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ADHESION OF PAINTS TO CONTAMINATED SURFACES

A THESIS

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by

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TO MOTHER ....

ABSTRACT

One of the main causes of premature failure of paint films is poor adhesion to substrate arising from the presence of contaminants at the interface. Chemical or mechanical treatment of the subtrate is normally used to ensure reasonable cleanliness of the surface, but in practice some contamination usually remains. Paints designed to accommodate such contamination would ensure that failures arising from this cause would be reduced.

In this work the effect of modifying the polymer structure with minor amounts of nitrogen containing groups or a combination of those with carboxyl groups has been studied in relation to the level of adhesion attained on deliberately contaiminated surfaces. Generally, improved adhesion has been achieved with both thermoplastic and thermosetting solvent thinned acrylic paints and also with emulsion type acrylic paints by such modification.

It is suggested that the mechanism of adhesion is of a chemical nature. This is based on the chemical reaction and the detection of an intermolecular compound between the monomeric form of the nitrogen containing compound and the contaminant. It was concluded that a similar behaviour would occur between the polymer carrying such a compound and the contaminant.

An examination of the effect of structural changes of the polymeric chain on the critical surface tension and cohesive energy density of the polymer and their relation to adhesion showed that the level of modification was too small to introduce any significant changes in these properties.

PREFACE

The bulk of this work was carried out at the Paint Research Association, Teddington, Middlesex, under the direction of the late [redacted] and later [redacted] and the supervision of Mr. K. W. Allen at The City University.

I am greatly indebted to all of them and also to [redacted] of The City University for their helpful guidance, constructive discussions and encouragement at all times.

The experimental work on infra-red and ultra-violet spectroscopy was carried out at The City University.

I would like to express my thanks to many of the staff of the Paint Research Association, particularly [redacted] and [redacted], and also to [redacted] and [redacted] of The City University, and to [redacted] for typing this thesis.

Finally I am indebted to the Paint Research Association for supporting the research and facilitating the birth of this thesis.

S. El-Muddarris

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CHAPTER ONE

INTRODUCTION

INTRODUCTION

The application of paints is an important factor in both the industrial and the domestic fields. Paints are generally applied to fulfil a utilitarian and aesthetic purposes.

Considerable effort has been made in recent years to obtain a better understanding of the merit of tailoring paint systems to meet the demands of coating specifications and technological requirements at an acceptable economic cost level.

This thesis is devoted to a study of the effect of chemical modification of the structure of the paint vehicle and its adhesion to a model of contaminated surfaces. In addition to devising new coating materials to accommodate such surfaces, an improvement in paint film adhesion is also an objective of this research. This is important because, if successful paints are to be developed they should show good average bond strength to substrates of practical industrial cleanliness level or at least have a safe level of adhesion which must always be at least as strong as the cohesive strength of the coating. Such coatings must therefore incorproate groups that will compete favourably for adsorption sites with the contaminant.

The main problem of adhesion failure of paints arised in the product finishing areas. This is largely because the surfaces of an industrial nature carry contaminants which interfere with intimacy of contact of the paint and the substrate and which themselves provide a weak layer of very low cohesive strength.

It was found that a more fruitful field of research to approaching the adhesion problem is in the modification of paint vehicle rather than in the approach of the use of additives as adhesion promoters. In normal practice, adhesion promoters which are effective in unpigmented film are often of little value in pigmented systems, presumably because the requirements for adsorption to, say, a metal oxide substrate were similar to those for adsorption of inorganic pigment surfaces. For this work, and as a model system, thermoplastic acrylic polymers are ideally suited for studying the effect of changing the polymeric structure upon adhesion of films particularly to contaminated surfaces. They are the simplest type of polymers amenable to controlled modification in the laboratory, and can well be characterised. They can be designed to produce films of acceptable physical properties simply by evaporation from solution. No complication arises from the production of other chemical groups by, for example, oxidation during film formation, or from changes in molecular weight or molecular weight distribution. Thus the chemical nature of the polymer film should be identical to that established with the original polymer.

The aims of this research have been achieved in so far as:

(1) Improving adhesion to dirty surfaces.

(2) Understanding the effect of chemical modification of the polymer backbone on adhesion.

(3) Extending the idea to the thermosetting and emulsion types of paints.

(4) Identifying the reasons for adhesion improvement by this method, where a chemical adhesion was involved.

(5) Determining the environmental effect, i.e. that of weathering on the performance of the paint systems.

(6) Offering a potentially viable coating system for contaminated metallic surfaces.

Inspite of the academic nature of this work some technological value was derived.

It was found that to overcome the problems of adhesion or intercoat adhesion failures the nature of the contaminants present at the interface should be identified prior to designing new systems, so that appropriate chemical groups can be utilized to scavenge the deleterious effect of such contaminants.

A considerable number of techniques as an indirect tool for identification of the mechanism of adhesion has been used. These include Infra-Red spectroscopy, solubility parameter and contact angle measurements. However, the study of phase diagram was a direct indication of chemical bonding of paints and contaminant.

CHAPTER TWO

PREVIOUS WORK

2.1. Classification of Polymerisation Reactions

The various methods of classifying polymerisation reactions have been extensively discussed[1]. Here, only the major classification scheme will be discussed in brief.

The most widely used classification is as follows:

1. By Stoichiometry of the Polymerisation

(a) Addition polymerisation in which the polymer molecule is formed by the addition of the monomer molecules together without the production of by-product small molecules. Thus the repeating unit which is normally named "a segmer" has the same weight as the monomer.

(b) Condensation polymerisation, where the formation of polymer molecules takes place from small molecules with concurrent production of by-product small molecules such as water, hydrogen chloride or ammonia. Here the sum of the weights of the repeating units is less than the weight of all the original monomer units that combined to form the polymer.

2. By Mechanism of Polymerisation

From this scheme, important information about molecular weights and rates of reaction are conveyed. The polymerisation processes are of two basic types, as chain reaction and as stepwise, which kinetically differ from each other. The properties of the polymers are different in molecular weight distribution and are usually different in kind.

The characteristics of chain-reaction polymerisation are as follows:

(a) A material of high molecular weight is formed at all stages, even during the first fraction of a second of reaction. The intermediate reaction mixture consists mainly of inactive polymer and unreacted monomer as in the free radical polymerisation of a vinyl type monomer.

(b) The polymer molecules formed do not react with one another to produce material of higher molecular weight.

(c) The "active centres" responsible for the reaction which are highly unstable are free radicals or ions, and the propagation step occurs rapidly relative to initiation. The mutual reaction between two of the intermediate in the free radical case, and the reaction between ions of opposite charge in the ions case, terminate the kinetic chain. The concentration of polymer molecules as a termination occurs is very low at a given instant.

In stepwise reaction polymerisation as in the polyesterification, the intermediates are relatively stable chemical compounds with functional groups characteristic of the monomer.

The growth of the polymer proceeds by a series of discrete reaction steps involving monomer and/or intermediate.

Other terms are normally used in this division including no-termination, dead-end, equilibrium, telomerisation, Diels-Alder and alternating intramolecular-intermolecular polymerisations.

3. By Nature of Propagating Species

This entails dividing reactions according to the chemical nature of the active centre in the propagation step, particularly common for vinyl polymerisation as ionic, free radical .... etc.

The ionic reaction may also be divided into anionic and cationic polymerisation.

Other terms for the polymerisation processes are also used mainly "co-ordinate" or a stereospecific if in the propagation step a complex with co-ordinate bonding is formed or it induces a measure of stereoregularity.

4. By Method of Initiation

Depending on the procedure used to effect initiation of the reaction, polymerisation can be given the names of catalysed, thermal, enzymatic, electrochemical, mechanochemical or radiation induced reactions.

5. By Medium of Reaction

Because of the theoretical differences in the behaviour of polymerisations and depending on the medium in which it is carried out, the major classes are:-

Bulk (undiluted monomer), solution, emulsion, suspension, solid-state and gaseous (vapour) polymerisation.

Homogeneous or heterogeneous polymerisation terms are also utilised. Because of the insolubility of the polymer in the medium the two terms become the same and the term precipitation polymerisation is introduced.

6. By Structure of Product

The chemical feature of the product gives rise to the following names, i.e. stereospecific for stereoregularpolymer, crosslinking, isomerisation polymerisation, cyclo, ring-opening, i.e. the loss of the cyclic structure of the monomer, block and graft copolymerisation and co-ordination polymerisation with co-ordinate covalent bonds.

Physical characteristics of the resulting polymer also describe reactions as bead or popcorn polymerisation. Polyesterification is also a term utilised when functional groups are involved in producing a polymer.

7. By Nature of Reactants

The vinyl polymerisation, diene, allyl, urea-formaldehyde condensation, ethylene oxide and Diels-Alder polymerisation are considered to belong to this group.

2.1.1. Monomer/Polymer Structure and Polymerisation Induced by Free Radicals

Because acrylic monomers have been used in this work, this discussion will be devoted to outlining some of their properties and how suitable vehicles for the coating industry are prepared to meet specific requirements.

The fundamentals of molecular architecture such as chemical composition, functionality, relative polarity and type and degree of polymerisation serve as guides for the selection of acrylic resins.

The term "acrylic" covers the entire field for both derivatives of acrylic or methacrylic compounds which are derived from methacrylic acid or their simple alkyl esters. All acrylic resins contain the functional group $CH_2=CH-CO-$ as acrylate or $CH_2=C(CH_3)-CO-$ as methacrylates. These resins are structurally macromolecules of a saturated carbon-carbon chain obtained by addition of the individual monomer units across the vinyl group.

Other well known monomers include ether-esters and methacrylate ester, acrylamide and dimethacrylates of glycols and glycol ethers.

The properties of acrylic ester polymers vary with the type of alcohol from which the acrylate or methacrylate ester is prepared. Table 1 illustrates[2] the marked differences in physical properties of the polymers as the alcohol portion is changed which may be attributed to the difference in the polarity of their polymeric back-bone. The polarisation effect of methyl group on the polymer when it is close to the back-bone, leads to a larger net of intermolecular force of van der Waal's forces of attraction in methacrylate than in acrylate polymers. Thus the polymer chains of methacrylates are more closely packed and aligned to a more symmetrical structure than the acrylate, giving rise to chain stiffness. In addition, differences in viscosity, solubility, mechanical and chemical properties are introduced. Easier rotation of segments about the main chain causes the acrylate polymers to be softer and more rubber-like than methacrylate.

TABLE 1

Effect of Side Group Chain Length on Polymer Properties

Polymer of	Tensile Strength, lb/in^2	Elongation, % at Break
Methyl methacrylate	10,500	1
Ethyl methyacrylate	5,400	25
n-Butyl methacrylate	500	300
Methylacrylate	1,005	750
Ethylacrylate	33	1,800
n-Butylacrylate	3	2,000

All acrylic monomers may be polymerised readily by free radical polymerisation and copolymerised with many other monomers such as styrene and vinyl acetate and amongst themselves.

Acrylic monomers undergo free radical polymerisation either in solutuon, or in bulk or in suspension or emulsion.

For this work the solvent polymerisation process which is comparatively simple was used.

The free radical polymerisation is a chain-reaction, the kinetics of which has been studied theoretically and experimentally in great detail elsewhere[3-5], and consisting of three main steps:

(1) Initiation

(2) Propagation

(3) Termination

(1) Initiation

All radical chain reactions have to be initiated by a process giving rise to free radicals and a small amount of initiator is commonly used, which decomposes relatively rapidly under the influence of heat or light. The choice of initiator depends on its decomposition temperature and the speed of the decomposition (or half-life) which controls the speed of the reaction. They can also be classified as free-radical, cationic, anionic and co-ordination initiators.

The application of initiator to maintain a continuity of the reaction by the generation of free radicals is not always necessary, however if the monomer has sufficiently strong ultra-violet absorption, then photo initiation is possible although not all such reactions proceed via free radicals rather than ions. Heat alone also suffices but only where the radical is highly resonance-stabilised as with styrene.

The amount of initiator used affects the molecular weight of the polymer produced and the degree of conversion. This is illustrated in Table 2.

Table 2.

Effect of Initiator Concentration on Product Viscosity (6)

Monomers(a)	Temperature of Polymerisation	Amount of Initiator di-t-butylperoxide	Product Viscosity in CPS at 50% total solids
HPMA 25	141	0.25	860
BA 41	"	0.50	525
S 33	"	0.75	453
AA 1	"	1.00	375
		1.25	290

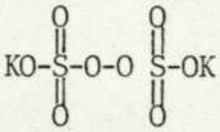
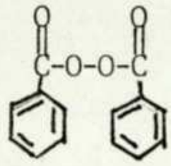
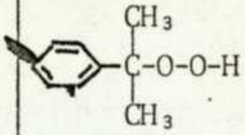
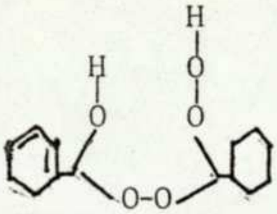
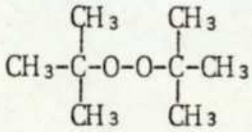
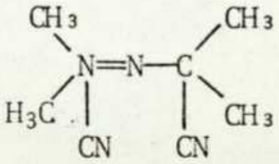
(a) Monomer-mixture including the initiator was fed at a constant rate for four hours into the refluxing xylene.

The decomposition reaction of the initiator and hence the constitution of the developing radical also depends on the type of solvent used.

Table 3 lists a number of initiators widely used on both the industrial and the laboratory scale for free radical reaction and a typical mechanism is given in Scheme 1.

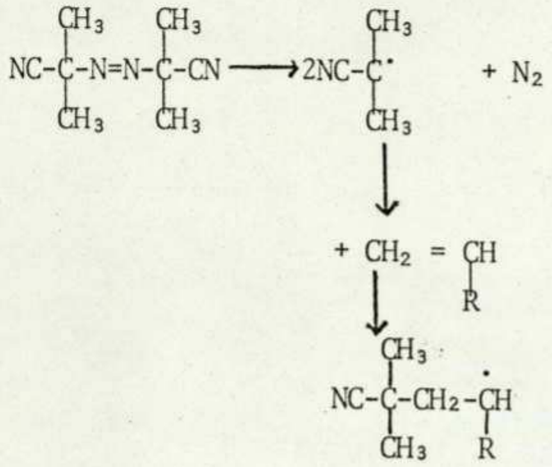
Table 3

List of Initiators Used for Radical Polymerisation

Name	Structure	Best Temperature for use (^{o}C)
Potassium persulphate	 $KO-\overset{O}{\underset{O}{S}}-O-O\ \overset{O}{\underset{O}{S}}-OK$	40 - 80
Dibenzoyl peroxide		40 - 90
Cumene hydroperoxide		90 - 100
Cyclohexanone peroxide		20 - 80
Di-t-butyl peroxide	 $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O-O-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$	80 - 150
Azobisisobutyronitrile		20 - 100

Scheme 1

Decomposition of Azo Initiator and Formation of Active Sites



The simplest possible reaction comprises three components and can be represented by:

$$I \longrightarrow 2\,R^{\cdot} \qquad R_i \qquad \text{or}$$

$$-d[R^{\cdot}]/dt = K_i\ [R.]^2$$

where R_i - is rate of initiation

K_i - specific velocity constant

By equating the rate of formation $R + M \rightarrow R\cdot$ (Kp) and destruction termination of radicals $2R. \rightarrow 2P$ (K_t), the radical concentration can be given by equation (1).

$$[R^{\cdot}] = (R_i/K_t)^{\frac{1}{2}} \qquad (1)$$

The rate of polymerisation (Rp) is the rate of consumption of monomer which is the rate of propagation and is equal to:

$$R_p = Kp\ [R\cdot]\ [M] \qquad (2)$$

Substituting for R· from equation (1) we obtain:

$$Rp = Kp\,[M]\;(Ri/K_t)^{\frac{1}{2}}$$

This clearly demonstrates that the rate of polymerisation is proportional to the monomer concentration and to the square root of rate of initiation.

The average kinetic chain length ν, which is the average number of monomer molecules consumed per chain started, is given by equation (3) and is also equal to the average degree of polymerisation (DP) in the absence of transfer reaction.

$$\nu = \frac{Rp}{Ri} = Kp\,[M]\;(Ri\;K_t)^{\frac{1}{2}} \qquad (3)$$

A variety of assumptions are made here including a constant concentration of reagents, lack of dependence of Kp and Kt on radical size and free diffusion of all species in the solution.

If the transfer reaction as given by $R^{\cdot} + XH \rightarrow RH + X^{\cdot} \rightarrow (K_{tr})$ is included, ideally it has no effect on the rate of reaction or on (ν) but it will reduce the average degree of polymerisation. The latter is the ratio of the rate of monomer consumption to the sum of the rates of the transfer and termination processes:

$$\bar{D}P = \frac{Kp\,[R.]\,[M]}{Kt\,[R.]^2 + K_{tr}[R\cdot]\,[XH]}$$

or

$$\bar{D}P = \frac{Kp\,[M]}{(R_iK_t)^{\frac{1}{2}} + K_{tr}[XH]}$$

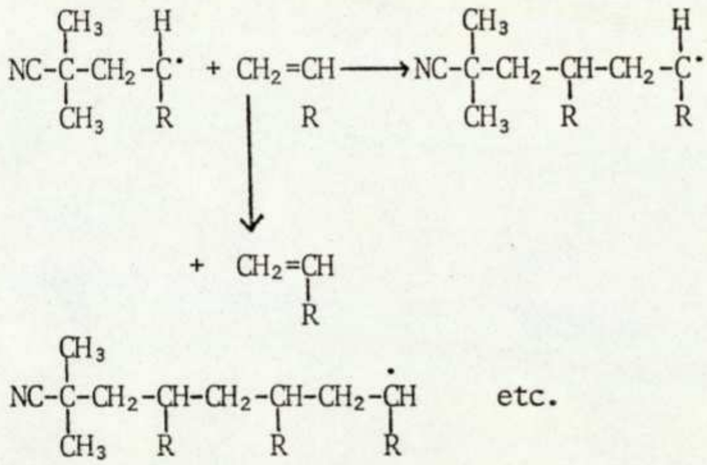
If a value of R_i is known, then in the light of these equations, expressions for Rp, ν, and DP can be obtained containing ratios of the velocity constants of $(Kp/K_t)^{\frac{1}{2}}$ and Kp/K_{tr}.

Various methods for the determination of the individual rate constants are reported in the literature[3], but differences are encountered.

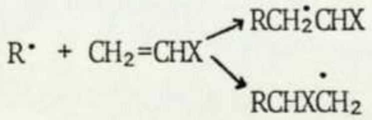
2. Propagation

The foramtion of a polymer molecule occurs when the ethylenic double bond of the monomer units add itself to the reactive site of the free radical, as shown schematically below.

$R^{\cdot} + M \longrightarrow R^{\cdot} \quad (Kp)$



The process can be visualised as occurring in either of two ways:



The first mode of addition would be preferred where X is able to contribute through resonance to the stabilisation of the radical. The second is sterically less favoured.

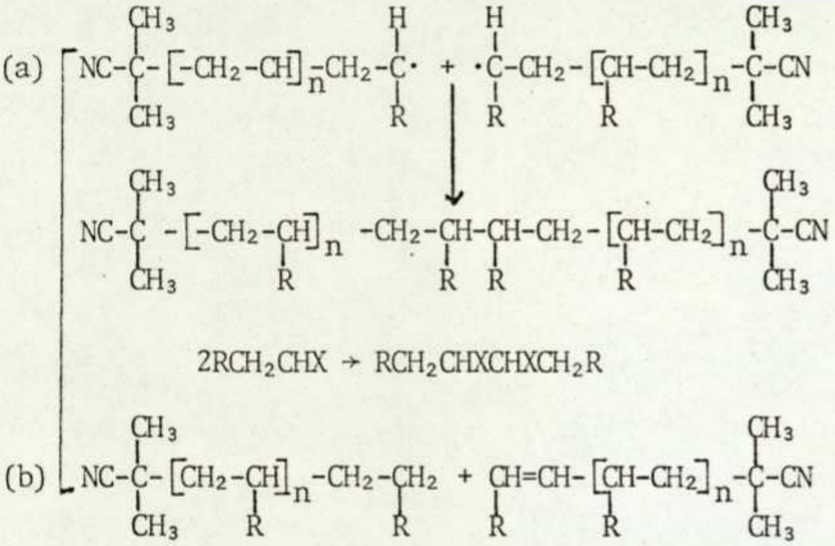
3. Termination

This process, as shown below in the diagram, involves two radicals hence the reactive sites on the polymer chain are rendered inactive by:

(a) combination process

(b) disproportionation process

$$2R\cdot \longrightarrow 2P \longrightarrow K_{tr}$$



(a)

$$NC-\overset{CH_3}{\underset{CH_3}{C}}-[-CH_2-CH]_n-CH_2-\overset{H}{\underset{R}{C}}\cdot + \cdot\overset{H}{\underset{R}{C}}-CH_2-[\underset{R}{CH}-CH_2]_n-\overset{CH_3}{\underset{CH_3}{C}}-CN$$

$$\downarrow$$

$$NC-\overset{CH_3}{\underset{CH_3}{C}}-[-CH_2-\underset{R}{CH}]_n-CH_2-\underset{R}{CH}-\underset{R}{CH}-CH_2-[\underset{R}{CH}-CH_2]_n-\overset{CH_3}{\underset{CH_3}{C}}-CN$$

$$2RCH_2CHX \rightarrow RCH_2CHXCHXCH_2R$$

(b)

$$NC-\overset{CH_3}{\underset{CH_3}{C}}-[CH_2-\underset{R}{CH}]_n-CH_2-\underset{R}{CH_2} + \underset{R}{CH}=CH-[\underset{R}{CH}-CH_2]_n-\overset{CH_3}{\underset{CH_3}{C}}-CN$$

$$2RCH_2CHX \rightarrow RCH_2CH_2X + RCH{=}CHX$$

An example of the first process is as with styrene and of the second is as with methylmethacrylate.

The retardation of the termination process is governed by the well-known phenomenon of Trommsdorf's effect[3,7] or the gell effect. In reactions that are allowed to proceed to say 20% conversion, the increasing viscosity of the medium tends to limit the diffusion of the macroradicals and in most polymerisations, termination is always to some extent diffusion-controlled. The velocity contant (K_t) is then a function of the viscosity of the solvent. As high conversion results in a retardation of propagation as well as of termination.

This principle is well supported by Klein[8], when a high solid polymerisation is required. Klein[8] showed that the molecular weight of copolymers of styrene, ethylacrylate, acrylic acid and hydroxypropylacrylate increases with increasing concentration of monomers at which polymerisation is carried out. This is so because the mobility of the growing polymer radicals are decreased where as the ability of the monomer to diffuse throughout the reaction mass is not diminished proportionally. The polymer continues to propagate at a high rate and decreases the chance for termination since the growing polymer chain have lost some of their mobility.

However, the molecular weight of acrylic polymers can be controlled with regulators or chain transfer agents such as mercaptan (n-t-butyl, dodecyl Mercpatans).

2.1.2. The Mechanism of Copolymerisation

When two different monomers, A and B are copolymerised to yield a product known as a copolymer, the rate of copolymerisation is generally slower than either of the corresponding homopolymerisations. The composition of the resultant copolymer containing units of both types is not a simple function of the concentration of the original monomers, but depends much more on the relative reactivity properties of the individual monomers.

Various treatments were given in the past to the mechanism of polymerisation reaction of systems involving two or more monomers. Wall[9], (1944) in a series of papers treated the subject of the rate of polymerisation of two or more monomers for structural studies of vinyl copolymers. His results were compared with the experimental data of Marvel and co-workers[10]. Branson and Simha[11] also attacked the problem. All these treatments involved the assumption that the propagation reactions involved only two distinct processes, i.e. the addition of each type of monomer to the growing chain.

However, Jenckel[12] recognised the existence of four distinct propagation processes, but with consideration of only those cases where certain simple relationships hold between the four propagation rate constants.

Alfrey and Goldfinger[13] however, in (1944) studied the mechanism of catalytic copolymerisation of two monomers without restricting conditions apart from treating the average molecular weight of the copolymer as "high". They proposed a number of equations describing the rate of polymerisation, average degree of polymerisation and shape of size distribution curves as variables of reaction conditions.

Alfrey and Goldfinger[13] treatment of the rate of copolymerisation was carried out by assuming two different initiation rates, four different propagation rates and two termination reaction rates.

Walling and Briggs[14] (1945), extended the theory of copolymerisation developed by previous workers[13,15,16] to the case of (n) monomers and the composition of the reaction product expressed in terms of the initial composition of the reaction mixture and the n(n-1) monomer reactivity ratios involved[15].

A discussion of the more general case of (n) monomers and experimental work on combination of styrene, MMA, acrylonitrile and vinylidene chloride was presented[14]. It was concluded that a general differential equation was developed which predicts the composition of the polymer formed in the copolymerisation of n-monomers in terms of monomer concentrations and the n(n-1) monomer reactivity ratios for all the two-component systems. The predicted and observed polymer compositions agree, and for any number of monomers.

A new method of computation of the composition of copolymers was proposed by Skeist[17] which permits evaluation of systems containing any number of components.

2.1.3. Theory and Practical Use of Monomer and Radical Reactivity Ratios

When two monomers are used M_1 and M_2, the four possible propagation growth reactions which can proceed, can be expressed in a simpler fashion, and in the light of the previous discussion as follows:-

(1) $R \sim M_1^{\bullet} + M_1 \xrightarrow{K_{11}} R \sim M_1^{\bullet}$

(2) $R \sim M_1^{\bullet} + M_2 \xrightarrow{K_{12}} R \sim M_2^{\bullet}$

(3) $R \sim M_2^{\bullet} + M_2 \xrightarrow{K_{22}} R \sim M_2^{\bullet}$

(4) $R \sim M_2^{\bullet} + M_1 \xrightarrow{K_{21}} R \sim M_1^{\bullet}$

where $M_1^{\bullet}$ and $M_2^{\bullet}$ are the derived radicals of monomer 1 and 2 respectively.

Mayo and Lewis[18] proposed a method for calculating the copolymer composition based on the copolymerisation parameter using the following equations:-

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \frac{r_1 [M_1] + [M_2]}{r_2 [M_2] + [M_1]} \qquad \text{(A)}$$

where: $r_1 = K_{11}/_{12}$ and $r_2 = \frac{K_{22}}{K_{21}}$ and are called the monomer reactivity ratios of 1 and 2 respectively.

This equation is the same as that derived by Alfrey and Goldfinger[13], and offers a direct determination of the composition of copolymers formed at any instant in time $d[dM_1/dM_2]$ as a function of the initial monomer concentration, of the conversion and the monomer reactivity ratio.

Solving equation (A) for the reactivity ratios we obtain:

$$r_2 = \frac{M_1}{M_2} \left[\frac{d[M_2]}{d[M_1]} \left(1 + \frac{[M_1]}{[M_2]} r_1\right) - 1 \right] \qquad \text{(B)}$$

The expressions (A) and (B) applies only for low conversion or under the condition where the monomer concentrations remain constant.

A study of the copolymerisation of styrene and methylmethacrylate[18] by a free radical mechanism suggests that the monomer reactivity ratios are independent of the composition of the monomer mixture, the extent and rate of conversion, small quantities of certain added materials, moderate proportions of benzene and ethylacetate as solvents and the presence or absence of benzylperoxide as initiator.

The practical significance of the rates is that if $K_{11} > K_{12}$ and $K_{22} > K_{21}$, then reaction in step (1) or in step (3) is dominating and theoretically a mixture of polymers will be formed. However, if $K_{12} > K_{11}$ and $K_{21} > K_{22}$ then a copolymer with a regular alternation of units along the polymer chain will be formed.

In an ideal copolymerisation situation, the four reactivity rate constants are equal and the addition of M_1 or M_2 depends on the concentration of the monomers in the mixture. The same mononer ratio in the copolymer will be found as it was originally.

If $r_1 > 1$ then the polymer radical react more rapidly with their own monomers than with copolymers. When $r_1 < 1$ the polymer radical reacts selectively with the comonomer. If $r_1r_2 = 1$, this indicates that the reactivities of both monomers with both radicals are the same and a random distribution of the monomer occurs. If $r_1r_2 \rightarrow 0$ then a pronounce tendency for alternation in the growing chain and 1:1 ratio of copolymers can be obtained.

A practical method of determining the rate of reaction is offered by Wilkinson et al[19], for several acrylic monomers and is based on gas chromatographic analyses of the unreacted monomers during solution or emulsion copolymerisation.

For this work the necessity for determining the kinetics of the reaction, and hence r_1, r_2 or r_3, during the course of the reaction did not arise. However, a different approach was explored for the determination of the copolymer composition of the end product via the elemental analysis (see section 3.7).

However, Alfrey and Price[20] offered a definite method and set of constants Q and e as a general measure of the relative reactivity of a monomer so as to avoid the need for characterisation of each addition of new monomer in a specific system.

Thus, the expression for the rate at which the monomer M_1 competes for its own radical $M_1^{\cdot}$ in step (1) is given by $K_{11} = P_1Q_1{}^{-e_1}$

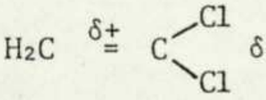
and in step (2) $K_{12} = P_1Q_2^{-e_1e_2}$ where P_1 is characteristic of the radical, $M_1^{\cdot}$. Q_1 and Q_2 are the mean reactivity of monomers, M_1 and M_2 respectively. e_1 is proportional to the charge on the end of radical $M_1^{\cdot}$. e_2 is proportional to the charge on the double bond of monomer, M_2.

The relative rates are: $r_1 = \frac{K_{11}}{K_{12}} = (\frac{Q_1}{Q_2})\ e^{-e_1(e_1-e_2)}$

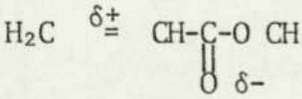
$$r_2 = \frac{K_{21}}{K_{22}} = (\frac{Q_1}{Q_2})\ e^{-e_2(e_1-e_2)}$$

Using these equations and published data of the monomer relative reactivity on copolymers of styrene, methylmethacrylate acrylonitrile and vinylidene chloride, Alfrey and Price calculated the Q and e values.

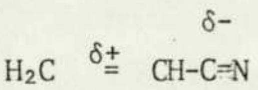
The (e) values are related to the electrical factors due to induced charges from substituent groups present on the carbons of the double bond. Substituents which are electron deficient (electrophile) such as -Cl, -COOR, $-NO_2$ and -CN groups tend to accept electrons and induce the double bond of the monomer to be positively charged. This may be illustrated as follows:



$H_2C \overset{\delta+}{=} C(Cl)_2\ \delta-$ Vinylidene chloride

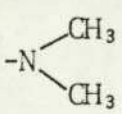


$H_2C \overset{\delta+}{=} CH\text{-}\underset{\overset{\|}{O}\ \delta-}{C}\text{-}O\ CH_3$ Methyl acrylate



$H_2C \overset{\delta+}{=} CH\text{-}\overset{\delta-}{C{\equiv}N}$

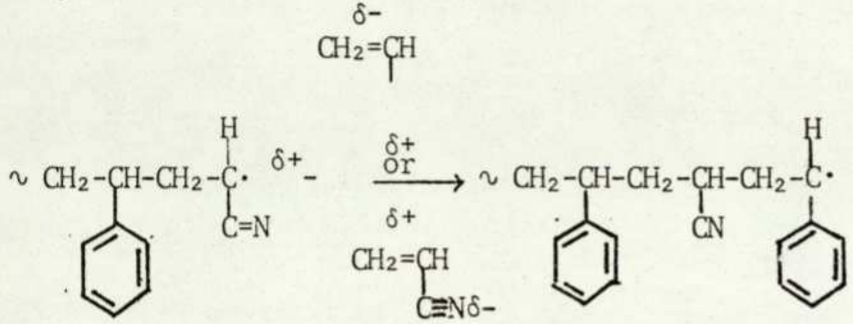
Substituents which are electron rich, e.g. $-CH_3$, $-C_6H_5$; $-O-CH_3$ and



$-N(CH_3)_2$ tend to donate electrons.

Radicals undergo such polarization and a polymer unit containing an electron deficient substituent on the end preferably adds a monomer with an electron rich substituent.

As an example is the case of the electron accepting radical (plus charged) adds itself to a styrene molecule rather than to an acrylonitrile.



To summarise, substituents which are electron rich tend to donate electrons and give negative (e) values. Electron deficient substituents tend to accept electrons and give positive values. The greater the difference in donor or acceptor properties between two monomers, the greater will be the alternating tendency in copolymerisation.

A list of Q and e values for some acrylic monomers can be found in the literature[21-23].

Copolymerisation proceeds more rapidly between monomers, with greatly different (e) values. Monomers with large differences in Q values and similar (e) values copolymerise with difficulty, if at all.

The addition of a monomer with a small Q value on a radical-containing chain, and with a high resonance stabilisation would lead from a lower to a higher form of energy or from a stable to an unstable state, which for thermodynamic reasons is unlikely. This is why vinyl chloride or vinyl acetate Q = 0.03 is not suitable for copolymerisation with styrene.

Ideal copolymers are formed when Q and e values are identical. Table 4 contains a list of Q and e values for some acrylic monomers which may be plotted to form a monomer map.

Table 4.

Q - e Values by Price and Alfrey[19]

Acrylates and Others	Q	e
Acrylic Acid	1.08	1.09
Methyl	0.43	.73
Ethyl	.34	.58
n-Butyl	.43	.53
2-Ethylhexyl	.36	.74
Styrene	1.00	-0.8
Vinyl acetate	.03	.3
Methacrylates		
Methacrylic acid	2.37	.83
Methyl	.74	.40
Ethyl	.64	.50
n-Butyl	.74	.39
Hexyl	.91	.31
Lauryl	.74	.20
Hydroxyethyl	.80	.20
Hydroxypropyl	.79	.20
Isobutyl	.77	- .04

2.2. The Effect of Polymer Structure on Adhesion

The progress in the fundamentals of polymer science facilitated the systematic improvement in the development of new synthetic adhesives. By studying variations in polymer structure, it is now possible to control the properties desired from a polymer to meet specific requirements. Control and knowledge of parameters such as flexibility, molecular weight, molecular organisation, crystallisation, cohesive strength and cross-linking are required to achieve the need for specific applications.

The approach to improving the adhesion of a variety of surface coating compositions by the chemical modification of polymer back-bone with functional groups or by the addition of adhesion promoters has been adapted by many workers and there are many patents and published sets of data. Czyzak[24] for example, in 1948, reported the contribution of polar groups to the adhesion of polymers to conducting surfaces such as steel and lead. In the late 1940's and beginning of the fifties, McLaren and co-workers (1948, 1949, 1951)[25-27], dealt with the peel strength as related to tack temperature and polarity of copolymers.

The importance of polar groups in promoting adhesion was recognised in 1948 when Hofrichter and McLaren[28] showed and proposed that the adhesion of polymers containing maleic acid to cellulose increased according to the equation : Adhesion = $K(COOH)^n$. This principle was used widely in the surface coating industry.

The participation of hydroxyl groups in adhesive bonding and the importance of their occasional point of attachment with the oxide layer of the metallic surface of epoxy resins and of poly(vinylbutyral) to glass was studied by Glazer[29] and was further emphasized by Waine[30].

Glazer[29] obtained a large increase in adhesive strength on an increase in hydroxyl groups per molecule of epoxy resins.

Voyurskii and associates[31], investigated the effect of the size, shape and polarity of polybutadienes and butadiene copolymers on adhesion to cellophane.

The importance of the hydroxyl group in adhesion was also studies by Koral and co-workers[32]. They observed an almost three-fold increase in adsorption on an iron (oxide) surface when poly-(vinyl acetate) was hydrolysed to the extent of 13%.

Black and Blomquist[33] studied the relationship of polymer structure to thermal deterioration of adhesive-steel bonds and their data pointed out the differences in adhesion based on variations in copolymer compositions, containing acrylonitrile and butadiene or acrylonitrile and acrylamide, with the observation that an increase in butadiene content or in the acrylamide increases adhesion. However, in the peel adhesion studies[34] of butadiene-acrylonitrile copolymers indicated that adhesion decreases with increasing concentration of acrylonitrile in the copolymer. In a U.S. patent[35] the effect of amine groups on adhesion was investigated.

The positive influence of hydroxyl and carboxyl groups on the side chain of acrylic polymers on adhesion in tension was recorded by Volfkovich and co-workers[36].

The concept of polymer design to adhesive properties of polymers was reviewed by Reynolds[37] in terms of increasing complexity of the polymer chains. The features of the backbone in linear polymers, the nature and effects of side-chains and the interaction of individual macromolecules with one another, and their effect on flexibility, molecular weights and cohesive strength and adhesion were illustrated. The effect of molecular weight on the cohesive strength of a copolymer of 2-ethyl hexyl-acrylate containing varying quantities of acrylic acid, between the low and high molecular weight produced something like 100% change in cohesive strength. Thus the properties of a high molecular weight polymer containing 2% AA can be equated by low molecular weight polymer containing just 3% AA. For the same amount of AA, the cohesive strength was higher for high molecular weight polymer than that for medium or low molecular weight resulting in the same order of adhesion as peel strength.

The increase in peel strength with increasing carboxyl content of ethylene acrylic acid copolymer was observed by Smarock and Bonotto[38]. Similar observations were also made in that small amounts of carboxyl functionality greatly improved the adhesion of a resin to metal[39,40].

The presence of the carboxyl groups in carboxylated polyesters was the most important structural feature which affected adhesion of coatings investigated by Jackson and Caldwell[41]. A number of linear polyesters with carboxyl groups attached to the polymer chain at uniform intervals were prepared by reaction of dianhydrides with hydroxyl-terminated polyester segments with predetermined molecular weights. These were effective in improving the adhesion when they were blended at 5 to 10% with cellulose acetate butyrate, vinylchloride copolymers, polystyrene and poly-methyl methacrylate. The substrates used were aluminium, brass, copper, chromium, steel, nylon 66 and poly(ethylene terephthalate). Particularly effective carboxylated polyester was obtained by reaction of pyromellitic dianhydride with a hydroxyl-terminated polyester prepared from 2,2-dimethyl-1-1,3 propane diol and equimolar amounts of terephthalic and isophthalic acids.

The introduction of functional groups in the side chain of acrylic polymers and copolymers and their effect upon peel adhesion to a pigmented epoxy ester coated steel substrate was studied by Mao and Reegen[42]. A series of copolymers of methyl-methacrylate with various co-monomers of alkyl methacrylates and alkyl-acrylates at a molar ratio of 9:1 respectively, were prepared and it was found that the peel strength generally increased with increase in the number of carbon atoms in the side chain of the comonomer. The acrylate series showed higher peel strength than the corresponding members of the methacrylate series. A similar trend was observed by Eich and Haarlammert[43], who reported that the adhesion of substituted polyacrylates and polyvinylethers increased with increasing length of the side chain. McLaren and co-workers[44] demonstrated the increase in adhesion of poly(alkylmethacrylate) as the alkyl group was changed from ethyl through n-butyl.

Mao and Reegen[42] also investigated the effects of polar groups as COOH and $CONH_2$ introduced in methylmethacrylate polymer via copolymerisation with acrylic acid, acrylamide, methacrylic acid and methacrylamide at various concentrations and observed that the presence of the acid enhanced the adhesion. The peel strength of the copolymer progressed as the concentration of the acid increased.

At 10 mole percent level, acrylic acid copolymers showed relatively high peel strength as compared to the acrylamide, methacrylic acid and methacrylamide. In the acrylamide series, however, the peel strength of the copolymer increased continuously up to 10 mole percent of the comonomer. Further increase in the acrylamide led to a lowering of adhesion. The author attributed this to the possibility of an increase in crystallinity of the copolymer for the methacrylic acid series and methacrylamide series neither comonomer seemed to enhance the peel strength of its copolymer with methylmethacrylate.

Similar results were obtained from adhesion studied carried out at the Paint Research Association by Brett and Kwasniok[45]. The relation between the polymeric structure of the paint medium and the ability of the film to form an adequate bond to surfaces contaminated in a controlled manner of thermoplastic acrylic polymers and copolymers varying in molecular weight and content of carboxyl, hydroxyl and acrylamide was demonstrated. It was found that increasing amounts of -COOH modification progressively increased the adhesion, OH modification however had no effect on adhesion, whereas $-CONH_2$ appeared to give a slight improvement at the 5% level of modification.

Mao and Reegen[42] further investigated the influence of functional groups such as nitrile, phenyl, chlorine, bromine hydroxyl in copolymers of methylmethacrylate or 10 mole percent and interpreted the results on the basis of electron availability as a chemical way of bonding. Both the benzyl methacrylate copolymer and the 2-phenylethyl methacrylate copolymer were also found to have high adhesion due to the π electrons of the aromatic rings.

On the basis of a study of the effect on adhesion of many monomer grafts containing specific chemical groups on a polypropylene polymer backbone, Lewis and Forrestal[46] concluded that, in general, acids or electron accepting groups increase adhesion to metals. Tertiary amines are not as effective as primary amines. In cases where polar groups increase adhesion, these investigators propose a chemical reaction or transfer of electrons across the interface between the metal surface and the polymer.

The most demonstrative examples correlating peel adhesion and electron availability of functional groups are provided by copolymers containing dimethylamino ethyl methacrylate and t-butylaminoethyl methacrylate[47]. Methyl methacrylate copolymers containing 10 mole % of the N-substituted amino monomers formed films that could not be peeled from the substrate. The presence of 2 mole % of the nitrogen-containing comonomer results in a twofold increase in peel adhesion.

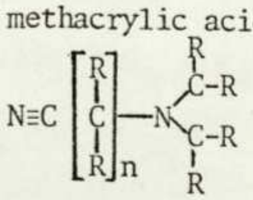
Nyquist and Yocum[48] recognised the beneficial effect of polymeric structural changes and electron availability concept on adhesion and studied the effects of modification of methylmethacrylate butylacrylate copolymer with 2-dimethylaminoethyl methacrylamide and 2-(1- aziridinyl)ethylmethacrylate.

The comonomers with an optimum level of 2% exhibited approximately the same adhesion promotion efficiency although this varied according to the substrate to which they were applied including tinplate, aluminium, galvanised steel, polyester and epoxy primers.

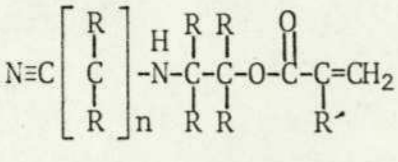
Gerber and Elisseva[49] studied the effect of functional groups of different chemical nature on the properties of acrylic coatings in terms of cohesive strength, adhesion, % elongation at break, vapour permeability (adsorption), and in hydrochloric acid atomsphere at 5% molar modification of n-butylmethacrylate with methacrylamide, methylolmethacrylamide, acrylonitrile glycidylmethacrylate, dimethylaminoethylmethacrylate and methacrylic acid.

Peel adhesion from aluminium foil was increased by the introduction of these groups apart from the amide group which showed no effect, the nitrile group on the other hand reduced adhesion. With the exception of CN group, all others increased the cohesive strength particularly the carboxyl and methylol groups.

The decrease in the protective properties under wet conditions with these groups was attributed to the positive electron density on the nitrogen atom and this decreases the adhesion values under such conditions. The hydrophobic character of (GMA) is responsible for the decrease in adhesion.

The application of cyanoalkylaminoethyl acrylates and methacrylates was claimed in a British and French patent[50] to improve the adhesion of acrylic polymer based latexes or non-aqueous coating compositions. These compounds as on 6' were prepared by reacting in a suitable solvent acrylic acid or methacrylic acid with an aziridine compound having the formula  . Examples of latices and lacquers containing small amounts of, e.g. 2-(2-cyanoethylamino)ethyl methacrylate in the copolymers were given.

The compounds may be in the form of an inorganic acid salt with the formula



$$N{\equiv}C\left[\overset{R}{\underset{R}{C}}\right]_n-\overset{H}{N}-\overset{R}{\underset{R}{C}}-\overset{R}{\underset{R}{C}}-O-\overset{O}{\overset{\|}{C}}-\underset{R'}{C}{=}CH_2$$

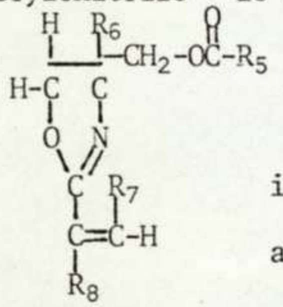
where R is hydrogen or alkyl.

