
7.9 Resistance to Microbiological Attack	208
7.10 Resistance to Insect and Rodent Attack	209
7.11 Stain Resistance	209
7.12 Toxicity and Health Aspects of Plasticisers	210
7.12.1 Plasticisers for Food-contact Application	210
7.12.2 Health and Safety	211
References	212

Chapter 8

Fillers in PVC—I. D. HOUNSHAM and W. V. TITOW	215
8.1 Introduction	215
8.2 Mineral Fillers	216
8.2.1 Silicates and Silicas: asbestos; talc; clay	216
8.2.2 Alkaline-earth Metal Sulphates	219
8.2.3 Calcium Carbonates	221
8.3 Calcium Carbonate Fillers—Nature, Properties and Applications	224
8.3.1 General Types: whiting; ground limestone, marble and calcite; ground dolomite; precipitated calcium carbonates	224

8.3.2	Surface Treatments: stearate treatments; organotitanate treatments; proprietary and miscellaneous treatments	225
8.3.3	Filler Properties and Selection Criteria: maximum particle size; particle size distribution and mean particle size; colour (dry brightness); refractive index; oil (or plasticiser) absorption; dispersion characteristics; cost.	228
8.3.4	Applications, and Effects of Filler Loading: flooring; plasticised compounds; rigid PVC	232
8.4	Functional Fillers	240
8.4.1	Reinforcing Fillers: asbestos (chrysotile) fibres; inorganic microfibres; glass fibres; carbon fibres; glass spheres; fine-particle calcium carbonate	240
8.4.2	Flame-retardant and Smoke-suppressant Fillers	247
8.4.3	Miscellaneous Functional Fillers: carbon black; metal powders; wood flour; starch; synthetic silicas	248
8.5	Some Filler Suppliers and Trade Names	251
	References	253

Chapter 9

	Stabilisers: General Aspects—W. V. TITOW	255
9.1	Introduction	255
9.2	Degradation of PVC Polymer	256
9.2.1	Thermal Degradation	256
9.2.2	Photochemical Degradation	260
9.3	Ideal Requirements for a Stabiliser, and General Factors Affecting Stabiliser Selection	261
9.4	Heat Stabilisers	263
9.4.1	Lead Compounds	265
9.4.2	Organotin Stabilisers: chemical nature and types; characteristics and applications	270
9.4.3	Compounds of Other Metals: metal compounds with stabilising effects in PVC; composite metal stabilisers	275
9.4.4	Organic (Miscellaneous) Stabilisers: esters of aminocrotonic acid; urea derivatives; epoxy compounds; organic phosphites; miscellaneous organic co-stabilisers	286

9.5	Antioxidants and UV Absorbers	292
9.5.1	Antioxidants	292
9.5.2	UV Absorbers	294
9.6	Main Modes of Stabiliser Action	299
9.6.1	Lead Stabilisers	299
9.6.2	Organotin Stabilisers	300
9.6.3	Other Metal-based Stabilisers	302
9.6.4	Organic Stabilisers, Antioxidants, UV Stabilisers	304
9.7	Some General Features and Common Faults of Stabilised Compositions	305
9.7.1	Plate-out	305
9.7.2	Sulphide Staining	308
9.8	Testing and Evaluation of Stabiliser Effects	311
9.8.1	Concept of Stability in Processing, Service and Tests	311
9.8.2	Heat Stability Testing	315
9.8.3	Light Stability Testing	328
9.9	Detection and Analysis of Stabilisers	330
	References	330

Chapter 10

	Commercial Stabiliser Practice—P. S. COFFIN	335
10.1	Introduction	335
10.2	Choosing a Commercial Stabiliser	337
10.3	The Importance of a Well-balanced Lubricant System	339
10.4	One-pack Systems and the Physical Form of Stabiliser Products	340
10.5	Hygiene and Environmental Considerations	341
10.6	UK Stabiliser Manufacturers—Product Ranges and Applications	342
10.6.1	Associated Lead Manufacturers Ltd	342
10.6.2	Ciba-Geigy Ltd	346
10.6.3	Durham Chemicals Ltd	348
10.6.4	Diamond Shamrock Polymer Additives Division	351
10.6.5	Victor Wolf Ltd	356
	References	356

Chapter 11

	Some Miscellaneous Components of PVC Formulations—W. V. TITOW	359
11.1	Lubricants	359

11.1.1	Functions, Nature and Effects	359
11.1.2	Interaction and Co-action of Lubricants with Other PVC Formulation Components: lubricant/stabiliser effects; mutual effects of lubricants and plasticisers; effects of polymeric modifiers; effects of fillers and pigments	364
11.1.3	Assessment of Lubricant Effects	367
11.1.4	Sources of Information on Lubricants and their Commercial Suppliers	370
11.2	Polymeric Modifiers	371
11.2.1	Processing Aids	372
11.2.2	Impact Modifiers: impact resistance—its nature, significance and measurement; the impact resis- tance of PVC; the nature, effects and applica- tions of polymeric impact modifiers for PVC .	375
11.3	Colourants	401
11.3.1	General Nature and Functioning	401
11.3.2	General Classification	403
11.3.3	Forms in which Colourants are Available . . .	405
11.3.4	Choice of Colourant—Main Considerations: general appearance and colour requirements; processability and stability in processing; stabil- ity and permanence in service; health and safety considerations	407
11.3.5	Some Commercial Pigments	410
11.4	Antistatic Agents	419
11.4.1	Static Electricity Charges on PVC: Phenomena and Tests	420
11.4.2	Nature and Use of Antistatic Agents	422
11.5	Flame and Smoke Retardants	424
11.5.1	General Mechanism of Burning of Polymers and Plastics	424
11.5.2	Flame Retardance and Smoke Suppression in PVC Compositions	427
	References	435

Chapter 12

Miscellaneous Properties of Special Interest in PVC Materials and Products—W. V. TITOW	439
12.1 Introduction	439

12.2	Low-temperature Properties	439
12.2.1	Cold Flex Temperature (Clash and Berg)	442
12.2.2	Cold Bend Temperature	442
12.2.3	Low Temperature Extensibility of Flexible PVC Sheet	442
12.3	Heat Resistance	443
12.4	Permeability	452
12.5	Environmental Stress Cracking and Crazing	466
12.6	Weathering Resistance	469
12.7	Resistance to Biological Attack	483
12.7.1	Microbiological Attack (Biodegradation)	483
12.7.2	Insect and Animal Depredations: attack by termites; attack by rodents	486
12.8	Chemical Resistance	487
12.9	Health Hazards	495
12.9.1	Vinyl Chloride Monomer	496
12.9.2	PVC Compounds and their Regular Constituents	498
12.9.3	PVC Decomposition Products	499
12.9.4	Peripheral Hazards	500
12.10	Burning Behaviour	501
	References	509

Chapter 13

Industrial Compounding Technology of Rigid and Plasticised PVC—W. HENSCHER and P. FRANZ		513
13.1	Introduction	513
13.2	Raw Materials	514
13.2.1	PVC Polymer and Fillers	514
13.2.2	Plasticisers	519
13.2.3	Other Additives	519
13.3	Upstream Equipment (Silo Storage to Weighing)	519
13.3.1	Silo Storage of PVC Polymer and Fillers: silo sizes; materials of silo construction; raw material intake (silo filling); raw material discharge; dust removal system	519
13.3.2	Conveying of PVC Polymer and Fillers: pneumatic conveying	525
13.3.3	Storage of Plasticisers: tank sizes; suitable con-	