FOOD PACKAGING MATERIALS

Aspects of Analysis and Migration of Contaminants

N. T. CROSBY

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Head of Food Additives, Contaminants and Information,
Laboratory of the Government Chemist, London

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PREFACE

Whilst glass, tinplate and paper have been widely used as food packaging materials for many years, plastics are a relatively recent innovation in this field. Major technological changes can introduce many benefits to mankind but at the same time they are liable to create new problems. Public concern over the use of chemicals and their release into the environment has increased markedly in the last ten years. This concern has been matched by a growth in legislative controls to protect the public in the home, at work and by general restrictions on pollution of the environment. No area is of greater importance than the nation's food supply. Hence the use of new chemicals, even though only in contact with food, as opposed to direct consumption as food additives, has to be examined with great care. Nevertheless, the development of the plastics industry has been a major technological achievement, and applications in the field of food packaging have contributed considerably to the conservation of scarce resources, so vital when the world's population is still increasing at a rapid rate. Furthermore, in protecting the food from contamination by outside chemical or microbiological agents, plastics assist in the development and maintenance of better food hygiene practices; the major area of concern at the present time.

Although plastics (i.e. the polymers) themselves are generally inert, monomers and chemicals used as processing aids may also be present in the finished product. Such chemicals may transfer from the plastic into the food during storage. Although not all such chemicals are harmful, there is a need to restrict the ingress of unnecessary non-nutritive substances into food. This has led to increasing activity from regulatory authorities, analytical chemists and toxicologists in an attempt to define and measure the migration problems and to quantify the risk arising from the use of plastics as food packaging materials. There is clearly no risk to the consumer even from harmful chemicals unless they are actually transferred from the plastic into the food. Hence, theoretical and experimental studies have been pursued to elucidate both the mechanism and the extent of the transfer process.

The science of food packaging is, therefore, truly multidisciplinary in so far as it encompasses parts of all the following activities: plastics and polymer technology, food science, physical chemistry, analytical chemistry, toxicology, national and international legislation—and probably many others too. Each of these subject areas has expanded rapidly in recent years so that an enormous volume of literature has accumulated. From this vast body of information, I have attempted to extract the relevant data likely to be of interest to both administrative and scientific staff in the food and plastics industries. Theoretical concepts and experimental evidence have been collated and assessed critically for the assistance of those working in industry, government or academic fields, who have undergone a basic training in science but have no specialist knowledge of food packaging. Parts of the book may also be of interest to students and those preparing for examinations such as the Mastership in Food Control. Whilst some principles and problems are discussed in depth and the bibliography provides access to an even more detailed treatment for the specialist, the primary aim has been to cover as many aspects of the subject as possible without excessive detail. Preference has been given to the more readily obtainable references whenever possible.

In the United States of America, the Department of Commerce has estimated that 280 kg of packaging materials go into the products used by each American every year. Packaging consumes about 80 per cent of all paper board produced, 65 per cent of all glass, 25 per cent of plastics, 22 per cent of paper, 15 per cent of wood and 7 per cent of steel. Obviously, this includes other areas as well as *food* packaging. However, it does underline the importance of packaging in the economy and the part played by materials other than plastics. Hence, whilst the major portion of the book is devoted to plastics, some consideration has also been given to the more traditional packaging materials such as glass, metals, ceramics and paper.

Most other books currently available have been written by specialists in the fields of plastics and polymer technology. It is hoped that a complementary view as seen by a food scientist and analytical chemist will be of some value.

N. T. Crosby

SPECIFICATION OF CONCENTRATIONS

Trace amounts of additives and contaminants in food are usually specified in terms of parts per million (ppm) or parts per billion (ppb). In scientific and technical journals, however, the system of units known as SI (Système Internationale d'Unités) has now been adopted almost universally. SI is an extension and refinement of the traditional metric system, which is both logical and coherent and possesses many advantages in scientific work. Nevertheless, the above units are still widely used and, in general, are more readily understood. They have been adopted throughout this book. The relationship between the various units is shown below:

$$1\ \text{ppm} \equiv 1\ \text{mg/kg}$$

$$1\ \text{ppb} \equiv 1\ \mu\text{g/kg} \equiv 0{\cdot}001\ \text{ppm}$$

The concentration of vinyl chloride in air or gaseous samples is usually specified as a ratio of volumes rather than as w/v or w/w where:

