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THE CHEMISTRY AND PHYSICS OF COATINGS

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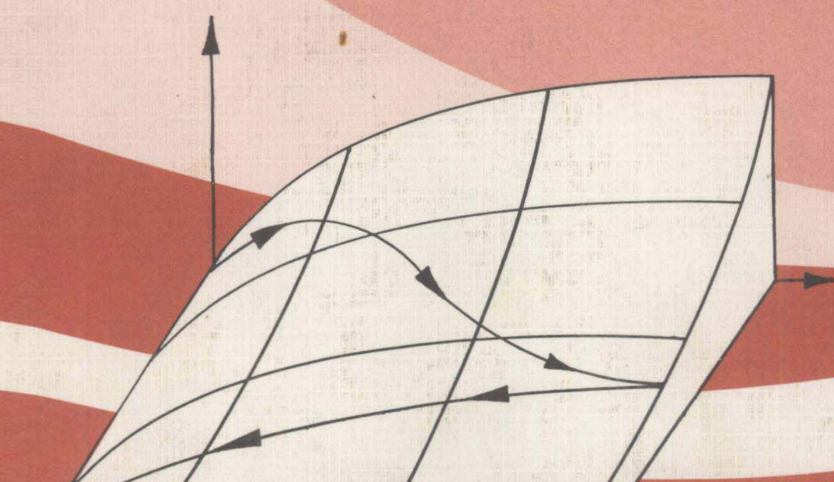

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Preface

This book is intended to expose some of the fascinating science encountered in the Coatings Industry to an audience well versed in chemistry, but perhaps having only nodding acquaintance with polymer science.

Though painting is one of the oldest polymer-based activities, it is also at the forefront of technology, and is an indispensable part of many manufacturing and construction processes. My fellow contributors and I describe, in simple terms, some of the remarkable variety of chemistry and physics which is called on to support the constant innovation in the Industry, and touch on the commercial and legislative background, without the extensive treatment of paint formulations for specific markets which forms a major part of most coatings text books.

The book is broadly organised in three sections. The first deals with economic and environmental aspects of the Coatings Industry, the second with the physics, and the third with the chemistry of coatings. Since it may be difficult for the uninitiated reader to grasp the contents of one section without some knowledge of the phenomena and terminology described in the others, we seek his forbearance and provide a glossary. A second purpose of the glossary is to supply systematic equivalents for the trivial chemical names frequently used in the Industry.

My co-authors are technologists, managers, and consultants within the industry, and I am indebted to them for finding time in their busy programmes to prepare their contributions. Any merit the work may have is due to them, whilst discontinuities and omissions are mine. We are grateful to Courtaulds Coatings (Holdings) Ltd. for its support of the work.

A.R. Marrion

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Chapter 1

Economics and the Environment: The Role of Coatings

A. MILNE

INTRODUCTION

The principal concerns of our confused world are still the fundamental ones of food, shelter, and warmth, aggravated by an awareness of a growing human population, its economic and material well-being, and even survival, set against the finite resources of non-renewable fossil fuels and minerals, and the unequal access to them. World population is about 5.5 billion and growing at about 2% annum^{-1}, giving a doubling period of 35 years. Global energy production is about 8000 million tonnes oil equivalent (TOE), which is an average of 1.5 t person^{-1} highly unevenly distributed.

The Times Atlas gives the energy distribution shown in Table 1.1, within which there are even greater extremes. Norwegians, for example, are amongst the 8 t consumers, but they also export a further 16 t head^{-1}, and import an equivalent value in consumer goods.

As a simple comparison, a car-owner doing 15 000 miles annum^{-1} at 30 miles gallon^{-1} (Imp) is using rather more than 0.5 t of crude oil on motoring alone.

There is a close relationship between energy consumption, gross

Table 1.1 *Distribution of per capita Global Energy Consumption*

Population %	*Tonnes Oil Equivalent*
6.3	>8
21.3	2–8
64.3	0.2–2
7.8	<0.2

domestic product, and standards of living. There is a remarkable consistency, for example, in the paint and coatings consumption of the developed world (Table 1.2). It is difficult, however, to see how the aspirations of two-thirds of the doubled world population, consuming less than 2 TOE can be satisfied, as well as satisfying the other demands of energy and resource conservation, acid rain reduction, and global warming.

