

5th Edition

Handbook of MATERIAL WEATHERING

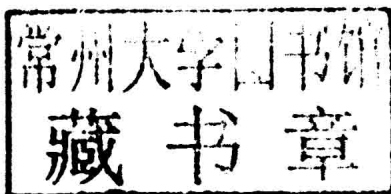
George Wypych



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Handbook of Material Weathering Fifth Edition

George Wypych



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4. Polymers--Biodegradation--Handbooks, manuals, etc.
5. Environmental testing--Handbooks, manuals, etc. I. Title.

PREFACE

The first edition of this book was published by ChemTec Publishing in 1990. The book had 18 chapters and 518 pages filled with the most up-to-date information on the subject of material weathering available in 1990.

Considering the size of the book and typesetting, the present edition is at least 3 times larger, in spite of the fact that two chapters were omitted from the fourth edition: Chapter 17. Stabilization and Stabilizers and Chapter 18. Biodegradation. Even without these two chapters the present 5th edition is larger than the previous edition. The reason is quite obvious – the field is systematically growing with new data, methods, and discoveries happening every day.

The reasons for eliminating the two chapters are as follows:

- If these two chapters would still be included in the book, the book would need to have two volumes which makes a book more difficult to use (separate table of contents and indices).
- In anticipation of the need for specialized monographic sources, the two chapters mentioned above were not updated in the previous edition, so information was already lacking novelty.
- Short chapters can only present brief review of the subject, whereas in applications detailed information is needed
- Two handbooks were published by ChemTec Publishing on the subjects of the omitted chapters:

Handbook of Material Biodegradation, Biodeterioration, and Biostabilization by

Falkiewicz-Dulik, M, Janda, K, and Wypych, G., 2010

Handbook of UV Degradation and Stabilization by Wypych, G, 2011

These two books give much broader and comprehensive information, such as it is required today, especially considering rapid changes which occurred recently because of health and safety concerns (biostabilization) and new discoveries (UV stabilization).

In addition, to present volume and the above two books, there is also a new book:

Atlas of Material Damage, Wypych, G, 2012

This book was written to emphasize importance of the material structure in photodegradation and photostabilization and also to account for the morphological changes which occur when materials degrade. This addition makes narrative of material degradation more comprehensive, showing new ways to deal with unstable materials.

I hope that the information provided in these four books will help readers to advance their studies on particular subjects of their research and that the results of these studies will be implemented in the future editions of these books, since we try to report current developments to foster future discoveries.

George Wypych
Toronto, 2013

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PHOTOPHYSICS

Photophysics, or physics of light, encompasses all ranges of electromagnetic radiation including UV, visible, and infrared radiation ranges which are important for weathering. The scope of photophysics interest includes:

- the nature of radiation
- the absorption of radiation by materials
- the radiation wavelength versus excitation energy
- the fate and utilization of absorbed energy
- the processes of energy transfer
- the emission of electromagnetic radiation.

If all photophysical properties of materials were known, studies of weathering would become a simple matter of prediction of results based on the laws of photophysics combined with the laws of photochemistry.

Unfortunately, many principles are only known in their fundamental form and cannot be directly applied to practical studies. On the other hand, most weathering studies fail because fundamental principles of photophysics have been violated.

1.1 NATURE OF RADIATION

1.1.1 RADIATIVE ENERGY

Visible light, infrared radiation, UV radiation, and γ -rays are each a distinct form of electromagnetic radiation. Each propagate in space as waves of electronic and magnetic fields. Electromagnetic waves can be reflected or refracted at a constant speed:

$$c = v \times \lambda \cong 3 \times 10^8 \text{ ms}^{-1} \quad [1.1]$$

where:

c	radiation velocity (in vacuum)
v	radiation frequency
λ	radiation wavelength

The fundamental theory of electromagnetic radiation developed by Maxwell is used today to explain some properties of radiation such as light spectrum and its diffraction, polarization, interference, etc. But some properties of radiation cannot be explained by Maxwell's theory. A corpuscular description of electromagnetic radiation, developed by Planck to quantum theory is used as a mathematical interpretation of the various properties of radiation. According to the quantum theory, electromagnetic waves carry discrete amounts of energy the magnitude of which depends on their frequency, as stated by Planck's Law:

$$E = h \times \nu \quad [1.2]$$

where:

E energy of radiation
 ν frequency of radiation
h Planck's constant.

Eq [1.2] can be used for calculating the energy of radiation of known wavelength. The excitation energy per mole can be obtained by multiplying molecular excitation energy by Avogadro's number:

$$E = N h \nu = \frac{N h c}{\lambda} = \frac{119627}{\lambda} \left[\frac{\text{kJ}}{\text{mol}} \right] \quad [1.3]$$

where:

E energy of radiation of a given wavelength, λ
N Avogadro's number = 6.022×10^{23} in mol^{-1}
h Planck's constant = 6.63×10^{-34} in J s
 ν frequency of radiation
c velocity of light = 2.998×10^8 in m s^{-1}
 λ wavelength of radiation in nm.

Table 1.1 gives the energy of radiation for some common energy sources.

