Paint and surface coatings

Theory and practice

Second edition

Edited by
R Lambourne
and
T A Strivens

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Preface to first edition

For many years I have felt that there has been a need for a book on the science and technology of paints and surface coatings that would provide science graduates entering the paint industry with a bridge between academia and the applied science and technology of paints. Whilst there have been many excellent books dealing with the technology there have not to my knowledge been any that have sought to provide a basic understanding of the chemistry and physics of coatings. Many of the one-time standard technological texts are now out of date (and out of print), so it seemed appropriate to attempt to produce a book that will, I hope, fill a gap. Nevertheless, it was with some trepidation that I undertook the task of editing a book covering such a diverse technology. The diversity of the technology is such that rarely will an acknowledged expert in one aspect of the technology feel confident to claim expertise in another. It therefore seemed to me that a work produced by a single author would not meet the objectives I had in mind, and I sought the help of friends and colleagues in the industry to contribute individual chapters on subjects where I knew them to have the requisite expertise. Fortunately, I was able to persuade sufficient contributions from individuals for whom I have the highest regard in respect of their knowledge and years of experience within the paint industry to satisfy myself of the ultimate authenticity of the book as a whole.

However, because of limitations of space it is impossible for a book of this kind to be completely comprehensive. Thus I have had to make decisions regarding content, and have adopted a framework which gives more space, for example, to the physics of paint and the physical chemistry of dispersions than most books of this kind. In doing so I have had to reduce the breadth (and in some cases the depth) of treatment of specific technologies. Thus, whilst the chapters on automotive painting and architectural paints are fairly detailed, the treatment of general industrial finishing is less an 'in depth' account of specific technologies, but is intended to illustrate the very wide range of requirements of manufacturing industry and the problems the paint technologist may encounter as a result of this.

In chapters dealing with the fundamental principles underlying the technology authors have been invited to provide critical accounts of the science and technology as it stands today. This is reflected in the extensive lists of references to original work mostly published within the last decade. It is hoped that readers wishing to delve further to increase their understanding will find these references a valuable source of information.

It is important to record that apart from the authors, a number of individuals have contributed to the production of this book. I would like to record my thanks to Dr Gordon Fettis, Research Manager of ICI Paints Division, for his support and encouragement from its inception, and for the use of many of the facilities of ICI in the production of the manuscript. Thanks are also due to Mrs Millie Cohen (of ICI) and Mrs Kate Slattery (of Bristol University) who between them typed the major part of the manuscript.

R Lambourne

Preface to second edition

When I was invited to edit the second edition of this book, I took the decision to retain as far as possible the original team of authors. In addition, valuable new chapters (20 and 21) on the use of computers in the paint industry and health and safety have been contributed by Mr J Bentley and Mr G R Hayward, respectively. Owing to the unfortunate and untimely death of Miss J F Rolinson, Chapter 3 on pigments has not been revised. Instead, thanks to Dr A G Abel, a completely new chapter on this subject has been provided.

I believe this resulting new edition will provide a useful text for those wishing to explore various aspects of paint technology and its underlying science, whilst its literature references will provide a useful start to the study of any particular aspect of that technology.

I would like to pay tribute to the team of authors, who have provided me with revised or new chapters, and for their support, help and encouragement in producing this second edition.

T A Strivens

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Paint composition and applications — a general introduction

R Lambourne

1.1 A short history of paint

Primitive men are credited with making the first paints about 25 000 years ago. They were hunters and cave dwellers and were probably inspired by the rock formations of their cave walls to outline and colour the shapes of the animals they hunted. It is possible that by creating these images they thought their power over their prey would be increased.

Chemical analysis of cave paintings discovered at Altamira (Spain) and Lascaux (France) show that the main pigments used by Palaeolithic artists were based upon iron and manganese oxides. These provide the three fundamental colours found in most cave paintings, namely black, red, and yellow, together with intermediate tints. Carbon from burnt wood, yellow iron carbonate, and chalk may also have been used. Surprisingly, there is no trace of a white pigment (the commonest pigment in use today) at Lascaux, where the natural colour of the rock was used as a pale background. However, white pigments do occur in some prehistoric paintings in Africa.

These earth pigments were ground to a fine powder in a pestle and mortar. Naturally hollowed stones are thought to have been used as mortars and bones as pestles, following the finds of such articles stained with pigments. The powdered pigments were probably mixed with water, bone marrow, animal fats, egg white, or vegetable sugars to form paints. They were applied by finger 'dabbing', or crudely made pads or brushes from hair, animal fur, or moss. Cave paintings have survived because of their sheltered positions deep in caves which were subsequently sealed off. These paints have very poor durability, the binders serving merely to make the pigments stick to the cave walls.