$$1\ \text{ppm} \equiv 1\ \text{ml/m}^3$$

and

$$1\ \text{ppb} \equiv 1\ \mu\text{l/m}^3$$

ABBREVIATIONS

Å	Angstrom = 10^{-8} cm
A_w	Water activity
ABS	Acrylonitrile butadiene styrene polymer
ADI	Acceptable daily intake
AN	Acrylonitrile
BGA	Bundesgesundheitamt (Federal Health Office of the West German Federal Republic)
BHA	Butylated hydroxyanisole
BHT	Butylated hydroxytoluene
BIBRA	British Industrial Biological Research Association
BPF	British Plastics Federation
b.pt.	Boiling point
BSI	British Standards Institution
b.w.	Body weight
DMA	Dimethylacetamide
DMF	Dimethylformamide
DNA	Deoxyribonucleic acid
ECD	Electron capture detector
EEC	European Economic Community
EVA	Ethylene vinyl acetate copolymer
FAO	Food and Agriculture Organisation of the United Nations
FDA	Food and Drug Administration, USA
FID	Flame ionisation detector
GLC	Gas-liquid chromatography
GM	Global (or total) migration
GRP	Glass reinforced plastics

HDPE	High density polyethylene
HIPS	High impact polystyrene
HSGC	Headspace gas chromatography
i.d.	Internal diameter
IUPAC	International Union of Pure and Applied Chemistry
LDPE	Low density polyethylene
LD_{50}	Dose required to kill 50 per cent of a group of animals
MS	Mass spectrometry
OPP	Orientated polypropylene
PAM	Polyamide
PE	Polyethylene (polythene)
PET	Polyethyleneterephthalate
PIRA	Paper and Board, Printing and Packaging Industries, Research Association
PP	Polypropylene
ppb	Parts per billion ≡ μg/kg
ppm	Parts per million ≡ mg/kg
PS	Polystyrene
PTFE	Polytetrafluoroethylene
PVC	Polyvinylchloride
PVDC	Polyvinylidenechloride
RH	Relative humidity
SAN	Styrene acrylonitrile copolymer
SI	Statutory Instrument
STP	Standard temperature and pressure
THF	Tetrahydrofuran
TLV	Threshold limit value
TWA	Time weighted average
UHT	Ultra high temperature
VCM	Vinyl chloride monomer
VDC	Vinylidene chloride
WHO	World Health Organisation

CONTENTS

Chapter 1

FOOD PACKAGING REQUIREMENTS

INTRODUCTION

From the earliest times Man has had to conserve and preserve his food so that an abundance obtained at harvest, or following a successful hunt, can be stored for use at a later date as a protection against famine until further supplies are obtained. Subsequent harvests, owing to adverse weather conditions, may be poorer in quality or quantity. Even today, the need to ensure an adequate supply of safe and nutritious food is a major problem for the developing countries throughout the world. Industrialised nations, such as those in the European Economic Community, have attempted to offset the vagaries of climate, which make food supplies so unpredictable, through a policy of financial intervention and market organisation designed to offer a fair standard of living to those working on the land as well as to ensure reasonable prices to consumers.

Few people would question the importance of good food, in adequate amounts, for the preservation of health. Wealthy, industrialised countries can 'make good' any shortages in supplies through imports. Currently, in the United Kingdom, about half of our food is imported. Hence, prime agricultural products worldwide have to be processed, or preserved, to a more stable form so that they can withstand transport, handling and storage over long periods of time. Very few foods, with the exception of some fruit and vegetables, etc., are consumed to any great extent in the raw state without cooking. Most foods are processed in some way, not only for reasons of preservation but also for palatability and to provide variety. Thus, basic ingredients as, for example, vegetable oils and starch can be used to prepare a wide range of manufactured products such as puddings, confectionery, desserts, etc. Changing social and work patterns in recent years have encouraged the growth and development of, so-called, 'convenience foods', with ramifications for the packaging industry as well. Hence, a food industry has evolved largely from the early nineteenth century onwards, when large numbers of the population began to move from the countryside into towns at the start of the industrial revolution.

