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ORGANOTIN POLYMERS AS COMPONENTS FOR MARINE ANTI-FOULING PAINTS

By

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(Grey College)

A thesis submitted to the University of Durham for the
Degree of Doctor of Philosophy

1982

To the memory of my Father Alf,
with love to my Mother Rita,
Anne and Jerry

ABSTRACT

The work described in this thesis is concerned with the synthesis of di-n-alkyl bis(hydroxy carboxylate)tin monomers and their reactions with several di- and poly-functional isocyanates to give polyurethanes with tin carboxylate units in the polymer backbone. These polymers were prepared for evaluation as components of marine anti-fouling paints.

The first chapter reviews the causes of marine fouling and the methods currently used to reduce corrosion and fouling.

The synthesis and characterisation of the di-n-alkyl bis(hydroxy carboxylate)tin monomers required for this work are described in Chapter Two; their polymerisation with commercial di- or poly-functional isocyanates being described in Chapter Three.

The polymers prepared by the methods described in Chapter Three were tested using an apparatus designed by the author which simulated a ship's passage through the water, this work is discussed in Chapter Four. The first set of polymers prepared (Chapter Three) were unable to withstand the physical stresses to which they were subjected and so a new set of co-polymers was synthesised using the organotin diols and commercially available diols as comonomers. The synthesis and testing of these copolymers is described in Chapter Five. The polymers prepared in Chapter Five were generally good film forming materials, their hardness being easily controlled, however their inclusion into paint systems was impracticable due to the ease of their hydrolysis and subsequent loss of film integrity.

ACKNOWLEDGEMENTS

Firstly I would like to thank the Science Research Council for their funding of this research project and also Camrex R. & D. Ltd. for their bursary award and their willingness to supply chemicals, photographs and technical advice. Thanks are also due to Dr. W.J. Feast who has been of great help and encouragement during the project; past and present members of Camrex's staff, Dr. R. Kay, Dr. K. Borer, Mr. A. Milne, Dr. S. Furtado and Mr. J. Chapman and also Professor W.K.R. Musgrave for finding financial support for the continuation of this research after the completion of the term of a normal S.R.C. studentship. Thanks are also due to Mrs. M. Cocks for recording the elemental analysis, Mrs. E.M. Nevins for the photographic work and to all other members of the department and Camrex R.& D. Ltd. for their support and encouragement.

I am greatly indebted to Mrs. M. Wilson for the typing of this thesis and eliminating some of my errors; those remaining are, of course, the author's responsibility.

Finally, but by no means least, I would like to express my appreciation to my family, Mrs. R. Tate and Mr. and Mrs. J.C. Lawrence, for their unfailing support, particularly during the more frustrating periods of the work.

MEMORANDUM

The work reported in this thesis was carried out in the Chemistry Department of the University of Durham between October 1977 and July 1981. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

AIDS FOR READER

KEY TO THE ABBREVIATIONS USED IN THE TABLES OF POLYMER SYNTHESIS AND APPENDICES

Solvents

Toluene	Tol.
Hexane	Hex.
Dimethyl sulphoxide	DMSO.
Acetone	Act.
Tetrahydrofuran	THF
Methyl ethyl Ketone	MEK
Methyl isobutyl ketone	MIBK
Solvesso	Sol.
Xylene	Xyl.
Oxytol acetate	Oxy.

Monomer 1. (Di-n-alkyl bis(hydroxy carboxylate)tin.

Di-n-butyl bis(o-hydroxy benzoate)tin	(1)
Di-n-octyl bis(o-hydroxy benzoate)tin	(2)
Di-n-butyl bis(m-hydroxy benzoate)tin	(3)
Di-n-octyl bis(m-hydroxy benzoate)tin	(4)
Di-n-butyl bis(p-hydroxy benzoate)tin	(5)
Di-n-octyl bis(p-hydroxy benzoate)tin	(6)
Di-n-butyl bis(3-hydroxy-2-naphthoate)tin	(7)
Di-n-octyl bis(3-hydroxy-2-naphthoate)tin	(8)
Di-n-butyl bis(12-hydroxy stearate)tin	(9)
Di-n-octyl bis(12-hydroxy stearate)tin	(10)
Di-n-butyl bis(mandelate)tin	(11)
Di-n-octyl bis(mandelate)tin	(12)
Di-n-butyl bis(glycolate)tin	(13)
Di-n-octyl bis(glycolate)tin	(14)

Monomer 2. (Diisocyanate)

Isophorone diisocyanate	(i)
Hexamethylene diisocyanate	(ii)
Trimethyl-hexamethylene diisocyanate	(iii)
Desmodur N	(iv)
DDI	(v)

Monomer 3. (Diol)

Ethane 1,2 diol	(A)
Propane 1,3 diol	(B)
Butane 1,4 diol	(C)
Teracol 1000	(D)
Teracol 2000	(E)

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APPENDICES -

CHAPTER ONE

THE CAUSES, CONSEQUENCES AND PREVENTION OF MARINE FOULING

1.1 Introduction

The work to be described in this thesis is concerned with the synthesis of polymers intended as potential components for marine antifouling paints. The first chapter of the thesis sets out the context of the work by reviewing the nature of the problem and previous attempts to overcome it.

Any submerged structure may be colonised by plant or animal organisms, in the case of artificial structures such as harbour installations, pipelines, drilling rigs and sea-going vessels; these plant and animal colonies are generally referred to as fouling. Marine fouling can cause problems by altering the way in which the structure performs in the marine environment. The economic penalty incurred by fouling can be very severe and consequently considerable efforts have been made over the years to reduce or eliminate the deposition of fouling on all types of structure. In this work we shall be mainly concerned with fouling of ships but it is important to realise that this is only one aspect of a more general phenomenon.

The practical importance of ship fouling may be briefly illustrated by reference to data taken from recent publications.[1-4] The major part of the propulsive power of a ship is used in overcoming frictional resistance and is therefore directly related to the condition of the submerged hull surface, only a relatively minor proportion of the energy expended depends on variations in ship design. Aertssen has pointed out that the only variable parameter on a painted ship to effect the total resistance is fouling and has been able to quantify this effect by analysing the performance of the container ship "The Dart

Europe".[1] He showed that after 295 days of service an increase of 8% in power was required to maintain constant speed, this extra power being required as a direct consequence of increased hull roughness caused by fouling. The economic consequence of increased frictional resistance was demonstrated by calculations reported by Banfield in 1972.[2] He indicated that for a very large crude carrier (VLCC) with a service speed of 16 kn. a loss of speed of 0.1 kn. would result in an increased annual running cost of over £40 x 10^3. A 1976 estimate of the cost of increased frictional resistance to the U.S. Naval Fleet was 150 x 10^6 \$/p.a.[3]

Not only does fouling cause extra expenditure on fuel to overcome increased frictional resistance but also the cost of hull preparation prior to repainting is an added penalty. It has been recently shown that for a relatively small tanker (28 x 10^4 tons dead weight of hull area 28.2 x $10^3 m^2$) the cost of removing fouling in 1977 would have been in the range £71 x 10^3 - £91 x 10^3 depending on the location in which the work was carried out.[4]

The evidence is thus overwhelming as to the necessity for an effective antifouling coating which will reduce these fouling related costs.

1.2 Types of Fouling

1.2.1 Plant Kingdom

(a) Bacteria and bacterial slimes

The bacteria which cause bacterial slimes are present in the sea water all the year round; they present a major fouling problem as settlement occurs within minutes of

Figure 1.1 Diatom colony on hull surface.

immersion. The slime is generated after the settlement of the bacteria by secretion of mucus, the species of bacteria being classified by this mucus. Once attached these bacteria begin to reproduce by cell division, the daughters not normally being released into the sea water but being held in the parents' mucilage thus very quickly the slime thickness and the fouled area increases. The slime thickness can vary from a few microns to several millimetres depending on the conditions, and this thickness directly affects the surface roughness.

These bacterial slimes are important because they can influence the rate at which toxins are released from an antifouling coating by forming a diffusion barrier on the surface, the slime can also trap spores and larvae of other fouling organisms thus promoting macro fouling.

(b) Diatoms

Diatoms are microscopic plants with a characteristic brown colour, they are similar to bacteria in size and again secrete mucus through their external siliceous shell although this is less slippery than that produced by the bacteria. Diatoms cause similar problems to those listed above.

(c) Seaweeds

These are algae and three main classes are found; namely, green, brown, and red seaweeds.

The commonest species of green seaweed is enteromorpha (seagrass) and this is found near the waterline forming a carpet up to 10 cm. thick and extending to a depth of several metres on the hull. Its success as a fouling organism stems from its ability to tolerate a wide spectrum of toxins and also its worldwide distribution. This marine algae exists as long 'grass like' filaments which contain up to five million cells in an average frond 7-8 cm. long, each cell being capable of producing eight zoospores (reproductive spores).[5] These spores leave the parent cell as free swimming zoospores directed by four flagellae, they settle preferentially in surface irregularities. When the zoospore makes contact with the surface the flagellae act as brushes and clean the point of settlement, a cement is released and within seconds the organism is firmly bound to the surface. It is at this stage that it is most vulnerable to toxins as it is surrounded by only a thin membrane, but within four hours a protective wall is formed and the zoospores begin to develop into the mature algae, after a few days it is already a few millimetres long and a centimetre or more within two weeks.

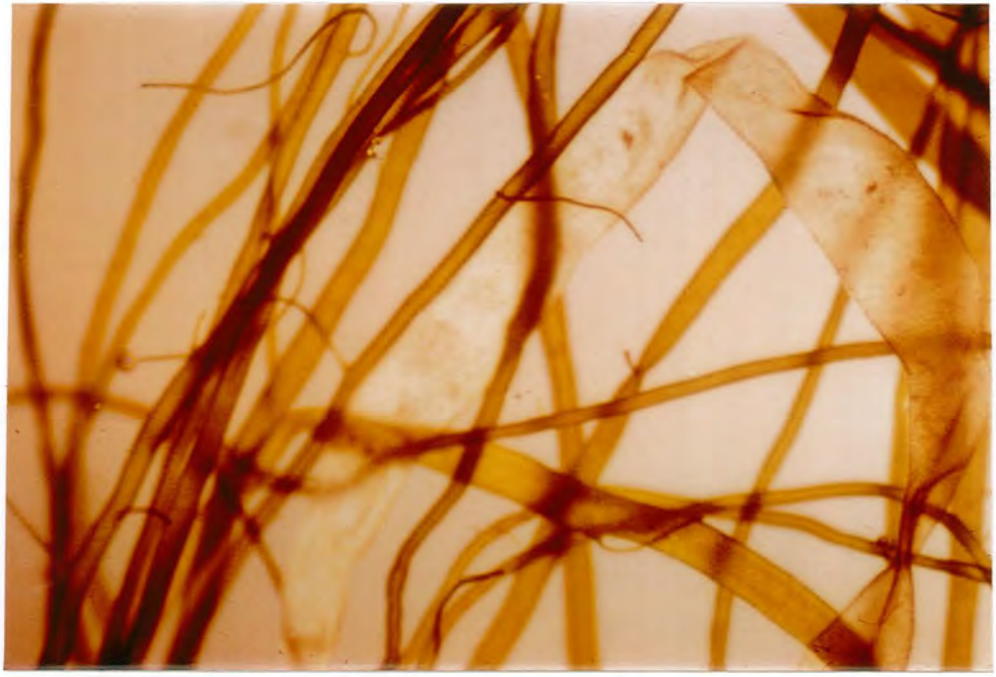


Figure 1.2 Living Enteromorpha Filaments

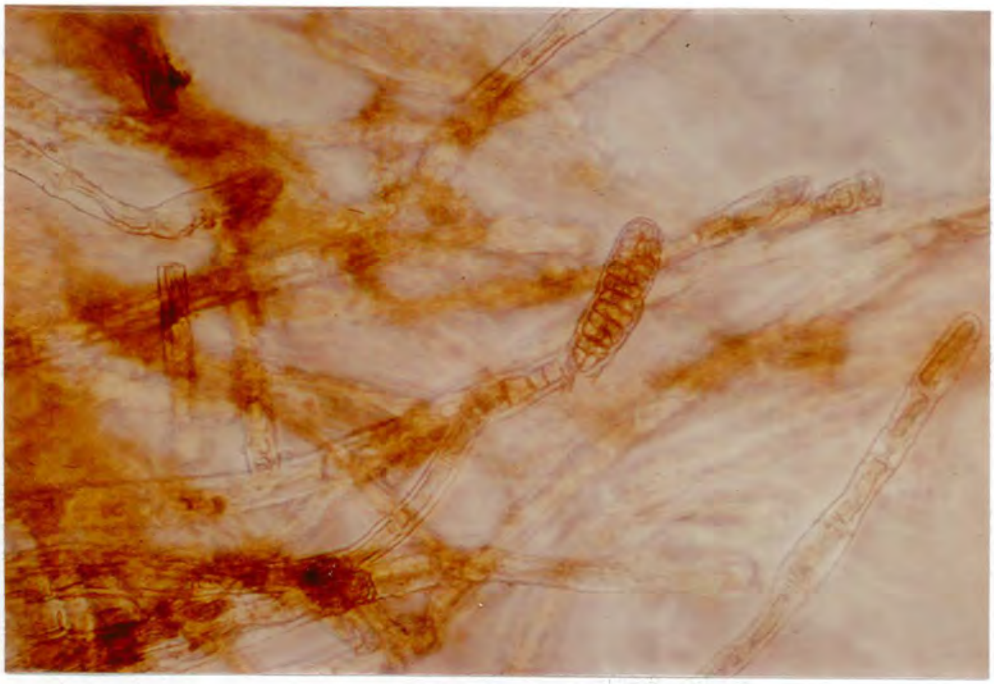


Figure 1.3 Living Ectocarpus Filaments.

The most common brown seaweed is ectocarpus which reproduces in a similar fashion to enteromorpha and again has worldwide distribution.[6] The plant is composed of two parts, the rhizoidal, a root-like part and an upright part supporting the spore bearing structure, this being branched and limp. Each plant is capable of producing 40×10^3 spores and each of these spores have two flagellae. They swim in the sea until a suitable settlement site is found (usually in surface defects) where they attach themselves and begin to develop a protective wall, this occurring at a slower rate than with enteromorpha; usually taking 24 hours, after which time growth of the new plant will have started. These seaweeds are found lower down on the hull than enteromorpha.

Figure 1.4 Heavily fouled hull showing enteromorpha (green) near water line and ectocarpus lower down

The commonest red seaweeds found are ceromium and polysuphonia, their reproduction and settlement behaviour is similar to that described above but these seaweeds are highly branched and much larger than either of the other two species; they are found much lower down on the hull where the light intensity is very low.

It has been shown that these fouling organisms, like the other seaweeds are most vulnerable to toxins during their settlement period; the resistance of the mature seaweeds to toxins is considerably higher than that of animal fouling organisms.[6,7]

1.2.2 Animal Kingdom

(a) Arthropods

This is a class of the animal kingdom which includes all organisms with a chitinous external skeleton and joined appendages, many of these have a skeleton which is hardened by calcareous deposits.

The barnacle (cirripedia), of which there are many different types, is the most common arthropod to be found on a ship's hull. It is an hermaphrodite, but sexual reproduction is preferred, asexual reproduction occurring only under adverse conditions. The eggs are produced in the parent shell, when the conditions are correct the nauplii (free swimming) larvae are liberated, and depending on the species they metamorphosise up to eight times, the final transformation producing the cypris (settling) larvae. The cypris larvae either swim or crawl around until they find a suitable area in which to settle, this is often a site which has previously been inhabited by a barnacle community. A protein, arthropodine, is secreted by mature barnacles and it is this which acts as a reference for renewed settlement.[7]

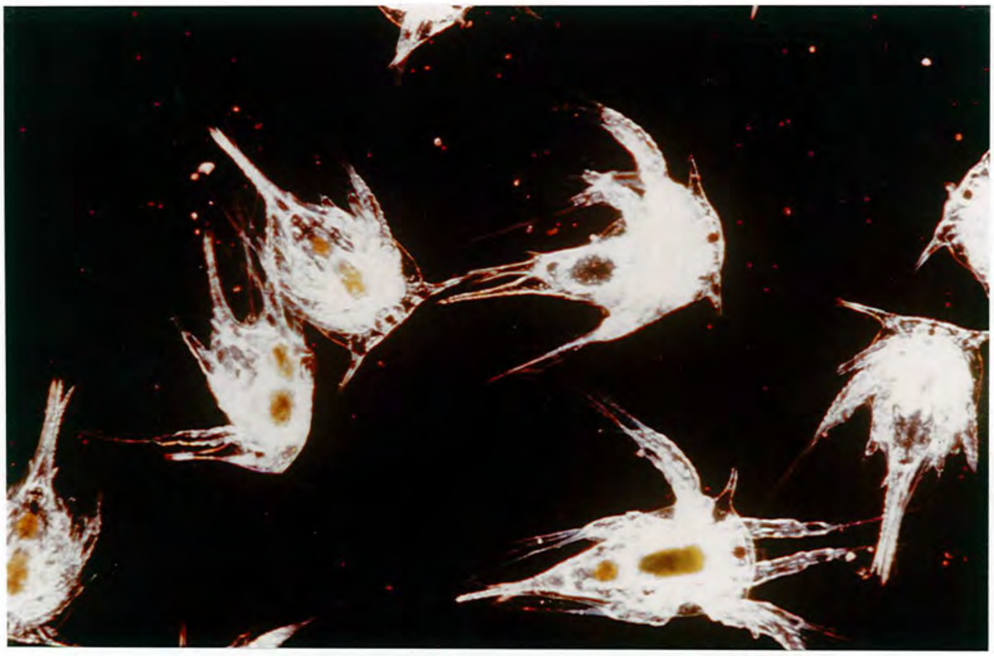


Figure 1.5 Free swimming naupli of the barnacle

Figure 1.6 Settling cypris larvae

The settling stage is the most vulnerable period for the young barnacles, the toxins in conventional anti-fouling coatings effectively kill the majority at this stage, hence on recently painted ships there is no serious fouling problem due to barnacles.[5] If they do survive and grow to their adult form not only do they cause increased surface resistance but also their shells tend to cut through the underlying coatings causing a corrosion problem.

Figure 1.7 Typical barnacle fouling in regions of anti-fouling coating failure

A particularly difficult type of barnacle fouling is that produced by the goose barnacle: its settlement and growth occurring rapidly and vigorously even in the open sea.

There are many other arthropods found in the sea, these include isopods, amphipods, crabs, shrimps and insects, but these only foul static structures and therefore do not present a fouling problem on seagoing vessels.

Figure 1.8 A Barnacle Colony

(b) Tubeworms (Annelids)

The coral effect on fouled underwater surfaces results from the activity of tubeworms. Reproduction can be either sexual, which results in free swimming larvae and thus a new area of infestation, or asexual when the parent acts as host to the new larvae which eventually bore holes through the calcareous shell of the parent and grow as new entities although still attached to the parent. This process produces a random frosted effect on the surface. As the creature grows the shell is extended; this continues until the death of the animal by which time there may be a large hard calcareous growth which remains attached to the surface and this can only be removed by abrasive treatments such as grit blasting. The presence of tube worms can be used as a good indication of the state of exhaustion of the matrix toxins in antifouling paints as they are normally vulnerable to toxins.

Figure 1.9 Typical calcareous growth resulting from tube-worm fouling

(c) Mussels (pelecypods)

The mussel is one of the few shellfish which foul vessels since generally shellfish are very susceptible to toxins not only during settling but also in the adult organism. This is due to their method of feeding and also the susceptibility of the settling larvae to toxins. Many mussels reproduce sexually although some species reproduce asexually, the resulting fertilised eggs being either held within the parent which releases free swimming larvae or the eggs are liberated into the water and hatch to produce the free swimming larvae. These larvae initially settle by means of a foot followed by the formation of a byssus (a web-like system of roots) which firmly secures the adult. Again the shell remains attached to the surface after the death of the organism and is difficult to remove.

Figure 1.10 Typical mussel colony on an antifouling coating

(d) Bryozoa

These may be divided into three main groups depending on their pattern of growth. Encrusting Bryozoa grow over the substrate to produce a network of shell growth similar to tube worms. Erect Bryozoa grow outwards from the substrate, and Stolonate Bryozoa have an intermediate pattern of growth. Reproduction is again sexual or asexual, the fertilised eggs either being retained by the parent or existing in the sea. Settlement occurs several hours after hatching, then the adult develops. The most susceptible time for poisoning Bryozoa is during the settling period, after which time it is difficult to kill this species of fouling.

(e) Sea Squirts

These produce free swimming larvae which become attached to a surface before metamorphosis can occur. The parent is a very lowly form of vertebrate existing as a sack through which water is filtered. They are not a common fouling organism on ships as, like mussels, they feed via filtration of water and so are very susceptible to toxins.

Figure 1.11 Mature Sea Squirt colony

(f) Hydroids

The free swimming hydroid larvae, produced either sexually or asexually, cements itself to a hard surface and grows into the adult. The adult is very firmly attached to the surface and resembles seaweed; it is quite resistant to toxins unlike the young free swimming hydroid which is easily poisoned.

Figure 1.12 Hydroids attached to a stone

(g) Protozoa

These are single cell animals which range in size from 0.002 mm to several centimetres. Their small size and their inability to form large colonies render them unimportant as fouling organisms. They do however provide, like the microfouling organisms in the plant kingdom, sites for settlement of other fouling organisms.

Generally plants are more resistant to toxins than animals because their method of feeding this involves the absorption of nutrients by osmosis which prevents the ingestion of the toxin whereas animals take in food and toxins directly and are therefore more easily killed. The resistance of fouling organisms to commonly used toxins is shown in Table 1.

TABLE 1 Resistance of commonly occurring fouling organisms towards currently used toxins

Resistance	Organism
Very High	Bacteria Diatoms
High	Ectocarpus Enteromorpha Hydroids Barnacles Polyzoans
Moderate	Barnacles Tubeworms Hydroids
Low	Weeds (Green & Red) Sea Squirts Mussels Oysters

1.3 The Fouling Mechanism

The authors of a U.S. Navy Report have summarised the factors affecting the settlement of fouling organisms;[8] the more important factors being the geographical location, the season, the movement of the water relative to the surface, the texture of the surface, the intensity of illumination and the presence of slime films.

The geographical and seasonal influence are of major importance as the reproduction of the fouling organism is governed by the water temperature consequently in some areas of the world's oceans no fouling may occur during the winter. The longer the summer season the greater the fouling as the reproduction of fouling organisms is far more prolific during the warmer season. Wherever there is a warm water current excessive fouling can be expected, as is found in the Gulf Stream. One of the implications of the geographical and seasonal factors is that it may be necessary to have several different types of anti-fouling paint that are suitable for the different areas in which ships operate.

The first step in fouling is settlement and this cannot occur when the ship is moving above 13 kn, thus a stationary ship is an ideal site for fouling. The majority of fouling occurs when the ship is in harbour, as here there is a higher water temperature, consequently a larger fouling population and the flow of water past the hull is usually very slow. Ships which spend a very short time in harbour are found to be relatively free from animal fouling although they have a large amount of plant fouling, this being due to the ease and rapidity of settlement of the latter.

The surface texture of the coating is important because imperfections in the surface provide sheltered environments where the fouling organisms can settle and be protected from the flow of water past the hull. The settlement of fouling on a moving ship is thought to be due to a combination of static flow patterns created on certain areas of the ship and also micro fouling organisms entraping the settling larvae of macro fouling organisms in their mucilage, thus enabling the larvae to grow into the adult form.

The light intensity plays an important role in plant fouling as this can only exist where there is sufficient light to allow photosynthesis to occur. Consequently the seaweeds requiring most light (green) are found near the water line, whereas those requiring less light (brown and red) are found lower down on the hull. Animal fouling is independent of the light intensity although some animal fouling organisms settle preferentially near the water line.

1.4 The frictional resistance to a ship's movement through water (Drag)

The total resistance to a ship's movement through water is normally defined as the force required to tow a ship at a given speed in calm waters. The total resistance is the sum of the frictional resistance and the residual resistance, the latter being a feature of the ship's design whereas the former is due to the tangential shear forces caused by the movement of water parallel to the ship's hull. It can be seen that only the frictional resistance can be influenced by the surface coatings or surface treatment.

In 1874 Froude showed experimentally that the frictional resistance for towed planks could be expressed by the equation:[9]

$$R_f = f.s.v^n$$

where R_f = frictional resistance, f = frictional coefficient, s = the wetted surface area, v = the velocity, and n = a number nearly equal to 2.

From the results Froude obtained it was obvious that the frictional resistance depended on the nature of the surface, the values of n being very nearly equal to two whereas the values of f varied greatly depending on the smoothness of the surface; these observations were not utilised until well into the twentieth century.

1.4.1 Flow around a ship's hull

The resistance caused by the flow of water around a ship's hull, the residual resistance, is governed by the hull geometry and operational speeds, this can be approximated to the flow around a plane plate for which the formulation below is applicable:

$$Re = \frac{vl}{\delta}$$

where v = the velocity of the flow past the hull, l = the distance from the bow of the ship and δ = the kinematic viscosity which is the ratio of the viscosity to density, the units being Stokes and the dimensions being l^2t^{-1}.

Re is called the Reynolds Number a dimensionless parameter, which provides a useful indicator of the type of flow around the hull; when its value is below 5×10^5 laminar flow is observed, whereas at a value $\geqslant 10^7$ the flow is turbulent, 5×10^5 and 10^7 are critical values of Re between which the flow changes from laminar to turbulent.

It has been shown by Izubuchi from tests on the Japanese destroyer 'Yudachi', that at normal operating speeds the residual resistance forms a relatively small proportion of the total resistance, Figure 1.13.[10,11] These results were in agreement with those obtained by the U.S. Navy using the U.S. Destroyer 'Hamilton' as the test craft.[8]

More recent work has demonstrated that the relative contribution of each of these resistance components to the total resistance depends on both the size and the speed of the vessel as shown by Figure 1.14.[12]

From this graph it is clear that the reduction of frictional resistance is of major importance for efficient operation, the residual resistance only becomes important at relatively high operating speeds and is effected by the design and

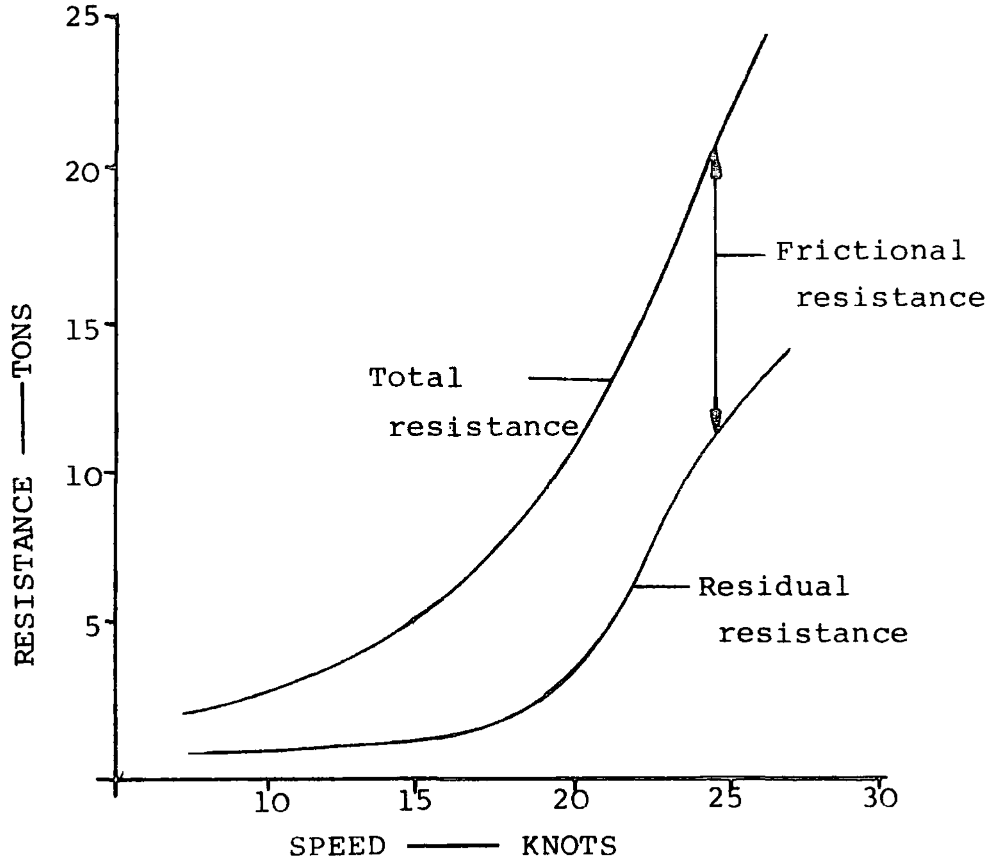


Figure 1.13 Graph of Speed versus resistance, showing the components of the total resistance

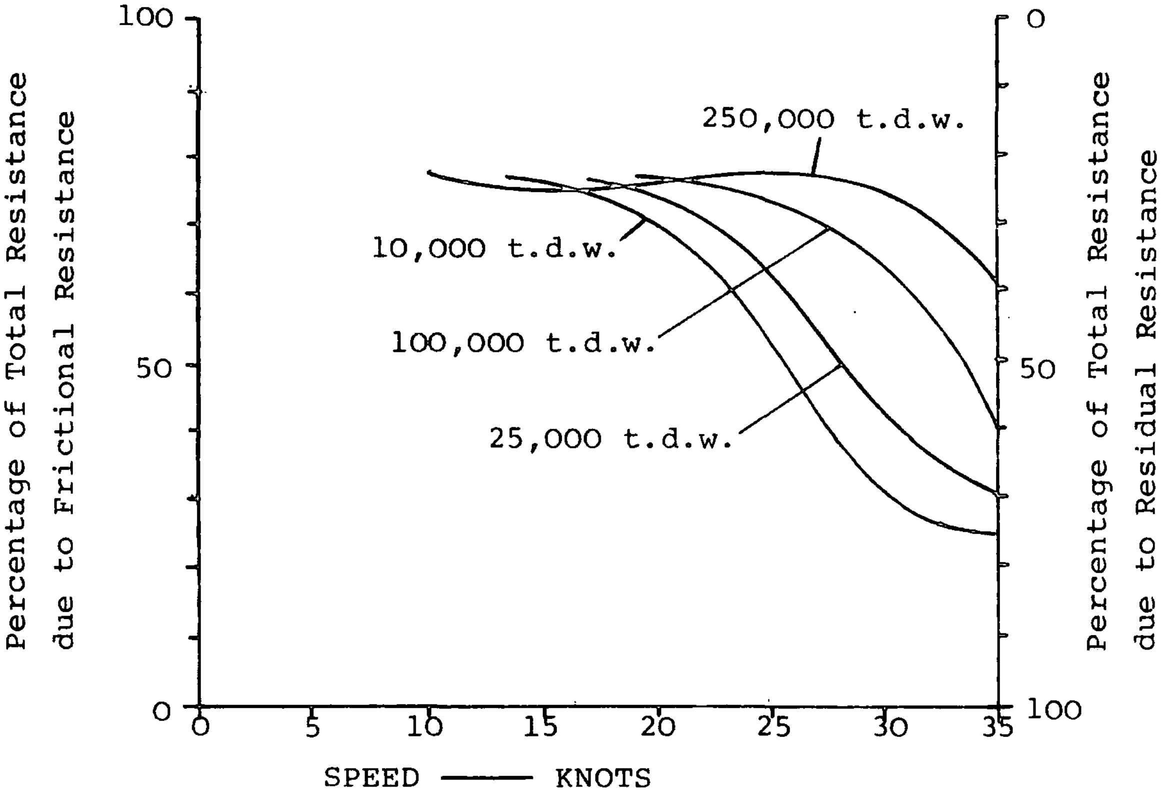


Figure 1.14 Relation between Frictional and Residual Resistance for ships of various sizes operating at different speeds

building of the vessel; most commercial vessels operate in the 10-20 kn range. A vast amount of research has been and continues to be conducted on design whereas, the frictional resistance can be very significantly lowered, with consequent economic benefit, by the application of a high performance antifouling.

The water around the hull of a ship moving at low speed can be divided into two parts; a laminar sublayer which is a continuous layer of water adjacent and parallel to the ship's hull and moving with the ship, the thickness of this layer being dependent on the speed of the ship; at greater distance from the hull flow becomes turbulent due to the shear forces created by the passage of water around the hull; the faster the ship moves the thinner the laminar sublayer. At a low Reynolds Number for a given ship operating under standard conditions a relatively thick laminar sublayer is present, with increasing speed (and therefore increasing Reynolds Number) the thickness of the laminar sublayer decreases and between certain Reynolds Numbers the laminar sublayer becomes discontinuous, Figure 1.15.

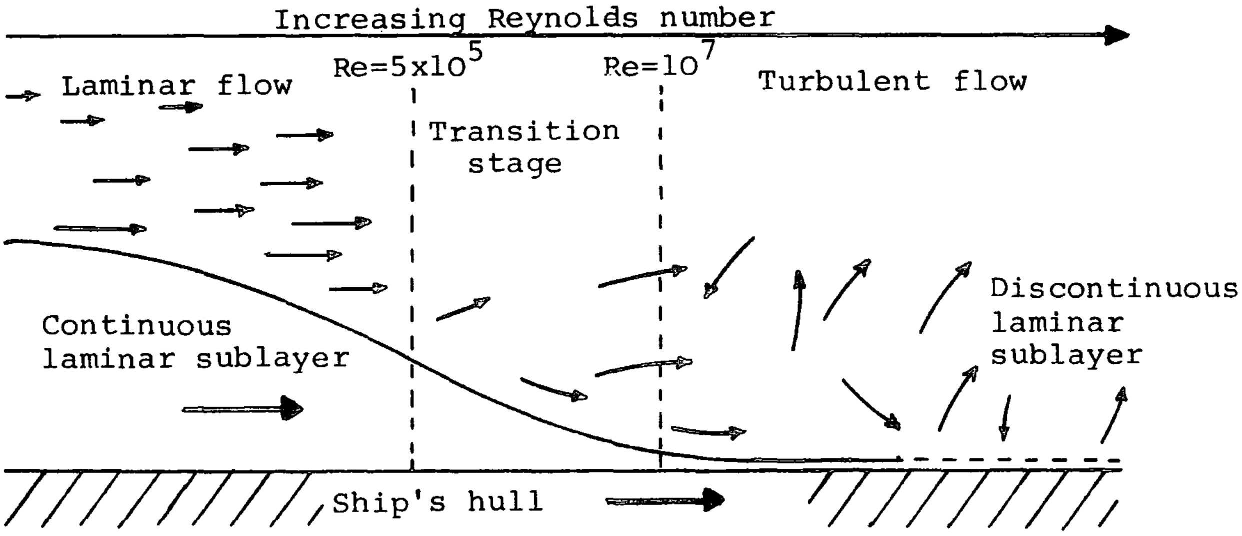
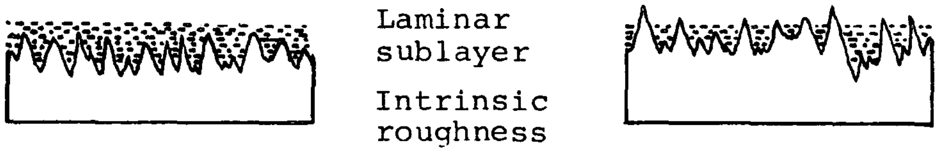


Figure 1.15 Changes in flow and laminar sublayer at increasing Reynolds Number

The smoother the hull, the lower the kinematic viscosity and so the greater the Reynolds Number. The increase in resistance created by turbulent flow (i.e. the energy required to produce turbulence) is thus related to the surface roughness and is directly proportional to the Reynolds Number.

A surface is considered to be rough if the peaks of roughness protrude through the thickness of the laminar sublayer, if the peaks are smaller and remain within the laminar sublayer the surface is considered to be hydrodynamically smooth, see Figure 1.16.



Laminar sublayer is covering the intrinsic roughness, the surface is thus hydrodynamically smooth.

Peaks of intrinsic roughness protrude through the laminar sublayer, the surface remains rough.

Figure 1.16

The thickness of the laminar sublayer is dependent on the velocity of the hull and it has been determined that for a ship operating at V knots a hydrodynamically smooth hull occurs when the surface roughness is less than or equal to $\frac{230}{V}$ μ, (see later, section 1.6). This criterion is very rarely satisfied even for a freshly painted hull.

1.5 Sources of hull roughness

Hull roughness is directly related to the frictional resistance and may be affected by numerous factors, these being described in the following sections.

1.5.1 Structure of the paint

As a consequence of the cost of dry docking and repainting, ship owners have sought shorter dry-docking times.

This has led paint manufacturers to compromise between adhesive paints that spray smoothly, but sag easily when sprayed thickly, and thixotropic paints which tend to ripple on the surface but can be applied in thicker coats without sagging. Both of these paint systems cause hull roughness, the former being less than the later.

1.5.2 Inadequate surface preparation

The removal of fouling organisms and the repair of surface defects to provide a smooth finish to which the new antifouling is to be applied is of major importance in producing a smoothly painted hull. This, however, is not always realised because of the cost of preparation, consequently in many instances surface roughness is built in in this way, the roughness increasing with each repainting.

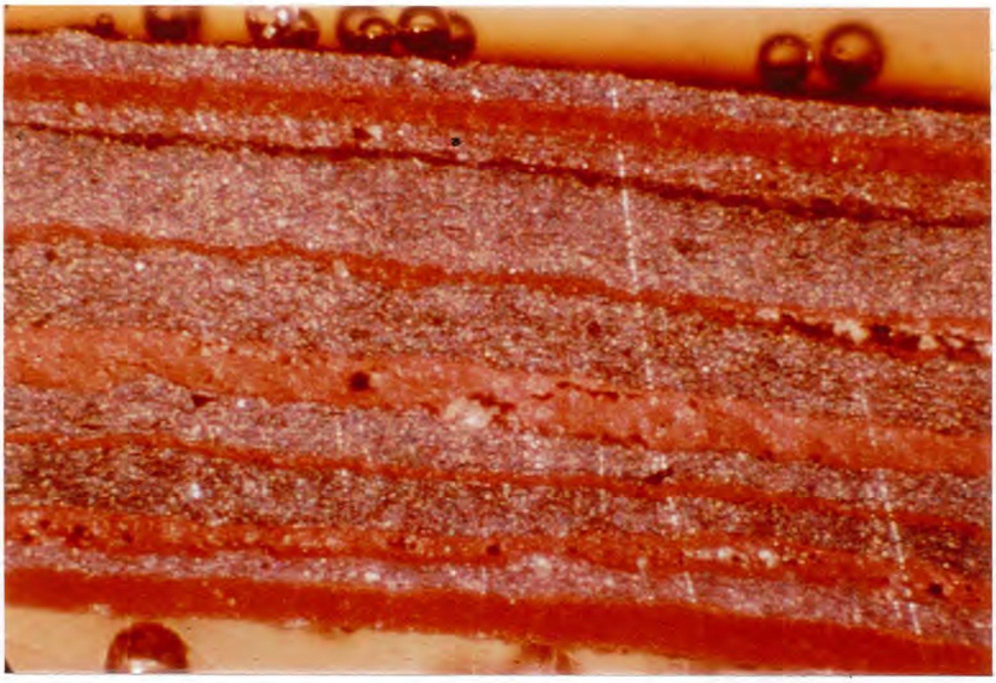


Figure 1.17 Build-up of paint layers

1.5.3 Poor application standards

The application of any coating system is really a skilled job but due to working conditions and pay, the average worker is either unskilled or untrained and consequently the manufacturers' spraying instructions are often not followed closely. The environment also plays an important role; for example, variations in humidity and wind speed can result in poor application.

1.5.4 Failure of the paint system

This occurs when the ship is in service and the main problems are: blistering, detachment and corrosion.

1.5.5 Mechanical damage

This includes berthing and grounding damage as well as that incurred from cable chafing.

1.5.6 Fouling

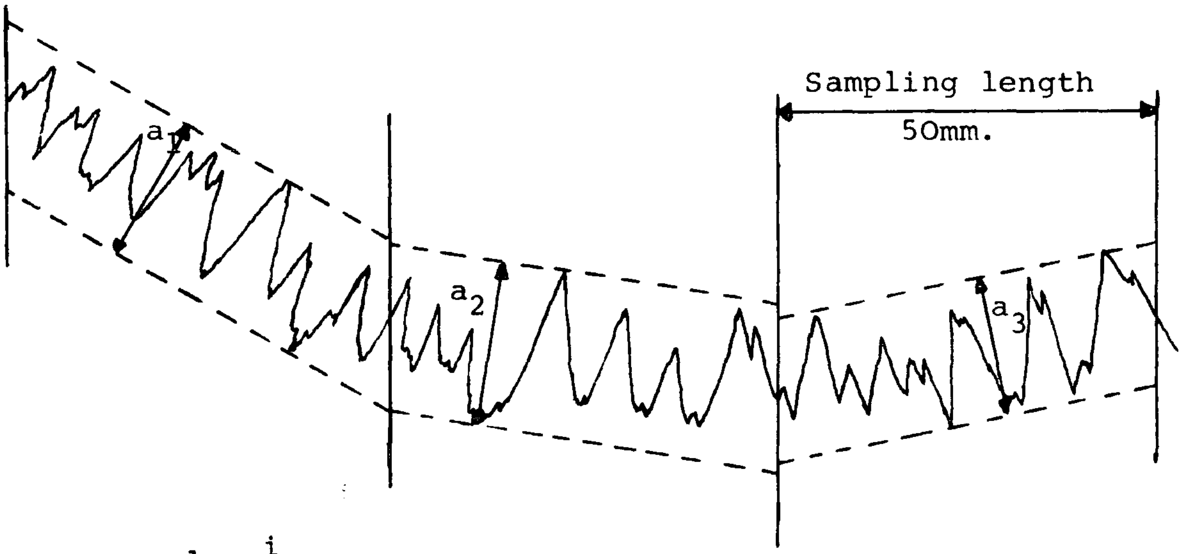
This is the major cause of hull roughness, it is caused by an ineffective or exhausted antifouling coating, thus the roughness caused by fouling increases with time.

1.6 Measurement of hull roughness

Surface roughness of a ship's hull is expressed as the maximum peak height to minimum valley depth over a distance of 50 mm, this is more commonly known as the mean apparent amplitude or MAA per 50 mm. This method of measurement gives reasonable correlation between hull roughness and ship's resistance.

Many instruments are available to measure surface roughness in the laboratory, Talysurf, Surfometer, Electron Microscope, etc. but it is only recently that the British Ship Research Association (BSRA) have developed an instrument which can measure the surface roughness of a ship's hull in dry dock.

The instrument (B.S.R.A. Roughness Gauge) consists of three wheels supporting a carriage through which protrudes a stylus. When the apparatus is pushed across the hull the stylus records the surface profile. The gauge's sample length is 50 mm and it measures the maximum peak to minimum trough distance as shown in Figure 1.18.



$$R_t(50) = \frac{1}{N} \times \sum_{1}^{i} a_i$$

Figure 1.18 Peak-to-trough method of analysis as used in B.S.R.A. Hull Roughness Gauge

This apparatus gives reasonable correlation with the standard laboratory instruments but it does not account for waves with a large wavelength as the sampling distance per measurement is too short and there is no fixed reference.

The results obtained by measuring a ship's roughness have to be corrected for defects which cause residual resistance, i.e. plate curvature, welds, etc. and then the surface roughness of the hull may be calculated, this being displayed usually as a histogram, Figure 1.20.

Figure 1.19 B.S.R.A. Roughness Gauge in use

To measure the ship's roughness in practice the hull is divided up into sections and each section is measured using the B.S.R.A. gauge before painting, the same procedure is followed after painting, sufficient measurements being taken to ensure a random sampling. The data may then be correlated to the ship's performance before and after painting to provide evidence for the increased fuel consumption due to surface roughness.

Scott has shown that the cost of surface roughness for a typical ship results in a one per cent increase in power to maintain the ship at a constant speed for every 10µ of roughness above 100µ.[13] The surface roughness of a new ship is generally about 130µ,[14,15] this figure increasing with service time for a ship painted with a conventional anti-

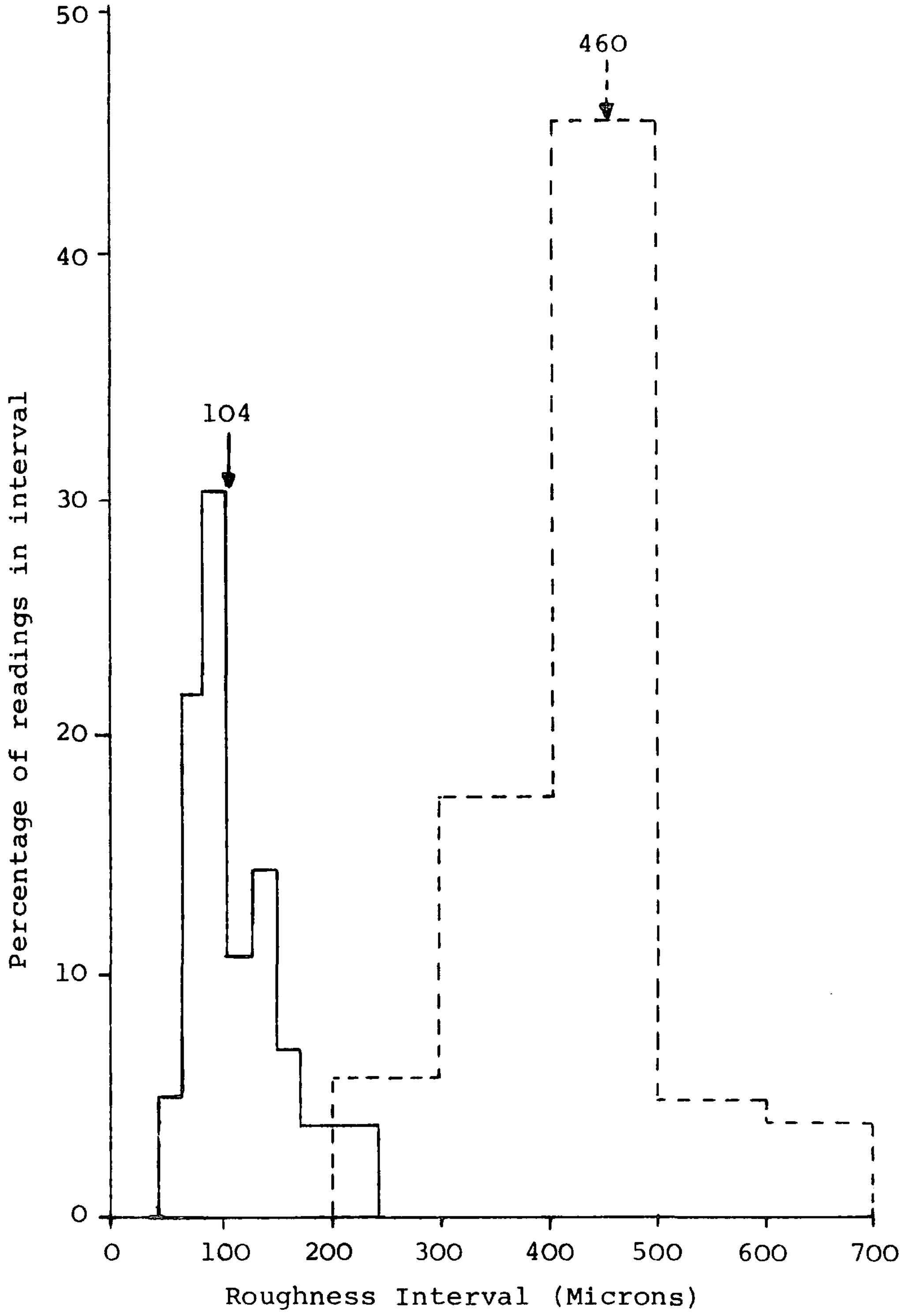


Figure 1.20 Hull roughness surveys on a six-year old vessel illustrating indocking roughness due to build up of systems detaching at various levels. The figure shows the average hull roughness on drydocking is 460μ and after full grit blast and repaint it is reduced to 104μ.

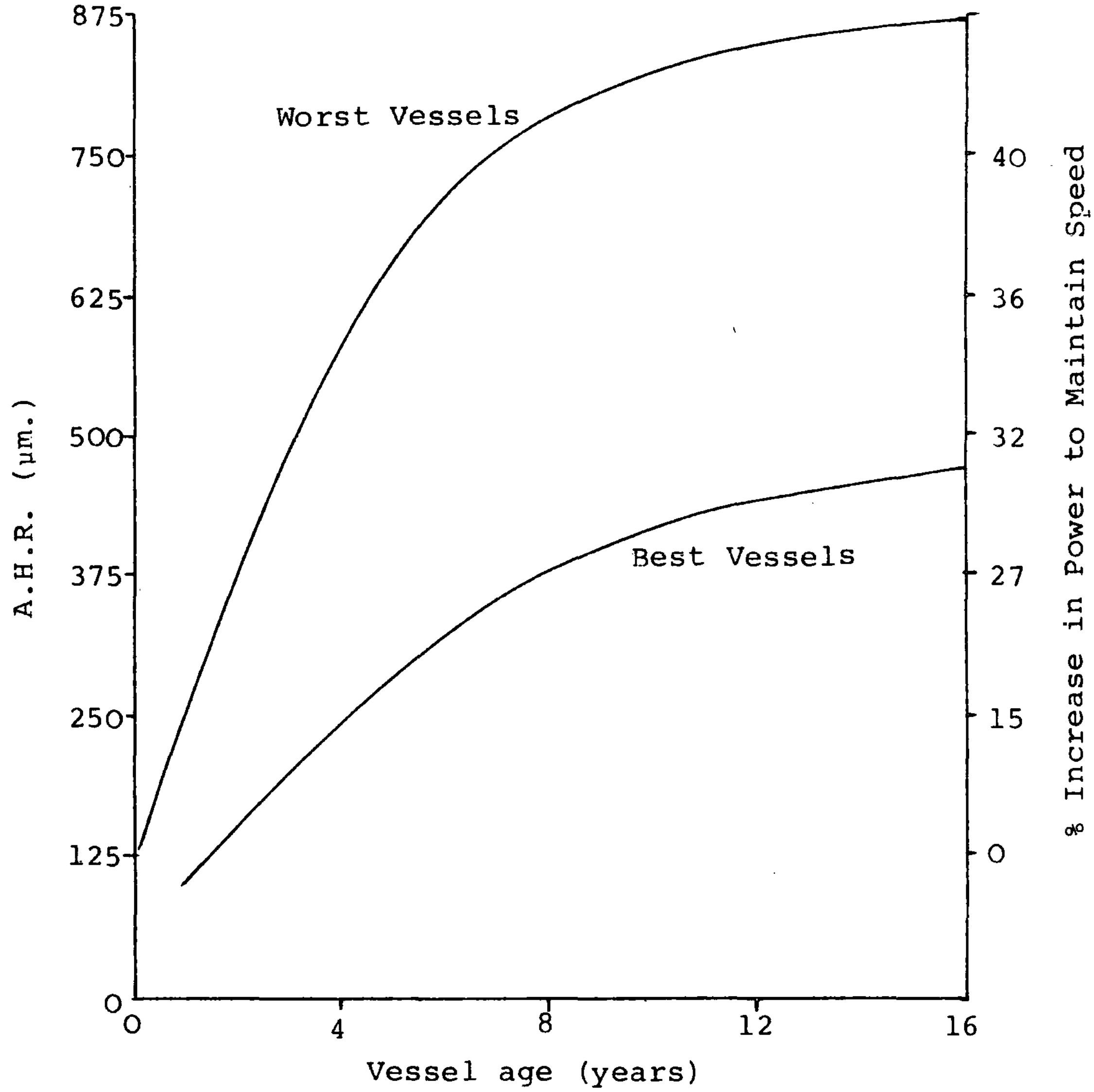


Figure 1.21 Increasing roughness with time of service for ships coated with a conventional antifoulant.

fouling preparation as was shown by the Norwegian Ship Research Institute,[14] Figure 1.21 and by Hacking and Rippon.[16]

1.7 Coating systems

The coating system on a ship is required to prevent corrosion and fouling, this being achieved by using an anticorrosive paint and an antifouling paint.

1.7.1 A brief history of antifouling procedures

Marine fouling has existed as long as boats have, the Phoenicians and Cartheginians used pitch and possibly copper sheathing on their ships to prevent fouling. Wax, tar, and bitumen are also recorded as being used as coatings although it is not clear whether they were used as antifoulings or to increase the water tightness of the ship's hulls. Both the Romans and the Greeks are known to have used lead sheathing as an antifoulant but one of the most common methods employed by these seafaring nations was to use natural resources. This involved anchoring the ship in fresh water or in areas of the Mediterranean where the alkalinity dropped to such an extent that the fouling organisms could not tolerate the conditions and so died, this occurs in estuaries draining some volcanic regions. The only other alternative was to beach the ship and physically remove the fouling, Figure 1.22.