The improvement in adhesion of methylmethacrylate to primed metal surfaces using modified polymer or polymers containing urea derivatives was claimed in British Patent[51]. These were effectively used as adhesion promoters which are specific to one particular type of substrate, i.e. primers.

A Dutch Patent[52] described thermoplastic acrylic finishes. Acrylic car finishes of the thermoplastic or lacquer type suffer from the disadvantage of poor adhesion to the primer. This was avoided by producing a copolymer of methylmethacrylate and glycidyl methacrylate and esterifying it with an aliphatic monocarboxylic acid whose only polar substituent, if any, is on OH group, e.g. Lauric acid. An aromatic acid is used for this purpose, e.g. benzoic acid.

The adhesion of coatings based on alkylmethacrylate polymers which show excellent gloss retention and durability, but have poor adhesion to many substrates including metals, glass, and conventional thermosetting sheet metal primers, was greatly improved[53] by the inclusion of a small proportion of acidic units and subsequent reaction with an alkylenimine or substituted alkylenimine. The latter class are known as aziridines, particularly ethylenimine (aziridine) and 1,2-propylenimine, or -2-methylaziridine.

In this way, the necessities for using operations like sealing or sanding or others prior to painting and restoration of the surfaces is eliminated. The imine-modified acidic units as adhesion promoters are either present in a separate polymer as an additive or are present in the alkylmethacrylate polymer backbond in an amount of 0.25%-5% of the total polymer weight.

Coating composition with the necessary balance of properties i.e. pigmentation with a variety of pigments and which have excellent adherence to acrylic lacquer coating, without sanding or buffing the coating before application, resistance to weathering and to water spotting which makes them well suited for use as an exterior finish or refinish for automobiles and trucks, have been claimed[54]. An acrylic oxazoline containing polymer consists of 30-70% MMA + <35% ester of an α,β-olefinically unsaturated mono carboxylic acid + < 10% acrylonitrile + 15 to 35% of an oxazoline compound with the formula  is suitable for finishing and refinishing lacquer coating.

The concept of the effect of structural changes on adhesion in other types of coatings was also explored particularly in problems related to blistering of coating and under wet conditions.

Moisture on a surface exposed to areas where mist and fog are very intense has harmful effect on the drying of the paint film and on its subsequent adhesion. Painting or priming presents a particularly difficult problem. Meler et al[55] overcame this problem by utilising phosphamino lipoid complexes prepared from phosphoric acid, esterified fatty acids and strong organic base choline. The residues of the latter have also anticorrosion properties. On application of the paint, the phosphoamino lipoids first anchor themselves with their polar groups on the surface. The oleophilic long chain groups of the esterified fatty acids act as bonding sites for the equally oleophilic binder, thus an oleophilic layer is formed on the surface which is capable of displaying water.

An interesting approach for preventing blistering and intercoat adhesion failures was explored by Heertjes and Jones[56]. In their adhesion studies of laminated unpigmented resin film to substrates they showed that blistering of a lacquer system on wood and combined blistering and corrosion on phosphated steel can be prevented or retarded when a resin film that forms a strong boundary layer with the substrate is used in combination with a top coat of a very stiff resin provided that no intercoat adhesion failure occurs. An example alkyd resin on wood and polyester resin film.

From the results of creep and the peeling off theory developed, prediction of the type of combination of two resins to give the best protection of the substrate against immersion in water can be made.

This phenomenon of the application of a strong boundary layer of invariable properties and with properties similar to the top film for adhesion improvement is in contrast with the theory of Bickerman of weak-boundary layer failure. Heertjes and Jones[56] also concluded that the boundary layer remains the same and that only the change in viscoelastic properties cause the change in the speed of peeling off of the film.

It has been reported[57] that the adhesion of alkyd resin-aminoplast resin coating compositions to metal surfaces was greatly improved by the modification or the addition of a relatively small amount of ungelled adduct of a polymer containing free hydroxyl groups and an anhydride of a discarboxylic acid, to give hard thermosetting coatings.

In acrylic thermosetting coating composition, the addition of 5% epoxide resin which is a polyglycidyl ether of phenolic compound as adhesion promoters was also claimed in a U.S. Patent[58].

The bonding of polyamide, rubber, PVC and rubber plasticised polyamide to metals, Cherkasskaya et al[59] found that the presence of functional groups, hydroxyl or nitrile resulted in adhesion promotion as a result of chemical and supplementary adsorption bonding. Polyamide containing sulpho groups had higher adhesion.

A study of the influence of the presence of functional groups in latex copolymers of alkylacrylates on the mechanical and adhesive properties of films was carried out by Sukarova et al[60]. 4-5 mole % of methyacrylic acid, methacrylamide and/or acrylonitrile were emulsion copolymerised with methylacrylate/butylacrylate monomers. The films were applied to an epoxide film of various thicknesses which was applied to glass. Modulii of elasticity, tensile strength, elongation at break and adhesion were measured.

It was concluded that the incorporation of small amounts of side polar groups in the chain of a linear polymer greatly affect the mechanical and adhesional properties of films and coatings. In addition, the ester interchange of polyalkylacrylate with carboxyl groups increased the adhesion, but the incorporation of amide and nitrile groups effectively decreased the adhesion. With increase in adhesion, internal stresses accumulate and are in no correlation with the tensile strength and modulii of elasticity of free films. Thus the incorporation of these or other polar groups in any polymer will affect the mechanical and adhesional properties and consequently coatings of required properties can be tailor-made.

A similar investigation on the effect of hydroxyl content of acrylic copolymers and those cured with polyisocyanates on the mechanical properties and adhesion to aluminium foil was carried out by Zorina et al[61]. The acrylic monomers chosen were methylmethacrylate, butylmethacrylate, butylacrylate and monomethylester of ethylene glycol methacrylate. Maximum adhesion was observed at 2.5% of hydroxyl content. The reduction in the MMA content to 40% results in increase in adhesion. However, the increase in the butylacrylate content decreases adhesion. An optimum ratio of these monomers was established for obtaining a suitable lacquer with the required properties.

The quantity of literature pertaining directly to methods of improving the adhesion to clean surfaces via the modification of the polymer structure as shown is relatively large. However, the aspect of improving adhesion to practical surfaces, i.e. surfaces which acquire contaminants under service conditions has been largely neglected. This deficiency has been relatively corrected in the topic of this thesis. The relevance to this topic of other work is outlined below.

New automobile engines after removal from post-assembly test stand, the still hot engines were normally coated with a solvent-oil based paint composition or engine enamel. These engines prior to being painted possessed an exterior oily surface resulting from the lubricating fluids used in the engine during their testing operation. This exterior oily surface made their subsequent painting difficult and the oil based paint led to certain pollution control problems. Thus a water based paint would have been considered desirable, but such was not known to be possible because of the incompatibility between water and oil. A solution to the above problem was offered in a U.S. Patent[62], by way of providing water reducible paint composition containing a special additive capable of altering the rheological surface tension characteristics of both the paint and the oily material on the surface. The additive used is C_3-C_{11} polyalkoxy compound of say 2,2-dimethoxypropane effective at 0.1-1.5% in alkyds, polyesters and acrylics water-reducible resin vehicles.

For effecting an adherent coating on the oily surfaces, the latter is maintained or must possess an elevated temperature upto as high as 95^{o}C. The coating composition has a pH of about 7.5.

In a study of the effect of additions of acids to an alkyd paint on its adhesion to aluminium cleaned only by solvent extraction, it was found[63] that sulphosalicylic acid, i.e. 3-hydroxy, 4-carboxy benzene sulphonic acid, acted as an adhesion promoter. To ascertain the level at which this acid is active and to examine the adhesion promotion mechanism, Prosser[64] postulated that at 1% addition the sulphonic acid group was strong enough to displace surface contamination layers of lubricants and attach firmly to the oxide surface of the metal. In addition, the OH and COOH groups of the attached acid then served to bind the alkyd by hydrogen bridging between suitable hydroxyls and oxygen.

A method of adhering unsaturated polyester resins to metal substrates was claimed in a U.S. Patent[65]. Unsaturated polyester resins have been used as coating materials for a great many substrates with exceptional strength and chemical resistance. However, it has been a problem to achieve good adhesion notably to metal substrates. The inventors of PPG Industries Inc.[65] discovered that modified unsaturated polyester reacted with polyphosphoric acid and cured by either ionizing irradiation or active light overcome this problem when coated to an iron phosphated treated cold rolled steel.

The addition of "low-shrink" or "low-profile" additives in polyester based resins which was necessary to overcome the shrinkage problem during moulding of fiber reinforced polyesters, created serious problems in finishing the cured part, namely the severe deterioration in adhesion of paints to the surface of the cured polyethylene based resin, due to the migration of the additives to the surface during polymerisation. However, addition of 7-15% of certain nitrogen containing vinyl monomers to the uncured low-shrink polyester increased the degree of adhesion between the thermosetting resin and overlying layers of paint[66]. The increase in paint adhesion produced by this invention is at least to the degree of conventionally formulated polyester based resins with the same paint and in many cases to a higher degree.

Vinyl monomers selected were acryl and methacrylamide, and dimethylamino ethylmethacrylate.

For this work the application of vinyl triethoxy silane as a modifier for the polymer chain was used. The literature covering their application to solve various problems are numerous.

In general, the application of trialkoxy silanes as coupling agents or adhesion promoters has been shown[67-77] to improve the strength of adhesive bonds of organic solids particularly those exposed to humid environments.

2.3. Fundamentals of Adhesion

2.3.1. Analysis of Bonding Forces and Their Contribution to Adhesion

The nature of the bonding forces which are responsible for producing adhesion of any species is of the very same nature as those that give (solids) their cohesive strength.

The forces have been classified as[78-80],

(a) Interatomic or (primary valency)

(b) Intermolecular or van der Waal's bonding; (secondary valency).

The primary forces are chemical bonding forces whose dissociation energies are very high of the order of 100 kcal/mole and which can be distinguished as:-

(1) Forces of attraction between ions.

The bond is based on the attraction between a positive and a negative ion.

The force of attraction, which obeys the inverse square law and is given by:

$F_i = q^+q^-/r^2$ where q^+ and q^- are charges of ions.

The interaction energy is equal to $U_i = q^+q^-/r$ = 140-250 kcal/mole.

(2) Covalent bonding forces.

This arises from a true sharing of electrons between two atoms with an interaction energy of 15-170 kcal/mole.

In specialised instances it is thought that bonds of this type do form in an adhesive joint as a classical case of chemical bonding.

Chemical cross-links are characteristics in the setting process of most structural adhesives where the chains join up to give a high cohesive strength. de Bruyne[81] (1947) has maintained that for many adhesives only van der Waal's forces are operative. However, substances such as protein, urea-formaldehyde and phenolformaldehyde and rubber do contain chemically reactive groups. Chemical bonds have been established in the sulphur vulcanisation for rubber-metal bonding[82] and have been suggested in the adhesion of phenolformaldehyde to aluminium alloys[83]. Chemisorption is not ruled out.

(3) Electrostatic bonding.

Skinner et al[84], (1953, 1954), found that when an adhesive is stripped from a metal surface an appreciable separation of electrostatic charge occurs if the break occurs at the adhesive adherend interface. His results indicated that these changes could only account for a very small part of the strength of the adhesive-adherend interface, but it is possible that under other conditions electrostatic charges may play a more important part. Derjaguin[85] (1955), maintains that electrostatic forces are the most important.

(4) Metallic bonding

This type of bond is found in metals. It involves the sharing of many electrons by many positive centres. The energy of attraction is between 27-83 kcal/mole. This type of bond is not significant in normal adhesive bonding.

The secondary intermolecular or van der Waal's forces are most important as they exist between all materials whether they are polar or not. These forces are additive of four types:

(a) Hydrogen bonds:

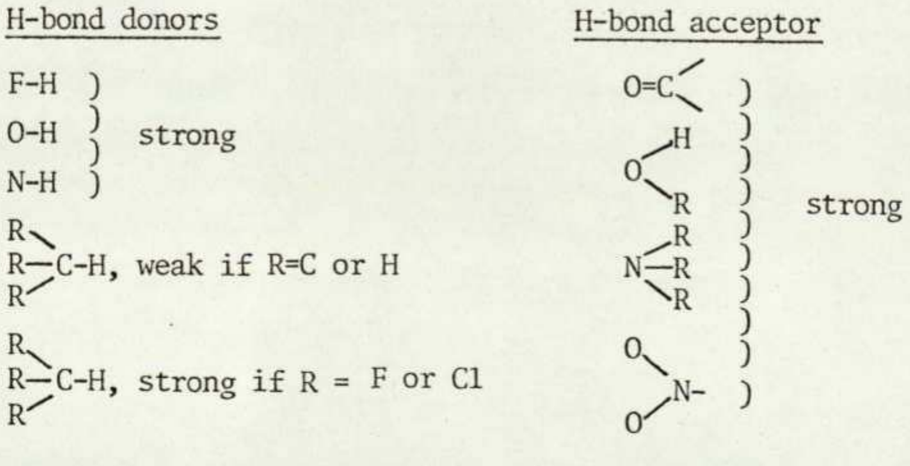
The hydrogen bond will form between molecules containing an active hydrogen and any other molecule containing an electronegative centre such as chlorine, oxygen or nitrogen. One pole of strong dipole attracted by two pole of another dipole, e.g. $\overset{+}{C}=\bar{O}$ $\overset{+}{H}-\bar{N}$. The classical case of hydrogen bonding occurs in water and alcohols and there is the strong interaction observed[86] between these and metal oxides, C=O---H-O, i.e. the hydrogen atom serves to link two electronegative atoms.

Hydrogen bonds can form in adhesive joints since they require only good molecular contact at a field of action of 2.6-3Å, and small activation energy with a relative strength of bonding energy of 12 kcal/mole.

If a carboxyl group (-COOH) is introduced in a simple non-polar polymer, e.g. polyethylene, the interaction to metal is further increased as a result of the special type of dipolar forces.

A specific case of the formation of hydrogen bonding is demonstrated in the remarkable adherence of the hydroxyl groups of epoxy resins to the electronegative oxygen atoms of aluminium oxidised through anodisation.

We can divide hydrogen bonds into donors and acceptors as illustrated below:



(b) Orientation forces or dipole-dipole interaction

A molecule contains a dipole when a positive and negative charge is separated at distance 'r'. As a result of the free rotation induced by the thermal energy or orientation energy $(\bar{\varepsilon})$, the average interaction potential energy between the two permanent isolated dipoles of 5 kcal/mole at distance 'r' with an average range of 4-5Å, was calculated by Keesom[87] as shown in equation (4).

$$\bar{\varepsilon}_o = -\frac{2}{3}\;\frac{\mu_1^2\,\mu_2^2}{KT\;r^6} \qquad (4)$$

where: μ_1 and μ_2 are the dipole moments of isolated molecules of type (1) and type (2), which are measured by Debye units, e.g. H-O = 1.6, >C=O = 2.5 and -C N = 3.8.

k - is Boltzmann constant

T - is the absolute temperature

The force can be represented by:

$$F = 4\;\frac{\mu^4}{KT}\cdot\;\frac{1}{r^7}$$

The validity of equation (4) ceases when steric hinderance prevents free molecular rotation. In addition there is attraction between molecules without permanent dipoles and the attraction between them does not fall off so rapidly with temperature. The energy of the forces produced by two interaction depends on the strength of the two dipoles and decreases with 6th power of the distance between centres.

The force is particularly interesting for strongly polarised molecules; the functional grouping (OH) with 1.9 Debye units is important to epoxy resins. This type of interaction can occur in bonding joints particularly with an adhesive containing polar groups.

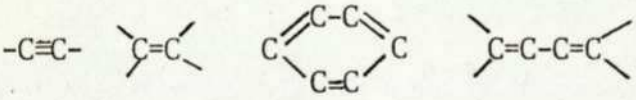
(c) Induction or Debye Forces

Debye[88] postulated that an interaction force is produced when a permanent (strong) dipole interacts with an induced dipole (weak), of nonpolar molecule because of its polarizability, i.e. separation of its charges. The potential energy ε_I which is independent of temperature is given by equation (5).

$$\bar{\varepsilon}_I = - \frac{1}{r^6} \left(\alpha_1 \mu_2^2 + \alpha_2 \mu_1^2\right) \qquad (5)$$

where α_1, α_2 - are the polari ability of molecules (1) and (2).

The force which can be expressed as $F = 12\alpha \ \mu^2 . \frac{1}{r^7{}_o}$ is weak with a field of action of 3.5 - 4.5 Å. Easily polarizable groups are



This phenomenon is particularly interesting in the case of metals which can be easily polarized. The superficial polarization explains not only the adherence of the organic lining films, but also the adsorption of gas and water.

(d) Forces between non polar molecules or dispersion effect

London[89] founded a theory for the interaction between non polar molecules of the same species, and postulated that the dispersion forces arise in all atoms and molecules whether charged or not, polar or non polar. At any instance in time a particular configuration of nuclei and electrons, the instantaneous dipole moment produces an electric field which interacts with the polarizability of an adjacent molecule (neighbouring) molecule and results in an instantaneous induced dipoles and mutual interaction to provide the dispersion force; $F = \frac{9}{2} h\nu\alpha \frac{1}{r^7}$ where:

h - Planck constant

ν - frequency of vibration

α - polarizability of the molecule

r - distance between molecules

The instantaneous electronic configurations and their dipoles show no directional preference and therefore no permanent dipole moment.

The attraction forces between molecules in which there is no permanent separation of charges but the assumed positive and negative charges are dissipated and created very fast and thus all are neutral.

With this concept London derived equation (6) for the interaction energy of two different species.

$$\varepsilon_{L_{12}} = -\frac{3}{4} \frac{\alpha_1 \alpha_2}{r^6} \frac{2I_1I_2}{(I_1 + I_2)} \tag{6}$$

where I_1, I_2 are the ionization potential of (1) and (2) and are tabulated for many compounds by Watanabe et al[90].

Some values of 'α' are given by Landolt and Bornstein[91], but it can be calculated from the index of refraction using Lorentz-Lorentz equation (7).

$$\alpha = \frac{n^2-1}{n^2+2} \cdot \frac{3\nu}{4\pi N_o} \tag{7}$$

where: n - refractive index

ν - molar volume

N_o - Avogadro's number

When the two molecules are of the same species equation (6) becomes:

$$\varepsilon_{L_{11}} = -\frac{3}{4}\;\frac{\alpha_1{}^2 I_1}{r_{11}{}^6} \tag{8}$$

Dispersion forces with short range action of 3.5-4.5Å, accounts for 75-95% of total molar cohesion of materials, and hence they are the major contributor to adhesion in joints. Thus the orientation effect is less important and the induction effect is practically negligible.

As these three energies, (b, c, d) decay with the increasing sixth power of the distance of separation (r), the attractive potential term (negative), i.e. the total interaction of a molecule of type (1) and one of type (2) can be expressed by equation (9).

$$\varepsilon_{12} = \frac{2}{3}\,\frac{\mu_1{}^2\mu_2{}^2}{KT} + \frac{3}{2}\;\frac{I_1 I_2 \alpha_1 \alpha_2}{(I_1 + I_2)} + \alpha_1\,\mu_2{}^2 + \mu_1{}^2 \tag{9}$$

For two molecules of identical species, i.e. $\alpha_1 = \alpha_2 = \alpha$; $\mu_1 = \mu_2 = \mu$ and combining equation (8) then equation (9) becomes:

$$\varepsilon_{11} = \frac{2}{3}\;\frac{\mu^4}{KT}\;\;\frac{3}{4}\;I\alpha^2 + 2\alpha\,\mu^2 \tag{10}$$

However, at small distances[79], a repulsive (positive) potential sets in rather suddenly and it is possible to represent it by formula (11).

$$\varepsilon_r = B\,e^{-cr} \tag{11}$$

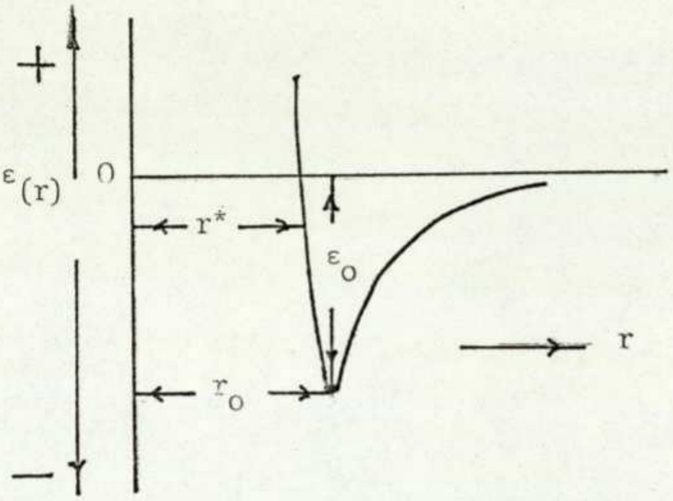
where B and C are constants.

For mathematical convenience ε_r is customarily represented by a high inverse power law, $\varepsilon_r = j/rn$ where $n = 12$.

The negative and positive forces of attraction are grouped together and can be represented by Lennard-Jones[92] potential energy 'ε' function, as shown in Figure 1, and in equation (12) bearing in mind that the force $F = -\frac{d\varepsilon}{dr}$

$$\varepsilon = \left(\frac{A}{r^6} - \frac{B}{r^{12}} \right) \qquad (12)$$

Figure 1.



The potential energy (ε) of a molecular pair passes through a minimum at which $\frac{d\varepsilon}{dr} = 0$, the negative potential minimum which is used to define an equilibrium distance (r_o) proportional to the cube root of molar volume ($V^{\frac{1}{3}}$).

If the molecules approach closer than the distance (r_o) the energy (ε) increases again and a distance (r^*) is equal to zero. The distance (r^*) may be regarded as an effective collision diameter for slow molecules.

Differentiation of equation (12) with respect to r yields

$$\frac{d\varepsilon}{dr} = 6 \frac{A}{r^7} - \frac{12B}{r^{13}}$$

$$r_o = \left(\frac{2B}{A}\right)^{\frac{1}{6}} \; ; \quad \varepsilon_o = - \frac{A^7}{4B}$$

$$\therefore \quad \varepsilon = \varepsilon_o \left[2\left(\frac{r_o}{r}\right)^6 - \left(\frac{r_o}{r}\right)^{12} \right]$$

A can be determined from van der Waal's constant (b).

Thus, the intermolecular energies (e.g. value) of ε_o give a direct measure of the intermolecular forces, if the molecular radii (the r_o's) are the same for two systems, then the forces are very simply related to energies.

2.4. Theories of Adhesion

The understanding of the nature of intermolecular forces has facilitated the advance of various theories to explain the adhesion phenomenon and there are four postulated theories. These are:

(1) Adsorption theory

(2) Electrostatic theory

(3) Diffusion theory

(4) Chemical interaction

In addition, it is also usually suggested that adhesion could be divided into two main types:

I. Mechanical adhesion

This is commonly referred to as interlocking of the adhesive into the pores or cavities in the adherend where it hardens and anchors itself somewhat below the surface.

II. Specific Adhesion

This is attributed to the attraction between smooth surface and adhesive arising from the primary and secondary valency forces which hold the atoms and molecules of the adherends themselves together.

(1) Adsorption Theory

This is based on the physical adsorption of molecules of either gases or liquids onto solid surfaces influenced by the physical forces of the types so far discussed. The formation of covalent bonds is reinforced by permanent dipoles or by chemisorption. Fresh surfaces are unavoidably exposed to air and adsorption of molecules occur because atoms at the surface of a solid, unlike those in the bulk are not surrounded on all sides by neighbours.

The adsorption theory emphasizes the occurrence of orientation of dipolar/non polar molecule when placed between two phases across which a change of dielectric constant occurs, with its non-polar part in the medium of least dielectric constant. However, in the solid adhesive orientation is restricted, but adhesives are applied as fluid. Experimental evidence does confirm that the polar part of molecules are held firmly in the surface and the hydrocarbon backbones cohere by van der Waal's force, away from the surface.

Evidence of the importance of orientation on adhesion improvement is provided by Glazer[29] by the introduction of hydroxyl groups on the surface of rubber and hydroxylating the double bond.

Sharpe[93] showed that monolayers orientated and interacted with the surface (as in the case of the reaction of the carboxyl groups with germanium crystal to form the salt), is an example of physical adsorption followed by chemisorption.

The work of Schonhirn[94] on the deposition of a monolayer of steric acid on aluminium and the improvement in adhesion with polyethylene indicates the link between orientation with adsorption theory as well as the diffusion theory. The adsorption theory can only be quantitatively discussed on the grounds of molecular contact and in terms of the adhesion between liquids and solids. This would involve the discussion of surface energies and wetting phenomenon. (See section 2.8).

2. The Electrostatic Theory

A contribution to adhesion has been thought to arise from contact or junction potentials between adhesive and substrate. This theory is developed by Deryagin[95] and his co-workers. Contact electrification is supposed to occur when adhesive and adherends are brought together and the asymmetric charge is sufficient to account for the bond strength.

Wake[96] reviewed this topic and summarised the situation with this statement "It is probable that charge dissymmetry which is known to exist at the moment of destroying an adhesive bond probably exists during the life of the bond and contribution to the force required to break it. This contribution may, as with thin evaporated metals on glass, be a major component, but it is by no means certainly so".

3. Diffusion Theory

Diffusion of polymer molecules into the adherends with the total loss of the interface can only occur under good molecular contact particularly between like molecules and when this is achieved, dispersion forces are adequate and no diffusion is necessary.

The diffusion theory is not favoured when different polymers are in contact due to the lack of solubility of one high polymer in another, but it is probably correct when considering the autohesion of tacky adhesives or heat seal adhesives.

Voyutskii[97] discussed the validity of this theory over a wide range of phenomena. Vasenin[98] examined the diffusion theory with a fundamental theoretical approach starting from a formulation of the condition for and rate of diffusion of small and long chain molecules into high polymer substrates. He found that the penetration of a long chain molecule into a polymeric substrate is limited to the diffusion of the end of the molecule to a depth of 10 or so carbon atoms. The growth of bond strength is achieved with time and as a function of molecular weight. Thus, the diffusion theory was formulated from the relation of theoretical adhesion values to physico-chemical parameters. The same can not be said for the adsorption theory since there has been a gap between say heats of adsorption and bond strengths.

However, for low energy solids the relationship between adhesion and interfacial free energy is claimed and in most important technological applications the adsorption theory has gained acclaim.

4. Chemical Interaction

A major contribution to adhesion is postulated to arise from actual chemicals. This is the conventional role of the adhesive formulator to build active groups into the adhesive which will chemically react with the substrate. This will only be successful if the number of active sites is also brought into consideration. A sufficiently high contact density must be achieved to obtain a successful bond. However, success in this direction has been achieved not by modifying the interface, but by changing the bulk adhesive properties. The role of adhesive morphology and structure must be excluded.

2.5. Effect of Nature of Surfaces, the Attraction Between Molecules and Layers of Molecules, and the Strength and Breaking of Joints

Before approaching the general question of paints and their action, it is convenient to discuss first the nature of the contact between a solid surface and an adhesive and the interaction between them.

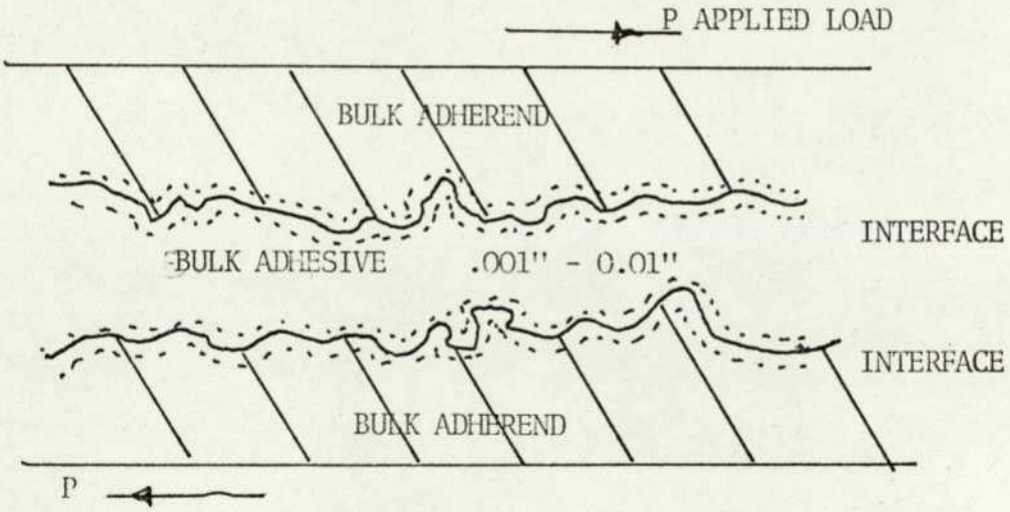
It is quite well known that the surface of any solid is different from the bulk material, and it is a special type of interface in which one of the phases is gaseous. A knowledge of the nature of interfaces between phases non of which is a gas is of great importance.

On an atomic scale, and however carefully a surface is prepared, it is very irregular and can resemble mountain ranges where peaks (asperities) have varying heights and peak to peak separation.

When two surfaces are brought together, they actually will touch at only a few of the asperities and high pressure are generated resulting in plastic flow, and formation of an area of true contact. The latter also depends on the ability of the adhesive to penetrate and fill the crevices which is a function of its viscosity preventing less than the total surface to be involved in the bonding process.

The force required to break asperity bonds is proportional to the true contact area and to the load force. Failure may occur in an adherend, at the interface or in the adhesive, depending on joint geometry, strain rates which are important to time dependent materials, the presence of weak boundary layers, which are loosely fastened to the base, chemistry of the materials, residual stresses due to shrinkage, and thermal and chemical environment effects.

An idealised sketch of an adhesive bond is shown below.



The performance of the adhesive joint is always judged by the strength of the joint, the purpose of which is to carry load and transmit it from one component to another, and is indicated by the applied load (P).

For the bulk region the distinct physical size and properties can be determined, but they are difficult to define for the interface which is a boundary layer area.

Theoretical calculations of the strength of cohesion forces of a perfect matter, i.e. the intermolecular and interatomic forces, between atoms and molecules for covalent and interatomic forces as a function of the distance between atoms and molecules for covalent and intermolecular forces, is known to be much higher than then realised.

For an ionic solid, sodium chloride and on the basis of ionic attraction, de Boer (1936)[99] calculated a cohesive strength of 400 kg/mm^2 and obtained 20 kg/mm^2 when he considered the physical forces alone. The breaking stress however was only 0.6 kg/mm^2. This can be attributed to the imperfections in the structure and to the flaws from which fractures propagate, and is reflected in the adhesion values. A similar mismatch occurs when two different bodies adhere with the concentration of flaws at the interface between the adhesive and the adherend.

Eley (1961)[100] calculated the normal force of adhesion required to pull-off a liquid leaving the solid surface covered with adsorbed film from purely thermodynamic grounds. For a linear hydrocarbon liquid of surface tension 30 engs/cm^2, or dyne/cm, the thermodynamic work of adhesion (W^+_{ASL}) which will be discussed later, was divided by a distance of (3×10^{-8} cm) over which the molecular forces fall to zero, (monolayer thickness of 3Å., an estimated force of 2000 kg/cm^2 or (27000 psi) was obtained. This value is much greater than is found in practice. For instance, Kraus and Manson[101] reported a tensile failing load of 183 kg/cm^2 for polyethylene/steel joints. Tabor[102] (1951), made similar calculations for direct tension, but Kemball[103] discussed the problem of the shear strength of joints in terms of the surface mobility of adsorbed molecules and assumed that the maximum variation of potential energy over a surface composed of regularly spaced atoms was 25% of the heat of adsorption. He arrived at a shear strength of 4.34×10^9 dyne/cm^2 (63000 psi) which drops to 1/10th of the stress as the mismatch in the wavelength between the periodicity of the surface imposed on it, becomes more pronounced.

It is clear that the ordinary forces of cohesion are more than adequate to account for the failing loads of joints, and as de Bruyne[81] pointed out that van der Waal's or London dispersion forces form an adequate basis for adhesion. More molecular contact of one substance with another, result in a bond as strong or stronger than either material, if strengths approaching the theoretical strength are realised in practice.

The review of the work on the experimental measurements of the van der Waal's forces, and the attraction at various molecular distances which falls off very rapidly with a sixth power law, carried out by Wake[96] led to the statement that "adsorptive forces are strengthened by long range forces, capable of bridging flaws of dimention equivalent to several molecular layers and biting, as it were, across the irregularities of the phase boundary".

2.6. Adhesion of Paints

In considering the adhesion of coatings to their substrates, the important aim is to obtain as much as possible a level of adhesion during the time available for formation of the film, with minimum surface preparation and regardless of the purpose the paint serves, it must adhere well for relatively long periods of time, i.e. the level must be maintained for the whole service life of the paint.

The success of multi-coat paint films, relies primarily on the ability of first coat to attach itself to the underlying surface.

In principle, successful coatings have been designed for a given application. However, many coatings, even some of the toughest paint films, flake or peel from their substrates, although the only significant external force operating is the weight of the film which is usually 1-50 mg/cm^2.

The reasons for this behaviour appears to involve the following:

(1) Anticipated stresses generated internally due to the differential dimentional changes in the volume of the film during film formation. Until the development of solventless type systems, half of the paint composition is comprised of a solvent or water, which on evaporation contracts the film (shrinkage).

(2) Unanticipated external stresses which are transmitted to the interior of the film as a result of thermal differential expansion, mechanical deformation arising from environmental

temperature changes. The effect of water is deleterious as it gets absorbed, the film blisters giving an osmoses effect and if there are water soluble products, the effect is even more drastic.

(3) Chemical changes of the paint film with loss of osmoses effect and poor adhesion as they form at the interface.

(4) Initial adhesion is low because of poor tolerance of the film to dirty surface, inadequate preparation before painting.

(5) Stresses occurring at the interface.

(6) Unsatisfactory painting and/or drying conditions.

(7) Inadequate preparation of paints before use and failure to maintain them in suitable condition during use.

These factors have been comprehensively studied by many workers[104-106].

2.7. Contamination of Surfaces

To improve the ability of paints to be retained, the surfaces are normally subjected to chemical or physical changes to overcome the defective structure of metal oxides. The oxide film inherets this property of low protective capacity because it is either too thick and fissured, too thin and permeable, or it is absorbent and is liable to attach contaminants, principally organic types deleterious to adhesion. In addition, "water" is also of crucial importance.

It was found[107] that the heat of immersion of powders in a series comprising water, alcohols, organic acids, esters and hydrocarbons, was invariably the highest with water as inorganic oxides. The surface of metal in a humid environment is likely to be covered with at least a monolayer of water, which is not displaced when the metal is painted[108]. This was also supported by the work of Haydon[109] who showed that the adsorption of polar molecules like amines and alcohols on metallic surfaces is actually onto a layer of water and not directly on the oxide.

Bowden and Tabor[110] in their studies of friction, found an equilibrium film two monolayers thick on very clear platinum. The thickness of such films may rise to 20 to 50 monolayers, particularly if the surface carries traces of soluble materials.

In a normal atmosphere, any clean surfaces will rapidly acquire a film of contaminant which can be detected by becoming progressively more hydrophobic on exposure and less water-wettable.

Important environmental surface defects which are usually present and are deleterious to adhesion are; the oxide films of unsuitable properties, corrosion products conducive to further corrosion, and invisible but strongly adsorbed organic contaminant.

The thickness of the oxide film formed on aluminium at room temperature and at 40-45% RH, was reported by Andreeva[111] to be in the range of 10-22Å as a result of oxygen adsorption.

Commercial metal strips are sheet metal and are prepared by cold-rolling a cast ingots, between rolls in roll mills down to the required gauge, by stamping and some metal parts are made by drawing, using a lubricant to reduce the power consumption and prevent cold welding of strip and roll. The sheet is then coiled and annealed. The surface may be buffed and polished.

As a result of this process, the metal surface will carry soils of the most diverse nature including:

(1) rolling lubricant residues, fatty materials and oxidation inhibitors

(2) drawing compounds, grinding lubricants containing sulphurised and chlorinated oils, corrosion preventives for preserving sheet in storage and transport, (inhibitors mineral oil and waxes), i.e. to prevent storage stains

(3) degradation products of these arising from oxidation or heating

(4) foreign matter, (dust imbeddes, metallic particles)

(5) moisture

The lubricant is usually a mineral oil containing surface active additives and is comprised from vegetable oils, soaps, esters and long chain alcohols.

Schey[112], Bizobahaty[113] and Guminski and Willis[114] have discussed the constitutions and the use of these components in rolling various substrates to include minor oil lubricants containing 5% rapeseed oil, phosphate esters, oleic acid, palm and colza oil and isopropyl alcohol.

The state of the surface of the substrate has a determining influence upon the penetration by the coating and hence on its long-life performance and adhesion. Therefore, it is important that the majority of deposits are removed which is an expensive operation.

Methods of removing contaminants and pretreatments of metal substrates were reviewed by Prosser[108,115].

The retention of rolling lubricants on cold rolled metal strip is believed to be firm and there is no evidence to suggest that all organic matter is removed by annealing. The presence of this residue, even if of the order of a monolayer is of importance to the paint technologist because it has an important bearing upon adhesion characteristics of paint films.

Evidence of the presence of a lubricant on aluminium sheet prepared from an ingot by rolling lies in the following circumstances:

(1) The sheet is very strongly hydrophobic in nature. The occurrence of interference colours from oily films on the bath surface in the acid pickling of steel strip even after rigorous solvent degreasing, is readily visible to the naked eye.

(2) The organic contaminant can be readily detected on aluminium sheet from the infra-red spectrum of the detritus. Johnson[116], who collected the residue by abrasion of the sheet even after solvent wash followed by a water-rinse and even after repeated abrasions, offered direct evidence of carbonyl and alkyl groups on

aluminium and phthalate esters on stainless steel strips.

(3) The sheet cannot be made hydrophilic by prolonged extraction with solvents.

(4) The adhesion of many film-formers to a solvent extracted sheet is poor.

It was suggested[108] that the lubricant may be physically entrapped in the oxide latice with some parts of its structure protruding which explains the great difficulty in its removal.

Prosser[63] measured the adhesion of ten different paints to aluminium sheet before chemical cleaning of the surface and concluded that the adhesion of this wide range of film-forming materials was poor. However, the adhesion was improved after chemical cleaning of the substrate.

The work of Prosser and Sherwood[117] confirmed the existence of firmly retained rolling lubricant on a cold-rolled aluminium after various cleaning procedures, in a model experiment using C^{14} labelled lubricants.

The effect of various treatments of the aluminium on the residual content showed that after petrol washing readily detectable amounts were found, after hot extraction with solvents, the residues corresponded to a monolayer, sulphochromating reduced the amount retained to about one tenth of the original value. Even after annealing at 350^{o}-$400^{o}C$, the residues constituted to $\frac{1}{2}$ monolayer, but the surface was water-wettable. They suggested that all surface treatments function by replacing a surface carrying organic contaminant by a fresh clean one.

The effect of deliberate contamination of steel with stearic acid, petroleum jelly and lanolin as commonly used rolling lubricants, at two different levels of contamination on the adhesion of epoxy/polyamide, epoxy ester polyurethane, chlorinated rubber, alkyds and styrene/butadiene copolymer, found that the paints were sensitive to stearic acid. None was sensitive to the lower level of petroleum jelly.

The adhesion level of various resin paints indicated significant correlation between adhesion and contamination level and the most deleterious contaminant is stearic acid which persists even after annealing.

It was felt therefore that paint designed to accommodate such contamination might ensure that failures arising from this cause could be considerably reduced, and investigations on the effect of tailor-making of a polymer on adhesion to "dirty" surfaces is an interesting topic of research.

2.8. The Role of Wetting and Spreading in Adhesion

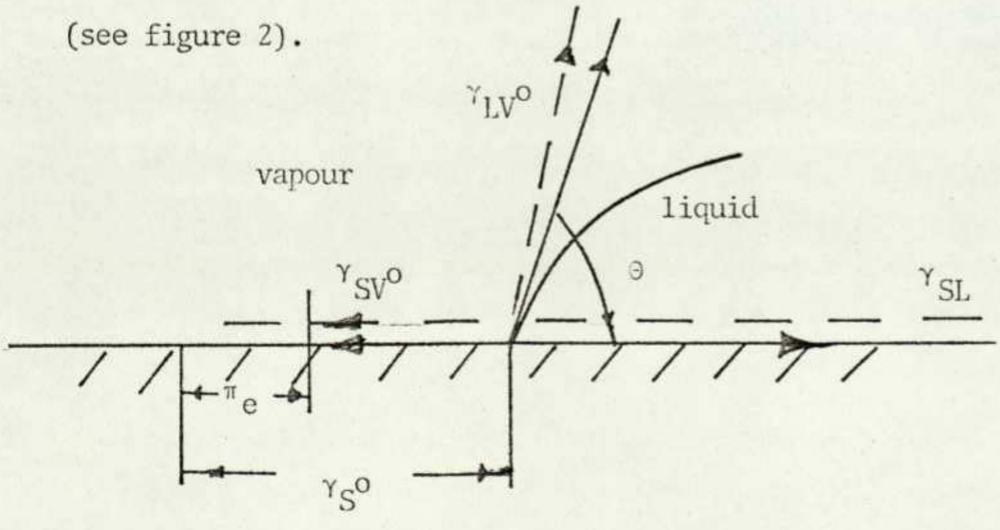
2.8.1. Thermodynamic Approach

The forces which operate at the surfaces of solids and liquids arise from the fact that the potential field around the molecules in the surface is unsymmetrical. This means that the attractive van der Waal's forces in the surface have a larger component into the bulk of the liquid or the solid than in any other direction. Consequently, a surface will always tend to reduce itself to a minimum and examples of this are the spontaneous condensation of fogs and aggregation of solids. It is this free energy which, when expressed in erg/cm^2 is equal to the surface tension in dyne/cm.

The liquid-solid interfacial free energy is a minimum when liquid and solid are the most perfectly matched to each other in each of the components of surface tension, separately, i.e. the polar component, the dispersion component and the induction component.

The classical description is usually done in terms of an equilibrium contact angle.

When a liquid is placed on a solid surface it spreads out until the forces operated attain equilibrium with each other. (see figure 2).



The thermodynamics of the solid-liquid interface is based on that of Young[118] for the contact angle, and that of Dupré[119] for the work of adhesion, i.e. the Young-Dupre equation demonstrates the relationship between the properties of wetting and contact angle to adhesion.

From figure 2, and if the solid is insoluble in the liquid, the equilibrium of the horizontal components of force by a vector argument and in terms of Young's relation requires that:

$$\gamma_{SV}^{o} = \gamma_{SL} + \gamma_{LV}^{o} \cos \theta \qquad (12)$$

where γ_{SV}^{o} and γ_{LV}^{o} are the free surface energy of the respective solid and liquid in equilibrium with the saturated liquid vapour.

γ_{SL} - is the free surface energy of the solid-liquid interface.

θ - is the contact angle between the solid and the liquid.

However, the work of adhesion, i.e. the decrease in free energy, required to separate 1 cm^2 of solid-liquid interface in vacuum leaving a perfectly naked solid surface is expressed by the Dupré equation:

$$W_{A(SL)} = \gamma_{S}^{o} + \gamma_{LV}^{o} - \gamma_{SL} \qquad (13)$$

where: γ_{S}^{o} - is the surface tension of the solid in vacuum, i.e. is the work necessary to create a new surface of 1 cm^2 in vacuo at $0^{o}K$ and is identical with the free surface energy of the solid at $0^{o}K$.

γ_{LV}^{o} and γ_{SL} are the same as in (12).