TABLE 1

UK MARKET FOR PACKAGING MATERIALS BY VALUE (£ MILLION)

Packaging material	Year 1971	1973	1977	1978	1979	Ratio 1979:1971
Tin plate	190	240	546	585	650	3·4
Fibreboard	151	205	423	492	585	3·9
Plastics (film plus containers)	100	165	448	450	746	7·5
Glass	94	114	283	316	354	3·8
Paper	85	108	182	198	226	2·7
Board	67	101	230	236	275	4·1
Aluminium foil	40	48	99	104	108	2·7
Cellulose (unconverted film value)	23	25	48·5	49	57	2·5

Abstracted from editions of *Packaging Review*, IPC Industrial Press Ltd, London.

Provision of food gradually developed into a specialised business as opposed to a personal or family operation hitherto. The formation of large armies to fight wars and, hence, the need for bulk food supplies also stimulated the growth of a food industry. In France around 1800, Appert showed that food could be preserved by heat treatment, without the use of chemicals, to destroy bacteria followed by a process of hermetical sealing to protect the food from subsequent contamination. For this work Appert was awarded a prize by Napoleon and from such origins the canning industry arose to the point where today, in the UK alone, some 6000 million cans of food are consumed annually. Other forms of packaging, e.g. glass, earthenware, wood, cloth and leather, have been used by primitive man from prehistoric times and some are still extensively used in modified form today (Table 1). These figures relate to packaging in general and cover the pharmaceutical and cosmetic industries as well as the food processing industry. In contrast, the use of various plastics for food packaging (Table 2) has only developed since around 1950, when there was a concomitant rapid rise in the number of food poisoning cases reported to

TABLE 2

UK CONSUMPTION OF PLASTICS IN PACKAGING ('000 TONS)

	1973	1979
LDPE	250	362
HDPE	75	134
PS	52	93
PP	90	79
PVC	56	61
PVDC	8	12
Polyester	—	3
Miscellaneous	5	7
Total	536	751

Abstracted from editions of *Packaging Review*, IPC Industrial Press Ltd, London.

the authorities (Table 3). Most probably this rise resulted from the growth in 'eating out' in restaurants, etc., following the end of World War II. The harmful effects of micro-organisms in foods have been described by Passmore.[1] The classical food poisoning micro-organisms are all bacteria, and following ingestion of contaminated foods, they produce symptoms of nausea, vomiting, diarrhoea or abdominal pain, depending on the organism. It has been estimated that 45 per cent of all meat and 60 per cent of poultry are contaminated by *Salmonella* spp. but they are heat sensitive and so destroyed on cooking. These organisms, which are responsible for

TABLE 3

REPORTED CASES OF FOOD POISONING IN THE UK

Year	Number of cases reported
1940	47
1944	275
1948	964
1955	8 961
1965	8 313
1970	8 088
1975	10 936
1977	10 365

From Annual Reports of the Chief Medical Officer of the Department of Health and Social Security, HMSO, London.

around two-thirds of all notified cases of food poisoning, can survive for long periods in frozen foods. Hence, poultry must be completely thawed before cooking to ensure complete destruction of all organisms at the centre of the carcass. Strict attention to hygienic handling and storage of fresh and cooked foods will prevent problems associated with food poisoning, both in the home and at mass catering establishments; so reducing the continuing upward trend in bacterial food poisoning (see Table 3). Undoubtedly, such cases represent only a fraction of the total number of incidents occurring in any one-year, particularly when only mild symptoms are involved. This need for better hygiene, together with the introduction of pre-packaging of foodstuffs, resulted in new outlets for plastics and a rapidly developing food packaging industry. Tables 1 and 2 show how, even in the 1970s, the growth in plastics for packaging has outstripped growth in other materials, despite economic pressures resulting from the change in crude oil prices during this period. Moreover, consideration of packaging materials consumption by volume instead of by value, shows that there has been little real growth except in the plastics sector.

Whilst packaging is required to fulfil a number of different functions, its primary role is to retard or prevent loss of quality (nutritional and aesthetic) and to give protection against environmental contamination. Some of these spoilage mechanisms and the measures taken to control their effects will now be considered in greater detail, since they influence the selection of the best material for packaging.

Food Spoilage Mechanisms

During growth, transport, processing and storage, food may deteriorate in quality or be lost in quantity through one or more of the following mechanisms:

(1) Depredation by macro-organisms, e.g. pests and vermin.
(2) Contamination by growth of micro-organisms, e.g. bacteria, fungi and yeasts.
(3) Chemical reaction brought about by enzymes, through oxidation or hydrolysis.
(4) Physical changes, e.g. loss of moisture with associated texture effects, ingress of gases, taint, radiation and mass transfer.