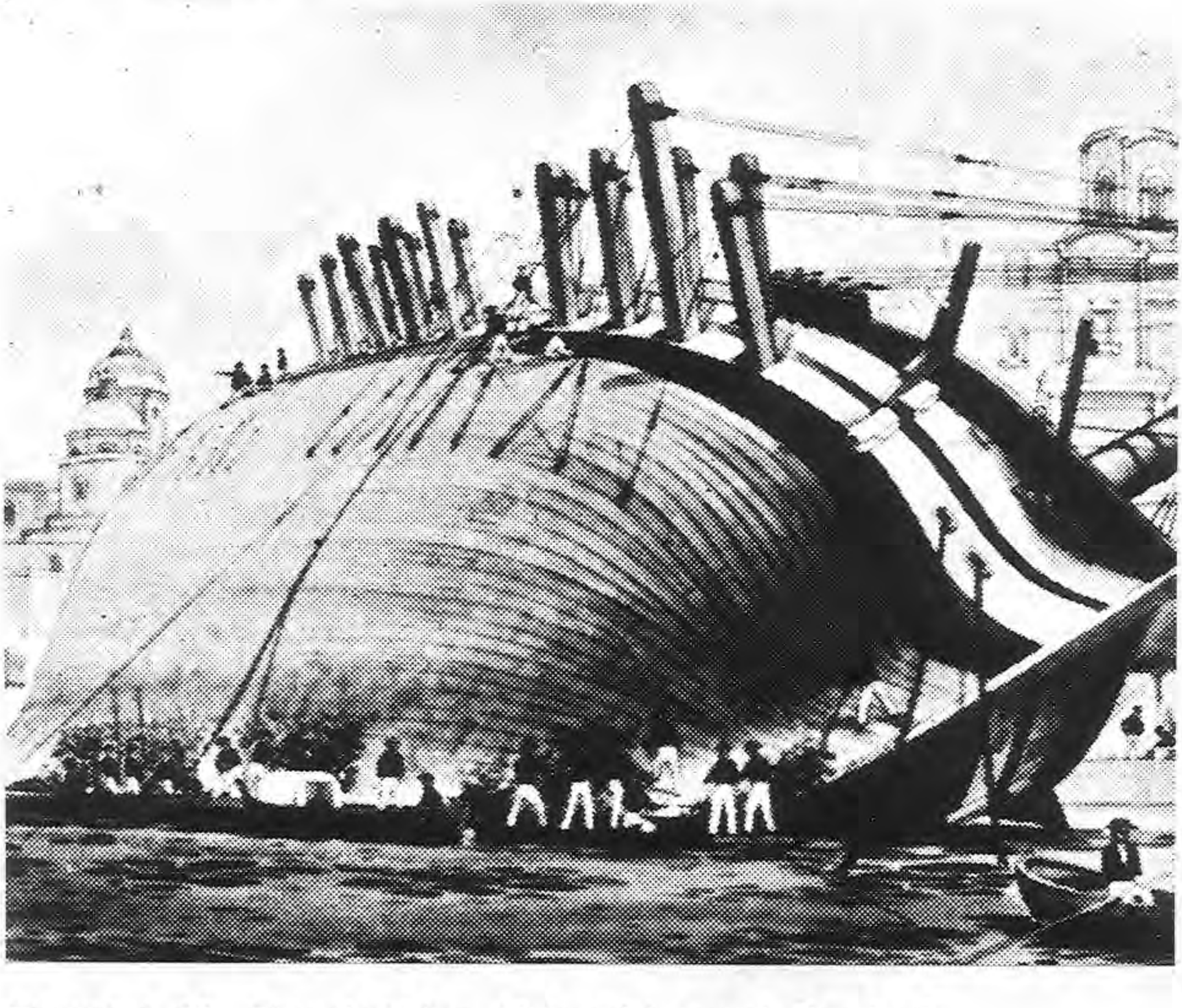


Figure 1.22 Illustration of beaching and physical removal of fouling

In the 15th Century came the total sheathing of ships with lead, while this provided relatively poor antifouling properties it did not prevent ship worm which attacked the wooden hulls. The sixteenth century saw the increased use of iron in the building of ships and it was noted that excessive corrosion occurred on any iron used in a sheathed ship's structure and so lead sheathing became obsolete. Copper sheathing was also used, this showed better antifouling properties than lead although again excessive corrosion of iron was observed.[17,18]

In 1824 Davy showed that the corrosion was due to the copper and other metals employed in the construction of the ship forming an electrolytic cell when immersed in sea water and not due to impurities in the iron as was first thought.[19,20]

With the advent of iron ships the problem of corrosion became more acute as a consequence of the different metals being employed (iron plate, rivets, etc.), therefore the ship owners required antifouling and anti-corrosive paints. Early use of copper sheathing proved almost disastrous owing to the electro-chemical corrosion eating through the iron plates resulting in frequent and expensive repairs.[21] This problem caused the Admiralty to consider the withdrawal of iron ships but owing to the lack of timber they were forced to continue using iron as the major construction material.[22]

It was realised that whereas wooden ships relied on wind for power, iron ships required some sort of fuel and as fouling increased so did the fuel consumption therefore there was a need for an efficient antifouling. Zinc sheathing was tried as this is electropositive with respect to iron and it was reported that the exfoliation (uncontrolled detachment of large areas) of the zinc was sufficient to prevent fouling and also protect the ship from corrosion although, unfortunately, the period for which it remained effective was relatively short.[23] Many methods and forms of sheathing were tried including sheathing first with a 'sealer' of pitch or a thin sheath of wood and then applying copper cladding, this however proved very expensive and therefore a cheaper method of fouling and corrosion prevention was sought.

Early records show the use of several types of antifouling coatings, these consisted of a binder and some toxin; the binder being tar, pitch or some sort of oil and a simple toxin, arsenic, sulphur, red lead, copper sulphide, etc., these being chosen for their antifouling activity: there is no available record of the effectiveness of these antifoulants. Extensive experimentation on the formulation of antifouling coatings began when it was realised that sheathing was not viable for iron ships. Many patents were issued in England, more than 300 before 1865 but many of them were useless.

Hay realised,[24] from the findings of Davy,[19,20] that the inclusion of electropositive metals or metal compounds in coatings could still result in electrolytic corrosion owing to the permeability of the coating. He devised a system whereby an impermeable layer was placed between the antifoulant and the iron hull, this sealer consisting of equal parts of pure vegetable pitch and rectified mineral spirit. The antifouling coating was then applied, this being the same as the sealer but with added copper I oxide as the toxin. By the end of the century antifouling coatings were applied over an alternative sealer, the sealer being an anti-corrosive coating based on shellac or varnish with the antifouling being either a hot plastic or shellac based paint which contained toxins.[8]

The development of antifouling and anti-corrosive coatings is still continuing owing to the ever increasing requirements imposed on the paint manufacturer by the ship owner.

1.8 Modern Anti-Corrosive Techniques

1.8.1 Impermeable coatings

The most commonly used method of preventing corrosion is to place an impermeable barrier between the sheet metal and the electrolyte (sea water). The type of anti-corrosive coating required is dependent on two main factors; the type of antifouling to be used and the situation of application on the ship. Obviously the antifouling and the anti-corrosive must be compatible, there must be good adhesion between them and also no reaction to impair the properties of either coating. Different areas of the ship require specific anti-corrosives; for example, around the steering gear, the hull and the splash zone where the environmental situations are very different.

Although it is not ideal, in practice only one anti-corrosive coating is used and this is based either on a chlorinated rubber resin or a pitch base, the system being chosen to be compatible with the antifouling to be used. Inevitably the coatings will not be continuous and pinhole free, and in service are likely to be damaged. There are also areas of the ship, such as steering gear, propulsion units and anchorage points which cannot be permanently coated, consequently other techniques to combat corrosion have been developed.

1.8.2 Cathodic Protection

The corrosion of metals in the marine environment is caused by the heterogeneous nature (chemical, physical and electrical) of the surface. In an electrochemical cell an electric current flows from certain points (local anodes) into and through the electrolyte (sea-water) to re-enter the metal at other points (local cathodes) as shown by the two half cell reactions below:

$$M \longrightarrow M^{+} \text{ (solvated)} + e^{-} \qquad \text{Anode}$$

$$X + e^{-} \longrightarrow X^{-} \text{ (solvated)} \qquad \text{Cathode}$$

The overall cell reaction being:

$$M + X \longrightarrow M^{+} + X^{-}$$

The local cathode remains free from corrosion while the anode acts as a site for corrosion hence the overall chemical reaction is the dissolution of metal ions at the anode and the formation of hydroxyl ions at the cathode. Cathodic protection is based on the fact that by making steel the only receiver of electric current (local cathode), by the use of either sacrificial anodes or impressed current anodes corrosion will be stopped.

(a) Sacrificial Anodic Protection (S.A.P.)

The anodes used here consist of a metal which is naturally anodic to steel, i.e. has a larger oxidation potential. The steel acts as the cathode and the anode dissolves leaving the steel protected from corrosion. Typically magnesium or zinc are used as the sacrificial anodes, lumps of the metal being attached to the hull below the water line. The number of these anodes varies although they are concentrated around areas where a breakdown in the anti-corrosive coating is expected, i.e. around the steering and propulsion units.

(b) Impressed Current Protection (I.C.P.)

With this system current for cathodic protection is supplied by the ship's generators and fed through the hull to anodes of suitable material. The anodes are permanent, typically constructed of platinised titanium or lead/silver alloy, and function by the liberation of chlorine

$$Cl^- \text{ (solvated)} \longrightarrow \tfrac{1}{2}Cl_2 \uparrow + e^-$$

S.A.P. systems are cheaper to instal than I.C.P., but the anodes need replacing from time to time whereas with I.C.P. the electrodes are maintenance free. With S.A.P. there is no means of regulating the current, this varying with the physical conditions whereas with I.C.P. the impressed current can be kept constant (normally computerised) thus ensuring maximum protection.

There is an area of over protection around the anodes in the I.C.P. method and so special coatings are necessary to prevent damage to the adjacent coatings. Deposits of magnesium carbonate and calcium carbonate can be formed around the cathode if there is chafing down to the steel thus reducing the current passing to the damaged area and so this tends to 'heal' any break in the coating.

1.9 Preparation of a Ship for Painting

The prefabricated sections of a ship are normally shop primed before they reach the shipyard to prevent corrosion before assembly. After the ship is assembled it is painted with several coats of anti-corrosive, chlorinated rubber (C.R.)

vinyl pitch or coal tar epoxy depending on the compatibility with the antifouling to be used. The ship is then coated with high build antifouling to obtain a high dry film thickness. The coatings are normally applied using an airless spraying technique which involves forcing liquid paint through a nozzel at high pressure (several thousand p.s.i.) causing the paint to atomise before reaching the surface.

When a ship is repainted certain problems have to be dealt with before a satisfactory surface for paint application can be obtained. Firstly all the fouling must be removed with the ship drydocked, this can be done by either scraping the ship by hand (a technology of possibly more than 2000 years' standing!) or using a high pressure water jet, the latter method is not as effective but is more economical for larger ships.

Figure 1.23 Removal of fouling using scrapers

Figure 1.24 High pressure water cleaning of a vessel in dry dock

The cleaned paintwork may then display several faults; there may be chafing damage, detachment of large areas where intercoat adhesion has failed, and corrosion.

Ideally a smooth surface should be obtained prior to repainting, either by grit blasting and by filling badly damaged areas with anti-corrosive primer. In practice this ideal is seldom realised as considerations of cost and time are dominant. With the ship prepared for repainting generally one coat of anti-corrosive is applied followed by two coats of antifouling; the latter is applied only below the water line as a consequence of relatively high cost.

Figure 1.25 Surface Corrosion on the Bows of a Ship

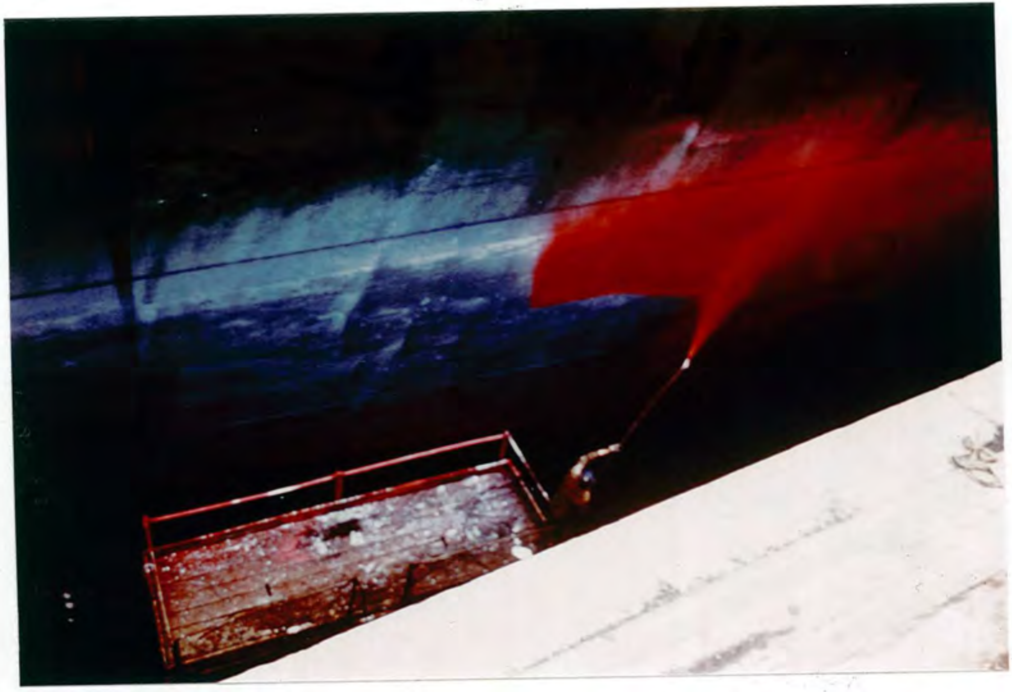


Figure 1.26 Spraying of a ship with Antifouling

Figure 1.27 A repainted ship

The cost of repainting a ship varies with the place of drydocking, the paint system used, the condition of the vessel and its size. As an example a 3-7 year old 280,000 d.w.t. supertanker (area of hull $27.2 \times 10^3 m^2$) might have an overall cost of a full recoating of the hull as high as £232,000,[4] this figure not including the drydocking charge or any account of lost revenue due to the ship being out of commission.

1.10 Antifouling Paints

The improvements in antifouling paints over the last few decades stem largely from the work carried out by the U.S. Navy during the Second World War when it was realised that the antifoulings available at the time were inadequate. A comprehensive report of this work is widely used as the standard source of information on the requirements and design of antifoulings.[8]

The advances made in the production of better antifouling paints in recent years can be ascribed to several factors:

(i) greater understanding of the fouling mechanisms,

(ii) better insight into the modes of action of antifouling paints, and

(iii) use of new materials in antifouling paints.

1.10.1 Formulation and Testing of an Antifouling Paint

There are two sets of criteria which must be applied when formulating antifouling paints, one set applying to the toxin and the other to the paint film.

With current conventional antifouling coatings toxins are the most important ingredients, since they are the components which prevent fouling. They function by controlled release of toxin from the paint matrix into the laminar sublayer thus in theory killing the fouling organism before settlement. The important characteristics of the toxins are:

(a) they should have a low solubility in sea water (<50 ppm) but, not of course be totally insoluble,

(b) they should have a wide spectrum of toxicity to marine fouling organisms,

(c) they should not create an ecological problem,

(d) they should be compatible with the paint medium in which they are placed and stable,

(e) they should be of reasonably low price, and

(f) they should not present an application problem.

Many toxins are patented each year most of which are of little use to the antifouling chemist as the above criteria are not satisfied. The main biocides which are used in commercially available antifoulings today are: copper I oxide, copper I thiocyanate, zinc oxide, bis tributyl tin oxide (TBTO) and triphenyl tin fluoride, often a combination of these being used to broaden the range of toxicity of the coating.

The role of the paint film is that it must be able to release the toxin at a rate which allows the prevention of fouling, while retaining its structural integrity so that its ability to adhere to the hull and withstand mechanical stresses is not reduced.

The paint formulation is dependent on the toxin and also the mode of release of the toxin. The compounds used in a successful paint formulation have generally been selected on the basis of a trial and error approach as there is at present no satisfactory method by which the antifouling nature of the paint can be predicted.

The ultimate test for an antifouling is to paint a ship's hull but prior to this cheaper and less expensive tests are conducted. Test panels coated with the new antifouling are immersed in sea water, usually under a raft in an estuary, the flow of water past these panels simulating the ship's passage through water. This tests the ability of the coating system to prevent fouling and also gives a guide to its active life and to the integrity of the film after prolonged exposure.
If a new coating system appears to be promising the next stage in testing is to attach coated bilge keel panels to a ship in service, the last stage before full scale ship trials are test patches (50-100m^2) painted on various ships. The expense involved in each of the test methods increases therefore it

Figure 1.28 B.S.R.A.'s raft for testing new antifouling paints, which is stationed in the estuary at Poole Harbour

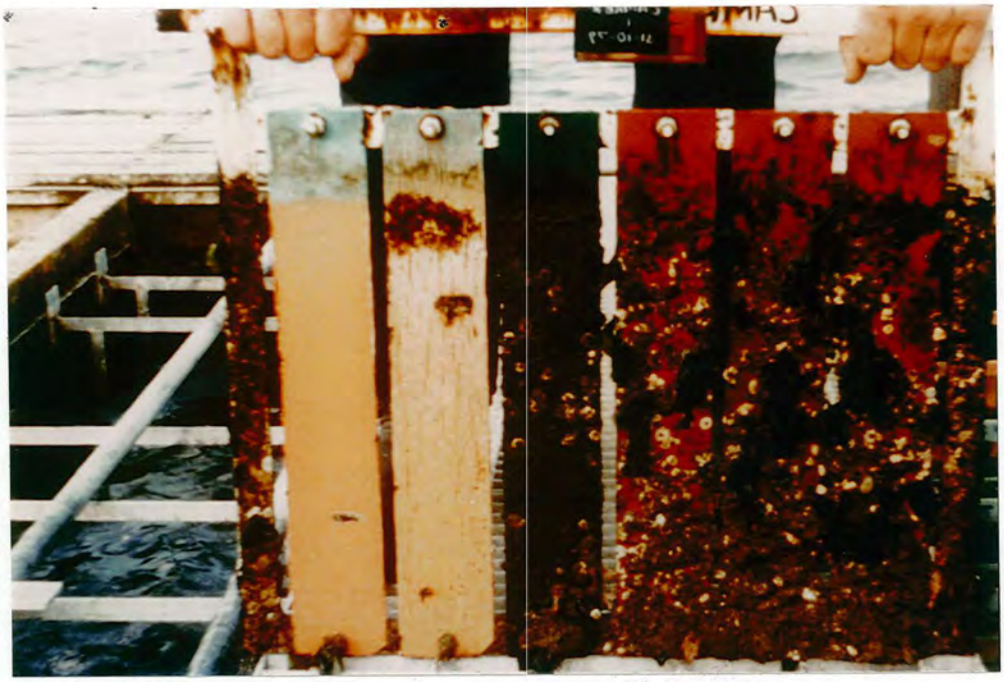


Figure 1.29 Panels coated with antifouling paints after several months' immersion in sea water

is essential that only antifoulings which are virtually certain to prove adequate are applied as test patches. The development of a new antifouling can take up to six or seven years due to the lengthy testing periods required.

The leaching of toxins from an antifouling coating can be determined very easily in the laboratory as can the lethal dose to the fouling organism, although it is impossible to apply this data to the real situation; generally a much higher leaching rate is required in practice than would be predicted on the basis of laboratory estimates. This illustrates that the factors which influence leaching rates form a complex matrix of interacting physical and chemical parameters impossible to quantify.

1.11 Types of Antifouling Paints

The effectiveness of conventional antifouling paints is determined by the efficiency with which the biocide is transported from the coating to the sea water immediately adjacent to the hull. It is necessary to obtain a constant release rate from the matrix and, until recently, only two types of antifoulings were available; namely, continuous contact and soluble matrix antifoulings. Recently, however, a new method for release of the toxin has become available and widely used, this utilises a sea water degradable matrix.

1.11.1 Continuous Contact

These coatings operate on the principle that close packing, either cubic or hexagonal, of the soluble biocide or fillers, is exceeded in the dry paint films, thus ensuring continuous contact between the soluble particles throughout the film. The required amount of this soluble material is 52% by volume for cubic close packing and 74% by volume for hexagonal close packing. With the appropriate criterion satisfied it can be assumed that each soluble particle is in contact with its neighbour and so a potential channel for water to enter the coating and dissolve the toxin exists, thus providing, in principle, a constant leaching rate. This process can be seen to occur by microscopic examination of the coating before and after immersion, Figure 1.30 and is also represented diagrammatically in Figure 1.31.

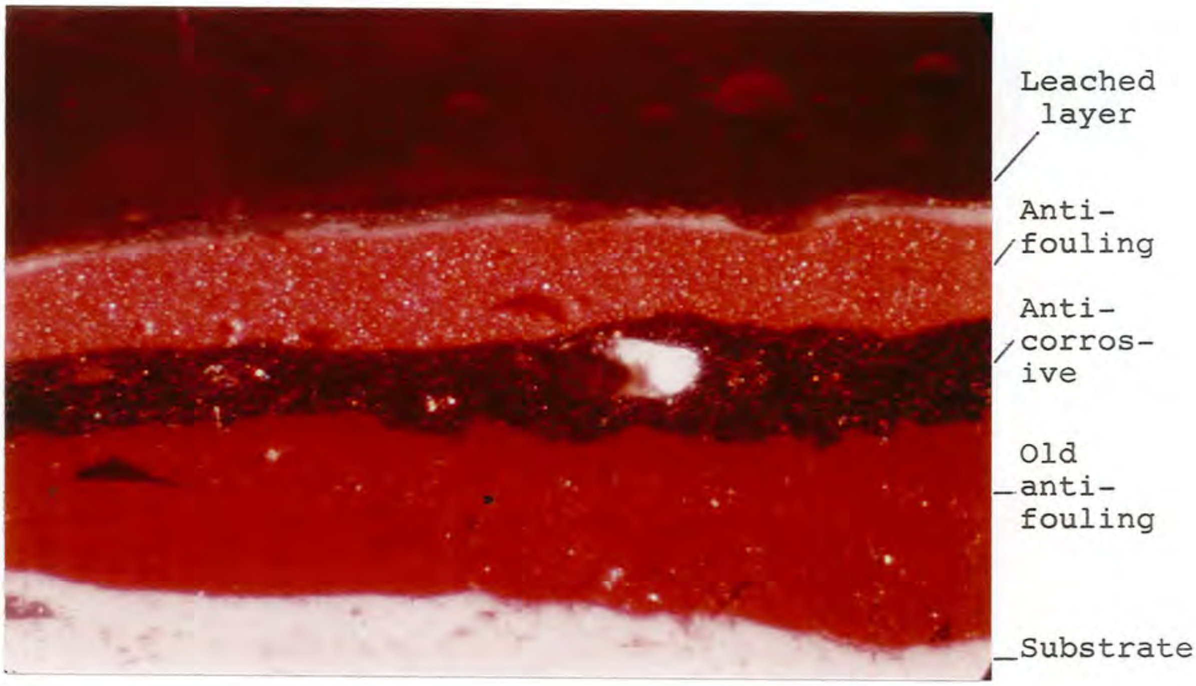
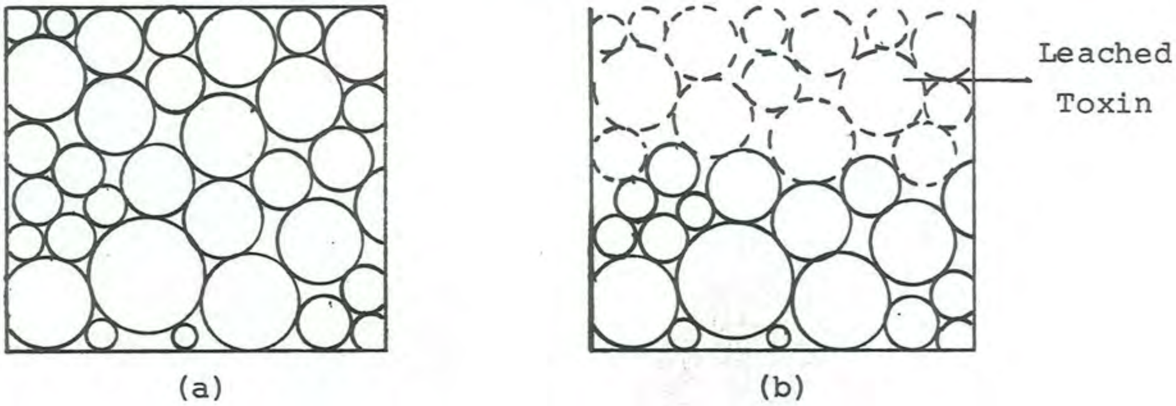


Figure 1.30 Cross-section of a paint flake removed from an in-service ship examined under a microscope



(a) (b)

Figure 1.31 The newly applied antifouling (a) and the same system after immersion (b), note the vacant pigment sites

The surface particles are the first to dissolve, their space being occupied by sea water. The surrounding particles are separated from this sea water by a thin film of the matrix, water diffuses through this film until the osmotic pressure is so great that the film fractures causing the release of the pigment (toxin) into the surrounding sea water, the rate of diffusion being dependent on the particle size.

As this process proceeds the relatively porous exhausted matrix of insoluble binder left after removal of toxin and filler builds up on the surface and begins to play an important role in determining the leaching rate, the rate decreasing exponentially. As a consequence of this decreasing leaching rate a very high initial leaching rate for toxins is required in order to extend the lifetime of the antifouling; thus the minimum leaching rate for copper I oxide to prevent fouling is $10\mu g/cm^3/day$ but in a new antifouling of this type the required rate can be as high as 30 or $40\mu g/cm^3/day$.

Marson assumed that the leaching rate was dependent on the diffusion characteristics of the solvated pigment through the exhausted matrix and the diffusion layer of the leachate (i.e. the area where the sea water is diffusing into the pigment) in direct contact with the surface of the unleached paint.[25] Using these assumptions he has shown that for a continuous contact coating the leaching rate is related to the physical properties of the pigment, the vehicle, the leachate and the conditions of exposure. He formulated an expression for ideal conditions which appears to correlate with laboratory data; unfortunately the number of variable parameters involved make it impossible to produce a reliable guide for the manufacture of antifoulings.

Most continuous contact coatings are based on a vinyl copolymer generally vinyl chloride 87%/vinyl acetate 13% (VYHH) or vinyl chloride 91%/vinyl acetate 3%/ vinyl alcohol 6% (VAGH) and rosin. Rosin is a natural polymer consisting almost entirely of a free acid (abietic) or a mixture of acids partly in the anhydride form. It is obtained as a residue, by the extraction of oil from oleoresin and is a solid, the colour of which determines its grade: the grade used extensively in the paint industry being classed as water white (WW) the purest form.

The antifouling activity of various combinations of Cu_2O, rosin, and the vinyl resin is as shown in Figure 1.32. It can be seen that compositions with high amounts of rosin are better antifoulants than those with a low content of rosin, this being due to the rosin-matrix being slightly soluble therefore alleviating the problem of the effect of the leached layer on the leaching rate.

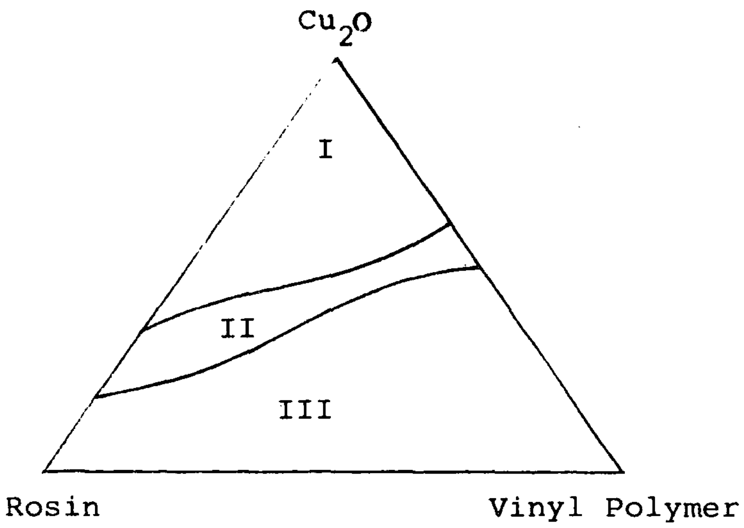


Figure 1.32 Antifouling Activity of Combinations of Cu_2O, Rosin and Vinyl Resin based on the results of Saroyan.[26]

I Good antifouling activity,
II Dubious antifouling activity,
III Insufficient antifouling activity.

Partington considered the effect of replacing the insoluble binder with extenders and he found that there was no significant effect in the performance until the volume of copper I oxide and the extenders exceeded that necessary for continuous contact.[27,28] At this point there is insufficient binder to surround both the copper I oxide and the extender and so the coating matrix will fail.

Extenders in theory can be used to regulate the leaching rate of toxins from the coating; the more soluble and the larger the particle size then the greater the leaching rate this being directly proportional to the percentage replacement. The depth to which the water penetrates is independent of the particle size of the extender, being affected only by the extender solubility, slow penetration being observed with a less soluble extender.

1.11.2 Soluble Matrix

This type of coating differs from the continuous contact antifouling in that the matrix is slightly soluble in sea water so that, in theory, as the matrix is dissolving a new toxic surface is constantly being exposed, thus the toxin is always on the boundary layer as illustrated in Figure 1.33.

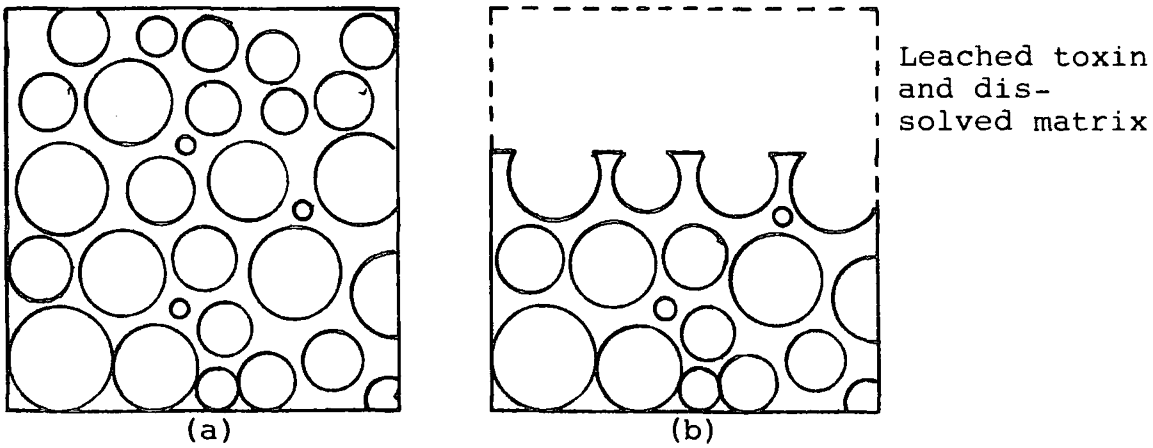


Figure 1.33 The newly applied antifouling (a) and the same system after immersion (b)

The percentage toxin content in this type of coating is low compared with continuous contact antifoulings, generally in the region of 10-25% by volume thus these are generally cheaper antifoulings owing to the toxin being the most expensive component in the paint. The soluble binder in this type of coating consists mainly of rosin, which, because of its carboxylic acid groups can react with the alkaline sea water forming water soluble salts.

The leaching of the toxin occurs by the solvation of the matrix, the toxin particles always being at the water coating interface, this in theory producing a uniform leaching rate. It is found, however, to decrease regularly with time, this being due to the fact that the toxin has to diffuse through the residual exhausted matrix on the surface.

Partington conducted research into the use of other resins such as coal tars, phenolic resins, synthetic resins and rosin derivatives, used in conjunction with rosin to form the paint matrix,[28] this allowed some empirical control of the leaching rate.

Research into the use of extenders has also been carried out and has shown that soluble extenders increase the leaching rate more than the inert extenders, both having a faster leaching rate than coatings without extenders.[28] The influence of the extender also depends upon the solubility of the matrix, the less soluble the matrix the smaller the effect of the extender. The explanation of this effect is probably related to the reactivities of the extender towards the binder material; for example, a common extender ZnO, may react with rosin to form soaps which affect the solubility of the matrix.

In general soluble matrix coatings have a shorter life than continuous contact coatings and so their uses are limited to ships that are continuously moving or as a "launching antifouling" to prevent fouling while the ship is being fitted out.

The graph below, Figure 1.34, shows the leaching rate of copper I oxide from a conventional antifouling; either a continuous contact or a soluble matrix, for the first six months there is excessive leaching of the biocide, the rate being exponential, after which time weed fouling begins to settle.

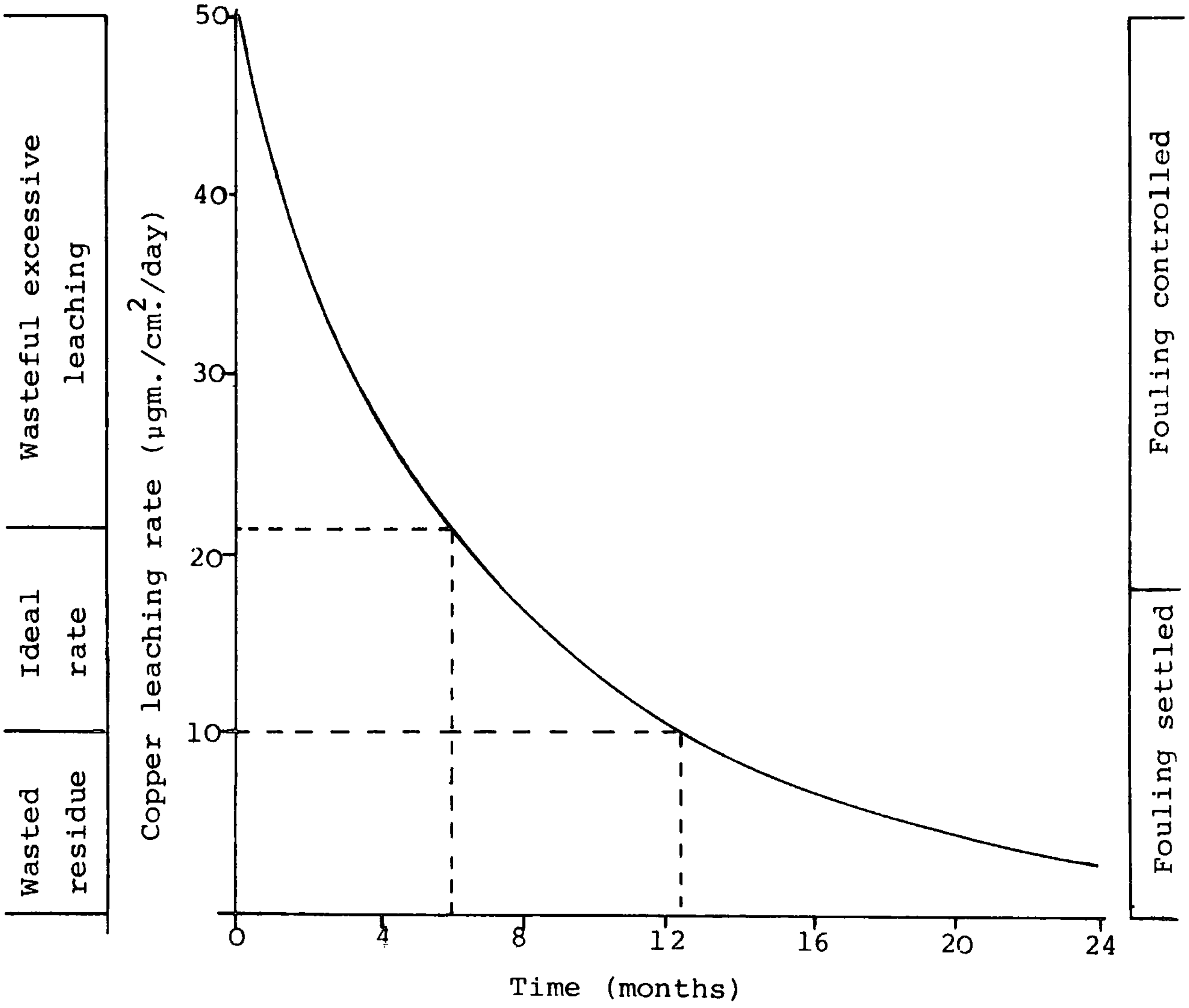


Figure 1.34 Biocide Leaching Rate from a Conventional Antifouling Paint

After thirteen months most types of fouling settle the leaching rate having dropped to below 10µg/cm^4/day the minimum required to prevent fouling; the paint system is now described as exhausted and needs replacing.

1.11.3 Organometallic Antifoulings

The development of this field started in the sixties, it arose because of the increased availability of cheap organometallic biocides, these being organo arsenicals, organo mercurials, organo leads and organo tins; the latter being used extensively in modern antifoulings as it is believed that they do not present a serious ecological problem.[29]

The major problem with copper I oxide and other commercially available biocides was that they were unsuccessful in the control of diatoms and bacteria, which, once they form the initial slime, affect the leaching rate of the toxin. Research carried out by the Institute of Organic Chemistry T.N.O. in the Netherlands and by the Tin Research Institute showed that the optimum biological activity of organo tin compounds occurs when the tin atom is trisubstituted, see Figure 1.35. The most active towards fungi being species of the type R_3SnX where X is a halogen or acid residue and R may be either aliphatic or aromatic, the toxicity of these trisubstituted tin compounds varies greatly depending on the R groups, Figure 1.36. Thus tributyl tin derivatives are very toxic whereas trioctyl tin derivatives are sufficiently non-toxic to be used as stabilisers in P.V.C. food and drink cartons.

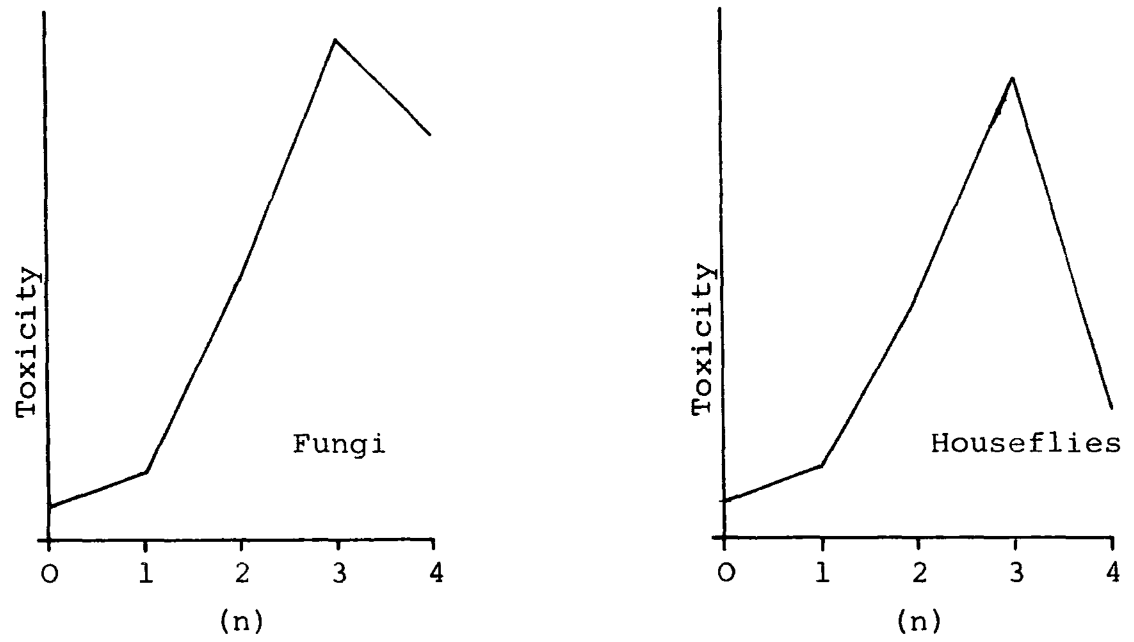


Figure 1.35 Variations of the toxicity of organo tin compounds R_nSnX_{4-n} with the number of organic groups bound to tin for Et_nSnCl_{4-n} towards fungi and Ph_nSnCl_{4-n} towards houseflies

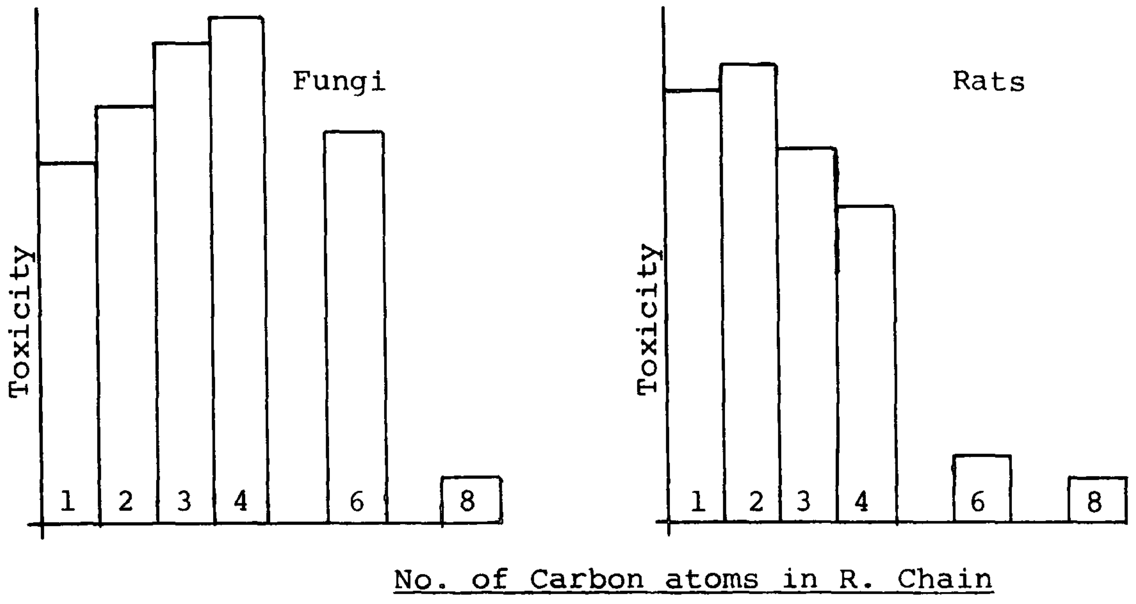


Figure 1.36 The toxic nature of organic groups bound to tin for $CH_3COOSnR_3$

It has also been shown that when R is kept constant in the derivatives of the type R_3SnX and X is varied the biological activity does not vary for a very large variety of X groups thus the biological activity is primarily due to the trialkyl tin units.

However, activity may be increased by the use of a specific biologically active anion X in the triorgano tin molecule (for example tributyl tin pentachlorophenoxide).[30] These tin derivatives are generally more effective against algae than against other fouling, Table 2.[31,32]

TABLE 2 Effectiveness of various toxins against fouling organisms

Antifoulant Toxin	Range of Activity (ppm.) of toxin in sea water	
	Algae	Barnacles
R_3SnX	0.01 - 5	0.1 - 1
Cu_2O	1 - 50	1 - 10
R_3PbX	0.1 - 1	0.1 - 1
RHgX	0.1 - 1	0.1 - 1

The original use of organotins was in crop protection, the first commercially available products being based on bis tributyl tin oxide (TBTO) and bis tributyl tin sulphide (TBTS), as the demand increased other useful organotins found application, for example triphenyl tins and other derivaties of the tributyl tins. Organotin compounds are of major importance as biocides, they eventually degrade to tin oxide which is non toxic whereas many of the other organometallic compounds are either stable or degrade to products which remain toxic.

Tin fluorides exist as high melting solids, whereas oxides, sulphides and chlorides are liquids or low melting point solids. The liquid organotins were difficult to incorporate into antifoulings because of the reactiveness towards acids or acid salts which resulted in uncontrollable leaching rates. The leaching rate of tributyl tin fluoride was too high whereas triphenyl tin fluoride leached too slowly although somewhat better antifouling activity was observed,[33] these early problems were overcome and organotin fluorides are now widely used in conventional antifouling paints together with other toxins to increase the biocidal range.

Since 'contact' and 'soluble matrix' antifouling systems exhibit an exponential leaching rate there is an 'overkill' in a newly applied antifouling.[34] An antifouling which exhibited a constant leaching rate with respect to time would be both financially and ecologically beneficial. Owing to the effectiveness of organo metallics as toxins towards fouling organisms much research has been conducted into organometallic polymers as components of antifouling paints, in the hope that these might give controllable leaching rates.

The criteria governing the inclusion of these organometallic polymers (O.M.P.s) into antifouling coatings being that they must be able to act as a resin base for the paint, maintain their integrity in sea water and also show some antifouling activity, this latter criterion being satisfied by the polymer hydrolysing and releasing toxic triorganotin derivatives.

The number of types of polymer which are in principle available are endless, polyvinyl derivatives, polyethers, polyurethanes, polyesters, polyolefins, etc. In practice relatively few appear to meet the requirements for useful coatings.

Research into the stability of various tin linkages to hydrolysis has shown that the tin carbon bond is very stable in contrast to the tin ether link which is hydrolytically unstable. A tin carboxylate linkage will hydrolyse and release the toxic tin salt at a rate appropriate for the satisfactory prevention of fouling: therefore intensive efforts have been made to synthesise polymers containing tin carboxylate linkages.[35,36]

Monteroso in 1962 patented a method of producing polymers of the type shown in Figure 1.37,[37,38] where R is a monovalent hydrocarbon radical and R´ is hydrogen or a monovalent radical

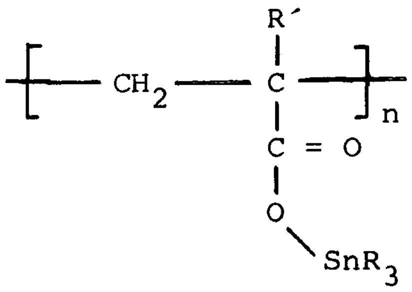


Figure 1.37 A typical trialkyl tin carboxylate polymer

The preparation of the monomer involved reacting triorganotin oxide with an unsaturated carboxylic acid, the reaction temperature being kept below 50°C to prevent polyester formation, the water produced being azeotropically removed. These monomers underwent ready free radical polymerisation at the vinyl group, Figure 1.38.

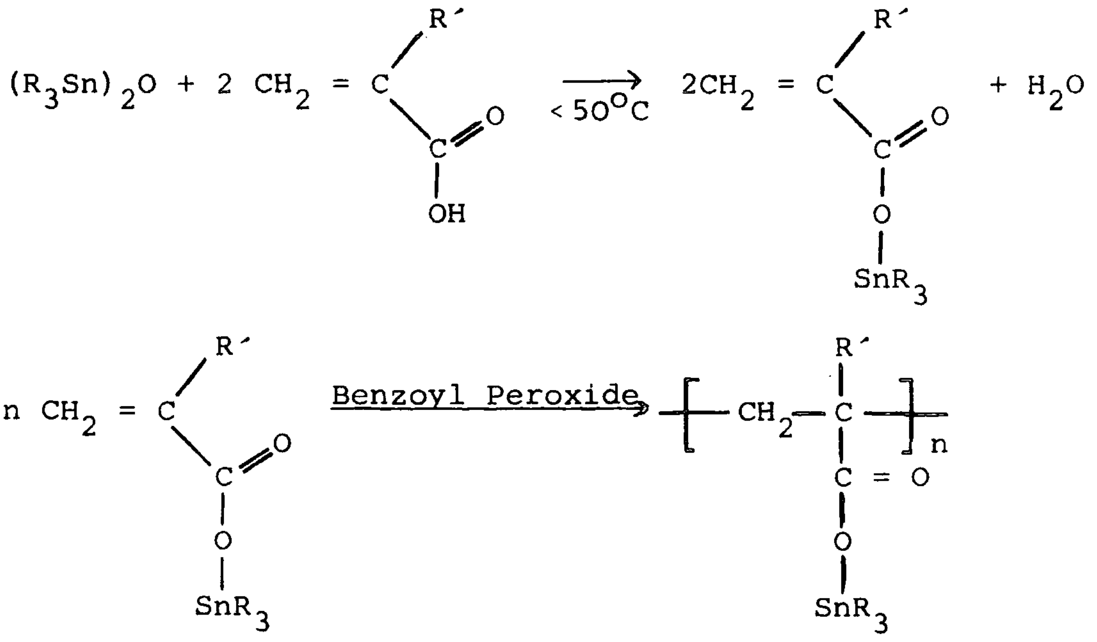


Figure 1.38 Synthesis of trialkyl tin carboxylate monomers and polymers

An alternative route of synthesis was the reaction between acrylic acid and trialkyl tin hydride,[39] this however proved less satisfactory.

Copolymers of vinyl acetate and/or vinyl chloride with the vinyl tin carboxylate were also prepared, variations in the observed physical and chemical properties being achieved by varying the molar ratios in the feedstock and the order of addition to produce what were claimed to be either random or block copolymers.

An American Company, M & T Chemicals, produced similar polymers to those described above.[40,41,42] They noted their biocidal and fungicidal properties and so incorporated them into simple paint formulations. The corresponding organotin sulphide polymers were also prepared,[43] these being formulated into paints. Little interest was shown in these polymers as resins for antifouling paints due to their expense compared to the conventional antifoulings. For some time these materials were too expensive for widespread use but with the rapid increase in fuel prices in the early 1970s came the necessity for better, more efficient antifoulings and these organotin polymers received more attention.

In 1974 Dyckman and Montemarano summarised the factors affecting the rate of hydrolysis of these polymers:

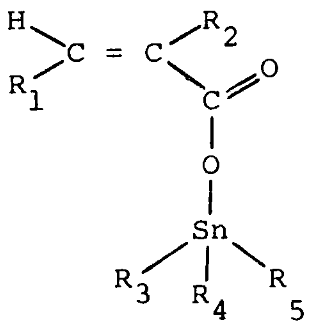
(i) the polymer type,

(ii) the degree of crosslinking within the polymer backbone,

(iii) the degree of substitution by organometallic groups along the polymer backbone, and

(iv) environmental conditions, sea water temperature, salinity, oxygen content, hydrogen ion concentration and turbulence.

A wide range of organotin carboxylate polymers has been prepared from unsaturated organotin monomers of the general formula shown in Figure 1.39. Using monomers of this type, homopolymers and random copolymers may be prepared by free radical initiated processes. High crosslinked copolymers may be prepared by co-polymerisation with unsaturated alkyd resins.[44]



where: $R_3R_4R_5$ are the same or different alkyl radicals with 2-6 carbon atoms or a phenyl radical.

R_1 and R_2 are alkyl radicals with a maximum of 2 carbon atoms, H atoms or phenyl radicals.

Figure 1.39 <u>Typical unsaturated organotin monomers</u>

James patented the use of organotin copolymers of the type shown in Figure 1.40 and noted that their antifouling properties were best when the polymer had a relatively low molecular weight,[45] providing that this was high enough to give a film forming material with the required mechanical properties. Workers of the Nippon Oil and Fats Co. Ltd.[46] claimed that the addition of unsaturated organic acids such as maleic, fumaric, acrylic or methacrylic acid improved the properties of these organotin polyacrylates with respect to hydrolysis, film forming character and adhesion. Russian workers claimed that polyorganotins based

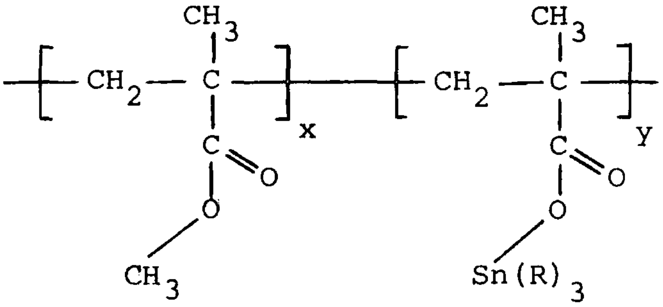


Figure 1.40 <u>Triorganotin/methyl methacrylate copolymer</u>

on bis(trialkyl tin)maleates (Figure 1.41) showed the required film forming and biocidal properties.[47]

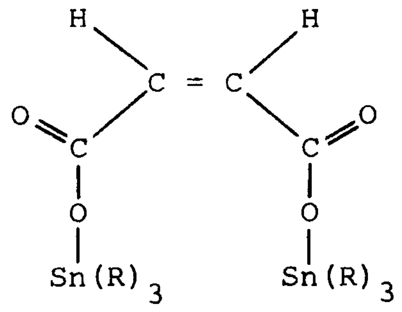


Figure 1.41 Bis(trialkyl tin)maleates used by Soviet workers

Organotin polymers have been extensively researched as a survey of the literature shows (ref. 48-71). Much of this work is repetitive with only minor changes in the details of preparation and formulations being reported, these subtle variations are primarily of interest to patent lawyers.

The formulation of these organotin polymers into paints requires as much work and research as their preparation so as to achieve the maximum antifouling activity and also ensure the compatibility of all the components of the paint. Leebrick formulated paints based on organotin resins with large volumes of inactive, non toxic pigments; the resulting coatings showed some antifouling activity, although this was insufficient to produce a marketable antifouling.[42] James, and Deeks *et al* incorporated soluble pigments into organotin resins and claimed to have greatly improved their antifouling properties, these coatings being the first commercially available antifouling paints based on organotin resins. They were used as non-corrosive antifoulings for aluminium hulled yachts.[45,72] The use of these organotin based paints for seagoing vessels proved disappointing due to their excessive 'erosion' or 'exfoliation' when in service although they appeared to act as reasonable antifoulings.

The methods of testing antifoulings were mentioned previously, correlation of data between static raft trials and in-service trials have shown that:

(a) the lifetime estimated for these antifoulings as a result of static raft trials were excessive,

(b) it was difficult to produce an antifouling with a service life of 18 months or longer,

(c) the organotin copolymer antifoulings when properly formulated were much superior to the conventional antifoulings,

(d) the difference between static and dynamic behaviour of tin copolymer antifoulings was dramatic,

(e) the mechanism by which the material was removed from the surface was controllable and so the terms exfoliation and erosion could no longer be used to describe the process.

As can be seen by these observations, the mode of action of these organotin resins is completely different to those previously described for contact and soluble matrix antifoulings. These organotin polymers are generally of the polyacrylate type with tributyl tin esters attached to the polymer backbone. The ester linkage is hydrolytically unstable in sea water (pH 8.0-8.2) which results in the formation of a polyacrylate salt and a solvated biocide, the triorgano tin hydroxide (Figure 1.42). The polyacrylate salt slowly begins to swell as it becomes solvated, and eventually dissolves, resulting in a new surface of the polymer being exposed. The rate of this solvation process is dependent on the polymer type, the number of organotin ester linkages in the polymer, the molecular weight of the polymer, the pigmentation of the

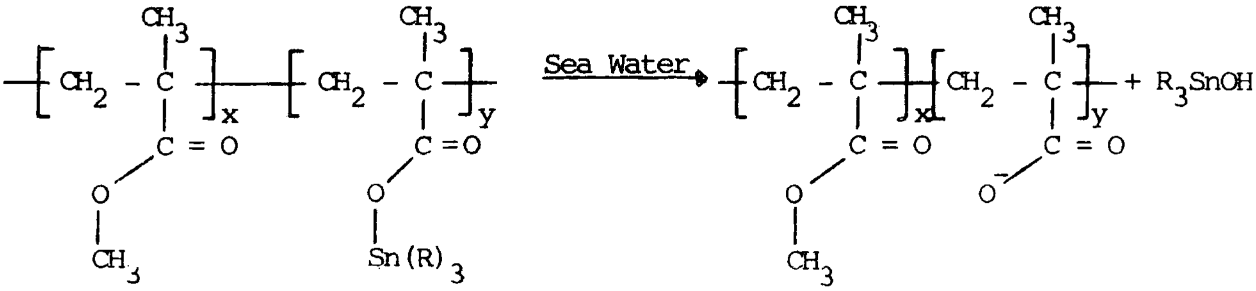


Figure 1.42 Sea water hydrolysis of organotin polymers

polymer and also variations in the environment to which it is exposed therefore in theory an antifouling of this type should be able to hydrolyse at a rate sufficient to prevent fouling and have a constant leaching rate. The leaching rate is now controllable unlike that of the conventional antifoulings and also the surface roughness of these coatings decreases with increased service time due to the hydrolysis of the resin therefore these antifoulings are described as polishing.

