

SECOND EDITION

# COLOUR

AND THE OPTICAL PROPERTIES  
OF MATERIALS



RICHARD J. D. TILLEY

 WILEY

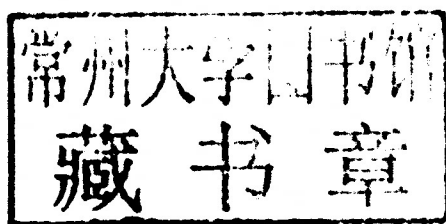


# Colour and the Optical Properties of Materials

An Exploration of the Relationship Between Light,  
the Optical Properties of Materials and Colour

**PROFESSOR RICHARD J. D. TILLEY**

Emeritus Professor, University of Cardiff, UK



A John Wiley and Sons, Ltd., Publication



This edition first published 2011  
© 2011 John Wiley & Sons, Ltd

*Registered office*

John Wiley & Sons, Ltd, The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, United Kingdom

For details of our global editorial offices, for customer services and for information about how to apply for permission to reuse the copyright material in this book please see our website at [www.wiley.com](http://www.wiley.com).

The right of the author to be identified as the author of this work has been asserted in accordance with the Copyright, Designs and Patents Act 1988.

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, except as permitted by the UK Copyright, Designs and Patents Act 1988, without the prior permission of the publisher.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic books.

Designations used by companies to distinguish their products are often claimed as trademarks. All brand names and product names used in this book are trade names, service marks, trademarks or registered trademarks of their respective owners. The publisher is not associated with any product or vendor mentioned in this book. This publication is designed to provide accurate and authoritative information in regard to the subject matter covered. It is sold on the understanding that the publisher is not engaged in rendering professional services. If professional advice or other expert assistance is required, the services of a competent professional should be sought.

The publisher and the author make no representations or warranties with respect to the accuracy or completeness of the contents of this work and specifically disclaim all warranties, including without limitation any implied warranties of fitness for a particular purpose. This work is sold with the understanding that the publisher is not engaged in rendering professional services. The advice and strategies contained herein may not be suitable for every situation. In view of ongoing research, equipment modifications, changes in governmental regulations, and the constant flow of information relating to the use of experimental reagents, equipment, and devices, the reader is urged to review and evaluate the information provided in the package insert or instructions for each chemical, piece of equipment, reagent, or device for, among other things, any changes in the instructions or indication of usage and for added warnings and precautions. The fact that an organization or Website is referred to in this work as a citation and/or a potential source of further information does not mean that the author or the publisher endorses the information the organization or Website may provide or recommendations it may make. Further, readers should be aware that Internet Websites listed in this work may have changed or disappeared between when this work was written and when it is read. No warranty may be created or extended by any promotional statements for this work. Neither the publisher nor the author shall be liable for any damages arising herefrom.

*Library of Congress Cataloging-in-Publication Data*

Tilley, R. J. D.

Colour and the optical properties of materials : an exploration of the relationship between light, the optical properties of materials and colour / Richard J. D. Tilley.  
p. cm.

Includes bibliographical references and index.

ISBN 978-0-470-74696-7 (cloth) – ISBN 978-0-470-74695-0 (pbk.)

1. Light. 2. Optics. 3. Color. I. Title.

QC355.3.T55 2010

535.6–dc22

2010025108

A catalogue record for this book is available from the British Library.

ISBN 9780470746967 [HB]

ISBN 9780470746950 [PB]

Set in 10/12pt Times Roman by Thomson Digital, Noida, India

Printed and bound in Singapore by Markono Print Media Pte Ltd.

# **Colour and the Optical Properties of Materials**

*To Anne, for her continued help and support*

# Preface

This book is concerned with colour. It is not primarily a textbook on optics, but focuses attention upon the ways that colour can be produced and how these ways govern device applications. However it is not possible to discuss colour without reference to numerous optical properties, so these, too, are explained throughout the text. Colour, though, remains the dominant theme.

When writing about colour and colour production from a scientific point of view one is beset by a number of language conflicts, arising from the historical importance of the subject. Much of this confusion is due to the fact that the terminology has arisen gradually, as a result of historical experiences that scientists of the day found difficult to understand and interpret. Thus, diffraction, scattering, reflection and refraction can all be considered to be scattering of photons, and the variety of terms in use only confuses the modern reader. Indeed, the nature of light itself leads to problems. Is it a series of waves or a spray of bullet-like photons? A light wave can apparently pass through holes in a metal foil that are far smaller than its wavelength. How can this be? Is the light, instead, a series of photons that can do this, and if so, how big is a photon?