Combination of equations (12) and (13) provides the Young-Dupré relation:

$$W_{A(SL)} = (\gamma_{S}^{o} - \gamma_{SV}^{o}) + \gamma_{LV}^{o} (1 + \cos \theta) \qquad (14)$$

This model neglects the presence on the free solid surface of an adsorbed film of vapour on retracting the liquid in equilibrium with the saturated vapour pressure (p_o) of the liquid. The adsorption must reduce the surface energy of the solid (otherwise the adsorption would not take place). This reduction which may be regarded as free energy decrease on immersion of a clean solid in the vapour of the liquid, thus giving a tension balance to the drop, is called the spreading pressure (π) and is given by:

$$\pi_e = (\gamma_S{}^o - \gamma_{SV}{}^o) \qquad (15)$$

Hence $W_{A(SL)}$ of equation (14) becomes:

$$W_{A(SL)} = \pi_e + \gamma_{LV}{}^o\ (1 + \cos\theta) \qquad (16)$$

However, the work of adhesion gained on wetting will be reduced by the contribution of the adsorption energy from the spreading pressure and a new quantity of work of adhesion can be defined to account for the presence of the adsorbed film as:

$$W^*_{A(SL)} = \gamma_{SV}{}^o + \gamma_{LV}{}^o - \gamma_{SL} \qquad (17)$$

Substituting equation (12) in equation (17) and resolving for W^*_A we obtain measureable quantities and a linear function of the surface tension of the wetting phase (γ_{LV}) and the cosine of the contact angle as:

$$W^*_{A_{SL}} = \gamma_{LV}{}^o\ (1 + \cos\theta) \qquad (18)$$

For complete wetting, i.e. when $\theta = 0$; $\cos\theta = 1$ and assuming that $\gamma_{LV}{}^o = \gamma_L$, a limiting value of $W^*_{A_{SL}}$ and $W_{A_{SL}}$ are obtained.

$$W^*_{A_{SL}} > 2\gamma_L \; ; \; W_{A_{SL}} > \pi_e + 2\gamma_L$$

The common practice is to neglect the term π_e, which is normally obtained form the adsorption isotherms of the gas on the solid, because it is small for low-energy solids on which $\Theta > 0$. For an alkane liquid such as heptane on teflon, PTFE, π_e is between zero and 2 ergs/cm^2. With this assumption, the free energy required to produce rupture is equivalent to the work of cohesion in the liquid, i.e. $W_C = 2\gamma_L$.

Since the free energy change is less by (π_e) therefore $W_{A_{SL}} > W_C$ and failure of an adhesive joint as was pointed out by Tabor[102] is expected to occur in the body of one of the adherends rather than at the interface between solid and liquid.

However, there is a discrepancy between the measured work of adhesion and the strength of the adhesive joints.

Harkins[107] and others have used the free energy of adhesion to estimate the force of adhesion. The results was several orders of magnitude higher than the experimental which was affected by the mode of separation assumed to be absolutely parallel which did not agree with the geometry of the samples.

A weak correlation was also found[120] between contact angle and adhesive strength.

This discrepancy is attributed to two factors:

(a) The thermodynamic work of adhesion is the work done in a reversible process, i.e. the approach in deriving the Young-Dupre relation does not apply to solids which undergo appreciable plastic flow before rupture. Hence the greater part of the energy is expended or dissipated in deforming the solid.

(b) Absence of force with which the adsorbed film will resist shear because the thermodynamic approach deals with energy changes when the liquid or vapour is placed or removed.

Nevertheless, the approach does help to understand the adsorption and growth of films at the interface and their spreading and wetting behaviour.

In the 1950's a model was proposed by Good and Girifalco[121,122], for determining and describing the properties of γ_{SL} and γ_{SV}.

In Young's equation, the meaning of γ_{SV} is a force acting parallel to the surface. But γ_{SV}, as Good pointed out, is a specific free energy, i.e. the change in free energy that accompanies a variation in area as given below:

$$\gamma_{SV} = \left(\frac{\partial G}{\partial A_{SV}}\right)_{T,\ P,\ Ni} \qquad (19)$$

where ∂A_{SV} can only be varied by translational motion perpendicular to the surface γ_S.

The vertical component of γ_{LV} is balanced by the elastic force in the solid, i.e. the elastic energy that is stored in response to the vertical component of force. When the solid is a purely elastic body, the deformation is reversible, otherwise there will be a plastic deformation.

Good offered a new derivation of Young's equation based on three steps of thermodynamic process, and stated that the only work done involving the solid is done in motion perpendicular to the surface. He obtained equation (20).

$$\gamma_{LV} \cos \theta_Y = \gamma_{SV} - \gamma_{SL} \tag{20}$$

γ_S can not be measured directly as γ_L because of three distinct reasons:

(a) shear strength of solid and of forces are generally anisotropic

(b) work of plastic deformation, cleavage and stress are properties with the right units; $\Sigma \left(\frac{\Delta G}{\partial A_{hkl}}\right) dA_{hkl}$

(c) every crystal face has its own energy, i.e. different energy density, $\gamma(hkl)$.

Good and Ginifalco[121,122] identified 'γ_S' with the free energy of reversible cleavage of the solid in vacuum, i.e. $\gamma_S \equiv \left(\frac{\partial G}{\partial A_S}\right) = \frac{\Delta G^{Cl}}{2}$, and the latter with the free enrgy of cohesion ΔG^C.

When the solid is in equilibrium with the vapour at pressure of (p) less than saturated pressure p_o, then

$$\pi_e = \gamma_S - \gamma_{SV}, \ p < p_o$$

Then Young's equation (20) becomes:

$$\cos \theta_Y = \frac{\gamma_S - \gamma_{SL}}{\gamma_{LV}} - \frac{\pi_e}{\gamma_{LV}} \tag{21}$$

As $\pi_e = 0$, then $\cos \theta = \frac{\gamma_S - \gamma_{SL}}{\gamma_{LV}}$ (22)

To test the relationship between strength and contact angle indirectly, and to eliminate the necessity of conducting measurements of the angle, a valuable concept of critical surface tension was formulated.

2.8.2. Critical Surface Tension

Zisman and co-workers[123-127] established that the wettability of low-energy organic surfaces, or of high-energy surfaces coated by an organic film is determined by the nature and packing of the surface atoms of the exposed groups of atoms and molecules. Making the assumption that the surface composition of the solid polymer was the same as that of the horizontally oriented polymer molecule Zisman measured the effect of surface constitution on the wettability. For this he[43,128] defined a critical surface tension term (γ_C) as an empirical parameter characteristic of the solid only and varying in a regular fashion with the structure of the surface.

"γ_C" is determined experimentally using the linear relationship between the cosine of the contact angle of an homologous series of liquids and their surface tension. Extrapolation to the line of cos $\Theta = 1$ gives γ_C value. Some deviation occurs in the obtained value of γ_C partiuclarly when the extrapolacion covered a region rather larger than that containing the data. However, the relation between the contact angle and the surface tension of the liquids can be related empirically[128] by the following equation:

$$\cos \Theta = a - b\ \gamma_{LV}{}^{o} \qquad (23)$$

where a and b are arbitrary constants.

Since γ_{LV} approaches γ_C as Θ approaches zero, then $1 = a - b\gamma_C$ and $a = 1 + b\gamma_C$. In addition, and by substituting for (a) in equation (23) we obtain:

$$\cos \Theta = 1 + b\ (\gamma_C - \gamma_{LV}) \qquad (24)$$

By eliminating cos θ between equation (18) $W_A^+ = \gamma_{LV} (1 + \cos \theta)$ and equation (24) a new expression can be obtained for the reversible work of adhesion, i.e.

$$W_A^* = (2 + b\gamma_C)\gamma_{LV}o - b\ \gamma_{LV}^2o$$

This equation is of a parabola with the concave side towards the surface tension axis and has a maximum value of W_A^* occurring at

$$\gamma_{LV}o = \frac{1}{b} + \tfrac{1}{2}\gamma_C$$

The maximum value is given by

$$W_A^* = \frac{1}{b} + \gamma_C + \tfrac{1}{4}\ b\ \gamma_C^2$$

Thus, the significance of this context for the relation between the strength of an adhesive bond and γ_C becomes apparent. Indeed, Levine et al[129] reported a linear relationship between γ_C and the tensile strength of variety of polymers bonded to metal buttons which were bonded on both sides by epoxy adhesive and broken in tension. As γ_C increased the tensile strength of bond increased.

2.8.3. Molecular Theories of Interfacial Forces

In 1953 and 1954, a theory of liquid-liquid interfacial tension was developed by Girifalco and Good[121,122,130], based on the theory of solubility of nonelectrolytes[79], and the Barthelot[131] geometric mean hypothesis for the attractive constant in the van der Waal's equation, i.e. $a_{12} = \sqrt{a_{11}a_{22}}$ where a_{11} and a_{22} are the attractive constants for molecules of species 1 and 2, and a_{12} is the attractive constant for interaction of molecules of species 1 and 2.

It was proposed that the free energy of adhesion between two phases may be given by the geometric mean of the free energies of cohesion of the separate phases.

$$|\Delta F^a_{12}| = 2\sqrt{\gamma_1\gamma_2} \tag{25}$$

Equation (25) can also be put in the following form to yield:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1\gamma_2} = |\gamma_1^{\frac{1}{2}} \quad \gamma_2^{\frac{1}{2}}|^2 \tag{26}$$

Good related the interfacial free energy 'γ_{12}' between the liquids to their surface free energies γ_1 and γ_2 to an interaction parameter (ϕ) which is the ratio between reversible work of adhesion ($\gamma_1 + \gamma_2 - \gamma_{12}$) and the geometric mean of the work of cohesion of the two components $2\sqrt{\gamma_1\gamma_2}$, i.e.

$$\phi_{\substack{12\\SL}} \equiv \frac{\gamma_1 + \gamma_2 - \gamma_{12}}{2\sqrt{\gamma_1\gamma_2}} \tag{27}$$

The general formula then becomes,

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\,\phi\,\sqrt{\gamma_1\gamma_2} \tag{28}$$

The validity of equation (26) was tested by the computation[121] of the values of ϕ_{12} which is a unique property of the pair of substances 1 and 2, for water-organic systems and for mercury vs. water and vs. various organic liquids using the literature values of surface tension and interfacial tension date. ϕ values ranged from 0.5 to 1.15.

To define the conditions for ϕ to be close to unity or otherwise, the attractive force across the interface or across a defined plane in a bulk liquid was separated into its components due to dispersion induction and dipole-dipole attractions[132]. Consequently, it was concluded that 'ϕ' should be close to unity when the cohesive forces within each separate phase and the forces acting across the interface are of the same type. Values of less than one were found when the forces were unlike, i.e. in cases when nonhydrogen bonding organic compounds vs. water, an organic compound vs. a liquid metal and a salt vs. a metal. ϕ can be computed for any pair of substances from the physical properties of the two substances.

As immisible phases < 1 and if the two phases are partially immisible then $\phi > 1$.

From Young's equations, i.e. $\gamma_{SV^o} = \gamma_{SL} + \gamma_{LV^o} \cos \Theta$ and $\pi_e = (\gamma_S{}^o - \gamma_{SV}{}^o)$ and solving for cos Θ, we obtain from equation (28) the following:

$$\cos \Theta = 2\,\phi \sqrt{\frac{\gamma_S}{\gamma_L}} - 1 + \frac{\pi_e}{\gamma_L} \qquad (29)$$

As $\pi_e = 0$ as explained previously, then

$$\cos \Theta = 2 \sqrt{\frac{\gamma_S}{\gamma_L}} - 1 \qquad (30)$$

This equation provides a method for determining γ_S by plotting $\cos\theta$ vs. $\frac{1}{\sqrt{\gamma_L}}$ and extrapolate the line to $\cos\theta = 1$.

This method was adopted later by Fawkes[133] and it is an improvement over Fox-Zisman plot for 'γ_C', although the points do not offer an easy way of drawing straight lines by the 'naked eye'.

Good later offered a more suitable method for determining γ_S, based on the use of the following equations obtained by solving equation (29) and (30) for γ_S,

$$\gamma_S = \frac{[\gamma_L(1 + \cos\theta) + \pi_e]^2}{4\phi^2\,\gamma_{LV}}$$

$$\gamma_S = \frac{\gamma_{LV}\,(1 + \cos\theta)}{4\phi^2}$$

Here, plot of $\gamma_{LV}\,(1 + \cos\theta)^2/\phi^2$ vs. γ_{LV} gives γ_S at the intercept of the best horizontal line.

Since γ_S is a property of the solid alone, then for a particular solid $\theta = \theta\,(\gamma_L, \gamma_{SL}, \pi_e)$. If $\pi_e = 0$ and if ϕ_{SL} is constant for an identified series of liquids, the largest value of γ_L for which $\cos\theta = 1$, i.e. $\lim_{\theta\to 0} \gamma_{LV} = \gamma_C$, then:

$$\gamma_C = \phi_{SL}^2\,\gamma_S \tag{31}$$

ϕ vary by at least 5% which when taken into account equation (31) becomes:

$$\gamma_C = \gamma_S\,\phi_{CSL}^2$$

Where ϕ_{CSL} is the value of ϕ for the member of the series of liquids for which $\gamma_{LV} = \gamma_C$ or the extrapolated value if the γ_{LV} of the lowest member of the series is greater than γ_C.

As ϕ differ by 50% for various series of liquids on a solid as ϕ depends on chain length, then γ_C can be different for a solid against say n-alkanes or alcohols.

Fowkes

Fowkes[128,80] derived an equation for the estimation of the interaction energies of a liquid interacting by dispersion forces on a non polar solid and for the discription of the role of dispersion forces on the contact angle of such a liquid. His equation also offers a method for calculating the dispersion force component of the surface energy of the solid.

Fowkes[133,134] proposed that the surface free energy of a liquid could be broken up into its dispersion, induction and dipolar components. The subdivision was exactly the same in concept as the subdivision of the energy of cohesion of the separate phases proposed by Girifalco and Good[121,122,130] as shown in their equation (26).

Because of the unbalanced action of the intermolecular forces on the surface molecules, an additional free energy emerges and consequently the surface energy of one phase is less than the surface energy of free surface. This reduction in the surface energy is controlled by the balance between the intermolecular forces in phase (1) and those in phase (2).

To put the above argument in a mathematical form, and if we assume (γ_1) is the surface energy of phase (1) at the interface with phase (2), then $\gamma_{1(12)}$ can be represented by:-

$$\gamma_{1(12)} = \gamma_1 - (\gamma_1\gamma_2)^{\frac{1}{2}} \qquad (32)$$

A similar expression can be written for phase (2), i.e.

$$\gamma_{2(12)} = \gamma_2 - (\gamma_1\gamma_2)^{\frac{1}{2}} \qquad (33)$$

The interfacial free energy (γ_{12}) is the sum of the free energies of the two surfaces comprising the interface and equation (32) and (33) can be combined to give:-

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1\gamma_2} \qquad (34)$$

$$\gamma_1 = \gamma_1^d + \gamma_1^p + \gamma_1^H \qquad (35)$$

The spreading of a hydrocarbon liquid in which dispersion forces are responsible for originating the intermolecular attraction over a polymeric surface then $\gamma_L{}^o = \gamma_L{}^d$ and equation (34) can be written as follows:

$$\gamma_{SL} = \gamma_S{}^o + \gamma_L{}^o - 2\sqrt{\gamma_S{}^{o^d}\ \gamma_L{}^{o^d}} \qquad (36)$$

Recalling Young's equation $\gamma_{SV}{}^o = \gamma_{SL} + \gamma_{LV}{}^o \cos\theta$ which in view of equation (15) i.e. $\pi_e = (\gamma_S{}^o - \gamma_{SV}{}^o)$ and its combination with equation (36) we obtain:-

$$\cos\theta = -\frac{\gamma_L{}^o}{\gamma_{LV}} + 2\frac{\sqrt{\gamma_S{}^o\ \gamma_L{}^o}}{\gamma_{LV}} - \frac{\pi_e}{\gamma_{LV}} \qquad (37)$$

or

$$\cos\theta = -1 + 2\sqrt{\frac{\gamma_S^d{}^o\ \gamma_L^d{}^o}{\gamma_{LV}}} \qquad (38)$$

This equation offers a method for determining $\gamma_S^d{}^o$ which is the dispersion force contribution to the surface free energy of the solid, i.e. the available energy of the solid surface for interaction with adjacent media, by measuring the contact angle and surface tension of liquids.

A graph of $\sqrt{\gamma_S^d o}$ $/\gamma_{LV}$ against cos Θ gives a straight line with a slope of $2\sqrt{S_o^d}$ and an intercept on the cos Θ axis of (-1).

Fowkes[80,128,133,134,135], developed an expression for the dispersion force part of the total work of adhesion, as $W_A = 2\gamma_{LV}$., Then

$$W_A^d = 2\ (\gamma_1\gamma_2)^{\frac{1}{2}} \qquad (39)$$

Fowkes determined γ_S^d of a variety of polymers, calculated the work of adhesion and estimated the tensile strength of adhesive bonds.

However, the dispersion force contribution to the theoretical maximum strength of say polyethylene and steel bond was calculated by Kraus and Manson[101] and Hoernschemsyer[136] and gave a value of 1.9×10^3 erg/cm^2. This is the energy of interaction which is the work which must be done in order to separate the two phases.

The calculated mean force required to pull polyethylene from steel was given as 3.9×10^4 kg/cm^2 and the actual strength measured was 3 tons/in^2.

This discrepancy is due to the assumption made in the calculation in that a perfect contact of flat surfaces is assumed whereas in reality the interface is never regular and failure occurs depending on the size of the penny-shaped cracks discussed by Sneddon[137] and others[100].

Equations (34) and (36) give a useful insight into the role of other types of forces, particularly the contribution of polar groups in an adhesive/adherend system. The contribution from dipole forces as calculated by Brunauer[138] from the dipole moment of a typical polar group and mirror changes in the metal gave an energy of 530 cal/mol which is small compared with the dispersion forces. This adds to the importance of dispersion forces as the major contributor to the observed bond strengths.

It was shown in 1970[139] that the Good-Girifalco model also makes it easy to compute $(\gamma)^d$ from molecular properties.

A molecular theory of work of adhesion was developed by Good and co-workers[80,130] to provide the following relation for the reversible work of adhesion W_A:

$$W_A = 2\,\phi_V\,\phi_a\,(\gamma_1\gamma_2)^{\frac{1}{2}} \tag{40}$$

where ϕ_V and ϕ_a identify the properties of the adjacent phases that cause a deviation from ideal interfacial interaction. ϕ_V is described by the molar volumes V_1 and V_2 of phase 1 and 2, and by (r_{12}), the intermolecular separation between monolayers of phase 1 and 2.

Then $$r_{12} \sim \phi_V^{\frac{1}{2}}\,(r_1 r_2)^{\frac{1}{2}} \tag{41}$$

Values of ϕ_V for several ratios of V_1/V_2 revealed that equation (41) deviates only by 12% from the geometric mean.

ϕ_a however is expressed as $\phi_a = \dfrac{a_{12}}{(a_1a_2)^{\frac{1}{2}}}$

Where a_{12}, a_1 and a_2 are the molar attraction constants which contained the induction, polar and dispersion.

This is similar to the equation derived by Gardon. (As seen later).

ϕ_a depends on the nature of the interaction forces in the two phases. If interaction is by dispersion forces, i.e. nonpolar molecules then $\phi_a = 1$. If the two liquids are of different polarity then $\phi_a < 1$. Water/nonpolar organic liquid $\phi_a = 0.5$.

First approximation of equation (40) assumes that $\phi_V = 1$, if the molar volume of the two components are the same or approaches 0.99, which is equivalent to the approximation for the lattice constant presented by Gardon[135], in his discussion of the theory of regular solutions. His recent development and that of Kaelble[135] with the deletion of the induction term in the classical statement of van der Waal's forces (see CED) contains the following information. In terms of the fractional dispersion and polar components,

$$\phi = \phi_a = (d_S d_L)^{\frac{1}{2}} + (p_S p_L)^{\frac{1}{2}} = 1 \tag{42}$$

As $- W_A = 2\phi(\gamma_L \gamma_S)^{\frac{1}{2}}$,

then substituting equation (42) in (40) and assuming $\phi_V = 1$, results in:

$$W_A = 2\,(\gamma_S \gamma_L)^{\frac{1}{2}}\,[(d_S d_L)^{\frac{1}{2}} + (p_S p_L)^{\frac{1}{2}}] \tag{43}$$

Equation (43) can be written in the following form if for each phase we write:

$$d = \frac{\gamma^d}{\gamma}\ ;\ \ p = \frac{\gamma^p}{\gamma}\ ;\ \ \gamma = \gamma^d + \gamma^p$$

Then, $$W_A = 2\,[(\gamma_S^d \gamma d_L^d)^{\frac{1}{2}} + (\gamma_S^p\ \gamma_L^p)^{\frac{1}{2}}] \tag{44}$$

Hence, the complete expression for the total work of adhesion would be:

$$W_a = W_a^d + W_a^p\ ;\ \ Wp = 2\,(\gamma_1^p\ \gamma_2^p) \tag{45}$$

In the light of Gardon[135] developments, however, Good gives the fractional dispersion component of surface tension in the following mathematical forms:

$$d = \frac{\gamma^{d}}{\gamma} = \frac{\frac{3}{4}\,\alpha^{2}\,I}{\frac{3}{4}\,\alpha^{2}I + 2\,\alpha^{2}\mu B + \frac{2\mu^{4}B^{2}}{3kT}} \qquad (46)$$

Fractional polar component and induction:-

$$P = \frac{\gamma^{p}}{\gamma} = \frac{2\,\mu^{4}B^{2}/3kT}{\frac{3}{4}\alpha^{2}I + 2\,\alpha^{2}\mu B + \frac{2\mu^{4}\,B^{2}}{3\,kT}} \qquad (47)$$

$$c = \frac{\gamma^{i}}{\gamma} = \frac{2\,\mu^{2}\alpha B}{\frac{3}{4}\alpha^{2}I + 2\mu^{2}\alpha B + \frac{2\mu^{4}B^{2}}{3\,kT}} \qquad (48)$$

$$\Delta G^{a} = 2(\gamma_S\gamma_L)^{\frac{1}{2}}\,[(d_Sd_L)^{\frac{1}{2}} + (p_Sp_L)^{\frac{1}{2}} + (i_Si_L)^{\frac{1}{2}}] \qquad (49)$$

As $\Delta G^{a} = -\gamma_S - \gamma_{LV} + \gamma_{SL}$, then we can write equation (49) with the aid of equations (47,48,42) in the following form:

$$\gamma_S + \gamma_L - \gamma_{SL} = 2\,[(\gamma_S^{d}\,\gamma_L^{d})^{\frac{1}{2}} + (\gamma_S^{p}\,\gamma_L^{p})^{\frac{1}{2}} + (\gamma_S^{i}\,\gamma_L^{i})^{\frac{1}{2}}] \qquad (50)$$

Since $\gamma_S = d_S^{d} + \gamma_S^{p} + \gamma^{i}$ and $\gamma_L = \gamma_i^{d} + \gamma_L^{p} + \gamma_L^{i}$ and since for any variables, $a-2(ab)^{\frac{1}{2}} + b = (a^{\frac{1}{2}} - b^{\frac{1}{2}})2$. Then equation (50) can be rarranged into the form,

$$\gamma_{SL} = [(\gamma_S^{d})^{\frac{1}{2}} - (\gamma_L)^{d})^{\frac{1}{2}}]^2 + [(\gamma_S^{p})^{\frac{1}{2}} - (\gamma_L^{p})^{\frac{1}{2}}]^2 + [(\gamma_S^{i})^{\frac{1}{2}} - (\gamma_L^{i})^{\frac{1}{2}}]^2 \qquad (51)$$

Good concluded that γ_{SL} is a minimum and work of adhesion is a maximum when the liquid and solid are exactly matched to each other in each of the separate components of their surface free energies.

A third approach to determining γ_S^{d}, γ_S^{p} is of Kaelble[135,140] which is based on the simultaneous solution of the following forms derived from equation (44) and (45):

$$\left.\begin{aligned} \left(\frac{Wa}{2}\right)_i &= \left(\sqrt{\gamma_L{}^d}\right)_i \sqrt{\gamma_S{}^d} + \left(\sqrt{\gamma_L{}^p}\right)_i \sqrt{\gamma_S{}^p} \\ \left(\frac{Wa}{2}\right)_j &= \left(\sqrt{\gamma_L{}^d}\right)_j \sqrt{\gamma_S{}^d} + \left(\sqrt{\gamma_L{}^p}\right)_j \sqrt{\gamma_S{}^p} \end{aligned}\right) \qquad (52)$$

Equation (52) was then rearranged into the following standard determinant forms:

$$D = \begin{vmatrix} \left(\sqrt{\gamma_L{}^d}\right)_i & \left(\sqrt{\gamma_L{}^p}\right)_i \\ \left(\sqrt{\gamma_L{}^d}\right)_j & \left(\sqrt{\gamma_L{}^p}\right)_j \end{vmatrix},$$

$$\gamma_S{}^d = \frac{\begin{vmatrix} (Wa/2)_i & \left(\sqrt{\gamma_L{}^p}\right)_i \\ (Wa/2)_j & \left(\sqrt{\gamma_L{}^p}\right)_j \end{vmatrix}^2}{D^2}, \qquad (53)$$

$$\gamma_S{}^p = \frac{\begin{vmatrix} \left(\sqrt{\gamma_L{}^d}\right)_i & (Wa/2)_i \\ \left(\sqrt{\gamma_L{}^d}\right)_j & (Wa/2)_j \end{vmatrix}^2}{D^2}$$

The relations express the half values of measured works of adhesion Wa/2 of characterised liquids (i) and (j) to a common solid (S). All the values in parenthesis are either measured or known. Thus for the interaction of two dissimilar liquids (i) and (j) to a common solid equation (46) may be solved to provide $\gamma_S{}^d$ and $\gamma_S{}^p$ directly. This method may be reapplied for all dissimilar combinations of liquids (i) and (j) to a common solid surface.

The subscripts (i) and (j) specify the liquid identification number which range from 1, 2 --- (n-1), n, and the numbers $1 \leq i < j$

have values i = 1, 2 --- (n-1), and j = 2,3, --- n.

This method was tested by Kaelble for a variety of liquids on various polymers in an attempt to explain the variation in the values of adhesion with the variations in the chemical constitutions of the polymer structure.

This method was applied for the calculation of γ_S^d and γ_S^p in this work for four modified paints using the results of Wa calculated from the experimental values of liquid surface tension and contact angle to surfaces of paints before and after bonding. (See section 3.18.1).

In conclusion there is a limit to the improvement in adhesion that can be attained by improving the wetting.

It has been pointed out by Huntsberger[80] that if the contact angle of an adhesive or coating (in its liquid form) on a solid is not zero, this will be conductive to the entrapment of air in pores or crevices of the solid and the existence of flaws or voids. These voids under load are loci of stress concentration, and hence are placed where failure is likely to be initiated.

The contact angle is a thermodynamic function and is a direct consequence of intermolecular forces. But because adhesive separation is an irreversible process, and strongly dependent on geometry and the presence of flaws, the thermodynamic "work of adhesion does not have any simple or direct relation to any measured <u>force</u>."

However, spreading and contact angle phenomena do have a direct influence on practical adhesive strength, via the rate of penetration of cracks and pores. Indees, pretreatment of a solid will improve adhesion if the contact angle of the adhesive or coating on the resulting surface is zero and particularly if the wetting liquid forms a liquid adsorbed film ahead of the advancing liquid front, and if the solid surface is initially free from adsorbed molecules of the penetrating material.

Wetting is critical to an adequate bond, but it only controls initial bonding in the fluid state, and it will have solidified before any load is applied. Other factors such as residual stresses cause failure at some place other than the interface. Penetration of an adhesive into the three dimentional complexity of rough adherend surface is partial even with adhesives having low contact angle.

Wetting is a rate dependent phenomenon as is affected by the viscosity of the adhesive and size of voids, the material takes time to flow, wet and reach an equilibrium position. The contact angle can be either advancing or receeding, and in the latter case a lower contact angle is left.

Most adhesives contain several components. The effect of low molecular weight species migrate a head of the base polymer causing increased contact angle and reduced wetting rates. Hence, the apparently good wetting materials can ultimately result in a lower quality bond.

2.9. Cohesive Energy Density of Polymers

2.9.1. Thermodynamic considerations

Van der Waals[78], in 1881, formulated equation (54) to describe the intermolecular forces for real gases. Thus, for one mole of gas:

$$P + \frac{a}{\nu^2} = \frac{RT}{\nu - b} \qquad (54)$$

Where:

P - is the external pressure

ν - is the molar volume

R - gas constant

T - absolute temperature

a - the attraction constant between molecules

b - volume of the molecule

An expression for the relation of 'a' for a mixture and a_1 and a_2 for pure components was derived by van der Waal yield equation (55):

$$a = N_1{}^2 a_1 + 2\,N_1 N_2\, a_{12} + N_2{}^2 a_2 \qquad (55)$$

Where (a_{12}) is the interaction between unlike molecular species, and

$$b = N_1 b_1 + N_2 b_2$$

The heat of mixing for unexpanded liquids, i.e. $v = b$ and according to van der Waal's theory, is given by equation (56):;

$$\Delta H^m = N_1 \frac{a_1}{b_1} + N_2 \frac{a_2}{b} - \frac{a}{b} \qquad (56)$$

If the interaction constant obeys the Berthelot[131] relation, i.e. $a_{12} = \sqrt{a_1 a_2}$

Then:

$$\Delta H^m = \frac{N_1N_2b_1b_2}{N_1b_1 + N_2b_2} \left(\frac{a^{\frac{1}{2}}}{b_1} - \frac{a^{\frac{1}{2}}}{b_2}\right)^2 \tag{57}$$

ΔH, can be zero only if $\left(\frac{a_1}{b_1}\right)^{\frac{1}{2}} = \frac{a_1^{\frac{1}{2}}}{b_2}$, which will be, if the two components have approximately equal critical pressures. $P_c = \frac{8a}{27\ b^2}$.

By substituting volumes, equation (57) becomes:

$$\Delta H^m = \frac{N_1N_2V_1V_2}{N_1V_1 + N_2V_2} \left(\frac{a_1^{\frac{1}{2}}}{V_1} - \frac{a_2^{\frac{1}{2}}}{V_2}\right)^2 \tag{58}$$

The thermodynamic equation of state (59) for the change in free energy, heat and entropy at <u>constant temperature</u>, i.e. 1st and 2nd law, can be instructively compared with equation (54).

$$P + \left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \tag{59}$$

Equation (59) is derived by differentiating E = H-TS, with respect to volume at constant temperature, $\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$ and since $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

Where E - is the internal energy

V - volume of the system

The comparison leads to the addition of "a repulsive" pressure term, i.e. $T\left(\frac{\partial P}{\partial T}\right)_V \simeq T\frac{R}{\nu - b}$ and an "attractive" pressure term $\left(\frac{\partial E}{\partial V}\right)_T = \frac{a}{V^2}$.

The former represents the tendency of a liquid or gas to expand and the latter is due to the cohesional forces between the molecules that contribute to internal energy (E) which define the intermolecular structure in the crystalline solid.

The structure of liquids and gases, however, is a function of a time and intermolecular distance, and is therefore specified in a more approximate manner.

When a polymer dissolves in a solvent, there are therefore two opposing factors at work. Firstly, the tendency of the system must assume a random state, i.e. that of complete solution, i.e. (repulsive pressure term). Secondly, the overcoming of the entropy of cohesion of the polymer, and that of the liquid, i.e. (attractive pressure term). In other words, the entropy 'S' of a system always tends to a maximum value.

Intermolecular bonds between polymer segments and between solvent molecules are therefore broken and new bonds are created between solvent molecules to polymer segments.

The two opposing effects are expressed thermodynamically by Gibbs free energy change at constant temperature for regular solutions as demonstrated in equation (60).

$$\Delta G = \Delta H - T\Delta S \qquad (60)$$

where ΔG - is the change in free energy

ΔH - is the change in heat content or enthalpy

T - is the temperature in K.

at constant pressure $\Delta G = dA + P\Delta V$.

In other words, ΔH is the heat absorbed by the system when polymer dissolves in the solvent and can be expanded in terms of the short range van der Waal's forces, acting between two solvent molecules and between two polymer segments. (Any specific chemical interactions are disregarded).

As (ΔG) with the negative sign is the driving force of a reaction, or a physical change, an increase in solubility is favoured by an increase in the entropy term $T\Delta S$, and by a decrease in enthalpy. In practical terms miscibility is favoured when higher temperatures are used.

Since thermodynamically ΔS is largely determined by the polymer itself, and is independent of the solvent, the choice of a suitable solvent of a particular polymer depends upon a minimum value of ΔH.

By relating the heat content change at constant volume to the latent heats of vaporization of the solvent and the polymer, and to the short range forces, equation (58) can take the form of equation (61):

$$\Delta H^M = \frac{N_S \quad n\,N_p}{N_S + n\,N_p} \left| \left(\frac{E_S}{V_S}\right)^{\frac{1}{2}} - \left(\frac{E_p}{V_p}\right)^{\frac{1}{2}} \right| \qquad (61)$$

where N_S and N_p - are the number of molecules of the solvent and of polymer respectively.

n - is the number of segments in one molecule of polymer

V_s and V_p - are the molar volumes of solvent and polymer

E_S and E_p - are the molar latent heats of vaporization at constant volume, which differ from that at constant pressure by an amount equal to the work of expanding at the given temperature, i.e. less RT = 580 cal/mole.

The quantity $(\frac{E}{V})$ is the energy of vaporization or sublimation per CC, or the "internal pressure" and is known as THE COHESIVE ENERGY

DENSITY. It was conveniently expressed by Hildebrand[79] in terms of its square root as the solubility parameter δ i.e.

$$(CED)^{\frac{1}{2}} = (\frac{E}{V})^{\frac{1}{2}} = \delta = \frac{a^{\frac{1}{2}}}{V}$$

The fundamental understanding of the physical significance of CED lies in the consideration of the interaction energy between two isolated molecules of low molecular weight material, and is a measure of the strength of the interaction, the nature of which is described(1) by dipole orientation, induction and dispersion forces. CED is numerically equal to the potential energy of one CC of material E/V but has the opposite sign, i.e. $\delta^2 = -E/V$, as the potential energy of a mole of material is $E = N_o \nu$ where N_o is the Avogadro number and ν is the potential energy of a single molecule, $\delta^2 = - N_o /V$.

2.9.2. Solubility parameters of solvents and solvent mixture

2.9.2.(i) Solubility parameter of solvents

The heat of vaporization per mole (ΔH_U) is used to compensate both for the potential energy per mole (E) and for the volume work which for a vapor phase obeying ideal gas laws is RT.

Therefore, CED of a solvent can be calculated from the heat of vaporization and molar volume using equation (62).

$$\delta^2 = \Delta H_\nu - RT/V \qquad (62)$$

However, to obtain ΔH_ν, there are four methods:

(1) Direct calorimetric determination, but this method is laborious and lacks accuracy.

(2) Bondi's[141] method which is based on calculations from group contributions based on the chemical formula.
This method will not be discussed because it is similar to Small's[142] method which will be described in section 2.9.3.

(3) Calculation from the boiling point by Hildebrand[79] rule which is illustrated in equation (63).

$$\Delta H_{\nu} = -2950 + 23.7\, T_b + 0.020\, T_b^2 \tag{63}$$

(4) Calculation from the variation of vapour pressure data with temperature using Clausius-Clapeyron[79] equation (64).

$$\frac{dP}{dT} = \frac{L}{T(V_V - V_L)} \tag{64}$$

where L - molar latent heat at constant pressure

V_V and V_L - are the molar volumes of vapour and of liquid respectively.

The application of the ideal gas law and neglecting V_L in comparison with V_V and integration of equation (64) results in equation (65).

$$\ln P_2 - \ln P_1 = \frac{L}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{65}$$

Substituting the vapor pressure data which are available in the literature[142,143] at T_1 and T_2 results in value of 'L' or ΔH_{ν}.

Since V = molecular weight/density, equation (62) becomes:

$$\delta = \left(L - 580 \times \frac{d}{M}\right)^{\frac{1}{2}}$$

Hence, 'δ' for a mixture of solvents is a linear volume function of the values of 'δ' for the separate components.

The cohesive-energy density is a measure of the strength of the interactions in a material, but does not contain information concerning the nature of these interactions. For characterising materials from this standpoint, Gardon[1] defined a new parameter, the fractional polarity 'p' which is equal to the fraction of total interactions due to dispersion fraction ($d_e = \frac{3I}{4}\alpha^2$), a polar fraction ($p_e = \frac{2}{3}\frac{\mu^4}{kT}$) and an induction fraction ($i = 2\alpha\mu^2$), i.e.

$$d + p + i = 1 \quad \text{and } p = 2\mu^4/3kT\varepsilon_{12} \qquad (63)$$

The significance of the term "ε_{12}" is described in section 2.3 by equation (9) and for the homogeneous phase by equation (10).

The fractional polarity 'p' can be calculated from equation (63) and (10), and Gardon[1] provided extensive tables containing values of 'p' in conjunction with CED (δ) and molar volume 'ν' of solvents.

To define the dependence of (d) or (i) upon the calculated values of 'p', the dispersion fraction d_e and the polar fraction p_e were calculated as follows.

The ionization potential (I) of most organic liquids lie between values of 8.5 and 11.4 eV, and we can assume a constant value of $I = 10 \text{ eV} = 1.602 \times 10^{-11}$erg.

Thus, $d_e = 1.2 \times 10^{-11}\alpha^2$

For a normal temperature, $T = 25^{\circ}C = 298K$, $k = 1.38 \cdot 10^{-16}$ erg/deg. and

$$p_e = 1.62 \times 10^{13}\mu^4$$

As $d + p + i = 1$

Then, $i_e = 1 - d - p = 2\alpha\mu^2 = 0.142\,(pd)^{\frac{1}{2}}\,\varepsilon_{12}$

$$\therefore \quad d = 1 - 0.9898\ p - 0.142\ (p - p^2)^{\frac{1}{2}} \tag{64}$$

$$i = 0.142\ (p - p^2)^{\frac{1}{2}} - 0.0102\ p \tag{65}$$

It was found[1] that (i) fraction is very small at its maximum value of 0.068 at $p = .47$. Thus, (i) can be neglected and $d + p = 1$.

For this work, equation (64) was used to calculate the solubility parameter of solvents used for the determination of CED of polymers.

The proportionality constant between the interaction constant ε_{12} in equation (9) and the potential energy ε_1 values of molecules of the same type as in equation (10) or of molecules surrounded by different kinds of molecules, is assumed to be the same if the molar volumes, shapes and packing of the (1) and (2) molecules are identical. This approximation underlies the Hidlebrand-Seatchard treatment[79] for the heat of mixing.

To conclude that the geometric-mean rule is an adequate approximation for the interaction of two nonpolar species, i.e. the interaction constant obeys Barthelot[131] relation $a_{12} = \sqrt{a_1 a_2}$, a dispersion interaction parameter "φ" is introduced as in equation (66) it should be unity.

$$\phi = \frac{\varepsilon_{12}}{(\varepsilon_1\ \varepsilon_2)^{\frac{1}{2}}} \tag{66}$$

To prove that $\phi = 1$, we equate equations (9) and (10) and neglect the induction force for any pair of organic liquids whose $I = 10$, i.e. $\mu_1 = \mu_2 = 0$, we obtain the following equation:

$$\frac{3}{2} \quad \frac{I_1\ I_2}{I_1 + I_2} \approx \frac{3}{4}\ (I\ \alpha^2)^{\frac{1}{2}} \tag{67}$$

When placing equation (67) in equation (9), and when there are only dispersion interactions, then,

$$\frac{\varepsilon_{12}}{\sqrt{\alpha_1 \alpha_2}} = \alpha = \phi = 2 \ (I_1 I_1)^{\frac{1}{2}} / (I_1 + I_2) \qquad (68)$$

Substituting, the ionization potential values for the highest and lowest limit in equation (68) we obtain that:

$$1 > \phi > 0.975 \ ; \ \text{i.e.} \ \phi \simeq 1$$

Equation (9) can be re-written in the following form (see section 2.8.3):

$$\begin{aligned} \varepsilon_{12} &= (\alpha_1\alpha_2)^{\frac{1}{2}} \ \left[(d_1 d_2)^{\frac{1}{2}} + (p_1 p_2)^{\frac{1}{2}}\right] \\ \therefore \ \phi &= (d_1 d_2)^{\frac{1}{2}} + (p_1 p_2)^{\frac{1}{2}} \end{aligned} \qquad (69)$$

Equation (69) was used for calculating ϕ of the solvents used in this work for the determination of CED of polymers. When the polar fraction of two molecular species are equal, $d_1 = d_2$; $p_1 = p_2$; and $\phi = 1$.

2.9.2.2. Solubility parameter of solvent mixtures

The knowledge of cohesive energy density of two component solvent mixtures is very important since it governs the technological aspects of polymer dissolution.

Kaelble[135] has shown that the internal energy 'U_m' of two component solvent mixtures is given by:

$$\delta^2_m = U_m = - n \ (x \ V_1 + x_2 \ V_2)(L_1 \ \phi_1^2 \ \alpha_{11} + L_2 \ \phi_2^2 \ \alpha_{22} + 2 \ L_{12}\phi_1\phi_2\alpha_{12}) \qquad (70)$$

Where:

n - number of moles

x_1, x_2 - mole fractions of components (1) and (2)

V_1, V_2 - molar volumes

L_1, L_1 - latice constants for (1-1) contacts and (2) contacts.

L_{12} - lattice constant for (1-2) contacts

$\phi_1\ \phi_2$ - volume fractions, i.e. $\phi_1 = \frac{V_1}{V_1 + V_2}$; $\phi_2 = \frac{V_2}{V_1 + V_2}$

$a_{11}a_{22}$ - attraction constants for (1-1) and (2-2) molecules respectively.

a_{12} - attraction constants between molecules of (1) and (2).

For one mole of solution n=1, and equation (70) can be divided by the molar volume of the mixture to obtain equation (71):

$$\delta_m^2 = - \frac{U_m}{\nu_m} = L_1\ \phi_1{}^2\ a_{11} + L_2\ \phi_2{}^2\ a_{22} + 2\ L_{12}\ \phi_1\phi_2\ a_{12}) \qquad (71)$$

As the energy energy density of pure component is $\delta^2 = - \frac{U}{V} = aL$, equation (71) becomes:

$$\delta_m^2 = (\phi_1\delta_1)^2 + (\phi_2\delta_2)^2 + 2\ L_{12}\ \phi_1\phi_2\ a_{12} \qquad (72)$$

Recalling equation (9) for the total interaction of two molecules (ε_{12}), equation (66)

i.e. $\phi = \frac{\varepsilon_{12}}{(\varepsilon_1\varepsilon_2)}^{\frac{1}{2}} = \alpha_{12} = \phi\ (a_1a_2)^{\frac{1}{2}}$

and substituting the value of $\phi = (d_1d_2)^{\frac{1}{2}} + (p_1p_2)^{\frac{1}{2}} = 1$ from equation (69) and $a_{12} = (a_1a_2)^{\frac{1}{2}}\ \{(d_1d_2)^{\frac{1}{2}} + (p_1p_2)^{\frac{1}{2}}\}$ into the last term of equation (72) and arranging in terms of $\delta^2 = - \frac{U}{V} = aL$. δ_m^2 is then :-

$$\delta_m^2 = (\phi_1\delta_1)^2 + (\phi_2\delta_2)^2 + 2\phi\ \phi_1\phi_2\ \delta_1\delta_2 \qquad (73)$$

Equation (73) was used to calculate 'δ_m' of solvent mixtures used in this work.

However, the solubility parameter of solvent mixture which is restricted to pure dispersion force or to selective combination of polar solvents in which $p_1 = p_2$; $\phi = 1$, equation (73) reduces to:

$$\delta_m = \phi_1 \delta_1 + \phi_2 \delta_2$$

This is the Scott and Magat[144] equation.

The developments in the thermodynamic of polymer solutions allowed a considerable advance in understanding the role of solvents of "solvent power" of a given liquid, and the solubility characteristics of polymers in solvents of a range of solubility parameters.

Burrell[145-147] pointed out the importance of the degree of hydrogen bonding of the solvent on its 'solvent power' and classified solvents into three classes of poor, moderate and strong hydrogen bondings. Aliphatic and aromatic hydrocarbons are poorly hydrogen bonded, the alcohols and carboxyl acids are strongly hydrogen bonded while ketones, esters, ethers and aniline are moderately hydrogen bonded.

In each class of solvents, polymers tend to dissolve in solvents of a range of solubility parameter and be insoluble in solvents outside this range. The ranges of sol. par. for a given polymer may differ in each of the hydrogen bonding classes.

Freeman and Rushman[148] determined the solubility parameter of polymers in solvents of a range of solubility parameters and concluded that 'δ' is of considerable value in comparing or predicting the solubility of polymers, particularly when considered in conjunction with the hydrogen bonding capacity of the solvent. Any solvent having 'δ' within the ranges of 'δ' for each degree of hydrogen bonding of the solvent, will dissolve the polymer regardless of chemical composition.

The technological importance of the prediction of the CED for a mixture of solvents is great, particularly when formulating lacquers and paints and for choosing the appropriate plasticisers or plasticizer mixtures which have the maximum compatibility with any given polymer system[149].