The pigmentation of these resins greatly affects their performance, if a soluble pigment or biocide is used and the level of inclusion is about that required for continuous contact the rate of hydrolysis is found to be increased.

This observation is rationalised by the fact that as the pigment leaches from the resin then the surface area of the polymer exposed to the sea water is increased resulting in the faster hydrolysis of the polymer.

The initial polymer will consist of coiled and fairly compact chains but on hydrolysis conformational changes will occur due to the solvation of the ionic polymer. This can result in the formation of highly crosslinked systems owing to the presence of multicharged cations in the sea water forming inter and intra molecular bridges between the anionic sites on the polymer chains which again affects the hydrolysis rate.

It has also been found that the incorporation of heavy metal biocides (zinc oxide,copper I oxide, copper I thiocyanate) into these polymers produces strong chelated structures which are insoluble even after prolonged exposure to sea water.

The main criteria in the design of these organotin antifoulings is to produce a film which undergoes hydrolysis at a rate sufficient to prevent fouling. It has been found that the inclusion of low molecular weight hydrophobic compounds, such as chlorinated paraffin wax, naphthalene, diphenyl ether and low molecular weight polybutene, into these organotin resins can give control of the polishing rate although their mode of action is not certain.[63] With the wide variety of resins, pigments and hydrophobic additives available, research into the systematic elucidation of the effects of the constituents of such paints is still an active area of research.[73]

Bennet and Millar claimed that a leaching rate of 1μg/cm^3/day of an organometallic biocide was sufficient to prevent fouling,[74,75] this in terms of polishing would correlate to 0.5μm/month for an organotin polymer of approximately 50% by weight of R_3Sn. This value has been found in practice to be a serious underestimation, the settlement of fouling being almost immediate, therefore to increase the performance of these polishing antifouling systems other biocides must be added.

To summarise the advantages of these types of organometallic antifoulings compared to the conventional antifoulings we have:

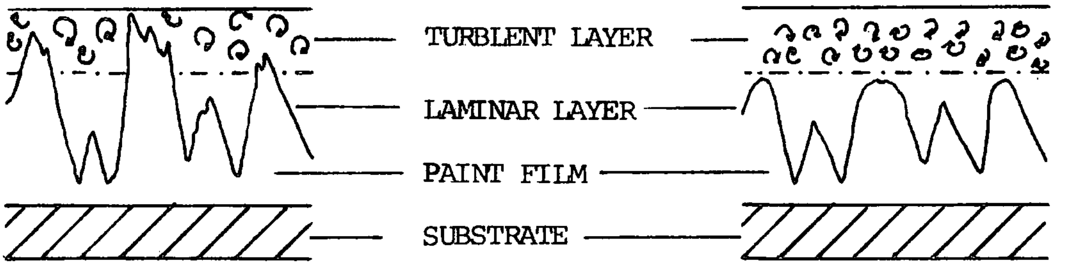
(a) the antifouling lifetime is proportional to the applied film thickness;

(b) there will be an approximately constant emission of biocide throughout the lifetime of the antifouling, making it easier in theory to produce a long life antifouling;

(c) the polishing of the surface ensures that there will be no accumulation of exhausted matrix, hence the surface roughness will decrease; and

(d) ideally when repainting the ship the surface should be smooth and fouling free therefore the drydocking time will be greatly reduced.

Milne and Hailes observed that with organotin antifoulings the rate of removal at the asperities of roughness was much greater than that on the depressed areas which resulted in the hull roughness decreasing with service time.[63] This observation may be rationalised by considering the peaks of roughness to protrude through the laminar sublayer into the turbulent layer where the eddy currents rapidly erode them until eventually they are confined in the laminar sublayer, Figure 1.43. The overall effect of this is a reduction in the frictional resistance with service time resulting in lower fuel consumption.[4]



Immediately after immersion

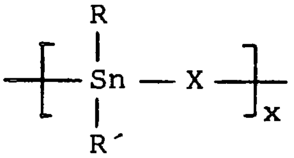
After several weeks service

Figure 1.43 Diagrammatic representation of how the peaks that protrude the laminar sublayer are eroded to produce a smoother surface

The commercially available polyorganotin paints are sold under the trade names S.P.C. (International Paints), C.Pol (Camrex), Nortic (Hempels), Sigma Plane (Sigma) and Takata-3-L (Nippon Oils and Fats) which are all based on the triorganotin carboxylate polymers previously described. The toxicity of the triorganotin compounds is high towards mammals, therefore they present a problem in their manufacture and application, if other less toxic resins could be prepared with the same polishing characteristics, then these would be preferred.

1.12 Diorganotin Polymers

The diorganotin analogues to the triorganotin compounds currently used in antifoulings are much less toxic (Figure 1.35), they are presently used for the stabilisation of P.V.Cs. and as catalysts for the room temperature curing of polyurethanes. Since they present no serious environmental hazard their incorporation into resins for antifouling paints could yield a hydrolysable and possibly polishing coating but this would have poor antifouling activity. Such diorganotin polymers would have the tin atom situated in the backbone of the polymer as shown in Figure 1.44.



$$-\left[\overset{R}{\underset{R'}{\mathrm{Sn}}} - X\right]_x-$$

where, R,R′ are organic groups and X is either organic or an inorganic group

Figure 1.44 A diorganotin polymer with the tin atom situated in the polymer backbone

There are presently four main types of diorganotin polymers, these being:

(i) organotin polyolefins,

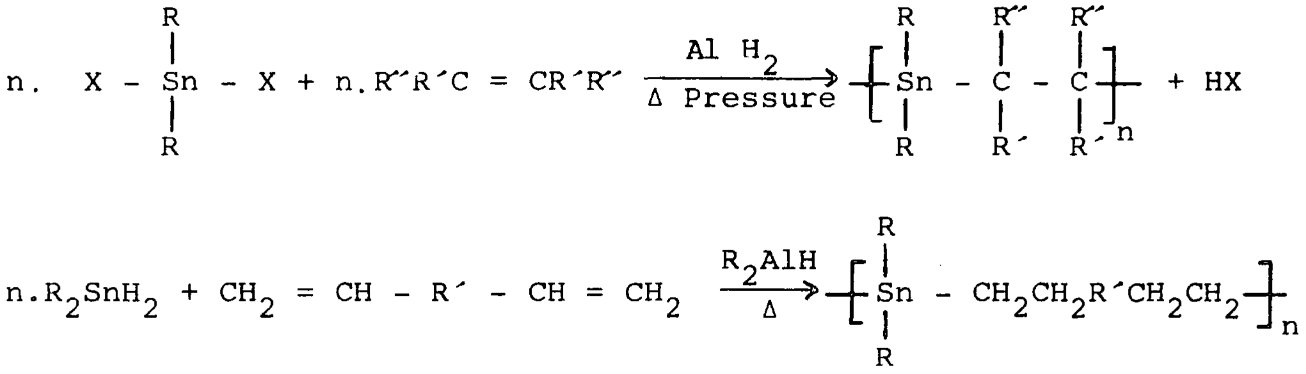
(ii) organotin polyethers,

(iii) organotin polyimines, and

(iv) organotin polyesters

1.12.1 Organotin Polyolefins

Organotin polyolefins can be prepared by treating olefins with organotin halides and hydrogen in the presence of aluminium at elevated pressures or using a diolefin and an organotin dihydride in the presence of an alkyl aluminium catalyst,[76,77] Figure 1.45.



$$n.\ X-\underset{R}{\overset{R}{Sn}}-X+n.R''R'C=CR'R''\xrightarrow[\Delta\ \text{Pressure}]{Al\ H_2}\left[\underset{R}{\overset{R}{Sn}}-\underset{R'}{\overset{R''}{C}}-\underset{R'}{\overset{R''}{C}}\right]_n+HX$$

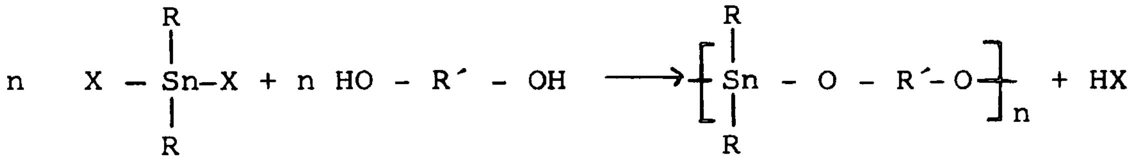
$$n.R_2SnH_2+CH_2=CH-R'-CH=CH_2\xrightarrow[\Delta]{R_2AlH}\left[\underset{R}{\overset{R}{Sn}}-CH_2CH_2R'CH_2CH_2\right]_n$$

Figure 1.45 Routes to Diorganotin polyolefins

The reaction between dialkyl tin dihydrides and diolefins in the presence of an alkyl aluminium catalyst has been found to produce both linear and crosslinked organotin polyolefins. Organotin polyolefins with interesting electrical properties have been prepared by reacting dilithium salts of diethynyl compounds with organotin dihalides, the resulting polymers being linear and filmformers.[78]

1.12.2 Organotin Polyethers

Carraher and Scherubel prepared these compounds using an interfacial technique; a diol forming one phase, with the diorganotin dihalides contained in an immisible organic phase. Because the hydrolysis of dialkyltin dihalides occurs in preference to alcoholysis the conventional aqueous/organic systems were not applicable to this synthesis,[79,80,81] Figure 1.46. The organotin polyethers are very susceptible to acid cleavage therefore triethylamine is dissolved in the diol to remove any acid produced during the polymerisation. The resulting organotin polyethers are of low to medium molecular weight the percentage yield varying with the monomers used and the reaction conditions. Infra red studies of the resulting polymers have shown the presence of Sn-Cl, Sn-OH and R-OH end groups but no $Sn-NEt_2$ or other similar end groups, this suggests that these polymers are stable towards weak base hydrolysis.[82]

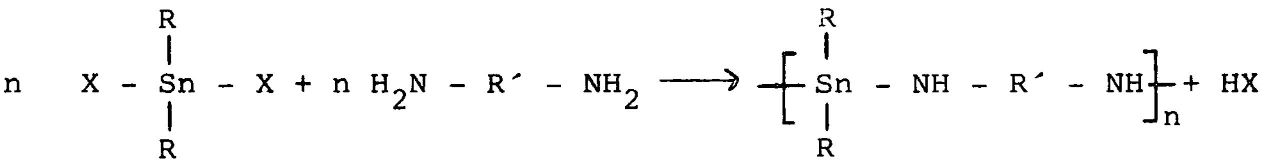


$$n\ X-\underset{R}{\overset{R}{Sn}}-X + n\ HO-R'-OH \longrightarrow \left[\underset{R}{\overset{R}{Sn}}-O-R'-O\right]_n + HX$$

Figure 1.46

1.12.3 Organotin Polyamines

These polymerisations were again carried out by an interfacial technique developed by Carraher and Winter using 2,5 hexenedione containing the dissolved diamine and a liquid hydrocarbon solution of the dialkyltin dihalide,[83,84,85] Figure 1.47. The factors influencing the molecular weight of the polymer were shown to be dependent on the size of the alkyl chain on the tin, the larger the chain then the higher the molecular weight, the leaving group X did not affect the molecular weight, and neither of these variables were found to alter the yield of the polymers.



$$n\ X-\underset{R}{\overset{R}{Sn}}-X + n\ H_2N-R'-NH_2 \longrightarrow \left[\underset{R}{\overset{R}{Sn}}-NH-R'-NH\right]_n + HX$$

Figure 1.47

1.12.4 Organotin Polyesters

Many organotin polyesters of the general structure shown in Figure 1.48 have been prepared by interfacial polycondensation methods as well as by direct reaction of the sodium salt of diacids with organotin dihalides.[86,87,88]

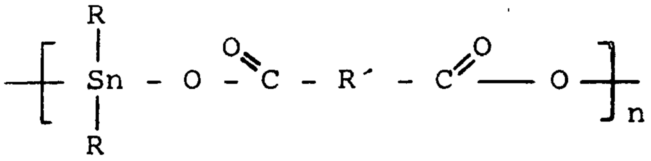


Figure 1.48

Andrews *et al* reacted dialkyltin diacetates with dicarboxylic acids producing organotin polyesters of molecular weights ranging from dimers to 3000.[89] Short chain acids generally lead to the formation of cyclic dialkyltin polyesters, while longer chain acids such as sebacic acid or conformationally rigid acids such as terephthalic acid lead to the formation of waxy linear polymers.[89] These polymers have been reported as exhibiting water repellency, being anti-fungal and it has been suggested, without experimental evidence, that they will show anti-bacterial activity.[90]

Reaction between the organotin dichloride in water and the alkali metal salts of carboxylic acids gave esters in high yields their structures being $R_2Sn(OOCR')_2$ and not tetraalkyl dicarboxy-distannoxanes $(R'CO_2SnR_2)_2O$ thus demonstrating that the reaction of the organotin halide with the carboxylate anion is faster than that with water.[87]

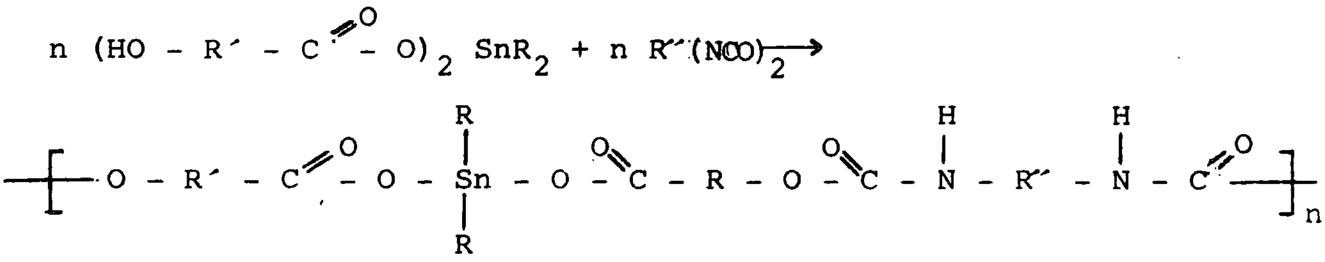
Thermal analysis of these polymers has shown them to be relatively stable, identical thermograms in air and under vacuum being recorded up to 240°C above which temperature oxidative degradation occurs in air.[91]

1.13 Diorganotin polymers as Components of Antifouling Paints

It has already been shown that diorganotin compounds are less toxic than their corresponding triorganotin analogues therefore it is logical to assume that their antifouling properties will be very poor. If the diorganotin polymer hydrolyses and dissolves at a rate sufficient to prevent the settlement of fouling then the surface should, in theory, remain free of such organisms; therefore it is necessary to consider which of the four previously described diorganotin polymers might exhibit such characteristics. Polyolefins are stable to acid and base hydrolysis whereas polyethers are very susceptible to hydrolysis, polyamines would be expected to undergo acid hydrolysis but not alkaline hydrolysis whereas Frankel *et al*[90] have shown that the polyesters are relatively stable towards both alkaline and acid hydrolysis therefore none of these polymer types would appear to be suited for incorporation into antifouling paints. However, since trialkyl tin carboxylate polymers which are currently used in antifouling paints are known to hydrolyse in sea water, it seems reasonable to suspect that the diorganotin polyesters will also undergo hydrolysis in the same environment, despite the reports of Frankel. The diorganotin polyesters described above do not exhibit the required film forming properties due to their low molecular weight therefore it was necessary to design a new polymer system with a high molecular weight which incorporated these tin-ester linkages.

The modern antifoulings are classed as high build, this means that the solvent content is low compared to the other components of the paint, therefore a high dry film thickness is achieved. There are various methods available to achieve this, one of them being the use of a two-pack system which consists of one pack containing the main constituents of the paint including a monomer or prepolymer and the second pack containing the curing agent and catalyst. The two packs are mixed either just prior to spraying or at the nozzle of the spray gun, the method used depending on the rate of reaction between the monomer or the prepolymer and the curing agent, the curing then occurs on the surface to which the coating is being applied. The two most common types of two-pack systems used in the paint industry are the urethane and epoxy systems.

The diorganotin class of compounds catalyse the urethane reaction therefore if a diorganotin di(hydroxycarboxylate) was prepared and reacted with a diisocynate the reaction should be autocatalytic and the resulting polymer should be of a high molecular weight, Figure 1.49. The following chapters describe the synthesis of such diorganotin di(hydroxy carboxylates) and their subsequent reaction with diisocyanates to produce polymers suitable for the incorporation into antifouling paints.



$$n\ (\mathrm{HO - R' - C(=O) - O})_2\ \mathrm{SnR_2} + n\ \mathrm{R''(NCO)_2} \longrightarrow$$

$$\left[\mathrm{O - R' - C(=O) - O - \overset{R}{\underset{R}{Sn}} - O - C(=O) - R - O - C(=O) - \overset{H}{N} - R'' - \overset{H}{N} - C(=O)} \right]_n$$

Figure 1.49 <u>Synthesis of polyurethanes containing backbone tin carboxylate units</u>

CHAPTER TWO

SYNTHESIS AND CHARACTERISATION OF MONOMERS

2.1 Introduction

The ever more stringent requirements of both the ship owner and the world's ecologists have stimulated the search for efficient antifouling paints that do not present a threat to the environment. The observation by Milne and Hailes that polymers containing triorganotin carboxylate groups undergo hydrolysis with the subsequent solvation of the polymer matrix has led to much research in this area.[63] Triorganotin polymers do not present a serious ecological problem by their hydrolysis but their uses have been extensively patented,[29] therefore new avenues of research into antifouling paints have been sought.

The area of research which will be discussed in this chapter is the synthesis and characterisation of dialkyl bis(hydroxy carboxylate)tin compounds, these being the precursors for the preparation of high molecular weight tin carboxylate containing polyurethanes.

2.2 Starting Materials

The criteria governing the choice of starting materials were that they be readily available, cheap and sufficiently pure to allow the large scale manufacture of the dialkyl bis(hydroxy carboxylate)tin monomers if the polymers prepared from them showed the required properties.

Two dialkyl tin oxides were used, di-n-butyl tin oxide and di-n-octyl tin oxide, both these compounds being supplied by Schering A.G., their specifications are listed in Table 2.1, the main impurities are likely to be mono and tri-alkyl tin derivatives.

	Di-n-butyl tin Oxide	Di-n-octyl tin Oxide
Structure	$(CH_3CH_2CH_2CH_2)_2SnO$	$(CH_3(CH_2)_6CH_2)_2SnO$
Molecular weight	248.92	361.14
Density	1.58	1.53
Melting point	Decomposes	Decomposes
Appearance	White Powder	White Powder
Purity	95%	95%

TABLE 2.1 Specification of the di-n-alkyl tin oxides used in the monomer syntheses.

The industrial preparation of these compounds involves the synthesis of a tetra-alkyl tin compound from tin^{IV} chloride.[92] Three reliable syntheses have been established using different alkylating methods as shown below:

(i) using Grignard reagents

$$SnCl_4 + 4RMgCl \longrightarrow R_4Sn + 4MgCl_2,$$

(ii) using Wurtz coupling

$$SnCl_4 + 4RCl + 8Na \longrightarrow R_4Sn + 8NaCl, \quad \text{and}$$

(iii) using Aluminium alkyls

$$3SnCl_4 + 4R_3Al \longrightarrow 3R_4Sn + 4AlCl_3.$$

The tetra-alkyl tin is reacted with an equimolar amount of tin^{IV} chloride and the resulting dialkyl tin dichloride hydrolised to give the dialkyl tin oxide (Figure 2.1)

$$\begin{tikzcd}
R_4Sn + SnCl_4 \arrow[r] & 2R_2SnCl_2 \arrow[d, "HCl"', "NaOH"] \\
& 2R_2SnO
\end{tikzcd}$$

Figure 2.1 Preparation of dialkyl tin oxides.

The hydroxy acids were used as supplied, they are listed in Table 2.2. A wide range of hydroxy acids were used with the objective of finding out how the polymer characteristics varied with the structure of the tin carboxylate moiety.

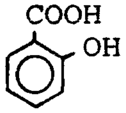
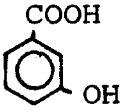
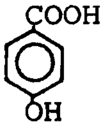
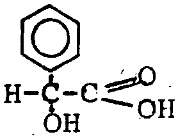
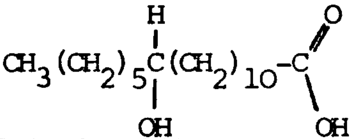
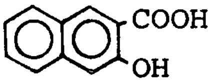
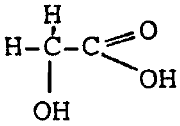
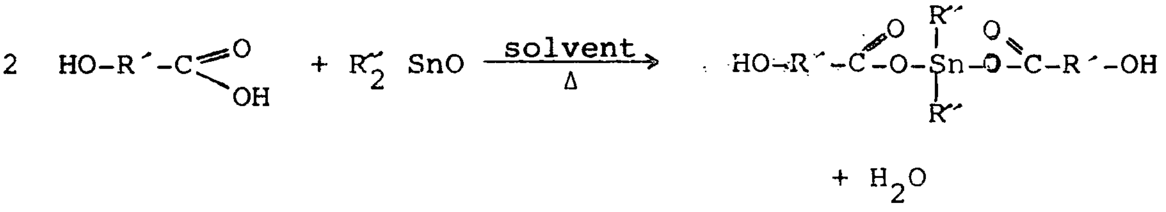
Hydroxy Acid	Supplier	Structure	Mol.Wt.	Melting Pt. °C	Purity (%)
o-Hydroxy benzoic acid	B.D.H.		138.12	157-162	99
m-Hydroxy benzoic acid	B.D.H.		138.12	201-204	99
p-Hydrozy benzoic acid	B.D.H.		138.12	215-217	99
Mandelic acid	B.D.H.		152.15	119-123	99.5
12-Hydroxy - stearic acid	Eastman	 $CH_3(CH_2)_5CH(OH)(CH_2)_{10}COOH$	300.48	73-77	98
3-Hydroxy - 2 - naphthoic acid	Fluka		188.18	216-220	95
Glycolic acid	Aldrich	 $H_2C(OH)COOH$	76.06	77-79	99+

TABLE 2.2 Suppliers and Specifications of the hydroxy acids used in the monomer synthesis

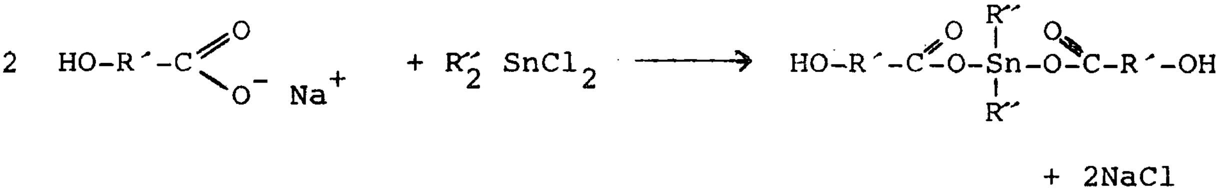
2.3 Choice of method for the monomer syntheses

Synthesis of the diorgano bis(hydroxy carboxylate)tin monomers from the reaction of a dialkyl tin oxide with a hydroxy carboxylic acid, and from the reaction of a dialkyl tin dichloride with the sodium salt of a hydroxy carboxylic acid, has been reported previously.[93] The route using dialkyl tin oxide as starting material relies on the azeotropic removal of water, while the route from dialkyl tin dichloride can be conducted using either an homogeneous solution or an interfacial technique, see Figures 2.2 and 2.3



$$2\ \mathrm{HO{-}R'{-}C(=O)OH} + \mathrm{R''_2SnO} \xrightarrow[\Delta]{\text{solvent}} \mathrm{HO{-}R'{-}C(=O){-}O{-}SnR''_2{-}O{-}C(=O){-}R'{-}OH} + \mathrm{H_2O}$$

<u>Figure 2.2.</u>

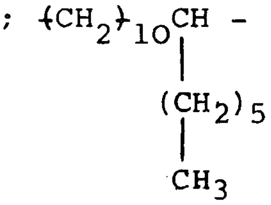


$$2\ \mathrm{HO{-}R'{-}C(=O)O^-\ Na^+} + \mathrm{R''_2SnCl_2} \longrightarrow \mathrm{HO{-}R'{-}C(=O){-}O{-}SnR''_2{-}O{-}C(=O){-}R'{-}OH} + 2\mathrm{NaCl}$$

<u>Figure 2.3.</u>

where R′ = ortho-, meta- or para phenylene;

2,3 naphthylene; phenylmethylene;



$\mathrm{{-}(CH_2)_{10}CH{-}}$ with $\mathrm{(CH_2)_5CH_3}$ on the CH

and R″ = butyl or octyl

Most of the work directed to the preparation of the dialkyl bis(hydroxy carboxylate)tins used the former route as the water produced could be azeotroped out of the reaction mixture using a Dean-Stark apparatus and this allowed the extent of the reaction to be monitored. The solvent used initially was toluene, it was thought that at the reflux temperature (∿112°C) decarboxylation might occur in some instances. To test this possibility the apparatus was swept with a stream of nitrogen and the effluent gas was bubbled through lime water. In no instance was carbon dioxide detected.

For some experiments the solvent was changed to hexane, which boils at 63°C to see if there was any variation in yield, but both solvents were found to give virtually quantitative yields. Toluene was generally more convenient since problems were encountered in regulating the boiling rate of hexane.

The thermal and interfacial reaction of a di-alkyl tin dichloride with the sodium salts of carboxylic acids was also investigated, the only difference being that there was no visual indication of the progress of these reactions as the sodium chloride remained in the reaction flask. All the experiments were carried out under dry nitrogen.

The criteria of purity were:

(i) carbon, hydrogen and tin analysis,
(ii) melting point, and
(iii) infra-red spectroscopic analysis.

The infra-red analyses were used mainly to show that reaction had occurred; a peak at $\sim 400\ cm^{-1}$ due to Sn=O stretching was present in the starting material but had disappeared after reaction. The peaks due to the carbonyl group, the hydroxyl group and the various C-H stretches were still observed.

Mass spectroscopic analysis was of little use since the splitting patterns were complex and no parent peaks were observed. Fragment ions containing tin were easily identified by the characteristic isotope peaks (Figure 2.4) as isotope patterns corresponding to the presence of the tin atoms were observed.

The experiments were initially carried out on a small scale to establish a familiarity with the procedure and to check that the synthesis worked, after this had been achieved a relatively large scale ($\sim$ 500g) preparation of monomer was undertaken.

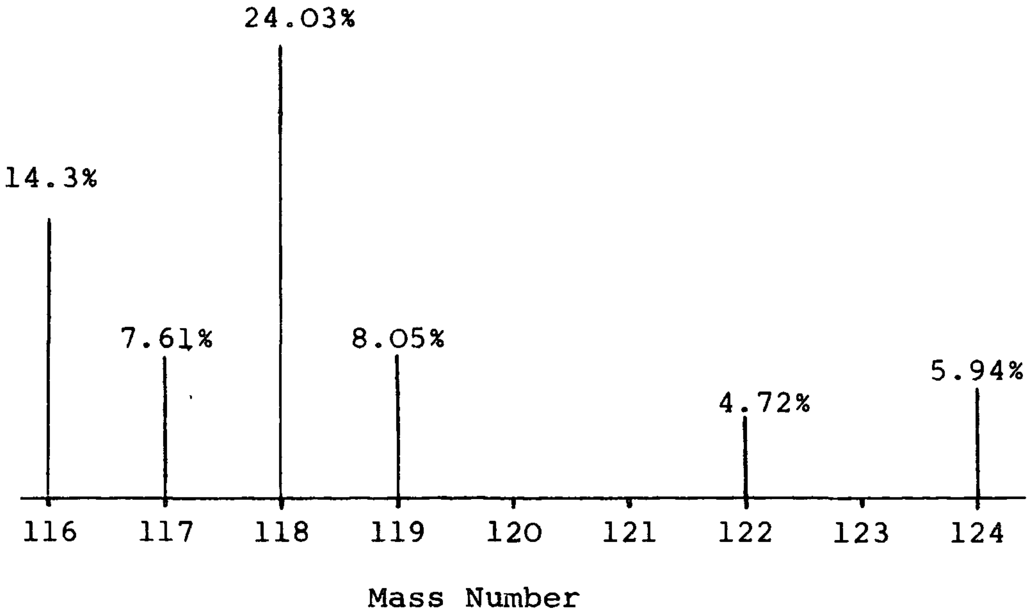


Figure 2.4 Isotope Peaks of Tin

2.4 Experimental

Various experimental procedures were examined in order to establish the most effective convenient synthesis for the required monomers, four typical experiments are presented below by way of illustration.

2.4.1 Attempted preparation of Di-n-butyl bis(hydroxy phenyl ethanoate)tin

A mixture of di-n-butyl tin oxide (15g, 0.06 moles), hydroxy phenyl ethanoic acid (mandelic acid) (18.9g, 0.12 moles) and toluene (500 ml) was heated under reflux using a Dean-Stark apparatus. After eight hours only 0.8 ml of water had been azeotroped out (theoretical 1.0 ml), the mixture remained as a thick white suspension throughout the process. Since removal of water appeared to have ceased, the mixture was filtered hot leaving a waxy white solid (30.25g, 92% mpt 175-176^{o}C).Evaporation of the toluene yielded a further 0.5g of this solid.

The product was dried, analysed, redried and re-analysed. The analytical results are recorded below in Table 2.3 and clearly demonstrate that the product was not sufficiently pure for use as a monomer in polymerisation studies.

	Calc.	Found	
		1	2
C	53.90	50.00	49.80
H	6.03	7.60	7.60
Sn	22.18	30.70	30.70

Table 2.3 Analytical Results for the Waxy White Solid

Infra-red spectroscopic analysis showed a band at 400 cm^{-1} assigned to the Sn=O stretching vibration which confirms that reaction was incomplete under these conditions.

2.4.2 Preparation of di-n-octyl bis(p-hydroxy benzoate)tin (A)

A mixture of di-n-octyl tin oxide, p-hydroxy benzoic acid (55.2g, 0.4 moles) and toluene (1200 ml), was heated under reflux as an experiment 2.4.1, 4.3 ml of water had been removed after two hours (theoretical 3.6 ml), the resulting clear solution was filtered hot and the toluene removed using a rotary evaporator to give a viscous light brown oil. This oil was dried under vacuum (0.5 mm Hg), and after several weeks a buff coloured solid was formed (134g, 92%, mpt 64°C).

Elemental analysis: Found, C, 58.2; H, 7.5; Sn, 16.9%; calculated for $C_{30}H_{44}O_6Sn$, C, 58.2; H, 7.16, Sn, 19.16%, this compound has been mentioned in the literature but no experimental data was presented.[92]

2.4.3 Preparation of di-n-octyl bis(p-hydroxy benzoate)tin (B)

This method differed from the previous preparation in that di-n-octyl tin dichloride and sodium o-hydroxy benzoate were used as the starting materials.

p-Hydroxy benzoic acid (136g, 1 mole) in warm water (5.0 ml) was neutralised with sodium carbonate (53g, 0.5 moles). After one hour, when the evolution of carbon dioxide had ceased, the sodium p-hydroxy benzoate was recovered by the evaporation of the water. The recovered salt was recrystallised from water and dried under vacuum (0.1 mm.Hg) for a day.

A mixture of sodium p-hydroxy benzoate (46.15g, 0.288 moles), di-n-octyl tin dichloride (60g, 0.144 moles) and toluene (500 ml) were heated under reflux for three hours and cooled overnight when a solid formed. A sample was removed and dried under vacuum (0.1 mm Hg 2 hours), infra-red spectroscopic analysis showed it to be a mixture of sodium p-hydroxy benzoate and di-n-octyl tin dichloride. The mixture was again refluxed for a further seven hours, filtered hot leaving a white solid (NaCl) residue and a yellow liquid solution. On cooling a white solid precipitated, this was removed before the remaining pale yellow solution was concentrated using a rotary evaporator yielding a light brown viscous liquid (62g, 70%). The product was dried under vacuum (0.5 mm.Hg) for two days after which time the infra-red spectrum was recorded, this was identical with the previously prepared sample of di-n-octyl bis(p hydroxy benzoate)tin, experiment 2.4.2.

In an attempt to further purify this material a sample was distilled under reduced pressure (120°C, 0.5 mm Hg), under these conditions the liquid decomposed to yield a product which was condensed in a glass trap cooled at -196°C. Infra-red and mass spectroscopic examination of this liquid established that it was a hydrocarbon with a molecular formula $C_{16}H_{32}$.

This observation rules out vacuum distillation (and indeed any high temperature process) for purification of these dialkyl tin dicarboxylates. The product presumably arises from a reaction in which the tin carbon bonds are broken possibly with concomitant formation of the tin-hydrogen bonds. Reactions in which a metal alkyl is converted to a metal carbene hydride are known.[94]

2.4.4 Preparation of di-n-butyl bis(hydroxy phenyl ethanoate)tin

Hydroxy phenyl ethanoic acid (mandelic acid) (50g, 0.33 moles) was neutralised with sodium hydroxide (8M.), phenalphthalene being used as indicator. The sodium hydroxy phenyl ethanoate solution was cooled to ∿2°C in an ice bath, and a solution of di-n-butyl tin dichloride (49.9g, 0.165 moles) in dichloromethane (200 ml) was added slowly (∿10ml/min) with rapid stirring. A white precipitate formed, the reaction was stopped after twenty minutes. The white solid was removed and washed with distilled water followed by dichloromethane and dried under vacuum (0.5 mm Hg) for two days yielding a white waxy solid (81.2g, 92%).

Infra-red analysis showed the band at 1050 cm^{-1} due to the Sn-O-C stretching was present along with other absorptions which were entirely consistent with the product being di-n-butyl bis(hydroxy phenyl ethanoate)tin.

Found: C, 54.0; H, 6.2; Sn, 22.1%,

Calculated for $C_{24}H_{32}O_6Sn$, C, 53.9; H, 6.03; Sn, 22.18%.

From these trial experiments it appears that di-alkyl bis(hydroxy carboxylate)tin compounds may be prepared from any of the above methods; however in the first method the reaction can be followed by the removal of water from the reaction vessel whereas in the other methods monitoring the extent of reaction is not so easily accomplished. The interfacial method involves the use of water as one of the solvents and although it is a much faster technique it has the problems associated with the total removal of water from the monomer which is essential for polymerisations involving urethane formation, consequently the preferred synthesis was that described in 2.4.2.

Several monomers were prepared on a relatively large scale (500g), the technique being the same as that used in 2.4.2 although there were minor variations in the conditions, the experiment details being shown in Table 2.4. The data for the characterisation of the monomers is shown in Table 2.5.

Compound	Diorganotin oxide. Weight (moles)	Hydroxy-carboxylic acid. Weight (moles)	Solvent (l.)	Reflux time (Hours)	Water evolved (ml.) (Theoretical)	Solubility of product*	Phase of product
Di-n-octyl bis (o-hydroxy benzoate) tin.	Di-n-octyl tin oxide. 306.97g. (0.85)	o-Hydroxy benzoic acid. 234.87g. (1.7)	Hexane (4.0)	3	15.6 (15.3)	Soluble	Liquid
Di-n-butyl bis (o-hydroxy benzoate) tin.	Di-n-butyl tin oxide. 211.58g. (0.85)	o-Hydroxy benzoic acid. 234.87g. (1.7)	Hexane (4.5)	4	15.4 (15.3)	Soluble	Solid
Di-n-octyl bis (m-hydroxy benzoate) tin.	Di-n-octyl tin oxide. 306.97g. (0.85)	m-Hydroxy benzoic acid. 234.87g. (1.7)	Toluene (5.0)	1	15.5 (15.3)	Soluble	Liquid
Di-n-butyl bis (m-hydroxy benzoate) tin.	Di-n-butyl tin oxide. 224.0g. (0.9)	m-Hydroxy benzoic acid. 245.6g. (1.8)	Toluene (2.5)	2	16.3 (16.2)	Soluble	Solid
Di-n-octyl bis (p-hydroxy benzoate) tin.	Di-n-octyl tin oxide. 306.97g. (0.85)	p-Hydroxy benzoic acid. 234.87g. (1.7)	Toluene (2.5)	1	15.4 (15.3)	Soluble	Liquid
Di-n-butyl bis (p-hydroxy benzoate) tin.	Di-n-butyl tin oxide. 249.0g. (1.0)	p-Hydroxy benzoic acid. 272.3g. (2.0)	Toluene (5.0)	1	18.2 (18.0)	Soluble	Solid
Di-n-octyl bis (3-hydroxy-2-naphthoate) tin.	Di-n-octyl tin oxide. 306.97g. (0.85)	3-Hydroxy-2-naphthoic acid. 319.9g. (1.7)	Toluene (5.0)	2	15.4 (15.3)	Soluble	Liquid
Di-n-butyl bis (3-hydroxy-2-naphthoate) tin.	Di-n-butyl tin oxide. 119.7g. (0.48)	3-Hydroxy-2-naphthoic acid. 181.1g. (0.96)	Toluene (3.0)	1	8.7 (8.7)	Soluble	Solid
Di-n-octyl bis (12-hydroxy stearate) tin.	Di-n-octyl tin oxide. 216.6g. (0.6)	12-Hydroxy stearic acid. 360.0g. (1.2)	Hexane (3.5)	4	9.3 (10.8)	Soluble	Solid
Di-n-butyl bis (12-hydroxy stearate) tin.	Di-n-butyl tin oxide. 186.75g. (0.75)	12-Hydroxy stearic acid. 450.0g. (1.5)	Toluene (4.0)	0.8	13.6 (13.5)	Soluble	Solid
Di-n-octyl bis (mandelate) tin.	Di-n-octyl tin oxide. 296.6g. (0.82)	Mandelic acid. 249.9g. (1.62)	Hexane (3.0)	0.6	16.5 (14.8)	Insoluble	Solid
Di-n-butyl bis (mandelate) tin.	Di-n-butyl tin oxide. 249.0g. (1.0)	Mandelic acid. 304.3g. (2.0)	Toluene (4.0)	0.5	18.7 (18.0)	Insoluble	Solid
Di-n-octyl bis (glycolate) tin.	Di-n-octyl tin oxide. 72.2g. (0.2)	Glycolic acid. 30.4g. (0.4)	Toluene (2.0)	1.0	3.8 (3.6)	Insoluble	Solid
Di-n-butyl bis (glycolate) tin.	Di-n-butyl tin oxide. 313.25g. (1.25)	Glycolic acid. 190.13g. (2.5)	Toluene (6.0)	0.6	25.0 (25.5)	Insoluble	Solid

* at reflux temperature

TABLE 2.4 Experimental Details for the Synthesis of the Di-n-alkyl bis (hydroxy carboxylate) tin Monomers

Compound	Appearance	Yield (%)	Molecular weight (g.)	Melting point(^{o}C)	Specific gravity	Analysis Found (Calculated) (%)
Di-n-octyl bis (o-hydroxy benzoate) tin.	White solid	90	619.366	25	1.18	C, 57.9 (58.17); H, 7.6 (7.16); Sn, 23.1 (19.16).
Di-n-butyl bis (o-hydroxy benzoate) tin.	White solid	95	507.000	78	1.18	C, 52.4 (52.1); H, 5.8 (5.57); Sn, 23.1 (23.4).
Di-n-octyl bis (m-hydroxy benzoate) tin.	Waxy buff coloured solid	95	619.366	86	0.83	C, 57.9 (58.17); H, 7.3 (7.16); Sn, 19.1 (19.16)
Di-n-butyl bis (m-hydroxy benzoate) tin.	White solid	95	507.000	137	1.03	C, 52.0 (52.1); H, 5.9 (5.57); Sn, 23.3 (23.4).
Di-n-octyl bis (p-hydroxy benzoate) tin.	Buff coloured solid	97	619.366	64	1.09	C, 58.4 (58.17); H, 7.4 (7.16); Sn, 19.01 (19.16).
Di-n-butyl bis (p-hydroxy benzoate) tin.	Buff coloured solid	95	507.000	104	1.16	C, 52.3 (52.7); H, 5.9 (5.57); Sn, 23.2 (23.4).
Di-n-octyl bis (3-hydroxy-2-naphthoate) tin.	Yellow solid	96	719.490	61	1.55	C, 63.2 (63.44); H, 7.1 (6.72); Sn, 16.4 (16.5).
Di-n-butyl bis (3-hydroxy-2-naphthoate) tin.	Yellow solid	99	607.240	104	1.53	C, 59.5 (59.2); H, 5.5 (5.31); Sn, 18.8 (19.55).
Di-n-octyl bis (12-hydroxy stearate) tin.	Waxy white solid	88	944.090	67	0.91	C, 66.0 (66.2); H, 12.0 (11.1); Sn, 13.2 (12.6).
Di-n-butyl bis (12-hydroxy stearate) tin.	Waxy white solid	97	831.873	80	0.97	C, 63.8 (63.5); H, 11.0 (10.66); Sn, 13.9 (14.27).
Di-n-octyl bis (mandelate) tin.	Wax white solid	87	647.240	157	1.15	C, 59.1 (59.37); H, 7.3 (7.47); Sn, 18.3 (18.35).
Di-n-butyl bis (mandelate) tin.	Waxy white solid	95	535.300	178	1.14	C, 54.1 (53.9); H, 6.4 (6.03); Sn, 21.9 (22.18).
Di-n-octyl bis (glycolate) tin.	Waxy white solid	93	495.130	267 Decomposed	1.17	C, 48.5 (48.71); H, 8.14 (8.02); Sn, 23.95 (23.01).
Di-n-butyl bis (glycolate) tin.	White solid	96	382.140	289 Decomposed	1.18	C, 37.64 (38.01); H, 6.32 (6.40); Sn, 30.97 (30.9).

Note The infra red spectroscopic data was consistent with the expected products.

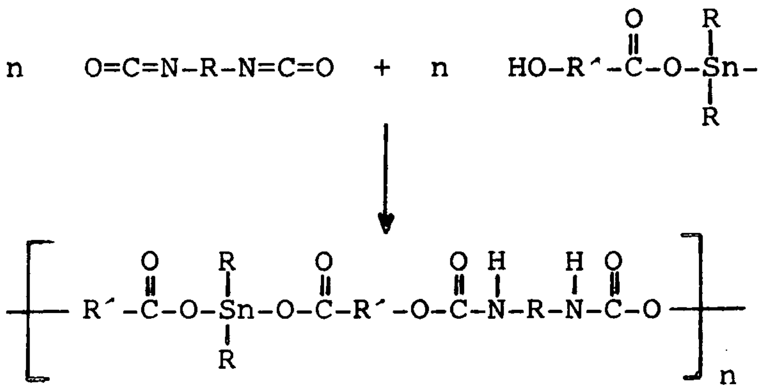
TABLE 2.5 Characterisation of monomers.

CHAPTER THREE

SYNTHESIS OF ORGANOTIN CARBOXYLATE CONTAINING POLYURETHANES

3.1 Introduction

The polymers synthesised for this research were polyurethanes, they were prepared from di-n-alkyl bis(hydroxy carboxylate)tin monomers (the diol component) and commercially available organic diisocyanates or polyisocyanates. The urethane reaction is usually very rapid due to the reactivity of the isocyanate group, and since the monomers used were difunctional the resulting organotin polyurethanes would be expected to be linear with a high degree of polymerisation, Figure 3.1.



$$n\ O{=}C{=}N{-}R{-}N{=}C{=}O + n\ HO{-}R'{-}\overset{O}{\overset{\|}{C}}{-}O{-}\underset{R}{\overset{R}{Sn}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}R'{-}OH \longrightarrow \left[R'{-}\overset{O}{\overset{\|}{C}}{-}O{-}\underset{R}{\overset{R}{Sn}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}R'{-}O{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{N}{-}R{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}O \right]_n$$

Figure 3.1

Organic isocyanates were first prepared in 1849 by Wurtz using a double decomposition technique, involving a dialkyl sulphate and potassium cyanate,[95] Figure 3.2.

$$R_2SO_4 + 2KOCN \longrightarrow 2RNCO + K_2SO_4$$

Figure 3.2

The potential uses of isocyanates were not realised until Bayer in 1937 discovered that reacting polyfunctional isodyanates with polyfunctional alcohols gave a new class of polymeric materials,[96] the polyurethanes. Today polyurethanes are very widely used and have found favour in many technologies including paints, fibres, rubbers, adhesives, foams, leather substitutes and so on. The ever increasing demand for new polyurethanes has led to a considerable amount of research directed towards the synthesis of isocyanates, and there are more than twenty-five published synthetic routes to isocyanates, although only a few of these have found industrial applications.

3.2 Synthesis of Isocyanates

3.2.1 Phosgenation of Amines

Hentschel, in 1884, showed that an isocyanate may be prepared from the reaction of phosgene with the salt of a primary amine.[97] Gattermann and Schmidt found that virtually quantitative yields of methyl isocyanate could be prepared by passing phosgene through molten methyl amine hydrochloride and treating the resulting methyl carbamyl chloride with lime,[98] Figure 3.3.

$$CH_3NH_2.HCl \quad + \quad COCl_2 \xrightarrow{250^{o}C} CH_3NHCOCl \quad + \quad 2HCl$$

$$2\ CH_3NHCOCl \quad + \quad 2CaO \longrightarrow 2\ CH_3NCO \quad + \quad CaCl_2 \quad + \quad Ca(OH)_2$$

Figure 3.3

This route was modified over the years to allow the synthesis of other higher boiling isocyanates and diisocyanates.[99,100]

Slocombe and Hardy found that by efficient mixing of the amine vapour with phosgene at 275°C a high yield of the isocyanate product (75-86%) was obtained,[101] however if the hydrogen chloride produced in the reaction was not removed the product was carbamyl chloride, this reaction occurring at a lower temperature,[102] Figure 3.4.

$$RHN_2 + COCl_2 \xrightarrow{275^\circ C} RNCO + 2HCl$$

$$RNCO + HCl \xrightarrow{25^\circ C} RNHCOCl$$

Figure 3.4

The phosgenation of amines is nowadays one of the important methods of synthesis both for small scale laboratory work and for the large scale industrial preparation of isocyanates. Many types of organic isocyanates are accessible via this route, the isolated product being dependent on the precursor used and the reaction conditions, see for example Figure 3.5.[103]

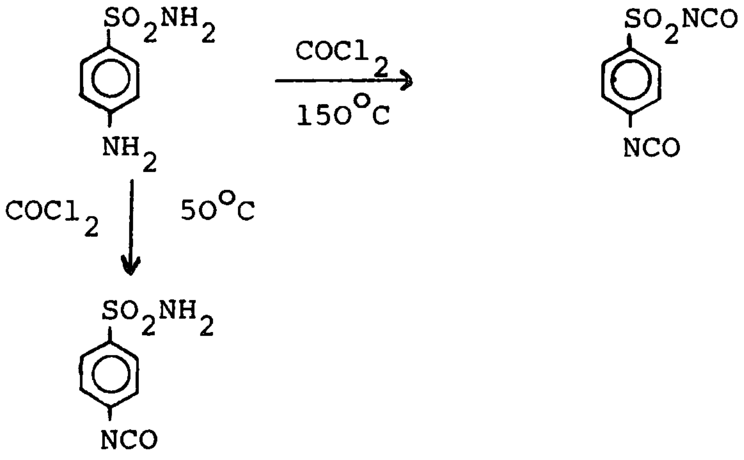


Figure 3.5

3.2.2 Alkenes with isocyanic acid

This reaction usually proceeds with difficulty but certain alkenes with electron releasing substituents will react, the yield being dependent on the stabilising effect of the substituent groups on the alkene,[104,105] see Table 3.1. The reaction is a typical electrophilic addition and involves the protonation of the olefin followed by the addition of the

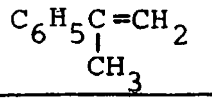
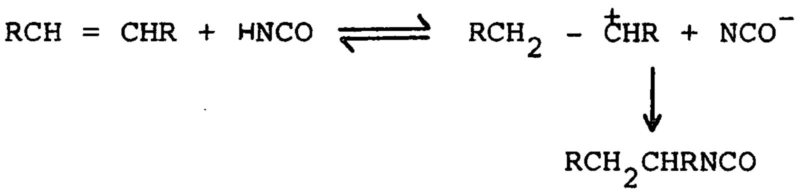
Alkene	Isocyanate	Yield
$(CH_3)_2C=CH_2$	$(CH_3)_3CNCO$	10%
 $C_6H_5\underset{CH_3}{\underset{\mid}{C}}=CH_2$	$C_6H_5C(CH_3)_2NCO$	5%
$C_6H_5OCH=CH_3$	$C_6H_5OC(CH_3)HNCO$	80%

Table 3.1

isocyanate anion, Figure 3.6. Simple alkenes such as ethene,



$$\begin{tikzcd}RCH=CHR + HNCO \arrow[r, shift left] & RCH_2-\overset{+}{C}HR + NCO^- \arrow[l, shift left] \arrow[d] \\ & RCH_2CHRNCO\end{tikzcd}$$

Figure 3.6

propene and but-1-ene have been found to undergo this reaction at high temperatures and pressures (200-600°C, several thousand p.s.i.).[106] Hoover and Rothrock noted that there was a possibility of cationic polymerisation of the alkene, but this was minimised by using a large excess of isocyanic acid.

3.2.3 Nitrocompounds with carbon monoxide

An aryl or alkyl nitro compound will react with carbon monoxide in the presence of a noble metal catalyst to produce an isocyanate,[107] Figure 3.7, the reaction occurs on the metal surface and is a single stage process. This method of synthesis is potentially much more important than the phosgenation reaction as it is much safer and cheaper although technical problems such as recovery and recycling of catalysts have still to be overcome. One of the major syntheses in

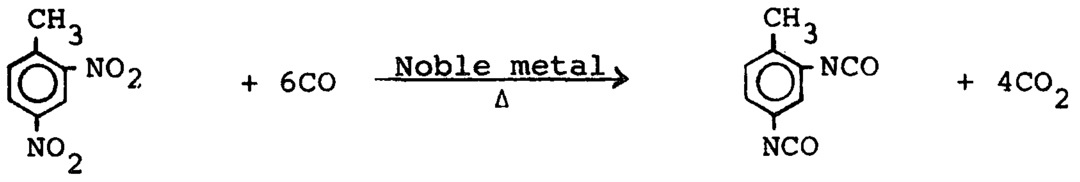


Figure 3.7

which this process may be used is that of methyl-2-4-diisocyanate benzene (toluene diisocyanate, TDI).

3.2.4 Curtius Rearrangement

This method is of little use industrially but is extensively used in the small scale syntheses of organic isocyanates. An acyl azide is obtained either from the reaction of sodium azide with an acyl chloride or by treating an acyl hydrazide with nitrous acid. The acyl azide is decomposed to give a nitrene which undergoes thermal rearrangement to give the isocyanate,[108] Figure 3.8.

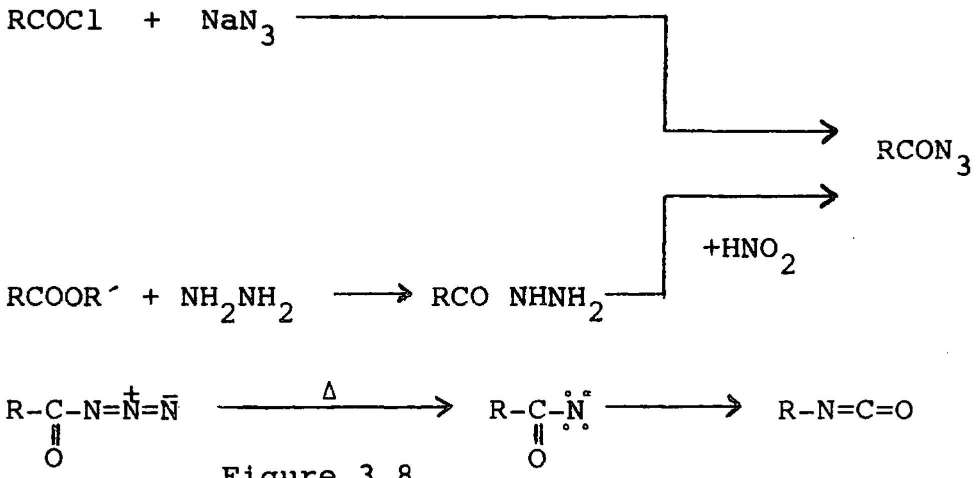


Figure 3.8.

Two other rearrangements involving the production of a nitrene and which may be used to make isocyanates are the Hofmann, Figure 3.9 and the Lossen, Figure 3.10, rearrangements; however, these are not extensively applied as in both methods an aqueous reaction medium is normally used with inevitable loss of product.[109]

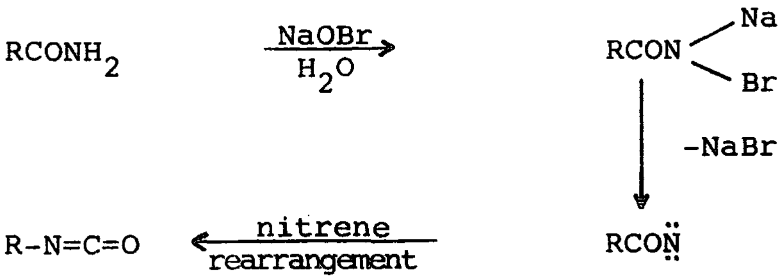
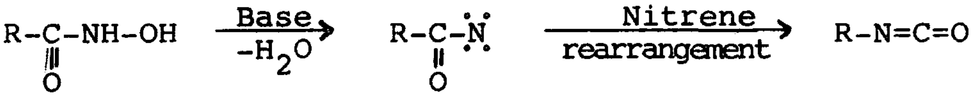


Figure 3.9 The Hofmann Rearrangement



$$\underset{\underset{O}{\|}}{R-C}-NH-OH \xrightarrow[-H_2O]{Base} \underset{\underset{O}{\|}}{R-C}-\ddot{N} \xrightarrow[rearrangement]{Nitrene} R-N=C=O$$

Figure 3.10 The Lossen Rearrangement

The Hofmann and the Lossen rearrangements may be more concerted than implied in the above figures, and in the extreme case the rearrangement may be synchronous with the elimination step with the nitrene having no distinct existence.

Many other methods for the synthesis of organic isocyanates may be found in the literature although they are more specific than those mentioned above.

3.3 Reactions of isocyanates

Isocyanates undergo many types of reactions, these include; addition to a double bond, ring formation, polymerisation of isocyanates and reaction with bases.