Other similar difficulties exist. A decaying and glowing fungus exhibiting bioluminescence does not produce light by the same mechanism as a light-emitting diode (LED) using electroluminescence, although both are termed luminescence. The termination '-chromic' suffers from the same lack of precision. Thermochromic molecules may or may not exhibit colour changes by the same mechanism as electrochromic thin films. The names do not supply any information about this. The units used in the measurement of light are equally confusing. This is because absolute measurements of energy, radiometric units, do not correspond to visual perception, measured in photometric units.

Many of these questions are resolved in this book, particularly with respect to light and colour. The explanations are taken at as simple a level that will allow an appreciation of the topic.

The book falls into three recognizable sections. Chapter 1 is introductory and covers ideas of light as rays, waves or photons. The emission and absorption of radiation is described, as is the difference in light from an incandescent source and light from a laser. Vision and the perception of colour (physiology or psychology), and related aspects are described in outline, as is the technical measurement of colour. These are specialist topics, and the information here is designed only to cover the need of subsequent chapters. Finally, the way in which light can interact with a material is summarized, as a prologue to later chapters.

Chapters 2–6 explain optical phenomena mostly in terms of light waves. Colour is generated when light waves comprising all colours (white light) are subdivided physically into a series of smaller wavelength ranges (i.e. colours). Traditional divisions of the topic are retained, although there is little to choose, theoretically, between labelling a process scattering, diffraction or reflection. Because of this, there is sometimes an ambiguity as to where a particular topic should be placed. For example, fibre Bragg gratings might be treated as multiple reflectors or as diffraction arrays. Mie scattering can be regarded as diffraction. The layout adopted here is one that fits best with the explanations involved.



Chapters 7–10 require a photon explanation to account for colour production. Fundamentally, the absorption and emission of light from atoms, ions and molecules forms the central theme, and for this a quantum mechanical approach is needed. Many of these processes are widely exploited in displays. Although these are technologically complex and require considerable engineering skills in production, the way in which they produce colour is always based upon recognisable physical and chemical principles. Because of this, displays are introduced throughout the text in terms of the appropriate colour-generating mechanism, rather than as a separate section.

The topics covered encroach upon physics, chemistry, biology, materials science and engineering and many aspects of these intertwined subject areas are touched upon. Students of all of these disciplines should find this book of relevance to some of their studies or interests. Readers who need more information can turn to the Further Reading sections at the end of each chapter. These include selected references to the original literature or substantial reviews and will allow them to take matters further. In addition, the website ([www.wiley.com/go/tilley\\_colour](http://www.wiley.com/go/tilley_colour)) that accompanies this book contains exercises and numerical problems which have been provided to illustrate and reinforce the concepts presented in the text. All readers are encouraged to attempt them. There are also introductory questions that appear at the start of each chapter which are designed to stimulate interest. The answers to these are found in the Chapter itself. In addition, the answers to these introductory questions and all the other exercises and problems are to be found on the accompanying website.

Unfortunately, some important light-related topics have been omitted. These include the important biological topics of photoperiodism in animals and plants and photosynthesis. Although colour is of importance in these topics, the specialist knowledge here is biological rather than optical, and information in this field is best reserved for biological texts.

It is a pleasure to acknowledge the considerable help and encouragement received in the preparation of this edition. The editorial staff of John Wiley & Sons have always given both assistance and encouragement in the venture. I am indebted to Professor D. J. Brown, University of California, Irvine, USA; Mr A. Dulley, West Glamorgan Archive Service, Swansea, Wales; Dr A. Eddington, Dr J. A. Findlay; Professor I. C. Freestone, University of Cardiff, Wales; Spectrum Technologies plc, Bridgend, Wales; Dr M. Sugdon, De La Rue Group; Dr R. D. Tilley, Victoria University of Wellington, New Zealand; Professor X. Zhang, University of California, Berkeley, USA; Dr P. Vukusic, University of Exeter, England; Dr G. I. N. Waterhouse, University of Auckland, New Zealand. All of them readily provided photographic material. To all of these I express my sincere thanks. Allan Coughlin gave encouragement and advice, and the members of staff of the Trevithick Library, University of Cardiff, Wales, were indefatigable in answering my obscure queries.

