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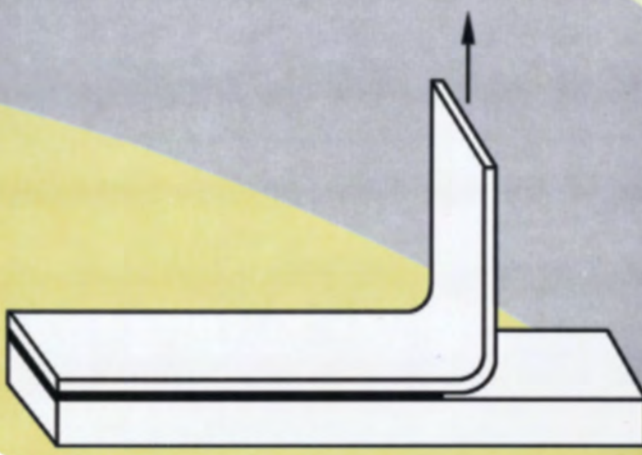
John Comyn



ADHESION SCIENCE

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THE ROYAL SOCIETY OF CHEMISTRY
Information Services

ISBN 0-85404-543-0
A catalogue record for this book is available from the British Library

Published by The Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge CB4 4WF, UK

Typeset by Vision Typesetting, Manchester
Printed by Athenaeum Press Ltd, Gateshead, Tyne and Wear, UK

Preface

The use of adhesives is widespread and growing, and there are few modern artefacts, from the simple cereal box to the magnificent Boeing 747, that are without this means of joining. This book sets out to explain the principles which underlie adhesive bonding, and other adhesion technologies such as sealing, printing and painting.

In about 25 years of researching adhesion, I have had to bear it in mind that engineers might need to understand my writings. I like engineers and have a high regard for the intellectual weight of their subject, but here I write unashamedly for chemists.

The structure of this book is that some basic polymer chemistry and theories of adhesion are dealt with in Chapter 1, and Chapter 2 basically describes the technology of surface treatment. The next four chapters describe the chemistry of adhesives and adhesion promoters, followed by a chapter on the rapidly developing field of surface analysis. Physical chemistry comes to the fore in Chapter 8 with surface thermodynamics. Engineering principles appear in Chapter 9, showing how the success or failure of adhesives chemistry can be assessed by measuring joint strengths. The major limitation on the use of adhesives in engineering structures is water, which is the main concern in Chapter 10.

As is appropriate for an introductory book, it is not fully referenced but has a recommended reading list. One disadvantage of this is that authors, many of whom are my friends and colleagues, are not directly acknowledged. However, any reader wishing to enquire further via the bibliography will soon find references to the original papers.

No scientific book is ever written without the help of others, and in this respect I thank Dr. D. M. Brewis of Loughborough University and Mr. T. P. A. Comyn of Leeds University for reading and commenting on the manuscript. I am most grateful to CSMA Ltd. for providing the XPS spectra of brass and glass in Chapter 7.

Adhesion is no different from other areas of science in that the ultimate aim is to formulate laws. So far we have written the 1st law of adhesive bonding, which states that '*If all else fails use bloody great nails*'.

John Comyn

Contents

Chapter 1

Introduction to Adhesion and Adhesives

Glues have been around for a long time; the ancient Egyptians used them in veneering the treasures of Tutankhamun and the ancient Greek word for glue is κολλα, from which we get colloid. In all centuries up to and including the 19th, glues originated from plants and animals; during the 20th century, however, synthetic chemicals have largely taken over, and the more respectable name of adhesive has been introduced. Animal glues were mostly based on mammalian collagen, which is the main protein of skin, bone and sinew, and the plant kingdom provided starches and dextrins from corn, wheat, potatoes and rice.

Nowadays adhesives are used in all types of manufacture, and in many cases have displaced other means of joining. A range of adhesives (hot melt, vegetable glues and emulsions) are used in making cardboard boxes, with rarely a staple to be seen. Apart from expensive handmade shoes, footwear is now adhesively bonded using hot melt adhesives for the basic construction, natural rubber latex for linings, and solvent based polyurethanes or polychloroprenes for sole attachment. Bookbinding is by hot melt adhesives.

Adhesive bonding is used increasingly in the construction of aircraft. Structural bonding began with the World War II De Haviland Mosquito, which was made of plywood. Modern civil aircraft are basically made of aluminium alloy, and rubber modified epoxide adhesives are increasingly used.