The reactive nature of isocyanates may be understood by considering the bonding arrangement in the group. The conventional formula is one of three resonance canonicals which can be drawn, these being shown in Figure 3.11. Consideration

$$R-\underset{+}{N}=\underset{-}{C}-O \longleftrightarrow R-N=C=O \longleftrightarrow R-\underset{-}{N}-\underset{+}{C}=O$$

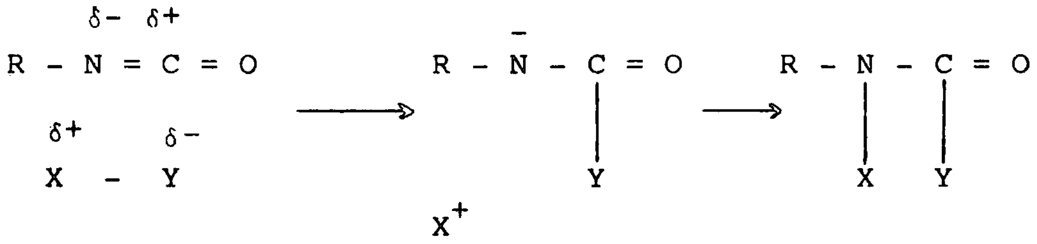
Figure 3.11

of these contributing canonicals suggests that the electron density will be greatest on the oxygen and least on the carbon, the nitrogen atom being intermediate with a net negative charge; thus we would expect that the carbon will be susceptible to nucleophilic attack,[110] and this is borne out in practice.

Extensive research has been carried out into the mechanism of the urethane reaction in various solvents, and a correlation between the rate of reaction of unsubstituted and substituted aryl isocyanates has been derived,[111]

$$\log\left(\frac{k}{k_o}\right) = \rho\sigma = 1.69\sigma$$

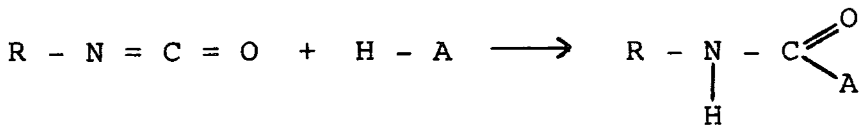
where k_o is the rate for the unsubstituted aryl isocyanate; k is the rate for the substituted aryl isocyanate; σ is a substituent constant for the substitution on the aryl ring, it depends on both the resonance and inductive effects of the substituent and, ρ is the reaction series constant based on the slope of the linear correlation. This is a typical Hammet linear free-energy relationship, substituents which are electron withdrawing are found to have a large positive σ value, i.e. such compounds are more reactive which would imply that attack on the isocyanate group occurs at an electrophilic centre. A mechanism is shown below, Figure 3.12.



$$\underset{\overset{\delta+}{X}\;-\;\overset{\delta-}{Y}}{R-\overset{\delta-}{N}=\overset{\delta+}{C}=O} \longrightarrow \underset{X^{+}}{R-\overset{-}{N}-\underset{|\atop Y}{C}=O} \longrightarrow R-\underset{|\atop X}{N}-\underset{|\atop Y}{C}=O$$

Figure 3.12

The most important reaction of isocyanates is the addition of bases, this involves nucleophilic attack on the isocyanate followed by protonation, the reaction occurring with any compound which has an active hydrogen, a fairly extensive list of examples is given in Figure 3.13.



where H - A = NH_3, RNH_2, RR´NH, H_2NOH, H_2NNH_2, H_2O, H_2S, H_2O_2, $RNHCONH_2$, RNHCOOR, ROH, ArOH, RSH, ArSH, H_2NCN, PH_3, HF, HBr, RCOOH, $CH_2(COOR)_2$, $CH_2(COCH_3)COOR$, RCH_2NO_2, $NaHSO_3$, R_2NOH, R_3SiOH.

Figure 3.13

The urethane reaction, which involves the reaction between an isocyanate and an alcohol is of major importance because it is used in the synthesis of high molecular weight polymers. This reaction is very fast, the rate depending on the isocyanate used, its substituents, the nucleophilicity of the attacking species and the steric interactions between the reactants.

3.4 The Urethane reaction

The urethane reaction can be represented as shown in Figure 3.14, this involves the nucleophilic addition of the alcohol to the isocyanate. The reaction was thought to follow a mechanism similar to that shown in Figure 3.14, but it has

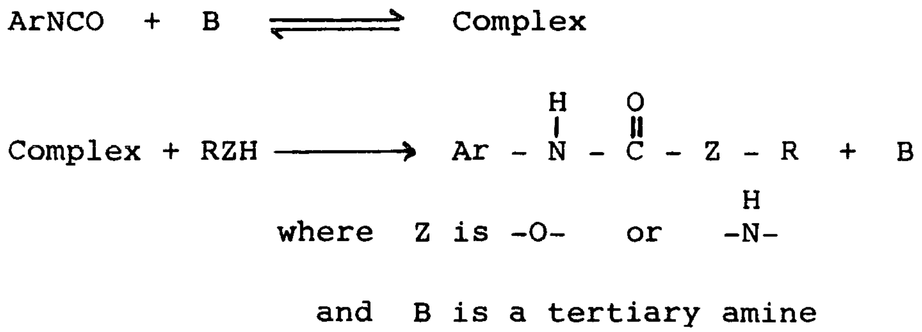
$$R - N = C = O + R'OH \longrightarrow R - \overset{\overset{H}{|}}{N} - \overset{\overset{O}{\|}}{C} - O - R'$$

Figure 3.14

been shown by Baker and others[112,113,114] to be much more complicated.

3.4.1 Base Catalysis of the Urethane Reaction

Baker and coworkers have conducted much research into the mechanism of base catalysis of the urethane reaction,[113,114] and have proposed that a base-isocyanate complex is involved as shown in Figure 3.15. This proposal was based on kinetic studies. Spectroscopic investigations have shown that when the base is a tertiary amine (which is the commonly used catalyst) it also complexes with the alcohol, which then complexes with the isocyanate,[115] Figure 3.16.



$$\mathrm{ArNCO} + \mathrm{B} \rightleftharpoons \mathrm{Complex}$$

$$\mathrm{Complex} + \mathrm{RZH} \longrightarrow \mathrm{Ar} - \overset{\mathrm{H}}{\overset{|}{\mathrm{N}}} - \overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}} - \mathrm{Z} - \mathrm{R} + \mathrm{B}$$

where Z is $-\mathrm{O}-$ or $-\overset{\mathrm{H}}{\mathrm{N}}-$

and B is a tertiary amine

Figure 3.15

$$\mathrm{R-O-H} + \mathrm{B} \rightleftharpoons \mathrm{R-O\cdots H\cdots B}$$

$$\mathrm{ArNCO} + \mathrm{R-O\cdots H\cdots B} \rightleftharpoons \mathrm{complex} + \mathrm{ROH}$$

$$\mathrm{Complex} + \mathrm{ROH} \longrightarrow \mathrm{RNHCOOR} + \mathrm{B}$$

Figure 3.16

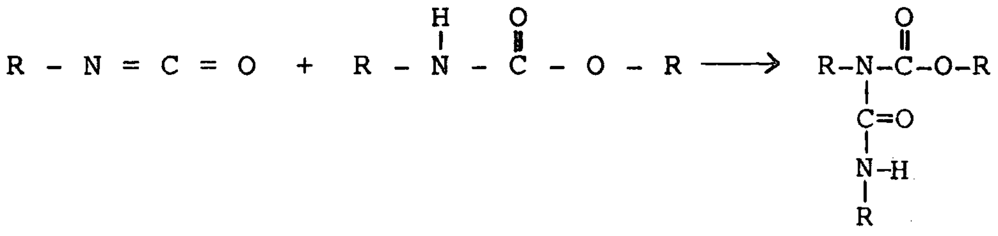
A mechanism proposed by Farkas and Strohm involved attack on the isocyanate by the ROH-B complex followed by a rearrangement to give the urethane directly rather than by the two steps shown in Figure 3.16.[116] These fine details of mechanism remain areas of dispute but are not of enormous practical significance.

The rate of catalysis is dependent on the concentration of the catalyst and also the specific velocity constants for the reaction involving the complex and the alcohol. Farkas has shown that the specific velocity constants are related to the steric interactions and the nucleophilicity of the catalyst, the smaller the steric interactions and the greater the nucleophilicity the more active is the catalyst.[117]

The reacting alcohol is also a base and therefore it would be expected to catalyse the urethane reaction. Baker has shown that the reaction is first order with respect to the alcohol when the concentrations of the reactants are equal, however, when the alcohol concentration is increased alcohol catalysis is observed, a $[ROH]^2$ term being included in the rate equation[112].

The urethane product is a base and it has also been found to catalyse the reaction, this catalysis only occurring when the reaction has gone to 50 or 60% completion.[118,119,120]

The elucidation of the mechanism of catalysis in the urethane reaction is further complicated by the formation of an allophanate from the reaction of the urethane with more isocyanate, Figure 3.17.

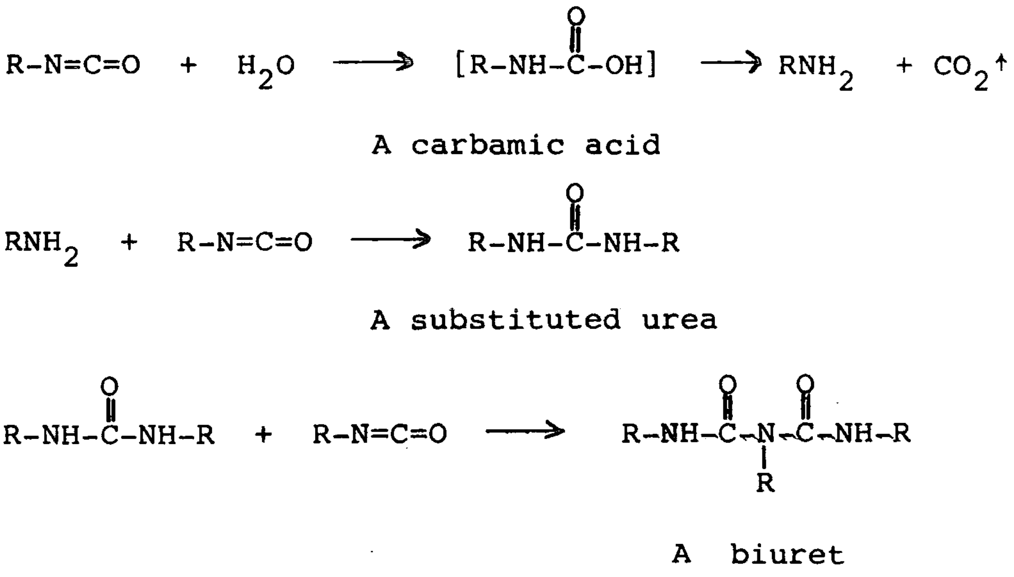


$$R-N=C=O + R-\overset{\displaystyle H}{\overset{|}{N}}-\overset{\displaystyle O}{\overset{\|}{C}}-O-R \longrightarrow R-\underset{\underset{\underset{\displaystyle R}{|}}{\underset{\displaystyle N-H}{|}}}{\underset{\displaystyle C=O}{\underset{|}{N}}}-\overset{\displaystyle O}{\overset{\|}{C}}-O-R$$

Figure 3.17

The inclusion of water in the reaction mixture adds one more complication since it reacts with free isocyanate groups to produce a primary amine and carbondioxide, this reaction being utilised in the manufacture of some polyurethane foams.

The amino groups produced in this reaction undergo further reaction with isocyanate moieties, Figure 3.18.



$$R\text{-}N{=}C{=}O + H_2O \longrightarrow [R\text{-}NH\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH] \longrightarrow RNH_2 + CO_2\uparrow$$

A carbamic acid

$$RNH_2 + R\text{-}N{=}C{=}O \longrightarrow R\text{-}NH\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH\text{-}R$$

A substituted urea

$$R\text{-}NH\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH\text{-}R + R\text{-}N{=}C{=}O \longrightarrow R\text{-}NH\text{-}\overset{O}{\overset{\|}{C}}\text{-}\underset{R}{\underset{|}{N}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH\text{-}R$$

A biuret

Figure 3.18

This brief review illustrates the actual complexity of what at first sight appears to be a very simple reaction.

3.4.2 Metal Catalysis

Many metal salts will catalyse the urethane reaction and it has been shown that organotin compounds are exceptionally good in this capacity. Hostettler and Cox found that the second order reaction between phenyl isocyanate and methanol in di-butyl ether or dioxane was effectively catalysed by di-n-butyl tin diacetate;[121] measured second order rate constants for this reaction are shown in Table 3.2. The effect of catalyst concentration on the related phenyl iso-

Catalyst	Mole % Catalyst	$k \times 10^4$ (litre $mole^{-1} sec^{-1}$)
None	-	0.51
Triethylamine	1	5.7
Di-n-butyl tin diacetate	0.0088	118

Table 3.2

cyanate-butan-1-ol reaction was shown to be given by the relationship,

$$k_2 = k_o + k_c \; [\text{catalyst}]^n .$$

where k_2 is the overall rate constant; k_o is the rate constant for the uncatalysed system, k_c is the rate constant for the catalysed system and n is 0.89 for di-n-butyl tin diacetate and 1.04 for triethylamine.

The mechanism proposed by Hostettler and Cox based on these observations involved the formation of a weak complex between the catalyst and one or both of the reactants.

Organotin catalysts were found to catalyse the aliphatic isocyanate-alcohol reaction to a far greater extent than the aromatic isocyanate-alcohol reaction,[122] a mechanistic rationalisation for these observations is shown below in Figure 3.19.

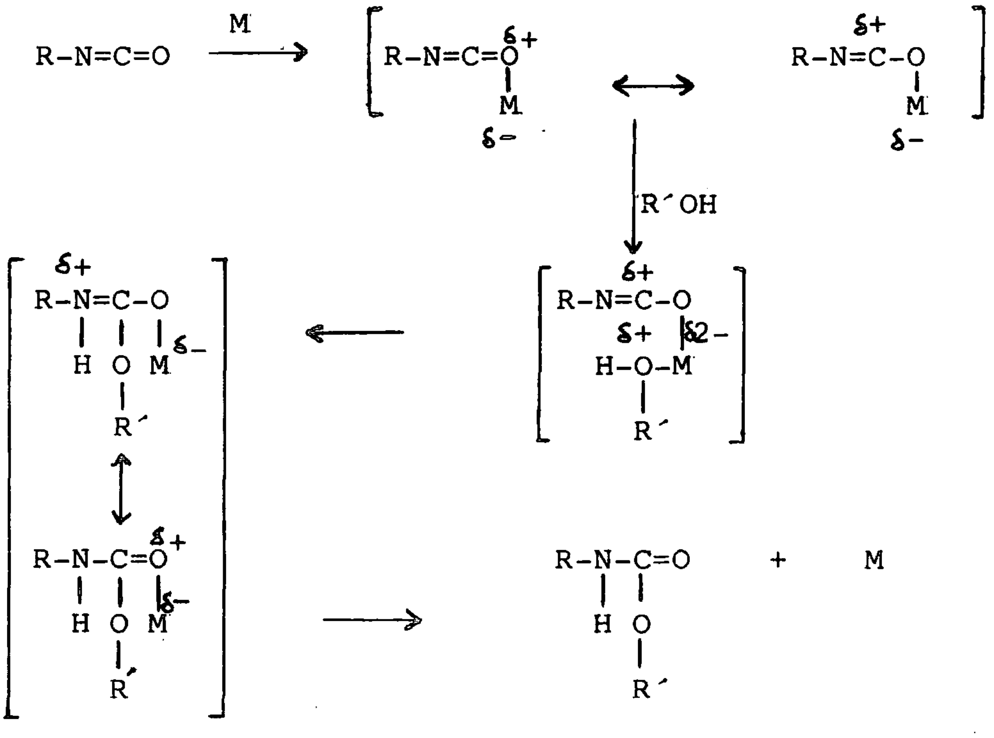


Figure 3.19 General scheme for the metal catalysed methane reaction

The coordination of both the alcohol and the isocyanate to the metal brings the two reactants very close together and therefore explains the large catalytic effect.

Proton nuclear magnetic resonance studies have shown that with metal catalysts the hydroxyl proton resonance is shifted down field from which it can be inferred that the metal atom is coordinated to the hydroxyl oxygen.[123] Attempts to probe catalyst isocyanate interactions by ^1H nmr. spectroscopy and ultra violet spectroscopy were inconclusive since observed shifts were very small. On the other hand determination of the molecular weight of di-n-butyl tin dilaurate-phenyl isocyanate mixtures by the depression of freezing point technique yielded conclusive evidence of association which may be interpreted as resulting from isocyanate coordination to tin.[124] Reegen and Frisch from this data postulated structures for separate tin complexes with 1-methoxy-2-propanol and phenyl isocyanate which subsequently underwent ligand exchange, Figure 3.20, followed by attack of the hydroxyl proton on the nitrogen of the isocyanate. This mechanism is essentially the same as that proposed by Britain and Gemeinhardt.[122]

The rate of complex formation is usually very fast, the rate determining step is the reaction between the ligands after complex formation, this being dependent on the coordination number of the metal, the configuration of the complex, and the ionic radius of the metal.

3.4.3 Solvent effects on urethane catalysis

The mechanisms described previously, 3.4.1 and 3.4.2 were postulated from studies of reactions carried out in solutions of low polarity. A solvent dependence was noted by some early workers who found that for a specific reaction the rate varied according to the solvent used.[125,126]

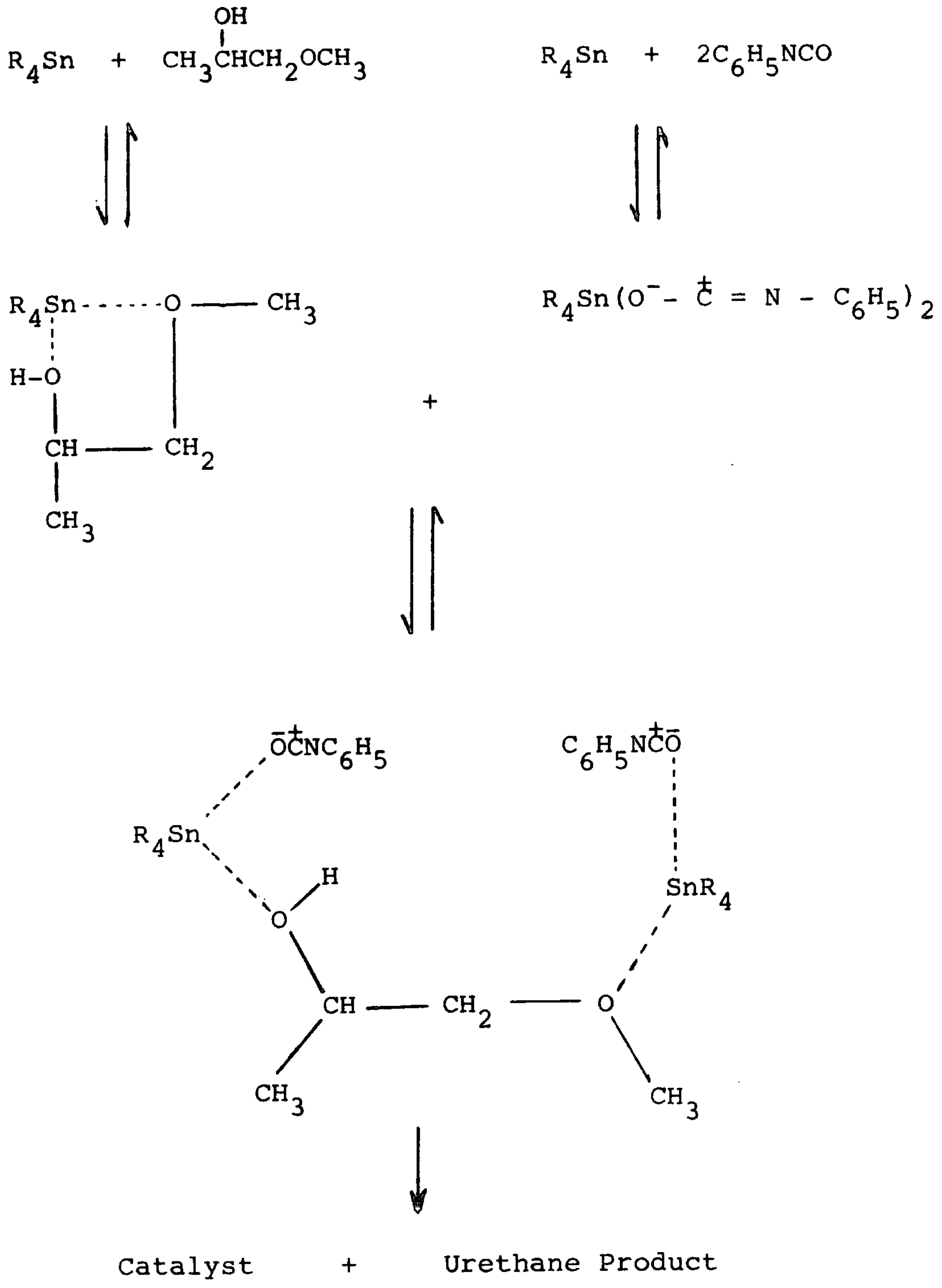

R4Sn + CH3CH(OH)CH2OCH3
R4Sn + 2C6H5NCO
R4Sn-----O—CH3
H-O
CH—CH2
CH3
R4Sn(O⁻- C⁺ = N - C6H5)2
+
⁻O C⁺NC6H5
R4Sn
H
O
CH — CH2 — O
CH3
C6H5NC⁺O⁻
SnR4
CH3
Catalyst + Urethane Product

Figure 3.20

Dabi and Zilka have shown that the situation is much more complex than was originally thought.[127] They have found that the polar aprotic solvents DMF and DMSO catalyse the reaction between butanol and phenyl isocyanate but inhibit the aliphatic isocyanate-butanol reaction. They suggested that the polar aprotic solvents form a charge transfer complex with the aryl isocyanate, Figure 3.21, and these complexes activate the isocyanate group towards electrophilic attack. They have also shown that hydrogen bonding between the alcohol and solvent inhibits the reaction, and that in the aliphatic isocyanate-alcohol system this reaction predominates over the charge transfer complex formation; presumably the aryl group is able to stabilise the developing charge on the nitrogen (Figure 3.21) whereas the alkyl group cannot.

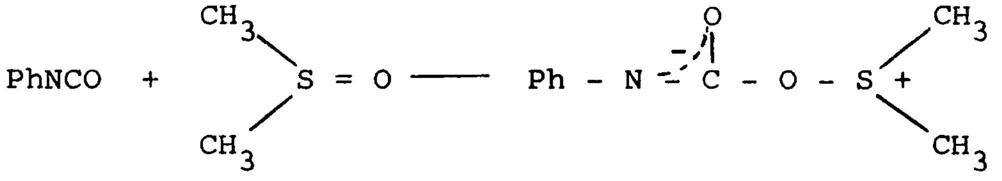


Figure 3.21

If a coordination catalyst is used, care must be taken to prevent the coordination sites being occupied by the solvent otherwise a lower catalytic activity will be observed.

3.5 Polymerisation of Isocyanates

Shashoua in 1959 synthesised N-substituted derivatives of nylon-1 from various organic isocyanates,[128] degress of polymerisation as high as 2000 were obtained. The reactions were carried out at low temperature (-20 → -100°C) in N,N dimethyl formamide in the presence of an anionic initiator, cyclic trimers resulted if the catalyst concentration was too great or the temperature too high, Figure 3.22.

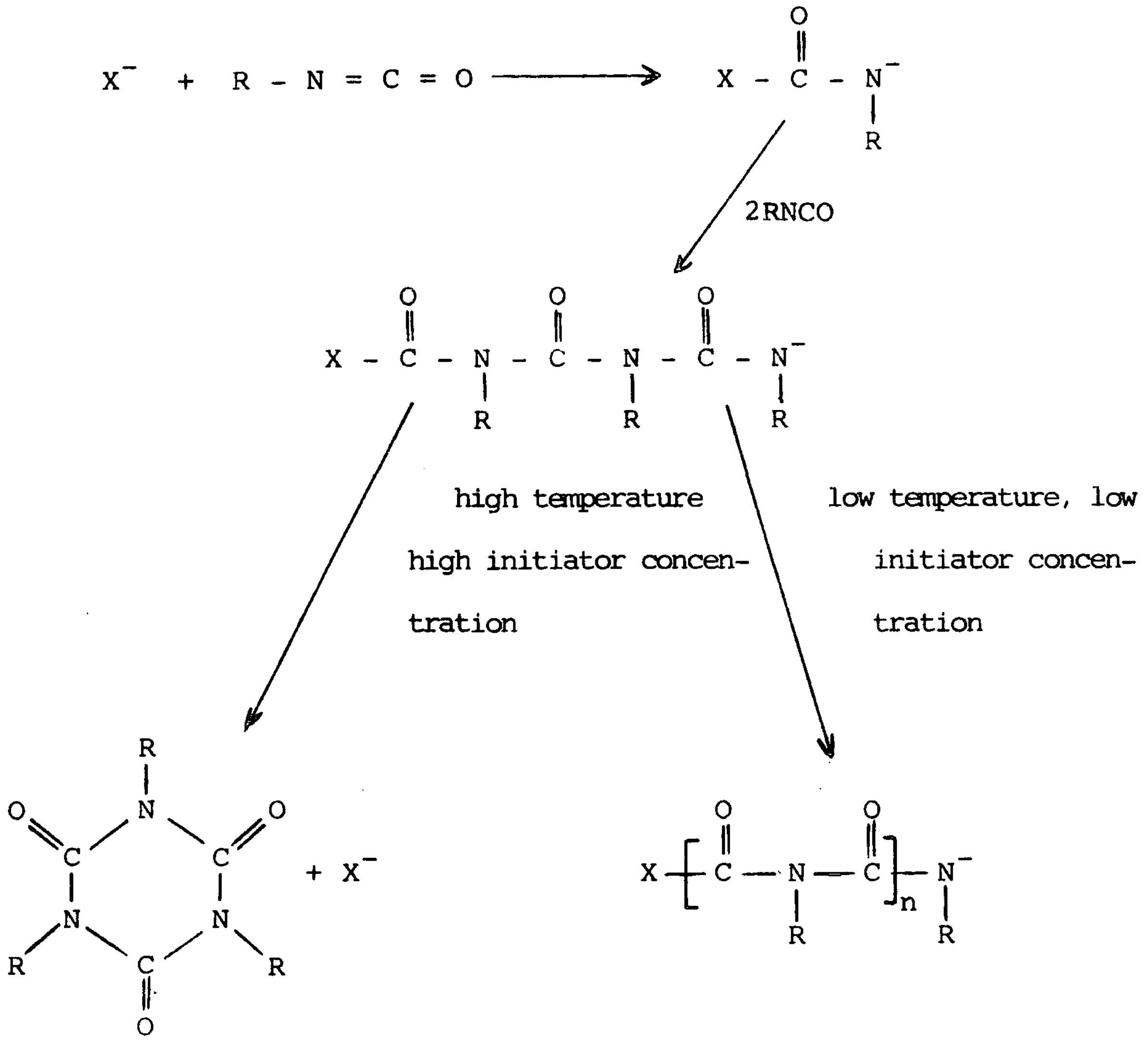


Figure 3.22 Anionic cyclisation and polymerisation reactions.

Cyclopolymerisation of the type shown in Figure 3.23 occurs with organic diisocyanates in N, N dimethyl formamide using sodium cyanide as initiator.[129,130]

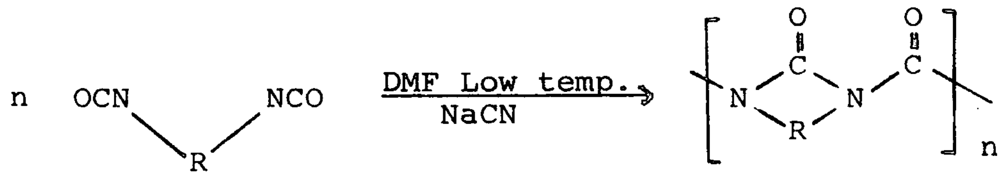


Figure 3.23 Anionic cyclopolymerisation of diisocyanates.

Block copolymers have been prepared by the copolymerisation of isocyanates with vinyl polymers obtained by anionic catalysis.[131] The polymers shown in Figure 3.24 contain a free isocyanate group which can react as previously described to produce a wide range of novel polymers.[131] Many other types of copolymers have been produced, these include copolymers from aromatic isocyanates and cyclic ethers or aldehydes.[132,133]

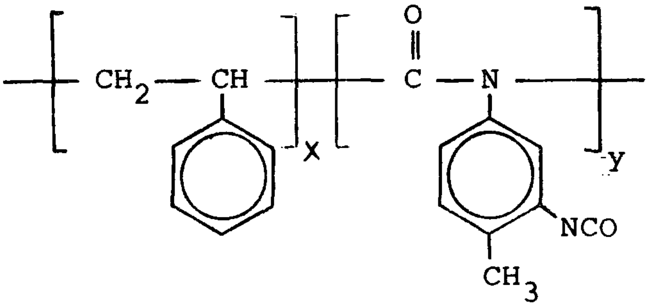


Figure 3.24

Isocyanates are easily dimerised and trimerised especially in the presence of an acid or base catalyst, the dimerisation occurring at low temperatures, this being easily reversible whereas the trimerisation occurs at elevated temperatures and is irreversible,[134] Figure 3.25. Aromatic isocyanates are much more likely to form these cyclic structures than their aliphatic counterparts.

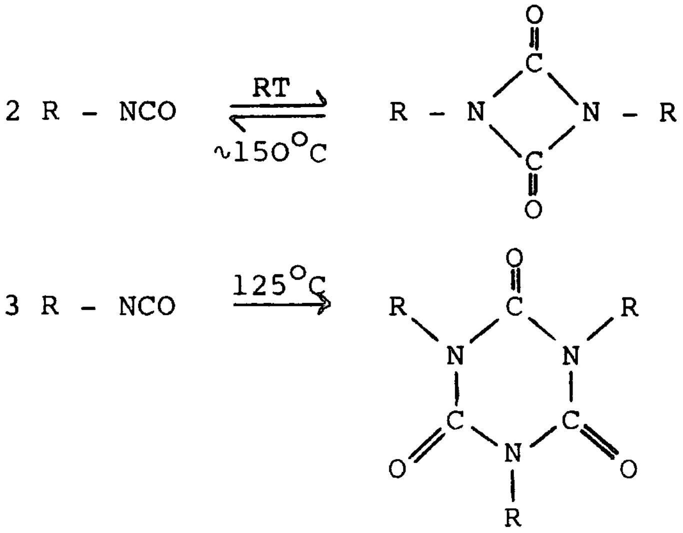


Figure 3.25 Cyclisation reations of isocyanates.

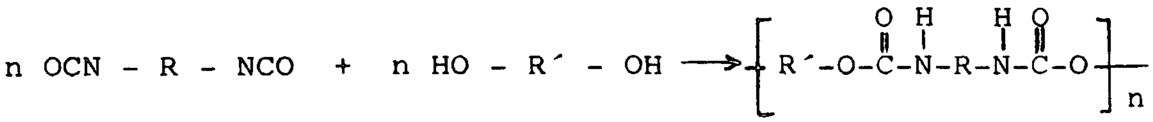
3.6 The Polyurethane Reaction

Polyurethanes were originally prepared by reacting a dihydric alcohol with a diisocyanate in an inert diluent such as chlorobenzene or toluene, by Bayer in 1937.[96] This method has now been superseded by the reaction of the two monomers in the melt at elevated temperatures (∿200°C), this facilitates the formation of high molecular weight polymers since the growing polymer remains in solution in the molten monomers, whereas precipitation at low molecular weight often occurs with solution polymerisation.

The problem of side chain reactions occurring in the synthesis of polyurethanes is very real. The reactions described above for the reactions of the monofunctional isocyanates illustrate the range of possible side reactions and the consequences of such reactions in polymer preparation are considerable. The formation of dimers, trimers, allophanates, biurets and amines may result in cross-linking and/or chain growth termination. If the latter predominates low molecular weight polymers will result. High monomer purity and precise reaction control is therefore very important in these reactions.

If a solvent is used in the polymerisation reaction it must be non-reactive towards both monomers and it must dissolve the growing polymer if a high molecular weight product is to be obtained.

The mechanism of the polyurethane formation is the same as that of the previously described urethane reaction, both in the catalysed and the non catalysed systems although steric interactions may reduce the reaction rate, Figure 3.26.



$$n\ OCN-R-NCO\ +\ n\ HO-R'-OH \longrightarrow \left[R'-O-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-R-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O \right]_n$$

Figure 3.26 The polyurethane reaction.

The reaction is spontaneous and exothermic but additional heat may be required to produce a high molecular weight polymer, the optimum temperature being between 100 and 180°C in which range both the monomers and the polymers are usually stable.

3.7 Experimental

3.7.1 Materials

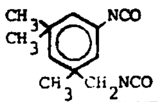
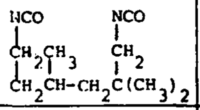
The diisocyanates were used as supplied, their suppliers, purity and physical properties are recorded in Table 3.3. The diorgano bis(hydroxy carboxylate)tin monomers were prepared as described in the last Chapter, they were stored at room temperature and under vacuum (ca. 1 mm.Hg.) to prevent the adsorption of water and were used without further purification. The solvent used was toluene, supplied as a general purpose reagent by Hopkins and Williams and purified by distillation from sodium, the 110-111°C fraction being collected and stored over a 4A molecular sieve and under nitrogen.

3.7.2 Initial Polymerisation Experiments

(a) Design of Reaction Vessel

The flat-bottomed cylindrical vessel was designed to give efficient mixing of the reactants, the clearance between the walls and bottom of the glass vessel and the propeller shaped paddle blade was very small (<2mm). To facilitate mixing a

TABLE 3.3 Physical, Chemical and Structural Data on the Isocyanates used in the Organotin Polyurethane Syntheses.

Isocyananate	Supplier	Structure	Molecular weight (NCO equivalent)	Density g.cm.$^{-3}$	Boiling point($^{\circ}$C)	Refractive index n_D^{25}	Appearance	Purity
Desmodur N75*	Bayer	Poly-functional aliphatic isocyanate	(255)				Viscous yellow oil	Commercial grade
Isophorone diisocyanate (IPDI)	Veba-Chemie		222.3 (111.2)	1.056	158°C @ 10 mm.Hg.	1.4829	Pale yellow oil	99.0% minimum
Tri-methylhexa-methylene diiso-cyanate (TMDI)	Veba-Chemie	 $OCN-CH_2-CH_2-CH(CH_3)-CH_2-C(CH_3)_2-CH_2-NCO$	210.3 (105.2)	1.011	149	1.4619	Pale yellow oil	99.0% minimum
Hexamethylene diisocyanate	Fluka	$OCN(CH_2)_6NCO$	168.2 (84.1)	1.045	61	1.453	Colourless oil	99.9%
Desmodur L67*	Bayer	Poly-functional aromatic isocyanate	(365)				Colourless viscous oil	Commercial grade
DDI.	Cornelius Chemicals	Di-funtional aliphatic isocyanate	600 (300)	1.02			Pale yellow oil	Commercial grade

* These are supplied as a 75% or 67% solution of the diisocyanate in a 1:1 xylene:ethyl glycol acetate mixture.

high speed stirrer motor was used and the connecting drive shaft was of ¼" stainless steel, an Edwards rotary shaft seal being used to stabilise the shaft and allow an inert purge gas to be used, see Figure 3.27. The vessel was fitted with a reflux condenser and a pressure equalised dropping funnel.

(b) Reaction between Di-n-butyl bis(hydroxy phenyl ethanoate) tin and Isophorone diisocyanate

The following polymerisation technique is essentially that described by Leebrick in 1964.[93]

A mixture of di-n-butyl bis(hydroxy phenyl ethanoate)tin (10g, 1.87×10^{-2} moles) and toluene (100ml) was introduced into the reaction vessel which was purged with dry nitrogen, the nitrogen atmosphere being maintained throughout the experiment. The vessel was heated from an oil bath (110°C) and the mixture stirred (750 rpm); the tin compound had a low solubility and remained as a fine white suspension, increasing the oil bath temperature to 175°C (rapid refluxing of the solvent) did not give any apparent increase in the amount of organotin monomer dissolved. Isophorone diisocyanate (4.15g., 1.87×10^{-2} moles) in dry toluene ($20cm^3$) was added rapidly to this suspension and after a few minutes a colourless solution formed. The system was heated at a bath temperature of 175°C for a further thirty minutes after which time the contents of the reaction flask were transferred to a florentine flask and the solvent removed using a rotary evaporator. The residual viscous oil in the florentine flask was dried in a vacuum oven overnight (1mm.Hg., @ 25°C) yielding a white solid (13.0g., 92% mpt.165°C). Infrared spectroscopic analysis showed that there was some residual isocyanate in the product (band at 2260 cm^{-1}), and confirmed the formation of the urethane linkage (bands at 3340 cm^{-1}

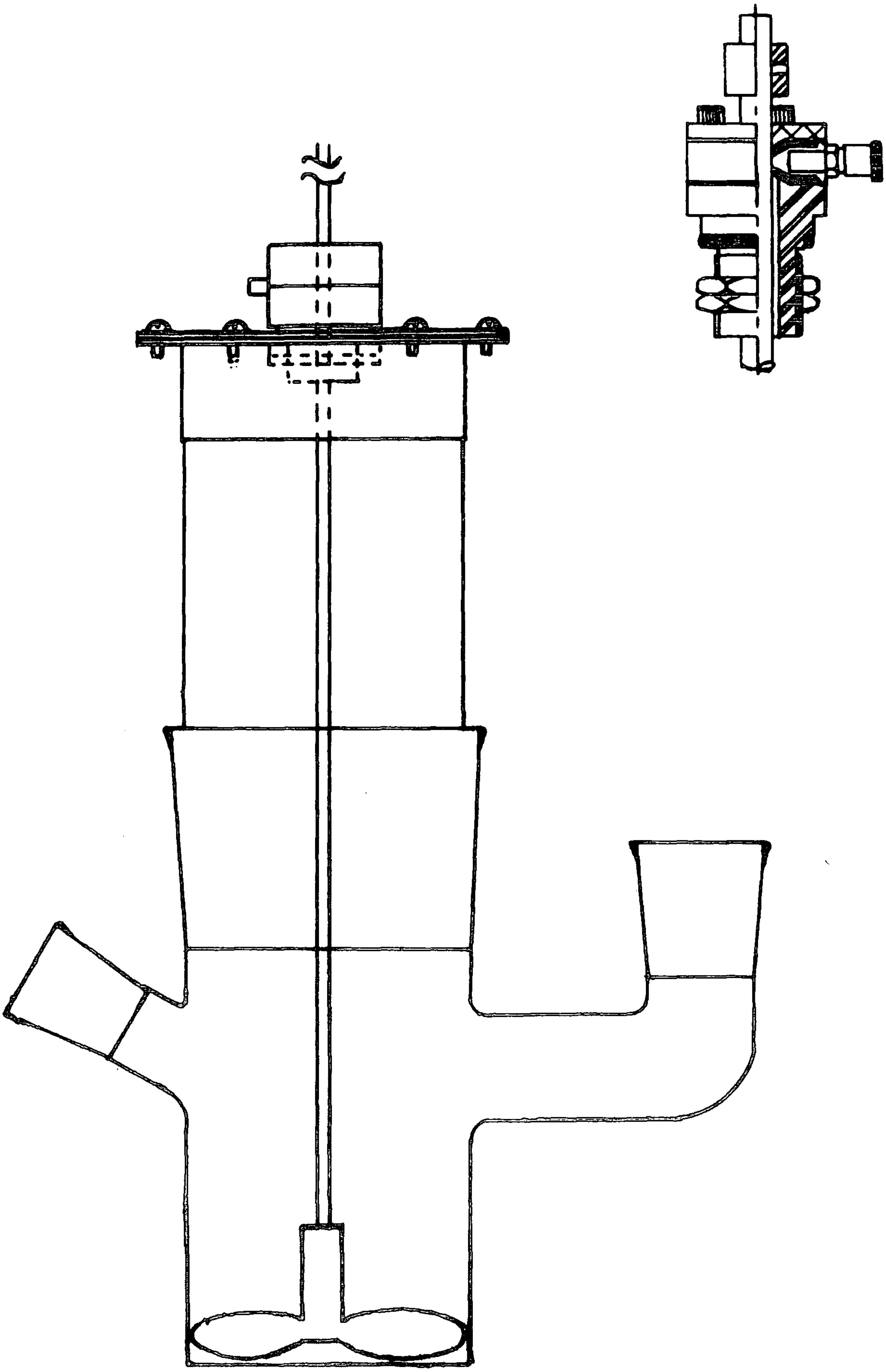


Figure 3.27 Reaction Vessel and Stirrer Gland

N-H stretching; and 1720 cm^{-1}, $>C=O$).

Reprecipation of the reaction product from toluene into 40-60 petroleum ether yielded a white solid; this compound, after drying, showed no i.r. evidence for the presence of isocyanate groups, which was probably due to the reaction of excess isocyanate with atmospheric moisture during handling.

A series of polymerisations of different diols and diisocyanates was carried out in the manner described above. The results of these polymerisations are recorded in Tables 3.4 and 3.5. Infra red spectroscopic analysis of the polymers obtained showed that in some experiments the isocyanate functionality was completely consumed but in other reactions there was residual isocyanate.

The feedstock compositions for the reactions reported in Tables 3.4 and 3.5 were based on the "hydroxyl equivalents" quoted by the suppliers for the diisocyanates, the i.r. evidence for unreacted isocyanate functionality suggested that in some instances 1:1 stiochiometry in the feedstock may not have been obtained, consequently the hydroxyl equivalents for IPDI and TMDI were determined as an analytical check.

(c) Determination of the hydroxyl equivalents of IPDI and TMDI

The method used is a modification of Siggia and Gordon's technique for analysis of hydroxyl groups using aryl isocyanates.[135] Di-n-butylamine (12.5g) was diluted to 500 cm^3 with dioxane which had been dried over sodium hydroxide pellets for two days. A known weight of the diisocyanate (approximately $2x10^{-3}$ moles) was placed in an Erlenmeyer flask and di-n-butylamine (20 cm^3) was added, the flask being stoppered and left to react for two hours. Distilled water (25 cm^3) was added

TABLE 3.4 Experimental Details for the Synthesis of the Organotin Polyurethanes.

Ref.	Monomer 1 g. Moles	Solvent (ml.)	Temp. (^{o}C)	Observation prior to add$^{n.}$ of Mon 2	Monomer 2 g. Moles	Solvent (ml.)	rpm.	Time (hrs)	Observations @ high temp.	Product	Yield g. (%)	Mpt. (^{o}C)	I.R. evidence for NCO group
2a	7. 5g. 8.23x10^{-3}	Tol(50)	115	Yellow solution	ii. 1.38g. 8.23x10^{-3}	Tol(20)	1000	0.5	Pale yellow solution	Yellow solid	6.21g. 97%	120	Present
2b	7. 5g. 8.23x10^{-3}	Tol(20)	170	Yellow solution	ii. 1.38g. 8.23x10^{-3}	Tol(10)	1000	1.5	Pale yellow solution	Yellow solid	6.0g. 94%	120	Present
3a	7. 5g. 8.23x10^{-3}	Tol(10)	160	Yellow solution	i. 1.83g. 8.23x10^{-3}	Tol(10)	1250	0.5	Yellow solution	Yellow solid	4.45g. 65%	118	Present
3b	7. 5g. 8.23x10^{-3}	Tol(10)	210	Yellow solution	i. 1.83g. 8.23x10^{-3}	Tol(10)	1000	2.0	Yellow solution	Yellow solid	2.67g. 31%	126	Present
4a	5. 5g. 9.86x10^{-3}	Tol(20)	190	Colourless solution	i. 2.19g. 9.86x10^{-3}	Tol(20)	1000	2.0	Viscous colourless sol$^{n.}$	Yellow solid	6.95g. 95%	145	Absent
4c	5. 5g. 9.86x10^{-3}	TOl(30)	200	Colourless solution	i. 2.19g. 9.86x10^{-3}	DMSO(30)	1000	1.5	Brown viscous oil	Yellow	4.97g. 68%		Absent
5a	5. 5g. 9.86x10^{-3}	Tol(20)	145	Colourless solution	ii.1.65g. 9.86x10^{-3}	Tol(20)	750	2.0	Viscous colourless sol$^{n.}$	Buff col solid	6.56g. 98%	134	Absent
6a	6. 5g. 8.07x10^{-3}	Tol(20)	120	Colourless solution	ii.1.36g. 8.07x10^{-3}	Tol(20)	750	0.75	Viscous colourless sol$^{n.}$	Buff col solid	5.89g. 93%	141	Absent
7a	5. 5g. 9.86x10^{-3}	Tol(15)	120	Colourless solution	i. 2.19g. 9.86x10^{-3}	Tol(15)	800	2.0	Viscous colourless sol$^{n.}$	Buff col solid	6.66g. 99%	155	Absent
7c	5. 5g. 9.86x10^{-3}	Tol(20)	120	Colourless solution	i. 2.09g. 9.80x10^{-3}	Tol(40)	800	3.0	Viscous colourless sol$^{n.}$	Buff col solid	5.9g. 83%	155	Absent

TABLE 3.5 Experimental Details for the Synthesis of the Organotin Polyurethanes.

Ref.	Monomer 1 g. Moles	Solvent (ml.)	Temp. (°C)	Observations prior to add$^{n.}$ of Mon. 2	Monomer 2 g. Moles	Solvent (ml.)	rpm.	Time (hrs)	Observations @ high temp	Product	Yield g. (%)	Mpt. (°C)	I.R. evidence for NCO group
8a	3. 5g. 9.86x10^{-3}	Tol(50)	150	Colourless solution	ii. 1.66g. 9.86x10^{-3}	Tol(80)	850	24.0	White suspension	Tan col. solid	6.5g. 97.5%	94	Absent
9a	4. 5g. 8.07x10^{-3}	Tol(20)	120	Colourless solution	ii. 1.34g. 8.07x10^{-3}	Tol(40)	400	27.0	Colourless solution	Tan col. solid	4.4g. 70.0%	96	Absent
10a	1. 5g. 9.86x10^{-3}	Tol(30)	100	Colourless solution	ii. 1.66g. 9.86x10^{-3}	Tol(30)	500	150.0	Tan coloured solution	Waxy tan solid	6.2g. 93.0%	74	Present
11a	2. 5g. 8.07x10^{-3}	Tol(50)	80	Colourless solution	ii. 1.36g. 8.07x10^{-3}	Tol(30)	500	120.0	Tan coloured solution	Tan col. solid	1.3g.	—	Present

to the flask and the excess di-n-butylamine was titrated against a standard 0.05M sulphuric acid solution. A blank was also run to determine the alkalinity of the di-n-butylamine. The results are shown in Table 3.6, the measured hydroxyl equivalents for the diisocyanates were in fairly good agreement with those given by the suppliers; IPDI, measured 112.3 quoted 111.2; TMDI measured 107.5 quoted 105.2. It appeared that the residual isocyanate must be arising from incomplete reaction rather than incorrect starting stoichiometry.

Iso-cyanate	Weight (g.)	Titre (cm^3)	Conc. of unreacted D.BA (moles)	Conc. of reacted D.BA (moles)	OH equivalent	
Blank		94.17	$9.4175x10^{-3}$			
Blank		94.17	$9.4175x10^{-3}$			
IPDI	0.5023	49.4	$4.4755x10^{-3}$	$4.94\ x10^{-3}$	112	112.3
IPDI	0.4916	50.4	$4.3775x10^{-3}$	$5.04\ x10^{-3}$	112.3	
IPDI	0.6030	40.6	$5.3575x10^{-3}$	$4.06\ x10^{-3}$	112.5	
IPDI	0.5074	49.05	$4.5125x10^{-3}$	$4.905x10^{-3}$	112.4	
TMDI	0.6167	36.80	$5.7375x10^{-3}$	$3.68\ x10^{-3}$	107.5	
TMDI	0.6560	36.55	$5.7625x10^{-3}$	$3.655x10^{-3}$	107.5	

Table 3.6

Next the hydroxyl equivalent was determined for the product from one of the preparations where incomplete isocyanate consumption was observed. The reaction of di-n-butyl bis(3-hydroxy-2-naphthoate)tin and IPDI was analysed using the above method, and found to have a hydroxyl equivalent of 730, from which it can be inferred that slightly less than one hydroxyl per molecule had reacted with the isocyanate.

(d) Further Polymerisations using the amended hydroxyl equivalents for the diisocyanates

Polymerisations were repeated using the previously described method but amended hydroxyl values were used to calculate the amount of diisocyanate required, the results are recorded in Tables 3.7 - 3.9, and confirm the trends established in the first polymerisation attempts.

3.8 Discussion

The "as prepared" monomers were found to be quite soluble in the reaction medium, however after prolonged drying their solubility generally decreased dramatically. In practice only the di-n-alkyl bis(o-hydroxy benzoate)tins and the di-n-alkyl bis(3-hydroxy-2-naphthoate)tins were readily soluble in toluene, significantly these two monomers were also the two which did not readily polymerise. Most of the monomers were found to precipitate from solution after several days, from which it can be inferred that an ordering of the monomer molecules occurs. It is known that trialkyl tin carboxylates of the type $R_3SnOOCR$ where R and R´ are alkyl groups exist in the solid phase as coordination polymers,[136,137] the tin atom being penta-coordinate, Figure 3.28. This structure also exists in concentrated solutions when the solvent is non polar however the degree of polymerisation decreases linearly with decreasing concentration. The structures shown in Figure 3.29 exist as chelated structures in both solid and solution phase, the tin atom being hexa-coordinate.[138,139]

TABLE 3.7 Experimental Details for the Synthesis of the Organotin Polyurethanes.

Ref.	Monomer 1 g. moles	Solvent (ml.).	Temp. (^{o}C)	Observations prior to add$^{n.}$ of Mon. 2	Monomer 2 g. moles	Solvent (ml.)	rpm.	Time (hrs)	Observations	Product	Yield g. (%)	I.R. evidence for NCO group
12a	6. 15g. 2.42×10^{-2}	Tol(30)	125	Colourless solution	i. 5.44g. 2.44×10^{-2}	Tol(50)	500	42.0	Tan coloured solution	Buff solid	17.8g. 87.0%	Absent
13a	5. 15g. 2.95×10^{-2}	Tol(30)	85	Colourless solution	iii. 6.4g. 3.0×10^{-2}	Tol(40)	500	3.0	Tan coloured solution	Buff solid	20.7g. 96.7%	Absent
14a	5. 15g. 2.95×10^{-2}	Tol(50)	120	Colourless solution	i. 6.65g. 2.99×10^{-2}	Tol(20)	400	42.0	Tan coloured solution	Buff solid	20.7g. 96.0%	Absent
15a	6. 15g. 2.42×10^{-2}	Tol(30)	100	Colourless solution	iii. 5.2g. 2.47×10^{-2}	Tol(40)	500	28.0	Tan coloured solution	Buff solid	18.2g. 90.0%	Absent
16a	3. 15g. 2.95×10^{-2}	Tol(50)	110	Colourless solution	iii. 6.4g. 3.0×10^{-2}	Tol(40)	500	52.0	Tan coloured solution	Buff solid	20.8g. 96.0%	Absent
17a	4. 15g. 2.42×10^{-2}	Tol(50)	100	Colourless solution	iii. 5.2g. 2.47×10^{-2}	Tol(20)	500	45.0	Tan coloured solution	Buff solid	19.7g. 96.0%	Absent
18a	1. 15g. 2.95×10^{-2}	Tol(20)	100	Colourless solution	iii. 6.4g. 3.03×10^{-2}	Tol(30)	600	95.0	Tan coloured solution	Oil+tan solid	20.9g. 97.0%	Present
19a	2. 15g. 2.42×10^{-2}	Tol(30)	110	Colourless solution	iii. 6.2g. 2.95×10^{-2}	Tol(30)	600	19.0	Tan coloured solution	Oil+tan solid	18.8g. 88.0%	Present
20a.	9. 15g. 1.8×10^{-2}	Tol(30)	110	Pale green solution	iii. 3.9g. 1.84×10^{-2}	Tol(30)	500	18.0	Pale green solution	White * solid	16.1g. 85.0%	Absent
21a	9. 15g. 1.8×10^{-2}	Tol(30)	120	Pale green solution	i. 4.1g. 1.82×10^{-2}	Tol(30)	500	22.0	Pale green solution	White * solid	18.3g. 96.0%	Absent

* NOTE These are waxy sticky materials.

TABLE 3.8 Experimental Details for the Synthesis of the Organotin Polyurethanes.

Ref.	Monomer 1 g. moles	Solvent (ml.)	Temp. (°C)	Observations prior to add$^{n.}$ of Mon. 2	Monomer 2 g. moles	Solvent (ml.)	rpm.	Time (hrs)	Observations	Product	Yield g.(%)	I.R. evidence for NCO group
22a	9. 15g. 1.8x10^{-2}	Tol(30)	110	Pale green solution	ii. 3.0g. 1.8x10^{-2}	Tol(30)	500	3.5	Pale green solution	White solid *	16.8g. 93.0%	Absent
23a	10. 15g. 1.59x10^{-2}	Tol(30)	120	Pale green solution	iii. 3.4g. 1.62x10^{-2}	Tol(30)	500	2.5	Pale green solution	White solid *	13.6g. 74.0%	Absent
24a	10. 15g. 1.59x10^{-2}	Tol(30)	130	Pale green solution	i. 3.56g. 1.59x10^{-2}	Tol(40)	500	4.5	Pale green solution	White solid *	10.1g. 55.0%	Absent
25a	10. 15g. 1.59x10^{-2}	Tol(30)	130	Pale green solution	ii. 2.67g. 1.59x10^{-2}	Tol(40)	500	4.5	Pale green solution	White solid *	17.4g. 98.0%	Absent
26a	7. 15g. 2.47x10^{-2}	Tol(20)	130	Dark yellow solution	ii. 2.47g. 2.47x10^{-2}	Tol(30)	600	24.0	Dark yellow solution	Brown solid	16.2g. 92.0%	Present
27a	11. 11.6g. 2.17x10^{-2}	Tol(30)	130	White fine suspension	ii. 3.65g. 2.17x10^{-2}	Tol(20)	500	1.75	White fine suspension	White solid	15.1g. 99.0%	Absent
28a	11. 15g. 2.8x10^{-2}	Tol(40)	130	White fine suspention	iii. 6.0g. 2.81x10^{-2}	Tol(30)	600	4.0	White fine suspension	White solid	20.9g. 99.5%	Absent
29a	11. 15g. 2.8x10^{-3}	Tol(40)	130	White fine suspension	i. 6.3g. 2.8x10^{-2}	Tol(30)	500	3.0	White fine suspension	White solid	21.0g. 99.0%	Absent
30a	12. 15g. 2.32x10^{-2}	Tol(30)	130	White fine suspension	ii. 3.9g. 2.32x10^{-2}	Tol(30)	500	6.5	Colourless solution	White solid	18.5g. 95.0%	Absent
31a	12. 15g. 2.32x10^{12}	Tol(40)	130	White fine suspension	iii. 4.9g. 2.37x10^{-2}	Tol(30)	500	8.0	Colourless solution	White solid	18.8g. 94.4%	Absent
32a	12. 15g. 2.32x10^{-2}	Tol(40)	130	White fine suspension	i. 5.2g. 2.32x10^{-2}	Tol(40)	500	4.7	Colourless solution	White solid	18.7g. 92.5%	Present

* NOTE These are waxy sticky materials

TABLE 3.9 Experimental Details for the Synthesis of the Organotin Polyurethanes.