Finally, my thanks, as always, are due to my wife Anne, who tolerated my hours reading or sat in front of a computer without complaint, and made it possible to complete this work.

Richard J. D. Tilley  
South Glamorgan  
May 2010

# Contents

## Preface

xv

<b>1 Light and Colour</b>	1
1.1 Colour and Light	1
1.2 Colour and Energy	3
1.3 Light Waves	5
1.4 Interference	7
1.5 Light Waves and Colour	9
1.6 Black-Body Radiation and Incandescence	10
1.7 The Colour of Incandescent Objects	13
1.8 Photons	14
1.9 Lamps and Lasers	16
1.9.1 Lamps	16
1.9.2 Emission and Absorption of Radiation	17
1.9.3 Energy-Level Populations	17
1.9.4 Rates of Absorption and Emission	18
1.9.5 Cavity Modes	21
1.10 Vision	23
1.11 Colour Perception	28
1.12 Additive Coloration	29
1.13 The Interaction of Light with a Material	33
1.14 Subtractive Coloration	37
1.15 Electronic 'Paper'	39
1.16 Appearance and Transparency	40
Appendix A1.1 Definitions, Units and Conversion Factors	43
A1.1.1 Constants, Conversion Factors and Energy	43
A1.1.2 Waves	43
A1.1.3 SI Units Associated with Radiation and Light	45
Further Reading	47
<b>2 Colours Due to Refraction and Dispersion</b>	49
2.1 Refraction and the Refractive Index of a Material	49
2.2 Total Internal Reflection	54
2.2.1 Refraction at an Interface	54



2.2.2	Evanescent Waves	54
2.3	Refractive Index and Polarisability	58
2.4	Refractive Index and Density	60
2.5	Invisible Animals, GRINs and Mirages	62
2.6	Dispersion and Colours Produced by Dispersion	65
2.7	Rainbows	68
2.8	Halos	75
2.9	Fibre Optics	75
2.9.1	Optical Communications	75
2.9.2	Optical Fibres	77
2.9.3	Attenuation in Glass Fibres	79
2.9.4	Chemical Impurities	80
2.9.5	Dispersion and Optical-Fibre Design	81
2.10	Negative Refractive Index Materials	84
2.10.1	Metamaterials	84
2.10.2	Superlenses	87
	Further Reading	89
<b>3</b>	<b>The Production of Colour by Reflection</b>	<b>91</b>
3.1	Reflection from a Single Surface	92
3.1.1	Reflection from a Transparent Plate	92
3.1.2	Data Storage Using Reflection	94
3.2	Interference at a Single Thin Film in Air	94
3.2.1	Reflection Perpendicular to the Film	96
3.2.2	Variation with Viewing Angle	97
3.2.3	Transmitted Beams	98
3.3	The Colour of a Single Thin Film in Air	99
3.4	The Reflectivity of a Single Thin Film in Air	101
3.5	The Colour of a Single Thin Film on a Substrate	102
3.6	The Reflectivity of a Single Thin Film on a Substrate	104
3.7	Low-Reflection and High-Reflection Films	105
3.7.1	Antireflection Coatings	105
3.7.2	Antireflection Layers	106
3.7.3	Graded Index Antireflection Coatings	108
3.7.4	High-Reflectivity Surfaces	110
3.7.5	Interference-Modulated (IMOD) Displays	110
3.8	Multiple Thin Films	111
3.8.1	Dielectric Mirrors	111
3.8.2	Multilayer Stacks	113
3.8.3	Interference Filters and Distributed Bragg Reflectors	114
3.9	Fibre Bragg Gratings	115
3.10	'Smart' Windows	119
3.10.1	Low-Emissivity Windows	119
3.10.2	Self-Cleaning Windows	121
3.11	Photonic Engineering in Nature	121
3.11.1	The Colour of Blue Butterflies	122
3.11.2	Shells	122