Table 1.1. Energy of various types of radiation

Type	Wavelength, nm	Energy, kJ/mol
Far UV	100	1196
Vacuum UV	200	598
Mercury lamp	254	471
Solar cut-off	295	406
Mid-range UV	350	341
End of UV range	390	306
Blue/green light	500	239
Red light	700	171
Near infrared	1000	120
Infrared	5000	24
Hard X-rays, soft γ -rays	0.05	2.4×10^6
Hard γ -rays	0.005	2.4×10^7
Laser	matching λ	as calculated per eq [1.3]

- the shorter the wavelength the larger the energy of radiation
- an unfiltered mercury lamp has radiation of higher energy than sunlight
- visible light and infrared radiation both carry energy which can be utilized during photochemical processes (see below)
- x-rays and γ -rays have so much higher energy than sunlight. Thus, the results of exposure are not comparable.

Table 1.2 shows the strength of selected bonds.

Table 1.2. Bond strength in polyatomic molecules

Bond	Strength, kJ/mol ⁻¹	Does sunlight have energy to break the bond?
C – H	420-560	no
C – C	300-720	depends on other substituents
C – Cl	320-460	depends on other substituents
C – N	120-300	yes
C – O	~1000	no
C = O	500-700	no
H – O	370-500	in most cases no
O – O	150-210	yes
S – O	>550	no
Si – Si	330-370	yes

PRINCIPLE OF DEGRADATION

“The amount of energy absorbed by a molecule must exceed the bond energy to cause degradation”

This principle of degradation carries two important messages:

- energy must be absorbed by a molecule for it to make any changes in molecular structure. This is the subject of further discussion in Section 1.2.
- a change in the energy of radiation source will affect weathering.

The radiation frequency is determined by the conditions under which it was formed. A hypothetical black body was postulated by Planck and used in the development of the law which bears his name. The black body, it is postulated, can absorb and emit radiation of any wavelength. Its characteristics are shown in Figure 1.1.

When the temperature of the radiation source increases, its emission spectrum is shifted to the left, meaning that it emits more UV and visible light. Figure 1.1 illustrates that the wavelength (or frequency of radiation) depends on the conditions of emission.

1.1.2 RADIATION INTENSITY

Table 1.1 indicates that the energy of laser light is the same as the energy of visible light or UV (depending on wavelength). But the fact that laser light is substantially more intense (focused or concentrated) is central to the following discussion.

Table 1.3 shows some units of radiation. Laser emits radiation from 1 mW (lasers frequently used in optical experiments) to 10 W (moderately powerful argon laser) and beyond. This power is emitted onto a very small surface area (laser light has high coherence, monochromaticity, and a small beam width) usually in the range from 10 μm² to 1 mm². Irradiance is calculated to be in the range of 10⁷-10⁸ W m⁻² (in fact the illuminated surface area is limited by and equal to the wavelength of radiation, and power can be as large as 100 W giving an irradiance of 10¹³ W m⁻²). For example, laser irradiance is

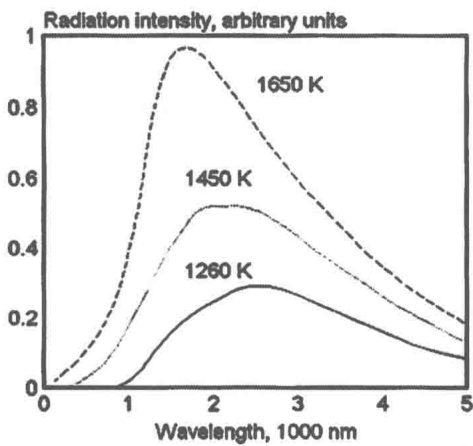


Figure 1.1. Radiation intensity vs. radiation wavelength and black-body temperature.

Table 1.3. Intensity of radiation

Quantity	Unit
Radiant energy	J
Radiant density	J m ⁻³
Radiant flux	W
Irradiance	W m ⁻²

$1.2 \times 10^{10} \text{ W m}^{-2}$ in the case of lasers used for welding.¹ If we compare these values with the mean intensity of sunlight on the Earth's surface (in the range of 10^3 W m^{-2}), it is easy to understand the difference between these two sources of radiation and to explain the effects produced (surface etching by laser beam versus minor changes or no changes at all by sunlight).

This illustrates the importance of the conditions under which the experiment is run and reported. It is useful to pursue the laser example. Laser light delivers 10^{12} to 10^{17} photons/cm³. At this intensity, several photons will react with a single atom causing high levels of excitation. Laser radiation also induces very strong electric fields which can be as much as 100 gigavolts per meter. This inevitably causes changes in orientation, dipole formation, ionization, etc.

The use of pulsed lasers, with their highly ordered (polarized) beams, can selectively excite the single isomer (in the mixture) which has the right configuration for energy absorption. This is why irradiation by chaotic radiation (e.g., sunrays) will

produce totally different results than radiations of high intensities (e.g., lasers).

The xenon lamp does not have enough energy to propagate through the entire thickness of a material nor can it excite so many atoms at once. The consequence of increasing irradiance in a Weather-O-Meter from 0.35 W m^{-2} which is the typical UV radiation of daylight, to higher values is difficult to predict because the change in irradiance does not simply increase the number of excited molecules but also causes the random formation of higher excited states. The proportion of both is difficult to predict.

1.1.3 RADIATION INCIDENCE

Two processes, reflection and scattering, determine the amount of energy crossing a surface of a specimen exposed to radiation. The geometrical relationship between incident, transmitted, and reflected beams is given by Snell's law:

$$n_1 \sin \theta_1 = n_2 \sin \theta_2 \tag{1.4}$$

where:

- n_1 and n_2 refractive indices
- θ_1 and θ_2 the angles illustrated in Figure 1.2.