Ref.	Monomer 1 g. moles	Solvent (ml.)	Temp. (^{o}C)	Observations prior to add$^{n.}$ of Mon. 2	Monomer 2 g. moles	Solvent (ml.)	rpm.	Time (hrs)	Observations	Product	Yield g. (%)	I.R. evidence for NCO group
33a	12. 15g. 2.32x10^{-3}	Tol(30)	130	White fine suspension	iv.9.12g. 2.32x10^{-2}	Tol(30)	600	6.0	Rubbery tan material	White solid	2.5g. 11.0%	Absent
34a	8. 15g. 2.08x10^{-2}	Tol(30)	130	Dark yellow solution	iv. 8.2g. 2.08x10^{-2}	Tol(30)	500	7.0	Brown gell	Brown solid	15.0g. 64.0%	Present
35a	9. 15g. 2.08x10^{-3}	Tol(30)	130	Pale green solution	iv. 7.1g. 2.08x10^{-2}	Tol30)	500	3.0	Viscous green solution	White solid	21.1g. 95.5%	Absent
36a	11. 15g. 2.8x10^{-2}	Tol(40)	130	White fine solution	iv. 11.0g. 2.77x10^{-2}	Tol(30)	500	3.0	Viscous green solution	White solid	25.8g. 99.0%	Absent
37a	10. 15g. 1.59x10^{-2}	Tol(30)	130	Pale green solution	iv. 6.3g. 1.59x10^{-2}	Tol(60)	500	7.5	Viscous green solution	White solid	18.5g. 82.2%	Absent
38a	6. 14g. 2.26x10^{-2}	Tol(30)	130	Colourless solution	iv. 8.9g. 2.26x10^{-2}	Tol(60)	500	6.0	Viscous tan solution	White solid	22.5g. 98.0%	Absent
39a	3. 15g. 2.95x10^{-2}	Tol(40)	130	Colourless solution	iv. 11.7g. 2.95x10^{-2}	Tol(60)	500	6.0	Viscous tan solution	White solid	26.1g. 98.0%	Absent

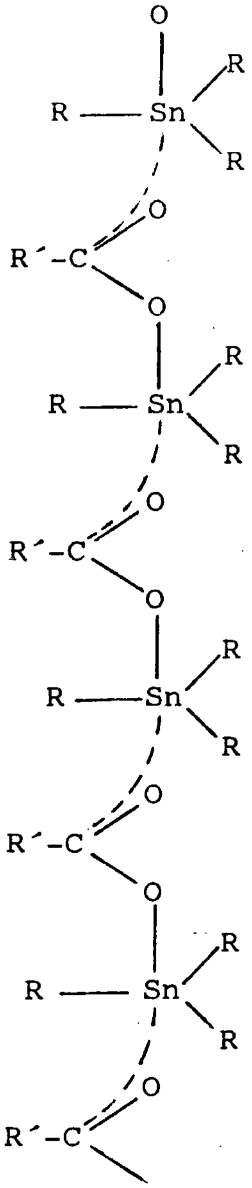


Figure 3.28

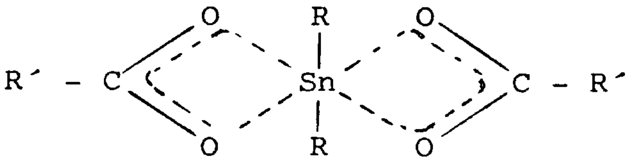


Figure 3.29

where R = CH_3, C_3H_7, C_4H_9;

and R´= H, CH_3.

The di-n-alkyl bis(hydroxy carboxylate)tin monomers used in this work have been previously claimed in the patent literature but no evidence relevant to their chemical or structural characterisation was presented. These monomers have four ligands, two of which contain potentially reactive groups, carbonyl and hydroxyl oxygen, the latter is the stronger donor. Earlier in this chapter the ability of the hydroxyl to coordinate to tin was discussed in relation to the catalysis of urethane forming reactions. In the following sections an attempt is made to correlate the solubilities and the melting points of the monomers with the type of coordination occurring.

3.8.1 Calculation of Solubility Parameters

Solubility parameters were calculated from first principles using the data for organotin compounds obtained from the Handbook of Chemistry and Physics (57th Edition). In order to calculate the latent heat of vapo risation, assuming it was independent of temperature, Hildebrand's equation was used, Figure 3.30, however this equation required the boiling

$$\Delta H_v = 23.7T_b + 0.02T_b^2 - 2950$$

where; ΔH_v = latent heat of vapo risation;

and T_b = boiling point of the compound at 760 mm.Hg.

Figure 3.30

point of the compound at 760 mm.Hg, which was not available therefore a correction was made, Figure 3.31.

$$\Delta t = \frac{(273.1 + t)\ (2.8808 - \log p)}{\phi + 0.15\ \ (2.8808 - \log p)}$$

where ; Δt = ^{o}C to be added to the observed boiling point;

t = observed boiling point (^{o}C);

p = observed vapour pressure (mmHg);

and ϕ = entropy of vaporisation at 760 mmHg, the values being extrapolated from the graph on page D.177 of the Handbook of Chemistry and Physics (57th Edition) assuming the compounds belong to group 1.

Figure 3.31

Using the expression shown in Figure 3.32 the solubility parameters of various organotin compounds were determined.

$$\delta = \left[\frac{(\Delta H_V - RT)D}{M}\right]^{\frac{1}{2}}$$

where; δ = solubility parameter (H);

ΔH_V = latent heat of vaporisation (cal mol^{-1});

R = gas constant (cal.K^{-1}.$mole^{-1}$);

T = temperature (K);

D = specific gravity;

and M = molecular weight (amu).

Figure 3.32

Solubility parameters are normally accessible via two approaches, namely the computation indicated in Figure 3.32 and a method based on the summation of group molar cohesion constants as indicated in Figure 3.33. No values for molar constants were available for tetrahedral tin with alkyl or carboxy-tin units, so these were calculated. Tabulated physical data for tetra-alkyl and tetra-aryl tin compounds allowed values of δ to be computed by the method indicated in

$$\delta = \frac{\Delta F_T . D}{M}$$

where δ = solubility parameter (H)

F_T = molar cohesion constants, values for CH_2 and CH_3 were those calculated by Hoy.[140] $cal^{\frac{1}{2}} ml^{\frac{1}{2}}$

D = specific gravity

and M = molecular weight (amu)

Figure 3.33

Figure 3.32; these δ values and tabulated group molar cohesion values for $-CH_2$ and $-CH_3$ were then used to solve for $F_{T_{\frac{1}{4}[(CH_2)_4Sn]}}$ using the expression given in Figure 3.33. The F_T values were computed for the central unit rather than for an isolated tetrahedral tin atom and this unit is expressed as $\frac{1}{4}[(CH_2)_4Sn]$. These values were found to decrease with increasing size of the aliphatic chain as shown in Table 3.10, this is not too unreasonable since the influence of the central tin unit on δ may be expected to decrease as the alkyl chain length increases.

Alkyl Chain	$F_{T_{\frac{1}{4}[(CH_2)_4Sn]}}$ ($cal^{\frac{1}{2}} ml^{\frac{1}{2}}$)
Methyl	214.38
Ethyl	193.12
Propyl	151.5
Butyl	142.0
Pentyl	111.5
Hexyl	71.4
Heptyl	36.4
Octyl	-15.7
Aryl	642.5

Table 3.10 Molar cohesion values for the $\frac{1}{4}[(CH_2)_3Sn]$ Group calculated from Data for R_4Sn compounds.

As a check for the molar cohesion constants found above the solubility parameters of several mixed tetralkyl tin compounds were calculated in two different ways:

(i) using tables of ΔH_V and boiling point (Figure 3.32) and (ii) using the $\frac{1}{4}[-\!(CH_2)\!-_4Sn]$ molar cohesion constant from Table 3.10 appropriate to the particular alkyl group (Figure 3.33. The results obtained were in relatively good agreement, the difference between the two δ values being at most 0.3H.

From these values of $F_{T_{\frac{1}{4}[-(CH_2)-_4Sn]}}$ the molar cohesion constants for $\frac{1}{2}[-\!(COO)\!-_2Sn]$ could be found using the same procedure and starting from physical data on di-n-butyl tin diacetate the value obtained was 381 $cal^{\frac{1}{2}}ml^{\frac{1}{2}}$.

The solubility parameters of the prepared monomers were then calculated using the above data and they were generally found to be between 8 and 9H. This would imply that suitable solvents for these monomers should be found amongst benzene, toluene, cyclohexane and cyclopentane but in practice only the ortho-hydroxy benzoates and the 3 hydroxy-2-naphthoates were soluble. Highly polar solvents such as DMSO and DMF were also ineffective as solvents for these materials.

In summary, we have calculated the expected solubility for these monomers on the assumption that they have a tetrahedrally substituted central tin atom. The expectation based on this model is not generally fulfilled in practice (there are two exceptions). It is known that tin can expand its coordination number to 5 and 6 and if this happens with these compounds a coordination polymerisation of the monomer may occur which would account for the discrepancy between the theoretical model and the experimental observation. The situation which remains to be explained is why two of the monomers are soluble, that is to say, that the originally expected behaviour is now regarded as anomalous.

3.8.2 Construction of models

Construction of a molecular model of di-n-octyl bis(o-hydroxy benzoate)tin indicates that a six-membered ring could easily be formed by the intra-molecular coordination of the hydroxyl oxygen to the central tin atom, (Figure 3.34).

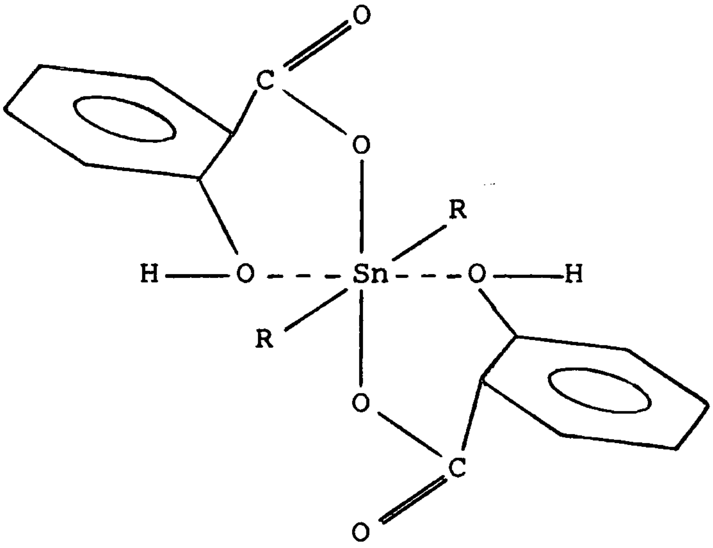


Figure 3.34

It seems reasonable that this hydroxyl coordination occurs in preference to the carbonyl coordination, Figure 3.35, since the hydroxyl group is a stronger donor and the steric interactions are much greater if the latter chelated four-membered ring structure is formed.[141] The same intra-molecular coordination

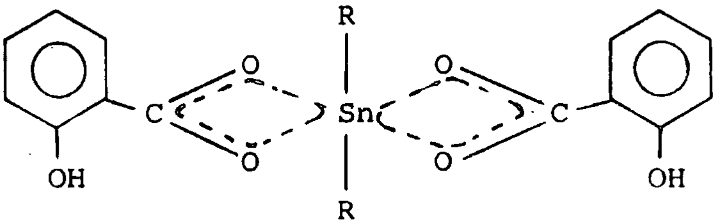


Figure 3.35

would also be expected to occur with the di-n-butyl analogue, and the di-n-octyl, di-n-butyl derivatives of 3-hydroxy-2-naphthoic acid.

The other monomers can reasonably be expected to coordinate inter-molecularly as they cannot attain the correct conformation for intra-molecular coordination, as a result a coordination polymer will be formed. With these monomers it is thought that intra-molecular coordination via the carbonyl unit is *initially* preferred and accounts for their "as-made" solubility, but with the passage of time inter-molecular coordination via the hydroxyl units predominates, and eventually the liquid samples begin to solidify due to the formation of coordination polymers.

3.8.3 Melting Point and Reactivity

On comparing the melting points of the di-n-butyl and the di-n-octyl tin analogues of the various hydroxy carboxylic acids it can be seen that the di-n-octyl derivatives have a lower melting point. This is what one would expect partly as a result of the steric requirements of the longer aliphatic chain, and partly as a consequence of its internal plasticising influence.

The melting points of the meta and para di-n-alkyl bis(hydroxy benzoate)tin compounds may be rationalised by considering their electron distributions, Figure 3.36. Considering

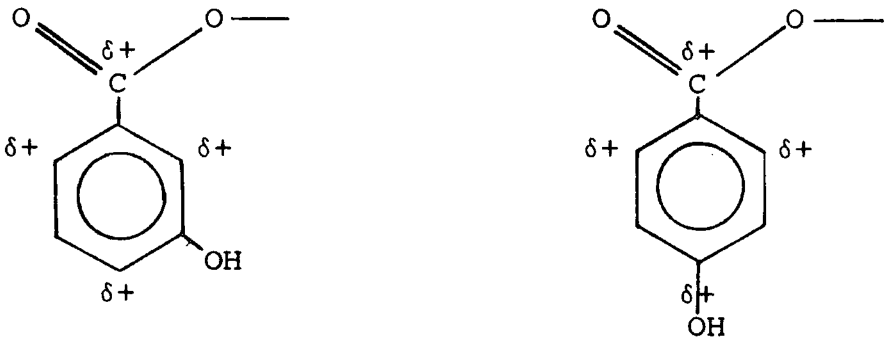


Figure 3.36

the para system there is a positive charge on the carbon atom next to the hydroxyl oxygen thus reducing its coordination power by the removal of electron density, in the meta system this will not be so pronounced. The melting points of the di-n-alkyl bis(m-hydroxy benzoate)tins are higher than the corresponding di-n-alkyl bis(p-hydroxy benzoate)tins which is what would be predicted as the former may coordinate more effectively.

This rationalisation of the melting points of the di-n-alkyl bis(hydroxy benzoate)tins can also be related to the proposed mechanism of organotin catalysis of the urethane reaction; thus in the case discussed above the meta hydroxy derivative was observed to be less reactive with isocyanates than the para derivative, which can be understood as being a result of the stronger coordination of the meta hydroxyl to the tin atom. This may be viewed as either reducing the availability of the meta hydroxyl or removing potential sites on the tin catalyst for the isocyanate.

The catalytic activity of the prepared di-n-alkyl bis(hydroxy carboxylate)tin compounds towards the urethane reaction appeared to be only very slight, but di-organo bis(carboxylate) tins are known to be very good catalysts for the urethane reaction, therefore it would appear that in these compounds all the coordination sites are filled resulting in a lower catalytic activity. This observation further substantiates the hypothesis that the monomers exist as coordination polymers.

CHAPTER FOUR

DESIGN OF TESTING APPARATUS

4.1 Introduction

Many different methods for testing antifouling paints and polymer resins used in conventional antifouling coatings were described in Chapter One. The use of hydrolysable polymers as components of antifouling paints has created a need for the rapid testing of the polymers to see if the film integrity is maintained under operating conditions and also a requirement for new methods of examining the surface to see if hydrolysis and/or ablation is occurring. Factors involved in the designs of the equipment used in this work are described below.

4.2 Design and Development of the Testing Equipment

The major requirements of the equipment were:

(a) that it should simulate the passage of a ship through sea water and,

(b) that it should provide reproducible results quickly. The method chosen was that of spinning the material under test in sea water.

The design of the test rig was based upon that of rigs used by Camrex Research and Development, Figure 4.1.

The rig used in this work had to be free-standing and portable therefore it was constructed using ¼" square section steel with a square base which was bolted to the floor, Figure 4.2. The method used for mounting the samples differed from that adopted by Camrex R.& D. in that they painted their samples radially on to a horizontal Tufnol disc, Figure 4.3, whereas on the author's rig the samples were detachable and mounted vertically on the surface of a Tufnol drum, Figure 4.4: the difference between the two methods being that the

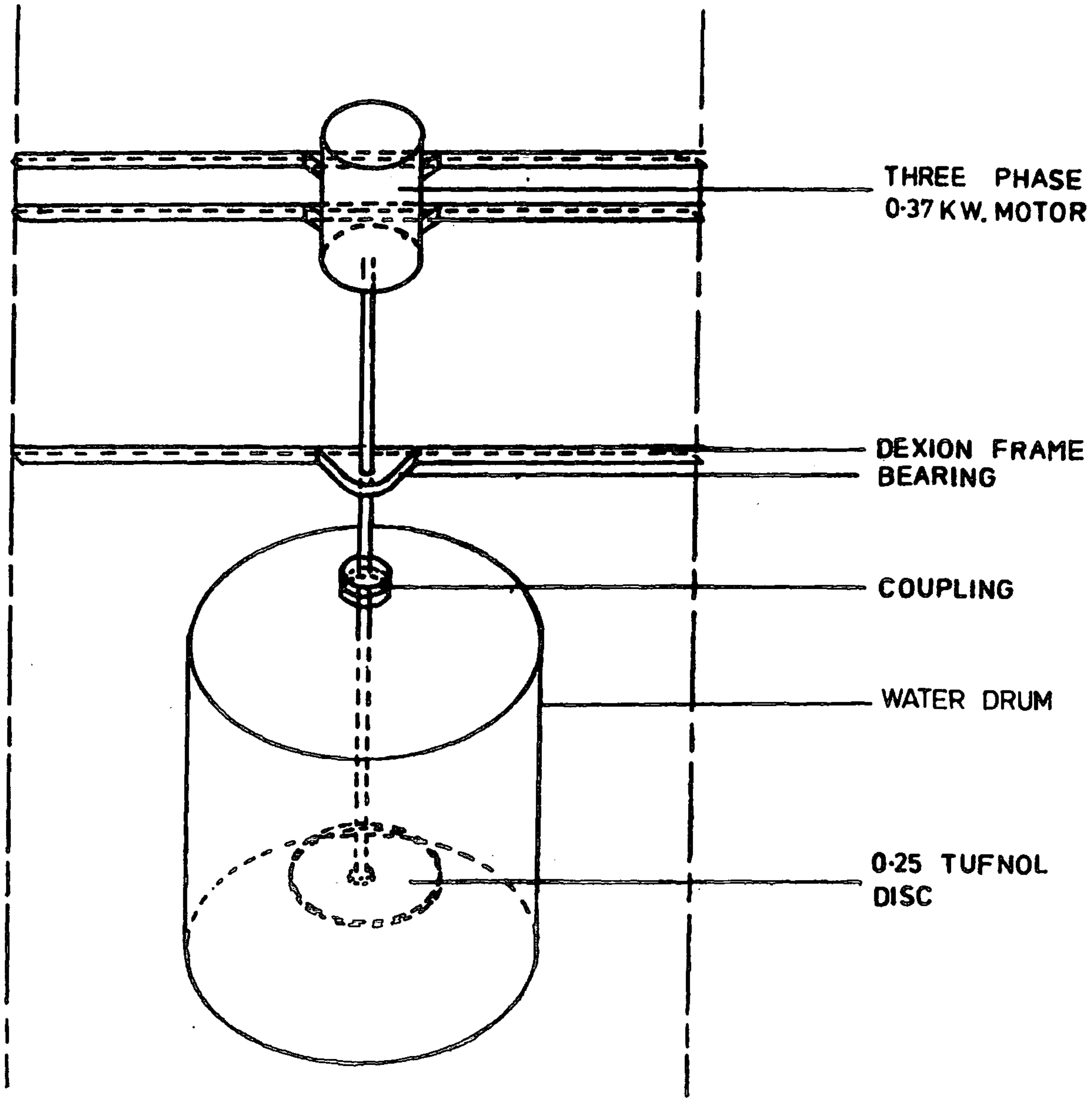


Figure 4.1 Camrex's Test Rig.

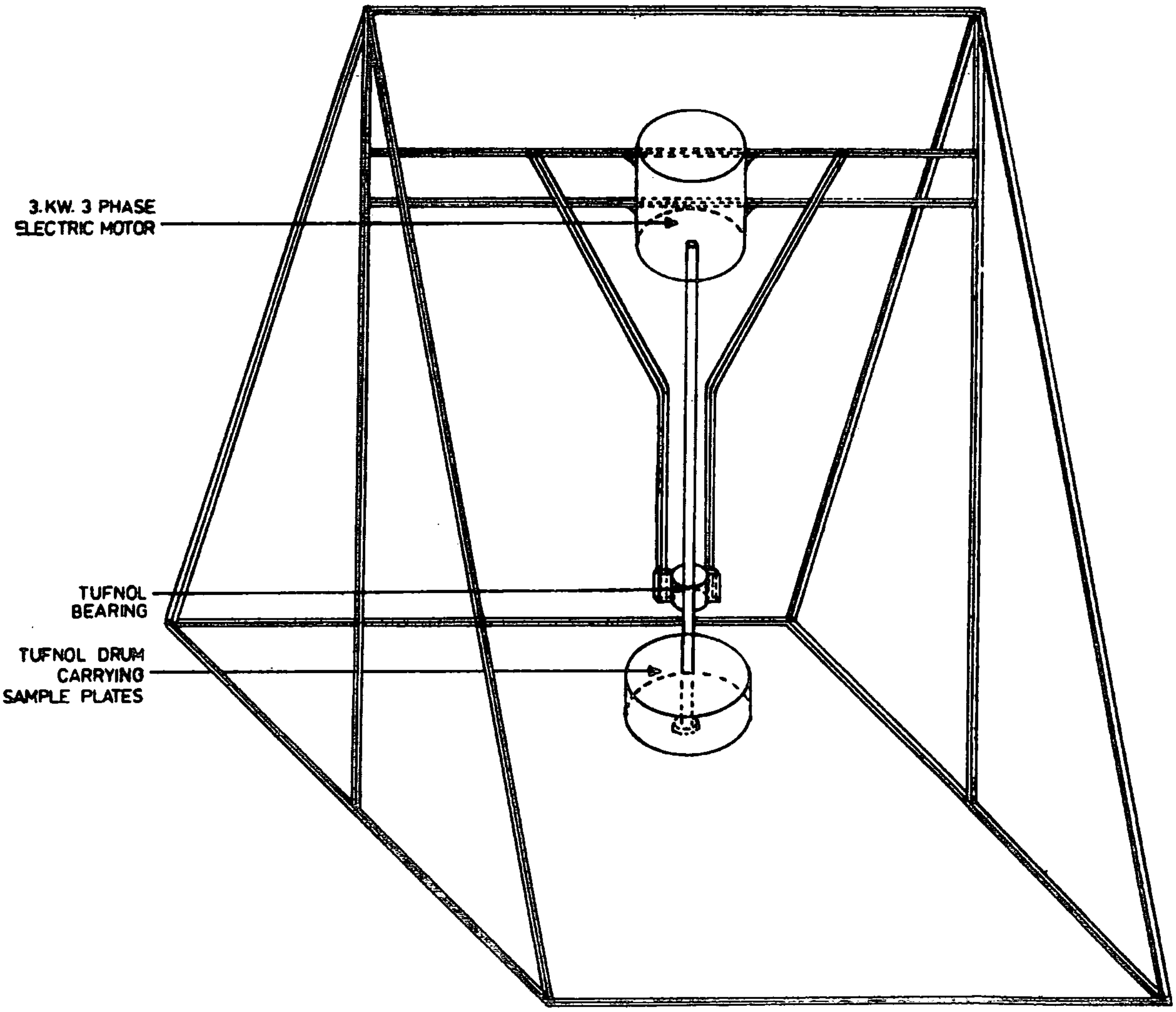


Figure 4.2 The Author's Test Rig.

Figure 4.3 <u>A Camrex Disc after sea water Trials</u>

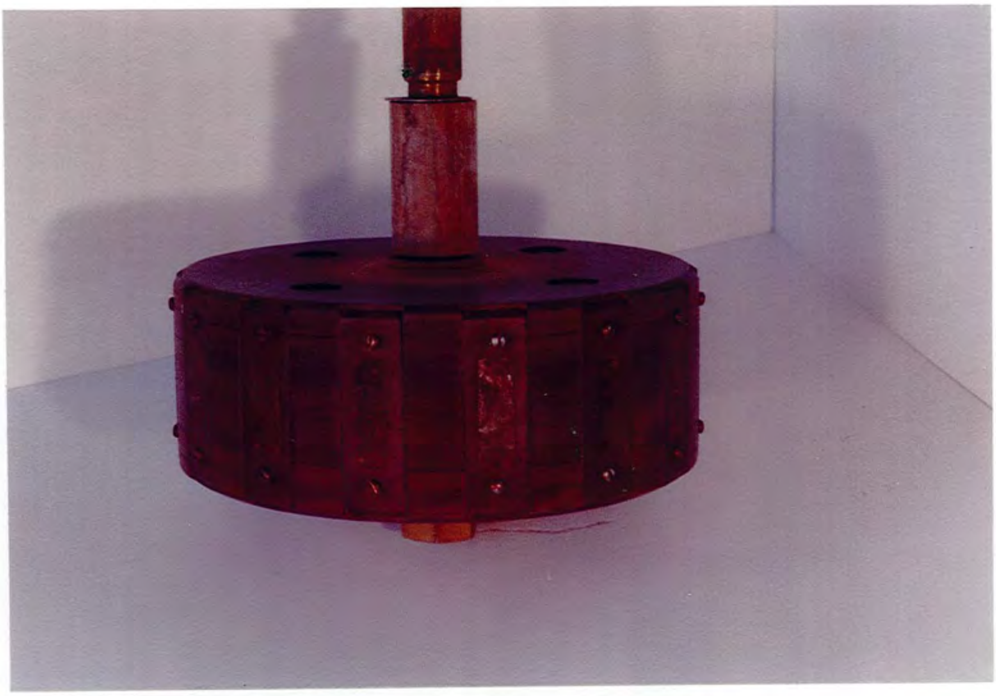


Figure 4.4 <u>The Author's Test Drum after Sea Water Trials</u>

samples mounted on the disc experience an angular velocity dependent on the distance of the segment of film from the centre of the disc whereas when the samples were mounted vertically on a drum the angular velocity experience by all parts of the film was constant and determined by the motor speed. It was thought that having detachable samples would allow weight loss to be monitored and used as evidence of polishing. Initially ground glass slides were used to mount the polymer samples but these were found to break frequently in operation due to centrifugal forces therefore these were replaced by small grit blasted stainless steel panels.

The tank which was used to contain the sea-water was a forty-five gallon oil drum, this enabled the flow of water across the test panels to be tangential, simulating the flow of water over a ship's hull.

Problems were encountered with the size of the motor required to drive the Tufnol drum, originally a single phase 0.37 k.w. motor being employed on the advice of engineers specialised in fluid mechanics, this was found to be inadequate although calculations using the appropriate design formulae indicated that it should have been suitable. The motor capacity was increased several times until a three-phase 3 k.w. motor was found to be capable of rotating the Tufnol drum at 1425 rpm. without overheating. It was interesting to note the difference between theory and practice in the choice of motor, the power required being about ten times greater than that computed according to apparently accepted design formulae. The motor was operating at 75% capacity (based on measuring the current consumption) and the peripheral speed of the drum was 37 knots (42 mph.). Baffels were required to prevent movement of the water in the tank resulting in the formation of a vortex therefore two pieces of Dexion frame were bolted vertically to the sides of the tank.

The test rig was initially found to rapidly overheat due to the energy dissipated into the water, consequently a cooling system was incorporated. The simplest way of cooling the water was to use a cooling coil, this consisted of six metres of six millimetre bore copper tubing which was coiled into the tank and cold tap water passed through at a rate of 5 litres per minute, this proved effective in maintaining a temperature of $18^oC \pm 2^oC$ during operation.

The panels on which the polymers were applied were made from 1" x 3½", 20 gauge stainless steel, the face to be used being lightly grit-blasted to improve the adheshion of the polymer to the surface.

4.2.1 Panel Preparation and Testing

The panels were washed in water, rinsed in acetone, dried and individually weighed, an area of ½" x 2½" was masked out on each panel and the polymers applied using a paint brush. When all the panels were touch dry the masking tape was removed; they were dried to constant weight under vacuum (0.5 mm. Hg at 20^oC) in order to calculate the mass of polymer on each panel.

The panels were attached to the drum in a specific position and geometry, the drum was immersed in the tank which was filled with artificial sea-water, a 7.0% solution of sea salt in distilled water, the system being left to stabilise for one hour before the motor and coolant were started. After four days the water pressure in the cooling coil dropped and the tank overheated, therefore the panels had to be re-coated as detailed above. The panels were tested for periods of between three and seven days after which time they were removed, washed under tap water, dried to constant weight under vacuum and then retested, the results are presented in Table 4.1, which also records observations regarding the integrity of the polymer films.

The initial tests were carried out using organotin anti-foulings prepared by Camrex Research and Development, panels 1-6 and panels 7-16 were commercial organotin resins, all these panels contained the tin atom linked to the backbone by an ester linkage whereas panels 17, 18 and 19 were polymers prepared during the period of research at Durham and contained the tin atom in the polymer backbone.

The weight losses recorded were very small therefore a large error is introduced to the percentage weight loss although it does give some information as to how the polymers withstand the effect of alkaline sea-water and their ability to adhere to the substrate, both of which are important determinants of the suitability of the resin for incorporation into an antifouling coating. Methods for the examination of the surface profile have been considered in order to try to assertain if hydrolysis and hence polishing of the coatings was occurring; these methods are discussed below.

4.2.2 Examination of the Surface Profile of the Polymer Film

Surface roughness can vary between two extremities, very long wavelength and relatively low amplitude or very short wavelength and relatively high amplitude, these being shown in Figures 4.5 and 4.6 respectively.

TABLE 4.1 Results of the Artificial Sea Water Trials of the Organotin Polyurethanes.

NUMBER OF DAYS TEST		5	9	13	19	21	28	34	41
PANEL NUMBER	POLYMER (WEIGHT)	TOTAL WEIGHT OF POLYMER LOST FROM PANEL							
1	A.310 (0.1910)	0.0047	0.0070	0.0073	0.0090	0.0155	0.0214	0.0255	0.0286
2	A.310 (0.1611)	0.0032	0.0156	0.0161	0.0166	0.0228	0.0275	0.0312	0.0339
3	A.306 (0.1707)	0.0090	0.0126	0.0139	0.0163	0.0258	0.0331	0.0371	0.0408
4	A.306 (0.1751)	0.0088	0.0118	0.0132	0.0156	0.0249	0.0324	0.0371	0.0389
5	A.264 (0.2426)	0.0079	0.0122	0.0127	0.0143^{L}	0.0216	0.0318	0.0355	0.0380
6	A.264 (0.2360)	0.0078	0.0112	0.0125	0.0139^{L}	0.0209	0.0270	0.0315	0.0322
7	OMP2 (0.1102)	0.0080	0.0098	0.0091	0.0112	0.0131	0.0142	0.0165	0.0186
8	OMP2 (0.0970)	0.0000	0.0013	0.0010	0.0022	0.0035	0.0045	0.0068	0.0069
9	Cl-1 (0.1171)	0.0010	0.0029	0.0020	0.0027	0.0051	0.0066	0.0073	0.0088
10	Cl-1 (0.0926)	0.0010	0.0043	0.0045	0.0061	0.0073	0.0091	0.0106	0.0122
11	Cl-2 (0.1091)	0.0018	0.0035	0.0025	0.0033	0.0044	0.0059	0.0073	0.0082
12	Cl-2 (0.0722)	0.0010	0.0026	0.0015	0.0030	0.0037	0.0043	0.0050	0.0067
13	Cl-3 (0.0830)	0.0015	0.0024	0.0023	0.0027	0.0038	0.0043	0.0059	0.0074
14	Cl-3 (0.0912)	0.0009	0.0027	0.0016	0.0030	0.0044	0.0057	0.0069	0.0084
15	OMP2 (0.1090)	0.0002	0.0028	0.0023	0.0038	0.0070	0.0102	0.0110	0.0133
16	OMP2 (0.1128)	0.0004	0.0028	0.0015	0.0035	0.0040	0.0051	0.0060	0.0068
17	16a (0.1745)	0.1324^{P}	0.1510	0.1581	0.1662				
18	16a (0.1506)	0.1193^{P}	0.1477	0.1495					
19	16a (0.1569	0.1115^{P}	0.1303	0.1330	0.1375				

NOTES Panels 1-6 were organotin antifoulings supplied by Camrex;
Panels 7-16 were organotin resin supplied by Camrex;
and Panels 17-19 were polymers prepared by the author and referenced as given in Synthesis Tables contained in Chapter 3.
Superscripts used; L, leached film; P, powdery film.

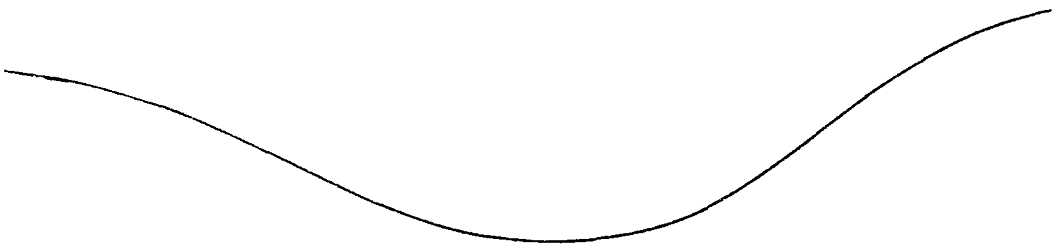


Figure 4.5 Long wavelength, relatively low amplitude

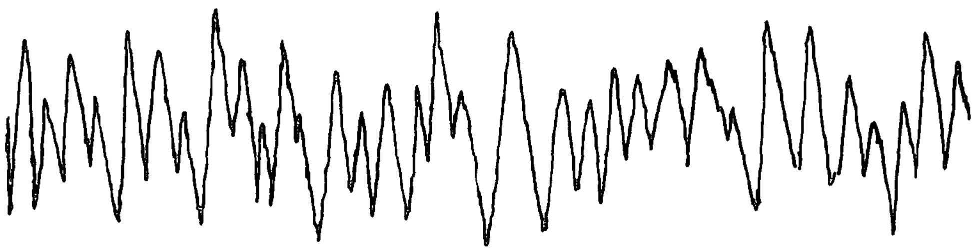


Figure 4.6 Short wavelength, relatively high amplitude

The manner in which surface roughness affects drag or frictional resistance has already been discussed; it will be recalled that drag increases when the asperities of roughness protrude through the laminar sublayer. A wave form of long wavelength and relatively low amplitude would not be expected to affect the drag significantly, however these wave forms will have superimposed upon them roughness of short wavelength and relatively high amplitude, Figure 4.7, which will consequently increase the drag. To measure the surface profile it is essential that the method used can detect the short wave length roughness; these values cannot be given as mean apparent amplitudes because this method of presenting data contains information about the long wavelength curves and is consequently biased.

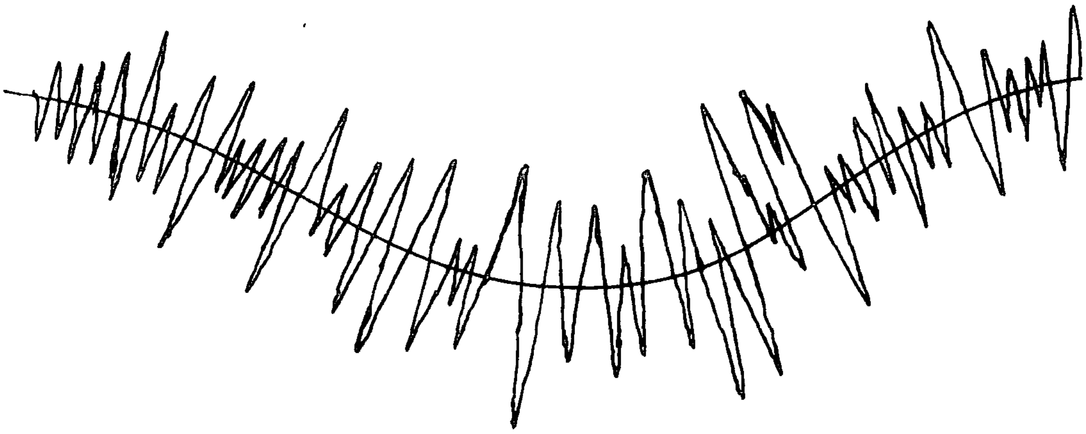


Figure 4.7 The combined wave form shown in Figures 4.5 and 4.6

The simplest non-destructive method of examining the surface profile is to use an instrument which tracks across the surface and records an enlarged trace of the profile on a chart recorder. The only instrument of this type that was readily accessible was a Talysurf, this operates by dragging a stylus across the surface, however it was found that for the films examined here the stylus pressure was too great, resulting in the surface being scratched and so the recording made was not very informative or reproducible.

One of the methods employed by Camrex Research and Development involved the painting of the whole surface of a test disc with the coating under examination. Spots of a non-eroding paint such as an acrylic emulsion were then placed radially on the coating as shown in Figure 4.8. The disc was then spun in sea water for a month and a radial set of samples of the coating including the spots were removed from the disc. Each of these samples was mounted in an epoxide resin, the mounted samples were then ground until a cross-section of the spot was obtained and then polished so that the

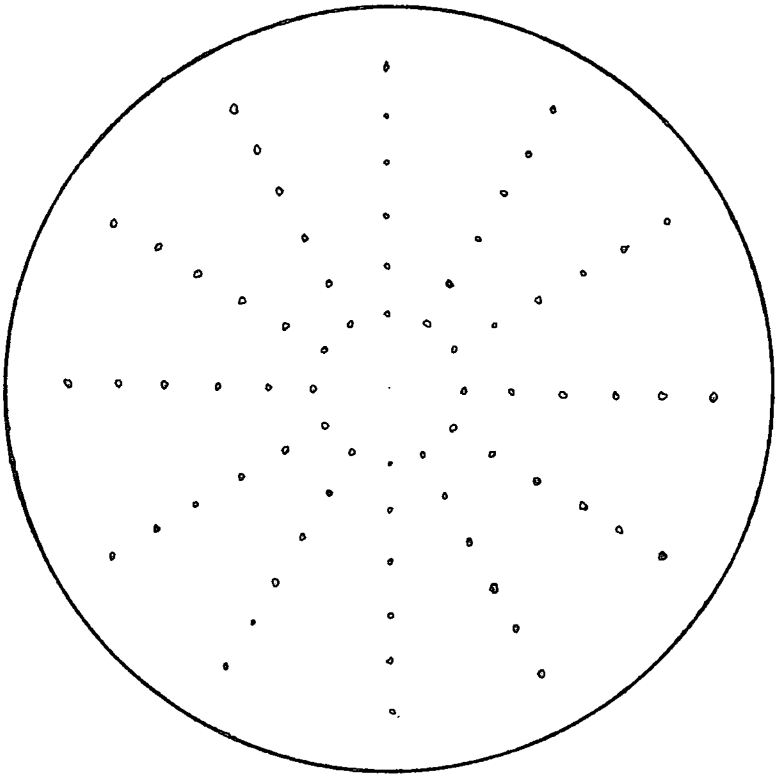


Figure 4.8 Disc coated with antifouling paint and radially spotted

surface could be examined with an optical microscope. The difference in thickness between the exposed surface of the coating and that under the spot was measured giving an indication of the extent of polishing, Figure 4.9

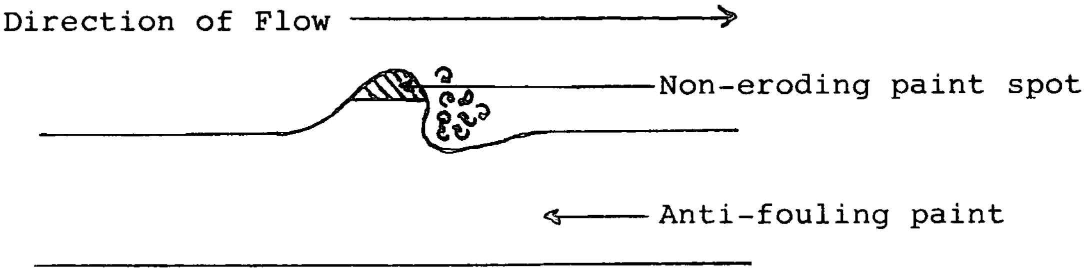


Figure 4.9 Diagrammatic representation of a sample of surface coating after ablation tests

It can be seen from Figure 4.9 that the coating on the trailing edge of the spot relative to the water flow has been more eroded than that of the coating on the leading edge. This effect can be explained if the water flowing across the non-eroding spot is turbulent on the trailing side and if the resulting eddy currents erode the coating more rapidly than the laminar flow, this is an acceptable qualitative hypothesis and can be related to the common phenomena of wind erosion of sand dunes and similar everyday fluid flow effects. The theory that the mechanism by which the surface of a ship coated with an organotin antifouling became smoother with service time depended on the roughness protruding through the laminar sublayer into the turbulent layer is supported by this evidence.

The above technique has two disadvantages. Firstly, it is destructive in that the paint has to be removed from the substrate for examination, and secondly, it does not allow rapid testing for a large number of samples at any one time as only two coating systems may be tested simultaneously (one on either side of the disc).

As there was no technique available for examining the surface profile of a large number of test materials it was decided to continue with the calculations of weight loss and to note changes in observable physical properties of the films after immersion since this seemed a reasonable way of making a first screening of new resins. The results shown in Tables 4.2 and 4.3 for some of the prepared organotin polymers were disappointing as the materials gave either brittle, powdery or sticky films, which, after relatively short periods of testing, became detached from the substrate, therefore they were not suitable materials for incorporation into antifouling paints.

In the following section attempts to use spectroscopic techniques to monitor changes in the films as a result of sea water immersion are described.

TABLE 4.2 Results of the Artificial Sea Water Trials of the Organotin Polyurethanes.

NUMBER OF DAYS TEST		5	7	15	19	24	38
PANEL NUMBER	POLYMER (WEIGHT)	TOTAL WEIGHT OF POLYMER LOST FROM PANEL					
1	$39a^{P}$ (0.1904)	0.1321	0.1322	0.1378	0.1415	0.1431	0.1518
2	$38a^{P}$ (0.2680)	0.1376	0.1765	0.1903	0.1928	0.1933	0.1998
3	$37a^{S}$ (0.2356)	0.2153	0.2174	0.2172	0.2193	0.2200	0.2183
4	$36a^{P}$ (0.1674)	0.1516	0.1655^{R}				
5	$35a^{S}$ (0.2679)	0.2596	0.2636	0.2656	0.2669	0.2669	
6	$29a^{P}$ (0.0857)	0.0855	0.0855^{R}				
7	$28a^{P}$ (0.1875)	0.1865	0.1870^{R}				
8	$27a^{P}$ (0.1266)	0.1256	0.1254^{R}				
9	$24a^{W}$ (0.1475)	0.0037	0.0076	0.0119	0.0137	0.0142	0.0215
10	$23a^{S}$ (0.0915)	0.0849	0.0864	0.0872	0.0881	0.0882	0.0872
11	$22a^{S}$ (0.1481)	0.0064	0.0128	0.0262	0.0347	0.0402	0.0622^{D}
12	$21a^{F}$ (0.1730)	0.0534	0.0680	0.0743	0.0764	0.0765	0.0791
13	$20a^{S}$ (0.0440)	0.0408	0.0409	0.0360	0.0367	0.0368	
14	$19a^{F}$ (0.1625)	0.0618	0.1043	0.1335^{R}			
15	$17a^{F}$ (0.2504)	0.1869	0.1992	0.2153	0.2220	0.2264	0.2391
16	$16a^{P}$ (0.3031)	0.3017	0.3021^{R}				
17	$15a^{F}$ (0.1754)	0.1276	0.1342	0.1446	0.1520	0.1600	0.1600
18	$29a^{P}$ (0.1928)	0.1880	0.1894	0.1895^{R}			
19	$32a^{P}$ (0.1803)	0.1767	0.1767	0.1798^{R}			
20	$31a^{P}$ (0.3013)	0.1974	0.2218	0.2429	0.2514	0.2549	0.2689

NOTE The polymers used are coded as to their reference given in the Synthesis Table contained in Chapter 3.

Superscripts used; D, Detached film; F, Film former; P, Powdery film; S, Sticky film; W, Waxy film; R, the film has run.

TABLE 4.3 Results of the Artificial Sea Water Trials of the Organotin Polyurethanes.

NUMBER OF DAYS TEST		5	19
PANEL NUMBER	POLYMER (WEIGHT)	TOTAL WEIGHT OF POLYMER LOST FROM PANEL	
4	$37a^S$ (0.2417)	0.1898	0.2014
6	$29a^P$ (0.0928)	0.0920	
7	$27a^P$ (0.1326)	0.1324	
8	$20a^S$ (0.1879)	0.1839	0.1841
14	$16a^P$ (0.2351)	0.2345	0.2345
16	$32a^P$ (0.0929)	0.0925	
18	$23a^S$ (0.1246)	0.1199	0.1209
19	$19a^F$ (0.1378)	0.1277	0.1376

NOTE The polymers used are coded as to their reference given in the Synthesis Tables contained in Chapter 3.

Superscripts used; F, Film former; P, Powdery film; S, Sticky film.

4.2.3 Spectroscopic examination of the effects of sea-water on polymer films

(a) Infra-red Spectroscopy

A.T.R.-I.R. allows the infrared spectrum of the surface of a material to be recorded and seemed an appropriate technique for this study. Aluminium foils were coated and immersed in sea water for several days, their spectra being recorded on a Perkin Elmer 597 infrared spectrometer using a Specac 25 Attenuated Total Reflection (A.T.R.) unit and a KRS-5 crystal before and after immersion. The starting films were glossy and clear, some of them acquired a matt white surface coating after immersion and this remained even after washing and drying. However there was no conclusive evidence for surface hydrolysis obtainable from these A.T.R.-I.R. studies. Very slight variations in the spectra of the samples tested before and after immersion were observed but these were insufficient for realistic assignment.

(b) ^{119}Sn N.M.R. Spectroscopy[142]

Tin nuclear magnetic resonance spectroscopy may be used to provide information about the environment of the nucleus under examination, and could therefore have considerable potential in the study of the alkaline hydrolysis of the di-n-alkyl bis(hydroxy carboxylate)tin containing polymers since reaction must inevitably alter the bonding around the tin atoms. A modified Perkin Elmer R.10 n.m.r. spectrometer was available for recording ^{119}Sn spectra of solutions, there was no facility for recording solid state spectra.

As a preliminary investigation the readily soluble monomer, di-n-butyl bis(3-hydroxy-2-naphthoate)tin, was studied. For solutions in acetone the ^{119}Sn chemical shift was found to be independent of concentration; however, successive additions of aliquots of pyridine resulted in changes in chemical shift of the forms shown in Figure 4.10. This demonstrates the

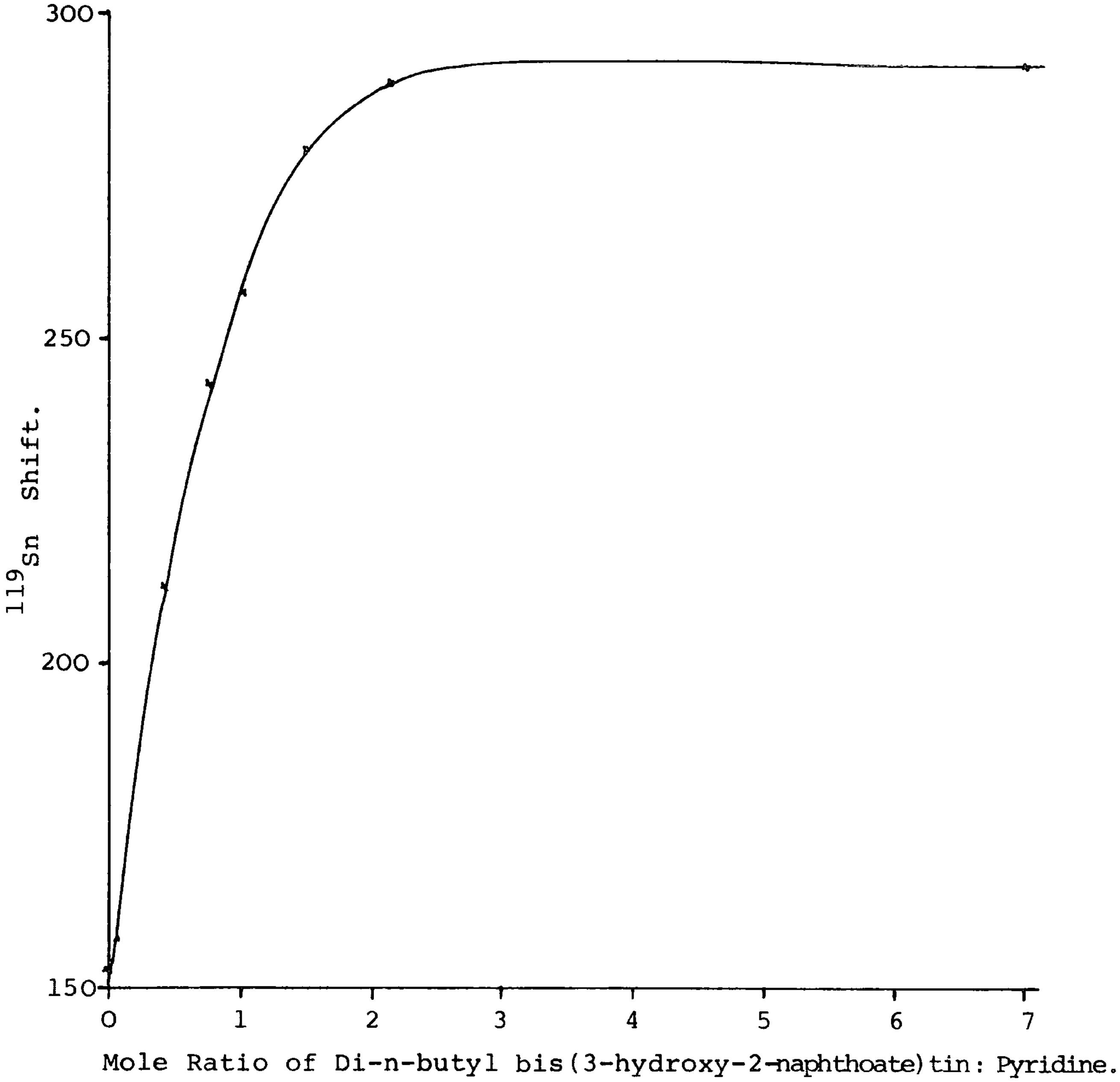


Figure 4.10 Graph of Mole Ratio of Di-n-butyl bis(3-hydroxy-2-naphthoate)tin: Pyridine against the observed ^{119}Sn shift

sensitivity of the shift to the environment of the tin nucleus and was encouraging. The observations can be interpreted in terms of a progressively increasing shift resulting from coordination of the base to the tin; at a tin:pyridine ratio of 1:2 all coordination sites are occupied and no further change in the shift with the addition of base is observed. On evaporation of solvent and the pyridine the starting material was recovered unchanged.

The tin-containing polymers were only slightly soluble in non-polar organic solvents, therefore in these solvents the tin concentration was very low resulting in a poor signal to noise ratio. Different polymers had different solubility characteristics in polar organic solvents and the shifts observed were very solvent dependent, probably due to coordination effects of the type indicated above. In attempts to see if hydrolysis of the tin-carboxylates could be monitored by ^{119}Sn n.m.r., so as to provide a rapid test of susceptibility to hydrolysis which might be correlated with the performance of polymers in sea water, it was decided to investigate the reaction of alkali on ethanolic solutions of both monomers and polymers containing tin. The ethanol solutions of these materials gave single tin resonances whose shifts were independent of concentration (see Appendix 2); however, an addition of small aliquots of alkali (sodium ethoxide in ethanol) all systems gave insoluble precipitates. This was disappointing and frustrated the objectives of the experiment. Attempts to use solvents more closely resembling water, such as ethanol/water or acetone/water mixtures were totally unsuccessful.

4.3 Molecular Weights of Polymers considered in this Chapter

The molecular weight and molecular weight distribution of a polymer are important characterising parameters. There are numerous methods available for the determination of these values, namely:

(a) End group analysis, this being accurate for low molecular weight polymers with readily determinable end groups, the number average molecular weight ($\bar{M}n$) being determined.

(b) Colligative Properties. In principle, three methods may be used, boiling point elevation (ebulliometry), freezing point depression (cryoscopy), and osmotic pressure (osmometry), these methods and variants on the same principles give the number average molecular weight for samples whose molecular weight is normally <50,000.

(c) Light Scattering. This method determines the weight average molecular weight ($\bar{M}w$) and is applicable to any polymer that is readily soluble in a solvent of differing refractive index to the polymer, however for polymers of $\bar{M}w$ <10,000 this method is inaccurate due to the intensity of the scattered light being too small to measure.

(d) G.P.C. and Viscosity Measurements. The above methods give data which can be readily related to a particular average molecular weight, $\bar{M}n$ or $\bar{M}w$. In practice it is generally desirable to obtain results more rapidly than the above techniques allow therefore Gel Permeation Chromatography (G.P.C.) and Viscometry measurements are commonly used, neither of these techniques is an absolute method, both requiring calibration with standard samples. At the time the work discussed here was carried out we had no G.P.C. facilities and viscometry was the method employed to indicate the molecular weight of the prepared polymers.

(d) The early work of Staudinger suggested that there was a correlation between the viscosity of polymer solutions of known concentration and their molecular weights. This has since been confirmed and is usually expressed in the form of the Mark-Houwick equation

$$[\eta] = kM^{\alpha}$$

where $[\eta]$ is the intrinsic viscosity and k and α are empirical constants which can only be determined from viscosity measurements on samples of known molecular weight, these values then being used to determine the molecular weight of polymers of closely related structures. Therefore viscosity studies on novel polymers are in general useful only to establish the order of magnitude of molecular weight. Nevertheless, this method is perhaps one of the most widely used, because it is cheap, quick and experimentally simple.