3.11.3	Labradorite	122
3.11.4	Mirror Eyes	125
Appendix A3.1	The Colour of a Thin Film in White Light	126
	Further Reading	127
<b>4</b>	<b>Polarisation and Crystals</b>	129
4.1	Polarisation of Light	129
4.2	Polarisation by Reflection	131
4.3	Polars	135
4.4	Crystal Symmetry and Refractive Index	137
4.5	Double Refraction: Calcite as an Example	138
4.5.1	Double Refraction	138
4.5.2	Refractive Index and Crystal Structure	140
4.6	The Description of Double Refraction Effects	143
4.6.1	Uniaxial Crystals	143
4.6.2	Biaxial Crystals	144
4.7	Colour Produced by Polarisation and Birefringence	147
4.8	Dichroism and Pleochroism	149
4.9	Nonlinear Effects	151
4.9.1	Nonlinear Crystals	151
4.9.2	Second- and Third-Harmonic Generation	153
4.9.3	Frequency Mixing	155
4.9.4	Optical Parametric Amplifiers and Oscillators	156
4.10	Frequency Matching and Phase Matching	157
4.11	More on Second-Harmonic Generation	160
4.11.1	Polycrystalline Solids and Powders	160
4.11.2	Second-Harmonic Generation in Glass	160
4.11.3	Second-Harmonic and Sum-Frequency-Generation by Organic Materials	161
4.11.4	Second-Harmonic Generation at Interfaces	162
4.11.5	Second-Harmonic Microscopy	162
4.12	Optical Activity	162
4.12.1	The Rotation of Polarised Light	162
4.12.2	Circular Birefringence and Dichroism	166
4.13	Liquid Crystals	168
4.13.1	Liquid-Crystal Mesophases	168
4.13.2	Liquid-Crystal Displays	169
	Further Reading	173
<b>5</b>	<b>Colour Due to Scattering</b>	175
5.1	Scattering and Extinction	175
5.2	Tyndall Blue and Rayleigh Scattering	176
5.3	Blue Skies, Red Sunsets	178
5.4	Scattering and Polarisation	181
5.5	Mie Scattering	184
5.6	Blue Eyes, Blue Feathers and Blue Moons	187
5.7	Paints, Sunscreens and Related Matters	188

5.8	Multiple Scattering	190
5.9	Gold Sols and Ruby Glass	191
5.10	The Lycurgus Cup and Other Stained Glass	193
	Further Reading	195
<b>6</b>	<b>Colour Due to Diffraction</b>	197
6.1	Diffraction and Colour Production by a Slit	198
6.2	Diffraction and Colour Production by a Rectangular Aperture	200
6.3	Diffraction and Colour Production by a Circular Aperture	202
6.4	The Diffraction Limit of Optical Instruments	203
6.5	Colour Production by Linear Diffraction Gratings	205
6.6	Two-Dimensional Gratings	208
6.7	Estimation of the Wavelength of Light by Diffraction	210
6.8	Diffraction by Crystals and Crystal-like Structures	211
6.8.1	Bragg's Law	211
6.8.2	Opals	213
6.8.3	Artificial and Inverse Opals	218
6.8.4	The Effective Refractive Index of Inverse Opals	221
6.8.5	Photonic Crystals and Photonic Band Gaps	223
6.8.6	Dynamical Form of Bragg's Law	224
6.9	Diffraction from Disordered Gratings	225
6.9.1	Random Specks and Droplets	225
6.9.2	Colour from Cholesteric Liquid Crystals	228
6.9.3	Disordered Two- and Three-Dimensional Gratings	230
6.10	Diffraction by Sub-Wavelength Structures	231
6.10.1	Diffraction by Moth-Eye Antireflection Structures	231
6.10.2	The Cornea of the Eye	233
6.10.3	Some Blue Feathers	234
6.11	Holograms	235
6.11.1	Holograms and Interference Patterns	235
6.11.2	Transmission Holograms	235
6.11.3	Reflection Holograms	237
6.11.4	Rainbow Holograms	239
6.11.5	Hologram Recording Media	240
6.11.6	Embossed Holograms	242
	Further Reading	243
<b>7</b>	<b>Colour from Atoms and Ions</b>	247
7.1	The Spectra of Atoms and Ions	247
7.2	Terms and Levels	252
7.3	Atomic Spectra and Chemical Analysis	254
7.4	Fraunhofer Lines and Stellar Spectra	255
7.5	Neon Signs and Early Plasma Displays	256
7.6	The Helium-Neon Laser	259
7.7	Sodium and Mercury Street Lights	262
7.8	Transition Metals and Crystal-Field Colours	264
7.9	Crystal Field Splitting, Energy Levels and Terms	270