The study of swelling of cross-linked gels in various solvents, which are more difficult to swell than those less fully polymerised, offers a useful way of obtaining information of the degree of cross-linking.

The phenomenon of mixing of two non-solvents to acting as a solvent is quite striking, say in the case of cellulose and PVC.

The concept of δ also has value in the consideration of the viscosity of polymer solutions.

Molecules in an extended form, i.e. (good solvent) contribute more to the viscosity of the solution than when they are folded, i.e. (poor solvent), and in this way the δ-value of the solvent should influence the viscosity of a solution, at an optimum value of δ resulting in highest viscosity. In lacquer formulation the addition of high volatility non-solvent to displace 'δ' for the mixture far from its optimum, thus obtaining a polymer content as high as possible for a given viscosity.

Burrel[150] reviewed the subject of the significance of (CED) concept in the surface coating industry, and its importance from the cost point of view to obtain the best ultimate film quality.

Gardon[151] using equation (31), related (δp) to the critical surface free energy (δ_c). He[80] also related it to the ultimate strength of materials and to the strength of an adhesive joint, and Schonhorn[152] to the surface tension.

2.9.3. Solubility Parameter of Polymers

In establishing the (CED) of polymers (nonvolatile materials), the dilemma is the same as in measuring the surface free energy of solids. The CED of nonvolatile substances cannot be measured directly. Just as the surface free energy of solids can be estimated from the interaction of a solid with non-solvent liquids, the (CED) of polymers can be determined by their interaction with good solvents.

The condition for maximum solubility of a polymer in a solvent is simply that the CED of the solvent shall be equal to that of the polymer. In other words, the CED of a polymer is normally taken equal to the CED of solvent or solvent mixture where the viscosity of the solution is at its maximum.

For polymers[1] the change in the sum of interaction energies between the interacting sites in 1 cm^3 substance varies in a relatively narrow range between 6-15 $cal^{\frac{1}{2}}/1.5$ cm.

Experimentally, the CED of polymers can be determined using two methods which are often quoted in the literature.

(1) The swelling measurements[153] involving the determination of $\delta_{solvent}$ in which cross-linked or crystalline polymers are swelled the most. $\delta_{polymer}$ is often dependent on the cross-linking density.

Baranwal[154] determined CED of natural rubber styrene-butadiene and ethylene-propylene terpolymers by swelling measurments.

Huglin and Pass[155] determined the CED of polytetrahydrofuran by the measurements of swelling coefficient $Q = \frac{(W-W_o)}{W_o p_s}$.

2. The viscosity measurements of polymer solution in a series of solvents. Normally the CED is taken equal to the CED of the solvent in which the intrinsic viscosity is at its maximum. This method is widely used. Yu et. al.[156] used it to measure the CED of ethylene-diethylfumarate copolymer. Mangaraj[157,158] extended Gee's method to estimate 'δ' of high polymers of cross-linked rubber from viscosity measurements, the plot of $|n|$ versus δ solvents yielded smooth curves similar to those obtained by plotting swelling coefficients against 'δ', and obtained values of δp comparable with those obtained by swelling measurements. In a series of publications, Mangaraj determined the CED of polyacrylates[158], polymethacrylates[159] and polyvinylester[160].

For this work, this method was used and the theoretical interpretations of Gardon[1] for the CED of solvents and solvent mixture were utilized.

3. Small's method[142]

This does not involve experimentation. Small's method was developed for estimating the value of the solubility parameter from chemical structure and assumed that the solubility parameter contribution of the different chemical groups or radicals in the molecule to the overall solubility parameter are additive and devised constituative molar attractive constants.

Hoy[167] re-examined these molar attraction constants over a broad spectrum of compounds using multiple regression analysis. He found that the only compounds which did not reliably yield to analysis were the acids, alcohols and other compounds which are capable of association.

The multiple regression analysis gave satisfactory results when the dimeric structure of a series of 14 carboxylic acids, and the modified equation of solubility parameter developed by Hildebrand and Scatchard[79] were used. Some 640 organic compounds were considered and the values of the solubility parameters were calculated from vapour pressure data.

The molar attraction constants generated in this way are given in Table 5.

The solubility parameter of polymers can then be calculated using Small's equation (74) and the new values of the molar attraction constants of Table 5.

Thus,

$$\delta\text{poly} = \frac{\Sigma F}{M_W} \cdot d \qquad (74)$$

where F - is the sum of molar attraction constants

δ = is solubility parameter $(\text{cal/cm}^3)^{\frac{1}{2}}$

M_W = is molecular weight of a repeating unit, g/mole

d = density (g/cm^3).

This method was also used to calculate the CED of synthesized polymers with the assumption that the degree of crystalinity is small and that the interaction between polymer segments were analogous to the interactions between small solvent molecules.

For copolymers and crystalline polymers, the CED is affected as the heat of mixing is also needed to melt the crystallites as the potential energy of the segment in the crystallites is higher than

TABLE 5

Molar Attraction Constants

(s, (cal cc)$^{\frac{1}{2}}$ mole^{-1})

Group	S	Group	S
$-CH_3$	148.3	-S-	209.42
$-CH_2-$	131.5	Cl_2	342.67
$>CH-$	85.99	Cl primary	205.06
$-\overset{\vert}{\underset{\vert}{C}}-$	32.03	Cl secondary	203.27
$CH_2=$	126.54	Cl aromatic	161.0
$-CH=$	121.53	Br	287.88
$>C=$	84.51	Br atomatic	205.60
$-CH=$ aromatic	117.12	F	41.33
$-\underset{\vert}{C}=$ aromatic	98.12		
-O- (ether, acetal)	114.98	Structure feature	
-O- epoxide	176.20		
-COO-	326.58	Conjugation	23.26
$>C=O$	262.96	Cis	- 7.13
-CHO	292.64	Trans	- 13.50
$(CO)_2O$	567.29	4 membered ring	77.76
-OH-	225.84	5 membered ring	20.99
-H acidic dimer	- 50.47	6 membered ring	- 23.41
OH aromatic	170.99	Ortho substituion	9.69
NH_2	226.56	Meta substitution	6.6
-NH-	180.03	Para substitution	40.33
-N-	61.08		22.56
C≡N	354.56		62.5
NCO	358.66	Base value	135.1

in the amorphous region.

Gardon[1] has collected numerous values of 'δ' polymers based on Small's method and the experimental methods as in (1) and (2).

CHAPTER THREE

WORK ON THERMOPLASTIC SYSTEMS

3.1. Experimental

3.1.1. Preparation of Thermoplastic Polymers

The base polymer, copolymers and terpolymers were prepared by a free radical solution polymerisation technique in toluene using 0.5% w/w 2,2'azobis(2-methylpropionitrile) as initiator.

The polymerisation was carried out in a three-necked round-bottomed 1 litre flask equipped with glass stirrer, thermometer, nitrogen gas inlet and water condenser.

Appropriate amounts of monomer or monomers, and equal weight of solvent and the initiator were put into the flask and it was maintained at 85 ± 2°C on a water bath.

The progress of the reaction was followed by determining the weight of non-volatile material (solids) remaining after heating a sample of the polymer solution for 30 minutes at 120°C. A 1-2g sample was pipetted into an accurately tared aluminium expendible dish at room temperature and weighed. This was then heated and the residue weighed accurately after cooling to room temperature. The polymerisation reaction was considered completed when at least 99% polymerisation conversion was obtained. The polymerisation conversion was calculated using equation (75):

$$\%\ \text{Polymerisation conversion} = \frac{2 \times R}{W} \qquad (75)$$

where R = weight of non-volatiles, grams

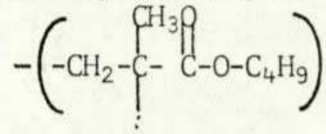
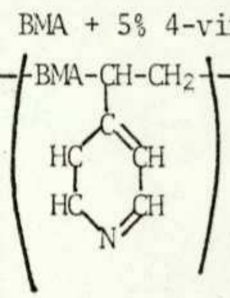
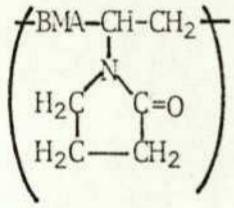
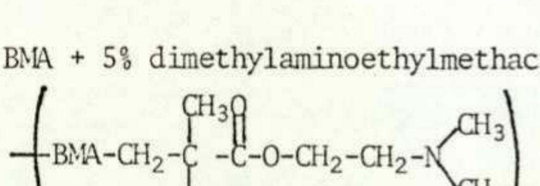
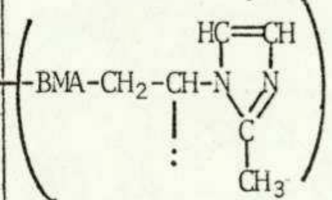
W = weight of sample used, grams

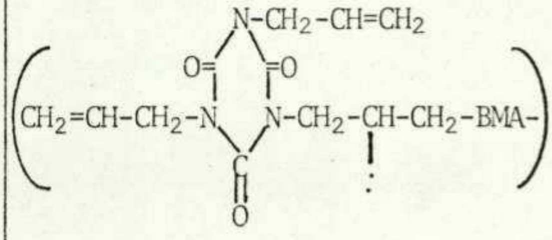
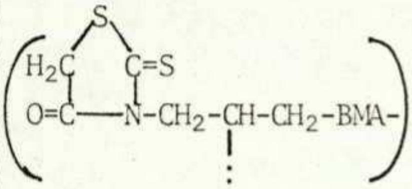
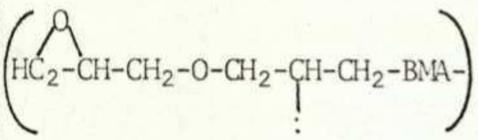
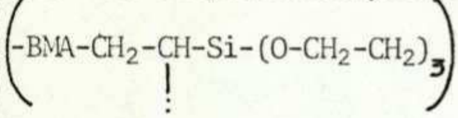
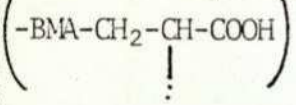
2 = conversion factor from 50% solution to 100% solid

The lengths of time found necessary for this complete reaction, together with the compositions used are given in Table 6.

TABLE 6

THE STRUCTURAL FORMULAE AND DETAILS OF PREPARATION OF THERMOPLASTIC POLYMERS

Monomer Composition (molar % ages)	Base monomer, g	co-monomer(s), g	Reaction Time, hours
	250 g total wt. of components		
n-butylmethacrylate (BMA)  $-\left(-CH_2-\overset{CH_3}{\underset{\vdots}{C}}-\overset{O}{\overset{\Vert}{C}}-O-C_4H_9\right)$	250.00	-	6
BMA + 5% 4-vinylpyridine 	240.63	9.37	16
BMA + 10% 4-vinylpyridine	231	19	28
BMA + 5% N-vinylpyrrolid-2-one 	240.13	9.87	24
BMA + 10% N-vinylpyrrolid-2-one	229.4	20.6	24
BMA + 5% dimethylaminoethylmethacrylate  $-\left(BMA-CH_2-\overset{CH_3}{\underset{\vdots}{C}}-\overset{O}{\overset{\Vert}{C}}-O-CH_2-CH_2-N\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}\right)$	236.25	13.75	24
BMA + 10% dimethylaminoethylmethacrylate	222.75	27.25	24
BMA + 5% 1-vinyl-2-methylimidazole 	240.37	9.63	24
BMA + 10% 1-vinyl-2-methylimidazole	230.5	19.5	42

BMA + 5% triallyl-s-triazine 2,4,6 trione 	228.87	21.15	30
BMA + 5% N-allylrhodanine 	234.9	15.1	24
BMA + 5% allylglycidylether 	239.85	10.15	30
BMA + 5% vinyltriethoxysilane  $\left(-BMA-CH_2-CH-Si-(O-CH_2-CH_2)_3\right)$	233.55	16.45	50
BMA + 1% acrylic acid  $\left(-BMA-CH_2-CH-COOH\right)$	248.73	1.27	24
BMA + 5% acrylic acid	234.5	6.5	36
BMA + 1% acrylic acid + 5% 1-vinyl-2-methylimidazole	239.0	1.3, 9.7	30
BMA + 1% acrylic acid + 5% 1-vinyl-2-methylimidazole	234.91	1.27, 13.82	24
BMA + 5% acrylic acid + 5% 1-vinyl-2-methylimidazole	233.6	6.58, 9.85	8
BMA + 5% acrylic acid + 5% dimethylaminoethylmethacrylate	229.4	6.5, 14.1	24

Solvent toluene - 250 g)
Initiator - 1.25 - 1.3 g) in every case

3.1.1. (i) Materials

1. Toluene was a reagent grade supplied by M & B, and was used as a solvent.
2. The initiator was 2,2'azobis(2-methylpropionitrile) supplied by BDH.
3. n-Butylmethacrylate as the base monomer was Koch-light laboratory grade material and it was distilled under vacuum at 0.5 mm Hg and 46°C to remove hydroquinone as stabiliser.

The physical properties[162,163] of n-butylmethacrylate are quoted as:

Boiling point	163-164°C
Density at 20°C	$d = 0.894$ g/cm^3
Refractive index	$n^{25} = 1.4215$
Heat of polymerisation	$\Delta H = 13.5$ kcal/mole
Acidity as methacrylic acid, %	0.01

The refractive index of freshly distilled monomer was determined using an Abbé refractometer of Bellingham and Stanley Ltd., and it was found to be $n^{25}_{D} = 1.4250$ which is in a good agreement with the reported value.

The acidity,[162(a)] which is almost entirely due to methacrylic acid was determined using the method described below.

Method

A 10 ml sample of the monomer was pipetted into a flask, diluted with about 10 ml of water and titrated with 0.1N sodium hydroxide solution using bromthymol blue indicator. The results are usually expressed in ml of 0.1 NaOH solution per 10 ml of sample.

% Acidity was calculated using the following expression:

$$\text{\% Acidity as methacrylicacid} = \frac{\text{ml 0.1N NaOH x 0.8609}}{\text{10 x specific gravity of sample}}$$

The expression was derived from the consideration that 1000 ml N NaOH are equivalent to 86.01 the molecular weight of methacrylic acid, and so if (y) ml NaOH are used then (X) grams of methacrylic acid will equal 86 y/1000, and is equivalent to 10 ml sample x specific gravity.

$$X = \frac{86\,y}{1000} \text{ grams, equivalent to 10 ml sample x Specific gravity}$$

and

$$\text{\% Acidity} = \frac{y \times 86}{1000 \times 10 \times SG} = \frac{y \times 0.86}{10 \times SG}$$

In view of the fact that the volume of NaOH used on titration of a 10 ml sample of n-butylmethacrylate was below 0.1 ml, it was considered that the % acidity is much lower than that reported by Blout[162].

4. Cumene hydroperoxide (Trigonox K-70) was supplied by Novadel Ltd. and it was used as initiator in the series of polymers prepared initially (see page), but it was abandoned because it yielded polymers of lower molecular weight and a slower rate of polymerisation.
5. Dimethylaminoethylmethacrylate was Koch-light laboratory grade material and it was distilled under vacuum at 2 mm Hg and at 50°C with flow of nitrogen to yield

a colourless liquid with refractive index n^{20}_{D} = 1.4420. This was used as a comonomer with n-butylmethacrylate.

6. 4-Vinylpyridine as a comonomer was Koch-light laboratory grade material, and it was distilled under vacuum at 2 mm Hg and at 50°C with flow of nitrogen to remove the 0.1% p-tertbutylcatechol as stabilizer and to give a colourless liquid with refractive index n^{20}_{D} = 1.5500. E.R. Blout[162] reported the refractive index as n_{D} = 1.545 and boiling point at 15-16 mm Hg pressure as 64-67°C.
7. N-vinylpyrrolid-2-one, was Koch-light laboratory grade 98% stabilized with 0.1% NaOH, was purified by distillation under vacuum at 2 mm Hg, and at 50°C with flow of nitrogen to give a colourless liquid with a refractive index n^{20}_{D} = 1.5135, density at 20°C = 1.043 g/cm^3 and BP. = 216°C. This was used as a comonomer with n-butylmethacrylate.
8. 1-Vinyl-2-methylimidazole or 1-vinyl-2-methylglyoxaline Koch-light laboratory grade, a dark brown liquid, stabilized with 0.1% picric acid, was purified by distillation under vacuum at 2 mm Hg and at 44°C to give a colourless liquid with a refractive index n^{20}_{D} = 1.5285, density at 20°C = 1.0188 g/cm^3, Boiling Point = 190°C and Frearing Point of -50°C. This was used as a comonomer.
9. Triallyl-s-triazine 2,4,6 trione, Ralph N. Emanuel laboratory grade as a comonomer, was purified by vacuum

distillation at 147-148^{o}C to yield a viscous and colourless liquid with a refractive index of n_D^{20} = 1.5145, or a white solid melting at 23.5^{o}C. This viscous liquid monomer is also called triallylisocyanurate [164], and can be obtained from the Plastics Division of Allied Chemicals with the following properties:

Boiling point	152^{o}C at 4 mm Hg
d_{25}	1.1583
n_D^{25}	1.5113
Solubility in water at 25^{o}C	0.37%

10. N-allylrhodanine a Ralph N. Emanuel laboratory grade, was a powder and was not purified further. It was used as a comonomer with n-butylmethacrylate. This compound melts at 46^{o}C and boils at 186^{o}C at 12 mm Hg[165,166].
11. Allylglycidylether, (1-allyoxy-2,3 epoxy propane) L. Light & Co. Ltd. was distilled under vacuum at 2 mm Hg and at 38^{o}C to yield a liquid with refractive index n_D^{20} = 1.4375. It was reported[164] that the refractive index of this monomer produced by Shell, was n_D^{20} = 1.4348, density was d^{20} = 0.9678 g/cm^3 and the boiling point was 154^{o}C.
12. Vinyltriethoxysilane, a product of Union Carbide designated as A-151[167], is a colourless liquid with a specific gravity of 0.894, refractive index n_D^{25} = 1.397 and boiling point (760 mm Hg) = 161^{o}C.

The monomer was distilled under reduced pressure to give a liquid with refractive index $n^{25}_{D} = 1.402$.

13. Acrylic acid was Koch-light material of pure grade and was used as comonomer without further purification. The experimental refractive index was $n^{20}_{D} = 1.4299$ which is in a good agreement with the value given by Blout[162] of $n^{20}_{D} = 1.4224$.

14. Stearic acid was B. Newton Maine Ltd., recrystallised from carbon tetrachloride and was used as a contaminant for metal surfaces.

3.1.1. (ii) Results and Discussion

The structural formulae and monomer composition of synthesized polymers, copolymers and terpolymers, as given in Table 6. It is anticipated that the rate and nature of polymerisation will be affected by the initiator used. The effect of the amount of initiator on the molecular weight distribution and on the rate of polymerisation was studied.

A polybutylmethacrylate (N3) was prepared using 0.5% 2,2-azobis-2-methylpropionitrile) on the weight of monomer. A similar polymer (N4) was also prepared using 1% initiator. The time for complete reaction for N3 was 6 hours, whereas for N4 it was 12 hours. Gel permeation chromatography used for determining the molecular weight distribution (see Section 3.2) gave the following results:

Ref. No.	M_n	M_w	M_{max}	D
N3 0.5% initiator	44520	94390	78380	2.12
N4 1.0% initiator	32580	82850	73820	2.54

These results confirm that a lower concentration of initiator is favourable, giving a higher molecular weight polymer, and 0.5% of initiator was used for preparing other polymers.

Initially cumene hydroperoxide was used as initiator for the preparation of the following polymers and copolymers:

Ref. No.	Type of polymer	Reaction time, hrs	Conversion %
P1	n-butyl methacrylate	22	99
N1	n-BMA + 5% dimethylaminoethylmethacrylate	32	75
N2	n-BMA + 5% 4-vinylpyridine	50	94

Azobismethylpropionitrile as initiator increases the rate of propagation of the polymer molecules. The reaction time was shorter and the degree of conversion was substantially better with this initiator and for these reasons it was favoured.

3.2. Characterisation of Thermoplastic Polymers

3.2.1. Gel Permeation Chromatography

3.2.1.(i) Experimental

Description of the Instrument

The Paint Research Assocation had a Waters gell permeation chromatography instrument which was used to study the polymers used in this work. Reference was made to assessments of the technical value of the method in this type of work at PRA by Rybicka[168,169].

The Gel Permeation Chromatography Instrument consists of two sets of stainless steel columns. The columns are packed with cross-linked polystyrene beads swollen in the solvent to form a gel. In packing the columns extreme care is needed to ensure that all the pores of the gel are filled with solvent and no air is trapped within the pores. The gels are prepared in such a way that their porosity is high, the pore sizes are well defined and the particles are small and rigid.

The solvent flow is split into two; one part flows through the set of analytical columns, the other flows through the reference columns. The sample in dilute solution is injected into a loop which can be connected with the solvent entering the analytical columns by manipulation of a valve.

After leaving the columns, the two streams of solvent flow through the differential refractometer. The difference in refractive index between the solution leaving the analytical columns and the solvent leaving the reference column, is recorded on a moving chart, the passage of each 5 millilitre batch of solvent being also recorded on the chart as a small vertical line.

Tetrahydrofuran was used as a solvent. This solvent is most convenient for separations carried out at room temperature as its refractive index is lower than that of a majority of polymers of interest to the paint industry (see Table 7), because it is sufficiently polar to overcome the adsorption effects on the gels, and because when sufficiently dry, it was found to be a good solvent for the majority of polymers.

Table 7

Typical Refractive Indices at 25°C

Tetrahydrofuran	1.404
Linseed oil	1.482
Alkyd	1.512
Phenolic resin	1.629
Acrylic polymer	1.490
Epoxy resin	1.583
Melamine resin	1.517
Polyester	1.520

Mechanism of Separation on GPC Columns

The total volume available to the solvent in the column consists of two distinct regions; the space between the particle size of the gel (void volume) and the space within the pores of the gel (pore volume). Only the space inside the pores of the gel plays a part in the separation of the solutes. The solvent penetrates through all the voids and pores. The molecules dissolved in the solvent can penetrate through the voids and through pores which are larger than their size, but they are excluded from pores smaller than the size of the molecule.

When a variety of pore sizes is available in the set of columns, the separation can be achieved between several sizes of molecules by the principle of gradual exclusion. The molecules larger than the largest size of the pores are completely excluded and can travel only through the void volume, i.e. they are not separated and leave the column first. The solution leaving the column contains gradually decreasing sizes of molecules appearing at the outlet at increasing elution volumes. The separation ends when the elution volume becomes equal to the total volume of voids and pores. (Elution volume is the volume of solvent leaving the columns from the moment of injection of the sample solution). As the solute molecules have always the choice between flowing through the voids and penetration into the pores, long columns and slow flow rates favour the separation, which is statistical in nature. This is also the reason why a single compound does not leave the column at a single elution volume, but appears as a Gaussian curve. The smaller the base of the curve the higher the efficiency of the separating system.

The elution volumes in the isothermal experiment are proportional to the logarithms of the sizes of the molecules in solution.

Type of Separation

The separation on GPC columns in a separation by size of the solute molecules. The size of the molecule depends not only on its molecular weight, but also on the bond length and bond angles and the general shape. The size of the molecule in solution depends on the type of solvent and the concentration. In GPC experiments, concentration is kept as small as is compatible with the sensitivity of the detector; 1 to 0.2% solutions being normally used. In dilute solutions the interactions of solute molecules are minimised. A good solvent for a given molecular species ensures that the molecules are fully extended, laminar flow of the solution also helping the extension of large molecules.

The distribution of sizes obtained in GPC experiments can be converted to a molecular weight distribution after careful calibration with a set of standards of known molecular weights of the same chemical type as the sample and under the same experimental conditions.

Calibration Procedure

A GPC apparatus with a system of six analytical columns four feet in length of nominal sizes of 60 Å, 100 Å, 400 Å, 1000 Å, 20,000 Å, and 30,000 Å, were used to obtain chromatograms of molecular size distributions of polymers used in this work.

The set of standards used to obtain calibration of elution volumes against the logarithms of equivalent chain length is given in Table 8.

The polystyrene standards are not pure compounds, but polymeric fractions of very narrow distribution.

The elution volumes were obtained using tetrahydrofuran as the solvent at 1 ml/min flow rate, a column temperature of 37^{o}C and 1 ml of 0.25% solution. The standards were either injected singly or in groups of two or three of very different size so as not to overlap. A flowing cell differential refractometer was used as detector. Using this component, detection depends on the difference of the refractive index of the solution and the solvent. Assuming that the refractive index of the eluted fractions remains the same as that of the unfractionated sample, the response of the detector may be taken as being proportional to the concentration of the solute. The fractions are eluted at increasing elution volumes (counts) in the sequence of decreasing molecular sizes.

The results of the separation are recorded on a chart, on which the elution volumes are marked on the abscissa in 1 ml units (counts) and ordinates give the increase of the refractive index of the eluate above that of the solvent; this increase is taken as proportional to the concentration of the solute. The figures obtained were used to plot a calibration curve on semilogarithmic graph paper; the elution volumes are plotted on the linear scale (abscissa), and the equivalent length in Å is plotted on the logarithmic scale (ordinates). The shape of the curve depends on the system of columns used and is approximately linear when the sizes of the molecules are in the range of the pore sizes of the gels filling the columns. When the logarithms of molecular weights are plotted against elution volumes, different curves are obtained for polystyrene, and for polyglycols. When the logarithm of chain lengths are plotted against elution volumes, all the standards used lie on a single smooth curve, which was a standard for subsequent work. The equivalent chain length calibration can be used for all the samples separated in the same experimental conditions.

Hendrickson and Moore[170] determined the elution volumes of 130 compounds using cross-linked polystyrene gel columns and were able to calculate the equivalent Ångstrom chain length from the structural elements of the compounds taking the known valence angles and the known interatomic distances. They found that the dimensions of the structural elements were additive in their effect on the elution volumes of the compounds. The elution volumes could be converted to the equivalent lengths by using a single calibration line for a large variety of compounds. The polystyrene unit conforms to this rule. The main polymer chain consists of CH-CH units with one pendant benzene ring hanging away from the main chain. The chain length per carbon atom is the length of the C-C bond (1.54 Å) multiplied by the size of half the C-C-C angle (109.5°), which comes to 1.25 Å. Two carbon atoms of the unit give the length of 2.50 Å. The molecular weight of the unit is 104, giving the Q factor of 41.6.

The Q factor is defined as the molecular weight per one Ångstrom unit length. In order to obtain the molecular weight from the equivalent Ångstrom length calibration line, a Q factor has to be determined for each type of polymer. When a sample consists of one chemical species, then the Q factor is constant throughout the distribution and can be calculated from the structural elements of the polymers.

The number average length may be calculated from the data of the experimental distribution by means of the following formula:

$$\overline{A_n} = \frac{\sum^{i} \frac{h_i}{A_i} \cdot A_i}{\sum^{i} \frac{h_i}{A_i}}$$

where h_i = ordinates of the experimental distribution taken at 0.5 ml intervals.

A_i = equivalent chain length read from the calibration line for the appropriate elution volume.

The weight average length may be similarly calculated from the data of the experimental distribution curve by means of the following formula:

$$\bar{A}_w = \frac{\Sigma^i h_i \cdot A_i}{\Sigma h_i}$$

Both number average length and weight average length can can be used to evaluate the Q factor if the corresponding molecular averages are determined by an independent method.

$$Q = \frac{\bar{M}_n}{\bar{A}_n} = \frac{\bar{M}_w}{\bar{A}_w}$$

The dispersion factor 'D' is the ratio of the weight average to the number average length. This factor gives the information about the broadness of the distribution.

There is an underlying assumption in this method of obtaining the Q factor that all the components of the distribution have a similar structure. If there is a reason to believe that this is not the case, the molecular weights of the fractions have to be determined. When the structural units of the fractions are known from the synthesis of the polymer, the length can be used to evaluate the Q factor and from that the molecular weight:

$$M = Q \times A$$

TABLE 8

MOLECULAR WEIGHTS AND CHAIN LENGTHS OF THE STANDARDS USED FOR CALIBRATION

Type	M_w	M_n	peak M = $\sqrt{M_n.M_w}$	Peak A Å	Elution Vol. in counts 1 count = 5 ml
Polystyrenes					
PS 5000	5000	4600	4800	117	36.1
PS 10000	10300	9700	10000	244	34.1
PS 19900	19850	19650	19750	480	32.9
PS 51000	51000	49000	50000	1220	31.1
PS 97200	98200	96200	97200	2360	30.02
PS 160000	173000	164000	171000	4160	29.22
PS 411000	411000	392000	402000	9800	27.75
PS 860000	867000	773000	830000	20200	26.8
PS 2000000	2145000	1780000	1987200	48000	26.5
Polypropylene glycols					
P 750		790		50.5	39.0
P 1200		1200		78.0	37.5
P 2020		2020		126	36.46
P 4000		3900		241	34.6
n-octadecane			254	26	42.65
n-hexatriacontane			506	47.5	39.7
lauryl alcohol			186.3	17.5	43.6
hexyl alcohol			102.2	10	46
p-t-octyl phenol			206	16.5	43.87
m-t-butyl phenol			150	10	46
phenol			94	8	46.7
o-dichlorobenzene			147		49.5

Peak M = the square root average of M_n M_w

Peak A = the length of the chain calculated from a model

Interpretation of Chromatograms

The total volume of the set of columns accessible to solvent is approximately 270 mls (54 counts). The void volumes is approximately 125 mls (25 counts) and the total volume of gel pores is 145 mls (29 counts). All the components of the sample appear on the chromatogram between 25 counts and 54 counts. The area under the peak is considered to be proportional to the amount of solues present in the sample injected (provided that their refractive indices are the same). The area under the peaks or under the broad distribution curve is calculated by measuring heights at equal distances throughout the chromatogram, the accuracy depending on the intervals between the heights measured. For fairly broad and smooth distributions it is often sufficient to measure the heights every 2.5 ml (0.5 count).

For the distributions composed of well resolved peaks, the peak heights have to be measured and heights at 1 ml distance from the peak taken. As mentioned earlier, a single compound appears on the chromatogram as a nearly symmetrical curve which can be approximated to a triangle, the base of this triangle in the case of these columns is about 8 mls (standard deviation 2 ml).

Broad Distribution Curves

A table is prepared of heights at half a count intervals and the appropriate sizes read from the calibration curve. The sum of all the heights is calculated and the individual heights are expressed as a percentage of the total. These heights can then be plotted on semilog graph paper, taking as the abscissa the logarithms of sizes, and as ordinates the percentage heights. In this way a size distribution is obtained from which the percentage of various sizes can be read. If the Q factor is known the distribution can be expressed taking logarithms of molecular weights as abscissa.

The table of these data can also be used to calculate the number average and the weight average molecular size and also the polydispersity D = M_w / M_n. When A_i is the Ångstrom size of point i and h_i is the height at this point, the values $A_i . h_i$ and h_i/A_i are calculated. The sum of all the products is divided by the sum of the heights to obtain the weight average molecular size, and the sum of the heights is divided by the sum of h_i/A_i to obtain the number average molecular size.

These data were used to characterise the distribution and to evaluate the Q factor. The chromatogram very often reveals the presence of a number of low molecular weight components which influence the M_n value to a great extent, making it insensitive to the presence of large molecular species.

3.2.1. (ii) Results and Discussion

Number and weight average molecular weights of polymers, copolymers and terpolymers calculated from GPC data are given in Table 9. The chromatogram for poly BMA is given in Figure 3 as a typical example of these.

The Q factor for these polymers was calculated as 56.8 from the molecular weight of the repeating unit divided by the lengths of the two carbon atoms as given on page .

Comparison of the data of Table 9 reveals that N6, N12, N18, N31, N32, N27 and N26 have much broader distribution than the base polymer. The distribution is biased towards higher molecular species. (Probably a higher viscosity due to the larger number of larger molecules).

It was also found that chromatograms of N31 and N32 contained an additional but lower in height peaks. The small peak corresponded to low molecular weight polymer with the following values of molecular weights.

	M_w	M_n	$Area_1$	$Area_2$
N31	1160	1105	8.8%	91.2
N32	1392	1322	12%	88%

The presence of low molecular weight species presumably those of polyallylrhodanine or polytriallylisocyanurate did not affect the adhesion, because the addition of allylrhodanine monomer as an additive to polybutylmethacrylate polymer solution reduced the adhesion by 50%.

TABLE 9

CHARACTERISTICS OF COPOLYMERS AND TERPOLYMERS

Ref. No.	Monomer Composition	M_w	M_n	D
N8	BMA	73368	34875	2.10
N6	BMA + 5% 4-vinylpyridine	104864	43219	2.43
N13	BMA + 10% 4-vinylpyridine	61896	31301	1.97
N9	BMA + 5% N-vinylpyrrolid-2-one	66671	33506	1.99
N14	BMA + 10% N-vinylpyrrolid-2-one	88601	42548	2.08
N5	BMA + 5% Dimethylaminoethylmethacrylate	66728	32023	2.08
N12	BMA + 10% Dimethylaminoethylmethacrylate	75907	33806	2.24
N18	BMA + 5% 1-vinyl-2-methylimidazole	49960	22620	2.21
N15	BMA + 10% 1-vinyl-2-methylimidazole	32893	19675	1.67
N31	BMA + 5% triallyl s-triazine 2,4,6-trione	85796	37221	2.30
N32	BMA + 5% N-allylrhodanine	92215	41384	2.22
N33	BMA + 5% allylglycidyl ether	98866	41174	2.40
N35	BMA + 5% vinyltriethoxysilane	95000	55500	1.71
N16	BMA + 1% acrylic acid	90351	42798	2.11
N26	BMA + 5% acrylic acid	85020	30670	2.77
N27	BMA + 1% acrylic acid + 5% 1-vinyl-2-methylimidazole	50550	22350	2.26
N28	BMA + 1% acrylic acid + 5% dimethylaminoethylmethacrylate	49436	22890	2.16
N19	BMA + 5% acrylic acid + 5% 1-vinyl-2-methylimidazole	50023	23855	2.09
N20	BMA + 5% acrylic acid + 5% dimethylaminoethylmethacrylate	81648	37719	2.16

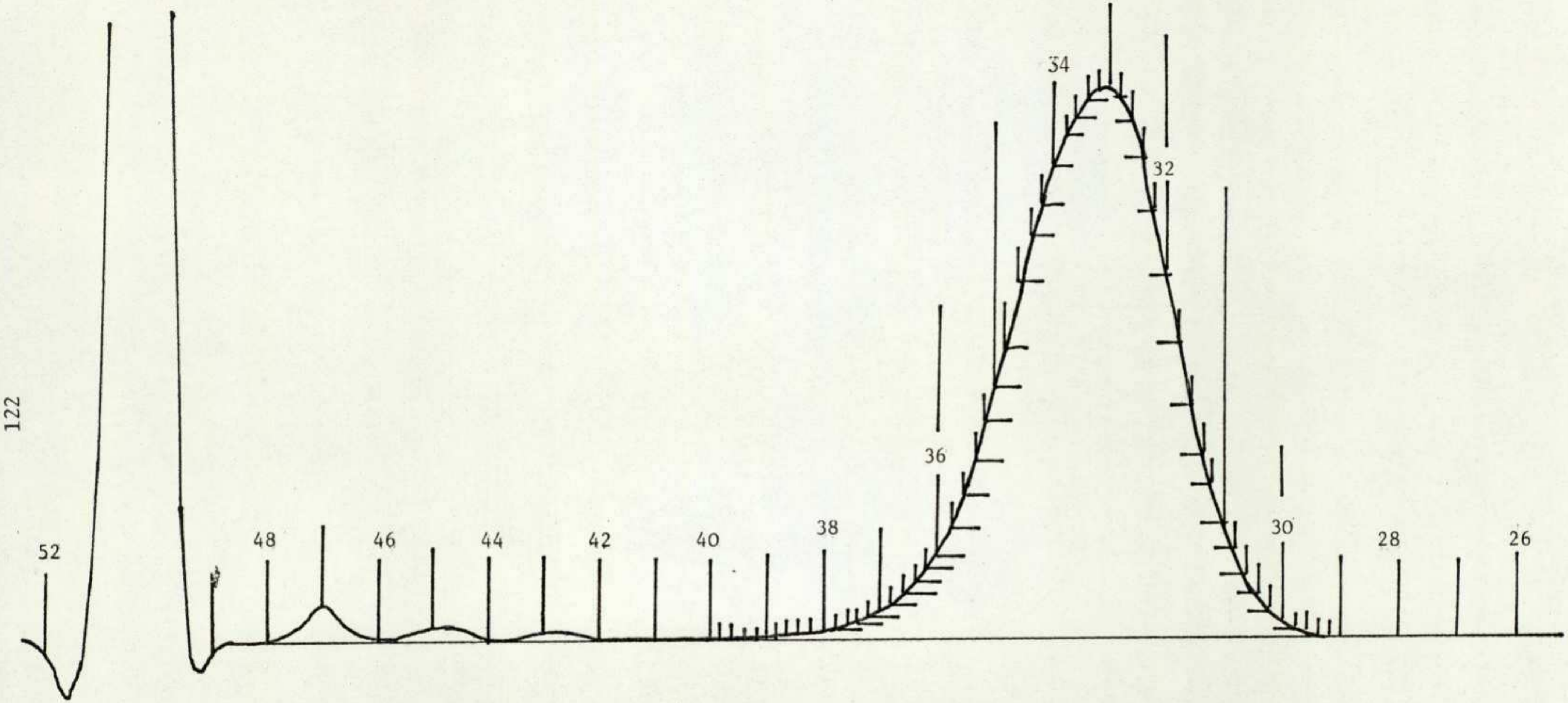


Figure 3. G.P.C. Chromatogram for n-Butylmethacrylate Polymer (N8).

3.3. Infra Red Spectroscopy

3.3.1. Experimental

A Perkin-Elmer model 137 infra-red spectrometer was used.

The infra-red spectra of freshly distilled monomers were determined from thin film between two sodium chloride plates.

Depending on the nature of a particular homopolymer a sample was either made in KBr disc or applied as a film from solutions onto sodium chloride plate with subsequent removal of the solvent by vacuum. (For preparation and properties of homopolymers see Chapter 3, section 3.7.1, 3.7.2).

For the copolymers, a solvent free sample was dissolved in methylene chloride of a spectroscopy grade to give a 10% solution. A film was spread on a sodium chloride plate using a capillary glass tube so that the thickness increased gradually. The solvent was removed under vacuum using a vacuum hot plate.

The position of the sodium chloride plate in the energy beam was adjusted so that the peak of the absorption at 1739 cm^{-1} did not exceed 0.7 absorbance, so that comparison of the various bands could be carried out quantitatively. This band at 1739 cm^{-1} is due to the stretching vibration of the ester carboxylic group[171,172].

The spectra were all run at a scanning rate of 12 minutes for the wavelength range 2.5 - 15 microns.

To increase the absorbance of minor bands, spectra were also obtained from thick films in some cases.

Thus, overall spectra were obtained for:

1. monomers
2. homopolymers

3. copolymers)
) for these, as both thin & thick films
4. terpolymers)

3.3.2. Results and Discussion

To ascertain the presence of various modifiers in the synthesized copolymers and terpolymers by infra-red spectroscopy, it was necessary to establish experimentally the specific bands of each modifier, in the monomeric and the polymeric forms. In addition, the application of literature values can be misleading because positions and intensities of the absorption bands can vary depending on the nature and composition of specific groups of compounds.

My results for the characteristics of the stretching vibrations of the sharp bands of monomers and homopolymers were tabulated in Table 10.

A comparison of various features of the spectra of copolymers and terpolymers of thick and thin films, of modifiers as homopolymer and monomers was made, and some literature references were reviewed.

Brownlie[173] reported that pyridines give a pair of bands in the 1600-1500 cm^{-1} as a result of the C=C and C=N links in the ring.

Cook and Church[174] in their studies on the correlations of the infra-red absorption bands of pyridine and substituted pyridines with their structures found similar absorption bands near 1600, 1570 and 1000 cm^{-1}.

Bellamy[171] reported that strong ring stretching vibration of CH around 3020 cm^{-1} and for C=C and C=N 1660-1590 cm^{-1}. For ring vibration, CH deformation the bands are near 1200 cm^{-1}, strong 1100-1000 cm^{-1}, strong 900-650 cm^{-1} and 710 cm^{-1}.

Bands featured in Table 10 indicate the similarity with the reported values and that pyridine ring was ddtected in the copolymers N6 and N13.

For N-vinylpyrrolidone similar band near 1625 cm^{-1} was observed in the copolymers N9 and N14.

Dimethylaminoethylmethacrylate in N5 and N12 was not detectable through the deformation mode of the CH_3 group attached to nitrogen which occurs at 1375 cm^{-1} or in the 1460-1430 cm^{-1} region. Bellamy[171] concluded that despite the constant frequency shown by CH_3 deformation attached to carbon (CH_3-C-1375 cm^{-}) and other elements the NCH_3 is too weak in intensity or too variable in position. The elemental analysis was sufficient confirmation.

For N18 and N15 the C=C and C-N ring aromatic vibration was demonstrated in the band 1650 $cm^{-1}$and 1540 cm^{-1}.

It was shown[164] that triallylisocyanurate monomer was characterised by sharp bands near 5.9 and 6.9 microns from carbonyl and double bonds respectively, with weak absorption occurring at 3.2 microns from CH bands. These bands were also found in the monomer and homopolymer. C-N link was detected in copolymer N31 at 1320 cm^{-1}.

In copolymer N32 the link C-N at 1330 cm^{-1} was found in thick film. The monomer N-allylrhodanine showed specific bands at 1740 cm^{-1} for the carbonyl group, -C-S- at 690 and -N-C=S at 1420 cm^{-1}.

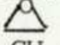
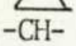
In conclusion, those bands which were characteristics for the modifiers were undetectable in certain copolymers because of the overlapping and the similarity in the bands of the base polymer (n-BMA) and only very few were identified.

TABLE 10

Stretching Vibrations of Characteristic Linkages in Modifiers as Monomers and Homopolymers and as in Copolymers

Name	Monomer	Homopolymer	Detected in copolymer
	stretching vibration	Wave number (cm^{-1})	
n-Butylmethacrylate		745, 1060, 1140, 1250, 1460, 1740, 2950 -C=O 1740 C-CH$_3$ -CH$_2$-C	-
4-Vinylpyridine	756, 790, 835, 930, 995, 1070, 1225, 1240, 1425, 1575, 1625, 3110 C=C and C=N 1625, 1575 Ring vibration, CH 3110 CH deformation 1225-1240 (S) 995-925 (S) 835	995, 1160, 1225, 1410, 1560, 1625, 2950, 3020 , 820	Thin film, 1625 Thick film 1560, 1625 1560
N-Vinylpyrrolidone	705, 855, 940, 990, 1055, 1300, 1400 1650, 1740, 3020 C=O 1740 -CH$_2$- 1300, 1400 C-C, C-N 1650 -CH- 3020, 855	840, 1290, 1320 1425, 1460, 1675 2950 1700 1290, 1320, 1425 1675 3020, 840	Thin film, 1625 1690-1700
Dimethylamino ethylmethacrylate	780, 800, 940, 1020, 1160, 1300, 1315, 1460, 1660, 1750, 2900, 3090	1725, 1150, 1450 2950, 2750	Thick film CH 2750 2310
	C=O 1750 C-N 1160 N-CH$_3$ 1460 deformation 1460-1430 of CH$_3$ attached to N CH$_2$=CH- (vinyl) 3090 as CH stretching C-CH$_3$ 1375, (1300-1315)	C=O 1725 C=N 1150 N-CH$_3$ 1450 -CH$_2$-CH- 2950 CH 2750	
1-Vinyl-2-methyl imidazole	885, 1160, 1275, 1360 1420, 1440, 1510, 1550, 1660, 3160	1275, 1650, 1420 2950, 3100, 3450	Thick film 1650 in N18, 1540 in N15
	C=C and C-N aromatic bands 1660 C-CH$_3$ - 1400-1450 CH$_2$=CH-N- 3150 N-CH$_3$ 1400-1450 -CH- 1360	C=C and C-N 1660 C-CH$_3$ 1420 -CH$_2$-CH- 2950	

Table 10 (cont.)