The intrinsic viscosity, $[\eta]$, is determined by the extrapolation of the inherent viscosity, η_{inh}, (logarithmic viscosity number) and the reduced viscosity, η_{red}, (viscosity number) to infinite dilution where η_{inh} and η_{red} are given by:

$$\eta_{inh} = (\ln\frac{t}{t_o})/c.$$

$$\eta_{red} = (\frac{t-t_o}{t_o})/c.$$

where t is the efflux time for a known volume of polymer solution to flow through a capillary, t_o is the efflux time for the pure solvent and c is the concentration of the polymer solution.

(d) Viscometry determinations were made using an Ubbelohde viscometer immersed in a thermostated water bath at 25.00 ± 0.01°C, the flow of a specific volume of pure solvent being timed automatically using a Wescan viscosity timer until three results were obtained to an accuracy of ±0.1 seconds. Successive known volumes of polymer solution were added to allow elution times at various concentrations to be determined, enabling the intrinsic viscosity at infinite dilution to be obtained by extrapolation. Many of the materials were found to dissolve in a variety of solvents but when diluted or left standing for any length of time they began to precipitate; the results shown in Table 4.4 are for the polymers that remained in solution, the viscosities being measured in pyridine unless otherwise indicated. The earlier studies of ^{119}Sn n.m.r. had shown that the polymers could be recovered unchanged from pyridine solutions.

Polymer	$[\eta]$dl/g
12a	4.853×10^{-2}
14a	5.25×10^{-2}
15a	6.55×10^{-2}
16a	4.3×10^{-2}
17a	3.68×10^{-2}
20a	3.16×10^{-2}
20a(1)	3.47×10^{-2}
20a(2)	2.63×10^{-2}
23a	2.92×10^{-2}

(1) Aniline

(2) Ethyl acetate

Table 4.4 Measured Intrinsic Viscosities for Polymers discussed in this Chapter

(d) These values of the intrinsic viscosities would normally be taken to indicate a very low molecular weight, and certainly they cannot be taken as an indication of high molecular weight materials.

The mode of preparations would have been expected to yield polymeric products; the structures of the di-n-alkyl bis(hydroxy carboxylate)tin monomers are undoubtedly correctly assigned and these monomers were analytically pure, their reactions with diisocyanates on a mole for mole basis resulted in complete consumption of isocyanate functionality. Such procedures ought to yield linear polymers and the fact that many of the materials were soluble or became swollen on the addition of solvent encouraged this conclusion, however it has to be acknowledged that some of these solutions were unstable and that precipitates that were deposited on long standing could not be redissolved. As would be expected when poly-functional isocyanates (of functionality >2) were reacted with the di-n-alkyl bis(hydroxy carboxylate)tin monomers the products were invariably insoluble hard resins. The low viscosity values obtained for the soluble materials are paralleled in other studies of metal carboxylate containing polymers and the authors of this earlier work attributed the low values to ionisation under the high dilution conditions required for the measurements.[143,144] Thus although the materials are not genuine high molecular weight polymers in dilute solution they may nevertheless be regarded as such in the solid state.

4.4 Summary

The results shown in Tables 3.4, 3.5, 3.7, 3.8 and 3.9 concerning the dried polymers were very disappointing, the polymers being micro crystalline powders or waxy sticky materials, the waxy sticky polymers being those prepared from the di-n-alkyl bis(12-hydroxy stearate)tin monomers whereas the polymers prepared from tin monomers whose hydroxyl groups were very close to the tin atom tended to be hard crystalline materials. The crystallinity was thought to be due to the ordering of the polymer chains by inter-molecular coordination of the urethane linkage to the tin atoms in the polymer backbone.

Infra red spectroscopic data yielded information concerning the polymerisation reaction but generally both infra red and ^{119}Sn nuclear magnetic resonance spectroscopic techniques were uninformative when attempts to study the hydrolysis of the polymers were made. The determination of the molecular weight of the polymers was also frustrating as the materials did not show ideal solution behaviour, however the results could be rationalised on the data reported by Matsuda.

The test method was found to have had "teething problems" although these were progressively reduced. The results obtained from the testing of the polymers were disappointing owing to the poor film forming properties of the polymers; modification of polymer structure in order to obtain good film forming properties will be discussed in the following chapter.

CHAPTER FIVE

MODIFICATION OF POLYMERS IN ORDER TO PRODUCE FILM FORMING POLYMERS

5.1 Introduction

The previously prepared copolymers were synthesised from di-n-alkyl bis(hydroxy carboxylate)tin monomers and various diisocyanates. It was noted in Chapter Four that the tendency towards crystallisation exhibited by these polymers probably resulted from coordination of the electronegative groups in the urethane linkage to the tin atoms in the polymer backbone. Some of the polymers prepared from the di-n-alkyl bis(12-hydroxy stearate)tin monomers were sticky waxy materials, this was thought to be a consequence of the greater separation of the tin atoms resulting in a reduction of the inter-chain coordinations, an alterative contributary effect might be the "internal plasticisation" caused by the pendant hexyl groups in these polymers.

The work described in this chapter is concerned with the synthesis of polyurethanes from a diisocyanate and two diols, a di-n-alkyl bis(hydroxy carboxylate)tin monomer and a second aliphatic diol. The aliphatic diols were used to effectively reduce the number of sites for coordination by increasing the separation between the tin atoms. Initially three aliphatic diols were used, namely, 1,2-ethanediol; 1,3-propanediol and 1,4-butanediol, these being supplied as general purpose reagents by Hopkins and Williams and used as supplied. The equipment used in the polymerisation reaction was the same as that described previously.

5.2 Experimental

5.2.1 Polymerisation of Di-n-butyl bis(12-hydroxy stearate)tin with Hexamethylene diisocyanate and 1,2-ethanediol

This preparation illustrates the general method used for the synthesis of the modified polymers. Di-n-butyl bis(12-hydroxy stearate)tin (20g., 2.4×10^{-2} moles) was heated in dry toluene (30 cm^3) at 110°C with rapid stirring (750 r.p.m.), and formed a colourless solution. Hexamethylene diisocyanate (8.088g., 4.408×10^{-2} moles) in dry toluene (20 cm^3) was added in a single rapid step, no changes in the physical properties of the solution being observed; after a further one and a half hours of heating and stirring 1,2-ethanediol (1.5 g., 2.4×10^{-2} moles) was added in a single rapid step. The temperature and stirring rate were kept constant throughout the reaction. The extent of reaction was monitored by the disappearance of the isocyanate band at 2270 cm^{-1} in the i.r. spectra, after two hours this had completely disappeared and the reaction was stopped. As the reaction mixture cooled a viscous pale green oil separated from the solution, this oil was recovered and dried (0.5mm Hg. 2 days) to give a white solid (28.5g., 96%).

Infra-red spectroscopic analysis of the product showed the presence of a urethane linkage (N-H, 3305; C=O, 1720 cm^{-1}), together with the characteristic tin-carboxylate stretching frequencies (1610 and 1540 cm^{-1}) from which it was inferred that the product was the required polyurethane.

This method of synthesis was used for the preparation of more than fifty polymers based on the use of different tin containing diols, aliphatic diols and isocyanates, the reaction conditions and observations being recorded in the Tables 5.1-5.5.

TABLE 5.1 Experimental Details for the Synthesis of the Organotin Polyurethanes.

Ref.	Monomer 1 g. moles	Solvent (ml.)	Observations prior to add$^{n.}$ of Mon 2	Monomer 2 g. moles	Solvent (ml.)	rpm.	Time (hrs)	Observations prior to add$^{n.}$ of Mon 3	Monomer 3 g. moles	Solvent (ml.)	Time (hrs)	Observations	I.R. evidence for NCO group	Dried Polymer Characteristics
A2	12. 20g. 3.09×10^{-2}	Tol(30)	White suspension	ii.10.39g. 6.18×10^{-2}	Tol(30)	750	0.75	Darker suspension formed	a. 1.9g. 3.06×10^{-2}	Tol(30)	2.0	Pale green solution	Absent	White crystall-ine material
A3	3. 10g. 1.97×10^{-2}	Tol(30)	Tan coloured solution	ii.6.635g. 3.95×10^{-2}	Tol(30)	750	0.75	Tan coloured solution	a.1.2243g. 1.97×10^{-2}	Tol(30)	2.0	Tan coloured solution	Absent	White crystall-ine material
A4	4. 10g. 1.61×10^{-2}	Tol(30)	Tan coloured solution	ii.5.431g. 3.23×10^{-2}	Tol(30)	600	0.55	Tan coloured solution	a.1.0g. 1.61×10^{-2}	Tol(30)	2.0	Tan coloured viscous sol$^{n.}$	Absent	Tan coloured cryst. material
A5	5. 10g. 1.97×10^{-2}	Tol(20)	Tan coloured solution	ii.6.635g. 3.5×10^{-2}	Tol(20)	700	0.50	Tan coloured solution	a.1.2243 1.97×10^{-2}	Tol(30)	1.0	Tan coloured viscous sol$^{n.}$	Absent	Tan coloured cryst. material
A6	10. 10g. 1.06×10^{-2}	Tol(30)	Colourless solution	ii.3.563g. 2.12×10^{-2}	Tol(20)	650	0.50	Colourless solution	a.0.658g. 1.06×10^{-2}	Tol(30)	2.0	Colourless viscous sol$^{n.}$	Absent	White crystall-ine material
A7	1. 10g. 1.97×10^{-2}	Tol(20)	Colourless solution	ii.6.635g. 3.96×10^{-2}	Tol(20)	700	0.50	Colourless solution	a.1.224g. 1.97×10^{-2}	Tol(30)	8.0	Colourless solution	Present	Green crystall-ine material
A8	5. 10g. 1.97×10^{-2}	Tol(30)	Tan coloured solution	i.8.86g. 3.95×10^{-2}	Tol(20)	600	0.50	Colourless solution	a.1.224g. 1.97×10^{-2}	Tol(30)	4.0	Colourless solution	Present	Yellow crystall-ine material
A9	9. 10g. 1.20×10^{-2}	Tol(20)	Colourless solution	i.5.399g. 2.40×10^{-2}	Tol(20)	800	0.50	Colourless solution	a.0.746g. 1.20×10^{-2}	Tol(20)	1.0	Colourless solution	Absent	Viscous yellow oil
A10	10. 10g. 1.06×10^{-2}	Tol(20)	Colourless solution	i.4.758g. 2.12×10^{-2}	Tol(20)	800	0.75	Colourless solution	a.0.637g. 1.06×10^{-2}	Tol(20)	0.25	Colourless solution	Absent	Viscous yellow oil
A11	10. 10g. 1.06×10^{-2}	Tol(20)	Colourless solution	v.12.711g. 2.12×10^{-3}	Tol(20)	800	0.75	Tan coloured solution	a.1.756g. 2.83×10^{-2}	Tol(20)	0.17	Tan coloured viscous sol$^{n.}$	Absent	Viscous yellow oil

NOTE All the reactions were carried out at 112°C.

TABLE 5.2 Experimental Details for the Synthesis of the Organotin Polyurethanes.

Ref.	Monomer 1 g. moles	Solvent (ml.)	Observations prior to add$^{n.}$ of Mon 2	Monomer 2 g. moles	Solvent (ml.)	rpm.	Time (hrs)	Observations prior to add$^{n.}$ of Mon 3	Monomer 3 g. moles	Solvent (ml.)	Time (hrs)	Observation	I.R. evidence for NCO group	Dried Polymer Characteristics
A12	10. 10g. 1.2x10^{-2}	Tol(20)	Colourless solution	v.13.188g. 2.35x10^{-2}	Tol(20)	850	0.33	Tan coloured solution	a.0.746g. 1.2x10^{-2}	Act(5)	0.33	Tan coloured viscous sol$^{n.}$	Absent	Viscous yellow oil
A13	10. 10g. 1.06x10^{-2}	Tol(20)	Colourless solution	v.12.711g. 2.12x10^{-2}	Tol(20)	850	0.50	Tan coloured solution	a.0.658g. 1.06x10^{-2}	Act(10)	0.25	Tan coloured viscous sol$^{n.}$	Absent	Viscous yellow oil
A14	5. 10g. 1.97x10^{-2}	Tol(20)	Tan coloured solution	v.22.953g. 3.82x10^{-2}	Tol(20)	700	0.50	Tan coloured solution	a.1.224g. 1.97x10^{-2}	Act(10)	0.17	Tan coloured viscous sol$^{n.}$	Absent	Viscous brown oil
A15	3. 10g. 1.97x10^{-2}	Tol(20)	Tan coloured solution	v.22.953g. 3.82x10^{-2}	Tol(20)	600	0.25	Tan coloured more viscous solution	a.1.224g. 1.97x10^{-2}	Act(5)	0.25	Tan coloured viscous sol$^{n.}$	Absent	Viscous brown oil
A16	4. 10g. 1.61x10^{-2}	Tol(20)	Tan coloured solution	v.19.375g. 3.23x10^{-2}	Tol(20)	750	0.50	Tan coloured more viscous solution	a.1.002g. 1.61x10^{-2}	Act(10)	0.25	Tan coloured viscous sol$^{n.}$	Absent	Viscous brown oil
A17	3. 5g. 9.85x10^{-3}	Tol(20)	Tan coloured solution	v.11.834g. 1.93x10^{-2}	Tol(20)	750	0.75	Tan coloured more viscous solution	a.0.611g. 9.86x10^{-3}	Act(5)	2.00	Tan coloured viscous sol$^{n.}$	Absent	Viscous brown oil
A18	9. 5g. 6.01x10^{-3}	Tol(20)	Colourless solution	ii.2.022g. 1.21x10^{-2}	Tol(20)	850	0.25	Colourless solution	b.0.457g. 6.02x10^{-3}	Act(10)	0.18	Colourless solution	Absent	Cream coloured solid
A19	10. 5g. 5.29x10^{-3}	Tol(20)	Colourless solution	ii.1.981g. 1.18x10^{-2}	Tol(20)	850	0.25	Colourless solution	b.0.403g. 5.3x10^{-3}	Act(10)	0.33	Colourless solution	Absent	Yellow film forming solid
A21	10. 5g. 5.29x10^{-3}	Tol(20)	Colourless solution	ii.1.981g. 1.18x10^{-2}	Tol(20)	750	0.50	Colourless solution	c.0.477g. 5.28x10^{-3}	Act(10)	0.50	Colourless solution	Absent	White crystalline solid
A22	9. 5g. 6.01x10^{-3}	Tol(20)	Colourless solution	ii.2.022g. 1.21x10^{-2}	Tol(20)	750	0.50	Colourless solution	c.0.542g. 6.01x10^{-3}	Act(10)	0.50	Colourless solution	Absent	Cream crystalline solid

NOTE All the reactions were carried out at 112°C.

TABLE 5.3 Experimental Details for the Synthesis of the Organotin Polyurethanes.

Ref.	Monomer 1 g. moles	Solvent (ml.)	Observations prior to add$^{n.}$ of Mon 2	Monomer 2 g. moles	Solvent (ml.)	rpm.	Time (hrs)	Observations prior to add$^{n.}$ of Mon 3	Monomer 3 g. moles	Solvent (ml.)	Time (hrs)	Observations	I.R. evidence for NCO group	Dried Polymer Characteristics
A23	5. 5g. 9.85×10^{-3}	Tol(20)	Colourless solution	i.4.431g. 1.97×10^{-2}	Tol(20)	750	0.33	Colourless solution	c.0.889g. 9.87×10^{-3}	Act(10)	0.50	Colourless solution	Absent	Cream crystalline solid
A24	10. 5g. 5.34×10^{-3}	Tol(20)	Colourless solution	i.2.399g. 1.07×10^{-2}	Tol(20)	700	0.50	Colourless solution	b.0.403g. 5.34×10^{-3}	Act(10)	0.66	Pale green solution	Absent	Viscous yellow oil
A25	10. 4g. 4.24×10^{-3}	Tol(20)	Colourless solution	i.1.903g. 8.47×10^{-3}	Tol(20)	750	0.50	Colourless solution	c.0.382g. 4.23×10^{-3}	Act(20)	1.00	Pale green solution	Absent	Tan coloured cryst. solid
A26	9. 5g. 6.01×10^{-3}	Tol(20)	Colourless solution	i.2.70g. 1.2×10^{-2}	Tol(15)	750	0.50	Colourless solution	b.0.456g. 6.02×10^{-3}	Act(20)	0.50	Pale green solution	Absent	Yellow crystalline solid
A27	9. 5g. 6.01×10^{-3}	Tol(20)	Colourless solution	i.2.70g. 1.2×10^{-2}	Tol(15)	750	0.50	Colourless solution	c.0.542g. 6.01×10^{-3}	Act(20)	2.00	Colourless solution	Absent	Viscous yellow oil
A28	9. 5g. 6.01×10^{-3}	Tol(20)	Colourless solution	v.6.594g. 1.1×10^{-2}	Tol(15)	750	0.50	Tan coloured solution	b.0.418g. 5.5×10^{-3}	Act(30)	2.00	Tan coloured solution	Absent	Viscous brown oil
A29	9. 5g. 6.01×10^{-3}	Tol(20)	Colourless solution	v.6.594g. 1.1×10^{-2}	Tol(30)	800	0.50	Tan coloured solution	c.0.495g. 5.49×10^{-3}	Act(20)	1.50	Tan coloured solution	Absent	Very viscous brown oil
A30	13. 5g. 1.3×10^{-2}	Tol(30)	White suspension	i.2.935g. 1.31×10^{-2}	Tol(30)	800	2.00	White suspension	a.0.406g. 6.53×10^{-3}	Act(30)	1.00	White suspension	Absent	Colourless film forming solid
A31	11. 4g. 7.47×10^{-3}	Tol(30)	White suspension	i.3.357g. 1.5×10^{-2}	Tol(30)	750	0.50	Yellow solution	a.0.464g. 7.47×10^{-3}	Act(20)	2.00	Pale yellow solution	Absent	White crystalline solid
A32	13. 5g. 1.31×10^{-2}	Tol(30)	White suspension	i.3.87g. 2.61×10^{-2}	Tol(30)	800	0.50	Yellow solution	a.0.811g. 1.306×10^{-2}	Act(30)	1.00	Pale yellow solution	Absent	White crystalline solid

NOTE All the reactions were carried out at 112°C.

TABLE 5.4 Experimental Details for the Synthesis of the Organotin Polyurethanes.

Ref.	Monomer 1 g. moles	Solvent (ml.)	Observations prior to add$^{n.}$ of Mon 2	Monomer 2 g. moles	Solvent (ml.)	rpm.	Time. (hrs)	Observations prior to add$^{n.}$ of Mon 3	Monomer 3 g. moles	Solvent (ml.)	Time (hrs)	Observations	I.R. evidence for NCO group	Dried Polymer Characteristics
A33	11. 4g. $7.49x10^{-3}$	Tol(30)	White suspension	i.3.357g. $1.49x10^{-2}$	Tol(20)	750	0.25	Pale yellow solution	b.0.569g. $7.48x10^{-3}$	Act(20)	0.50	Pale yellow solution	Absent	White crystalline solid
A34	11. 3g. $5.6x10^{-3}$	Tol(30)	White suspension	i.2.518g. $1.12x10^{-2}$	Tol(20)	750	0.25	Pale yellow solution	c.0.505 $5.61x10^{-3}$	Act(30)	0.50	Pale yellow solution	Present	White crystalline solid
A35	13. 5g. $1.3x10^{-2}$	Tol(30)	White suspension	i.5.87g. $2.61x10^{-2}$	Tol(20)	800	0.50	Pale yellow solution	b.0.994g. $1.31x10^{-2}$	Act(30)	0.50	Pale yellow solution	Absent	White crystalline solid
A36	13. 5g. $1.31x10^{-2}$	Tol(20)	White suspension	i.5.87g. $2.61x10^{-2}$	Tol(20)	800	0.50	Pale yellow solution	c.1.176g. $1.3x10^{-2}$	Act(30)	3.00	Pale yellow solution	Absent	White crystalline solid
A37	13. 5g. $1.31x10^{-2}$	Tol(20)	White suspension	v.15.68g. $2.61x10^{-2}$	Tol(30)	750	0.25	Pale yellow solution	b.0.995g. $1.31x10^{-2}$	Act(30)	0.50	Pale yellow solution	Absent	Very viscous yellow oil
A38	13. 5g. $1.31x10^{-2}$	Tol(30)	White suspension	v.15.68g. $2.61x10^{-2}$	Tol(30)	750	0.25	Pale yellow solution	c.1.178g. $1.31x10^{-2}$	Act(30)	0.50	Pale yellow solution	Absent	Very viscous yellow oil
A39	13. 5g. $1.31x10^{-2}$	Tol(30)	White suspension	v.15.68g. $2.61x10^{-2}$	Tol(30)	750	0.33	Pale yellow solution	a.0.810g. $1.31x10^{-2}$	Act(30)	0.50	Pale yellow solution	Absent	Viscous yellow oil
A40	9. 5g. $6.01x10^{-3}$	Tol(30)	Colourless solution	i.7.213g. $3.2x10^{-2}$	Tol(30)	750	0.50	Colourless solution	b.1.987g. $2.61x10^{-2}$	Act(20)	0.33	Colourless solution	Absent	Yellow crystalline solid
A41	9. 5g. $6.01x10^{-3}$	Tol(30)	Colourless solution	v.7.216g. $1.2x10^{-2}$	Tol(30)	800	0.50	Tan coloured solution	c.0.542g. $6.01x10^{-3}$	Act(20)	1.00	Tan coloured solution	Absent	Very viscous yellow oil
A42	9. 5g. $6.01x10^{-3}$	Tol(30)	Colourless solution	v.&.216g. $1.2x10^{-2}$	Tol(30)	700	0.50	Tan coloured solution	b.0.457g. $6.02x10^{-3}$	Act(20)	1.25	Tan coloured solution	Absent	Very viscous yellow oil

NOTE All the reactions ware carried out at 112°C

TABLE 5.5 Experimental Details for the Synthesis of the Organotin Polyurethanes.

Ref.	Monomer 1 g. moles	Solvent (ml.)	Observations prior to add$^{n.}$ of Mon 2	Monomer 2 g. moles	Solvent (ml.)	rpm.	Time (hrs)	Observations prior to add$^{n.}$ of Mon 3	Monomer 3 g. moles	Solvent (ml.)	Time (hrs)	Observations	I.R. evidence for NCO group	Dried Polymer Characteristics
A43	10. 2.5g. 2.65x10^{-3}	Tol(30)	Colourless solution	v.3.018g. 5.03x10^{-3}	Tol(30)	750	0.25	Tan coloured solution	a.0.156g. 2.5x10^{-3}	Act(20)	1.00	Tan coloured solution	Absent	Tacky yellow solid
A44	10. 1g. 1.06x10^{-3}	Tol(20)	Colourless solution	v.1.271g. 2.12x10^{-3}	Tol(30)	800	0.50	Tan coloured solution	b.0.081g. 1.06x10^{-3}	Act(20)	1.00	Tan coloured solution	Absent	Waxy yellow solid
A45	10. 1g. 1.06x10^{-3}	Tol(20)	Colourless solution	v.1.271g. 2.12x10^{-3}	Tol(30)	800	0.25	Tan coloured solution	c.0.096g. 1.06x10^{-3}	Act(20)	1.00	Tan coloured solution	Absent	Yellow film forming solid
A46	3. 5g. 9.86x10^{-3}	Tol(20)	Tan coloured solution	i.4.43g. 1.97x10^{-2}	Tol(30)	700	0.50	Tan coloured solution	a.0.612g. 9.86x10^{-3}	Act(20)	2.00	Tan coloured solution	Present	Tan coloured cryst. solid
A47	5. 5g. 9.86x10^{-3}	Tol(30)	Colourless solution	i.4.43g. 1.97x10^{-2}	Tol(30)	950	0.25	Colourless solution	a.0.612g. 9.86x10^{-3}	Act(20)	1.00	Tan coloured solution	Absent	Cream crystalline solid
A48	5. 5g. 9.86x10^{-3}	Tol(30)	Colourless solution	i.4.43g. 1.97x10^{-2}	Tol(30)	950	0.25	Colourless solution	b.0.751g. 9.86x10^{-3}	Act(20)	1.00	Tan coloured solution	Absent	Cream crystalline solid
A49	5. 5g. 9.86x10^{-3}	Tol(30)	Colourless solution	v.11.834g. 1.97x10^{-2}	Tol(30)	950	0.50	Tan coloured solution	b.0.751g. 9.86x10^{-3}	Act(20)	2.00	Tan coloured solution	Absent	Viscous brown oil
A50	5. 5g. 9.86x10^{-3}	Tol(30)	Colourless solution	v.11.834g. 1.97x10^{-2}	Tol(30)	950	0.50	Tan coloured solution	c.0.889g. 9.86x10^{-3}	Act(20)	0.33	Tan coloured solution	Absent	Viscous yellow oil
A51	3. 5g. 9.86x10^{-3}	Tol(30)	Tan coloured solution	i.4.43g. 1.97x10^{-2}	Tol(20)	950	0.33	Tan coloured solution	b.0.751g. 9.86x10^{-3}	Act(20)	3.00	Tan coloured solution	Absent	Tan coloured cryst. solid

NOTE All the reactions were carried out at 112°C.

5.3 Testing of Polymer Samples

The polymers which were thought on the basis of their physical appearance to be suitable for further testing were painted as solutions on to 1" x 3" x 1/8"* grit blasted stainless steel panels in a similar manner to that previously described in Chapter Four. The panels were mounted on to the drum and spun in sea water, periodically they were removed, dried to constant weight and their weight loss with respect to time were recorded, Table 5.6, together with information about the integrity of the film.

From the above table it can be seen that these polymers disintegrate very rapidly compared to the commercial products used as standards, Cl-1; Cl-2; Cl-3 and OMP2. These failures were due to two factors, firstly, poor adhesion to the substrate and secondly loss of film integrity during testing. The polymers used were all film formers although their degree of resilience towards cracking varied considerably and it is thought that many of them disintegrated rather than polished.

The testing of the samples listed in Table 5.6 was terminated when it was established that the sea water was contaminated with iron ions; these ions arose from the breakdown of the coating system on the water tank, and were known to inhibit the polishing of established ablative coating systems. To overcome this problem a plastic drum liner was installed and the rig was moved to Camrex's test station at Blyth, on the

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* The panel thickness was increased to 1/8" from 20 gauge to allow grit blasting without any deformation of the panel; this necessitated the manufacture of a new Tufnol drum to mount the samples on.

TABLE 5.6 Results of the Artificial Sea Water Trials of the Organotin Polyurethanes

NUMBER OF DAYS TEST		8	13	17	25
PANEL NUMBER	POLYMER (WEIGHT)	TOTAL WEIGHT OF POLYMER LOST FROM PANEL			
1	C1-1 (0.1426)	0.0075	0.0107	0.0119	0.0179
2	C1-2 (0.1420)	0.0068	0.0083	0.0091	0.0093
3	C1-3 (0.0601)	0.0206	0.0297	0.0312	0.0328
4	OMP2 (0.0695)	0.0030	0.0035	0.0058	0.0066
5	A2 (0.1151)	0.0069	0.0081	0.0127	0.0441
6	A1 (0.0714)	0.0010	0.0025	0.0039	0.0061
7	A3 (0.1947)	0.0412	0.0580	0.0734	0.1020
8	A4 (0.0562)	0.0246	0.0246	0.0306	0.0357^{D}
9	A5 (0.1756)	0.0419	0.0861	0.1211	0.1614
10	A6 (0.0838)	0.0036	0.0081	0.0510	0.0529
11	A9 (0.0371)	0.0090	0.0156	0.0180	0.0300
12	A11 (0.0764)	0.0019	0.0029	0.0041	0.0052
13	A10 (0.0562)	0.0451	0.0471	0.0486	0.0541
14	A12 (0.0285)	0.0232	0.0265^{D}		
15	A13 (0.0546)	0.0018	0.0021	0.0039	0.0186^{D}
16	A15 (0.0688)	0.0618^{D}	0.0630	0.0651	0.0654
17	A15 (0.0728)	0.0614	0.0677^{D}		
18	A16 (0.0534)	0.0458	0.0494^{D}		

NOTE Panels 1-4 were coated with commercial organotin resins supplied by Camrex;

Panels 5-18 were coated with polymers prepared by the author and referenced as given in the Synthesis Tables contained in this Chapter.

Superscript used D, Detached film

Northumbrian coast, where a flowing sea water supply was available; this also reduced the probability of the tank overheating during a test run.

A second set of panels was coated with a further set of polymers and tested using a flowing sea water supply, the results being shown in Table 5.7. The surface profiles of some of these panels were recorded using a Surfometer; although similar in principle of operation this instrument differed from the Talysurf described in Chapter Four in that the stylus pressure was very low, thus minimising damage to the surface of the film and the tracking distance was longer and allowed a profile to be recorded between two reference points, as shown in Figure 5.1.

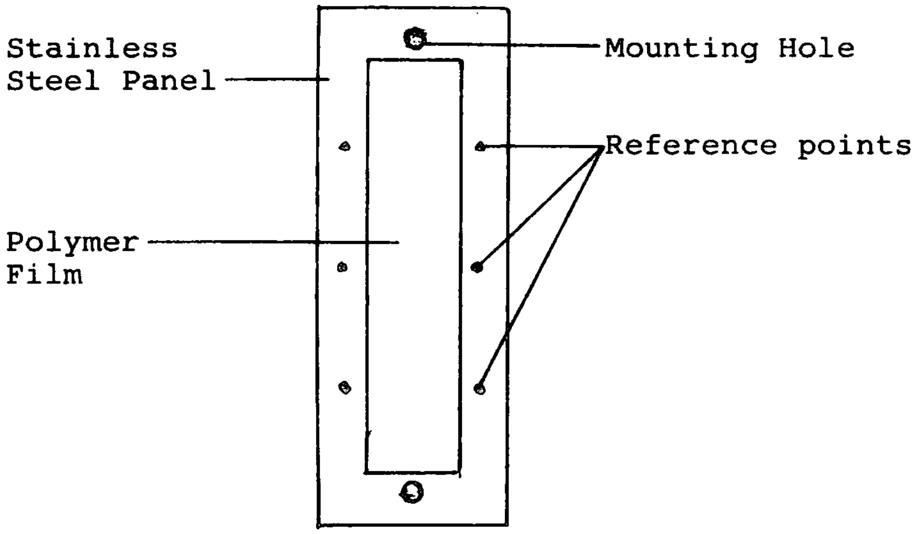


Figure 5.1 A Prepared Stainless Steel Panel.

Problems were encountered with this method as the films were applied to the substrate using a brush so the surface profiles were very rough and not of uniform thickness, unlike those applied by Camrex where the coatings used were viscous and

TABLE 5.7 Results of the Sea Water Trials of the Organotin Polyurethanes.

NUMBER OF DAYS TEST		9	22	31	51
PANEL NUMBER	POLYMER (WEIGHT)	TOTAL WEIGHT OF POLYMER LOST FROM PANEL			
1	A34 (0.0511)	0.0053	0.0085	0.0087	0.0096
2	A33 (0.0398)	0.0397^{D}			
3	A40 (0.0579)	0.0057^{B}	0.0114	0.0133	0.0136
4	A27 (0.0352)	0.0163	0.0259	0.0283^{D}	
5	A26 (0.1452)	0.1121^{R}	0.1348	0.1380^{D}	
6	A10 (0.0688)	0.0523^{R}	0.0619	0.0623	0.0632
7	A9 (0.0996)	0.0437^{R}	0.0665	0.0839	0.0924
8	C1-1 (0.0516)	0.0115^{D}	0.0185	0.0228	0.0261
9	A50 (0.0769)	0.0623^{R}	0.0673	0.0686	0.0688
10	A49 (0.0748)	0.0625^{R}	0.0648	0.0663	0.0669
11	A19 (0.0592)	0.0023	0.0052	0.0080	0.0084
12	A6 (0.0789)	0.0011	0.0028	0.0047	0.0055
13	A1 (0.0536)	0.0009	0.0021	0.0037	0.0046
14	A2 (0.0980)	0.0960^{D}			
15	A40 (0.0646)	0.0035	0.0065	0.0080	0.0095

NOTE Panel No. 8 was coated with a commercial organotin resin the remaining fourteen panels were coated with polymers prepared by the author and referenced as given in The Synthesis Tables contained in this Chapter. Superscripts used; B, Brittle film; D, Detached film; R, The film has run.

therefore they could be applied with a drawdown cube resulting in a very smooth film of uniform thickness (Appendix Three). As a consequence of this roughness it was virtually impossible to correlate the roughness data although in some cases it was possible to observe slight changes in the surface profile but no conclusive proof was obtained for the polishing of the film.

The tests carried out at Durham and Blyth using the polymers described in this chapter had demonstrated the ability of some of the polymers with backbone tin carboxylate units to withstand the physical forces likely to be encountered if they were to be used as an antifouling resin; however the behavioural characteristics of a coating system are effected by pigmentation, therefore some simple paints were formulated with these polymers and tested.

5.4 Pigmentation and Testing of Polymer Samples

There are three main criteria which influence the effects of pigmentation:

(i) The pigment: the pigment chosen was calcium sulphate as this is inert, non-toxic and not very soluble in sea water thus it was acting more as an extender. The calcium sulphate used was supplied by B.D.H. as a commercial grade material.

(ii) The particle size: the calcium sulphate used had a large variation in particle size therefore it was ground using an Ultra Turax high speed homogeniser until the maximum particle size was 50μm.

(iii) The percentage pigmentation: this was generally kept low so as to maintain the integrity of the film as some of the polymers used were brittle.

A fairly wide cross-section of polymers was used to rapidly determine the effects of pigmentation.

5.4.1 Preparation of Pigment

Calcium sulphate (130g.) and toluene (345g.) were stirred at 10,000 r.p.m. for one hour, the particle size being determined periodically using a grind gauge. The calcium sulphate was found to settle out very quickly when the agitation was stopped, therefore a suspending agent, Airosil 200 (2g.), was added and the system again ground for thirty minutes, after which time the maximum particle size was 50μm.

5.4.2 Preparation of the Pigmented Polymers

Weighed aliquots of the suspended pigment were added to solutions of the polymers, these pigmented polymers were then stirred to give a uniform dispersion before painting out. An approximate pigment content of the dry polymer film was obtained by this procedure (see Table 5.8).

5.4.3 Panel Preparation

The stainless steel panels were grit blasted, washed under running water, dried and sprayed with an aluminium based primer to prevent contact between the pigmented polymer under test and the metal substrate, thus reducing any anomalies arising due to iron ions interacting with the polymer. The primed panels were dried to constant weight before the application of the pigmented polymer samples, the method employed being the same as that described previously. The newly prepared panels were attached to the drum and the test routine started; unfortunately the submersible sea water pump broke down and a member of Camrex's staff disconnected the cooling coil therefore the tank overheated

TABLE 5.8 Results of the Sea Water Trials of the Pigmented Organotin Polyurethanes.

NUMBER OF DAYS TEST			14
PANEL NUMBER	POLYMER (WEIGHT)	% PIGMENT	TOTAL WEIGHT OF POLYMER LOST FROM PANEL
1	A11 (0.0430)	27	0.0026
2	A2 (0.0398)	18.5	0.0002
3	A3 (0.1445)	17.4	0.0386
4	A6 (0.0546)	23	0.0031
5	A19 (0.0562)	22.5	0.0167
6	4a (0.1793)	29	0.0624
7	5a (0.1793)	29	0.1644
8	6a (0.2249)	22	0.1502
9	A38 (0.1872)	21	0.1327
10	9a (0.1562	20	0.1366
11	A50 (0.1122)	31	0.0798
12	A1 (0.2122)	50	0.0469
13	A2 (0.1555)	50	0.0695
14	A3 (0.1639)	50	0.0998
15	10a (0.2352)	22	0.2253

NOTE Panels 6, 7, 8, 10 & 15 are coded as to their reference given in the Synthesis Tables contained in Chapter 3, the remaining panels are coded as to their reference given in the Synthesis Tables contained in this Chapter after twenty-eight days and the testing was thus terminated, the limited set of results are shown in Table 5.8.

5.5 The use of Low Molecular Weight Hydroxy Terminated Polymers to produce film forming organotin polymers

The polymers prepared using the three diols as co-monomers showed a slight improvement in the film forming properties of the organotin polymers compared to those described in Chapter Three. The inclusion of a flexible polymeric diol into the organotin polymer instead of a low molecular weight diol could enhance the film forming properties of the polymer by:

(a) reducing the coordination and hence the crystallinity, and

(b) introducing a soft segment into the polymer to give more flexible structures.

Polytetramethylene ether glycols were used as the origin of the 'soft segment' these being supplied in two molecular weights, 1,000 and 2,000, by DuPont under the trade names Teracol 1000 and Teracol 2000. The materials were hydroxy terminated with a narrow molecular weight distribution; they were white low melting point solids, readily soluble in toluene, and cheap; therefore they were ideally suited for the large scale manufacture of any successful organotin polymer which may have results from these studies.

5.5.1 Experimental

The method of synthesis of the organotin polyurethanes containing these prepolymers was identical to that previously described, the monomers, reaction conditions, observations and film forming characteristics are tabulated in Tables 5.9 - 5.14, the abbreviations used in these tables being shown

TABLE 5.9 Experimental Details for the Synthesis of the Organotin Polyurethanes.

Ref.	Monomer 1 g. moles	Solvent (ml.)	Observations prior to add$^{n.}$ of Mon 2	Monomer 2 g. moles	Solvent (ml.)	rpm.	Time (hrs)	Observations prior to add$^{n.}$ of Mon 3	Monomer 3 g. moles	Solvent (ml.)	Time (hrs)	Observations	Dried Polymer Characteristics and Film Forming Properties
T1	14.5.429g. $1.1x10^{-2}$	Tol(30)	White suspension	i.4.929g. $2.19x10^{-2}$	Tol(20)	1000	1.50	White suspension	e.21.95g. $1.09x10^{-2}$	Tol(50)	2.00	White suspension	White waxy solid Poor film
T2	12. 5g. $7.73x10^{-3}$	Tol(30)	White suspension	i.3.469g. $1.54x10^{-2}$	Tol(30)	900	1.50	Colourless solution	d.7.723g. $7.72x10^{-3}$	Tol(50)	1.50	Colourless viscous sol$^{n.}$	Cream coloured very viscous oil
T3	12. 5g. $7.73x10^{-3}$	Tol(30)	White suspension	i.2.602g. $1.16x10^{-2}$	Tol(30)	900	1.50	Colourless solution	d.3.862g. $3.86x10^{-3}$	Tol(50)	2.00	Colourless viscous sol$^{n.}$	Cream coloured very viscous oil
T4	12. 5g. $7.73x10^{-3}$	Tol(30)	White suspension	i.2.168g. $9.65x10^{-3}$	Tol(30)	900	1.25	Colourless solution	d.1.931g. $1.93x10^{-3}$	Tol(50)	2.00	Colourless viscous sol$^{n.}$	Tacky cream coloured material
T5	12. 10g. $1.55x10^{-2}$	Tol(30)	White suspension	i.3.903g. $1.73x10^{-2}$	Tol(30)	900	1.00	Colourless solution	d.1.871g. $1.87x10^{-3}$	Tol(50)	2.00	Colourless viscous sol$^{n.}$	Tacky cream coloured material
T6	12. 10g. $1.55x10^{-2}$	Tol(30)	White suspension	i.4.163g. $1.85x10^{-2}$	Tol(30)	900	1.00	Colourless solution	d.3.089g. $3.09x10^{-3}$	Tol(50)	4.00	Colourless viscous sol$^{n.}$	Tacky cream coloured material
T7	14. 10g. $2.02x10^{-2}$	Tol(30)	White suspension	i.5.446g. $2.42x10^{-2}$	Tol(30)	900	15.0	White suspension	d.4.003g. $4.00x10^{-3}$	Tol(50)	6.00	White suspension	White solid and a colourless film forming material
T8	14. 10g. $2.02x10^{-2}$	THF/ACT 50/50 (30)	White suspension	i.5.446g. $2.42x10^{-2}$	Tol(20)	1400	15.0	Yellow solution	d.4.003g. $4.00x10^{-3}$	Tol(50)	4.00	Yellow sol$^{n.}$ + White solid	Tan coloured brittle film forming material
T9	3. 10g. $1.97x10^{-2}$	Tol(10)	Tan coloured solution	i.5.541g. $2.47x10^{-2}$	Tol(20)	900	1.00	Tan coloured solution	d.4.934g. $4.93x10^{-3}$	Tol(30)	1.00	Tan coloured solution	Tan coloured tough film forming material
T10	3. 10g. $1.97x10^{-2}$	Tol(30)	Tan coloured solution	i.6.649g. $2.96x10^{-2}$	Tol(30)	900	1.00	Tan coloured solution	d.9.868g. $9.87x10^{-3}$	Tol(30)	1.00	Tan coloured viscous sol$^{n.}$	Tacky tan coloured film forming material

NOTE All the reactions were carried out at 112^{o}C and infra red examination of the products showed that there was some unreacted isocyanate present.

TABLE 5.10 Experimental Details for the Synthesis of the Organotin Polyurethanes.

Ref.	Monomer 1 g. moles	Solvent (ml.)	Observations prior to add$^{n.}$ of Mon 2	Monomer 2 g. moles	Solvent (ml.)	rpm.	Time (hrs)	Observations prior to add$^{n.}$ of Mon 3	Monomer 3 g. moles	Solvent (ml.)	Time (hrs)	Observations	Dried Polymer Characteristics and Film Forming Properties
T11	9. 10g. 1.2×10^{-2}	Tol(30)	Colourless solution	i.3.24g. 1.44×10^{-2}	Tol(30)	900	1.00	Colourless solution	d.2.402g. 2.4×10^{-3}	Tol(30)	1.00	Colourless solution	Tacky white coloured material
T12	9. 10g. 1.2×10^{-2}	Tol(30)	Colourless solution	i.2.97g. 1.32×10^{-2}	Tol(30)	850	1.00	Colourless solution	d.1.202g. 1.2×10^{-3}	Tol(30)	1.00	Colourless solution	Tacky white coloured material
T13	9. 10g. 1.2×10^{-2}	Tol(30)	Colourless solution	i.2.754g. 1.23×10^{-2}	Tol(30)	950	1.00	Colourless solution	d.0.293g. 2.93×10^{-4}	Tol(30)	1.00	Colourless solution	Tacky white coloured material
T14	10. 10g. 1.59×10^{-2}	Tol(30)	Colourless solution	i.3.747g. 1.67×10^{-2}	Tol(30)	950	1.00	Colourless solution	d.0.794g. 7.94×10^{-4}	Tol(30)	1.00	Colourless solution	Pale yellow tacky film forming material
T15	14. 10g. 2.02×10^{-2}	Tol(30)	White suspension	i.4.994g. 2.22×10^{-2}	Tol(30)	950	1.00	Colourless solution	e.4.043g. 2.02×10^{-3}	Tol(30)	1.00	Colourless sol$^{n.}$+ ppt.	Pale yellow soft film forming material
T16	14. 10g. 2.02×10^{-2}	Tol(30)	White suspension	i.4.767g. 2.12×10^{-2}	Tol(30)	1500	1.00	Colourless solution	e.2.022g. 1.01×10^{-3}	Tol(30)	1.00	Colourless sol$^{n.}$+ ppt.	Pale yellow brittle film forming material
T17	4. 10g. 1.66×10^{-2}	Tol(30)	Tan coloured solution	i.3.903g. 1.73×10^{-2}	Tol(30)	900	1.00	Tan coloured solution	e.2.425g. 1.21×10^{-3}	Tol(30)	1.00	Tan coloured solution	Tan coloured slightly tacky film forming material
T18	4. 10g. 1.66×10^{-2}	Tol(30)	Tan coloured solution	i.3.812g. 1.69×10^{-2}	Tol(30)	900	1.00	Tan coloured solution	e.1.616g. 8.08×10^{-4}	Tol(30)	1.00	Tan coloured solution	Tan coloured film forming material
T19	5. 10g. 1.97×10^{-2}	Tol(30)	Colourless solution	i.4.871g. 2.17×10^{-2}	Tol(30)	950	1.00	Colourless solution	e.3.943g. 1.97×10^{-3}	Tol(30)	1.00	Colourless solution	Colourless slightly soft film film forming material
T20	5. 10g. 1.97×10^{-2}	Tol(30)	Colourless solution	i.5.314g. 2.37×10^{-2}	Tol(30)	950	1.00	Colourless solution	d.3.943g. 3.94×10^{-3}	Tol(30)	1.00	Colourless solution	White material

NOTE All the reactions were carried out at 112°C and infra red examination of the products showed that there was some unreacted isocyanate present.

TABLE 5.11 Experimental Details for the Synthesis of the Organotin Polyurethanes.

Ref.	Monomer 1 g. moles	Solvent (ml.)	Observations prior to add$^{n.}$ of Mon 2	Monomer 2 g. moles	Solvent (ml.)	rpm.	Time (hrs)	Observations prior to add$^{n.}$ of Mon 3	Monomer 3 g. moles	Solvent (ml.)	Time (hrs)	Observations	Dried Polymer Characteristics and Film Forming Properties
T21	5. 10g. $1.97x10^{-2}$	Tol(30)	Colourless solution	i.4.65g. $2.07x10^{-2}$	Tol(30)	900	1.00	Colourless solution	e.1.972g. $9.86x10^{-4}$	Tol(30)	1.00	Colourless solution	White brittle film forming material
T22	5. 10g. $1.97x10^{-2}$	Tol(30)	Colourless solution	i.4.761g. $2.12x10^{-2}$	Tol(30)	900	1.00	Colourless solution	e.2.957g. $1.48x10^{-3}$	Tol(30)	4.00	Colourless solution	White good film forming material
T23	3. 10g. $1.97x10^{-2}$	Tol(40)	Tan coloured solution	ii.3.648g. $2.17x10^{-2}$	Tol(30)	800	1.00	White suspension	d.1.972g. $1.97x10^{-3}$	Tol(30)	2.00	Cream viscous solution	White tacky film forming material
T24	3. 10g. $1.97x10^{-2}$	Tol(30)	Tan coloured solution	ii.3.471g. $2.07x10^{-2}$	Tol(30)	900	1.00	White suspension	d.0.956g. $9.86x10^{-4}$	Tol(30)	2.00	Cream viscous solution	White good film forming material
T25	3. 10g. $1.97x10^{-2}$	Tol(30)	Tan coloured solution	iii.6.211g $2.96x10^{-2}$	Tol(30)	850	1.00	Tan coloured solution	d.9.858g. $9.86x10^{-3}$	Tol(30)	1.00	Cream viscous solution	White tacky film forming material
T26	3. 10g. $1.97x10^{-2}$	Tol(30)	Tan coloured solution	iii.4.969g $2.37x10^{-2}$	Tol(30)	850	1.00	Tan coloured solution	d.3.943g. $3.94x10^{-3}$	Tol(30)	1.00	Cream viscous solution	White slightly tacky film forming material
T27	3. 10g. $1.97x10^{-2}$	Tol(40)	Tan coloured solution	iii.4.554g $2.17x10^{-2}$	Tol(30)	900	1.00	Tan coloured solution	d.1.972g. $1.97x10^{-3}$	Tol(30)	1.00	Cream viscous solution	White slightly soft film forming material
T28	3. 10g. $1.97x10^{-2}$	Tol(30)	Tan coloured solution	iii.4.347g $2.07x10^{-2}$	Tol(3o)	900	1.00	Tan coloured solution	e.1.972g. $9.86x10^{-4}$	Tol(30)	1.00	Cream viscous solution	White slightly tacky film forming material
T29	3. 10g. $1.97x10^{-2}$	Tol(30)	Tan coloured solution	iii.4.244g $2.02x10^{-2}$	Tol(30)	1000	1.00	Tan coloured solution	e.0.986g. $4.83x10^{-4}$	Tol(30)	1.00	Cream viscous solution	White slightly tacky film forming material
T30	3. 10g. $1.97x10^{-2}$	Tol(30)	Tan coloured solution	iii.4.192g $2.0x10^{-2}$	Tol(30)	950	1.00	Tan colcured solution	e.0.493g. $2.42x10^{-4}$	Tol(30)	1.00	Cream viscous solution	White good film forming material

NOTE All the reactions were carried out at 112°C. and infra red examination of the products showed that there was some unreacted isocyanate present.

TABLE 5.12 Experimental Details for the Synthesis of the Organotin Polyurethanes.

Ref.	Monomer 1 g. moles	Solvent (ml.)	Observations prior to add$^{n.}$ of Mon 2	Monomer 2 g. moles	Solvent (ml.)	rpm.	Time (hrs)	Observations prior to add$^{n.}$ of Mon 3	Monomer 3 g. moles	Solvent (ml.)	Time (hrs)	Observations	Dried Polymer Characteristics and Film Forming Properties
T31	11. 5g. 9.34×10^{-3}	Tol(30)	White suspension	i.2.519g. 1.12×10^{-2}	Tol(30)	950	0.75	Colourless solution	d.1.868g. 1.87×10^{-3}	Tol(30)	1.00	Colourless solution	White brittle film forming material
T32	11. 10g. 1.87×10^{-2}	Tol(30)	White suspension	i.6.295g. 2.80×10^{-2}	Tol(30)	950	0.75	Colourless solution	d.9.342g. 9.34×10^{-3}	Tol(30)	1.00	Colourless solution	White slightly soft film forming material
T33	11. 10g. 1.87×10^{-2}	Tol(30)	White suspension	i.5.605g. 2.49×10^{-2}	Tol(30)	950	0.75	Colourless solution	d.5.605g. 5.61×10^{-3}	Tol(30)	1.00	Colourless solution	White brittle film forming material
T34	11. 10g. 1.87×10^{-2}	Tol(30)	White suspension	i.4.616g. 2.06×10^{-2}	Tol(30)	950	0.75	Colourless solution	e.3.737g. 1.87×10^{-3}	Tol(30)	1.00	Colourless solution	White brittle film forming material
T35	11. 10g. 1.87×10^{-2}	Tol(30)	White suspension	i.5.036g. 2.44×10^{-2}	Tol(30)	950	0.75	Colourless solution	e.7.475g. 3.74×10^{-3}	Tol(30)	1.00	Colourless solution	White slightly soft film forming material
T36	11. 10g. 1.87×10^{-2}	Tol(30)	White suspension	i.5.456g. 2.43×10^{-2}	Tol(30)	950	0.75	Colourless solution	e.11.21g. 5.60×10^{-3}	Tol(30)	1.00	Colourless solution	White slightly soft film forming material
T37	5. 10g. 1.97×10^{-2}	Tol(30)	Colourless solution	i.5.314g. 2.37×10^{-2}	Tol(30)	950	1.00	Colourless solution	d.3.943g. 3.94×10^{-3}	Tol(30)	1.00	Cream viscous solution	White brittle film forming material
T38	5. 10g. 1.97×10^{-2}	Tol(30)	Colourless solution	i.5.757g. 2.56×10^{-2}	Tol(30)	950	1.00	Colourless solution	d.5.915g. 5.91×10^{-3}	Tol(30)	1.00	Cream viscous solution	White good film forming material
T39	5. 10g. 1.97×10^{-2}	Tol(30)	Colourless solution	i.5.314g. 2.37×10^{-2}	Tol(30)	950	1.00	Colourless solution	e.7.886g. 3.84×10^{-3}	Tol(30)	1.00	Cream viscous solution	White slightly soft film forming material
T40	5. 10g. 1.97×10^{-2}	Tol(30)	Colourless solution	i.4.871g. 2.17×10^{-2}	Tol(30)	950	1.00	Colourless solution	e.3.943g. 1.97×10^{-3}	Tol(30)	1.00	Cream viscous solution	White good film forming material

NOTE All the reactions were carried out at 112°C and infra red examination of the products showed that there was some unreacted isocyanate present.

TABLE 5.13 Experimental Details for the Synthesis of the Organotin Polyurethanes.

Ref.	Monomer 1 g. moles	Solvent (ml.)	Observations prior to add$^{n.}$ of Mon 2	Monomer 2 g. moles	Solvent (ml.)	rpm.	Time (hrs)	Observations prior to add$^{n.}$ of Mon 3	Monomer 3 g. moles	Solvent (ml.)	Time (hrs)	Observations	Dried Polymer Characteristics and Film Forming Properties
T41	5. 10g. 1.97x10^{-2}	Tol(30)	Colourless solution	i.4.65g. 2.07x10^{-2}	Tol(30)	900	1.00	Colourless solution	e.1.972g. 8.86x10^{-4}	Tol(30)	1.00	Cream viscous solution	White brittle film forming material
T42	5. 10g. 1.97x10^{-2}	Tol(30)	Colourless solution	iii.4.974g 2.31x10^{-2}	Tol(30)	900	1.00	Colourless solution	d.3.943g. 3.94x10^{-3}	Tol(20)	1.00	Cream viscous solution	White good film forming material
T43	5. 10g. 1.97x10^{-2}	Tol(30)	Colourless solution	iii.4.352g 2.07x10^{-2}	Tol(30)	900	1.00	Colourless solution	d.0.986g. 9.96x10^{-4}	Tol(30)	1.00	Cream coloured solution	White brittle film forming material
T44	6. 10g. 1.61x10^{-2}	Tol(30)	Colourless solution	i.4.352g. 1.94x10^{-2}	Tol(30)	900	1.00	Tan coloured solution	d.3.229g. 3.23x10^{-3}	Tol(20)	1.00	Tan coloured solution	White slightly soft film film forming material
T45	6.10.831g. 1.75x10^{-2}	Tol(3o)	Colourless solution	i.4.321g. 1.93x10^{-2}	Tol(30)	900	1.00	Tan coloured solution	d.1.749g. 1.75x10^{-3}	Tol(30)	3.00	Tan coloured solution	White slightly brittle film forming material
T46	6.11.523g. 1.86x10^{-2}	Tol(30)	Colourless solution	i.4.806g. 2.14x10^{-2}	Tol(30)	900	1.00	Tan coloured solution	d.2.791g. 2.79x10^{-3}	Tol(30)	3.00	Tan coloured solution	White slightly brittle film forming material
T47	6.11.992g. 1.94x10^{-2}	Tol(30)	Colourless solution	i.5.131g. 2.28x10^{-2}	Tol(30)	900	1.00	Tan coloured solution	d.3.41g. 3.41x10^{-3}	Tol(20)	3.00	Tan coloured solution	White slightly brittle film forming material
T48	6.11.206g. 1.81x10^{-2}	Tol(30)	Colourless solution	i.5.08g. 2.26x10^{-2}	Tol(30)	850	1.00	Tan coloured solution	d.4.523g. 4.52x10^{-3}	Tol(20)	3.00	Tan coloured solution	White slightly soft film forming material
T49	6.9.361g. 1.51x10^{-2}	Tol(30)	Colourless solution	i.3.742g. 1.67x10^{-2}	Tol(30)	850	1.00	Tan coloured solution	e.3.629g. 1.81x10^{-3}	Tol(30)	1.00	Tan coloured solution	White slightly tacky film forming material
T50	6.12.352g. 1.99x10^{-2}	Tol(30)	Colourless solution	i.4.703g. 2.09x10^{-2}	Tol(20)	850	1.00	Tan coloured solution	e.1.994g. 9.97x10^{-4}	Tol(30)	2.00	Tan coloured solution	White solid and yellow oil

NOTE All the reactions were carried out at 112°C and infra red examination of the products showed that there was some unreacted isocyanate present.