7.9.1	Configurations and Strong Field Energy Levels	270
7.9.2	Weak Fields and Term Splitting	271
7.9.3	Intermediate Fields	273
7.10	The Colour of Ruby	277
7.11	Transition-Metal-Ion Lasers	281
7.11.1	The Ruby Laser: A Three-Level Laser	281
7.11.2	The Titanium–Sapphire Laser	282
7.12	Emerald, Alexandrite and Crystal-Field Strength	283
7.13	Crystal-Field Colours in Minerals and Gemstones	284
7.14	Colour as a Structural Probe	287
7.15	Colours from Lanthanoid Ions	288
7.16	The Neodymium ( $\text{Nd}^{3+}$ ) Solid-State Laser: A Four-Level Laser	290
7.17	Amplification of Optical-Fibre Signals	294
7.18	Transition Metal, Lanthanoid and Actinoid Pigments	295
7.19	Spectral-Hole Formation	297
Appendix A7.1	Electron Configurations	300
A7.1.1	Electron Configurations of the Lighter Atoms	300
A7.1.2	The 3d Transition Metals	301
A7.1.3	The Lanthanoid (Rare Earth) Elements	301
Appendix A7.2	Terms and Levels	302
A7.2.1	The Vector Model of the Atom	302
A7.2.2	Energy Levels and Terms of Many-Electron Atoms	304
A7.2.3	The Ground-State Term of an Atom	306
A7.2.4	Energy Levels of Many-Electron Atoms	306
Further Reading		307
<b>8</b>	<b>Colour from Molecules</b>	309
8.1	The Energy Levels of Molecules	309
8.2	The Colours Arising in Some Simple Inorganic Molecules	311
8.3	The Colour of Water	315
8.4	Chromophores, Chromogens and Auxochromes	316
8.5	Conjugated Bonds in Organic Molecules: The Carotenoids	317
8.6	Conjugated Bonds Circling Metal Atoms: Porphyrins and Phthalocyanines	319
8.7	Naturally Occurring Colorants: Flavonoid Pigments	323
8.7.1	Flavone-Related Colours: Yellows	323
8.7.2	Anthocyanin-Related Colours: Reds and Blues	324
8.7.3	The Colour of Red Wine	328
8.8	Autumn Leaves	332
8.9	Some Dyes and Pigments	333
8.9.1	Indigo, Tyrian Purple and Mauve	335
8.9.2	Tannins	337
8.9.3	Melanins	337
8.10	Charge-Transfer Colours	340
8.10.1	Charge-Transfer Processes	340
8.10.2	Cation-to-Cation (Intervalence) Charge Transfer	341
8.10.3	Anion-to-Cation Charge Transfer	345
8.10.4	Iron-Containing Minerals	346

8.10.5	Intra-Anion Charge Transfer	348
8.11	Colour-Change Sensors	349
8.11.1	The Detection of Metal Ions	349
8.11.2	Indicators	350
8.11.3	Colorimetric Sensor Films and Arrays	353
8.11.4	Markers	354
8.12	Dye Lasers	355
8.13	Photochromic Organic Molecules	358
	Further Reading	361
<b>9</b>	<b>Luminescence</b>	<b>363</b>
9.1	Luminescence	363
9.2	Activators, Sensitisers and Fluorophores	365
9.3	Atomic Processes in Photoluminescence	368
9.3.1	Energy Absorption and Emission	368
9.3.2	Kinetic Factors	370
9.3.3	Quantum Yield and Reaction Rates	371
9.3.4	Structural Interactions	374
9.3.5	Quenching	374
9.4	Fluorescent Lamps	379
9.4.1	Halophosphate Lamps	379
9.4.2	Trichromatic Lamps	381
9.4.3	Other Fluorescent Lamps	382
9.5	Plasma Displays	383
9.6	Cathodoluminescence and Cathode Ray Tubes	385
9.6.1	Cathode Rays	385
9.6.2	Television Tubes	386
9.6.3	Other Applications of Cathodoluminescence	389
9.7	Field-Emission Displays	390
9.8	Phosphor Electroluminescent Displays	391
9.9	Up-Conversion	394
9.9.1	Ground-State Absorption and Excited-State Absorption	395
9.9.2	Energy Transfer	399
9.9.3	Other Up-Conversion Processes	401
9.10	Quantum Cutting	402
9.11	Fluorescent Molecules	405
9.11.1	Molecular Fluorescence	405
9.11.2	Fluorescent Proteins	407
9.11.3	Fluorescence Microscopy	409
9.11.4	Multiphoton Excitation Microscopy	410
9.12	Fluorescent Nanoparticles	411
9.13	Fluorescent Markers and Sensors	412
9.14	Chemiluminescence and Bioluminescence	413
9.15	Triboluminescence	416
9.16	Scintillators	416
	Further Reading	418