The Egyptians developed the art of paint-making considerably during the period circa 3000–600 BC. They developed a wider colour range of pigments which included the blues, lapis lazuli (a sodium silicate–sodium sulphide mixed crystal), and azurite (chemically similar to malachite). Red and yellow ochres (iron oxide), yellow orpiment (arsenic trisulphide), malachite green (basic copper carbonate), lamp-black, and white pigment gypsum (calcium sulphate) all came into use during this period. The first synthetic pigment, known today as Egyptian Blue, was produced almost 5000 years ago. It was obtained by calcining lime, sodium carbonate malachite, and silica at a temperature above 830 °C. The Egyptians also developed the first lake pigments. These were prepared by precipitating soluble organic dyes onto an inorganic (mineral) base and 'fixing' them chemically to form an insoluble compound. A red dye obtained from the roots of the madder plant was used in the first instance. This is no longer used other than in artists' colours ('rose madder') because it fades rapidly on exposure to sunlight, and it has been replaced by alizarin. Lake pigments still, however, represent an important group of pigments today. Red lead was used in preservative paints for timber at this time, but was more extensively used by the Romans. The resins used were almost all naturally occurring gums; waxes which were applied molten as suitable solvents were unknown. Linseed and other drying oils were known, but there is no evidence that they were used in paints.

The Greeks and Romans in the period 600BC–AD400 almost certainly appreciated that paint could preserve as well as decorate objects. Varnishes incorporating drying oils were introduced during this period. However, it was not until the thirteenth century that the protective value of drying oils began to be recognized in Europe. During the Middle Ages much painting, especially on wood, was protected by varnishing. The varnish was made by dissolving suitable resins in hot linseed, hempseed or walnut oil, all of which tend to darken with time.

By the late eighteenth century, demands for paints of all types had increase to such an extent that it became worthwhile for people to go into business to make paint and varnishes for others to use. In 1833, J W Neil advised varnish makers always to have an assistant present during the varnish making process, for safety. 'Never do anything in a hurry or a flutter . . . a nervous or timorous person is unfit either for a maker or assistant, and the greatest number of accidents occur either through hurry, fear or drunkenness.' This admonition is indicative of the increase in scale of manufacture and the dangers of use of open-pan varnish kettles.

The industrial revolution had a major effect on the development of the paint industry. The increasing use of iron and steel for construction and engineering purposes resulted in the need for anti-corrosive primers which would delay or prevent rusting and corrosion. Lead- and zinc-based paints were developed to fulfil these needs. It is interesting to note that one of the simplest paints based upon red lead dispersed in linseed oil is still probably one of the best anti-corrosive primers for structural steel. Lead-based paints are being superseded not because better products have been produced, but because of the recognition of their toxicity and the hazards attendant upon their use.

An acceleration of the rate of scientific discovery had a growing impact on the development of paints from the eighteenth century to the present day. Prussian blue, the first artifical pigment with a known chemistry, was discovered in 1704. The use of turpentine as a paint solvent was first described in 1740. Metal driers, for speeding up the drying of vegetable oils, came into use about 1840.

The basis of formaldehyde resin chemistry was laid down between 1850 and 1890 although it was not used in paints until the twentieth century. Likewise, it was discovered in 1877 that nitrocellulose could be made safe to use as a plastic or film, by plasticizing it with camphor, but it was not until after the First World War that it was used in any significant amount in paints. The necessary impetus for this to happen came with the mass production of the motor car. Vast quantities of nitrocellulose were manufactured for explosives during the war. At the end of the war, with the decline in the need for explosives, alternative outlets for nitrocellulose needed to be found, and the mass production of motor cars provided the necessary market. The war had accelerated the exploitation of the discoveries of chemistry and the growth of the chemical industry. New coloured pigments and dyestuffs, manufactured synthetically, became available, and in 1918 a new white pigment, titanium dioxide, which was to replace white lead completely, was introduced. Titanium dioxide improved the whiteness and 'hiding' or obliterating power of paint, but when originally introduced it contributed to more rapid breakdown of paints in which it was used because of its photoactivity. Subsequent research has overcome this problem and ensured that the modern pigmentary forms of titanium dioxide can be used in any type of composition without suffering any disadvantage of this kind.

The most recent influences on coating developments are related to environmental considerations, and the need to conform to health and safety legislation. Cost/benefit relationships have also become more important in an increasingly competitive world market and have influenced formulation practice markedly.

Subsequent chapters of this book will be largely concerned with developments that have taken place in the twentieth century, of which most have occurred within the last fifty years.

1.2 Paint or surface coating?

The terms 'paint' and 'surface coating' are often used interchangeably. Surface coating is the more general description of any material that may be applied as a thin continuous layer to a surface. Purists regard the term 'surface coating' as tautological. However, it has been used widely in the UK and in North America to distinguish painting from other forms of surface treatment, such as electroplating, anodizing, and the lamination of polymer film onto a surface. Paint was traditionally used to describe pigmented materials as distinct from clear films which are more properly called lacquers or varnishes. We shall be most concerned with paint in the context of this book; but, as we shall see, modern painting processes may include composite systems in which a total paint system comprises several thin films, some, but not all, of which may be pigmented. We shall use both terms as appropriate to the context in which specific paint compositions are being discussed.

The purpose of paints and surface coatings is two-fold. They may be required to provide the solution to aesthetic or protective problems, or both. For example, in painting the motor car the paint will be expected to enhance the appearance of the car body in terms of colour and gloss, and if the body is fabricated out of mild steel it will be required to give protection against corrosion. If the body is formed from glass fibre reinforced plastic the paint will only be required for aesthetic purposes. There are obviously very sound economic reasons why it is attractive to colour only the outer surface of articles that might otherwise be self-coloured by using materials of fabrication, e.g. plastics that are pigmented, particularly if a wide choice of coloured effects is required. This topic will be developed in the chapters on paints for specific markets (Chapters 9–13).

In considering the nature of paints it will become abundantly clear that the rela-