TABLE 5.14 Experimental Details for the Synthesis of the Organotin Polyurethanes.

Ref.	Monomer 1 g. moles	Solvent (ml.)	Observations prior to add$^{n.}$ of Mon 2	Monomer 2 g. moles	Solvent (ml.)	rpm.	Time (hrs)	Observations prior to add$^{n.}$ of Mon 3	Monomer 3 g. moles	Solvent (ml.)	Time (hrs)	Observations	Dried Polymer Characteristic and Film Forming Properties
T51	6.9.928g. 1.6×10^{-2}	Tol(30)	Colourless solution	i.3.78g. 1.68×10^{-2}	Tol(30)	850	1.00	Tan coloured solution	e. 1.603g. 8.01×10^{-4}	Tol(30)	1.00	Tan coloured solution	White brittle film forming material
T52	6.9.746g. 1.57×10^{-2}	Tol(30)	Colourless solution	i.3.781g. 1.683×10^{-2}	Tol(20)	850	1.00	Tan coloured solution	e.2.203g. 1.1×10^{-3}	Tol(30)	1.00	Tan coloured solution	White brittle film forming material
T53	6.10.227g. 1.65×10^{-2}	Tol(30)	Colourless solution	i.4.024g. 1.79×10^{-2}	Tol(20)	900	1.00	Tan coloured solution	e.2.802g. 1.4×10^{-3}	Tol(30)	1.00	Tan coloured solution	White solid and yellow oil
T54	6.11.105g. 1.79×10^{-2}	Tol(30)	Colourless solution	i.4.371g. 1.94×10^{-2}	Tol(20)	900	1.00	Tan coloured solution	e.3.049g. 1.52×10^{-3}	Tol(30)	1.00	Tan coloured solution	White good film forming material
T55	6.8.17g. 1.32×10^{-2}	Tol(30)	Colourless solution	iii.3.05g. 1.45×10^{-2}	Tol(40)	900	1.00	Tan coloured solution	d.1.319g. 1.32×10^{-3}	Tol(30)	1.00	Tan coloured solution	White slightly soft film forming material
T56	6.8.06g. 1.3×10^{-2}	Tol(30)	Colourless solution	iii.2.96g. 1.41×10^{-2}	Tol(30)	900	1.00	Tan coloured solution	d.1.041g. 1.04×10^{-3}	Tol(30)	1.00	Tan coloured solution	White slightle soft film forming material
T57	6.9.277g. 1.49×10^{-2}	Tol(30)	Colourless solution	iii.3.37g. 1.61×10^{-2}	Tol(30)	900	1.00	Tan coloured solution	d.1.048g. 1.05×10^{-3}	Tol(20)	1.00	Tan coloured solution	White good film forming material
T58	6.8.392g. 1.35×10^{-2}	Tol(30)	Colourless solution	iii.2.99g. 1.42×10^{-2}	Tol(30)	900	1.00	Tan coloured solution	e.1.355g. 6.77×10^{-4}	Tol(20)	1.00	Tan coloured solution	White slightly soft film forming material
T59	6.4.171g. 6.73×10^{-3}	Tol(30)	Colourless solution	iii.1.47g. 7.01×10^{-3}	Tol(20)	900	1.00	Tan coloured solution	e.0.539g. 2.86×10^{-4}	Tol(20)	1.00	Tan coloured solution	White good film forming material

NOTE All the reactions were carried out at 112°C and infra red examination of the products showed that there was some unreacted isocyanate present.

in the key.

The final column in the tables describes the characteristics and film forming properties of the dried polymer. On inspection of this column it can be seen that the observed physical properties can be regulated by varying the concentration of the 'soft segment' in the polymer. The greater the percentage of the polytetramethylene ether glycol used the softer and more pliable is the organotin polyurethane. It was found experimentally that if an organotin polymer was too soft and gave a tacky film, repetition of the polymerisation using a lower mole ratio of the polytetramethylene ether glycol to the organotin polyurethane gave a more rigid material, therefore a technique was now available for synthesis of organotin polymers with the desired film forming properties, all these polymers were readily soluble in toluene.

5.5.2 Preparation of Test Panels

The panels used to test this latest set of organotin polyurethanes were made from Tufnol in order to totally exclude the possibility of the polymers coming into contact with steel; the method of spraying stainless steel panels with an aluminium based primer being abandoned as it was observed that in the previous testing routine the primer was degraded. The test panels were prepared as described previously and dried for two days in a vacuum oven (0.1mm Hg), their surface profiles and weights being recorded before testing. The panels were spun in sea water for several days after which time they were removed, washed and dried to constant weight in a vacuum oven (0.1mm Hg), their weights and surface profiles again being recorded. The test routine was continued for several weeks and although monitoring by weighing proved to be unreliable due to the slightly absorbent nature of the Tufnol panels, useful information on the ability of the films to withstand the physical stresses and the chemical environment was obtained and they appeared to be promising in this respect, the results being shown in Tables 5.15 and 5.16. The surface profile measurements were again of little use owing to the previously discussed problems of this technique and to the scratching of the soft films during measurement. Owing to the problems encountered in the use of Tufnol panels it was decided to revert back to the use of stainless steel panels, the contamination caused by these panels being deemed as very small compared to that inherent in the sea water.

The test panels were prepared as previously described, the Teracol organotin polymers used were either new materials or previously tested materials that had shown the desired properties, the results being shown in Table 5.17.

The results, after prolonged testing, were very disappointing in that all the polymers became very brittle, therefore being of little use for the incorporation into antifouling paints. The polymer T51 showed good film forming properties on both Tufnol and stainless steel panels up to 23 or 28 days, Tables 5.16 and 5.17 respectively. The surface of the polymer appeared to acquire a hard powdery surface during testing which could be scraped off the film whereas the bulk polymer remained a relatively tough material. Examination of the polymer after 70 days' testing on a stainless steel panel revealed that it had become brittle and lost its film forming properties, this presumably being due to total hydrolysis of film. Infra-red analysis of polymer samples removed after 23 days and 70 days yielded no

TABLE 5.15 Results of the Sea Water Trials of the Organotin Polyurethanes.

NUMBER OF DAYS TEST		14	21	57
PANEL NUMBER	POLYMER (WEIGHT)	TOTAL WEIGHT OF POLYMER LOST FROM PANEL		
1	T36 (0.0544)	0.0119	0.0105	0.0509^{G}
2	T38 (0.0505)	0.0013	0.0012	0.0064^{G}
3	T39 (0.1234)	0.1213	0.0952	0.1062^{B}
4	T18 (0.1464)	0.1354	0.1201	0.1464^{B}
5	T32 (0.0432)	0.0964	0.0835	0.0355^{D}
6	T33 (0.1047)	0.2270	0.2006	0.2386^{D}
7	T34 (0.1401)	0.1536	0.1490	0.2107^{B}
8	T26 (0.2566)	0.0350	0.0177	0.0600^{D}
9	T27 (0.1607)	0.0036	-0.0230	0.0178^{D}
10	A6 (0.1530)	0.0059	0.0074	0.0059^{G}
11	A1 (0.1140)	0.0024	-0.0446	-0.0447^{G}
12	T35 (0.1204)	-0.1488	-0.1853	-0.0498^{R}
13	T16 (0.1195)	0.0162	-0.0122	0.0498^{R}
14	A2 (0.0855)	0.0110	-0.0282	-0.0323^{G}
15	T29 (0.0866)	0.2812	0.2583	0.2971^{G}

NOTE The panels were coated with polymers prepared by the author and referenced as given in the Synthesis Tables cotained in this Chapter. Superscripts used; B, Brittle film; D, Detached film; G, Good film; R, the film has run.

TABLE 5.16 Results of the Sea Water Trials of the Organotin Polyurethanes.

NUMBER OF DAYS TEST		16	23
PANEL NUMBER	POLYMER (WEIGHT)	TOTAL WEIGHT OF POLYMER LOST FROM PANEL	
1	T55 (0.1064)	0.0567^{G}	-0.0542
2	T56 (0.1077)	0.1649^{R}	0.0622
3	T56 (0.1104)	0.0596^{G}	-0.0573
4	T54 (0.0944)	0.0604^{G}	-0.0430
5	T52 (0.1083)	0.0713^{R}	-0.0200
6	T51 (0.0891)	0.0630^{G}	0.0578
7	T49 (0.0554)	0.0577^{R}	-0.0374
8	T48 (0.1789)	0.0859^{R}	0.0049
9	T47 (0.0368)	0.0652^{G}	-0.0616
10	T46 (0.0467)	0.0577^{G}	0.0267
11	T45 (0.0819)	0.0915^{G}	-0.0750
12	T44 (0.1295)	-0.0880^{R}	0.0381
13	T6 (0.0766)	0.2787^{R}	-0.0366
14	T42 (0.1256)	0.1581^{D}	0.0752
15	T6 (0.0483)	0.0597^{G}	-0.0586

NOTE The panels were coated with polymers prepared by the author and referenced as given in the Synthesis Tables contained in this Chapter.
Superscripts used; D, Detached film; G, Good film; R, the film has run.

TABLE 5.17 Results of the Sea Water Trials of the Organotin Polyurethanes.

NUMBER OF DAYS TEST		14	28	70
PANEL NUMBER	POLYMER (WEIGHT)	TOTAL WEIGHT OF POLYMER LOST FROM PANEL		
1	T6 (0.0958)	0.0259^{D}	0.0517	0.0766
2	T29 (0.0446)	0.0241^{D}	0.0321	0.0433
3	T33 (0.1353)	0.0758^{R}	0.1000	0.1286
4	T35 (0.0596)	0.0595^{D}		
5	T36 (0.0972)	0.0758^{D}		
6	T38 (0.1838)	0.0607^{R}	0.0790	0.0919
7	T45 (0.1576)	0.0016^{G}	0.0079	0.0205
8	T46 (0.1366)	0.0027^{G}	0.0041	0.0123
9	T47 (0.1231)	0.0012^{G}	0.0023	0.0086
10	T51 (0.1852)	-0.0037^{G}	0.0093	0.0148
11	T55 (0.1396)	0.0070^{G}	0.0112	0.0321
12	T56 (0.1647)	0.1367^{R}	0.1383	0.1400
13	T54 (0.0883)	-0.0026	0.0018	0.0044
14	T16 (0.0619)	0.0328^{D}		
15	T58 (0.1756)	0.0439^{G}	0.0492	0.0615

NOTE The panels were coated with polymers prepared by the author and referenced as given in the Synthesis Tables contained in this Chapter.

Superscripts used; D, Detached film; G, Good film; R, the film has run.

conclusive proof for hydrolysis occurring, static tests on the Teracol 1000 analogue, T44, (Table 5.13) and subsequent attenuated total reflection (A.T.R.) infrared analysis showed some slight differences before and after immersion in sea water. Using A.T.R. however it is very difficult to obtain data exclusively about the surface of the polymers owing to the fact that this technique samples quite a thick surface layer (150nm.) and so gives a spectrum which is the sum of bulk plus surface material.

The Teracol, organotin polyurethanes do appear to be the best diorganotin polymers produced during this research, however their ability to withstand prolonged immersion is poor, and this shortcoming rules them out as candidates for use in antifouling coatings. Formulation of these resins into antifouling paints using only pigments and extenders would prove unsatisfactory as the hydrolysis of the resin is too rapid. If they were considered for use a second resin would be required to retain the film's integrity. The work involved in carrying out these formulations would be considerable as would the task of continuing the synthesis of new diorganotin resins. At this stage of the investigation it was decided to terminate the project.

5.6 Conclusions

The objectives of this work were the synthesis of low toxicity polymeric resins with tin dicarboxylate units in the polymer backbone. The sea water degradation of such materials was to be investigated and compared with that of those resins which contain tin carboxylate units in the side chains and which are currently used in ablative antifouling coatings. A further objective was to try to gain a better understanding of the polishing process observed with ablative coatings.

Many resins were prepared and it was established that by suitable structural modification it was possible to produce film forming resins which could withstand both the physical and chemical environments likely to be encountered by real marine coatings. The development of rapid testing procedures was in part successful but the resins prepared by the author and examined by these tests were generally greatly inferior to those already in commercial use. Why this should have been the case is not completely clear but some speculative explanations may be advanced.

The current hypothesis for the mechanism of polishing and ablation proposes that the resin used, a copolymer of methyl methacrylate with tributyl tin methacrylate, is hydrolysed *in situ* with the loss of the toxic tributyl tin hydroxide moiety and the slow solvation and removal of the ionic polymer surface thus exposing a new surface. This process is compounded of a large number of steps at a molecular level and small variations in a formulated paint can have a great effect on the overall ablation rate. The tin containing resins' part in this process requires that initially the tin carboxylate unit is hydrolysed, at this stage the polymer remains intact and the process of its solvation and eventual removal will depend on an array of factors which include, the molecular weight of the resin; the extent of entanglement; the rate of penetration of water into the surface of the film; the rate at which the other components dissolve; and possibly several other factors. For example it is known that increasing the proportion of tributyl tin carboxylate units increases the polishing rate as does the addition of a very soluble extender;

whereas the presence of significant concentrations of iron ions inhibit ablation, this usually being attributed to the resin becoming insoluble due to crosslinking occurring via iron carboxylate units.

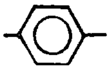
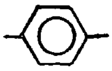
In the case of the resins with tin dicarboxylate units in the polymer backbone we have a different situation, and all the resins examined in this work failed to show uniform ablation; generally the films were disrupted and underwent mechanical failure. Those films which survived testing for reasonable periods were heavily loaded with aliphatic ether sequences and were relatively hydrophobic. As a qualitative conclusion it could be suggested that hydrolysis is probably very rapid and that in the systems looked at here we have two broad types:

(a) Those having a high concentration of backbone tin dicarboxylate units which are fairly polar and susceptible to rapid hydrolysis and penetration by water. These are effectively broken into low molecular weight fragments and consequently there is a rapid degradation of the film.

(b) Those having a relatively low concentration of backbone tin dicarboxylate containing units and a high proportion of hydrophobic material. These materials do not undergo hydrolysis as readily as the resins of type (a) owing to the lack of tin carboxylate units and the slow penetration of the water into the film, therefore they survive the test conditions far longer. Even with these polymers eventually catastrophic failure is the rule rather than the slow uniform polishing which was hoped for.

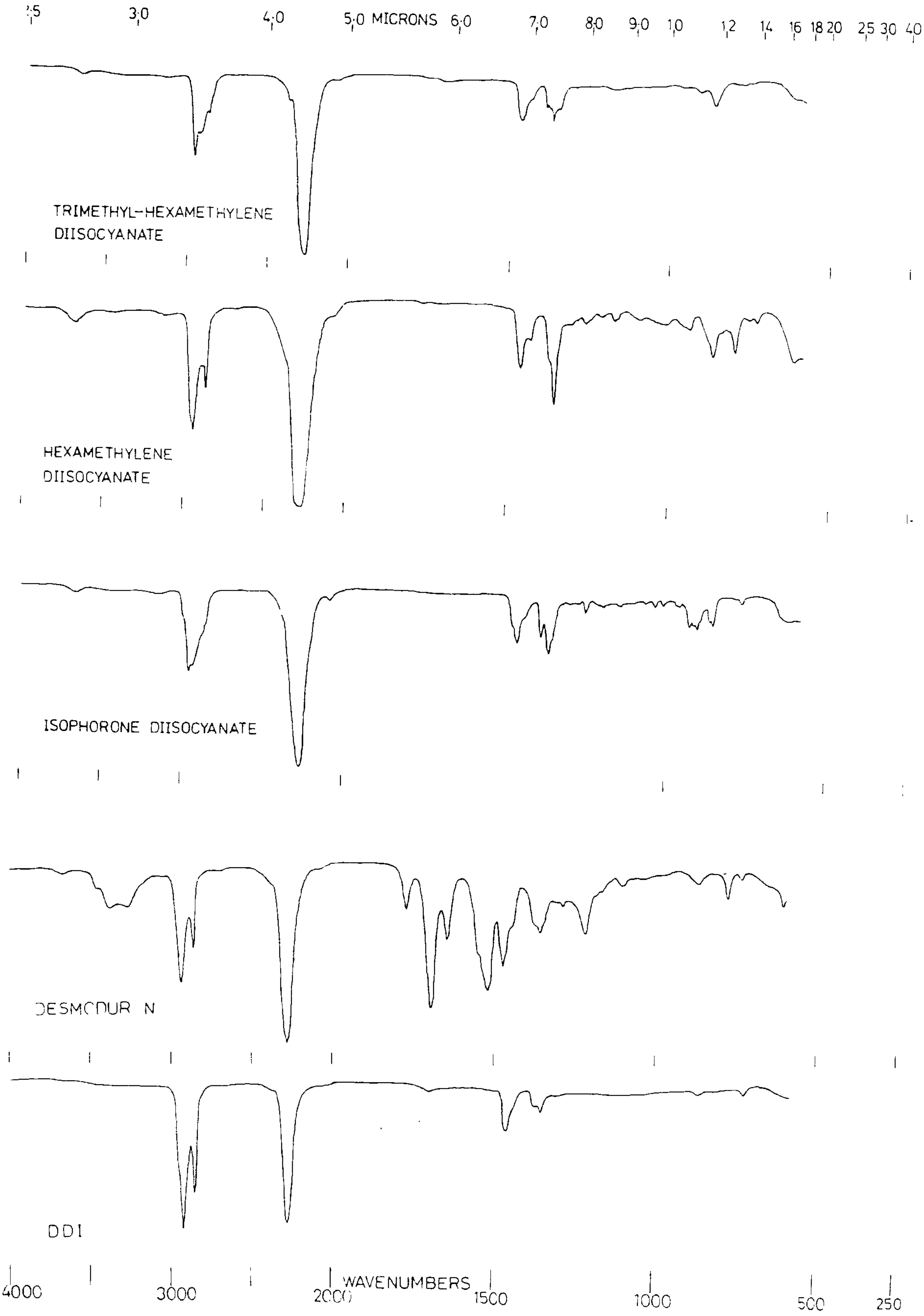
It would therefore seem that this type of approach is unlikely to yield useful resins for ablative marine antifouling coatings, on the other hand the mechanism by which these multi-variable systems act is clearly very complex and it would be foolish to make sweeping dogmatic generalisations.

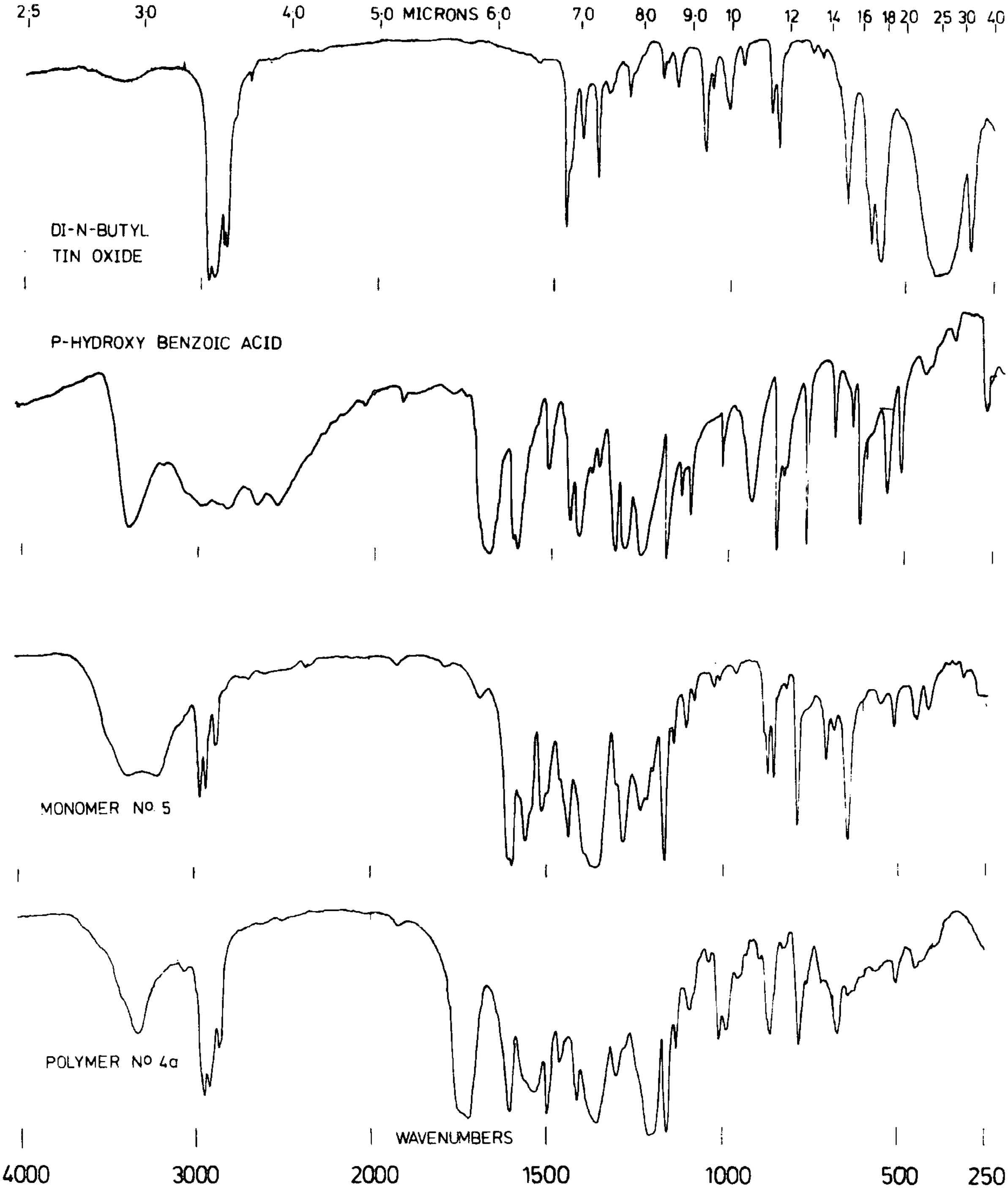
At the conclusion of an investigation it is usual to consider further avenues for research in the area. It would seem that an effective ablative and polishing coating requires a resin which becomes solvated and is removed at a slow rate, while allowing the remaining film to retain its physical integrity. The history of these tin containing resins is that the hydrolysis was intended to produce a toxin which would prevent settlement of fouling organisms, the valuable and novel polishing effect was an example of serendipity. If a non toxic polishing antifouling is required then it may well be that the expensive tin containing polymers are not really essential and what is needed is simply a resin which dissolves at an appropriate rate while at the same time being able to maintain its film integrity.

If the author was continuing to work on this problem the investigations of sea water solubility of polymers as a function of polar side group concentration (-OH,-COOH, OH, COOH, etc.), backbone type and molecular weight would probably be the first project undertaken.

APPENDIX ONE

INFRA RED SPECTRA


2·5
3·0
4·0
5·0 MICRONS
6·0
7·0
8·0
9·0
10
12
14
16
18
20
25
30
40
TRIMETHYL-HEXAMETHYLENE DIISOCYANATE
HEXAMETHYLENE DIISOCYANATE
ISOPHORONE DIISOCYANATE
DESMODUR N
DDI
4000
3000
2000
WAVENUMBERS
1500
1000
500
250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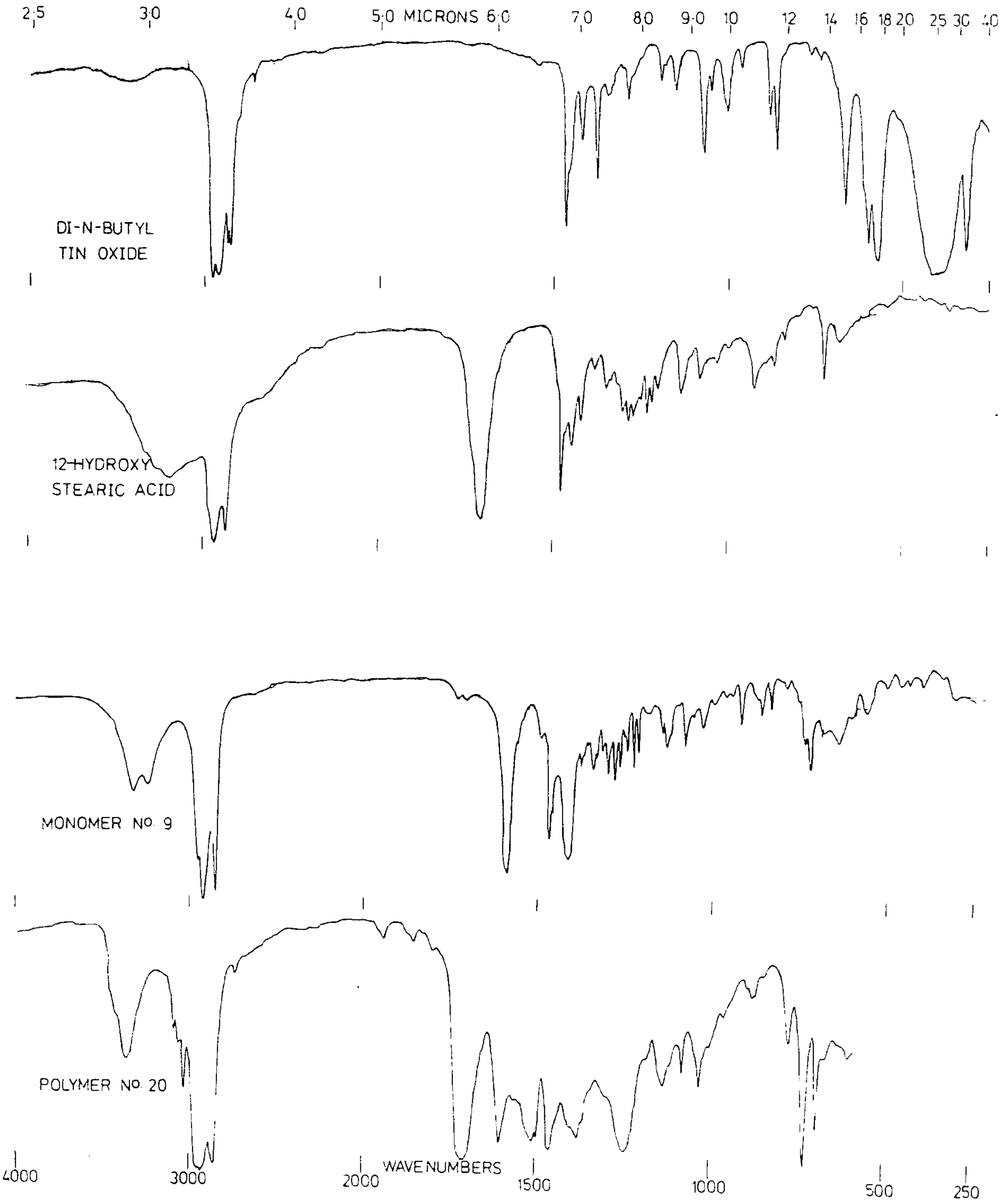
3.0
4.0
5.0 MICRONS 6.0
7.0
8.0
9.0
10
12
14
16
18
20
25
30
40
DI-N-BUTYL TIN OXIDE
P-HYDROXY BENZOIC ACID
MONOMER No 5
POLYMER No 4a
WAVENUMBERS
4000
3000
2000
1500
1000
500
250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3.0
4.0
5.0 MICRONS 6.0
7.0
8.0
9.0
10
12
14
16
18
20
25
30
40
DI-N-BUTYL
TIN OXIDE
12-HYDROXY
STEARIC ACID
MONOMER No. 9
POLYMER No. 20
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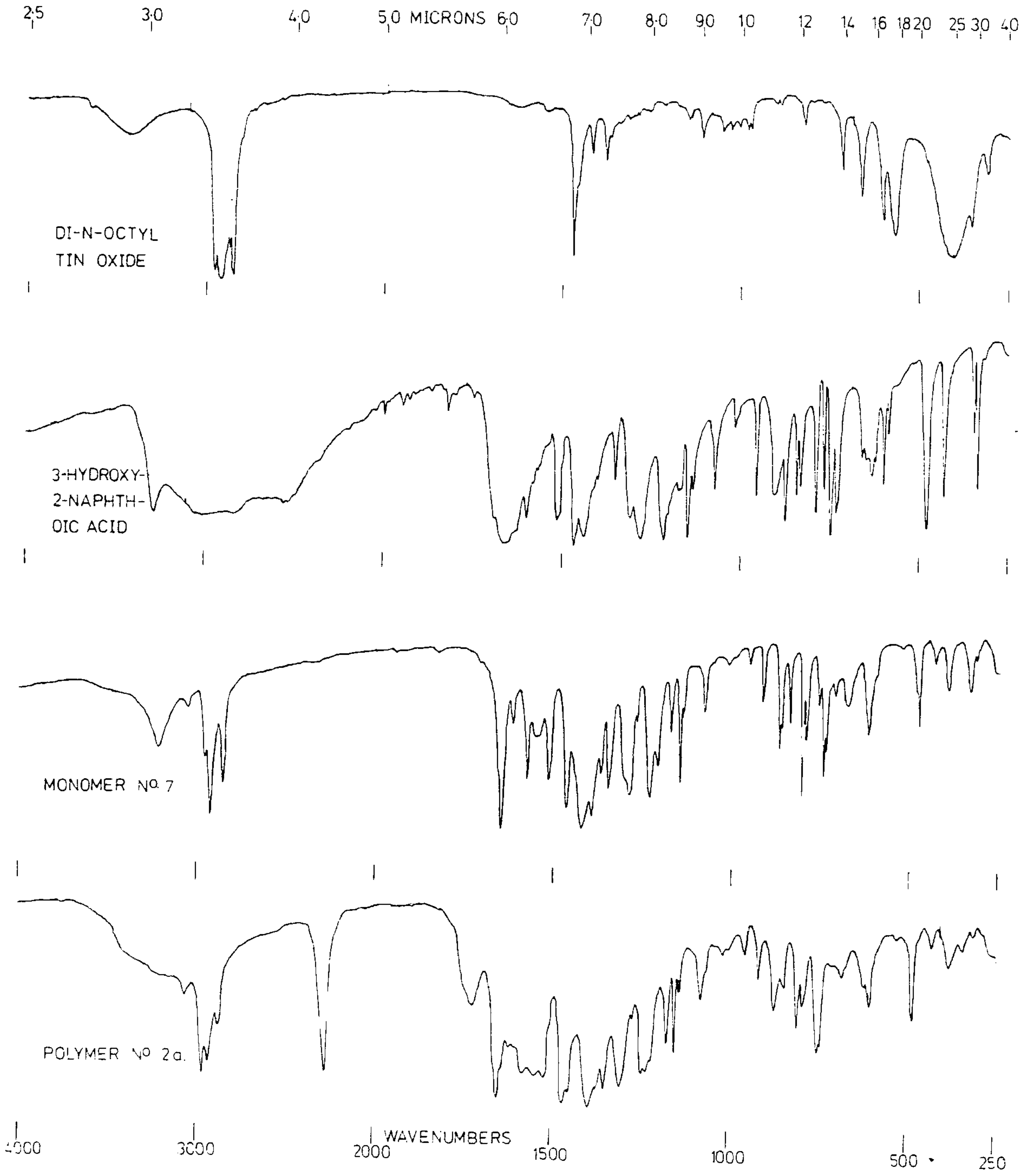
2000
WAVENUMBERS
1500
1000
500
250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3.0
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5.0 MICRONS 6.0
7.0
8.0
9.0
10
12
14
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18
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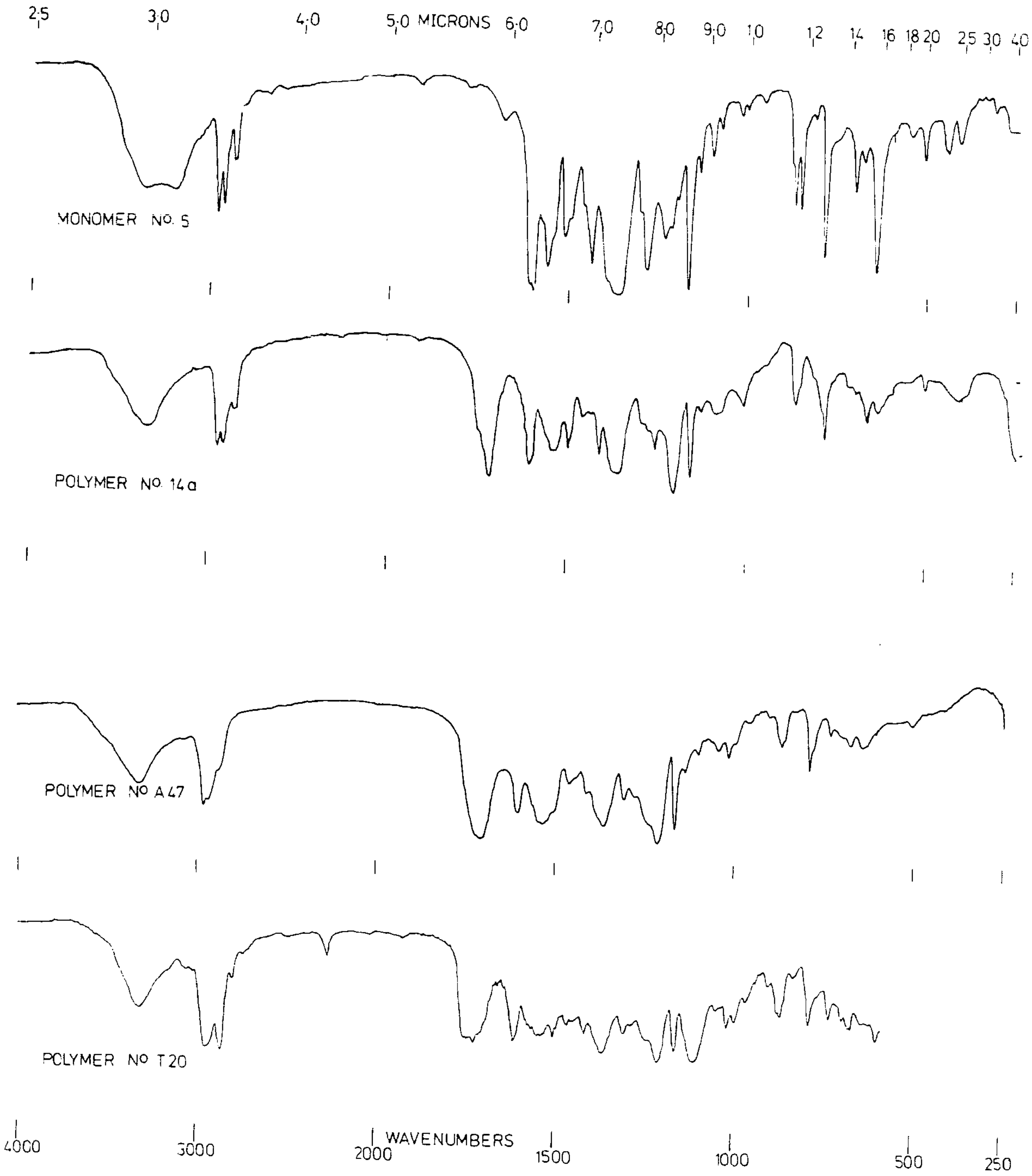
25
30
40
DI-N-OCTYL TIN OXIDE
3-HYDROXY-2-NAPHTHOIC ACID
MONOMER No. 7
POLYMER No 2a.
4000
3000
2000
WAVENUMBERS
1500
1000
500
250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3·0
4·0
5·0 MICRONS
6·0
7·0
8·0
9·0
10
12
14
16
18
20
25
30
40
MONOMER No. 5
POLYMER No. 14a
POLYMER No A 47
POLYMER No T 20
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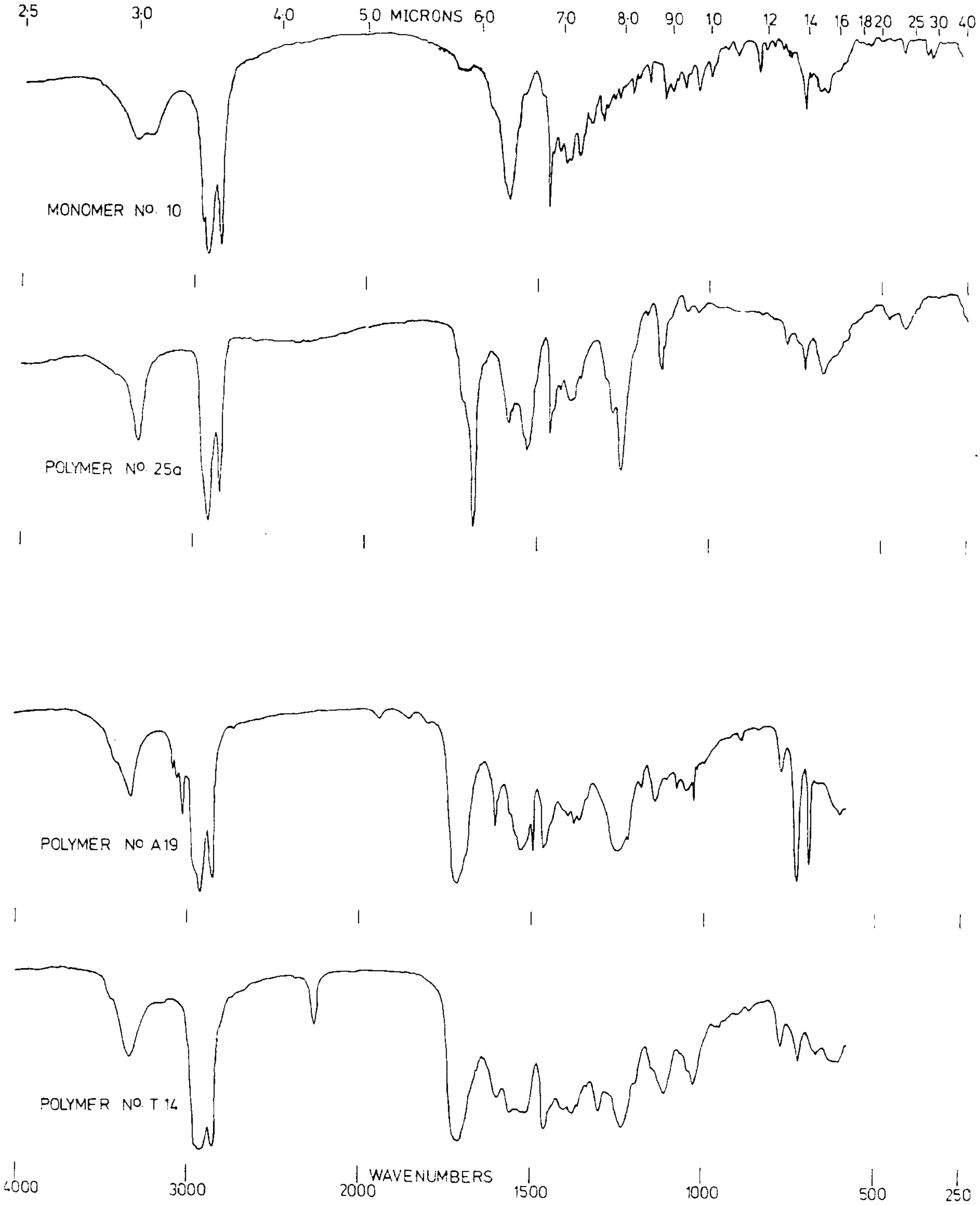
2000
WAVENUMBERS
1500
1000
500
250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3.0
4.0
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8.0
9.0
10
12
14
16
18
20
25
30
40
MONOMER No. 10
POLYMER No. 25a
POLYMER No A19
POLYMER No. T 14
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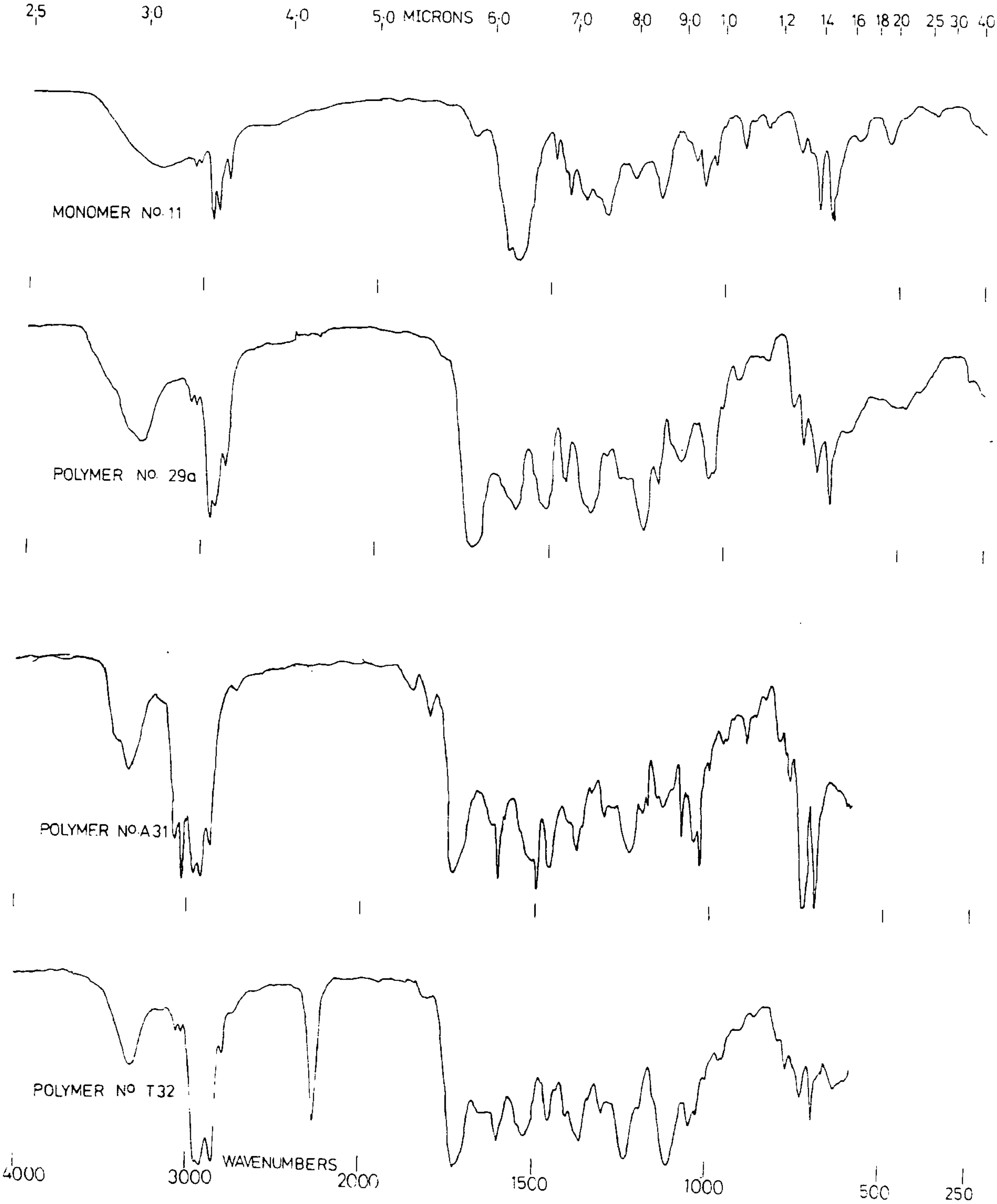
3000
2000
WAVENUMBERS
1500
1000
500
250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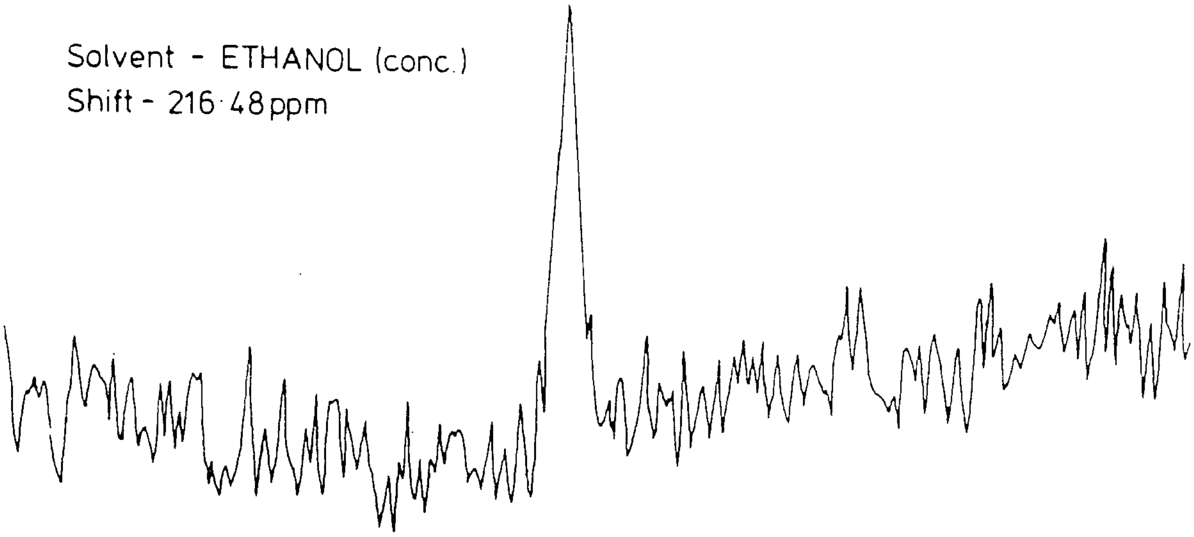
3.0
4.0
5.0 MICRONS
6.0
7.0
8.0
9.0
10
12
14
16
18
20
25
30
40
MONOMER No. 11
POLYMER No. 29a
POLYMER No. A31
POLYMER No T32
4000
3000
WAVENUMBERS
2000
1500
1000
500
250

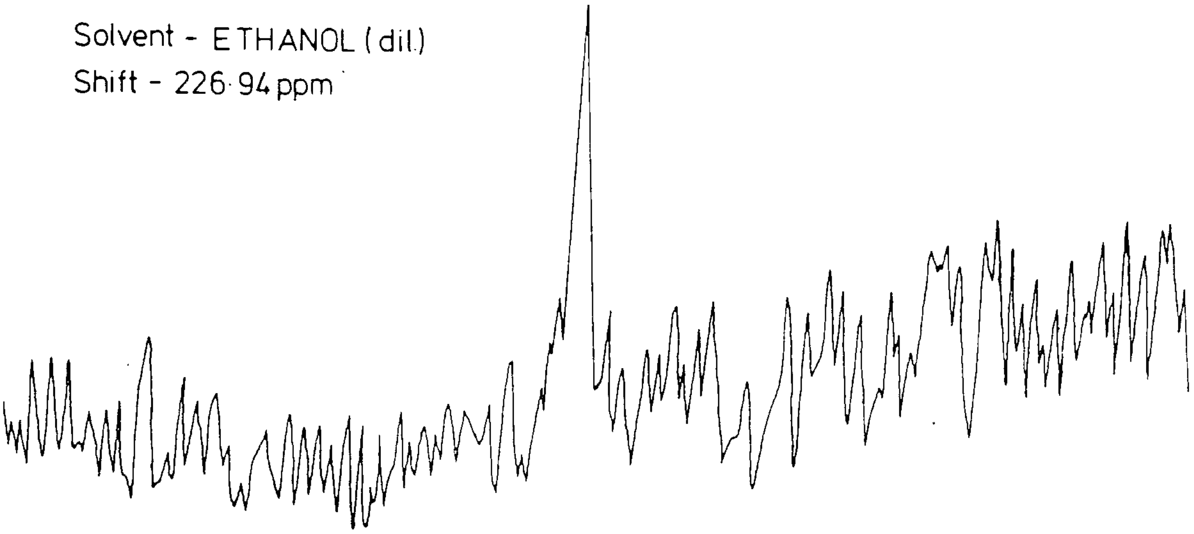
APPENDIX TWO

^{119}Sn N.M.R. SPECTRA

Di-n-butyl bis(3-hydroxy-2-naphthoate) tin



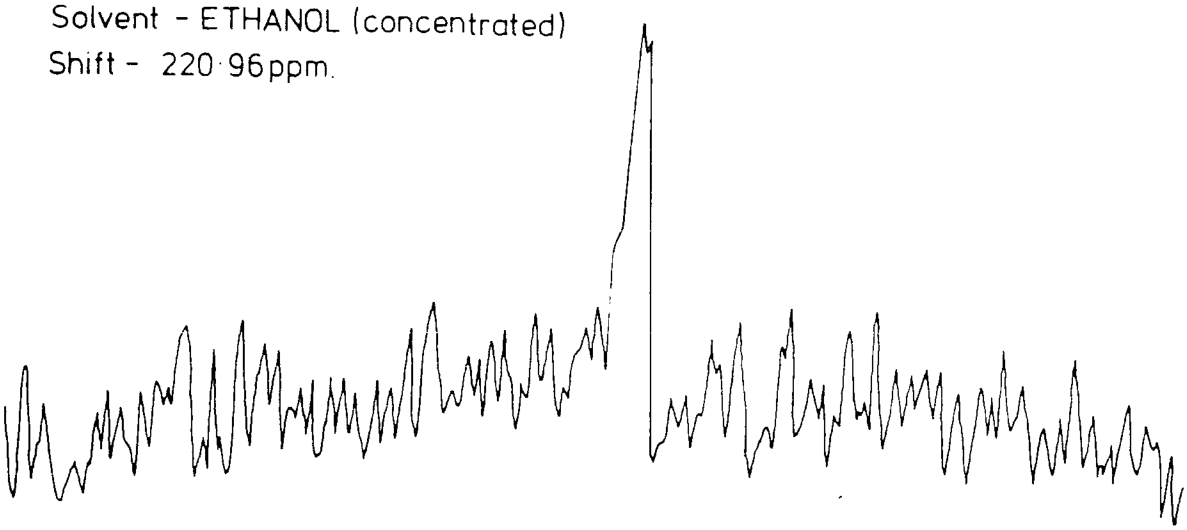
Solvent - ETHANOL (conc.)
Shift - 216·48 ppm



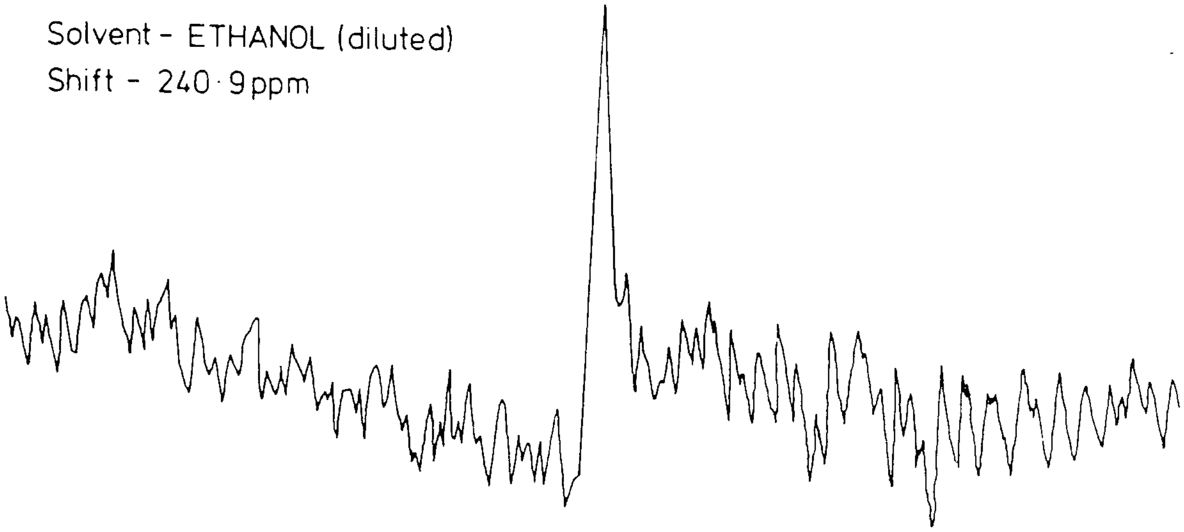
Solvent - ETHANOL (dil.)
Shift - 226·94 ppm

Di-n-butyl bis(o-hydroxy benzoate) tin

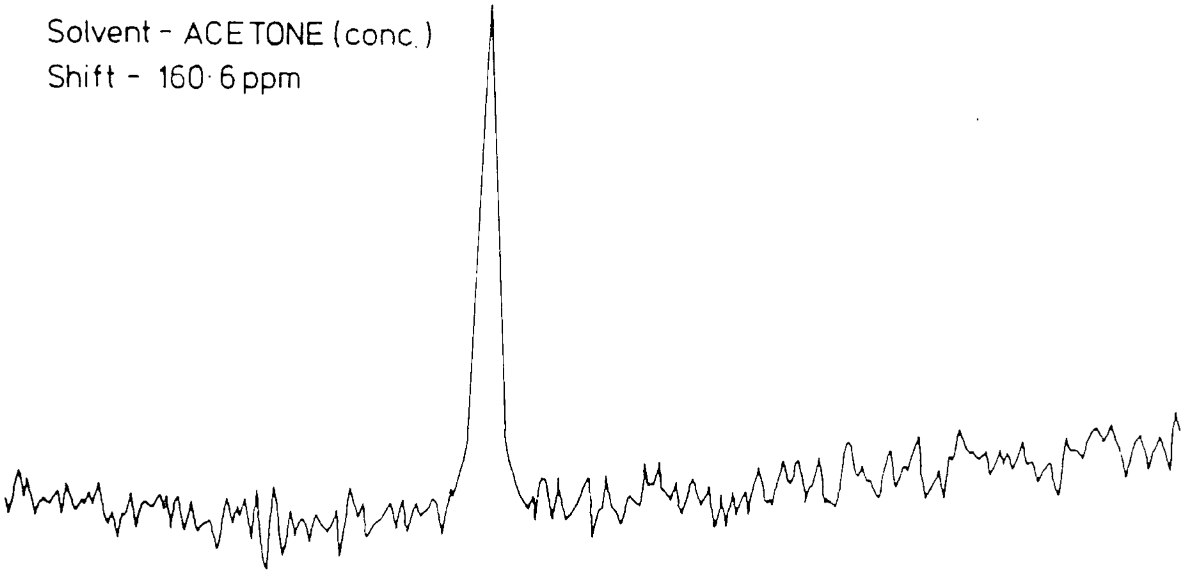
Solvent - ETHANOL (concentrated)
Shift - 220·96ppm.