Triallyliso-cyanurate	760, 1340, 1425, 1475, 935, 1675, 1730, 3110 C-N 1320 CH deformation 769 C=O 1675 CH 3110	769, 930, 1320, 1460, 1690, 2950, 3090 C-N 1320 CH deformation 769 C=O 1690 CH 3090	Thick film 770, 1320
N-allylrhodanine	690, 1175, 1190, 1330, 1420 1740, 2950, 3450 C=O 1740 C-N 1330 -C-S- 690 (600-700) -N-C=S 1420 (1500-1470)	-	C-N, 1330 cm^{-1}
Allylglycidylether	765, 855, 920, 995, 1100, 1140, 1160, 1250, 1425, 1650, 2880, 3000, 3180, 3500 -CH$_2$-O-CH$_2$- ether linkage (1150-1060), 1100, 1140, 1160  epoxy 1250 -CH- 2880-3180, 855 CH$_2$=CH-CH$_2$ C-C 1650 1460 -CH$_2$- 1425	755, 855, 910, 1100, 1160, 1250, 1340, 1390, 1450, 1660, 1725, 2890 2950, 3500 -CH$_2$-O-CH$_2$- 1100, 1160  1250 -CH- 2890 -CH$_2$-CH- 2950 C-C 1660 -CH$_2$- 1450 C=O 1725	Thick film 6.05 6.85 longer 1650, C-C 1460 -CH$_3$ None coincide
Vinyltriethoxysilane	760, 785, 965, 1015, 1080, 1105, 1160, 1295, 1395, 1610, 2900, 2975, Si-O-C 1090-1020 -CH$_3$ 2900, 2975 CH$_2$=CH- vinyl CH out of plane 965 CH in plane defor. 1295	700, 775, 955, 1080, 1105, 1160, 1290, 1390, 1610, 2900, 2975, Si-O-C 1080 -CH$_3$ 2900, 2975 -CH$_2$-CH- vinyl CH out of plane 995 CH in plane defor. 1290	770-790
Acrylic acid	1725, 3100, 1650, 1440 1625 C=O 1725	3400, 2940, 1725, 1460, 1400 C=O 1725 OH- 3400-3500 (3420) -OH dimeric acid 2940 OH bending 1400	N26 3280 2.9) 5.9) N16
N19			14.8 thick
N20			7.9 thick
N28			2.8, 6.9, 7.1
N27			14.8 thick

3.4. Analytical Methods

3.4.1. Experimental

(a) Determination of carboxyl groups in acrylic copolymers and terpolymers

The carboxyl groups in copolymers and terpolymers containing acrylic acid were determined by the measurement of acid values. The acid value is defined as the number of milligrams of potassium hydroxide required to neutralise the acidity of one gramme of the substance.

One to two grammes of the polymer were dissolved in 25 ml of Benzene:Ethanol mixture (2:1 v/v). This was then titrated with N/10 KOH in methanol using phenolphthalein as indicator.

The acid value was calculated from the equation

$$\text{Acid value} = \frac{V \times N \times M}{A} \text{ mg KOH/1 gramme polymer}$$

Where V - is the volume of KOH solution consumed on titration

N - is normality of KOH

M - is equivalent weight of KOH

A - is weight of sample, gramme

The theoretical acid value was calculated using the following equation:

$$\text{Acid value} = \frac{N \times W}{45 \times x} \text{ mg KOH/1 gramme polymer}$$

where N - is equivalent weight of KOH, gramme

W - is number of carboxyl groups in one gramme copolymer

45 - is molecular weight of carboxyl group

x - is mole % of acid modifier

and the results are given below.

(b) Determination of Amine Value

The amine value[175] is the number of milligrams of potassium hydroxide equivalent to the basicity in one gram of sample.

The polymer solid was obtained by removing the solvent and unreacted amines under vacuum at 80°C.

One to two grammes of the polymer solid was dissolved in 25 ml of an appropriate solvent. i.e. acetone; N5, N12. The sample was then titrated with N/10 HCl using bromo-cresol green as an indicator.

The amine value was then calculated using the equation:

$$\text{Amine value} = \frac{V \times N}{w} \text{ mg KOH/1 gram polymer}$$

where V - is the volume in millilitres of N/10 HCl consumed on titration

N - is equivalent weight of potassium hydroxide

w - is the weight of solvent-free polymer grammes.

This method was used to establish the amount of dimethylaminoethylmethacrylate, via an amine value of copolymers N5, N12.

The theoretical amine values were also calculated using the corresponding amounts of nitorgen caontaining monomers used in the preparation of the copolymers.

(c) Elemental Analysis

Carbon, nitrogen and oxygen were determined by Butterworths Micro-Analytical Services, Teddington.

3.4.2. Results and Discussion

The theoretical and experimental acid values of acid containing copolymers and terpolymers are given in the table below and it will be seen that there is generally good agreement.

Reference Polymer	Acid value, mg KOH/1 g polymer	
	Theoretical	Experimental
N16	3.97	3.7
N26	20.20	19.8
N27	4.00	3.9
N28	3.90	3.8
N19	20.50	17.6
N20	20.14	18.5

The theoretical and experimental amine values of two copolymers N5 and N12 are shown below.

For N9 and N14, it is not possible to measure the amine value as there is no free tertiary nitrogen to titrate. Instead the nitrogen content was determined by F. B. Straus at 10 Carlton Road Oxford. Nitrogen content was also carried out for N6.

Reference Polymer	Amine Value mg KOH/g copolymer	
	Theoretical	Experimental
N5	19.50	18.65
N12	38.70	35.2

The results of the elemental analysis for carbon, hydrogen and nitrogen are given in the table below. The theoretical values which were calculated are in good agreement with the experimental.

Ref. olymer	C %		H %		N_2 %	
	Theoretical	Experimental	Theoretical	Experimental	Theoretical	Experimental
N8	67.50	67.20	9.88	9.82	Abs	Abs
N6	68.06	67.62	9.74	9.97	.499	.51
N13	68.54	68.98	9.62	9.80	1.013	1.13
N9	67.49	66.91	9.79	9.72	.497	.34
N14	67.37	68.06	9.72	9.75	1.039	.74
N5	67.25	67.30	9.84	10.10	.49	.51
N12	66.90	66.94	9.83	9.81	.972	1.01
N18	67.57	67.79	9.76	9.78	.998	.54
N15	67.53	68.30	9.67	10.00	2.022	1.56
N31	66.78	66.80	9.54	9.36	1.426	1.18
N32*	66.03	66.20	9.51	9.69	.488	0.29
N33	67.43	69.00	9.81	10.04	Abs	Abs
N35^x	66.48	66.78	9.83	9.66	Abs	Abs
N16	67.52	67.35	9.84	9.94	Abs	Abs
N26	64.71	66.64	9.39	9.68	Abs	Abs
N27	67.48	68.59	9.74	10.19	1.005	.69
N28	67.16	66.65	9.82	9.57	0.493	.48
N19	67.11	67.75	9.65	9.91	1.021	.70
N20	66.78	66.48	9.73	9.68	0.503	.52

*N32 : $S_{Theo} = 2.23\%$ $S_{Exp} = 2.02\%$

^{x}N35 : $Si_{Theo} = .96\%$ $Si_{Exp} = 0.46 \pm 0.02\%$

3.5. Density Measurements

3.5.1. Experimental

The densities of polymers and copolymers were determined using 25 ml density bottles at 25°C.

The known absolute density of distilled water at various temperatures[175,176], was used to calibrate the volume of the density bottles.

Each polymer sample was prepared as powder thus: a polymer solution in toluene was applied onto a Melinex film, left to dry at 25°C for one week and then the retained solvent was removed under vacuum in a vacuum oven at 60°C to a constant weight. This solvent-free polymer was ground to a powder.

Calibration[177] was carried out by determining the volume of the density bottle employing the following steps:

1. The density bottle was cleaned with chromic acid, rinsed with distilled water and acetone dried and brought to a constant weight - M.
2. The density bottle was filled with freshly boiled distilled water at a temperature below 25°C. The bottle was capped, (ensuring that air bubbles are avoided), with the overflow orifice open. The excess overflowed water was removed with tissues. The bottle was left at a constant room temperature at 25°C. The excess overflow of water was wiped away. The outside of the bottle was wiped and the filled bottle was immediately weighed - 'N'.
3. The volume of the bottle was calculated using the equation

$$\nu = \frac{N - M}{q}$$

where ν = volume of container in cubic centimeters

q = absolute density of water in grams per cubic centimetre at specified temperature (0.997044 g/cm^3)

N = weight of bottle and water, grams

M = weight of dry bottle, grams.

4. The mean of three determinations of ν was obtained to provide the value of 'V' as the volume of the density bottle in cubic centimetres.
5. The procedure in 1-4 was repeated substituting methanol for the distilled water. The weight of the methanol filled bottle was recorded as W_2 and the weight of the empty bottle as w, if different from M.
6. The density of methanol was then calculated using the following equation:

$$D_{\text{methanol}} = \frac{W - w}{V} \quad g/cm^3$$

7. The empty container was then filled with the polymer powder to $\frac{1}{3}$ of the volume of the bottle and the weight was recorded as W_3.
8. The bottle with polymer powder was filled with methanol and the weight was recorded as W_4.
9. The density of the polymer, D, was then calculated using the following equation:

$$D_{\text{polymer}} = \frac{W_3 - M}{(W - M) - (W_4 - W_3)} \times D_{\text{methanol}}$$

Three determinations of the density of the polymer were carried out and the mean was taken.

3.5.2. Results and Discussion

The densities of polymers shown in Table 11 are all lower than those reported[178] and higher than for commercial acrylic resins[179]. The lower or higher values may be attributed to the differences in the molecular weights, method of preparation.

TABLE 11

Density of Polymers at 25°C

Polymer Reference No.	Density* g/cm	Published values with references
N8	1.0570	1.13 - 1.19[178]
N6	1.0518	.95 - 0.97[179]
N13	1.0432	
N9	1.0474	
N14	1.0487	
N5	1.0587	
N12	1.0458	
N18	1.0580	
N15	1.1620	
N31	1.0600	
N32	1.0880	
N33	1.0520	
N35	1.0330	
N16	1.0501	
N26	1.0578	
N27	1.0400	
N28	1.0395	
N19	1.0798	
N20	1.0670	

*Each value reported is the mean of 3 determinations

3.6. Cohesive Energy Density

3.6.1. Theoretical Calculations

The solubility parameters of thermoplastic polymers were calculated as shown in Table 12, using Small's[142] method, the molar attraction constants of Hoy[161] and assuming a random structure for the polymers. For full discussion of the method see Section 3.16.

TABLE 12

Calculated Solubility Parameter of Polymers

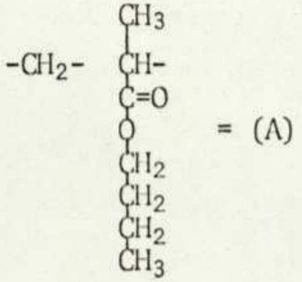
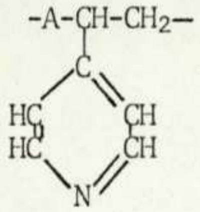
Polymer Ref. No.	Proposed structure of repeating unit of Polymer molecule	Molecular weight of repeating unit gm/mole	Density 'd' gm/cc	Groups	Molar Attraction constants $(cal.\ cc)^{\frac{1}{2}} mole^{-1}$	Sum of Molar Attraction Constants ΣF	Solubility Parameter $(cal.\ cc)^{\frac{1}{2}}$ $\delta = d.\frac{\Sigma F}{M}$
N8	 $-CH_2-CH(CH_3)-C(=O)-O-CH_2-CH_2-CH_2-CH_3$ = (A)	142	1.057	$(-CH_2-)$ (CH_3-) $-\overset{\vert}{\underset{\vert}{C}}-$ $-COO-$ Base value	131.5 x 4 148.3 x 2 32.03 326.58 135.1	1316.31	9.79
N6		(5/100 x 105)+ 95/100 x 142 = 140.15	1.0518	As (A) + $-\underset{\vert}{CH}-$ $-CH_2-$ C aromatic N CH aromatic Base value six membered ring	As (A) + 85.99 131.50 98.12 61.08 117.12 x 4 135.1 -23.41	(95/100 x 1316.31) +5/100 x 956.86) = 1298.34	9.74
N13	as N6	(10/100 x 105) + (90/100 x 142) = 138.3	1.043	As N6	As N6	(90/100 x 1316.31 +(10/100 x 956.86 =1280.365	9.66

Table 12 cont...

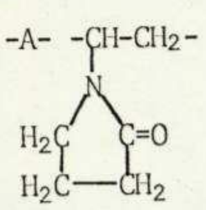
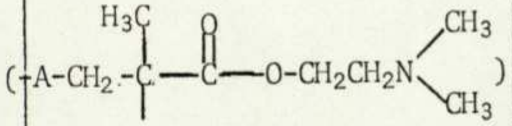
N9		(5/100 x 111) + 95/100 x 142 = 140.45	1.047	As (A) + N ring -CH- -CH$_2$- ring -CH$_2$- C=O ring Base value five membered ring	61.08 85.99 131.50 x 3 131.5 262.96 135.1 20.99	95% x 1316.31 + (5/100 x 1092.13) = 1305.09	9.73
N14	As N9	(90/100 x 142) + (10/100 x 111) = 138.9	1.049	As N9	As N9	(90/100 x 1316.31 + (10/100 x 1092.13) = 1293.89	9.77
N5		(95/100 x 142) + (5/100 x 157) = 142.75	1.059	As (A) + -CH$_2$- -CH$_3$ -C- -COO- N Base value	131.5 x 3 148.3 x 3 32.03 326.58 61.08 135.1	(95/100 x 1316.31) +(5/100 x 1394.19) = 1320.204	9.79
N12	As N5	(90/100 x 142) + (10/100 x 157) = 143.5	1.046	As N5	As N5	(90/100 x 1316.31) +(10/100 x 1394.19) =1324.098	9.65

Table 12 cont..

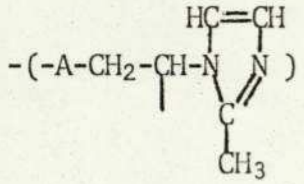
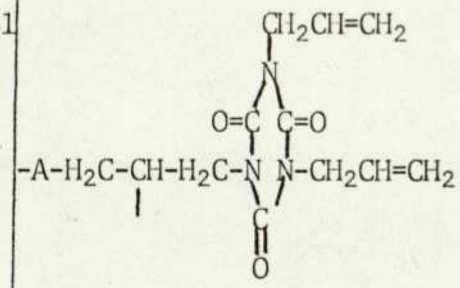
N18		(95/100 x 142) + (95/100 x 108) = 140.3	1.059	As (A) + -CH- $-CH_2-$ \N/ $-CH_3$ -CH= aromatic >C= aromatic Base value five membered ring	 85.99 131.50 61.08 x 2 148.30 117.12 x 2 98.12 135.1 20.99	(95/100 x 1316.31) +(5/100 x 976.45) =1299.31	9.81
N15	As N18	90/100 x 142) + (10/100 x 108) = 138.6	1.162	As N18	As N18	(90/100 x 1316.31) + (10/100 x 976.4) = 1282.319	10.75
N31		(95/100 x 142) + (5/100 x 249) = 147.35	1.06	(A) + -N- >C=O $-CH_2-$ -CH- $CH_2=$ -CH= Base value six membered ring	 61.08 x 3 262.96 x 3 131.5 x 4 85.99 126.54 x 2 121.53 x 2 135.1 23.41	(95/100 x 1316.31) + (5/100 x 2192.44) = 1360.12	9.78

Table 12 cont...

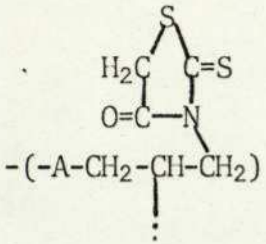
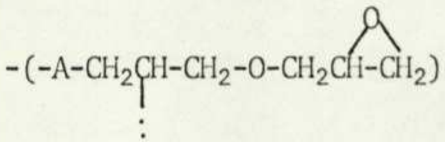
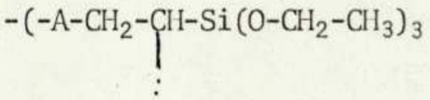
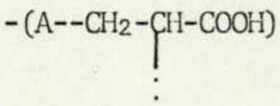
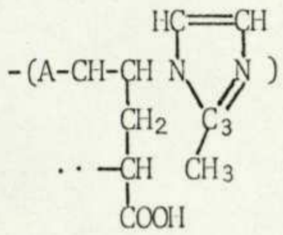
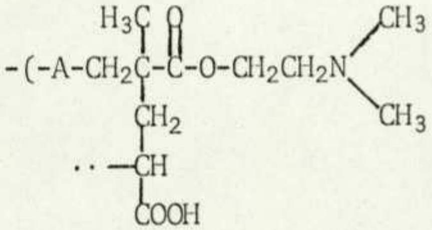
N32		(95/100 x 142 + (5/100 x 173.12) = 143.556	1.067	(A) +  -CH$_2$- allyl -CH$_2$- ring -CH- >N- >C=O >C= Base value five membered ring	 209.42 x 2 131.5 x 2 131.5 85.99 61.08 262.96 98.12 135.1 20.99	(95/100 x 1316.31) +(5/100 x 1477.58) =1324.37	9.84
N33		(95/100 x 142) + (5/100 x 114) = 140.6	1.052	 -O- -CH$_2$- -CH- Base value	176.2 114.98 131.5 x 4 85.99 x 2 135.1	(95/100 x 1316.31) + (5/100 x 1124.26) = 1306.707	9.78
N35	 $-(-A-CH_2-\underset{\vdots}{CH}-Si(O-CH_2-CH_3)_3$	(95/100 x 142) + (5/100 x 190) = 144.4	1.033	-Si- -CH$_2$- -CH- -O- -CH$_3$ Base value	 131.5 x 4 85.99 114.98 x 3 148.3 x 3 135.1	(95/100 x 1316.31) +(5/100 x 1746.35) =(1337.81)	9.57
N16	 $-(A--CH_2-\underset{\vdots}{CH}-COOH)$	(99/100 x 142) + (5/100 x 172) = 141.3	1.050	-CH- -CH$_2$- -COO- -H Base value	85.99 131.5 326.58 (-50.47) 135.1	(99/100 x 1316.31) +1/100 x 628/7) =(1309.43)	9.73

Table 12 cont...

N26	As N16	(95/100 x 142) + (5/100 x 72 = 138.5	1.0578	As N16	As N16	(95/100 x 1316.31) +(5/100 x 628.7) 1285.073	9.79
N27		(94/100 x 142) + (1/100 x 72) + (5/100 x 108) = 139.6	1.04	As (A) + N18 + N16	As (A) + N18 + N16	(94/100 x 1316.31) +(1/100 x 628.7) +(5/100 x 976.4) =1297.32	9.66
N28		(94/100 x 142) + (1/100 x 72) + (5/100 x 157) = 142.05	1.04	As (A) + N5 + N16	As (A) + N5 + N16	(94/100 x 1316.31) +(1/100 x 628.7) +(5/100 x 1394.19) =1313.32	9.62
N19	As N27	(90/100 x 142) + (5/100 x 108) = 136.8	1.0798	As N27	As N27	(90/100 x 1316.31) +(5/100 x 628.7) +(5/100 x 976.4) =1264.93	9.98
N20	As N28	(90/100 x 142) + (5/100 x 72) + (5/100 x 157) = 139.25	1.067	As N28	As N28	(90/100 x 1316.31) +(5/100 x 628.7) +(5/100 x 1394.19) =(1285.82	9.85

3.6.2. Results and Discussion

Calculated cohesive energy densities of synthesized polymers are recorded in Table 13.

The values for the various copolymers and terpolymers were all very similar to the value of 9.79 for the unmodified polymer N8 except for N15.

The experimental values of cohesive energy densities of modified (18) and unmodified (N8) polymers were determined by measurement of viscosities of polymer solutions in order to establish the effect of chemical modification of the polymer chain on adhesion as a result of possible alteration of CED. (See Section 3.16).

TABLE 13

Calculated Cohesive Energy Density of Polymers

Reference No.	Solubility Parameter, δ, $(cal/cc)^{\frac{1}{2}}$
Stearic Acid	8.82
N8	9.79*
N6	9.74
N13	9.66
N9	9.73
N14	9.77
N5	9.79
N12	9.65
N18	9.81
N15	10.75
N31	9.78
N32	9.84
N33	9.78
N35	9.57
N16	9.73
N26	9.79
N27	9.66
N28	9.62
N19	9.98
N20	9.85

* δ literature = 8.7 (1)

3.7. Composition Distribution

3.7.1. Experimental

It is relevant to investigate the composition distribution or proportion of the reactants in the macromolecular chain of a particular polymer. This is important in understanding the basic physical and chemical characteristics of the polymer.

Since polymeric compositions are characterised by segmer or repeating units, the method of identification would involve the determination of the ratio of n-butylmethacrylate units to the modifier units in the final copolymer and its relation to the initial monomer ratio.

An extraction principle was adopted. This was based on the removal from the final product, of any free homopolymer of one of the reactants by the application of the appropriate solvent/nonsolvent system and the subsequent analyses of the remaining portion of the copolymer.

3.7.2. Preparation of pure homopolymers of the modifiers

The solubility characteristics of poly n-butylmethacrylate, poly 4-vinylpyridine, poly-N-vinylpyrrolidone and polyacrylic acid in organic solvents are reported in the literature[178]. However, availability of samples of these homopolymers was essential because the knowledge of the ultraviolet absorption spectra of the homopolymers became imperative for explaining the results of adhesion of paints after artificial weathering.

Poly(4-vinylpyridine) was prepared in ethanol, and in accordance with a reported method[180] for bulk homopolymerisation of vinylpyridines by heating the monomer for six hours at 40°C and in the presence of 1% benzoyl peroxide.

Poly(N-vinylpyrrolidone) was made in methanol using 0.1% azobisisobutyronitrile as the initiator and heating at 65°C for 2 hours. This polymer was also obtained[181] by the vinyl polymerisation using hydrogen peroxide as an initiator.

Polydimethylaminoethylmethacrylate was prepared in ethanol using 0.5% azobisisobutynonitrile as initiator at 80°C.

Poly(1-vinyl-2-methyl imidazole) was homopolymerised in toluene using 0.5% azobisisobutynonitrile at 80°C for one hour to yield on removal of solvent a powdery yellowish polymer.

Poly(triallyl-s-triarine 2,4,6-trione or (cyclic N-allylimide) TALC) was prepared by bulk polymerisation of the monomer at 160°C in air and in accordance with the procedure of Gillham[182].

Polyallylglycidylether

Vinyl type homopolymerisation of the pure monomer was reported by various workers and was conducted under various conditions.

Shell reported[183] the homopolymerisation by air blowing at 220°C or by heating with peroxide.

It was also claimed[184] that 40% polymer was obtained.

A polymer with a molecular weight of 500 has been synthesized[185] using solution polymerisation technique in benzene with the application of 3% di-t-butylperoxide at 155°C.

In the present work, pure monomer with the physical characteristics described in Section 3.1.1.(i) was polymerised in accordance with British Patent[186] as 50% in benzene solution using 3% di-t-butylhydroperoxide and heating at 200°C for 5 hours and in the presence of oxygen. The solvent was then removed under vacuum to yield clear viscous liquid.

Poly-(Vinyltriethoxysilane):

Wagner et al[187] almost converted the pure vinyltriethoxysilane monomer to colourless viscous liquid polymer, having M.W. of 5000 to 8000, using 0.1% di-t-butylperoxide as catalyst, and heating at 135°C for 16 hours.

Mixer and Bailey[188] covered some novel aspects of the peroxide-catalysed homopolymerisation of the monomer in argon atmosphere at 125°C and suggested a chain transfer mechanism as an important reaction in this case.

The homopolymer was made in xylene and following the conditions of Wagner[187] the solvent was removed and the polymer was tested for solubilities.

3.7.3. Method of Extraction

In duplicate, and to an accurately weighed sample of ground solvent-free copolymer, a suitable solvent was added. The mixture was warmed, and then left to stand for a week with occasional shaking to ensure complete leaching and dissolution of the homopolymer.

After this period of contact, the solvent was removed by filtration and the sample was for a second time subjected to the same procedure. Then the copolymer remaining was dried under vacuum to a constant weight and analysed for elemental composition, for acid value and for percentage weight loss.

Organic solvents were not used because a substantial proportion of the copolymer would have been extracted.

It was also found necessary to aim at extracting the homopolymer portion of the modifiers rather than of the polybutylmethacrylate because the former consistituted only a small proportion in the copolymer chain.

In certain cases, it was not possible to find a suitable solvent/nonsolvent system. In the absence of any reliable data on the solubility characteristics of the homopolymers, they were synthesized and their solubilities were assessed in various solvents.

Calculation of the Monomer and the Copolymer Segmer Ratios

Because a homopolymer consists of a sequence of identical segmers, whereas a copolymer contains more than one segment species, this argument followed.

The ratio of the repeating n-butylmethacrylate units to the modifier units in one macromolecule of the copolymer was expressed by:

$$xA + yB + zC \quad = \quad X \qquad (76)$$

where x, y or z - is the number of molecules in monomer A, B and C respectively which give one molecule of polymer

X - is percentage experimental value of nitrogen, sulphur or silicone before and after extraction.

Equation (76) can take the form of the following equation in terms of molecular weights of A, B for one gram copolymer (N6), through 0.51% N_2.

$$\frac{14\,y}{x\,M_A + y\,M_B} \times 100 = X$$

Substituting the appropriate values and resolving for x and y yields that

$$\frac{x}{y} = 18.6$$

Now if $y = 1 \quad \therefore \quad x = 18.6$.

3.7.4. Results and Discussion

The solubility characteristics of the homopolymers (not recorded in literature) in various organic solvents are recorded in Table 14.

The results of the elemental analysis for nitrogen, carbon and hydrogen before and after extraction of free homopolymers are given in Table 15.

Tables 16 and 17 show the theoretical and experimental distribution molar ratios of the reactants as monomers and polymers, which were calculated using equation (76). (y and z were taken as unity).

These calculations indicated that the molar ratio of n-butylmethacrylate units to modifier's units in the final copolymer (column (2) Table 16) was not greatly different from the initial monomer ratio (column 1), i.e. for every one segmer of modifier there are the "x" segmer numbers of n-butylmethacrylate.

Juve[189] et al showed that the elemental analyses for nitrogen in polyvinylpyridine homologs were lower by 25% than those calculated in the monomer. Subsequently when these monomers were used as modifiers for butadiene rubbers, Juve found that their ratio in the final copolymers was lower than the theortical.

In this work the nitrogen content in copolymers containing

4-vinylpyridine (N6, N13) and hence, the ratio, agrees very well with the theoretical values.

Since homopolymerisation of allylrhodanine was not attempted due to the absence of any information regarding the conditions or methods of syntheses, its solubility characteristics were not established. Although such characteristics were attained for homopolymer of triallylisocyanurate, allylglycidylether and vinyltriethoxysilane, suitable solvent/nonsolvent systems were unascertainable. Hence a lack of data on composition distribution resulted.

As an alternative route, the extraction of polybutylmethacrylate by cyclohexane failed to show the presence of any residues of polytriallylisocyanurate or poly N-allylrhodanine, although substantial amounts of lower molecular weight species were detected from GPC analyses of the parent copolymers N31 and N32. True representation of the composition distribution was based on such analyses.

For the identification of the composition of acid containing copolymers and terpolymers, the acid values were used as a tool. Consequently, the molar ratio in monomer and in copolymer mixtures of N16 and N26, were calculated before and after extraction and it was found that 0.078% mole and 1.9% mole as polyacrylic acid was present respectively.

For the analyses of terpolymers N27 and N19 double extraction was carried out. The first was to extract any free polyacrylic acid by water and the second was to extract simultaneously polyacrylic acid and poly 1-vinyl-2-methylimidazole.

The composition of N27 before and after extraction was practically the same and this was also confirmed by the identical acid values. However, this did not resemble the theoretical 'X' value of butylmethacrylate.

In N19 terpolymer, the double extraction confirmed that there was appreciable amounts of poly VMI, and BMA/acrylic acid copolymer because the acid value remained unchanged.

Terpolymers N28 and N20 were subjected to a single simultaneous extraction to remove poly DMAEMA and polyacrylic acid because both are soluble in water and dilute acids.

Acid values and nitrogen content proved that the distribution was similar before and after extraction.

In general, after extraction, there was a tendency for nitrogen content to increase in value. However, in most cases, the values of 'X', column 3 of Table 16, and column 4 of Table 17, suggested that the amount of free homopolymer of modifiers at 100% conversion was very small.

Copolymers normally consist of a mixture of polymers, whose copolymer composition is subject to a composition distribution function, and is dependent on the rate of copolymerisation of the mixture of monomers. Such rate is controlled by the values of the relative reactivity ratios say r_1, r_2 etc. which describe the rate of addition of radical monomer (1) with monomer (1) and monomer (2), and of radical monomer (2) with monomer (2) and monomer (1). (see section 2.1.2).

Since the values of these parameters are unknown the general picture of the composition distribution presented here must be regarded as approximate.

Table 14

The Solubility Characteristics of Homopolymers

Homopolymer	Solvent	Nonsolvent
Poly(dimethylaminoethylmethacrylate	ethanol, H_2O, methanol dilute HCl	cyclohexane
Poly(1-vinyl-2-methylimidazole)	Methanol, partially soluble in water, dilute acid, ethanol	hexane, cyclohexane
Poly(tri-allylisocyanurate), cyclic N-allylimide	toluene, acetone (partially S), MEK (PS), benzene (S to PS), methylene chloride partially soluble to soluble, chloroform, carbon tet. (PS), diethylether (PS)	ethanol, ethylene glycol, water 0.1N HCl, methanol cyclohexane
Poly(allylglycidyl ether)	PS Benzene, xylene, dioxane, methylene-chloride, toluene chloroform, carbon tet.	ethanol, methanol water, cyclohexane diethylether
Poly(vinyltriethoxysilane)	Cyclohexane, carbon tet. methylene chloride, benzene, toluene, xylene, hexane, chloroform, carbon tetrachloride	water, methanol, ethanol (cold)

Key (S) - Soluble
(PS) - Partially Soluble

Table 15

Experimental Elemental Analyses Before and After Extraction

Reference Polymer	C %		H %		N_2 %	
	Before	After	Before	After	Before	After
N8	-	67.2	-	9.82	-	Abs
N6(1)	67.62	67.93	9.97	9.87	.51	.71
N13(1)	68.98	66.9	9.8	10.23	1.13	1.00
N9(1)	66.91	68.14	9.72	10.16	0.34	.48
N19(1)	68.06	67.43	9.75	10.06	.74	.68
N5(1)	67.3	67.15	10.10	10.02	.51	.47
N12(1)	66.94	67.89	9.81	10.04	1.01	1.26
N18(1)	67.79	66.98	9.78	9.52	.54	.63
N15(1)	68.30	66.62	10.00	9.72	1.56	1.73
N27(1)	68.59	67.18	10.19	9.95	.69	.73
N27(2)	68.69	69.22	10.19	10.85	.69	.71
N28(1)	66.65	67.2	9.57	10.26	.48	.51
N19(1)	67.75	66.92	9.91	10.34	.70	.80
N19(2)	67.75	66.91	9.91	10.43	.70	.17
N20(1)	66.48	66.51	9.68	9.88	.52	.53

Table 16

Composition Distribution of the Number of Segmer Species in the Chains of Copolymers

Ref. No.	Extracting Media	Monomer Mixture	Polymer Mixture		
		Theoretical	Experimental calculated using the results of elemental analyses		
		Calculated using weights of monomers	Before Extraction	After Extraction	
		x, $y^{(+++)}$	x	x	Total wt loss
		(1)	(2)	(3)	
N6	Aqueous in HCl	19	18.6	13.2	.609
N13	"	8.99	7.99	9.12	.1
N9	Aqueous in HCl	19.02	28.2	19.76	.33
N14	"	8.71	12.54	13.72	.54
N5	Aqueous in HCl	19.02	18.23	19.87	.46
N12	"	9.04	8.66	6.72	.32
N18	Aqueous in HCl	19.00	35.75	30.54	.36
N15	"	9.00	11.88	10.64	.13
N31	Clear solution in cyclohexane	19	23.3	-	-
N32	"	18.98	32.77	-	-
		3.2*	3.66		
N33	Clear solution in cyclohexane	28.8	-	-	-
++ N35	Absence of suitable solvent	18.99	20.09	-	-

* Using the value of sulphur content
++ Using the value of silicon content
+++ y = 1

TABLE 17

Composition Distribution Ratios of the Number of Segmer Species in the Chain of Acid Copolymers and Terpolymers

Ref. No.	Extracting Media	Monomer Mixture			Polymer Mixture						Acid Value mg KOH/1 g Resin		Total weight loss of Extractable materials on 250 g Copolymer
		Theoretical ratio calculated using weights of monomers			Experimental Ratio Calculated Using the Results of Elemental Analysis								
					Before Extraction			After Extraction			Before	After	
											Extraction		
		x	y	z*	x	y	z*	x	y	z*			
	(1)	(2)			(3)			(4)			(5)		%
N16	Water	99.3	1	-	101.25	1	-	105.5	1	-	3.8	3.5	.439
N26	Water	18.29	1	-	18.54	1	-	23.57	1	-	19.8	12.1	4.48
N27	(1) Water	36.75	1.97	1	54.86	1.97	1	(1) 51.77	1.97	1	3.9	3.87	.51
	(2) Aqueous IN HCl							(2) 53.27	1.97	1		4	.288
N28	In Aqueous HCl	37.26	1.97	1	38.33	1.97	1	35.95	1.97	1	3.8	14.94	.328
N19	(1) Water	36.58	1.97	1	54.1	1.97	1	(1) 47.11	1.97	1	17.6	16.7	.26
	(2) Aqueous IN HCl							(2)227.25	1.97	1	17.6	18.6	.342
N20	Aqueous IN HCl	36.48	1.97	1	35.42	1.97	1	(1) 34.5	1.97	1	20.14	20.14	.331

(*) Z = 1

3.8. Preparation of Paints

3.8.1. Experimental

Paints were prepared using rutile titanium dioxide (R-CR)[190,191] as a pigment at a pigment-Binder ratio of 1:1 (by weight of the solid polymer). It has good tint retention and milling performance is good. It belongs to the coated and refined type which is produced by surface treatment coated with various thicknesses of silica and alumina oxides, but is organically untreated.

The absence of organic coating for this work is essential so that any interference arising from such coatings on the results of adhesion is eliminated.

Appropriate amounts of polymer as a solution in toluene and of pigment were placed in a paint pot and ball-milled until a reading of above 8 was observed on the Mils scale of a Hegman-gauge, which is used to measure the fineness of grind[192,193], i.e. a quality control test for the degree of dispersion. The latter is a relative term, and what is actually measured is the particle size of the coarsest fraction of a dispersion.

The viscosity of each paint was adjusted to 4 poise by the addition of extra toluene. The viscosity was measured by using the ICI Rotathinner.

3.8.2. Results and Discussion

The level of pigmentation of 1:1 pigment-binder ratio was chosen in these studies after careful comparison of the results of adhesion measurements obtained at a lower lever of pigmentation, i.e. 0.25:1. These results are summarized in Table 18, and suggest that the joint strength is very much lower than that obtained at 1:1 pigment:binder ratio as shown in the last column.

The following considerations highlight the reasons for this difference in adhesion values as the pigment level is changed.

Table 18

Adhesion of Acrylic Paints at 0.25:1 Pigment:Binder Ratio after 4 Days Drying

Ref. No.	Mean joint strength $N/m^2 \times 10^4$	No. of results	Standard devn. $N/m^2 \times 10^4$	Error SD/Mean strength %	Mean joint strength at 1:1 pigment:binder ratio, $N/m^2 \times 10^4$
N8	310.13	4	23.00	5.1	608.50
N6	352.17	6	28.26	8.0	551.30
N13	354.23	5	38.86	10.97	1019.98
N9	344.58	4	34.45	10.00	514.80
N14	305.99	6	26.18	8.56	992.40
N5	470.70	6	39.09	8.35	717.43
N12	869.05	6	48.43	5.63	2281.18/37 (*)

* The area of Adhesion Failure, for others, it is 100%.

The effect of the change in the level of pigmentation on the physical properties of paints in relation to tensile strength[194] and weathering[195] have been thoroughly studied.

If the tensile strength of a paint film is measured[194], it is found that the value will often increase by an order of magnitude or more from that determined on the unpigmented vehicle. It reaches a maximum at the critical pigment volume concentration (CPVC). The concept of CPVC in the formulation of paints has become firmly established in the coatings industry. It is recognised that coating formulations pass through a 'critical point', if pigment volume is increased by increments over the pigment volume concentration range. The typical effects achieved are schematically illustrated in Figure 4. Depending upon the specific test a critical or transition point can be ascertained more or less readily. Moisture vapour permeability, rusting, blister resistance, scrub and stain resistance are affected. Extensibility is found to decrease and a decided peak is found in the tensile strength of the coatings composition at this point. Beyond this point, it decreases again to a value of zero at 100% pigment. Figure 5.

Either of these tests may consequently be employed to detect the CPVC of the specific pigment/vehicle combination employed.

Asbeck[194] demonstrated that the increase in tensile strength of a pigmented coating with increasing pigment content below the CPVC can be largely attributed to the changes resulting in the true strain rate imposed on the polymer matrix due to increased pigment loading. The addition of pigment to the coating matrix is equivalent to shortening portions of the specimen of resin contained in the composition, and consequently, the true strain rate imposed upon the resin is increased significantly at a given standard testing rate as the pigment volume concentration of the system approaches the CPVC.

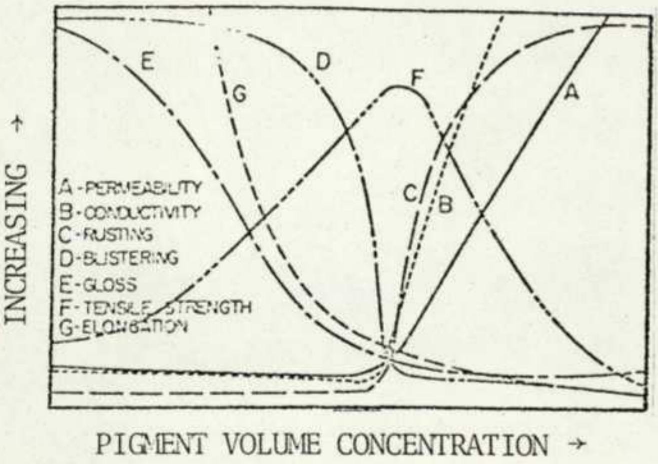


Figure 4. Critical Pigment Volume and Coatings Performance

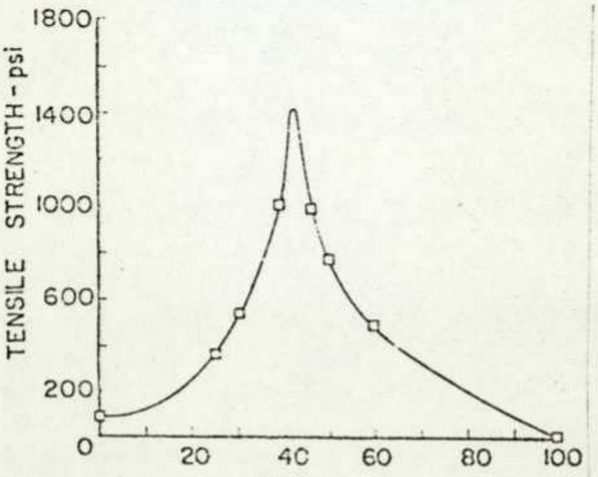


Figure 5.

3.9. Preparation of Substrate Prior to Painting

3.9.1. Preparation of Aluminium Surface

3.9.1.(i) Experimental

Aluminium sheet thickness conforming to BS 1470* Grade SIC-Y_2H (hard) was used.

*'Wrought aluminium' and aluminium alloys for general engineering purposes. Sheet and strip. Maximum permissible impurities were quoted as Cu 0.10%; Si 0.5%; Fe 0.7%; Mn 0.1%; Total 1.0%.

The aim of the procedure used for the preparation of the surface was to produce a standard surface prior to a deliberate controlled contamination with stearic acid.

Recommended practices for preparation of aluminium and aluminium-alloy surfaces for painting[196] cover four types of treatment. These are solvent cleaning, chemical treatments, anodic treatment and mechanical treatment.

It was decided to use a combination of solvent cleaning and chemical pretreatments. The procedure is as follows:

Aluminium panels were cut to 10.16 x 15.2 cm, washed in a warm solution of Teepol, and rinsed with water to remove loosely adhering soil and grit.

Solvent cleaning does not disturb the natural oxide film on the metal, and a vapour degreasing method was used. The panels were suspended in a vapour-phase degreaser containing trichlorethylene (ICI degreasing plant). They were allowed to remain in the vapour compartment until they attain the temperature of the vapour, at which time condensation on the panels no longer occurs, i.e. normally 15 minutes. After this stage the panels were handled with tweezers.

The panels were first etched for two minutes in a bath containing 36 ml of concentrated nitric acid, 3 mls of hydrofluoric acid, 100 mls of distilled water, then rinsed in distilled water.

In the next stage, etching treatment confined to British Standards[197] was carried out in a bath containing 100 g of pure sodium dichromate in 1000 mls of distilled water and 170 mls of pure sulphuric acid (SG = 1.84), for 20 minutes at 54°C ± 2°C. The panels were washed thoroughly and as rapidly as possible in cold water, and dried between sheets of blotting paper. These were immediately contaminated as described below because prolonged standing in the laboratory may affect the nature of the oxide film.

3.9.1.(ii) Results and Discussion

It is well known that variation in surface treatment produces end conditions which differ, and which do not necessarily yield identical results when paints are applied.

To eliminate the effects arising from the variations in the nature of the oxide film structure obtained using different techniques, on the adhesion of polymers in general[198,199], and in particular on the distribution and the packing of the stearic acid when applied, it is essential that a standard procedure for aluminium pretreatment is used.

The standard aluminium surface prepared by chromic-sulphuric acid pickle is one generally used prior to painting or bonding[197,200,201].

This method of surface preparation was also used by Bottrell[202] to determine its effect on surface roughness, degree of wettability and the form of the angle at the boundary.

This acid pretreatment gives a rise in surface area and adhesion is normally increased by direct interaction of the oxide and the adhesive[203].

There are a number of oxides of aluminium. Their structures and densities are widely different. The properties of these oxides have been fully reviewed[204,205].

The simplest structure of the oxides is that of α- Al_2O_3 or corundum, and γ- Al_2O_3 [206].

In addition to the oxides, there are the important hydrated forms, bayerite β-$Al_2O_3.3H_2O$ or β-$Al(OH)_3$ and boehmite α-$Al_2O_3.H_2O$, or α-$AlO(OH)$.

Aluminium exposed to air or oxygen at 20°C becomes covered with an amorphous oxide film reaching a limiting thickness of about 35Å in seven days[207].

The chromic-sulphuric acid pretreatment of aluminium[200], leads to the formation of a film of hydrated oxide. The hydrated oxide formed on aluminium in water below 75°C is bayerite (β-Al_2O_3, $3H_2O$) and above this temperature is boehmite (α-Al_2O_3, H_2O), although it appears that some boehmite begins to be formed at 60°C and its proportion increases with temperature[208]. Some authors quote the transition temperature as 71°C[198].

The reaction which is probably occurring in the acid dichromate etching solution is:

$$2Al + Cr_2O_7^{2-} + 14H^+ \rightarrow Al^{3+} + 2Cr^{3+} + 7H_2O$$

This was supported by Peckham[209] who measured the weight loss of aluminium together with the aluminium and chromium ions concentrations.

At $63^{o}C$ and at least for 25 minutes, one mole of aluminium passes from the solid to the solution as one mole of chromium (III) is formed by reduction.

The films produced by the chromic-sulphuric acid pretreatment are considered to have a structure similar to that produced by anodic oxidation, i.e. by anodising in pore-forming electrolyte[208,210]. The film is generally considered to consist of a thin barrier layer next to the metal covered with a thicker porous layer. The latter layer consists of hexagonal prisms of alumina with cylindrical pores running from the top surface to the barrier layer, Figure 6.

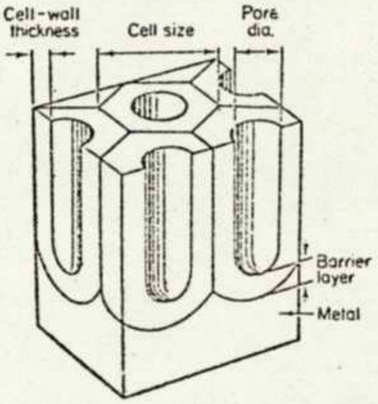


Figure 6. Cell and pore structure of porous anodic films on aluminium

The cell and pore dimensions depend upon current density, voltage applied, and the electrolyte used. The pore diameter is 120Å for oxide formed in 15% sulphuric acid and 330Å for that formed in 4% phosphoric acid[211,212].