Table 1.2 *Global paint market*

Territory	*Production* $/10^6$ t	*Population* $/10^6$	*Per capita* /Kg year^{-1}
USA	4.9	250	20
EEC	5.3	340	15.6
Former USSR	3.3	220	15
Japan	1.9	120	15.8

What has all this to do with coatings? A great deal. Somewhat serendipitously, but from historically very sound roots, the coatings industry finds itself an inconspicuous but significant contributor to the solution to some of the problems. We are able to say, with a degree of complacency, that we have always been in the business of conservation as well as decoration. We are not, however, allowed that degree of complacency. Seen from the outside as major users of heavy and toxic metals, volatile hydrocarbons, halogenated monomers and polymers, highly reactive chemicals, and carcinogens, we are perceived as part of the problem rather than as part of the solution. Part of the purpose of this book will be to see how the industry can rise to the challenge of changing priorities and demands being put upon it. Increasingly, environmental concern is followed by legislative constraints. The original concerns of the environmental movement, for example, were with the basic extractive industries, wood, water, coal, iron, and agricultural products, and more recently with oil, gas, uranium, and renewables and non-renewables of all kinds. What follows in this book is an outline of some of the ways in which the industry is responding, and can respond, to the changing demands being put upon it. For the more fortunate 20% of the world population, for example, with a disposable energy budget of 5–8 TOE head^{-1}, it is not difficult to make alternative choices and there is an increasing preference for, and an increasing value being put upon, clean air, clean water, natural beauty, and an increasing willingness to pay for them. No doubt these would be preferences of the other 80% also!

The most economic solution to most problems, following directly from the Second Law of Thermodynamics, is the reduction and elimination of pollution at source. Indeed, if we can express our problem in concentration terms we can get a first approximation to the cost, as in equation (1):

$$\Delta G = RT \ln C_1/C_0 \qquad (1)$$

where ΔG is Gibbs free energy change, R is the Boltzmann constant, T is absolute temperature, and C_1 and C_0 are the starting and finishing concentrations, always remembering that in the real world, efficiencies of real reactions are rarely more than 20%. That gives us a molar cost for pollutant and effluent recovery. Hence the emphasis on total elimination at source, and the emphasis in this book of strategies for avoidance of problems. Forethought would seem to be one of the few thermodynamically efficient processes! If the objective is energy conservation then recovering dilute liquid and gaseous pollutants very quickly becomes self-defeating in energy terms.

In the following chapters therefore, the authors respond to demands to remove solvents, by formulating coatings on liquid oligomers, use little or no solvent, as powder coatings without solvent, use liquid only at elevated temperature for a few minutes, or in the form of aqueous latices or non-aqueous dispersions. There is an emphasis on doing more with less by radical improvements to the performance of coatings. Each new technique and material creates its own problems and opportunities. Highly reactive monomers and oligomers are more likely to be hazardous almost by definition, and water, from an environmental viewpoint, would seem to be an ideal dispersant in everything except boiling point and latent heat of evaporation, while under ambient conditions it brings its own problems at low temperature and high humidity.

FUNCTIONS OF COATINGS

Why coatings? Why not simply paints? Historically there was no distinction. Leonardo da Vinci used essentially the same materials and methods of preparation and application as the house painters of his day, and the present professional association in the UK, 'The Oil and Colour Chemists Association', is only now seeking a title more in keeping with the present role of its members. When we make the distinction between paint and coatings we imply a distinction between functions which are largely decorative and aesthetic in the former, and have a more serious purpose in the latter. Indeed there are several serious purposes, and they would usually be expressed in specific terms. Some of the specific purposes are:

the prevention of corrosion, either actively, by the inclusion of anticorrosive pigments, or passively by providing an adhesive and impermeable barrier; providing either slip or slip resistance; impact and abrasion resistance; resistance to contamination; or hygienic properties, such as fungal, bacterial, or fouling resistance. Whatever the desired end property, what they have in common can in general be expressed in economic terms and calculated in terms of:

(i) energy savings,
(ii) reduced down-time,
(iii) increased life-time,
(iv) capital savings,
(v) materials substitution.

The distinction between paint and coatings, even in economic terms is more apparent than real, since even aesthetic choices can be accommodated in standard economic theory in terms of willingness to pay for some benefit, or willingness to pay for the elimination of some undesired consequence, the 'Hedonistic Price Principle'.