<b>10 Colour in Metals, Semiconductors and Insulators</b>	<b>419</b>
10.1 The Colours of Insulators	420
10.2 Excitons	421
10.3 Impurity Colours in Insulators	424
10.4 Impurity Colours in Diamond	424
10.5 Colour Centres	429
10.5.1 The F Centre	429
10.5.2 Electron and Hole Centres	430
10.5.3 Surface Colour Centres	434
10.5.4 Complex Colour Centres: Laser Action	434
10.5.5 Photostimulable Phosphors	435
10.6 The Colours of Inorganic Semiconductors	436
10.6.1 Coloured Semiconductors	436
10.6.2 Transparent Conducting Oxides	437
10.7 The Colours of Semiconductor Alloys	440
10.8 Light Emitting Diodes	441
10.8.1 Direct and Indirect Band Gaps	441
10.8.2 Idealised Diode Structure	443
10.8.3 High-Brightness LEDs	445
10.8.4 Impurity Doping in LEDs	446
10.8.5 LED Displays and White Light Generation	446
10.9 Semiconductor Diode Lasers	448
10.10 Semiconductor Nanostructures	449
10.10.1 Nanostructures	449
10.10.2 Quantum Wells	451
10.10.3 Quantum Wires and Quantum Dots	454
10.11 Organic Semiconductors and Electroluminescence	457
10.11.1 Molecular Electroluminescence	457
10.11.2 Organic Light Emitting Diodes	459
10.12 Electrochromic Films	463
10.12.1 Tungsten Trioxide Electrochromic Films	465
10.12.2 Inorganic Electrochromic Materials	467
10.12.3 Electrochromic Molecules	468
10.12.4 Electrochromic Polymers	468
10.13 Photovoltaics	471
10.13.1 Photoconductivity and Photovoltaic Solar Cells	471
10.13.2 Dye-Sensitised Solar Cells	472
10.14 Digital Photography	474
10.14.1 Charge Coupled Devices	474
10.14.2 CCD Photography	476
10.15 The Colours of Metals	477
10.16 The Colours of Metal Nanoparticles	478
10.16.1 Plasmons	478
10.16.2 Surface Plasmons and Polaritons	479
10.16.3 Polychromatic Glass	481
10.16.4 Photochromic Glass	482
10.16.5 Photographic Film	484



10.16.6 Metal Nanoparticle Sensors and SERS	486
10.17 Extraordinary Light Transmission and Plasmonic Crystals	487
Further Reading	488

<b>Index</b>	491
--------------	-----

# 1

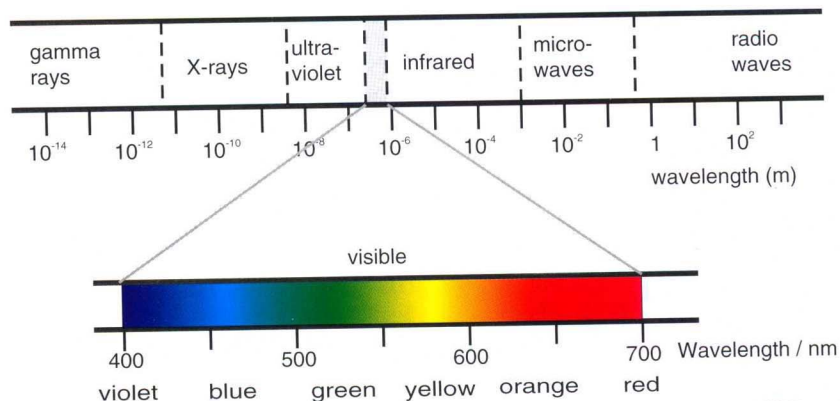
## Light and Colour

- **What is colour?**
- **Why do hot objects become red or white hot?**
- **How do e-books produce 'printed' words?**