Pests such as weevils and other beetles, ants, flies, cockroaches, or worms may contaminate growing as well as stored crops. Strict quality control of raw materials is essential therefore to prevent contamination of the finished product. Many species of insects can develop at water activity (A_w) levels below 0·3, but multiplication is prevented at temperatures below 15°C. Vermin (such as rats and mice) consume the crop, and sometimes the packaging material, as well as (cf. insects) causing contamination by mechanical transmission of disease-producing organisms as they move from excrement to food, thereby resulting in the destruction and condemnation of the total consignment. The presence of micro-organisms in foods, whilst in many cases[1] producing disease, sickness, possible loss of life and further wastage, can also be beneficial. Fermentation processes and the ripening of cheese are examples of beneficial changes occurring as a result of microbiological inoculation. Chemical changes are mainly undesirable in that hydrolysis or oxidation often lead to the production of off-flavours, e.g. rancidity, although many alcoholic beverages improve on keeping through chemical reactions such as esterification. Enzymes, proteinaceous compounds naturally occurring in the tissues of plants and animals, continue to act after the harvesting of crops or the death of the animal. In some cases these changes are undesirable, e.g. the browning action in apples. Hence, vegetables are usually blanched prior to freezer storage. Alternatively, some enzymatic changes are encouraged, e.g. the hanging of game to develop flavour before cooking and eating. Physical changes involve principally a loss of moisture with associated textural changes. The absorption of volatile compounds may produce problems of taint, although the useful storage life of some foods may be prolonged in atmospheres of carbon dioxide or nitrogen.

Micro-organisms, including moulds, yeasts and bacteria, develop rapidly under favourable environmental conditions. Hence, most control mechanisms are designed to change these conditions so as to make them less favourable to growth.

Control Mechanisms

Whilst some of the above agents produce desirable changes in the organoleptic qualities of a food, the majority lead to loss of appearance, taste, nutritional quality and safety. Hence, a number of preventive measures have been devised over the years to control or retard loss of crops and food products, and any associated deterioration in quality. These measures can be grouped as follows:

(1) Reduction of moisture; drying, salting.
(2) Chemical preservation using sulphur dioxide, nitrate/nitrite, pesticides, organic acids and their derivatives, acidulants (pickling), antioxidants.

(3) Use of high temperatures; canning, pasteurisation.
(4) Use of low temperatures; refrigeration, freezing.
(5) Irradiation.
(6) Packaging, for protection and for a controlled environment.

Since all forms of life require water for growth and even survival, dehydration of food is an effective means of restricting deterioration caused by fungi and other micro-organisms. The reduction in water activity can be effected by simple drying, or by the use of sugar (as in jams), or salt (through osmotic effects), or by smoking. In the latter case, whilst the main change is a reduction in moisture content, some chemical action through the presence of phenolic compounds and formaldehyde in the smoke, may also occur. A reduction in moisture content may also produce important savings in transport costs. Chemical preservatives comprise a wide and heterogeneous group of products, from insecticides and fungicides used in agriculture, to simple inorganic and organic preparations added during food manufacture to kill-off various groups of micro-organisms, or to restrict their growth. A more detailed account of the science and technology of food preservation can be found in a recent review.[2] Most organisms grow rapidly at human body temperature (37 °C). Hence, a change in temperature, away from this optimum, should prevent or reduce their rate of growth by the creation of an unfavourable environment. High temperatures may effect a complete sterilisation or, alternatively, only partial stabilisation may be obtained. Usually the heat treatment is sufficient to kill any pathogenic organisms, fungal spores and to inactivate enzymes by denaturation. The heat treatment itself may lead to some loss of food quality. Hence, only the minimum necessary to safeguard the product is carried out. In the case of milk there are a number of heat treatment processes designed to kill pathogenic organisms only (pasteurisation) or all micro-organisms (sterilisation). Milk in the cow's udder is probably sterile but it readily picks up contaminating organisms in passing through the teat and into the milking pail or from other dairy equipment. Milk becomes sour in a few hours unless kept cool. The pathogenic organisms present in milk are all heat sensitive but there is a non-linear relationship between the temperature and time of heating required for safety. Some examples of suitable conditions for pasteurisation are given below:

40 min at 57 °C
10 s at 71 °C
$<$2 s at 75 °C

As the temperature is increased, less time is required. However, the time