Easiest to calculate are the immediate and direct benefits, the producer surplus and the consumer surplus, since they are the everyday transactions of supplier and consumer. We can illustrate (i)–(iv) above for the case of antifouling use, for example, since this is one of the few areas where the benefits are most readily calculated, in energy and monetary terms, and since all antifoulings (to date) have used biocides which come under specific legislation, to which both suppliers and users have had to accommodate. Antifouling coatings are thus a paradigm for many of the constraints being imposed by increasingly stringent legislation, one of which is the possibility that when other and incompatible preferences are being expressed, the solution is sub-optimum in the very area for which the coating was designed, *i.e.* maximum energy conservation at least cost. As coatings, antifoulings also illustrate at least two of the less expected functions which can be built into coating materials. Permanence is usually regarded as a desideratum in a coating; self-polishing antifoulings are designed to disappear, and smoothness, usually an aesthetic consideration in a coating, is here intimately connected to the turbulent flow over the surface, again with desirable energy-saving consequences. Marine fouling and hull roughness increase the drag on vessels, and that increase can be readily translated into fuel consumption. The world fleet of some 39 000 vessels burns 184 million t of heavy fuel oil, at a cost of $100 (US) t^{-1}, or $18.4 billion. The base line, the cost of doing nothing, would mean that the whole fleet would burn 40% more fuel, an increase of 72 million t. In practice since most vessels operate close to maximum power, the fleet would have to increase by a similar amount. For comparison, the UK sector of the North Sea produced at maximum, just over 100 million t of oil annum^{-1}.

The increase in the price of oil, in 1973, from about £5.00 t^{-1} to £50.00, and in 1979 to £100 t^{-1}, required a radical improvement in antifouling performance and in antifouling lifetime. The improvement took the form of the self-polishing tri-butyl tin copolymer antifoulings. Improvements in fouling protection, and in ship roughness, save 4% of fuel, 7.2 million t, valued at $720 million.

At the same time ship-owners demanded much longer lifetimes between drydocking. Traditionally vessels had docked on an annual basis. This was increased to 30 months and the current maximum is 5–7 years. The average improvement in 10 years (1976–86) was from 21 to 28 months. This has a value of $820 million. Since average docking was for about 9 days, two days annum^{-1} extra trading was also available, worth $420 million. Capital savings are more difficult to calculate but a typical 200 000 DWT tanker will carry about 1 million t annum^{-1}, so the above 7.2 million t oil saving is, itself worth 7 tankers at $80 million each, worth in annual opportunity cost some $500 million. So, for a modest improvement in antifouling performance, a total saving of about $2.5 billion is obtained. This is obtained also at no nett increase in price of antifoulings. The global antifouling market is about 25 million l, at $8 l^{-1}, so the $2.5 billion benefit is purchased for approximately $200 million, a benefit-cost ratio of 11.5. Both producers (the coatings manufacturers) and the consumers (the ship-owners and operators) are happy. In the language of cost-benefit analysis there is clearly a producer and consumer benefit. Resources are saved (oil and steel to make seven vessels), and those very environmental aspects on which such weight is placed, acid rain and the alleged 'greenhouse effect', benefit to the extent of 560 000 t and 23 million t respectively. But the producer and consumer are no longer the only participants in the transaction. Tri-butyl tin is a 'Red List' pesticide, and it has measurable environmental effects both on economic crops (oysters) and non-economic species such as the dog-whelk, *Nucella lapillus*. No one, it is thought, has yet evaluated these environmental impacts, but the case serves to illustrate some of the ramifications of environmental risk-benefit analysis. For example, using the 'Hedonistic Price Method', one would be required to put a value on the pleasure of finding dog-whelks on a particular stretch of coast, or to put a value on bio-diversity. Exactly how much pleasure, to how many people, for what period is discussed in the literature. Alternative methods available are the 'Contingent Valuation Method', which claims to be able to put a value on the existence of a resource whether one uses it or not, or might wish to in the future, and the 'Replacement Cost Method', which attempts to evaluate the cost of recreating a damaged habitat or ecosystem. Consideration of human safety and health require one to estimate a value-of-statistical-life. This is commonly done in the transport field where the values of investment in accident prevention have to be calculated, but the methods apply equally in the fields of industrial accidents and the handling and use of hazardous materials.

This would seem to take us into territory remote from the design of coatings fit for a variety of purposes, but the process has been considered for one of the many raw materials in the coatings field, and will be so increasingly in other areas. Such considerations are clearly the preoccupations of those 20% of the population burning 8 t of oil equivalent; they are unlikely to feature strongly in the minds of those burning less than 2 t.