Treatment with boiling water seals the porous alumina[213], and this leads to blocking of the pore from the mouth probably by hydration of the oxide.

In this work the oxide film presented to the paint prior to painting is masked by the presence of stearic acid molecules which act as a barrier. Adhesion results are related to the ability of the applied paint to overcome this barrier probably by chemical interaction.

Electron micrographs and scanning electron micrographs of replicas of sulphochromated aluminium are given in Figures 7 and 8 respectively, showing the porous structure.

3.9.2. Contamination of Aluminium Surface

3.9.2.(i) Experimental

0.2% Solution of the stearic acid as a contaminant, in isopropyl alcohol was prepared. The panels were artificially contaminated by pipetting, using a micropipette, the appropriate volume of the solution on the aluminium panels which were put on a glass-plate levelled using a spirit level, to give, on evaporation, an acid coverage of 40 microgrammes/cm^2. A short heating treatment (1 - 2 minutes) at 60°C ensured that stearic acid was not loosely packed on the surface, but melted to give an even coating.

Scanning electron micrographs were taken. The National Physical Laboratory S1 instrument was used at 20kV and a stage angle of 45°. Photographs were prepared in a magnification range 34X to 3.2KX.

Conventional two-stage replica electron micrographs were prepared from the sample previously examined by scanning electron microscopy.

A negative replica of the surface was formed from an aqueous

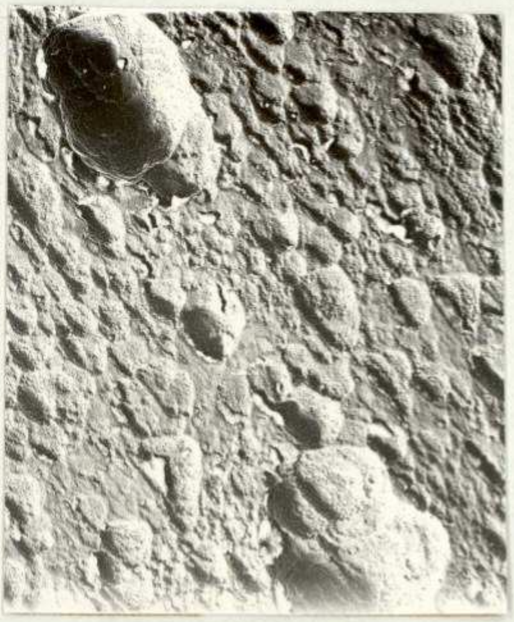


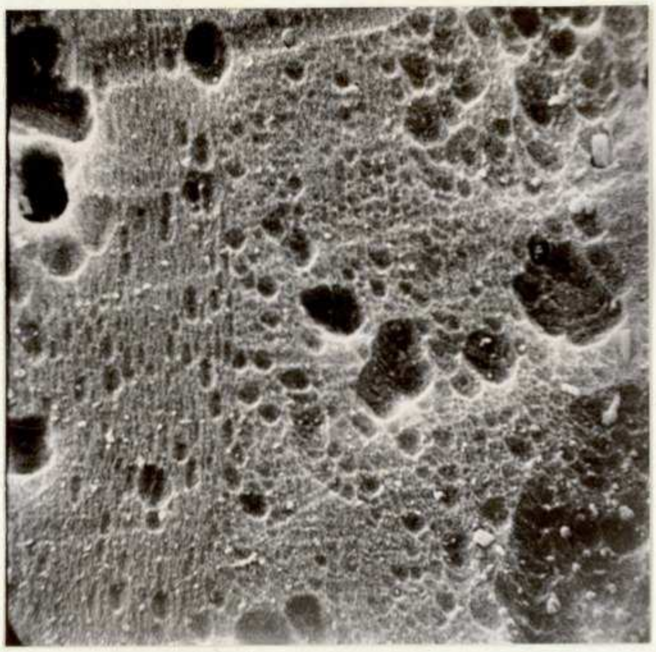
Figure 7. Electron micrograph of sulphochromated aluminium (M1368)

Original Magnification 6,000X

6,300X

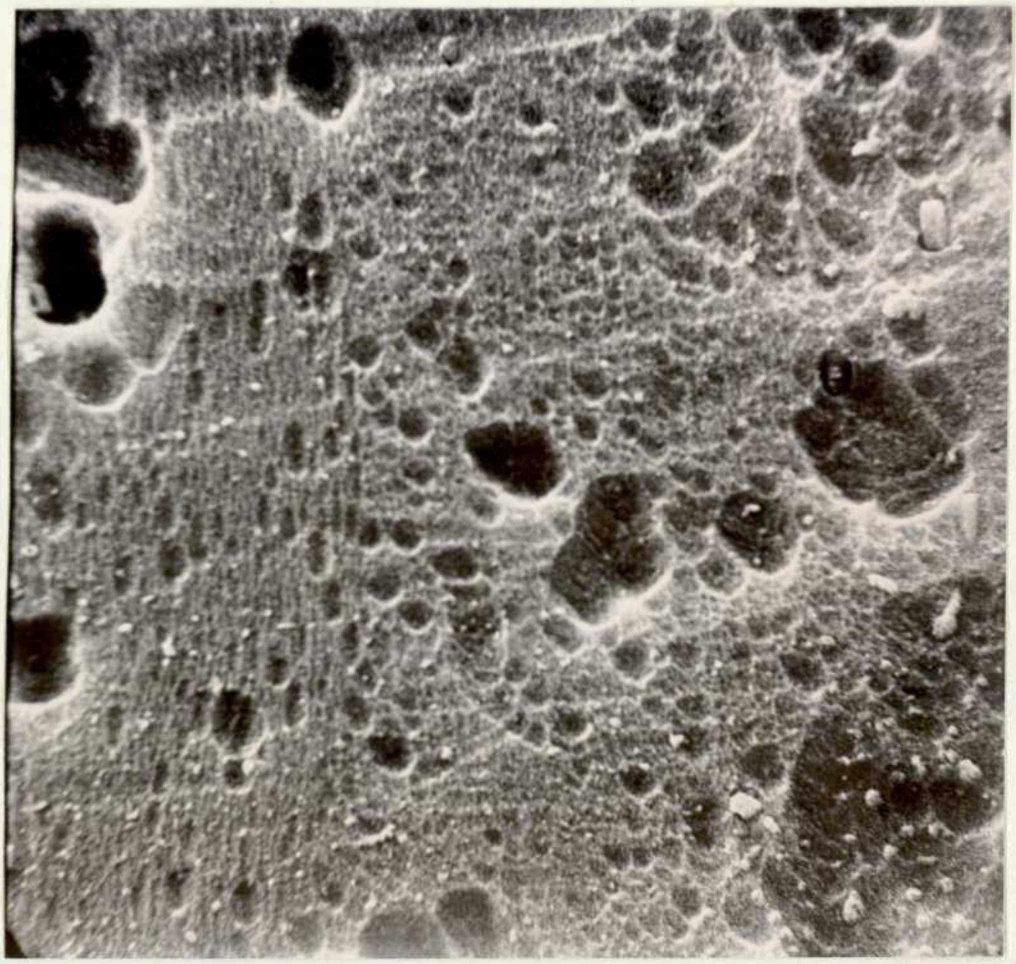
Figure 8. Scanning electron micrograph of replicas of sulphochromated aluminium

S5/3



Original
Magnification 1.8KX X = 3½

1.8KX X = 5



solution of polyvinyl alcohol. The dry film was stripped and the surface replicated with carbon. The polyvinyl alcohol was removed by floating carbon side up on warm water.

After picking up the carbon replica on electron microscope grids, it was shadowed at 15^{o} with Au/Pd alloy through the back of the grid. Electron-micrographs were prepared at magnifications of 2500X and 6000X.

The above method of replication forms an extraction replica of the surface, i.e. a replica is formed of the surface but loose material including stearic acid, is removed with the replica.

This accounts for the difference between M 1370 (sulpho-chromated aluminium contaminated with 40 $\mu g/cm^2$ stearic acid - area 'cleaned' by previous replication) and M1371 (sulpho-chromated aluminium contaminated with 40 $\mu gm/cm^2$ stearic acid - virgin area). In the latter case the stearic acid was removed from the surface and appears as an electron-dense region of the photographs (i.e. white).

3.9.2.(ii) Results and Discussion

Scanning electron micrographs of the contaminated surface are shown in Figure A.

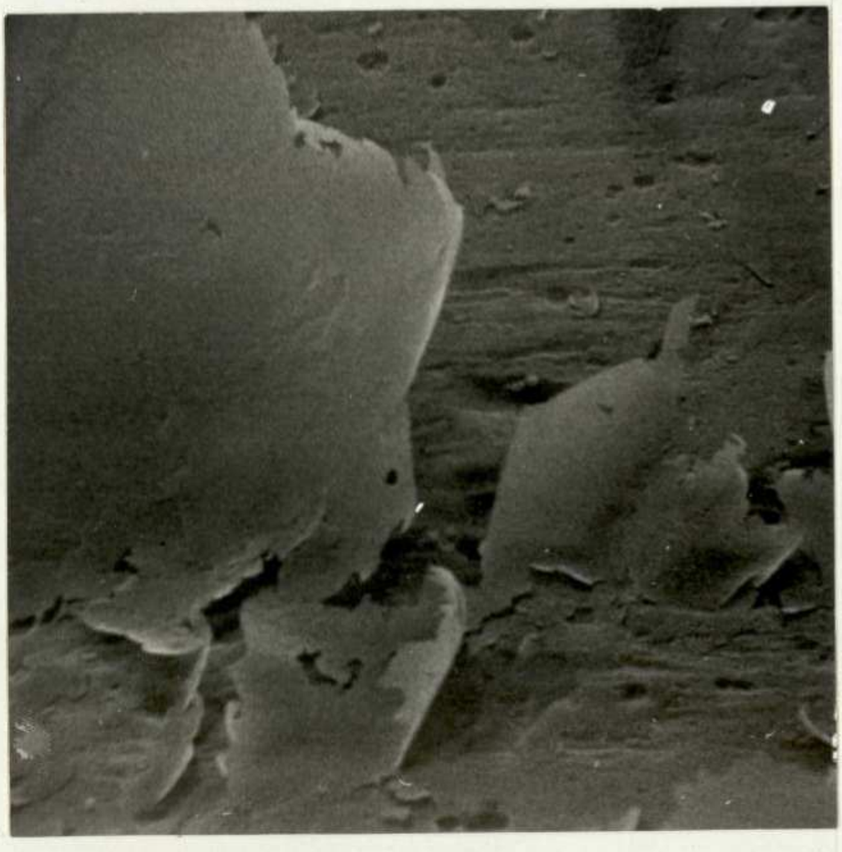
These are of a single area and features may be traced from photograph to photograph giving a zoom effect.

The contaminant layer is clearly visible as a discrete coating flaking from the surface. Emphasis should not be put upon the crakcs and flakes observed. It is quite possible these are formed during evacuation.

The electron micrographs of the surface are shown in Figure B. Most photographs show broadly similar features to those shown in scanning electron microscopy.

Figure A. Scanning electron micrograph of replica of contaminated aluminium.

S2O/12
Original Magnification
170X



S2O/15
Original Magnification
1.6KX

Figure B. Electron micrographs of replica sulphochromated aluminium contaminated with 40 $\mu gm/cm^2$ stearic acid.

Original Magnification 6000X

3 4

b_1 Area cleaned by previous replication (M 1370)

b_2 virgin area (M 1371)

3.9.3. Method of Painting the Surface

3.9.3.(i) Experimental

Paints prepared as described in Section 3.8 were applied to artificially contaminated panels by a spinning technique using PRA home-made spinner to give a final dried film thickness of 20-25 microns. To deposit 25 micron films of paint at 1:1 pigment:binder ratio on 25.8 cm^2 area, 0.105g of dried paint is needed. This was calculated from the equation

$$W = V \cdot x$$

where V is total volume of the pigment and the resin
d is the total density of the pigment and the resin
W weight of paint

3.10. Adhesion Test Method Used

3.10.1. Experimental

In the early nineteen-fifties, and under a U.K. Ministry of Supply Contract, work began at the Paint Research Association to develop a sensitive and accurately reproducible method for adhesion testing of paints to metal substrates.

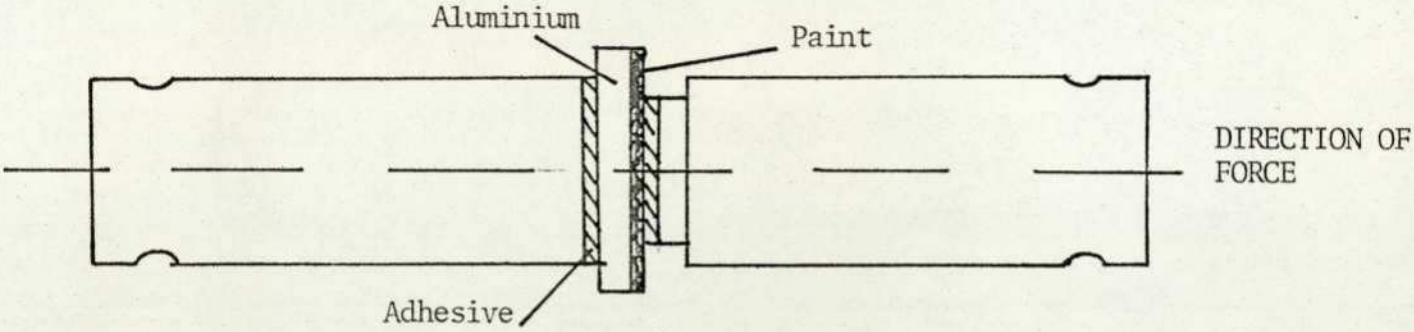
Progress in this development was described[214,215]. Further elaboration of techniques was covered in a paper by the Joint Services Research and Development committee on Paints and Varnishes[216].

As a result, a direct pull-off method for adhesion testing was established and this was used in this work.

The essential features of the method are as follows:

Discs of 3 mm in diameter were stamped out in a flypress from the painted aluminium panels. A disc was glued between two steel cylinders (rods) 25 mm in diameter, the end of one cylinder being turned down to 19 mm diameter.

The set-up is diagrammatically illustrated below.



The normality of the faces of the cylindrical rods was maintained by facing off with a surface grinder on each occasion before reuse and care was taken to ensure that the sheet metal used for preparing test panels was of uniform thickness and undistorted. The unpainted face of the disc was also abraded uniformly and solvent wiped before gluing to minimise the possibility of failure at the glue line.

The painted face of the disc was very lightly abraded for the same reason and cleaned with tissues. The smaller-ended rod was placed against the painted face of the disc (thus concentrating the pull force on this side of the disc), and a joint made with the solvent-free, cold-curing epoxy/amine adhesive[217].

This adhesive (AY105:HY951 used as 100:11 parts by weight) can give joint strengths of up to 6891.8 x 10^4 N/m^2, but it is extremely sensitive to moisture. In order to avoid difficulties with the low molecular weight hardener, the mixture was allowed to partially cross-link before use. For a 5 g sample this takes about 30 minutes at 25°C - the usable life being about 1 hour. This procedure reduces the moisture sensitivity of the adhesive, prevents migration of the hardener, and eliminates free polyamines. Great care was taken during the spreading of the adhesive as moisture adsorption at this stage is particularly harmful. Thus the spreading of the adhesive was carried out in a special cabinet flushed continually with dried air.

The complete sandwich test specimen was held in an alignment rack under 4.45 kg spring pressure load until the adhesive was thoroughly cured (normally 48 hours at 20-25°C is sufficient).

It has been found[104] that alignment of the assembly is of critical importance for the slightest bending moment applied to the adhesive joint results in uneven stressing and propagation of a peeling fracture across the surface.

The test specimen was then subjected to a tensile pull on a

Hounsfield tensiometer operated at a controlled rate of loading and at room temperature 20-22^{o}C.

The load at which the joint fractures was recorded in tons and was converted to a bond strength in lb/cm^2, and hence to N/m^2 [218]. In evaluating test results, it is essential to record the locus and type of failures, i.e. adhesion failures occurring at the paint/metal interface, cohesion failure occurring in the paint or failure in the adhesive. The measured joint strength alone may give a misleading impression.

Each result is the mean of sets of five to eight determinations.

3.10.2. Results and Discussion

The direct pull-off method was criticised[219] on the grounds that the cold-curing adhesive may penetrate into the paint film. The effects and the extent of this effect (if any) is of course very difficult to assess on the paint film and hence on paint film adhesion. However, the high viscosity and the large molecular size of the adhesive molecules achieved by allowing the partial cross-linking of the adhesive before application, minimise the danger of possible attack on the paint film. Furthermore, in any test method of adhesion, interfering factors exist and normally the adhesion of a system is not normally known by an independent method without the influence of one factor or another.

From tests on the pull-off method, Huntsberger[220], who measured the adhesion of two conventional paint systems for comparison, showed that the order of the reproducibility of the joint strength obtained from replicate specimens prepared and tested at the same time was 15%. Adhesion tests carried out by the author gave reproducibility of better than 10% and good reproducibility of 3% particularly on uncontaminated aluminium.

The unequivocal measure of adhesion by this method was confirmed by the results of the tests[220] which agreed with that expected from paints in service and by the results accumulated from experiments carried out at the Paint Research Association extending over many years.

3.11. Results of the Effects of Chemical Modification of the Polymer Chain on Adhesion to Standard Surface

3.11.1. Results

The results of a series of tests of adhesion of selected paints on cleaned and uncontaminated aluminium surfaces are given in Table 19. The paints chosen were those based on unmodified n-butylmethacrylate (N8); on an imidazole modified copolymer (N18) and on a copolymer modified with acrylic acid (N26). It seemed necessary to have these results for comparison with the main body of results with contaminated aluminium surfaces; and also to help in proposing an explanation for the improvements in adhesion which were achieved with the various modified polymer paints.

The results of the main body of the tests with the various paints based on the whole range of modified polymers are given in Table 20.

All these results were obtained with the test techniques described in 3.10 using stearic acid contaminated aluminium surfaces described in 3.9.2. The paints were allowed to dry for four days at 25°C ± 1°C and 60% Relative Humidity.

Table 19

Adhesion of Paints to Uncontaminated Aluminium After Four Days Drying

Ref. No.	Mean value of joint strength, $N/m^2 \times 10^4$	No. of Observations	Std. Devn. (δ) $N/m^2 \times 10^4$	Area of Adhesion Failure, %	Error in δ, %
N8	2869.7	4	136.5	8	4.8
N18	3058.1	6	76.7	5	2.51
N26	3053.8	5	157.3	55	5.15

Table 20

Adhesion of Theromplastic Polymer Paints to Contaminated Aluminium After Four Days Drying

No.	Ref. No.	Mean value of joint strength, $N/m^2 \times 10^4$	No. of Obser- vations	Standard Devn. (δ) $N/m^2 \times 10^4$	Area of Adhesion Failure, %	Error: $\frac{\delta \times 100}{\text{Mean Value}}$, %
1	N8	608.5	5	62.7	100	10.3
2	N6	551.3	6	42.7	100	8.3
3	N13	1019.9	6	102.0	100	10.0
4	N9	514.8	5	60.7	100	11.8
5	N14	992.4	8	86.8	100	8.8
6	N5	717.4	5	98.6	100	13.7
7	N12	2281.2	7	205.4	35	9.0
8	N18	2089.6	5	202.9	20	9.7
9	N15	2316.3	7	90.9	35	3.9
10	N31	1896.6	6	142.7	60	8.0
11	N32	2234.3	6	153.7	65	7.0
12	N33	1056.5	5	97.2	100	9.2
13	N35	1275.0	6	92.7	100	7.27
14	N16	2079.9	8	75.1	20	3.6
15	N27	2343.2	6	172.9	10	7.4
16	N28	2179.1	7	177.1	40	8.1
17	N26	2359.1	7	162.6	75	6.9
18	N19	2047.6	5	270.2	1	13.2
19	N20	2403.0	6	215.2	20	8.96

3.11.2. Comments on Results

In comparison, the reproducibility of the joint strengths of these paints to uncontaminated aluminium was better than that to contaminated aluminium. This can, in addition to the expected experimental error, be attributed to the presence of the contaminant and the nature of its distribution on the surface. The reliability of the pull-off method of adhesion testing was also confirmed from the results in Table 19 where the standard deviation was small.

In this work the technique used for applying stearic acid on the surface was not as that previously used by other investigators [221,222,94]. They aimed to obtain a well-defined surface, i.e. a surface with a mono- or a specific number of multilayers of fatty acids, for special purposes.

It was apparent[94] that when a monolayer of stearic acid was applied to sulphochromated aluminium employing Sher and Chanley's technique[222], the layer distributed itself in such a way that the carboxyl group was attached to the metal and the hydrocarbon portion was stuck out. A schematic diagram of this situation was given by Eley[223] and is illustrated in Figure 9.

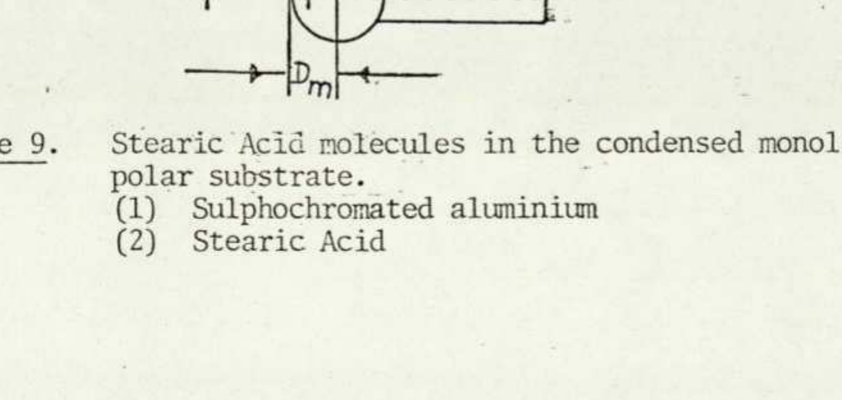


Figure 9. Stearic Acid molecules in the condensed monolayer on a polar substrate.
(1) Sulphochromated aluminium
(2) Stearic Acid

Allen and Patel[224], who studied the adsorption of long-chain fatty acids dissolved in n-heptane, on iron oxide, barium sulphate and (anatase) titanium dioxide, came to a similar conclusion. They interpreted their results on the basis of molecular orientation at the interface, in that fatty acid molecules are adsorbed so that the polar head, i.e. carboxyl group is resting at the interface and the first six $-CH_2-$ elements form a loop above the surface extending into the liquid. The seventh $-CH_2-$ element would rest on the interface whereas the eighth and subsequent elements lie above the interface.

Blodgett[221] who deposited two distinct series of successive layers of calcium stearate (i.e. one at a time) onto glass, found that the layers of odd number, that is, 1 or 3 or 5 ......, etc. molecules deep, were oriented with $-CH_3$ groups in the opposite direction from layers of even number, i.e. 2, 4, 6 ....., etc. The first layer with $(-COO)_2Ca$ "heads" was next to the glass and the $-CH_3$ groups away from the glass. The latter surface is not wetted by water and would form an angle of $>90^\circ$. A $-COOH$ surface however is completely wetted by water.

This type of alternate orientation of successive layers is usual in fatty acids. Muller[225,226] and others have shown by x-ray analysis that the molecules in crystals of fatty acids are oriented end to end, in opposite directions. In further studies, he[227] found that the length of a pair of molecules of stearic acid crystals arranged end to end was 48.84 Å, and that the axis of the chains was inclined at an angle of $\beta = 63^\circ 38'$ with the plane in which the carboxyl group lay, giving as in $\beta = 43.75$ Å spacing between consecutive carboxyl planes. Each $-CH_2-$ group contributes 1.257 Å to the chain as was calculated on the theory[226] that the chain is a zig-zag in which the lines joining the centres of successive carbon atoms are inclined at the tetrahedral angle $109^{o}28'$, the diameter of the carbon atoms being 1.54 Å.

Blodgett[221] who deposited films of stearic acid on polished chromium from distilled water at pH 5.2 - 5.4 and pH 4.2, found from the refractive index of 1.48, that the thickness per layer of stearic acid was 22.9 Å.

Clarke et al[228] obtained, by means of x-ray diffraction, 46.05 Å as the thickness of two monomolecular films of stearic acid, turned in opposite directions. The difference in spacing is affected by the degree of constraint imposed on the molecules of fatty acids while crystallisation is taking place.

The experiments of Harkins and Morgan[229] on the spreading of thin films on water and on salt solutions gave at zero force of compression on water, an area per molecule of 19.2 $Å^2$ for stearic acid.

The application of these different values of thickness per layer of stearic acid, and the amounts used in the experiments of this work, i.e., 40 $\mu g/cm^2$, the expected numbers of layers of stearic acid on the sulphochromated aluminium, were calculated as shown overleaf.

Investigator	Thickness per layer, Å (t)	Shape of film	Volume of layer $\frac{(w/d=40\times10^{-6})}{.94}$, x 10^{-24}	No. of layers
Muller[227]	21.88	Crystal	420.096	194.88
Blodgett[221]	22.90	Deposited	439.68	185.82
Clark[228]	23.03	Deposited	442.08	184.77

The sequence of these layers (≈ 185) is presumably random and an uneven coverage of the surface was inevitable. Obviously the first layer adjacent to the sulphochromated aluminium should resemble that of Schonhorn[94], Allen[224], Blodgett[221], i.e. the -COOH group oriented on the aluminium surface, and the $-CH_3$ free. Because these methods were not necessary to use in this work, a precise picture of the distribution of the subsequent layers of stearic acid relative to the first was not established. However, these layers should orient themselves in a reproducible fashion and generally in accordance with the information given by the previous investigators.

From the electron and the scanning electron micrographs, it was apparent that stearic acid was present as a discrete coating flaking from the surface. This presents the true picture of the accumulation of contaminants similar to that in an industrial environment. The forces that would operate, therefore are:

(a) Cohesion, that is, the interaction forces between the -COOH groups of the stearic acid molecules themselves, van der Waal's dispersion forces between adjacent chains;

(b) the interaction forces between the -COOH groups of the stearic acid molecules and the aluminium surface, and

(c) between the groups of the aluminium surface itself.

The stearic acid layers, because of the heating treatment of the surface, will undoubtedly diminish in thickness due to the thermal agitation of the molecules. As a result, the rigidity of the film is diminished; the forces exerted by the molecules in their constrained upright position become sufficient to expand the film in a lateral direction. The stearic acid flakes flow on the surface giving a layer composed of $-CH_3$. The latter was predominantly apparent by the measurements of contact angle of water on such a surface. Zisman[230] reported a receding contact angle of water of 100^o on a stearic acid surface and quoted bulk shear strength of 200 kg/cm^2 when measuring the adhesion of ice to organic solids. Water would spread on -COOH surface (turns upside down for more polar substrates). Blodgett[221] gave 90^o as a contact angle of water on a $-CH_3$ surface.

The contact angles and the critical surface free energy of stearic acid-contaminated aluminium were determined (see 3.17) and values of Exper. $\Theta_{H_2O} = 91^o42'$ on baked surface. Exper. $\Theta_{H_2O} = 105^o$ on unbaked surface, and 21-23 $dyne.cm^{-1}$ were obtained. This range of values is similar to the value obtained by Shafrin and Zisman[123], on a close-packed monolayer of $-CH_3$.

Having established the nature of the surface of the top layer, the bonding phase presented to the paint can still be quite a complex one. The paint must possess the ability to displace quite a thick layer of contaminant, and bonding to one monolayer is quite different to bonding to multi-layers.

Schonhorn[94] demonstrated that the absorption of a condensed monomolecular layer of polar/nonpolar material, i.e. stearic acid between carefully prepared hydrophilic and hydrophobic surfaces (sulphochromated aluminium and polyehtylene), afforded a bonding phase of a high degree of orientation, uniformity and specificity. Thus he obtained a bond strength exceeding the cohesive strength of polyethylene, and adhesional failure was minimised.

He explained that the role of this type of monolayer was a bridge between the polar and nonpolar adherends, its carboxyl group is anchored in the porous aluminium and the aliphatic portion is mechanically encapsulated in the molten adhesive. The former is strongly held because the adsorption energy for such a layer calculated using Eley's approach[223] and assuming a range of action 2×10^{-8} cm was -700 erg/cm^2 and an interfacial force of approximately 1300 tonnes/cm^2 was obtained[94]. However, the force required to break real bonds never approaches the calculated from theory[231] and the limiting consideration is the cohesive strength of the weaker adherend. Because of the presence of multilayers of stearic acid the bond strength of the n-butylmethacrylate paint is low due to the weak adhesion of the monolayers to themselves[230], bulk shear 200 kg/cm^2, and due to the fact that the paint possesses less chemical activity than the modified paints.

In Table 20 the results of adhesion tests clearly demonstrate the improvement in adhesion achieved by the modification of the polymer structure with a suitable modifier. The locus of failure was also transformed from 'adhesion' to a mixture of adhesion/cohesion which was detected visually, and the true interfacial adhesion force must have been even greater than was measured.

The apparent differential effect of chemical modification of the simple n-butylmethacrylate paint on the joint strength and the type of adhesion failure, does not suggest that there was a weak boundary layer failure (WBL), within the stearic acid film, because if there was, the joint strength and type of failure should have been the same for all and within the experimental error. These results do not appear to agree with Bickerman's[232] statement that "all apparent adhesion failure is properly cohesive failure of a weak layer". Here, stearic acid is the weak layer.

The degree of the effectiveness of modifiers of a basic or acidic nature, on adhesion to uncontaminated aluminium (see Table 19), particularly those derived from a heterocyclic ring via imidazole (N18) or from acrylic acid (N26) was practically the same. An enhancement in adhesion of about 6.5% over that of unmodified n-butylmethacrylate is not very significant. However, the importance of the application of the chemical modification of a simple polymer back-bond technique with a suitable modifier, for adhesion improvement, is more pronounced when the adherend is "contaminated", although some 30% and 22% reduction in the adhesion of copolymers N18 and N26 respectively, was experienced, compared to the uncontaminated results.

The incorporation of 5% molar 4-vinylpyridine in n-butylmethacrylate polymer chain N6, was insufficient to cause any improvement in the level of adhesion, but a further increase in pyridine level produced a significant improvement in adhesion to contaminated aluminium (N13).

A similar behaviour was observed with copolymers containing 5% or 10% molar N-vinylpyrrolid-2-one, (N9) and (N14) respectively.

Copolymers containing 5% or 10% molar of an aliphatic amine, i.e. dimethylaminoethylmethacrylate gave some improvement at the lower level of modication (N5), but an increase in the number of active sites of the modifier on the polymer chain (N12) enhanced the adhesion tremendously, with a substantial decrease in the area of adhesion failure, a value of an interfacial strength probably approaching the cohesive strength of the weaker adherend, i.e. the copolymer.

Favourable results were also given with copolymers containing 5% (N18) or 10% (N15) molar 1-vinyl-2-methylimidazole. Both copolymers showed an excellent adhesion, with a substantial reduction in the area of adhesion failure, and comparable to that obtained by the use of 1% or 5% molar acrylic acid respectively.

Modifications of n-butylmethacrylate with allyl derivatives at 5% molar showed that both triallylisocyanate (N31) and allylrhodanine (N32) gave a significant increase in adhesion compared with the control; the latter being particularly effective and similar to N15 and N26. Allylglycidyl ether was comparable to N13 and N14. (A detailed description is in the distribution and GPC sections).

Trialoxy silanes are normally recommended in the monomeric form as adhesion promoters to glass or metal surfaces[67-77], and it was of interest to examine their behaviour when reacted into an acrylic polymer chain. The vinyltriethoxysilane as a co-monomer at 5% molar improved the adhesion to contaminated aluminium and surpassed the 10% molar of vinylpyridine and N-vinylpyrrolidone.

It was reported[233] that acrylic carboxyl groups in an acrylic polymer paint promoted adhesion to stearic acid contaminated aluminium. In the present studies the effects of combination of carboxyl and monomers of a basic nature in a single polymer chain were examined to see whether any further enhancement of adhesion over that obtained with carboxyl groups alone was possible. This combination does not suggest any outstanding benefits over that obtained with 5% molar acrylic acid (N26).

3.12. Phase-Equilibria, Chemical Interaction and the Formation of an Intermolecular Compound

3.12.1. Experimental

To explore some of the reasons responsible for adhesion improvement, particularly the possibility of chemical interaction of the modifiers and the contaminant, the monomer 1-vinyl-2-methylimidazole (VMI) was selected as a representative of the nitrogen-containing modifiers, and acrylic acid for the acid containing paints.

To illustrate the formation of an intermolecular compound, the most convenient way was to determine the temperature/concentration diagram of the two components.

In stoppered sample tubes, freshly distilled monomer was mixed with purified stearic acid at various molar weight ratios.

The monomer (VMI) was found to be an excellent solvent for stearic acid but at concentrations over 50%, the mixtures, containing undissolved acid, were heated initially to obtain homogeneous samples and cooled prior to conducting the measurements.

The melting point of each mixture was determined using Kofler melting point apparatus, fitted with a hot-stage thermometer and a microscope. Each value was an average of two or three determinations.

For mixtures which were liquid at ambient temperature, particularly those containing less stearic acid, it was found necessary to deep freeze them and to cool the hot stage, prior to each determination. In this way it was possible to carry out accurate measurements of melting point below 30°C.

3.12.2. Results and Discussion

3.12.2.(i) 1-Vinyl-2-methylimidazole

The percentage molar ratios of VMI/stearic acid mixtures and their melting point values, are given in Table 21, and the diagram for this system in Figure 10.

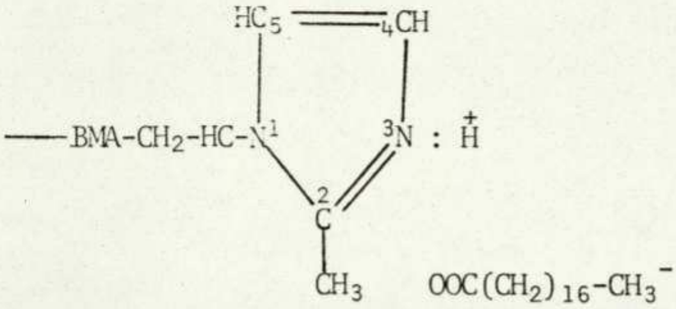
The maximum at the point (C) indicated the formation of a compound at equimolar quantities, and with a congruent melting point i.e. when the solid compound was heated to 35.5°C, it melted to a liquid of identical composition and behaved like a simple pure component. Point (E) is the eutectic of compound/stearic acid.

This was a clear indication that adhesion in this system could be due to chemical bonding. This was also supported by the following analyses.

From the literature information given of the chemistry of VMI,[234-240], and diagram A, it was shown[234] that the acid dissociation constant ρka of IV2MI is 7.09 compared to ρka of pyridine of 5.25 and the nitrogen atom at 3-position was assigned a negative charge, supports the co-ordination with the pyridine type. The electron density of this position i.e. the tertiary nitrogen, which increases its negative charge in relation to the substitution of the 2nd position, gives the molecule its basicity and also plays a role in quaternization of the molecule if necessary[241].

This property of the imidazole ring accommodates the attachment of stearic acid to paints containing VMI, i.e. (N18, N15, N26 and N19) and to paints having similar character. Diagram A illustrates such attachment.

Diagram A



The bond presumably is very much stronger than that formed with pyridine. Paints containing the latter (N6, N13) gave much lower adhesion values, because pyridine[88] is a base with $K_b = 2.3 \times 10^{-9}$ which is a weaker base than aliphatic amines ($K_b \sim 10^{-4}$). The third Sp^2 orbitals of nitrogen contains a pair of electrons giving the basicity to the pyridine ring and the availability to share them with acids. But these electrons are held more tightly, and are less available for sharing with acids than the pair of electrons of an aliphatic amine, say in DMAEMA, which occupies an Sp^3 orbital.

The presence of 5% molar of 4-vinylpyridine as a comonomer with n-butylmethacrylate was not sufficient to boost the adhesion to stearic acid contaminated aluminium. However, the higher content of pyridine gave better adhesion due to the increase in the number of active sites on the copolymer chains for compound formation.

It was found that[243] imidazole and methacrylic acid were not reactive, no product could be obtained. This suggests that in terpolymers N27 and N19, acrylic acid and imidazole were free to join n-butylmethacrylate during polymerisation and without reacting with each other.

Table 21.

Melting Points of Mixtures of Stearic Acid/1-Vinyl-2-Methylimidazole

Stearic Acid, Mole, %	Melting Point, °C
0	- 50
6.97	0
14.96	17
18.18	18
20.1	23
24.9	24
27.57	25
36.30	29
43.69	31.5
46.20	32.0
50.00	35.5
55.00	31
60.25	43.0
77.30	59
100	70

Each melting point was the mean of 3 observations

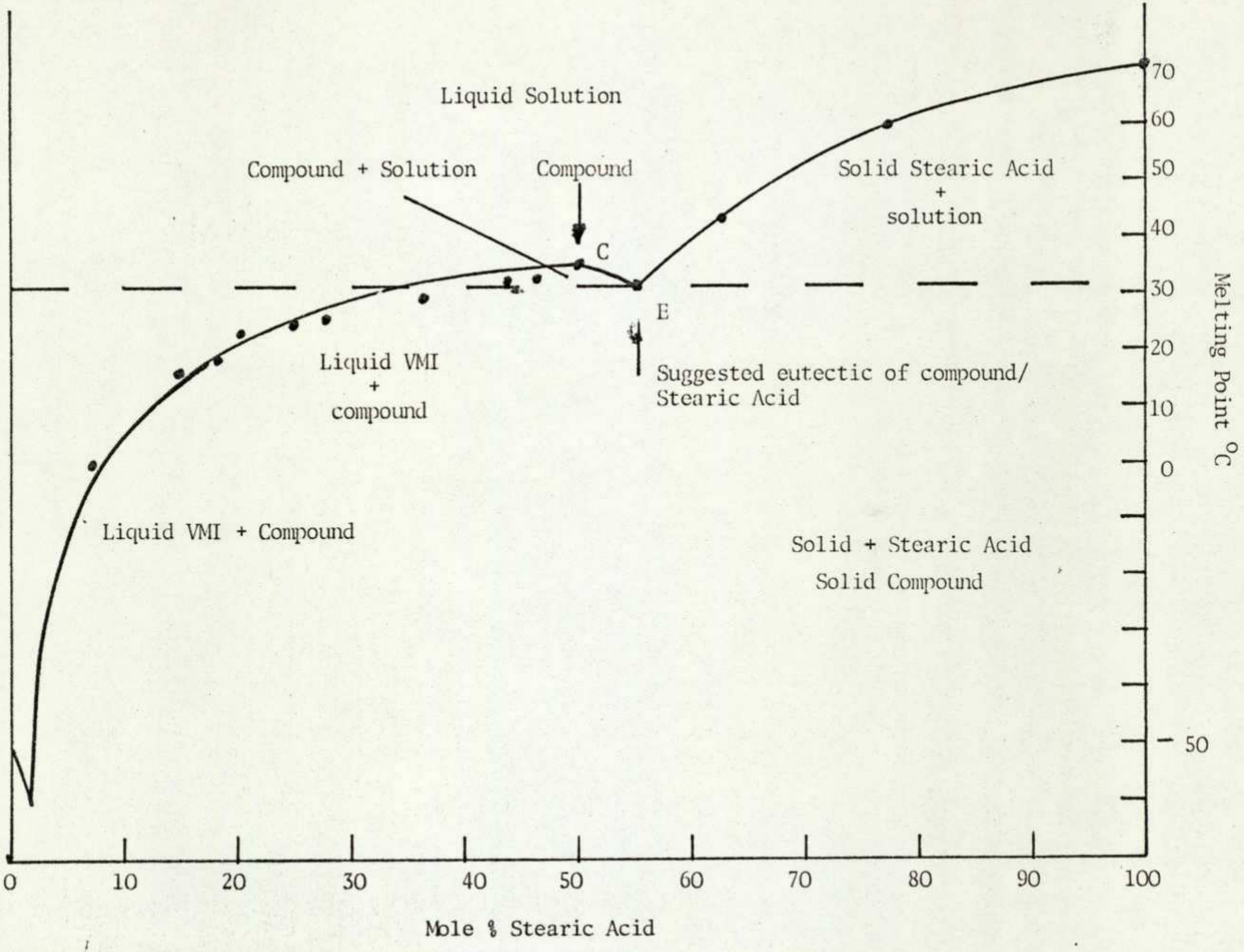


Figure 10. Phase diagram of Stearic Acid/1-Vinyl-2-methyl imidazole

Dowbenko et al[243] found that in general metal salt complexes of imidazole derivatives (including 1-vinyl-2-methylimidazole) were suitable as one-pack latent curing agents for epoxy resins, and produced a desirable increase in the mechanical properties of the adhesive bond.

Imidazole derivatives also improve the mechanical properties when used in adhesives[224-246].

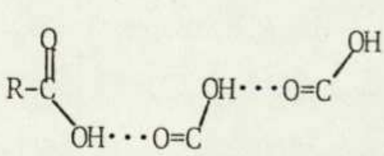
These findings suggest that the improved adhesion with the copolymer containing VMI, was also a result of further hardening of the film with an increase in the mechanical properties under the conditions of test, (particularly after artificial weathering).

The principle pattern in the behaviour of the other nitrogen containing modifiers can therefore be considered as being similar to that of 1V2MI. Therefore, the improvement in adhesion of nitrogen containing paints to stearic acid contaminated aluminium is the result of chemical interaction and molecular association.

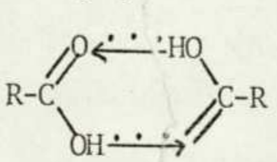
3.12.2.(ii) Acrylic Acid/Stearic Acid Systems

(a) Acrylic Acid as a monomer

Acids in general[242,171], can exist in monomeric or open chain form (I), or in cyclic or dimeric form (II).



(I)



(II)

Carboxyl groups are polar and form hydrogen bonds with each other and with other kinds of molecules.

Carboxylic acids nearly always occur as cyclic dimers (II), and a pair of molecules are held together not by one but by two hydrogen bonds which are stronger than those of open chain[171].

The information available from the infra-red spectrsocopy analysis suggests that the true nature of the vibrational mode of the carbonyl group frequencies (ν C=O) of the two forms is that, the open-chain system has a single vibration directly related to the force constant of the bond, whereas the cyclic dimers shows two modes of symmetric and anti-symmetric vibrations of the pair of carbonyl groups. As a result, a change will occur in the νCO.

Bateuv[247] reported the following values of (ν C=O) for acrylic acid:-

νCO -	liquid dimer,	1695 cm^{-1}
	liquid chain,	1724 cm^{-1}
	terminal unassociated groups	1740 cm^{-1}

This indicates a large difference in the open and chain cyclic forms of association, and Bellamy[171] suggested that the 1724 cm^{-1} frequency refers to some other forms as one in which (OH) group of one molecule is associated with the π cloud of the double bond of the next.

Stearic acid spectra in carbontetrachloride and benzene, showed[248] a C=O stretching band at 1760 cm^{-1} (monomer) and 1711 cm^{-1} (dimer). KBr disc and solid film spectra were almost identical and showed only a single carbonyl stretching vibration at 1702 cm^{-1} indicating a stronger hydrogen bond in the solid state than in solution. The C=O stretching vibration of stearate ions is close to

1410 cm^{-1}.

For carboxylic acids[172], the (νOH) stretching vibration of the monomeric form lies near 3600 cm^{-1}, and the dimeric form gives rise to a broad absorption region with many submaxima between 3000 cm^{-1} and 2500 cm^{-1}.

These findings are in good agreement with the experimental values of the carbonyl and hydroxyl stretching vibrations of the acrylic acid monomer and crystallised stearic acid, as summarised in the table below, and suggest that the former exists in the two forms of open and cyclic chains. Thus, the assumption that dimerisation of acrylic acid and the contaminant was a strong possibility, and was confirmed by a comprehensive study of the melting point/concentration relationship of mixtures of acrylic acid and stearic acid.