Rubber-to-metal bonds are used for engine, transmission and exhaust mountings in automobiles and in railway bogie suspensions. Mass produced car bodies are made of spot-welded mild steel; weight and fuel consumption can be reduced with aluminium bodies, which are more difficult to spot-weld. The large-scale bonding of car bodies is a prize that awaits the adhesives industry. A recent achievement was the bonding of steel rails in the new Manchester tramway.

Human beings can be repaired by adhesives. This includes the use of UV-curing cements in dentistry and acrylic bond cements in orthopaedic surgery. It has been said that cyanoacrylate adhesives were used for short term repairs during the Vietnam War.

Adhesives are not the only materials that must stick or adhere. Adhesion is essential for printing inks, sealants, paints and other surface coatings, and at interfaces in composite materials such as steel or textile fibres in rubber tyres and glass- or carbon-fibres in plastics. Mother nature uses adhesion rather than mechanical fasteners (nuts and bolts, nails, staples, *etc.*) in constructing plants and animals, and some animals are masters at the exploitation of adhesion. Here I am thinking of barnacles sticking to anything that floats in the sea and the remarkable ability of many insects to walk on ceilings.

A disadvantage of adhesives as a means of joining is that they are generally weakened by water and its vapour. Also, their service temperature ranges are less than for metal fasteners (nuts, bolts, welds, staples, *etc.*), being limited by their glass transition temperature and chemical degradation. Advantages include their ability to join dissimilar materials and thin sheet materials, the spreading of load over a wider area, the aesthetic and aerodynamic exteriors of joints, and application by machine or robot.

BASIC PROPERTIES

What is an adhesive and what are its basic properties? A definition is *a material which when applied to the surfaces of materials can join them together and resist separation.* The terms *adherend* and *substrate* are used for a body or material to be bonded by an adhesive. Other basic terms are *shelf-life*, for the time an adhesive can be stored before use, and *pot-life*, the maximum time between final mixing and application.

Basically an adhesive must do two things:

(i) It must wet the surfaces, that is it must spread and make a contact angle approaching zero, as is illustrated in Figure 1.1. Intimate contact is required between the molecules of the adhesive and the atoms and molecules in the surface. When applied the adhesive will be a liquid of relatively low viscosity.

(ii) The adhesive must then harden to a cohesively strong solid. This can be by chemical reaction, loss of solvent or water, or by cooling in the case of hot melt adhesives. There is an exception to this, and

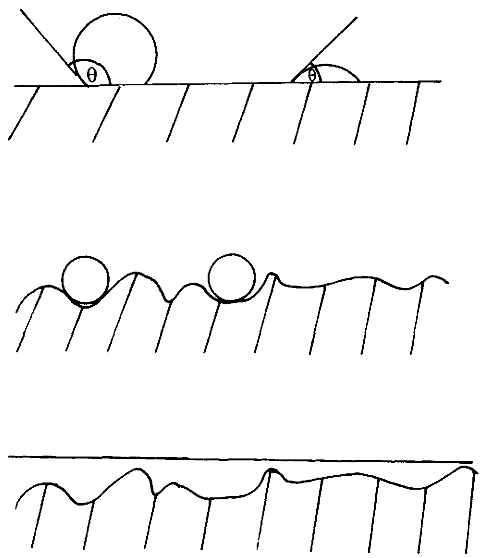

Figure 1.1 *Top: liquid droplets making a high and low contact angle on a flat, solid surface. Centre: high contact angle leading to no spreading on a rough surface. Bottom: wetting on a rough surface.*

that is pressure-sensitive adhesives which remain permanently sticky. These are the adhesives used in sticky tapes and labels.

BASIC CHEMISTRY

All adhesives either contain polymers, or polymers are formed within the adhesive bond. Polymers give adhesives cohesive strength, and can be thought of as strings of beads (identical chemical units joined by single covalent bonds), which may be either linear, branched or crosslinked as illustrated in Figure 1.2.

Linear and branched polymers have similar properties and it is not easy to distinguish them, and they will flow at higher temperatures and dissolve in suitable solvents. These latter properties are essential in hot melt, and solvent-based adhesives, respectively.

Crosslinked polymers will not flow when heated, and may swell, but not dissolve, in solvents. All structural adhesives are crosslinked because this eliminates creep (deformation under constant load). Automotive tyres are crosslinked natural or synthetic rubber, and if they crept they would permanently deform during parking, and a rough ride would follow.