Item (v) in the above list of criteria, materials substitution, is by far the most important aspect of the 'added value' of coatings. There is an inverse relationship between the value and abundance of metals in the Earth's crust. Platinum, gold, silver, copper, and tin, are rare, precious, and coinage metals, comprising no more than 71 $g\,t^{-1}$ of the Earth's crust, while iron and aluminium at 5.8% and 8.8% of the Earth's crust respectively are by far the most abundant. Coated steel performs many of the functions which would otherwise require much more expensive metals and alloys, such as copper, bronze, or stainless steel or much more expensive coating processes such as ceramic coating, electroplating with expensive metals such as nickel or chromium, vacuum metallising, or plasma coating. Coatings therefore fulfil some of the ambitions of the alchemists, in transmuting some of the properties of base metals into gold. This is 'added value'. Global production of iron and steel is about 700 million t $annum^{-1}$, or about 9 t $person^{-1}$ (average $lifetime)^{-1}$ of 70 years. Iron and aluminium occur in large deposits, in high concentration at or near the Earth's surface. The major component of the cost is the energy required to reduce them to the metallic state. They are thermodynamically unstable in our oxidising atmosphere, and tend to revert to the original oxides, as corrosion products. The materials thus substituted at great energy cost, require to be conserved.

We are also highly uneven in our admiration of corrosion products. We admire the patina on copper and bronze, but have only a limited admiration for galvanised iron, and none at all for rust. There was an attempt some years ago amongst new-brutalist architects to get us to like rust, and the metallurgists complied by producing a uniformly rusting steel, Cor-Ten® steel; but we refused to love it. So one of our primary coatings objectives has been, since the Bronze Age, the substitution of semi-precious metals by iron and steel. We can get some idea of how much this is worth to the users in the form of an approximate cost-benefit.

At the stage of iron ore, about 50% Fe, the cost of iron is about £13 t^{-1}. The energy requirement is 60–360 GJ t^{-1}, and at a cost of 2.2 p (kW h^{-1}), or an oil price of £67 t^{-1}, the energy content of a tonne of steel is about £100, *i.e.* most of the cost is 'pure' energy. The added value of a coating is difficult to calculate, depending both on the gauge of the steel, the thickness of the coating and the end use. For some applications the uncoated steel would be of zero value even for the shortest period of time, *e.g.* a beer can uncoated inside or outside, but for a long term use, a bridge or a ship say, calculation is possible.

An uncoated ship, in sea-water would suffer severe corrosion in five years or less. An adequately coated one might avoid serious repair for 15–25 years. A super-tanker might cost $80 million. If, by coating the lifetime is tripled, then the saving is $160 million on 16 000 t of steel, or $10 000 t^{-1}. The coating enhances the value by fifty times. If the steel plate is 15 mm thick, and protected on both sides with 250 μm of a polymer coating, then 120 kg (1 m^2), of fabricated steel, worth $1250, is protected for 25 years for about $2 of polymer, a benefit-cost ratio of 600 times.

In those areas where coated steel replaces, say, stainless steel, similar benefits are achievable. Indeed, in the area of chemical resistance, coated mild steel is suitable for most likely cargoes, with stainless steel used for only the most aggressive chemicals. In the case of both steel and aluminium, the energy required for remelting is a small fraction of that required for the original reduction. Coating, in both cases, ensures that almost the total original weight of metal is available for recycling. These two illustrations of direct energy saving and resource conservation are the principal contributions of coatings to the community.

Chapter 2

Volatile Organics—Legislation and The Drive to Compliance

D.J. WIGGLESWORTH

ATMOSPHERIC POLLUTION AND THE COATINGS INDUSTRY

Volatile Organic Compounds (VOCs) are substances which contain carbon and which evaporate readily, though a few of these materials such as the oxides of carbon are not generally classed as VOCs. Most solvents used in paint, perfumes, adhesives, inks, aftershave, *etc.* are VOCs and other VOCs are present in various household chemicals, petrol, dry cleaning fluids, car exhaust fumes, cigarette, and bonfire smoke, *etc.* Within Europe some 40% of all VOC emissions to the atmosphere arise from natural sources such as that invigorating smell of pine needles in some forests, emissions from animals and agriculture in general, *etc.* Some estimates of total world VOC emissions put the natural contribution at around 90%. Most of the adverse effects of VOC emissions arise because of the type of VOC, the local concentration, or the combination with other air pollution, and because of the concentration effect much of the difficulty caused by VOCs arises from anthropogenic releases.

Carbon dioxide, nitrogen oxides (NO_X), and sulfur dioxide are not VOCs but are also emitted to the atmosphere and, either alone or in association with VOCs, contribute to a range of current or potential atmospheric pollution effects, the most well known examples of which are reviewed below.

The Hole in the Ozone Layer

Some 15 to 30 miles above the Earth, in that level of the atmosphere called the stratosphere, there is a layer in which the concentration of ozone is