### 1.1 Colour and Light

Colour is defined as the subjective appearance of light as detected by the eye. It is necessary, therefore, to look initially at how light is regarded. In fact, light has been a puzzle from earliest times and remains so today. In elementary optics, light can usefully be considered to consist of light *rays*. These can be thought of as extremely fine beams that travel in straight lines from the light source and thence, ultimately, to the eye. The majority of optical instruments can be constructed within the framework of this idea. However, the ray concept breaks down when the behaviour of light is critically tested, and the performance of optical instruments, as distinct from their construction, cannot be explained in terms of light rays. Moreover, colour is not conveniently defined in this way. For this, more complex ideas are needed.

The first testable theory of the nature of light was put forward by Newton (in 1704) in his book *Optics*, in which it was suggested that light was composed of small particles or 'corpuscles'. This idea was supported on philosophical grounds by Descartes. Huygens, a contemporary, thought that light was wavelike, a point of view also supported by Hooke. Young provided strong evidence for the wave theory of light by demonstrating the interference of light beams (1803). Shortly afterwards, Fresnell and Arago explained the polarisation of light in terms of transverse light waves. However, none of these explanations was able to refute the particle hypothesis completely. Nevertheless, the wave versus particle theories differed in one fundamental aspect that could be tested. When light enters water it is refracted (Chapter 2). In terms of corpuscles, this implied a speeding up of the light in water relative to air. The wave theory demanded that the light should move more slowly in water than in air. The experiments were complicated by the enormous speed of light, which was known to be about



**Figure 1.1** The electromagnetic spectrum. Historically, different regions have been given different names. The boundaries between each region are not sharply defined but grade into one another. The visible spectrum occupies only a small part of the total spectrum

$3 \times 10^8 \text{ m s}^{-1}$ , and it was not until April 1850 that Foucault first proved that light moved slower in water than in air, and seemingly killed the corpuscular theory then and there. Confirmation of the result by Fizeau a few months later removed all doubt.

Over the years the wave theory became entrenched and was strengthened by the theoretical work of physicists such as Fresnel, who first explained interference and diffraction (Chapter 6) using wave theory. Polarisation (Chapter 4) is similarly explained on the assumption that light is a wave. The wave theory of light undoubtedly reached its peak when Maxwell developed his theory of electromagnetic radiation and showed that light was only a small part of an *electromagnetic spectrum*. Light was then imagined as an electromagnetic wave (Figure 1.1). Maxwell's theory was confirmed experimentally by Hertz, whose experiments led directly to radio.

The problem for the wave theory was that waves had to exist in something, and the 'something' was hard to pin down. It became called the *luminiferous aether* and had the remarkable properties of pervading all space, being of very small (or even zero) density and having extremely high rigidity. Attempts to measure the velocity of the Earth relative to the luminiferous aether, the so-called aether drift, by Michelson and Morley, before the end of the nineteenth century, proved negative. The difficulty was removed by Einstein's theory of relativity, and for a time it appeared that a theory of light as electromagnetic waves would finally explain all optical phenomena.

This proved a false hope, and the corpuscular theory of light was revived early in the twentieth century, principally by Einstein. Since 1895, it had been observed that when ultraviolet light was used to illuminate the surfaces of certain metals, negative particles, later identified as electrons, were emitted. The details of the experimental results were completely at odds with the wave theory. The electrons, called *photoelectrons*, were only observed if the frequency of the radiation exceeded a certain minimum value, which varied from one material to another. The kinetic energy of the photoelectrons was linearly proportional to the frequency of the illumination. The number of photoelectrons emitted increased as the intensity<sup>1</sup> of the light increased, but their energy remained constant for any particular light source. Very dim illumination still produced small numbers of photoelectrons with the appropriate energy.

<sup>1</sup> The imprecise expression 'intensity' has largely been replaced in the optical literature by well-defined terms such as irradiance (Appendix 1.1). The term intensity is retained here (in a qualitative way to designate the amount of light) because of the historical context.