	ν C=O cm^{-1}		ν OH cm^{-1}	
	dimer	chain	dimer	chain
Acrylic acid monomer	1695	1724	3150 2750	1450 bending
Stearic acid	1700	-	2940 2850	-
AA homopolymer	1695	1724	2940 2850	3410 1400) 1150) bending

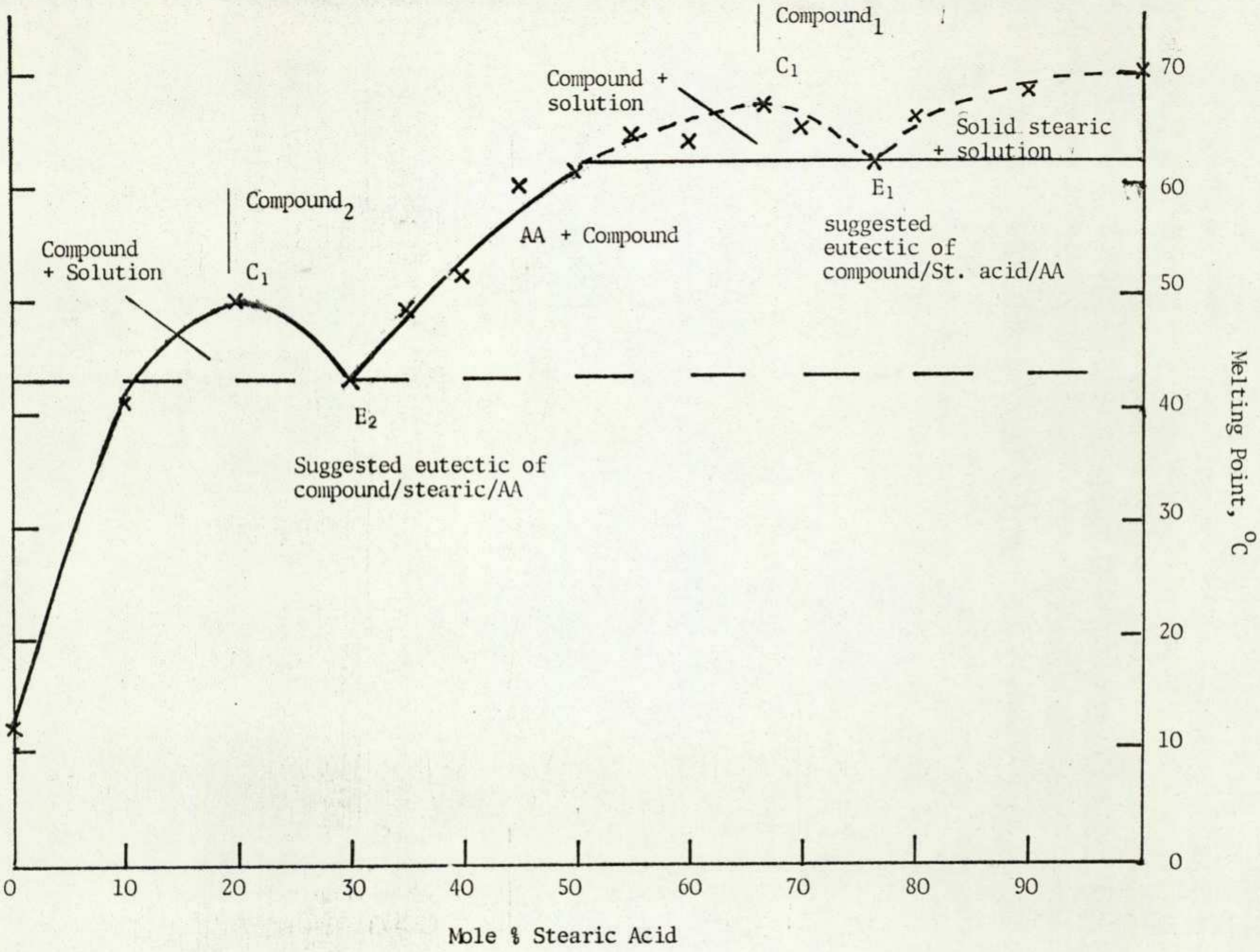
The melting points of such mixtures are given in Table 22 and is illustrated in figure 11.

The characteristic feature of the diagram was in the appearance of two maxima. The first at 66.7% and the second at 20% stearic acid, i.e. the formation of two compounds at molar ratios of 2 stearic/1 acrylic and 1 stearic/4 acrylic acid respectively, with the corresponding euotectics at 76.5% mole % and 30 mole %. Evidence for a stable or unstable compound at 1:1 ratio was quite tenuous.

TABLE 22

Melting Points of Mixtures of Stearic Acid/Acrylic Acid

Stearic Acid Mole %	Melting Point ^{o}C
0	70
90	68
80	66
76.5	62
70	65
66.7	67
60	64
55	64.5
50	61
45	60
40	52
35	49
30	43
20	50
10	41
0	12



<u>Figure 11.</u> Phase-diagram of Stearic Acid/Acrylic Acid

(b) Acrylic Acid in the Copolymer Chain

The significance on adhesion improvement of dimerisation of carboxyl groups built in the polymer backbone with those present on the aluminium surface is a function of the number of free -COOH available. This was demonstrated by copolymer (N26) with 5% molar AA, which showed better adhesion (N16) with 1% AA. Although addition of -COOH did not necessarily mean an increase in adhesion to uncontaminated aluminium.

On the basis of the findings in paragraph (a) and on the assumption that stearic acid distributed itself in the bulk of the copolymers (N16) or (N26) when these were applied as solution in toluene and formed a dimer with carboxyl groups of the acrylic acid it was possible to perform two things:-

(1) Calculate approximately how much was needed to form a dimer.

(2) Detect the decrease in acid value of a mixture of stearic acid and copolymer solution (N16).

For the first item, the total -COOH available on the metal (x) can be calculated from the equation $x = \frac{NW}{M}$, where

W - is the weight of stearic acid used = 40 mg/cm^2

N - Avagadro's number

M - molecular weight of stearic acid.

Then:

$$x = \frac{6.02 \times 10^{23} \times 40 \times 10^{-6}}{284} = 8.54 \times 10^{16}/\text{cm}^2 \ \text{COOH}$$

For 2StAC/1AA $= 4.23 \times 10^{16}/\text{cm}^2$ COOH

Similarly the number of COOH in the copolymers which were available for providing adhesion in pigmented 1% or 5% molar acrylic acid modified n-butylmethacrylate copolymer was calculated, assuming that none was adsorbed onto titanium dioxide pigment. 0.105 g paint was spread on 6.45 cm^2, i.e. 0.0162 g paint/cm^2. At 1:1 pigmentation the amount of resin was 0.0081 g, i.e. the amount of acrylic acid present was either (x_1) in (N16) or (x_2) in (N26):-

$$x_1 = \frac{6.02 \times 10^{23}}{72} \times 4.05 \times 10^{-5} = 33.86 \times 10^{16}$$

$$\frac{x_1}{x} = \frac{33.86 \times 10^{16}}{8.5 \times 10^{16}} = 4 \quad \text{Excess -COOH groups of AA}$$

$$x_2 = \frac{6.02 \times 10^{23}}{72} \times 2.106 \times 10^{-4} = 176 \times 10^{16}$$

$$\frac{x_2}{x} = \frac{1.76 \times 10^{16}}{8.5 \times 10^{16}} \approx 21 \quad \text{Excess COOH groups of AA.}$$

There was no evidence from adsorption isotherms[248] that multilayer adsorption of stearic acid occurred on titanium dioxide, but stearic acid was hydrogen bonded to the pigment surface and not in the bulk. The pigment contained stearate ion and acid ion chain. In addition, the amount of adsorbed acid was much less than the amount of stearate ion, and ion formation occurred at specific sites on the pigment surface.

The calculated values of the carboxyl groups of acrylic acid in the paint as active sites were five fold excess in N26 than N16 and adhesion was proved to be better with the former.

For item (2), the acid values of mixtures of the base polymer (N8) and (N16), containing the same small increments of stearic acid were determined by simple titration against 0.1N alcoholic potassium hydroxide solution using phenolnaphthaline as indicator. The results are given in Table 23.

The trend for the acid values of the solutions containing stearic acid and acrylic acid to decrease was apparent and this was a further indication of dimerisation.

It was of interest to know what would happen if for example a mixture of two homopolymers of n-butylmethacrylate and acrylic acid were made, what sort of behaviour would they show in relation to adhesion and would they be more efficient when they are built in the polymer chain, or when they are introduced as additives from a homopolymer solution.

These questions were answered by further investigations into the concept of adhesion promoters. (see paragraph 3.13).

Basically a mixture of two homopolymer solutions of the above materials were incompatible because polyacrylic acid is normally prepared in water. However, a suitable method was devised for obtaining clear solutions.

TABLE 23

Mixture in toluene	Stearic acid g x 10^{-2}	Volume of alcoholic KOH.N = 0.0845, ml	Acid Value, mg KOH/weight of mixture	Acid Value AV solution - AV N16
Stearic acid	0.99	0.53*	-	-
	3.97	1.76	-	-
	4.97	2.18	-	-
Stearic acid + 0.5 g (N8)	0.99	0.52	4.83	-
	3.97	1.76	15.46	-
	4.97	2.18	18.80	-
0.5 g N16		.38	3.59	-
Stearic acid + 0.5 g N16	.99	.83	5.88	2.29
	3.97	2.10	18.41	14.82
	4.97	2.55	21.95	18.34

* average of two determinations

3.13. Adhesion Promoters

3.13.1. Experimental:

Copolymers of n-butylmethacrylate with 20% and 50% molar acrylic acid were prepared as 50% solution in toluene and acetone respectively using the solution polymerisation technique. These were prepared as adhesion promoters i.e. to use as an additive in a homopolymer solution rather than built in the homopolymer backbone and to illustrate the difference in the ability of carboxyl groups to improve adhesion by the two methods of their introduction in paints.

The theoretical and experimental acid values of the copolymers are given in the table below.

Reference	Composition	acid value, mg KOH/1g resin	
		Theoretical	Experimental
N21	n-Butylmethacrylate + 20% Acrylic Acid	87.9	66.9
N22	n-Butylmethacrylate + 50% Acrylic Acid	261.6	236.7

Copolymers (N21) and (N22) were added to the homopolymer of n-butylmethacrylate so as to obtain a polymer solution containing an equivalent number of carboxyl groups to a 1% molar modification of the acrylic acid introduced by copolymerisation with n-butylmethacrylate, i.e. (N16).

Some difficulties were experienced during the addition of copolymer (N22) to n-butylmethacrylate due to the inhomogeneity of the solutions, the precipitation of either occurred. However, these were overcome by the application of a slower and graduate rate of addition of the n-butylmethacrylate to the warm solution of the copolymer, i.e. adhesion promoter. Thus, copolymer solutions were obtained with the following characteristics:-

Ref. No.	Composition	M_w	M_n	D	acid value
N29	A mixture of n-butylmethacrylate and N21	110500	49500	2.23	4
N30	A mixture of n-butylmethacrylate and N22	87800	46500	1.91	3.00

Paints were made at 1:1 pigment:binder ratio, and their adhesion was tested after 4 days drying.

3.13.2. Results and Discussion

The joint strength of n-butylmethacrylate paints containing carboxyl groups as additives to stearic acid contaminated aluminium are given in the table below. The values of adhesion of a homopolymer (N8) and copolymer (N16) paints are also included for comparison.

Reference Number	Joint strength after 4 days drying, N x 10^4/% Area of adhesion failure		
N8	608.5 / 100		
N16	2079.9 / 25		
N29	507.2 / 100		
N30	589.2 / 100		

These results confirmed that the role of carboxyl groups in promoting adhesion was more effective when they were built into the polymer chain than as additives, and that the mechanical properties of the copolymer were equally important features to consider in the interpretations of the reasons of adhesion improvement in addition to chemical bonding. The type of fracture therefore was 100% adhesion and was controlled by the breaking down of the hydrogen bonds between the carboxyl groups of stearic acid and acrylic acid homopolymer (the latter was not part of the copolymer matrix), rather than by the breaking of the same bonds but with a mixture of adhesion and cohesion, as previously experienced with such systems.

3.14. Effect of Artificial Weathering on Adhesion

The British Standard method of test[249] for the resistance of paints to artificial weathering is an accelerated one and it simulates the conditions of natural weathering.

The onset and the degree of failure of paint films exposed to natural weathering are influenced by the variation in intensity and wavelength distribution in daylight, on a diurnal and annual basis, air temperature, relative humidity, rainfall and atmospheric contamination. These variations in weathering parameters prevent the application of a precise time scale to describe the relationship between natural and artificial weathering. In accelerated weathering these variables can be controlled and more meaningful results are obtained. Generally 12 weeks of continuous exposure to artificial weathering will produce the same effects on paint film performance as that experienced after three to four years exposure to natural weathering. The 500 hours of artificial weathering therefore gives approximately one year of natural weathering which is probably a reasonable period for detecting changes in paint properties.

3.14.1. Experimental

The apparatus and the procedure used to carry out the artificial weathering test were those specified in British Standard[249].

The apparatus (see Figure 12) consists of the following:

1. A drum 1.2m in diameter, with a lid which can be raised or lowered.
2. A frame consisting of two galleries for mounting the panels at an angle of 10-15° to the vertical.

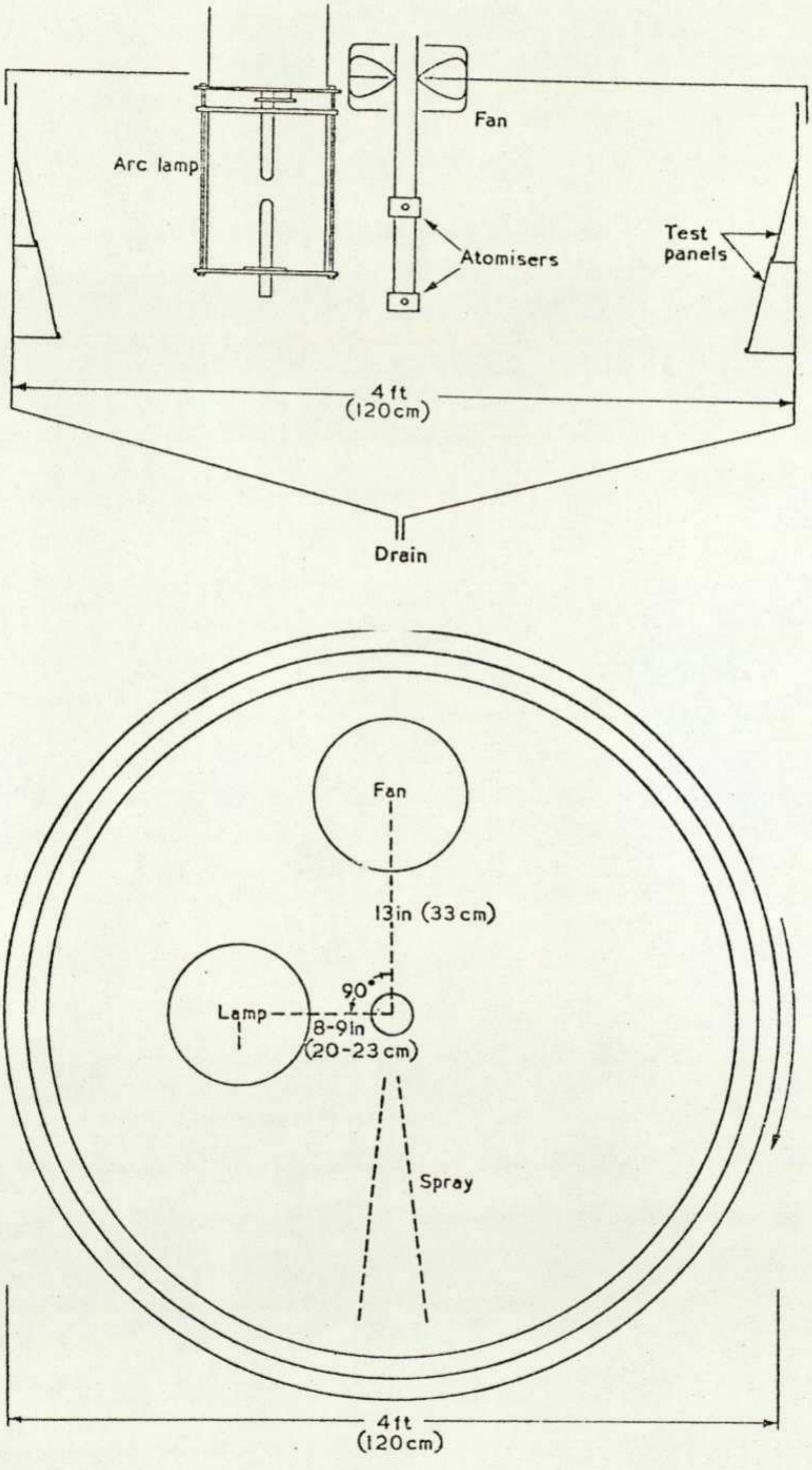


Figure 12. Diagram of Artificial Weathering Apparatus

3. A carbon DC arc lamp enclosed in a borosilicate glass cylinder, mounted with its axis vertical to, and 215 ± 15mm away from the axis of the drum. The arc is formed between two uncored carbons, 15mm in diameter, the upper 305mm long is the positive carbon which burns at a rate of 4mm/hour. This lamp is the source of ultra-violet radiation.
4. Two water atomizers, centrally placed; each discharges 1500ml of water per hour at an air pressure of approximately 48 kN/m^2. This ensures that the panels are finely sprayed and each is evenly wetted. The temperature of the water in the atomizers does not exceed 30^oC.
5. A ventilating fan, diametrically fitted into the lid, blows air at a rate of approximately 500 m^3/hr and in a direction opposite to the direction of the water sprays.

Painted aluminium test panels 100mm x 150mm were prepared in accordance with the procedure outlined in section 3.9, dried for four days at 25^oC and 60% relative humidity (no sunlight) and were then subjected to the artificial weathering test. After a period of 500 hours of exposure to the artificial conditions, the panels were taken out from the drum, wiped with tissues, dried for 24 hours at 25^oC and 60% RH, and were then used to prepare specimens for adhesion tests.

3.14.2. Results and Discussion

The results for the evaluation of adhesion of paints to stearic acid contaminated aluminium after 500 hours artificial weathering are given in Table 24.

After 500 hours of artificial weathering, practically all paints based on chemically modified n-butylmethacrylate polymer exhibited a remarkable performance in maintaining the high level of initial adhesion, i.e. adhesion after 4 days drying, and also relative to the adhesion of unmodified base polymer (N8).

TABLE 24

ADHESION OF THERMOPLASTIC POLYMERS AS PAINTS TO CONTAAMINATED ALUMINIUM AFTER 500 HOURS ARTIFICIAL WEATHERING

No.	Ref. No. of paint	Mean value of joint strength $N/m^2 \times 10^4$	No. of Observ-vations	Std Dev δ $N/m^2 x10^4$	Area of Adhesion Failure, %	Error = $\frac{\delta \times 100}{\text{Mean value}}$ %	Joint Strength before weathering
1	N8	482.4	5	44.38	100	9.2	608.5
2	N6	510.7	5	71.67	100	14.0	551.3
3	N13	603.7	6	64.09	100	10.6	1019.9
4	N9	516.9	4	37.22	100	7.2	514.8
5	N14	1068.9	6	107.51	100	10.1	992.4
6	N5	954.8	5	112.75	100	11.2	717.4
7	N12	2953.1	6	216.26	80	7.3	2281.2
8	N18	2260.5	6	201.72	10	8.9	2089.6
9	N15	2219.2	7	154.85	6	6.8	2316.3
10	N31	1780.2	5	104.76	100	5.9	1896.6
11	N32	2332.9	7	135.079	5	5.8	2234.3
12	N33	1028.9	5	82.70	100	8.0	1056.5
13	N35	1935.9	5	157.41	80	8.1	1275.0
14	N16	1170.2	7	37.90	100	3.2	2079.9
15	N27	2173.9	6	113 .03	33	5.2	2343.2
16	N28	2126.1	6	135.08	92	6.4	2179.1
17	N26	2017.2	8	126.12	26	6.3	2359.1
18	N19	1897.3	6	110.54	62	5.8	2047.6
19	N20	3199.2	6	120.61	83	3.8	2403.0

The results in Table 24 show that copolymer (N6) containing 5% molar 4-vinylpyridine which was inactive initially, had an even lower activity after artificial weathering, but it was at least comparable to (N8). At 10% molar modification, the significant improvement in initial adhesion was not maintained after artificial weathering and some 40% of it was lost.

The effect of 5% molar N-vinylpyrrolid-2-one (N9) on adhesion after artificial weathering was similar to that of 4-vinylpyridine (N6), but at 10% molar (N14), the initial increase in adhesion was improved further by about 8%.

The introduction of 5% molar dimethylaminoethylmethacrylate in n-butylmethacrylate polymer chain (N5) which gave some 17% improvement in the initial adhesion over that of (N8), gave a further 33% increase in adhesion after artificial weathering. The significant increase in the level of the initial adhesion particularly marked at the higher degree of modification, i.e. 10% dimethylaminoethylmethacrylate (N12), was substantially increased after artificial weathering. The area of adhesion failure was no longer 100% but was reduced to 80% (this polymer is the best with regard to adhesion after artificial weathering. Similar results were also obtained with terpolymer containing 5% molar dimethylaminoethylmethacrylate and 5% molar acrylic acid).

5% Molar 1-vinyl-2-methylimidazole in n-butylmethacrylate polymer chain (N18) demonstrated a further increase in joint strength (8%) after artificial weathering with a substantial reduction in the area of adhesion failure. The effect on adhesion from 10% molar (N15) although comparable to that of 5% molar after 500 hours artificial weathering, was lower by 4% compared to its excellent initial adhesion. This is in contrast to the beneficial effect on adhesion shwon after artificial weathering using a higher level of modification of dimethylaminoethylmethacrylate (N12).

A copolymer of n-butylmethacrylate with 5% molar trially-s-triazine-2,4,6- trione (N31) showed after artificial weathering a 6% reduction in the joint strength compared to the significant increase in the initial adhesion.

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Paint based on n-butylmethacrylate with 5% molar allylrhodanine (N32) gave some 4% improvement after artificial weathering compared to the initial adhesion.

The third allyl derivative used as a modifier, i.e. allylglycidyl ether with butylmethacrylate (N33) at 5% molar, did not maintain the same improved level of adhesion it gave initially, but an undefined increase was observed.

n-Butylmethacrylate polymer chain containing 5% molar vinyltriethoxy silane (N35) showed some 50% improvement in adhesion after artificial weathering.

Copolymers with only 1% or 5% acrylic acid suffered a reduction in adhesion after artificial weathering.

For the effect of the combination of carboxyl and nitrogen-containing monomers in a single polymer chain on the adhesion to contaminated aluminium after artificial weathering, the results suggest that the addition of 1% or 5% acrylic acid with 5% 1-vinyl-2-methylimidazole to the n-butylmethacrylate polymer chain (N27 and N19 respectively), was not as beneficial as already obtained by the use of 1-vinyl-2-methylimidazole alone. However, the combination showed its merits with terpolymers containing 5% dimethylaminoethylmethacrylate and 1% acrylic acid (N28) or 5% acrylic acid (N20) as compared to the copolymers (N5) or (N16) and (N26) respectively. A remarkable performance was exhibited by terpolymer containing 5% acrylic acid and 5% dimethylaminoethylmethacrylate.

To attempt an explanation of these results it is essential to consider the combined effects from factors associated with the accelerated 'artificial weathering' test. These factors are:

1. The increase in temperature
2. The effects of water spray (simulation of rainfall)
3. The effects of ultraviolet radiation produced by the carbon arc lamp.

By virtue of these, chemical and physical changes in paint films will occur, the extent of which will depend on the chemical nature of the film itself. Each factor is responsible for introducing a particular change, but the final and overall change in the paint film and in its performance must be attributed to a combined effect.

Effect of Temperature

Earlier work carried out at the Paint Research Association[250] to investigate the effect of high temperature on adhesion showed that at 120°C, the adhesion of n-butylmethacrylate based paint and those modified with acrylic acid and hydroxyethylacrylate to stearic acid contaminated aluminium was only marginally better than that at room temperature.

In the artificial weathering drum, an average of 47°C is reached as a result of the heat generated from the carbon arc lamp. It follows that the contribution of an increase of 20°C on adhesion value is even less significant.

The reduction in adhesion of copolymer (N18) to uncontaminated aluminium after artificial weathering and the large difference between the joint strengths of n-butylmethacrylate paint to contaminated and uncontaminated aluminium (see Table 24), are additional indications of the negligible effect of temperature on adhesion.

However, the high value of adhesion of paints particularly those containing vinylpyrrolidone, dimethylaminoethylmethacrylate, allylrhodanine and vinyltriethixysilane, can be influenced by the higher rate of release of retained solvent and hardening of the film. These two factors are normally accelerated at a higher temperature. However, changes in mechanical properties of paints, in primary and secondary forces and cross linkages either within the paint or across the interface, increase in stress due to differences between thermal coefficients of paint and adherend and increase in weak layer(s) with increasing temperature, and in general, factors responsible for the change in bond strength with temperature. These have not been explored in this work.

Effect of Water

The effect of water on the adhesion of paints contaminated aluminium can be explained in reference to work carried out at the Paint Research Association[251]. The object was to find whether the chemical modification of n-butylmethacrylate had any special merit in improving adhesion under adverse conditions such as water soaking.

The adhesion termed 'wet adhesion' was measured using the pull-off technique with a suitable fast curing adhesive as described elsewhere[252]. The adhesion to contaminated aluminium of modified and unmodified paints was measured immediately after 48 hours water soaking at 25°C, and after 48 hours water soaking followed by drying for 24 hours at 25°C.

The base n-butylmethacrylate paint after 48 hours water soaking, showed only a very poor adhesion (which was not possible to measure), and the adhesion was not recovered after a drying cycle of 24 hours. However, the 'wet adhesion' of selected copolymers (N5, N18, N27, N28) was not so drastically reduced and water had little effect of paint based on a terpolymer containing 1-vinyl-2-methylimidazole and acrylic acid (N27). Recovery in 'wet adhesion' of these copolymers and terpolymers after 24 hours drying was remarkably good and was essentially complete. (In the absence of the contaminant n-butylmethacrylate paint which showed good adhesion initially (see Table 20) performed well after 48 hours water soaking with only 13% reduction and with a complete recovery after a drying cycle of 24 hours).

It was apparent that the adhesion of the base n-butylmethacrylate paint after artificial weathering did not totally collapse as compared to the low level of initial adhesion. This discrepancy may be attributed to the dissimilarity in the methods of exposure of paint film to water. In the latter method, the paint was totally immersed in water whereas in the former the water was sprayed on the paint panel which were placed at an angle allowing the water to drain continuously.

Although there may be some deleterious effect from water on adhesion of the n-butylmethacrylate paint, it should be negligible for modified paints which gave a lower adhesion because their adhesion is recoverable after the drying cycle. The paints prior to the adhesion testing after artificial weathering were normally subjected to a similar cycle.

Effect of Ultraviolet Radiation

Photodegradation of a polymer is a degradation process initiated by light and takes place in air or oxygen. It generally implies the use of ultraviolet radiation.

The electromagnetic spectrum with the portion of the ultra-violet spectrum between 2000Å and 4000Å is shown in Figure 13 in the expanded form.

When a polymer photolytically degrades it means that the polymer will:

(a) absorb directly the incident radiation and it must therefore have a strong absorption band in the region of the wavelength of the light used.

(b) undergo homolysis, i.e. to give radicals at different sites and is influenced by the energy of the incident light.

(c) undergo chain scission which is revealed by a fall in molecular weight of the sample by breaking one of the backbone C-C bonds.

(d) cross-link indicated by a rise in molecular weight and the formation of an insoluble gel.

The source of light in accelerated weathering was from an enclosed carbon arc lamp which was relatively constant spectral distribution and intensity, contrary to natural weathering.

The spectral composition of the light emitted by this arc

[redacted]

Figure 13. The Electromagnetic Spectrum

in the visible and ultraviolet regions was determined by Neville[253] who showed that the carbon arc gives much more intense radiation between 355 nm and 420 nm than in the visible spectrum above 420 nm wavelength.

The diagram in Figure 14 shows the distribution of the light output from the carbon arc and daylight as a relationship between 100% relative spectral energy and (300-600) wavelength (nm). Neville[253] named these three most intense bands at 355 nm, 385 nm and 420 nm as the 'cyanogen bands'.

In comparison it is clearly visible that the radiation of the carbon arc lamp below 350 nm is negligible, whereas daylight contains considerable energy between 300 to 350 nm. Consequently the pigmented acrylic polymers, copolymers and terpolymers are vunerable to the effects of ultraviolet radiation at the 'cyanogen bands'.

Neville[253] also showed that the percent amount of absorption by titanium dioxide pigment at 355 nm, 385 nm, and 420 nm, was 95%, 85% and 15% respectively. Hence, the pigment acts as an additional filter incorporated in the film, giving a protective shield against the degradation of the media.

The protective effect of titanium dioxide on the binder was also shown by Dunderdale[254]. However, the pigment also assists the degradation by a photo-catalytic mechanism.

Neville[253] demonstrated the enormous difference in the absorption coefficient of rutile titanium dioxide, as shown in Figure 15 (approximately 10^4 mm^{-1}) and various clear (unpigmented) polymer films (0.1 - 10 mm^{-1}) in the range of wavelength 280 - 450 nm. Polymer films included linseed pentaerythritol alkyd, silicone

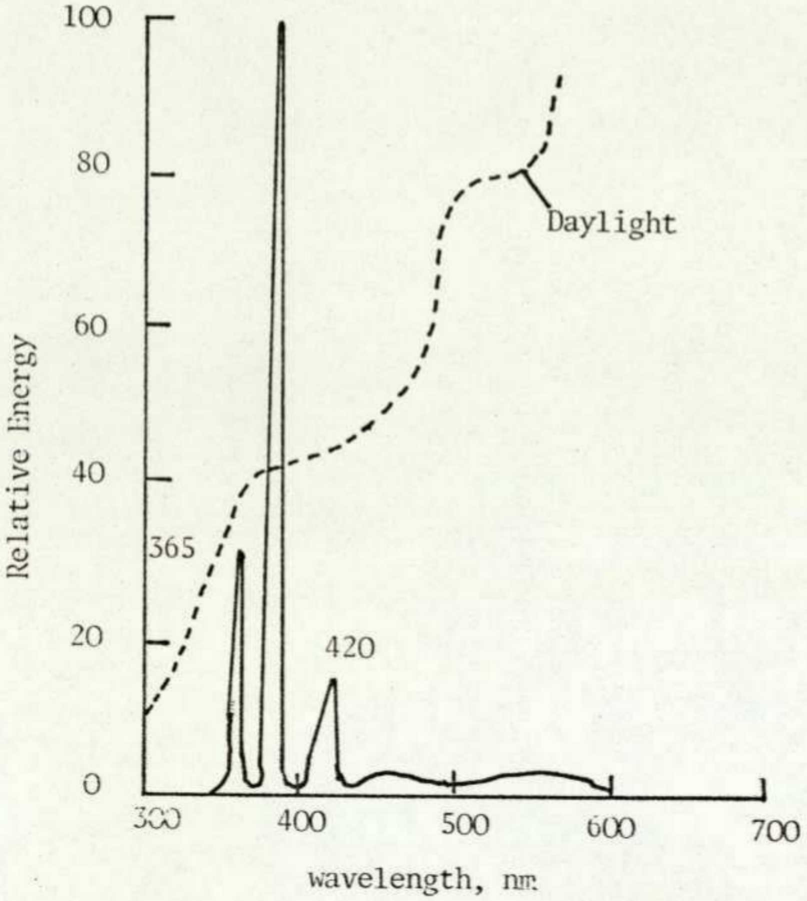


Figure 14. Emission Spectrum of Enclosed Carbon Arc

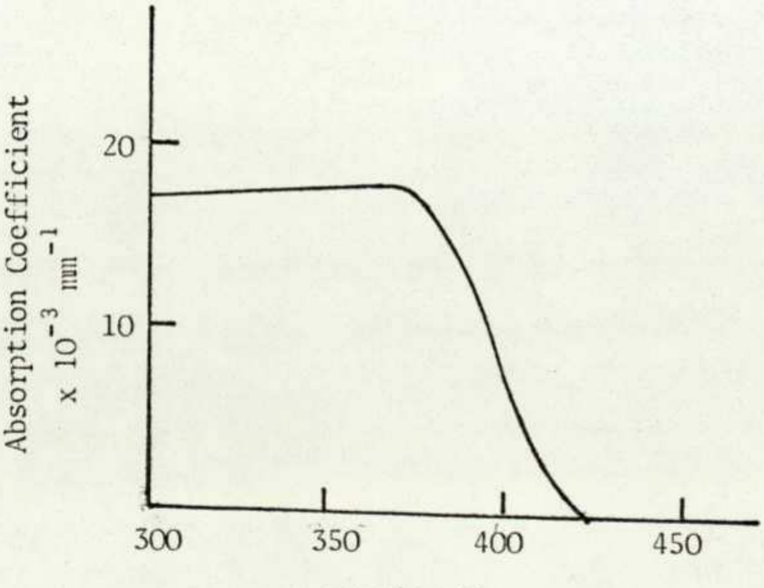


Figure 15. Absorption Coefficient of Rutile Pigment

modified alkyd, melamine/nitrocellulose, acrylic/melamine/formaldehyde (thermosetting), moisture curing polyurethane, silicone polyester, vinyl chloride, and thermoplastic acrylics.

From the graphical illustration,[253] the maximum absorption coefficient of thermoplastic acrylic film is 1.6 mm^{-1} at 284 nm or between (1.6 - 0.2 mm^{-1}) at (280 - 440 nm). In other words, the absorption coefficient of films in general was increased steadily as the wavelength was reduced.

Hughes[255] classified roughly the media of paint films into light-sensitive and light stable groups and correlated within the former group, the dependence of rate of degradation of the media on U.V. absorption coefficient. Thus he multiplied the measured absorption coefficients of film (0.1 - 10 mm^{-1}) by the energy distribution of the light of the carbon arc lamp to obtain (K_m - weighted absorption coefficient, mm^{-1}) values over 300 - 400 nm. He assumed that the rate of degradation is proportional to K_m, and derived a degradation rate constant a_m as the quotient of rate of mass loss M_o, $mgm^{-2}h^{-1}$, and weighted absorption coefficient K_m, i.e.

$$a_m = M_o/K_m$$

The degradation rate constant, a_m is a measure of the durability of the clear films and depends on film thickness, permeability, U.V. absorption and chemical structure. Small values of a_m indicate stable films.

For thermoplastic acrylic film $M_o = 2.5$ mg/m2h , $K_m = 0.15$ mm^{-1} and hence $a_m = 14$. This is high. However Hughes[255] showed that the absorption and distribution of U.V. energy by the medium in paint films is enormously reduced, and it is one thousandth of the radiation absorbed by the clear film, at 10% pigmentation. In the paint film, the pigment is responsible for most of the total absorption.

The spectral reflectance/wavelength relationship of rutile titanium dioxide[256] shows that above 390 nm, titanium dioxide strongly reflects the greater part of the visible spectrum. Below this value the reflectance is zero. This suggests that half of the radiation of the carbon arc lamp is absorbed by titanium dioxide and in accordance with Neville's findings[253], and the other half is reflected. Then the media presumably will not undergo a severe photodegradation process in view of the fact that titanium dioxide gave an additional protection and assuming that, the residual light scattered will not be absorbed sufficiently strongly to degrade the film, and the energy absorbed was dissipated as heat and is lost without causing deterioration to the binder.

These considerations do not imply that the modifiers themselves are not capable of absorbing ultraviolet radiation in the wavelength region of 350 - 420 nm. For this purpose, and for the purpose of supporting the idea that the deterioration or improvement in the adhesion of the base polymer and copolymer paints is a function of the differences in U.V. absorption, their U.V. Spectra were determined. Details of this work are included in Section 3.15.

The ultraviolet energy absorbed by the modifier or modifiers will depend on an efficiency parameter peculiar to the modifier. For modifiers capable of absorbing the energy, acceleration of degradation process with loss of adhesion will occur or further hardening of the film resulting in a higher tensile strength and hence higher adhesion.

In addition, the part of the U.V. energy that is absorbed by the pigment causes additional breakdown of the medium near the pigment/medium interface.

In general, paint films[257] after artificial weathering suffer the loss of gloss, and the appearance of chalking as a result of weight loss and the appreciable contraction of the film.

To illustrate the combined effects of water, temperature and U.V., and omitting the effect of the contaminant and the possibilities of its interaction with the modified paints, the adhesion of base n-butylmethacrylate paint (N8), the same modified with 5% molar 1-vinyl-2-methylimidazole (N18), and n-butylmethacrylate with 5% acrylic acid (N26) to uncontaminated aluminium after 500 hours artificial weathering, was measured. The results are given in Table 25.

TABLE 25

ADHESION OF PAINTS TO UNCONTAMINATED ALUMINIUM AFTER 500 HOURS ARTIFICIAL WEATHERING

	UNCONTAMINATED					CONTAMINATED
Ref. No.	Mean value of joint strength, N/m^2 10^4	No. of observations	Standard deviation (δ) $N/m^2.10^4$	Area of adhesion failure, %	Error in (δ)	Joint Strength, $N/m^2.10^4$
N8	2419.71	5	95.11	25	3.9	482.4 ± 44.4
N18	2690.56	6	46.86	20	1.7	2260.5 ± 201.7
N26	3075.12	6	122.32	90	3.98	2017.2 ± 126.1

Uncontaminated Surface

The reduction of 15.7% and 12% in the adhesion of n-butylmethacrylate paint (N8) and its copolymer containing 5% 1-vinyl-2-methylimidazole (N18) respectively, were presumably due to the combined harmful effects of water, heat and ultra-violet radiation. In contrast, the adhesion of the copolymer of n-butylmethacrylate and 5% acrylic acid (N26) was not affected by these factors and very small increase was obtained, indicating that other factors are responsible; such as the change in mechanical properties as a result of the introduction of carboxyl groups in the polymer chain.

The effectiveness of the chemical modification in promoting adhesion of n-butylmethacrylate with 1-vinyl-2-methylimidazole (6.6%) or with 5% acrylic acid (6.4%), after 4 days drying, was essentially good after artificial weathering, giving 11.2% increase respectively.

Contaminated Surface

It was shown previously that n-butylmethacrylate paint displayed poor adhesion to stearic acid contaminated surface after 4 days drying, due to the absence of chemical activity to displace the contaminant. A similar behaviour was encountered after artificial weathering with further reduction of 20% in joing strength and indication of a weak boundary layer failure.

The adhesion of the copolymer of n-butylmethacrylate with 5% 1-viny-2-methylimidazole (N18) after artificial weathering was increased by 8.2%. By contrast, the presence of the contaminant reduced the activity of the carboxyl groups in maintaining the higher level of adhesion of four days drying of copolymer (N26), resulting in a 14.5% decrease.

The loss of adhesion of N18 as a result of the presence of the stearic acid contaminant after 4 days drying was 31.7% but half of this loss was recovered after artificial weathering. The improvement, i.e. of 8.2% must be attributed to the more favoured conditions of an accelerated rate of interaction between stearic acid and the imidazole.

It is apparent that further improvement in adhesion was obtained by the introduction of dimethylaminoethylmethacrylate (N5, N12), allyrhodanine (N32), vinyltriethoxysilane (N35) and 5% dimethylaminoethylmethacrylate with 5% acrylic acid (N28) in n-butylmethacrylate polymer chain after artificial weathering.

Although, and in the presence of stearic acid there is this apparent increase in adhesion, after artificial weathering with the above monomers, but some reduction in the adhesion after artificial weathering was inevitable due to the effect of ultraviolet radiation, water and heat.

Heat will lead to expansion of the film, water can cause blisters and U.V. promotes photochemical reduction and oxidation processes resulting in surface topographical changes due to pigemnt migration, leaching of the oxidative products as gases and soluble materials. This statement is also confirmed by the results of adhesion to uncontaminated surface and the reduction in adhesion occurred with the other copolymers. It follows that the degree of this reduction or increase is a function of the degree and nature of interaction of the contaminant and the modifiers, the degree of oxidation of the contaminant through the unsaturation[258] by the effect of ultraviolet radiation (as seen with the results of N26), and the effect of U.V. radiation on each particular modifier. A fundamental factor in all U.V. curing or destruction of a material is its U.V. absorbance. Hence, the necessity for the determination of U.V. absorption spectra of the copolymers, became important.

3.15. Ultra-violet Spectrophotometry, Absorption Spectra of Binders

3.15.1. Experimental

Initially a selection of suitable solvents for the determination of U.V. spectra of the copolymers or the homopolymers of the modifiers was made. Suitable solvents included ethanol, methylene chloride, hexane, methanol and water.

The concentrations of the polymer solutions were adjusted in situ and by the addition of extra solvent or extra polymer until a satisfactory shape of the adsorption spectrum was obtained. In some cases very concentrated solutions were used.

The method of preparation and the solubility characteristics of the homopolymers were discussed in Section 3.7.

The spectra were obtained using Model 137 Perkin-Elmer Spectrophotometer (slit 25).

3.15.2. Results and Discussion

The U.V. absorption spectra of the contaminant, the homopolymers of the modifiers and copolymers were obtained. Their specific wavelengths which were possible to detect are shown in Table 26 and Table 27 respectively.

The application of U.V. absorption technique for studying the rate of chemical reactions is not recommended for these systems because of the difficulty in finding the right solvent which will dissolve the contaminant, the homopolymer, the copolymer and have the appropriate absorption bands for quantitative measurements.

The U.V. absorption spectra of the homopolymers were included in these series of experiments to establish whether the copolymers contained the same absorption bands, which are specific for each modifier. In certain cases this was the case. But in others, the same bands were very difficult to detect due to the low level of modifier concentration in the copolymers.

Basically the homopolymers of the modifiers and the copolymers have maximum intensity of absorption close to or at the same wavelengths, i.e. between 200 - 220 nm.

The shift in the position of the medium or weak intensity absorption bands, and their appearance or disappearance, are the results of the differences in the composition of the polymer chain.

It is conceivable to assume that a greater proportion of available U.V. energy will be absorbed by paints containing those modifiers which possess similar U.V. absorption intensity bands at similar wavelengths to those of the carbon arc lamp, i.e. above 300 nm.

Paints containing N-vinylpyrrolidone (N9, N14), dimethylaminoethylmethacrylate (N5, N12), 365 and 376 nm; 1-vinyl-2-methylimidazole (N18, N15) 380 nm; triallylisocyanurite (N31), 344 and 387 nm; N-allylrhodanine (N32), 394 nm; allylglycerylether (N33), 388 nm; and vinyltriethoxysilane (N35), 377 nm, fall under this category.

Practically all the copolymers would absorb the radiation of the carbon arc lamp due to the presence of the modifiers and regardless of whether they exist in the homopolymeric or copolymeric forms. By the application of special filters, it has been recently demonstrated[259,260], that wavelengths shorter than 310 nm have a most pronounced effect on paint films.

The homopolymer of 1-vinyl-2-methylimidazole showed a weak absorption band at 380 nm which is inside the most intense region of U.V. emission spectrum of the enclosed carbon arc lamp, and could have had a significant effect on the adhesion of the paint containing the monomer as a copolymer. The band was only apparent at very high concentration of the homopolymer in ehtanol and consequently it did not appear in the spectrum of the copolymers which contain only 5% or 10% modification.

For the imidazole and its simple alkyl derivatives, Grimmett[240], observed that they have little absorption in the near-ultraviolet due to their high aromatic stability. Schubert[261] and Pozharskii[262] found that alkyl groups introduced at any position in the imidazole ring produce a small bathochromic shift of the absorption band at 207 - 208 nm. When 1-vinyl-2-methylimidazole was homopolymerised or when it was linked with n-butylmethacrylate, the vinyl group produced similar shift at 210 - 211 nm respectively.

The amount of U.V. energy absorbed by paints (N6 and N13) via 4-vinylpyridine was probably insignificant because the maximum intensities of the copolymers of pyridine rings in general[263,264] were below 300 nm which is outside the emission spectral distribution of the carbon arc lamp.

The ultra-violet absorption spectrum of 2-vinylpyridine (monomer) was determined[109] as 200 - 300 nm with a maximum at 277.5 nm. The U.V. absorption spectrum of 3-vinylpyridine was reported by Swain et.al.[264], and covered the range 200 - 300 nm wavelength with maxima at 240 and 280 nm. As expected the U.V. spectrum for homopolymeric 4-vinylpyridine covered the same range of wavelengths with intensities at 209, 258, 252, and 265 nm.