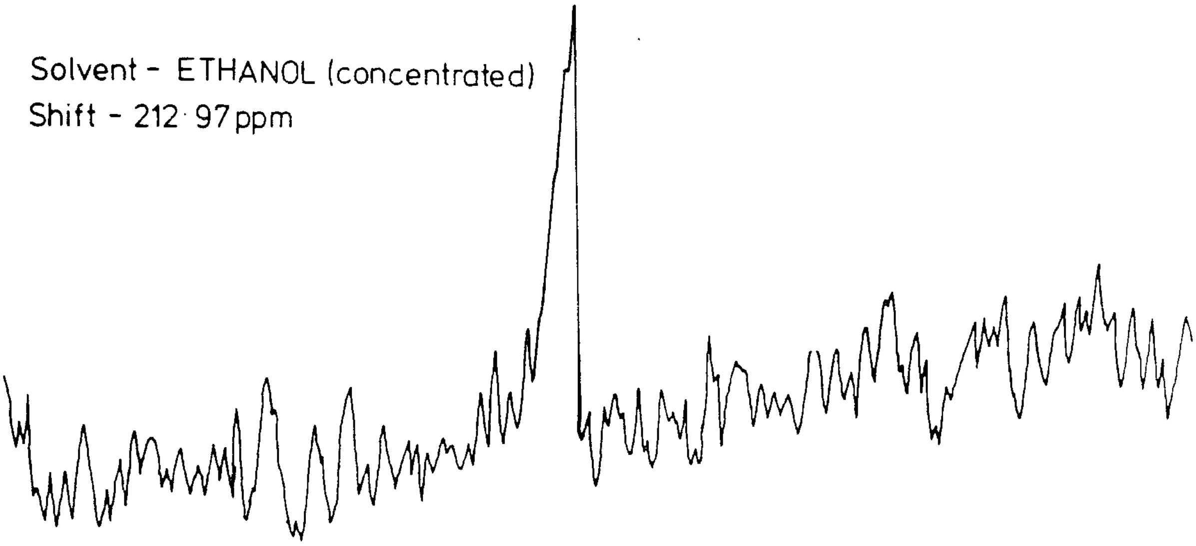
Solvent - ETHANOL (diluted)
Shift - 240·9ppm



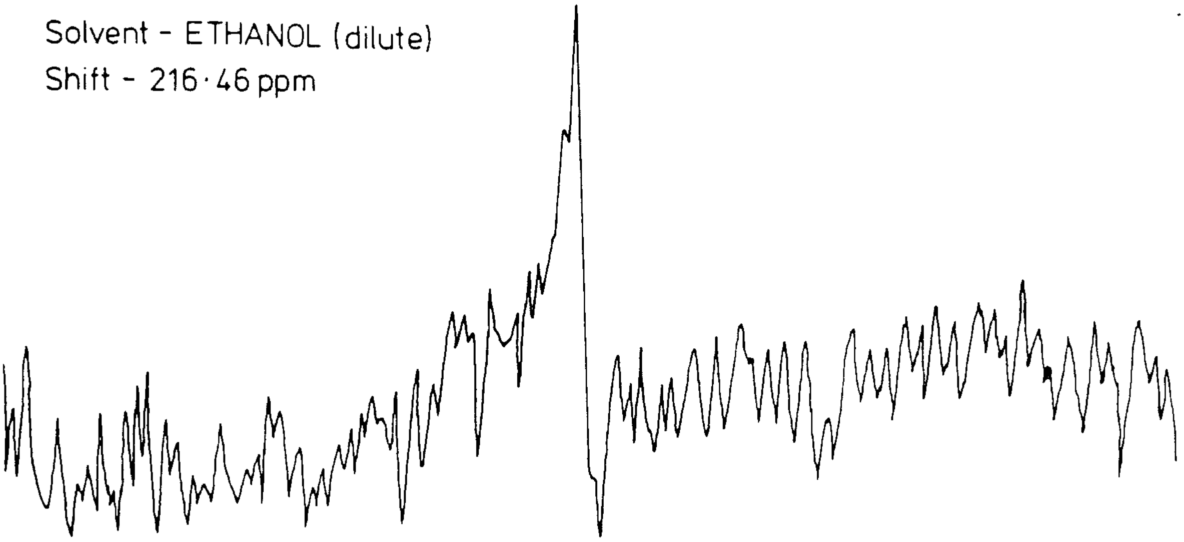
Solvent - ACETONE (conc.)
Shift - 160·6ppm



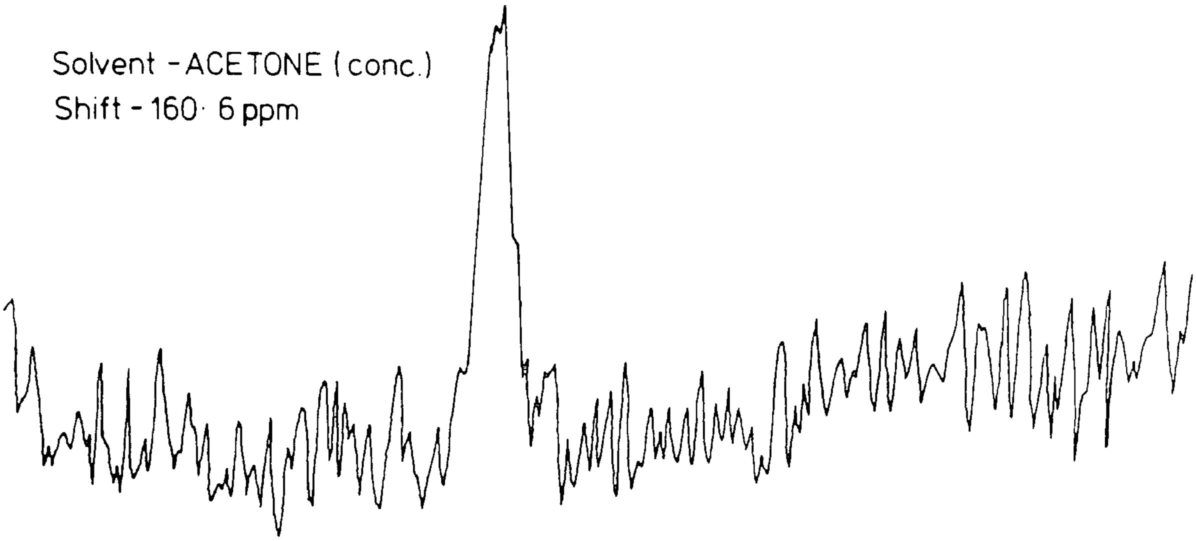
Di-n-octyl bis(3-hydroxy-2-naphthoate) tin



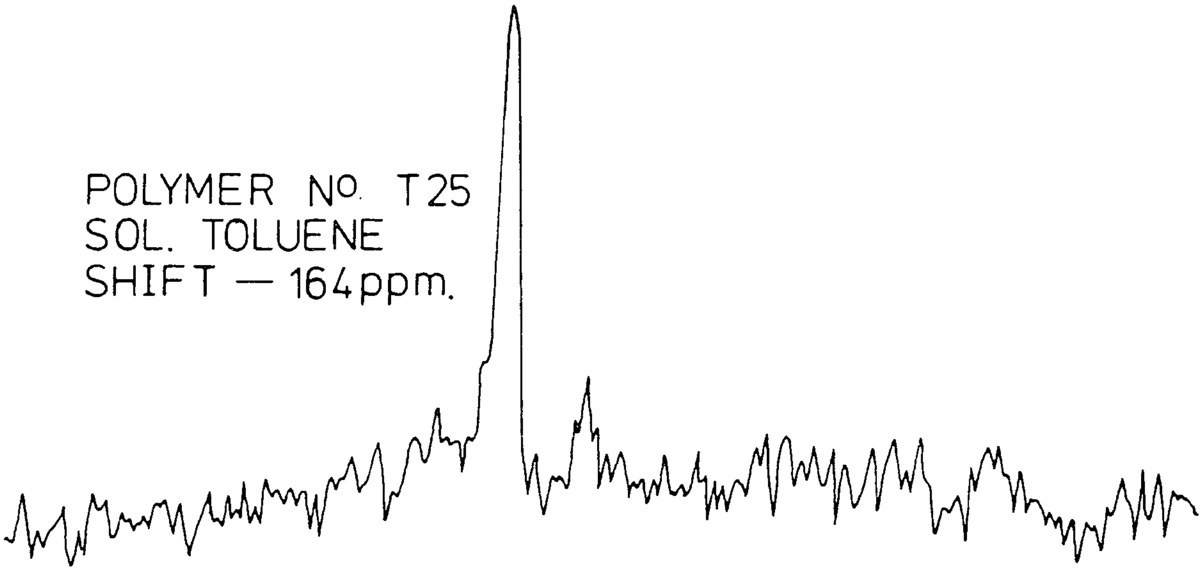
Solvent - ETHANOL (concentrated)
Shift - 212·97 ppm



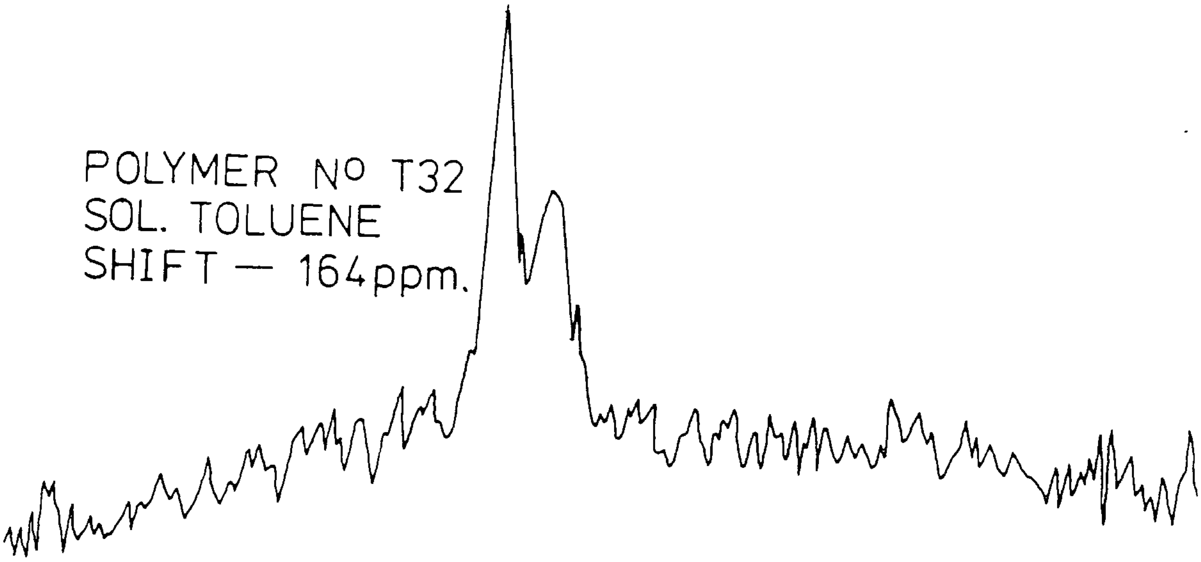
Solvent - ETHANOL (dilute)
Shift - 216·46 ppm



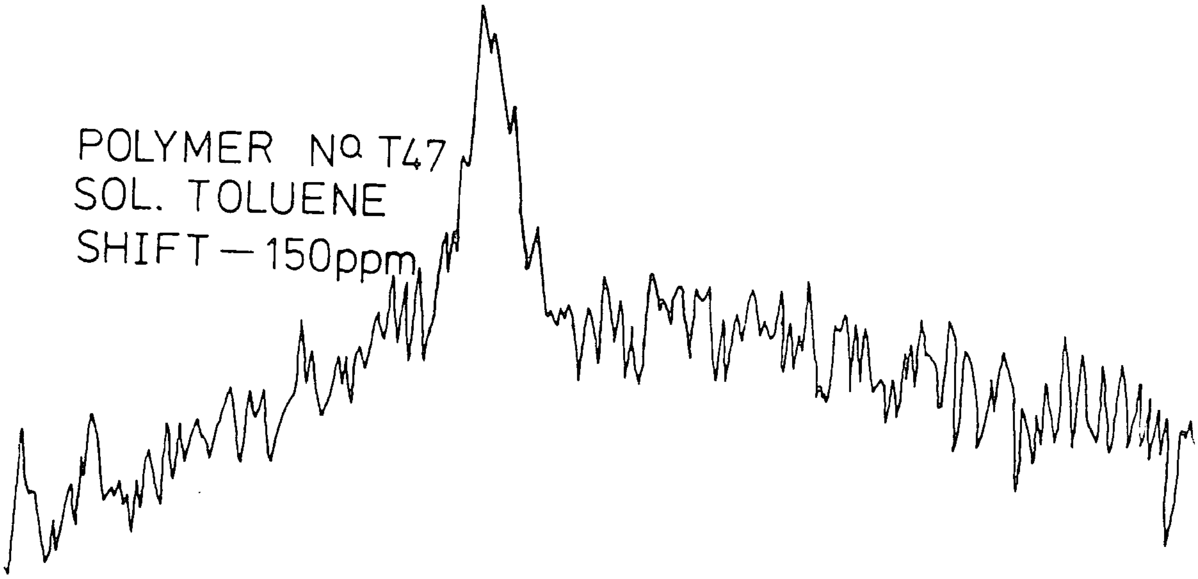
Solvent - ACETONE (conc.)
Shift - 160·6 ppm



POLYMER No T25
SOL. TOLUENE
SHIFT — 164ppm.



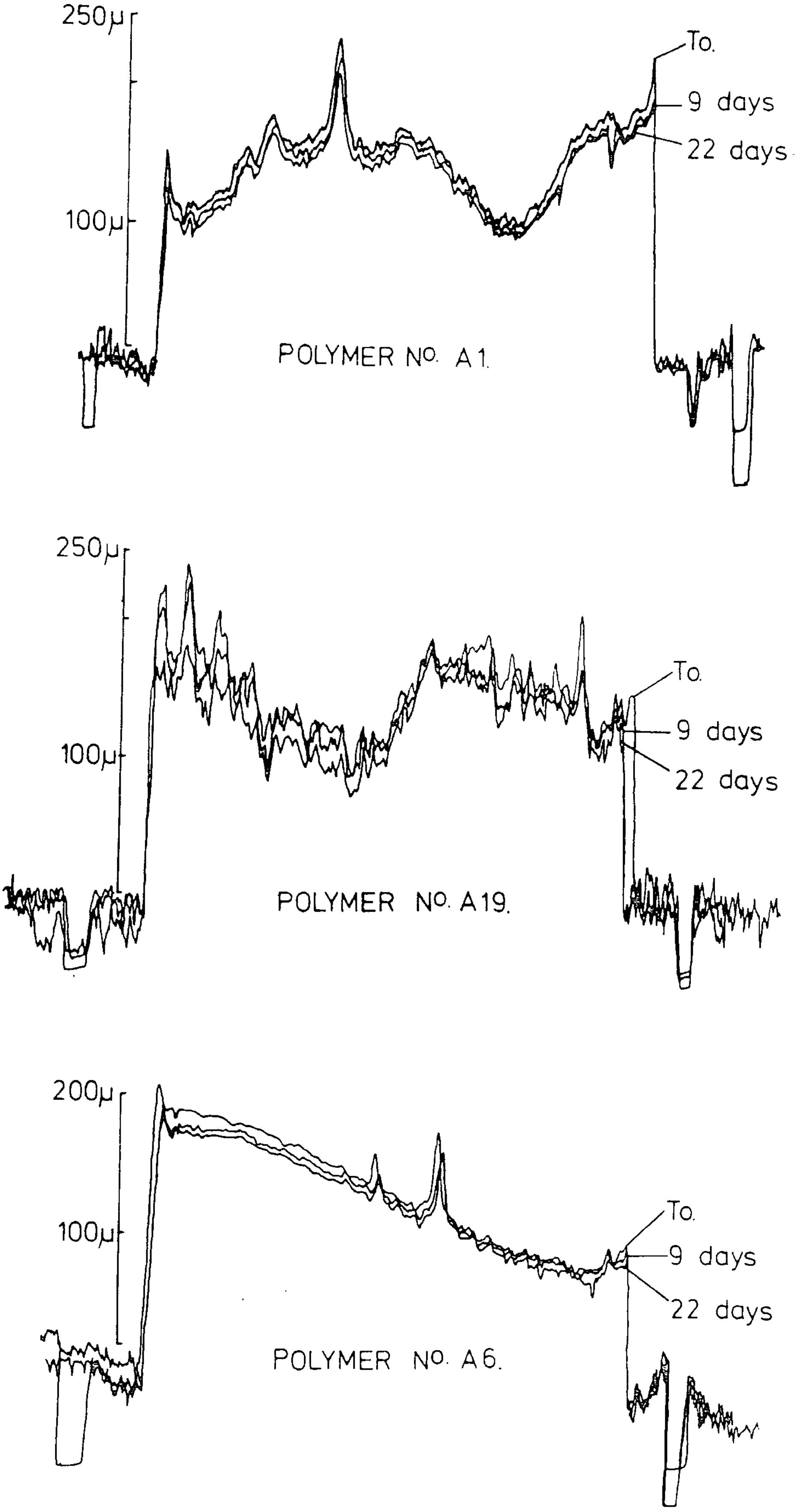
POLYMER No T32
SOL. TOLUENE
SHIFT — 164ppm.



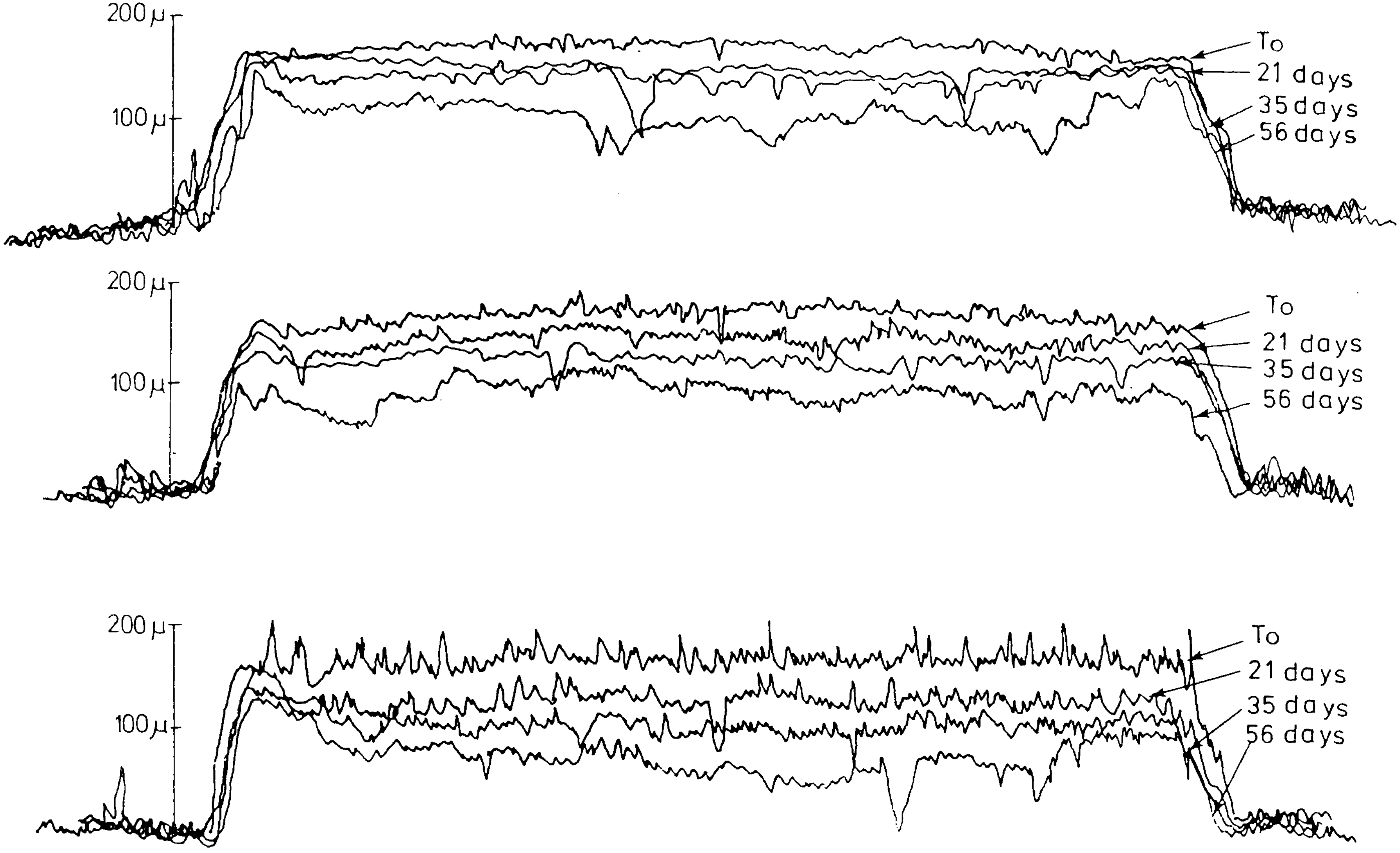
POLYMER No T47
SOL. TOLUENE
SHIFT — 150ppm.

APPENDIX THREE

SURFACE ROUGHNESS PROFILES



Surface Roughness Measurements on Polymers Prepared by the Author.



Surface Roughness Measurements on Polishing Paint Systems.

APPENDIX FOUR

OUTLINE OF WORK CARRIED OUT AT CAMREX R. & D. LTD.

1. Introduction

The work reported in this thesis was supported by an S.R.C. CASE award, these grants are intended to provide the student with experience of industry as well as a training in research methods. The objectives of the author during the periods of work at Camrex R.& D. Ltd. were:

(i) to obtain an understanding of the paint industry,

and (ii) to formulate the di-n-alkyl bis(hydroxy carboxylate)tin monomers.

The work carried out is described below.

Paint Formulation and Analysis using Commercial Resins

The paints formulated in this section were conventional continuous contact antifouling and were based on a chlorinated rubber resin (Alloprene R.10), the toxin used was I.C.I.'s A.24 (2-amino-3 chloro 1-4 naphthalenedione).

1.1 Formulation A

			Weight (g)	S.G.	Volume
1.	Alloprene R.10		36	1.6	22.5
2.	Special Pitch No.5		80	1.151	69.5
3.	Copper I Oxide		749	5.79	129.36
4.	Tricresyl Phosphate		54	1.157	46.67
5.	Rosin		34	1.1	30.9
6.	I.C.I.'s A.24		47	1.52	30.9
7.	Bentone 34	Bentone	7.5	1.8	41.66
		Solvesso	42.5	0.875	48.57
8.	Xylene		50.0)	0.864	120
9.	Xylene		54.0)		

Volume solids = 70%

S.G. = 2.15

Experimental

A stock solution of Alloprene R.10 (a low molecular weight chlorinated rubber) in xylene was prepared by mixing Alloprene R.10 (400g.) with xylene (600g). Xylene (item 8) was weighed into a ball mill (an earthenware pot used to grind the solid constituents of the paints to a required particle size, together with a plasticiser, tricresyl phosphate (item 4). Finely ground rosin (item 5) was added followed by the special pitch No. 5 (item 2); finally copper I oxide (item 3) and Bentone 34 (item 7), (a structuring agent used to give the paint its supporting framework) were added and the mixture ground overnight using a ball mill. The grind was tested using the grind gauge (a simple device used to find the maximum particle size in a paint sample) and found to be under 60 µm, which was acceptable. Alloprene R.10/xylene stock solution (items 1 and 9) was added and the mixture milled for a further fifteen minutes, then sieved to remove any large unground particles. The viscosity of the sieved paint was measured (4.2 poise at 20°C) using a cone and plate viscometer, and then a test panel was painted to check that the paint had film forming properties.

Analysis

(i) Determination of total solids by the Microscope Slide Technique

This involves placing a small paint sample on a pre-weighed microscope slide, the weight of 'wet' paint applied was determined by difference. The slide was then warmed in an oven (at *ca.* 50°C) and dried to constant weight, at which time no solvent remains in the paint so the total solids may be calculated. This analysis was carried out in duplicate and it was found that the two determinations were in good agreement (within 2%) with an average percentage total solids in the paint of 77%.

(ii) Determination of the ash content

This method is used to determine the amount of inorganic non volatile material in the paint.

A clean dry crucible and lid were weighed and then approximately one gram of paint was accurately weighed into the crucible. This was warmed in an oven to remove the solvent and then heated to red heat with a bunsen burner until no further loss of weight occurred. The determination was carried out in duplicate and it was found that the agreement was again good (within 2%) with an average ash content of 57%.

(iii) Specific Gravity (S.G.)

The determination of the specific gravity of the paint was carried out using a weighing cup, the volume of this being accurately known, by finding the weight of paint contained in the cup the specific gravity can be found, this being 2.27 for the formulation A.

1.2 Formulation B

		Weight (g)	S.G.	Volume
1.	Xylene	100		
2.	Rosin	68	1.1	61.8
3.	Tricrysyl Phosphate	36	1.157	31.1
4.	Copper I Oxide	755	5.79	130.4
5.	I.C.I.'s A.24	96	1.52	63.2
6.	VAGH	43	1.34	32.1
7.	Xylene	43		
8.	M.I.B.K.	86	0.8022	107.2
9.	Xylene	30		
Total Xylene 1 + 7 + 9		173	0.865	200

Volume solids = 51%

S.G. = 2.0

Experimental

VAGH (item 6), a copolymer of vinyl chloride, vinyl alcohol and vinyl acetate, was added to xylene (item 7) with slow stirring, when the addition was complete the M.I.B.K., methyl isobutyl ketone (item 8) was added.

Rosin (item 2) was dissolved in xylene (item 1) followed by the addition of: tricrysyl phosphate (item 3), copper I oxide (item 4) and I.C.I.'s A.24 (item 5), the mixture being continually stirred. The sample was too viscous to ball mill and so more xylene (item 9) was added and the mixture milled overnight, the resulting particle size was less than 60 μm. The prepared solution of VAGH was added, and the paint was milled again for fifteen minutes, then sieved. The viscosity was adjusted to 4.6 poise by the addition of M.I.B.K. (item 8).

Analysis

(i) Determination of Total Solids

This was carried out as previously described and found to be 72%.

(ii) Determination of Ash Content

The ash content was determined to be 53% by the above method.

(iii) Specific Gravity

This was found to be 2.0.

A third formulation was prepared, this was based on an organometallic resin, OMP 2, the resultant paint belonged to the class of self-polishing coatings.

1.3 Formulation of Anti-Fouling 54E

			Weight (g)	S.G.	Volume
1.	OMP 2		152.5	1.18	129.2
2.	Copper I Oxide		305	5.79	52.6
3.	Captam		49	2.00	24.5
4.	$CaSO_4\frac{1}{2}H_2O$		26	2.32	11.2
5.	T.B.T.O.		11	1.17	9.4
6.	Sylodex		10	2.60	3.8
7.	Thixatrol		5	1.20	4.2
8.	Bentone 34	Bentone	4.4	1.80	2.4
		Solvesso	24.6	0.875	28.2
9.	Xylene (total)		239	0.864	276

Volume solids = 44%

S.G. = 1.5

Experimental

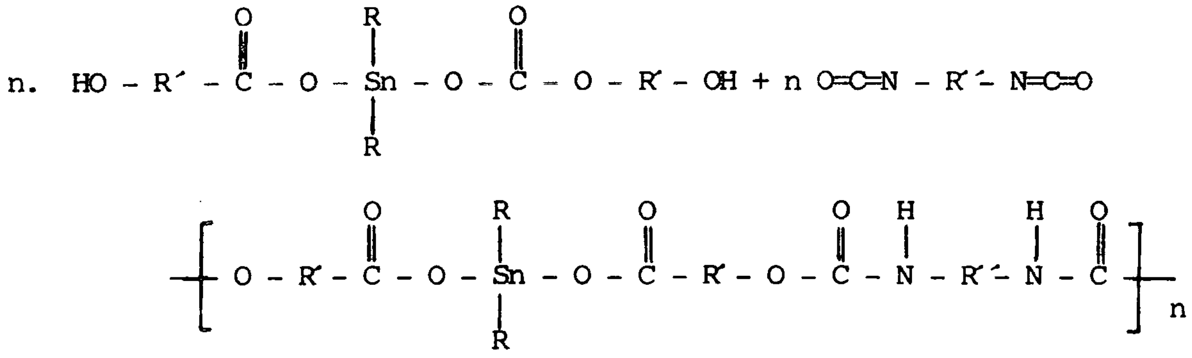
The method employed in this preparation involved the use of a high speed disperser, the components being added in the above order. The temperature of the mixture was allowed to rise above 55°C so that the thixatropic properties of the paint changed. It was transferred to a ball mill and milled overnight with xylene (130g. of item 9). The viscosity was then adjusted to 12.5 poise by the addition of xylene (item 9).

Analysis

The solids content of the paint was 47%; the ash content 31%, and the specific gravity 1.14, these being determined using the previously described methods.

2. Formulations using Di-n-alkyl bis(hydroxy carboxylate)tin monomers

The difference between the previous three paints and the paints to be formulated on the di-n-alkyl bis(hydroxy carboxylate)tin monomers is that whereas the above paints are single component (pack) paints and harden by the evaporation of solvent, the paints formulated with the di-n-alkyl bis(hydroxy carboxylate)tin monomers should harden (cure) by the reaction with another monomer (diisocyanate) according to the process depicted below.



$$n.\ HO-R'-\overset{O}{\overset{\|}{C}}-O-\underset{R}{\underset{|}{\overset{R}{\overset{|}{Sn}}}}-O-\overset{O}{\overset{\|}{C}}-O-R'-OH+n\,O{=}C{=}N-R''-N{=}C{=}O$$

$$\left[O-R'-\overset{O}{\overset{\|}{C}}-O-\underset{R}{\underset{|}{\overset{R}{\overset{|}{Sn}}}}-O-\overset{O}{\overset{\|}{C}}-R'-O-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-R''-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}\right]_n$$

The di-n-alkyl bis(hydroxy carboxylate)tin is formulated into the paint and the diisocyanate is added when the paint is required, thus this type of paint is known as a two-pack paint.

It was decided to examine formulations including two different pigmentations for each monomer and four diisocyanates. The pigmentations included anhydrous calcium sulphate which can adsorb water, the removal of water from the paint is important since it reacts with the diisocyanate forming carbon dioxide, which causes foaming, and the resulting amine group can react further with other isocyanate groups forming a highly cross-linked polymer.

The two pigmentations used were:

(a) Based on anhydrous calcium sulphate,

and (b) Based on zinc oxide with a small amount of anhydrous calcium sulphate.

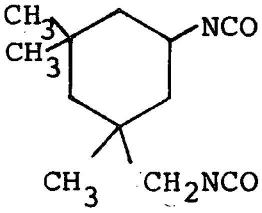
In both pigmentations a thixatrope was used, aerosil which gives structure to the paint.

The four curing agents (diisocyanates) selected were chosen, because they could be obtained as pure samples and also because they provided a wide range of structural types. The four diisocyanates used were:

(1) Desmodur N.75 and N. 62.5. Desmodur N is a polyfunctional aliphatic isocyanate supplied as a 'neat liquid', or a 75% solution in ethyl glycol acetate : xylene (1:1). This solution N.75 and a more dilute solution N.62.5 were used in this work, the solutions were light tan coloured liquids with NCO equivalent weights of 255 and 315 respectively.

(2) Desmodur L.67 and L.60.5. These are solutions of a polyfunctional isocyanate in ethyl glycol acetate : xylene (1:1), the L.67 (67% w/w) solution was supplied and the L.60.5 was prepared by addition of solvent. The NCO equivalent weights are 362 and 401 respectively.

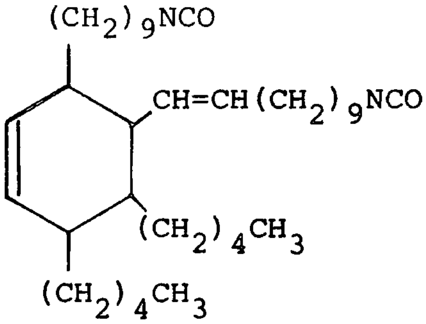
(3) IPDI. This is a diisocyanate of the structure:



Isophorone diisocyanate
(3 isocyanatomethyl-3,5,5-trimethyl-cyclo hexyl isocyanate)

It is supplied as a 'neat' liquid and has an NCO equivalent weight of 111.2, and

(4) DDI. This is a liquid aliphatic diisocyanate with the structure



It is supplied as a 'neat' liquid and has the NCO equivalent weight of 300.

The criteria for the inclusion of these di-n-alkyl bis(hydroxy carboxylate)tin monomers into paint systems are listed below:

(i) The di-n-alkyl bis(hydroxy carboxylate)tin compounds must be soluble, preferably very soluble as limiting the amount of solvent keeps the paint price down and also allows a large amount of solids to be applied in one coat.

(ii) The viscosity must be such as to allow the paint to be workable, in practice this means in the range 5-10 poise.

(iii) The solvent used must be acceptable; i.e. no health hazard, a high flash point, and non-reactive with isocyanates.

Two paint formulations were initially used to prepare paints based on di-n-alkyl bis(hydroxy carboxylate)tin compounds, these being shown below:

(a) With $CaSO_4\frac{1}{2}H_2O$

Tin Monomer	200g
$CaSO_4\frac{1}{2}H_2O$	47g
Aerosil 200	3.0g
Xylene	As required

(b) With ZnO and $CaSO_4\frac{1}{2}H_2O$

Tin Monomer	200g
ZnO	93g
$CaSO_4\frac{1}{2}H_2O$	4.8g
Aerosil 200	3.0g
Xylene	As required

2.1 Experimental Procedure

The monomer was dissolved in the required amount of xylene, the other compounds were added in the order stated above, the viscosity being adjusted by the addition of xylene and the formulation was ball milled until the particle size was less than 60 μm. The paints prepared by this method are shown below

Monomer	Pigmentation	Wt. of xylene (ml.)	Volume Solids	S.G.
Dioctyl bis (o-hydroxy benzoate) tin	1	30	84%	1.25
	2	51	76%	1.42
Dioctyl bis (o-hydroxy benzoate) tin	1	135	56%	1.07
	2 (no aerosil)	155	53%	1.19

Formulations using other monomers were unsuccessful due to the low solubility of the monomers in xylene and other organic solvents, therefore the monomers were dissolved at elevated temperatures and partially cured with the isocynates, this method is commonly used by resin manufacturers to solubilise low solubility materials.

The partial curing was achieved by the addition of the diisocyanate to the monomer and some solvent. The monomer was dissolved in hot solvent and the diisocyanate added initially as pre-weighed aliquots but this gave successive 5% increments in the extent of cure and the procedure was changed to dropwise addition which allowed a much more sensitive control of the extent of cure.

The partial curing of the monomer is shown in the following tables together with the paint formulations used.

Monomer (g.)	Solvent (g.)	Isocyanate Weight % Cure	Observations	Pigmentation used
1. 30g.	MEK. 17g.	N62.5. 4.75g. 12%	Colourless solution	a.
1. 30g.	MEK. 18g.	N62.5. 4.75g. 12%	Colourless solution	b.
1. 30g.	MEK..16g.	IPDI. 1.5g. 11.4%	Colourless solution	a
3. 30g.	MEK. 15g.	IPDI. 3.175g. 24%	Colourless solution	a
3. 30g.	MEK/Sol. 10/10g.	N75. 7.76g. 25%	Crystalline material	Not formulated
3. 30g.	MEK/Tol. 18/2g.	N62.5. 4.25g. 11.4%	Colourless solution	b.
3. 30g.	MIBK. 20g.	L67. 17g. 40%	Crystalline material	Not formulated
4. 40g.	Xyl/MIBK. 11/10g.	N75. 7.5g. 22%	Colourless solution	a.
4. 40g.	Xyl/MIBK. 12/10g.	L67. 9.5g. 20%	Colourless solution	a.
4. 10g.	Xyl/MIBK. 15g.	IPDI. 7g. 50%	Crystalline material	Not formulated
5. 30g.	MIBK. 15g.	N62.5. 0.5g. 1.4%	Light brown solution	a.
5. 30g.	MIBK. 22g.	N62.5. 0.25g. 0.67%	Light brown solution	b.
5. 30g.	MIBK. 14g.	L67. 4.2g. 10%	Decomposed	Not formulated

Monomer (g.)	Solvent (g.)	Isocyanate Weight % Cure	Observations	Pigmentation used
5. 30g.	MEK. 14g.	L60.5. 1g. 2.1%	Colourless solution	a.
5. 30g.	MEK. 14g.	L60.5. 1g. 2.1%	Colourless solution	b.
5. 30g.	MEK. 12g.	IPDI. 0.25g. 1.9%	Colourless solution	a.
5. 30g.	MEK. 12g.	IPDI. 0.25g. 1.9%	Colourless solution.	b.
7. 30g.	MEK/Tol 10/10g.	L60.5. 2g. 5%	Yellow crystalline material	Not formulated
7. 30g.	MEK. 15g.	N62.5. 9.375g. 30%	Yellow solution	a.
7. 30g.	MEK. 18g.	N62.5. 9.25g. 29.7%	Yellow solution	b.
7. 30g.	MEK/Tol. 10/10g.	IPDI. 1.35g. 12%	Yellow crystalline material	Not formulated
8. 30g.	MIBK. 15g.	L67. 6g. 19%	Yellow solution	a.
8. 30g.	MIBK. 8g.	N75. 6.6g. 30%	Yellow solution	a.
8. 30g.	MIBK. 13g.	N75. 6.6g. 30%	Yellow solution	b.
8. 30g.	Oxy. 8g.	IPDI. 0.45g. 4.8%	Yellow solution	a.
8. 30g.	Oxy. 12g.	IPDI. 1.29g. 13%	Yellow solution	b.
8. 30g.	MIBK. 8g.	DDI. 1.08g. 4.3%	Yellow solution	a.

Monomer (g.)	Solvent (g.)	Isocyanate Weight % Cure	Observations	Pigmentation used
9. 30g.	MEK. 15g.	N62.5. 17.5g. 77%	White insoluble material	Not formulated
10. 30g.	Xyl/MIBK. 10/10g.	DDI. 9.5g. 50%	White insoluble material	Not formulated
10. 30g.	Xyl. 20g.	L67. 10.17g. 40%	White insoluble material	Not formulated
10. 30g.	MIBK. 10g.	N62.5. 2.28g. 12%	White insoluble material	Not Formulated
11. 30g.	MEK. 15g.	N62.5. 3g. 8.5%	White insoluble material	Not formulated
11. 30g.	Sol/MIBK. 10/10g.	IPDI. 2.5g. 20%	White insoluble material	Not formulated
11. 30g.	MEK/Sol.	L60.5. 3.03g. 7%	White insoluble material	Not formulated
12. 30g.	Sol. 15g.	IPDI. 0.86g. 25%	White insoluble material	Not formulated

3. Testing of the Pigmented Coatings

The partially cured pigmented monomers were cured to 100% by mixing with the required amount if isocyanate. The paint was then coated on to a test disc using a 100μm drawn-down cube, as described in Chapter Three. The dried films were examined and then tested for polishing using the Camrex Spinning Disc procedure described in Chapter Three. The observations and results are recorded in the following tables.

Monomer	Isocyanate	Pigmentation	Volume solids (Viscosity)	Observations after Disc Trials
1.	N75.	a.	70% 10 Poise	No polishing observed
1.	N75.	b.	72% Gelled	No polishing observed
1.	IPDI.	a.	75% 0.4 Poise	After 13 days the film had disappeared
2.	N75.*	a.	84% 2 Poise	No polishing observed
2.	L67.*	a.	79% Gelled	No polishing observed
2.	IPDI.*	a.	91% 1.2 Poise	No polishing observed
2.	N75.*	b.	86% Gelled	No polishing observed
2.	167.*	b.	78% Gelled	No polishing observed
2.	IPDI.*	b.	88% Gelled	No polishing observed
3.	IPDI.	a.	71% 10 Poise	After 23 days the film had disappeared

* These formulations were not partially cured

Monomer	Isocyanate	Pigmentation	Volume solids (Viscosity)	Observations after Disc Trials
4.	N75.	a.	71% 10 Poise	No polishing observed
4.	L67	a.	68% 10 Poise	No polishing observed
5.	N62.5.	a.	68% 5.4 Poise	No Polishing observed
5.	N62.5.	b.	70% 1.5 Poise	No polishing observed
5.	L67.	b.	64% 2.4 Poise	No polishing observed
5.	IPDI.	a.	80% 1.8 Poise	After 40 days the film had disappeared
5.	IPDI.	b.	74% 1.2 Poise	No polishing observed
6.	N75.*	a.	68% 3.8 Poise	No polishing observed
6.	L67.*	a.	65% 8.8 Poise	No polishing observed
6.	IPDI.*	a.	70% 3.6 Poise	No polishing observed
6.	N75.*	b.	68% 3.2 Poise	No polishing observed
6.	L67.*	b.	54.5% 7.8 Poise	No polishing observed
6.	IPDI.*	b.	70% 3.5 Poise	No polishing observed

* These formulations were not partially cured.

Monomer	Isocyanate	Pigmentation	Volume solids (Viscosity)	Observations after Disc Trials
7.	N75.	a.	68% 10 Poise	No polishing observed
7.	N75.	b.	70% Gelled	No polishing observed
8.	N75.	a.	80% 10 Poise	No polishing observed
8.	N75.	b.	77% 9.5 Poise	No polishing observed
8.	IPDI.	a.	85% 2.4 Poise	No polishing observed
8.	IPDI.	b.	83% 2.5 Poise	Film thinned after prolonged testing
8.	L67.	a.	71% 4.4 Poise	Film thinned after prolonged testing
8.	L67.	b.	75% 5.1 Poise	Film thinned after prolonged testing

3.1 Conclusions of the Disc Trials

It can be seen from the results that the only coatings to show polishing are those in which the diisocyanate, IPDI, was used, at the time it seemed likely this was probably due to the fact that a linear, non cross-linked polyurethane was formed, thus enabling hydrolysis of the Sn-O bond and the solvation of the remaining structure to occur. With the polyfunctional isocyanates the initial hydrolysis may occur at the surface but the solvation may be hindered by the size and crosslinked structure and so polishing was not observed.

These initial results achieved in the first year of the project were moderately encouraging. A more detailed analysis of this type of system is discussed in the main body of the thesis, unfortunately this initial promise was not fulfilled in practice.

APPENDIX FIVE

RESEARCH COLLOQUIA, SEMINARS AND LECTURES

The Board of Studies in Chemistry requires that each postgraduate research thesis contains an appendix listing:

(a) all research colloquia, research seminars and lectures arranged by the Department of Chemistry during the period of the writer's residence as a postgraduate student;

(b) all research conferences attended and papers read out by the writer of the thesis, during the period when the research for the thesis was carried out.

1. Research Colloquia, Seminars and Lectures
University of Durham Chemistry Colloquia

Academic Year 1977-1978

19 October - Dr. B. Heyn (Univ. of Jena, D.D.R.), "Sigma-organo molybdenum complexes as alkene polymerisation catalysts".

27 October - Professor R.A. Filler (Illlinois Institute of Technology, U.S.A.), "Reactions of organic compounds with xenon fluorides".

2 November - Dr. N. Boden (Univ. of Leeds), "N.m.r. spin-echo experiments for studying structure and dynamical properties of materials containing interacting spin-Y_2 pairs".

9 November - Dr. A.R. Butler (Univ. of St. Andrews), "Why I lost faith in linear-free energy relationships".

7 December - Dr. P.A. Madden (Univ. of Cambridge), "Raman studies of molecular motions in liquids".

14 December - Dr. R.O. Gould (Univ. of Edinburgh), "Crystallography to the rescue in ruthenium chemistry".

25 January - Dr. G. Richards (Univ. of Oxford), "Quantum pharmacology".

1 February - Professor K.J. Ivin (Queens Univ., Belfast), "The olefin metathesis reaction, mechanism of ring opening polymerisation of cycloalkenes".

3 February - Dr. A. Hartog (Free Univ., Amsterdam), "Surprising recent studies in organo-magnesium chemistry".

22 February - Professor J.D. Birchall (Mond Division, I.C.I.), "Silicon in the biosphere".

1 March - Dr. A. Williams (Univ. of Kent), "Acyl group transfer reactions".

3 March - Dr. G. van Koten (Univ. of Amsterdam), "Structure and reactivity of arylcopper cluster compounds".

15 March - Professor G. Scott (Univ. of Aston), "Fashioning plastics to match the environment".

22 March - Professor H. Vahrenkamp (Univ. of Freiburg, Germany), "Metal-metal bonds in organometallic complexes".

19 April - Dr. M. Barber (UMIST), "Secondary ion mass spectra of surfaces and adsorbed species".

16 May - Dr. P. Ferguson (C.N.R.S., Grenoble), "Surface plasma waves and adsorbed species on metals".

18 May - Professor M. Gordon (Univ. of Essex), "Three critical points in polymer chemistry".

22 May - Professor D. Tuck (Univ. of Windsor, Ontario), "Electrochemical synthesis of inorganic and organometallic compounds".

24 & 25 May - Professor P. von R. Schleyer (Univ. of Erlangen, Nürnberg): I - "Planar tetra-coordinate methanes, perpendicular ethenes and planar allenes".

II - "Aromaticity in three dimensions".

III - "Non-classical carbo-cations".

21 June - Dr. S.K. Tyrlik (Acad. of Sci., Warsaw), "Dimethylglyoxime-cobalt complexes - catalytic black boxes".

23 June - Professor G. Mteescu (Case Western Reserve Univ., Ohio), "A concerted spectroscopy approach to the characterisation of ion and ion-pairs: facts, plans and dreams".

8 September - Dr. A. Diaz (I.B.M., San Jose, California), "Chemical behaviour of electrode surface bonded molecules".

15 September - Professor W. Siebert (Marburg, W. Germany), "boron heterocycles".

22 September - Professor T. Fehlner (Notre Dame, U.S.A.), "Ferraboranes: synthesis and photochemistry".

Academic Year 1978 - 1979

12 December - Professor D.J.M. Stirling (Univ. of Bangor), "Parting is such sweet sorrow - the leaving group in organic chemistry".

31 January - Professor P.D.B. de la Mare (Univ. of Auckland, New Zealand), "Some pathways leading to electrophilic substitution".

14 February - Professor B. Dunnel (Univ. of British Columbia), "The application of n.m.r. to the study of motions of molecules in solids".

14 March - Dr. J.C. Walton (Univ. of St. Andrews), "Pentadienyl radicals".

28 March - Dr. A. Reiser (Kodak Ltd.), "Polymer photography and the mechanism of cross-link formation in solid polymer matrices"

25 April - Dr. C.R. Patrick (Univ. of Birmingham), "Chlorofluorocarbons and stratospheric ozone: an appraisal of the environmental problem".

1 May - Dr. G. Wyman (European Research Office, U.S.Army), "Excited state chemistry of indigoid dyes".

2 May - Dr. J.D. Hobson (Univ. of Birmingham), "Nitrogen-centred reactive intermediates".

8 May - Professor A. Rchmidpeter (Inst. of Inorg.Chem., Munich Univ.) "Five-membered phosphorus heterocycles containing dicoordinate phosphorus".

9 May - Professor G. Maier (Lahn Giessen Univ.), "Tetra-tert-butyltetrahedrane".

9 May - Dr. A.J. Kirby (Univ. of Cambridge), "Structure and reactivity in intramolecular and enzymic catalysis".

16 May - Dr. J.F. Nixon (Univ. of Sussex), "Some recent developments in platinum-metal phosphine complexes".

23 May - Dr. B. Wakefield (Univ. of Salford), "Electron transfer in reaction of metals and organometallic compounds with polychloropyridine derivatives".

13 June - Professor I. Ugi (Univ. of Munich), "Synthetic uses of super nucleophiles".

25 September - Professor R. Soulen (Southwestern Univ., Texas), "Applications of HSAB theory to vinylic halogen substitution reactions and a few copper coupling reactions".

Academic Year 1979 - 1980

21 November - Dr. J. Miller (Univ. of Bergen), "Photochemical reactions of ammonia".

28 November - Dr. B. Cox (Univ. of Stirling), "Macrobicyclic cryptate complexes: dynamics and selectivity".

5 December - Dr. G.C. Eastmand (Univ. of Liverpool), "Synthesis and properties of some multicomponent polymers".

12 December - Dr. C.I. Ratcliffe, "Rotor motions in solids".

18 December - Dr. K.E. Newman (Univ. of Lausanne), "High pressure multinuclear n.m.r. in the elucidation of mechanism of fast simple inorganic reactions".

30 January - Dr. M.J. Barrow (Univ. of Edinburgh), "The structures of some simple inorganic compounds of silicon and germanium - pointers to structural trends in group IV".

6 February - Dr. J.M.E. Quirke (Univ. of Durham), "Degradation of chlorophyll - a in sediments".

23 April - B. Grievson B.Sc. (Univ. of Durham), "Halogen radiopharmaceuticals".

14 May - Dr. R. Hutton (Waters Associates), "Recent developments in multi-milligram and multi-gram scale preparative high performance liquid chromatography".

21 May - Dr. T.W. Bentley (Univ. of Swansea), "Medium and structural effects on solvolytic reactions".

10 July - Professor D. Des Marteau (Univ. of Heidelberg), "New developments in organonitrogen fluorine chemistry".

2. Durham University Chemical Society

Academic Year 1977 - 1978

13 October - Dr. J.C. Young and Mr. A.J.S. Williams (Univ. of Aberystwyth), "Experiments and considerations touching colour".

20 October - Dr. R.L. Williams (Metropolitan Police Forensic Science Dept.), "Science and trime".

3 November - Dr. G.W. Gray (Univ. of Hull), "Liquid crystals - their origins and applications".

24 November - Mr. G. Russell (Alcan), "Designing for social acceptability".

1 December - Dr. B.F.G. Johnson (Univ. of Cambridge), "Chemistry of binary metal carbonyls".

2 February - Professor R.A. Raphael (Univ. of Cambridge), "Bizaree reactions of acetylenic compounds".

16 February - Professor G.W.A. Foules (Univ. of Reading), "Home winemaking".

2 March - Professor M.W. Roberts (Univ. of Bradford), "The discovery of molecular events at solid surfaces".

9 March - Professor H. Suschitzky (Univ. of Salford), "Fruitful fissions of benzoduroxans".

4 May - Professor J. Chatt (Univ. of Sussex), "Reactions of coordinated dinitrogen".

9 May - Professor G.A. Olah (Case Western Reserve Univ. Ohio), "Electrophilic reactions of hydrocarbons".

Academic Year 1978 - 1979

10 October - Professor H.C. Brown (Purdue Univ.), "The tool of increasing electron demand in the study of cationic processes".

19 October - Mr. F.C. Shenton (Public Analyst, Co. Durham), "There is death in the pot".

26 October - Professor W.J. Albery (Imperial College, London), "Photogalvanic cells for solar energy conversion".

9 November - Professor A.R. Katritsky (Univ. of East Anglia), "Some adventures in heterocyclics".

16 November - Dr. H.C. Fielding (Mond Division, I.C.I.), "Fluorochemical sufactants and textile finishes".

23 November - Dr. C. White (Sheffield Univ.), "The magic of chemistry".

18 January - Professor J.C. Robb (Birmingham Univ.), "The plastics revolution".

8 February - Mr. C.G. Dennis (Vaux Ltd.), "The art and science of brewing".

1 March - Professor R. Mason (Govt. Scientific Advisor), "The Scientist in defence policy".

10 May - Professor G. Allen (Chairman, S.R.C.), "Neutron scattering for polymer structures".

Academic Year 1979 - 1980

18 October - Dr. G. Cameron (Univ. of Aberdeen), "Synthetic polymers - twentieth century polymers".

25 October - Professor P. Gray (Univ. of Leeds), "Oscillatory combustion reactions".

1 November - Dr. J. Ashby (I.C.I. Toxicological Laboratory), "Does chemically-induced cancer make chemical sense?"

8 November - Professor J.H. Turnbull (R.M.C. Shrivenham), "Luminescence of drugs".

15 November - Professor E.A.V. Ebsworth (Univ. of Edinburgh), "Stay still, you brute: the shape of simple silyl complexes".

24 January - Professor R.J.P. Williams (Univ. of Oxford), "On first looking into biology's chemistry".

14 February - Professor G. Gamlen (Univ. of Salford), "A yarn with a new twist - fibres and their uses".

21 February - Dr. M.L.H. Green (Univ. of Oxford), "Synthesis of highly reactive organic compounds using metal vapours".

28 February - Professor S.F.A. Kettle (Univ. of E. Anglia), "Molecular shape, structure and chemical blindness".

6 March - Professor W.D. Ollis (Univ. of Sheffield), "Novel molecular rearrangements".

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AIDS FOR READER

KEY TO THE ABBREVIATIONS USED IN THE TABLES OF POLYMER SYNTHESIS AND APPENDICES

Solvents

Toluene	Tol.
Hexane	Hex.
Dimethyl sulphoxide	DMSO.
Acetone	Act.
Tetrahydrofuran	THF
Methyl ethyl Ketone	MEK
Methyl isobutyl ketone	MIBK
Solvesso	Sol.
Xylene	Xyl.
Oxytol acetate	Oxy.

Monomer 1. (Di-n-alkyl bis(hydroxy carboxylate)tin.

Di-n-butyl bis(o-hydroxy benzoate)tin	(1)
Di-n-octyl bis(o-hydroxy benzoate)tin	(2)
Di-n-butyl bis(m-hydroxy benzoate)tin	(3)
Di-n-octyl bis(m-hydroxy benzoate)tin	(4)
Di-n-butyl bis(p-hydroxy benzoate)tin	(5)
Di-n-octyl bis(p-hydroxy benzoate)tin	(6)
Di-n-butyl bis(3-hydroxy-2-naphthoate)tin	(7)
Di-n-octyl bis(3-hydroxy-2-naphthoate)tin	(8)
Di-n-butyl bis(12-hydroxy stearate)tin	(9)
Di-n-octyl bis(12-hydroxy stearate)tin	(10)
Di-n-butyl bis(mandelate)tin	(11)
Di-n-octyl bis(mandelate)tin	(12)
Di-n-butyl bis(glycolate)tin	(13)
Di-n-octyl bis(glycolate)tin	(14)

Monomer 2. (Diisocyanate)

Isophorone diisocyanate	(i)
Hexamethylene diisocyanate	(ii)
Trimethyl-hexamethylene diisocyanate	(iii)
Desmodur N	(iv)
DDI	(v)

Monomer 3. (Diol)

Ethane 1,2 diol	(A)
Propane 1,3 diol	(B)
Butane 1,4 diol	(C)
Teracol 1000	(D)
Teracol 2000	(E)