Future experimentation should include studies in the rate of weight loss of paints, gloss, and degree of cross-linking are recommended.

TABLE 26

THE ULTRA VIOLET ABSORPTION INTENSITIES OF MODIFIERS AS HOMOPOLYMERS

Monomer	Homopolymer	Solvent	Wavelength, nm, In order of decreasing intensity of absorption		
			Max.	Med.	Weak
-	n-Butylmethacrylate	Cyclohexane	219	-	-
240,280	4-Vinylpyridine	Ethanol	209	258,252,265	-
235 methanol	N-Vinylpyrrolidone	Methanol	209	262,269,256,265	254,248 244
-	Dimethylaminoethyl-methacrylate	Ethanol	209	294	
235 ethanol	1-Vinyl-2-methylimidazole	Ethanol	210	-	380
208 Ethanol	Triallylisocyanurate	Methylene Chloride	263	270,257,249,247, 244	299,318, 350
-	Allyl-rhodanine as (monomer)	Ethanol	207	260,298,346,386,456	
208,240	Allylglycidylether	Methylene chloride	246		
-	Vinyltriethoxysilane	Hexane	199	266,259,269,273	-
195	Acrylic Acid	Water	208	262	307
Stearic acid		Cyclohexane, Ethanol	215		

TABLE 27

THE ULTRA VIOLET ABSORPTION INTENSITIES OF COPOLYMERS

Ref. No.	Copolymer	Solvent	Absorption Intensities at wavelengths, nm		
			max.	med.	weak
N8	n-Butylmethacrylate (nBMA)	Cyclohexane	219	-	-
N13	nBMA + 10% 4-vinyl-pyridine	Cyclohexane	219	259	-
N14	nBMA + 10% N-vinyl-pyrrolidone	Methylene chloride	214,247	-	275,292, 347
N12	nBMA + 10% Dimethylamino-ethylmethacrylate	Cyclohexane	216	365,376	-
N15	nBMA + 10% 1-Vinyl-2-methyl-imidazole	Ethanol	211	-	-
N31	nBMA + 5% TAST, 2,4,6 Trione	Methylene chloride	243	262,298	344,387
N32	nBMA + 5% Allylrhodanine	Cyclohexane	216	260,294, 260,394	468,514
N33	nBMA + 5% Allylglycidyl-ether	Cyclohexane, Methylene Chloride	221	262,298, 341	388
N35	nBMA + 5% Vinyltriethoxy-silane	Cyclohexane	216	-	297,377
N26	nBMA + 5% Acrylic Acid	Cyclohexane	212	270	256,263 328,341, 345,349

3.16. Characterisation of Bulk Properties of Synthesized Polymers

3.16.1. Experimental

The cohesive energy density of two polymers, mainly polybutylmethacrylate N8 and its copolymer with 1-vinyl-2-methylimidazole N18, were determined using the method based on the measurements of the viscosities of their polymer solutions.

The determination of the viscosity of fluids is based on their property to resist a shearing force under laminar flow conditions when passing through capillary of a glass viscometer.

Two distinct types for quantitative expression of viscosity are known; The dynamic viscosity (η), and the kinematic viscosity (ν).

The dynamic viscosity measured in Poise or Centipoise $ML^{-1}T^{-1}$, 1 g/cm/sec. is the tangential force on unit area of either of two parallel planes at a unit distance apart.

The kinematic viscosity, measured in stokes or centistokes L^2T^{-1}, equals to the quotient of the dynamic viscosity and the density of the fluid, thus:

$$\nu = \eta/p \quad \text{or} \quad \nu = Ct$$

where C - is the viscometer constant and

t - is the time of flow in seconds.

It is necessary to calibrate the viscometer and to apply the corrections outlined below.

Densities of the solvent and polymer solution mixtures were determined using 25 ml density battles at $25^{\circ} \pm .05^{\circ}C$ and in accordance with the procedure outlined in Section 3.5.

Polymer solutions at 0.5% concentrations were made in volumetric flasks using solvent free polymer samples prepared as described in Section 3.5.

All solutions were filtered using cintered glass filters prior to each flow time determination.

(a) Calibration of Viscometer

To meet the precision requirements of British Standard (B.S. 188 : 1957, part 5), the Ubbelohode suspended level viscometer was made of borosilicate glass tubing to size '0' and as specified in method ASTM D445-61:1P71/64. The viscometer is not an absolute instrument and therefore calibration is necessary to obtain true values of viscosity.

Liquids of known viscosity are usually used, and in this work hexane and toluene were chosen.

There are numerous types of viscometers but the Ubbelohode type (see Figure 16) has a number of advantages over the U-tube, mainly it avoids the complication of having to introduce an accurately reproducible and exact volume and decreases the variation in hydrostatic head during measurements. As the liquid emerges from the lower end of the capillary tube (5), it flows down the sides of bulb (B) only, due to the spherical shoulder and air vent (tube 3).

The method of manipulation of viscometer consists of the following operations: the sample is charged through tube (1), then tube (3) is closed and suction is applied to tube (2) until the liquid reaches a satisfactory level in bulb (D). This ensures that the liquid has the same environment when it enters and leaves bulb (C). The liquid is held at this level by closing tube (2), then tube (3) is opened to the atmosphere to allow the sample to drop away from the capillary. The turbulence of the flow of the liquid is minimised by the conical shape of the entrance and exit of the capillary.

The flow time is then recorded which is the time taken for the bottom of the meniscus to pass from the top edge of Mark (E) to the top edge of Mark (F).

The flow time is measured repeatedly until three successive times are obtained which do not differ from their mean by more than 0.1 percent.

Accurate results depend on absolute cleanliness and control of a constant temperature. Cleaning of the viscometer between determination is carried out according to British Standard (B.S. 188:1957, pp 12). The variation of the coefficient of viscosity with temperature is controlled by suspending the viscometer in a thermostatically controlled water bath using special holders.

(b) Precautions, Corrections and Sources of Error

1. Kinetic Energy Correction

The Poiscuille's law for the flow of liquid through a cylindrical tube, i.e. $V = \frac{\pi P R^4}{8 \eta L}$ is applied to the flow in a capillary viscometer with a correction for kinetic energy of efflux in the form of the equation:

$$\nu = \frac{\pi d^4 hg.t}{128 \ L_V} - \frac{mV}{8\pi L} \cdot \frac{1}{t} \qquad (77)$$

where: ν - kinematic viscosity

V - volume of liquid flowing in time (t), cm^3

h - mean head of liquid, cm

g - acceleration due to gravity, cm/sec/sec

V - volume of liquid which flows in time t in cm^3 per second.

L - corrected length of capillary, i.e. the actual length plus the Couette correction which may be taken as three times the diameter of the capillary, cm

M - a constant with small positive value up to 1.5

Equation (77) corresponds to the one used in practice, i.e.

$$\nu = Ct - \frac{B}{t} \qquad (78)$$

where $C = \frac{\pi d^4 hg}{128\ LV}$ and $B = \frac{mV}{8\pi L}$

if $m = 1$ then $B = 3.98\ \frac{V}{L}$

Paiscuille's law applies strictly to that portion of the tube in which the velocity has become constant, and the applied pressure is used to give kinetic energy to the liquid and to overcome the viscous resistance.

Equation (77) includes the correction for kinetic energy (B), i.e. the work done in overcoming the viscous resistance in the capillary itself as a result of the applied pressure, and the correction for the small amount of energy expended in overcoming the viscous forces between the converging and diverging streamlines at the entrance and exit respectively of the capillary. The latter is referred to as Couette correction, and takes the form of a hypothetical increase in the length of the capillary.

In equation (78) when (t) is large the term $\frac{B}{t}$ becomes very small and can be neglected, and the equation takes the form of $\nu = Ct$, and hence the dynamic viscosity $\eta = Ct\,\rho$. In this work, the term $\frac{B}{t}$ was not neglected in the calculations.

Calculation of constants

Comparison of two liquids with viscosities ν_1, ν_2 and flow times of t_1, t_2, the values of (C) and (B) may be calculated using the following equations, (79) and (80).

$$B = \frac{t_1 t_2 (\nu_2 t_1 - \nu_1 t_2)}{t_2^2 - t_1^2} \qquad (79)$$

$$C = \frac{\nu_2 t_2 - \nu_1 t_1}{t_2^2 - t_1^2} \qquad (80)$$

where: ν_1 and ν_2 - are the viscosities of hexane and toluene respectively, which were taken from the literature at 25°C

t_1 and t_2 are the flow times, when hexane and toluene were passed through, seconds.

(c) Calculation of minimum flow times

The percentage error x, due to omitting the kinetic energy correction is given by:

$$x = 100 \frac{B}{Ct^2} \text{ , and since } B = 3.98\ V/L$$

$$= \frac{398V}{Ct^2L}$$

$$\therefore \qquad t = \sim 20 \sqrt{\frac{V}{XCL}}$$

If x is to have a maximum value of 0.1%, then t must have a minimum value given by:

$$t = 20 \sqrt{\frac{V}{0.1\ LC}} = 63 \sqrt{\frac{V}{LC}}$$

In the experiments $V = 3.5\ cm^3$, $L = 9$ cm

$C = .00127$, $t = 1102$

(d) Drainage Errors

The true volume of the liquid emerging from the bulb is normally reduced by an amount equal to that of the film adhering to the walls of the bulk. However, a correction is not usually applied.

The error in the Ubbelohole viscometer is reduced because it has a second bulk of similar shape above the main bulb giving the same drainage conditions when the level of liquid passes the upper and lower marks.

(e) Streamline and Turbulent flow

At high rates of flow, the assumption of streamline flow in the derivation of Poiscuille's equation is deviated; and can be characterised by a dimensionless quantity known as Reynold number.

$$(Re) = \frac{\nu d \rho}{\eta}$$

where: ν is the mean velocity

d is the diameter of the tube

ρ is the density

when $Re > 2000$ turbulent flow occurs and when $Re > 4000$ streamline flow occurs.

Errors due to turbulent flow in these experiments were avoided because the flow rates were slow and (d) was very small.

3.16.2. Results and Discussion

Initially toluene/methanol was used as solvent/nonsolvent system. However, the value of solubility parameter of the mixture was not low enough to allow for the construction of a defined relationship of the titration curve, i.e. $[\eta \text{ versus } \delta_{mixture}]$.

Other combinations of solvent mixtures were investigated. The choice was limited because the homopolymer is soluble in a variety of solvents and insoluble in very limited ones.

A computer programme was written for calcuating the solubility parameter of combinations of various solvent/nonsolvent systems using the data of Gordon[1] for the solubility parameter and fractional polarity (ρ), and the following equations.

$$d = 1 - 0.9898\ \rho - 0.142\ (\rho-\rho^2)^{\frac{1}{2}} \qquad (64)$$

$$\Phi = (d_1d_2)^{\frac{1}{2}} + (\rho_1\rho_2)^{\frac{1}{2}} \qquad (69)$$

$$\delta^2 m = (\phi_1\delta_1)^2 + (\phi_2\delta_2)^2 + 2\ \Phi\ \phi_1\phi_2\delta_1\delta_2 \qquad (73)$$

The definitions of the symbols are discussed previously. See section 2.9.1. The molar volumes of solvents were taken at various percentages of concentrations.

The calculation was carried out for the following combinations:

Ethyl-n-butyrate / Ethanol
Butylacetate / Ethanol
Toluene / Ethanol

Cyclohexane / Ethanol

Cyclohexane / Ethanol

However, cyclohexane / ethanol combination was chosen because δ_m was low enough.

The specific viscosity was calculated using the following relation and with the aid of a computer programme.

$$\eta_{\text{specific}} = \frac{\eta_{\text{solution}} - \eta_{\text{solvent}}}{\eta_{\text{solvent}}}$$

The results of the viscosity and δ_m of solvent mixture cyclohexane/ethanol is given in Table 28, for 0.5% solution of polybutylmethacrylate in Table 29, and for 0.5% solution of copolymer polybutylmethacrylate + 5% 1V2MI, in Table 30.

The values of η_{sp} are plotted against δ_m in Figure 17 and smooth curves have been drawn covering most points.

The precise value of the solubility parameter at η_{sp} maximum is 8.94 $\text{cal/cc}^{\frac{1}{2}}$ and is identical for both polymers. This shows that the interaction forces in the bulk of the modified and unmodified polymers are the same, although a stronger solvation of the modified polymer in polar solvent is apparent, giving a higher viscosity which is not due to a higher molecular weight.

The purpose of the following discussion is to outline the relationship between adhesion and solubility parameter in terms of polymer structural changes observed by other investigators and its relevance to the present work.

Engel and Fitzwater[265] demonstrated a relationship between the solubility parameter of solvents used in organosols and their peel adhesion to tin. A maximum of peel strength was obtained from the polymer dissolved in the most efficient solvent, which aided the dispersion of the polymer in the dried film.

Sherlock et al[266,267], studied the effects of surface cleanliness, phosphate coatings and oxide films on the adhesion of (PVC) to steel, and obtained a similar relationship between peel adhesion and cohesive energy density of solvents used.

The difference in the role of the solvent was that in Engel's studies it was as a means of dissolving the polymer where in Sherlock's, it was a cleaning solvent.

The best cleaning power in removing contaminants of rolling lubricants which had a markedly adverse effect on adhesion of the polymer to steel substrate[267] was n-butanol ($\delta = 11.2$). This value is very close to that of unpolymerised diallylphthalate ($\delta = 11.3$), being one of the components of the coating which exhibited maximum peel adhesion.

In this work, the effectiveness of the presence of the modifiers in the polymer backbone in "cleaning the contaminated metal surface" and in accordance with the above findings, was not apparent. Calculated values of solubility parameter (SP) (see Section 3.6) of modified polymers were practically the same, because the amounts of modifiers added were too small to introduce significant changes in solubility parameters and to bring it closer to the solubility parameter of stearic acid $\delta = 8.89\ \text{cal/cc}^{\frac{1}{2}}$. In addition, the change was also too small to observe experimentally, and the improvement in adhesion is an indication to a specific interaction to stearic acid rather than alteration in CED.

However, using Small's method[142] the (δ) of the modifiers in the monomeric form are given in Table 31. A plot of δ_{monomer} against joint strength gave a relationship as in Figure 18, similar to that plotted by Engel[265] and Sherlock[266,267]. But this does not agree with the idea that if two compounds are to be mutually soluble then their solubility parameter must not differ by more than approximately 1.1 units[142] or substances with similar molar volumes and solubility parameter have greater mutual solubilities.

δ_{stearic} acid is not very close to 'δ' of most of the modifiers with the exception of DMAEMA and N-allylrhodanine which gave good adhesion. In fact, δ_{stearic} is close to δ n-butyl methacrylate monomer which has poor adhesion.

TABLE 28

VISCOSITY OF SOLVENT MIXTURES AT 25°C CYCLOHEXANE/ETHANOL

C = viscometer constant .00127

B = 69.624, stopwatch correction 1.0033

% Ethanol by volume	Density (ρ) g/cm^3	Flow time seconds	Viscosity, centipoise $\eta = C\,t\,\rho$ $\eta = (Ct - \frac{B}{t})\,\rho$	δ_m Equation (73)
0	.7748	971 ± .2	.8999	8.2
10	.7736	903.5 ± .1	.8280	8.45
20	.7732	909.9 ± .4	.8342	8.76
25	.7724	914.7 ± .2	.8385	8.94
30	.7726	930.96 ± .5	.8556	9.13
35	.7733	944.6 ± .4	.8706	9.33
40	.7731	955.6 ± .4	.8819	9.54
50	.7746	980 ± .3	.9090	9.99
60	.7763	1008.6 ± .5	.9407	10.47
70	.7738	998.8	.9276	10.99
80	.7752	1074.7	1.0078	11.54
90	.7765	1096.5	1.0320	12.11
100				12.7

TABLE 29

VISCOSITY OF 0.5% SOLUTION OF POLYBUTYLMETHACRYLATE IN CYCLOHEXANE/ ETHANOL

C = .001267, B = 69.957, Stopwatch correction = 1.0007

% Ethanol by volume	Density ρ g/cm^3	Flow time seconds	Viscosity, centipoise $\eta = C\ t\ \rho$ $\eta = (Ct - \frac{B}{t})\ \rho$	Specific Viscosity $\eta_{sp} = \dfrac{\eta_{poly} - \eta_{solution}}{\eta_{solution}}$
0	.7755	1040.9 ± .9	.9706	.0785
10	.7740	988.3 ± .5	.9143	.1042
20	.7738	998.8 ± .5	.9276	.1118
25	.7730	1012	.9377	.1183
30	.7739	1028.3 ± .5	.9556	.1168
35	.7743	1040.5 ± .5	.9689	.1128
40	.7756	1047.2 ± .5	.9772	.1081
50	.7766	1070 ± .2	1.0020	.1023
60	.7774	1092.9 ± .1	1.0267	.0913

TABLE 30

VISCOSITY OF 0.5% SOLUTION OF COPOLYMER n-BUTYLMETHACRYLATE + 5% MOLAR 1-VINYL-2-METHYLIMIDAZOLE (N18) IN CYCLOHEXANE/ETHANOL

C = .001276, B = 69.957

% Ethanol by volume	Density (ρ) g/cm^3	Flow time, (t) seconds	Viscosity (η) centipoise $\eta = (Ct = \frac{B}{t}) \cdot \rho$	Specific Viscosity $\eta_{sp} = \frac{\eta_{poly} - \eta_{solution}}{\eta_{solution}}$
0	.7758	1033.3 ± .1	.9631	.0703
10	.7729	987.7 ± .2	.9124	.1019
20	.7732	1009.7 ± .6	.9355	.1213
25	.7739	1015.3 ± .2	.9422	.1240
30	.7730	1029.2 ± .1	.9554	.1166
35	.7743	1046.7 ± .1	.9751	.1199
40	.7735	1057.8 ± .2	.9855	.1175
50	.7752	1074.7 ± .0	1.0078	.1085
60	.7765	1096.5 ± .0	1.0320	.0970

TABLE 31

THE SOLUBILITY PARAMETER OF MODIFIERS AS MONOMERS BY SMALL'S METHOD(142)

	Monomer	Density g/cm^3	Molecular weight	Solubility parameter $\delta, (cal/cc)^{\frac{1}{2}}$	Joint strength $N/m \times 10^4$
1.	Stearic acid	.94	284	8.89	-
2.	n-Butylmethacrylate	.894	142	8.73	608.5
3.	4-Vinylpyridine	.97	105	9.71	785.6 (N6+N13)
4.	N-Vinylpyrrolidone	1.043 (1)	111	10.77	753.6 (N9+N14)
5.	Dimethylaminoethylmethacrylate	.9321 (*)	157	8.7	1500 (N5+N12)
6.	1-Vinyl-2-methylimidazole	1.0188 (1)	108	9.72	2203 (N18+N15)
7.	Triallyl-5-triazine,2,4,6-trione	1.1583	249	10.66	1896 N31
8.	N-allylrhodanine	1.0	173.12	8.84	2234.5
9.	Allylglycidylether	.9678	114	10	1056.5
10.	Vinyltriethoxysilane	.894	190	9.96	1274.98
11.	Acrylic acid	1.0511	72		2219.5

(1) Determined at 20°C ± 1

(*) V. D. Gerber, V. E. Elisseeva, LAK. KRAC. MAT. 1, 1970.

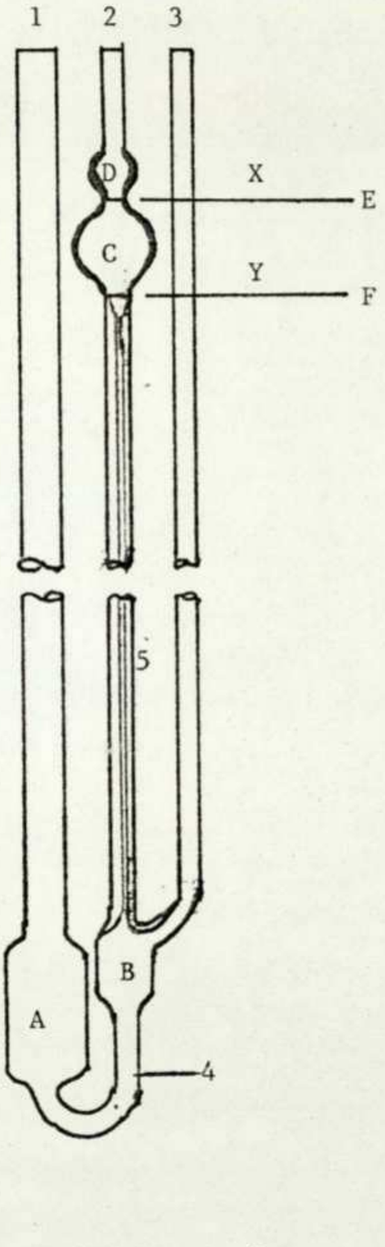


Figure 16. Suspended Level Viscometer
Size 'O'

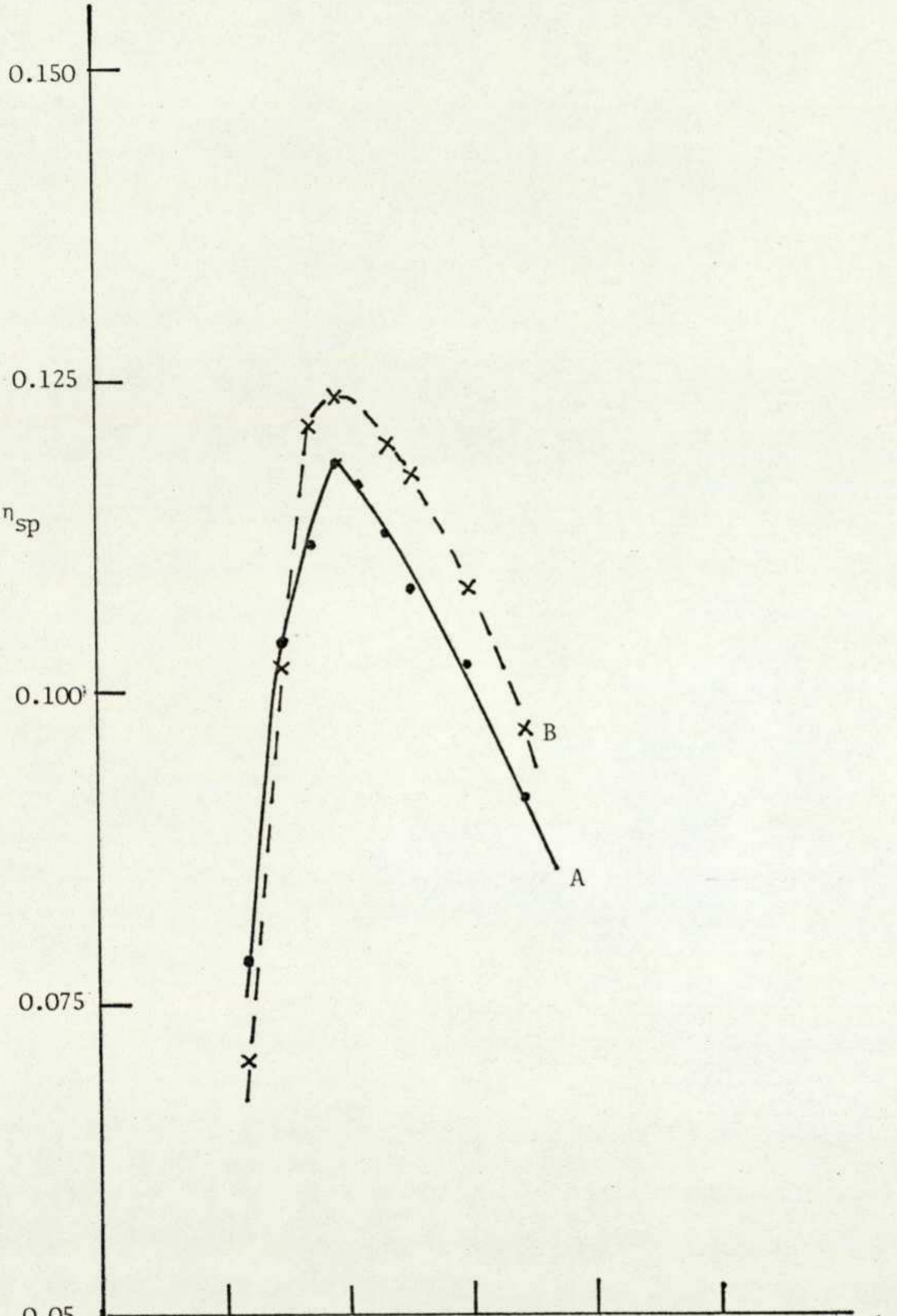


Figure 17. Specific Viscosities (η_{sp}) of Dilute Solutions of Polymers Plotted Against Solubility Parameter (δ_m) of Mixtures of Cyclohexane and Ethanol 25^{o}C.

A n-Butylmethacrylate (N8)
B n-Butylmethacrylate + 5% molar VMI (N18)

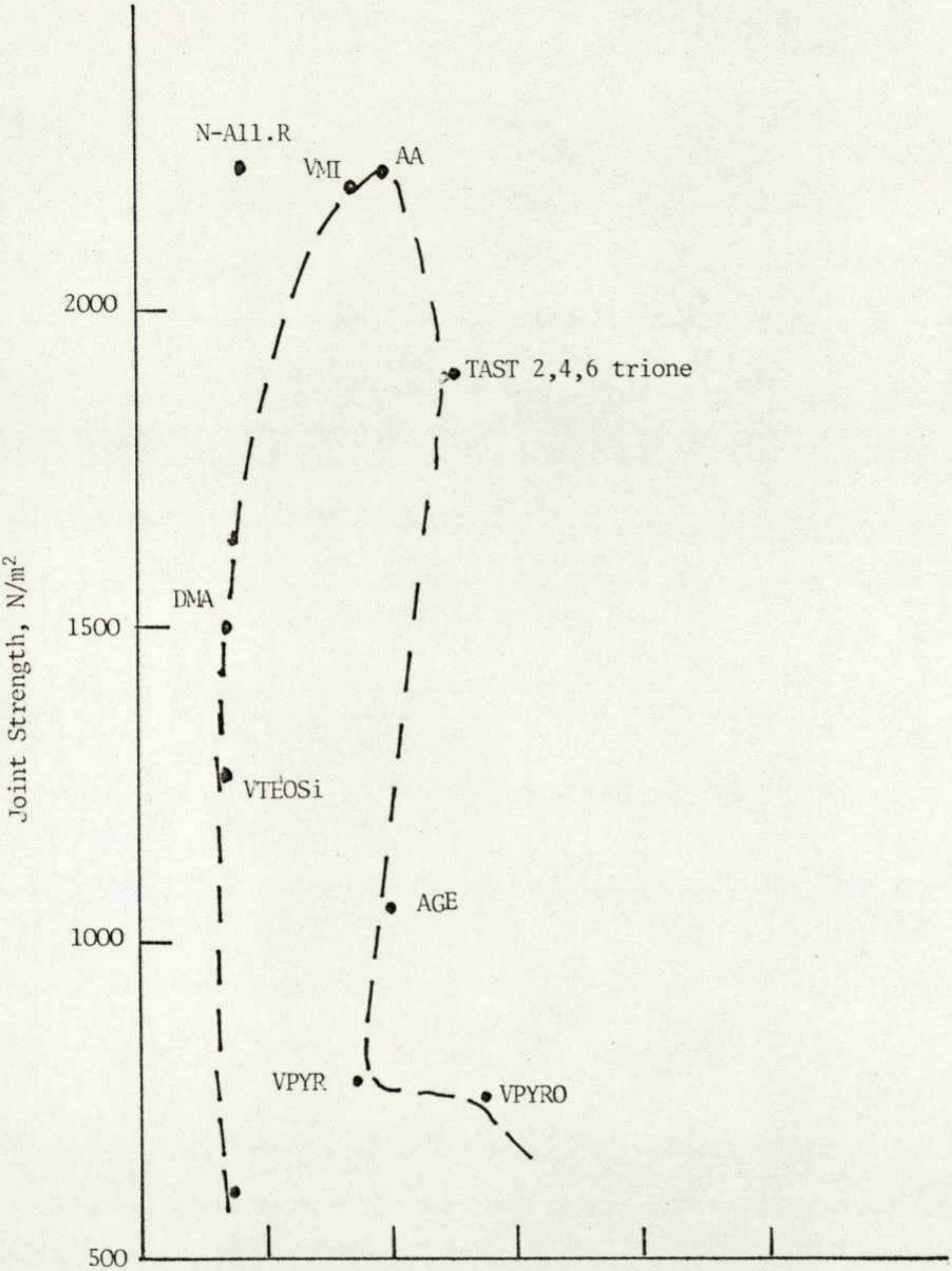


Figure 18. The Relationship Between the Solubility Parameter of Monomers (modifiers) and Joint Strength of Copolymers Containing Them

3.17 Characterisation of Surface Free Energy of Paints

3.17.1. Experimental

The critical surface free energy of paints were determined using Zisman's technique discussed in 2.8.2.

The contact angle of wetting of liquids of various chemical nature was measured for the following surfaces:

(1) stearic acid contaminated aluminium

(2) aluminium painted with paints based on polybutylmethacrylate (N8), its copolymers with dimethylaminoethylmethacrylate (N5), 1-vinyl-2-methylimidazole (N18), and acrylic acid (N16), i.e. (TOPSIDE).

(3) paint surfaces immediately after breaking the adhesive bonds, i.e. (UNDERSIDE).

(4) aluminium surface immediately after breaking the adhesive bonds.

The measurements were carried out at 20°C ± 2°C and 60% relative humidity using a goniometer eye piece fitted to adjustable stand. The volume of the drop was 0.001 ml and was controlled by a micrometer volumetric syringe. The readings of the contact angle of both sides of the drop of each liquid were taken at the first minute of contact with the surface. The final value was an average of 14 - 16 readings.

3.17.2. Results and Discussion

The results of the contact angle measurements are summarised in Tables 32, 33, 34, 35 and 36. Graphical representations of plots of cosine of the contact angle against the surface tension of the liquids (γ_L) are shown in Figures 19, 20, 21, 22 and 23.

The work of adhesion (W_A) was calculated using Young-Dupre's equation and ignoring the value of the equilibrium spreading pressure coefficient of adsorbed film of the vapour of the liquid i.e. (π_e). which may be important with water and dimethylformamide even if not with the other liquids. The values of W_A are included in Table 37.

Values of 'γ_C' is normally taken at the point of intersection of the extrapolated straight line and the horizontal line where cos θ equals to unity.

For the stearic acid contaminated surface, 'γ_C' is 21 dyne/cm when n-alkanes were used and 23 dyne/cm when other liquids were used.

This value is similar to the value obtained by Zisman[123,127] for a close packed monolayer of a high molecular weight fatty acid of 22-24 dyne/cm, i.e. the crystal phase of $-CH_3$.

Precise values of γ_C for the other surfaces however, was difficult to define, because γ_C lay within a narrow band of 28-33 dyne/cm.

However, as can be seen from Table 37, a consideration of the effect of individual liquid on the values of W_A and in relation to the interaction with each surface lead to the following conclusions.

The total work of adhesion W_A when using o-xylene, decalin and n-hexadecane are essentially the same for top and underside of paint films. Hexadecane also gives practically the same W_A for the metal side after breaking the bond and to contaminated aluminium.

For poly n-butylmethacrylate (N8), there is evidence of polar interaction with water, DMF and formamide which is unchanged for top and underside of paint surface. For the metal side after breaking the bonds, this interaction is reduced considerably with water and formamide and to some extent with DMF. The stearic acid contaminated aluminium gives the same pattern and so it is clear that separation has occurred with the stearic acid adsorbed to the aluminium.

If now to add W_A values for glycerol, ethylene glycol and tricresylphosphate (TCP) (is entirely dispersion forces and is unchanged), the total value of W_A for top surface is 74.1, for underside 71.0; this slightly lower value might be accounted for by some of the long chain of the stearic acid being on the surface, but with a stearic acid substrate W_A = 53.4 and metal W_A = 51.5 substrate, it looks as though film has the same surface.

With copolymer N18, there is a strong polar reaction of the topside with water at 93.3, DMF at 101, and to some extent glycerol and formamide are also reacting at 83. This polar component is markedly reduced on the underside. Again, tricresylphosphate which is entirely dispersion is unchanged, for both, and for the metal and stearic acid contaminated surface. For the metal side water and DMF is also reduced compared to the stearic acid surface.

Total W_A for glycerol,ethylene glycol, and TCP for the topside is 76.5, for underside it is 70.2 for metal 56.1 and for stearic acid 56.47. These reductions in polar components suggest that there is the possibility that stearic acid absorbed into the paint film has influenced this. If so, and to confirm this the water drop should be unstable and the angle will gradually drop in time as the stearic acid molecules embeded in the paint film starts to turn over toward the water molecules. Thus, the kinetic behaviour of water drop on the underside of paint film of N18 copolymer was studied and the results are as follows:

Time Minutes	Average	W_A
1 min	78° 43'	87.4
2 min	70° 6'	96.98
6 min	56° 13'	113.37
10 min	40° 9'	127.82
14 min	37° 57'	130.50

On the topside of paint the angle was stable and had an average value of 73° 38' ± 1° 8', $W_A = 93.6$.

For copolymer N5 again there is a strong polar component on the topside with water; DMF and formamide which is reduced on the underside of paint film. TCP is unchanged. The total value of W_A with glycerol, ethylene glycol and TCP for topside is 75.8 and for underside is 70.2, metal 44.7 and stearic acid 57.0.

For N16 Top and undersides are substantially the same.

W_A value for glycerol, ethylene glycol and tricresylphosphate is 75.7, and for underside is 71.

TABLE 32

DETERMINATION OF CRITICAL SURFACE TENSION UTILIZING ZISMAN'S TECHNIQUE

(a) γ_C of aluminium contaminated with stearic acid

No.	Liquid	Liquid surface tension γ_L	cos θ	$W_A = \gamma_L(1+\cos\theta)$
	Water on sulpho-chromated Al		.993	145.1
1.	Water	72.8	- .261	53.8
2.	Glycerol	63.4	- .157	53.45
3.	Dimethylformamide	58.2	.833	107.78
4.	Formamide	58.2	.029	58.2
5.	Ethylene glycol	47.7	.184	56.47
6.	Tricresylphosphate	40.9	.495	61.14
7.	Decalin	29.9	.882	56.3
8.	n-Hexadecane	27.6	.914	52.8
9.	Dodecane	25.4	.937	49.2
10.	n-Decane	23.9	.969	47.1
11	n-Octane	21.8	.991	43.4

TABLE 33

(b) γ_C of topside of paint N8 (n-butylmethacrylate), underside of paint after breaking the bonds and metal side after breaking the bonds.

No.	Liquid	Liquid surface tension γ_L	Topside of paint		Underside of paint after breaking the joint		Metal side after breaking the joint	
			cos Θ	W_A	cos Θ	W_A	cos Θ	W_A
1.	Water	72.8	.218	88.7	.205	87.7	- .456	39.6
2.	Glycerol	63.4	.217	77.2	.133	71.8	- .263	46.7
3.	Dimethylformamide	58.2	.712	99.6	.735	101	.574	91.6
4.	Formamide	58.2	.381	80.4	.488	86.6	- .365	40
5.	Ethylene glycol	47.7	.471	70.2	.392	66.4	-	-
6.	Tricresylphosphate	40.9	.829	74.8	.826	74.7	.377	56.3
7.	O-xylene	30.1	.991	59.9	.975	59.5	-	-
8.	Decalin	29.9	.969	58.8	.972	58.96	-	-
9.	n-Hexadecane	27.6	.999	55.2	.999	55.2	.988	54.87

TABLE 34

(C) γ_C of TOPSIDE OF PAINT N5 (n-butylmethacrylate + 5% dimethylaminoethylmethacrylate), underside of paint after breaking the joint and metal side after breaking the bonds.

No.	Liquid	TOPSIDE OF PAINT		Underside of paint after breaking the bonds		Metal side after breaking the bond	
		cos Θ	W_A	cos Θ	W_A	cos Θ	W_A
1.	H_2O	.295	94.3	.192	86.8	- .542	33.3
2.	Glycerol	.307	82.9	.041	65.99	- .472	33.5
3.	Dimethylformamide	.716	99.9	.711	99.6	.415	82.4
4.	Formamide	.455	84.7	.3	75.7	- .429	33.2
5.	Ethyleneglycol	.478	70.5	.441	68.74	-	-
6.	Tricresylphosphate	.812	74.1	.854	75.8	.366	55.9
7.	O-xylene	.97	59.3	.947	58.6	-	-
8.	Decalin	.991	59.5	.946	58.2	-	-
9.	n-Hexadecane	.992	54.97	.995	55.1	-	-

TABLE 35

(d) γ_C OF TOPSIDE OF PAINT N18 (n-butylmethacrylate + 5% vinyl-2-methylimidazole), UNDERSIDE OF PAINT AFTER BREAKING THE JOINT AND METAL SIDE AFTER BREAKING THE BONDS.

No.	Liquids	Topside		Underside after breaking the bonds		Metal side after breaking the bonds	
		cos Θ	W_A	cos Θ	W_A	cos Θ	W_A
1.	H_2O	.282	93.3	.164	84.74	- .261	53.8
2.	Glycerol	.311	83.1	.0505	66.6	- .224	49.2
3.	Dimethylformamide	.73	100.7	.733	100.9	.505	87.6
4.	Formamide	.426	83	.211	70.5	- .308	40.3
5.	Ethylene glycol	.505	71.79	.442	68.78	-	-
6.	Tricresylphosphate	.829	74.8	.844	75.4	.54	63
7.	O-xylene	.993	60	.961	59	-	-
8.	Decalin	.97	58.9	.964	58.7	-	-
9.	n-Hexadecane	.999	55.2	.994	55.0	.972	54.42

TABLE 36

(e) γ_C OF TOPSIDE OF PAINT N16 (n-butylmethacrylate + 1% acrylic acid), UNDERSIDE OF PAINT after breaking the joint and metal side after breaking the bonds.

No.	Liquids	TOPSIDE		UNDERSIDE		METAL SIDE	
		cos Θ	W_A	cos Θ	W_A	cos Θ	W_A
1.	H_2O	.271	92.5	.207	87.9	-.223	56.6
2.	Glycerol	.261	80	.103	69.9	-.56	27.9
3.	Dimethylformamide	.74	101.3	.689	98.3	.641	20.9
4.	Formamide	.387	80.7	.326	77.2	-.233	44.6
5.	Ethylene glycol	.493	71.2	.412	67.35	-	-
6.	Tricresylphosphate	.86	76.1	.851	75.7	.438	58.8
7.	O-xylene	.951	58.7	.96	59	-	-
8.	Decalin	.968	58.8	.97	58.9	-	-
9.	n-Hexadecane	.997	55.13	.998	55.14	.981	54.68

TABLE 37

WORK OF ADHESION BETWEEN LIQUIDS AND TOP AND UNDERSIDE OF PAINTS BASED ON CONTACT ANGLE MEASUREMENTS

No.	Liquid	n-butylmethacrylate (N8)			nBMA + 5% 1V2MI (N18)			nBMA + 5% DMAEMA (N5)			nBMA + 1% AA (N16)			Stearic Acid contaminated Al
		top side	under side	metal side	top side	under side	metal side	top side	under side	metal side	top side	under side	metal side	
1.	Water	88.8	87.7	39.6	93.3	84.7	53.8	94.3	86.8	33.3	92.5	87.9	56.6	58.8
2.	Glycerol	77.2	71.8	46.7	83.1	66.6	49.2	82.9	66	33.5	80	69.9	27.9	53.5
3.	Dimethylformamide	99.6	101	91.6	100.7	100.9	87.6	99.9	99.6	82.4	101.3	98.3	20.9	107.8
4.	Formamide	80.4	86.6	40	83	70.5	40.3	84.7	75.7	33.2	80.7	77.2	44.6	58.2
5.	Ethylene glycol	70.2	66.4	-	71.8	68.8	-	70.5	68.7	-	71.2	67.4	-	56.5
6.	Tricresylphosphate	74.8	74.7	56.3	74.8	75.4	63	74.1	75.8	55.9	76.1	75.7	58.8	61.1
7.	O-xylene	59.9	59.5	-	60	59	-	59.3	58.6	-	58.7	59	-	-
8.	Decalin	58.8	58.9	-	58.9	58.7	-	59.5	58.2	-	58.8	58.9	-	56.3
9.	n-Hexadecane	55.2	55.2	54.9	55.2	55	54.42	55	55	-	55.1	55.1	54.7	52.8

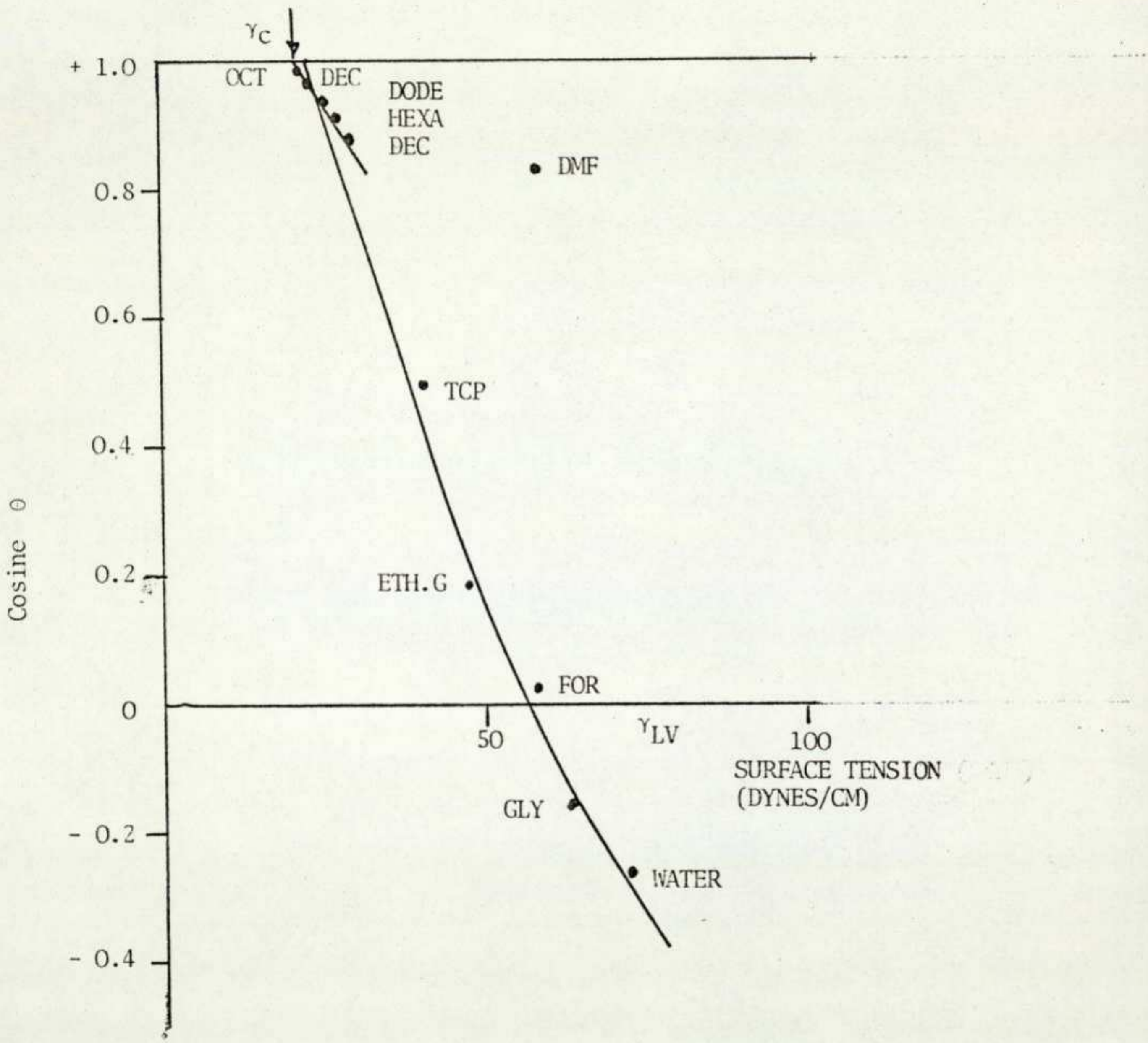


Figure 19. Cosine of Contact Angles vs. γ_{LV} for Various Liquids on Stearic Acid Contaminated Aluminium.

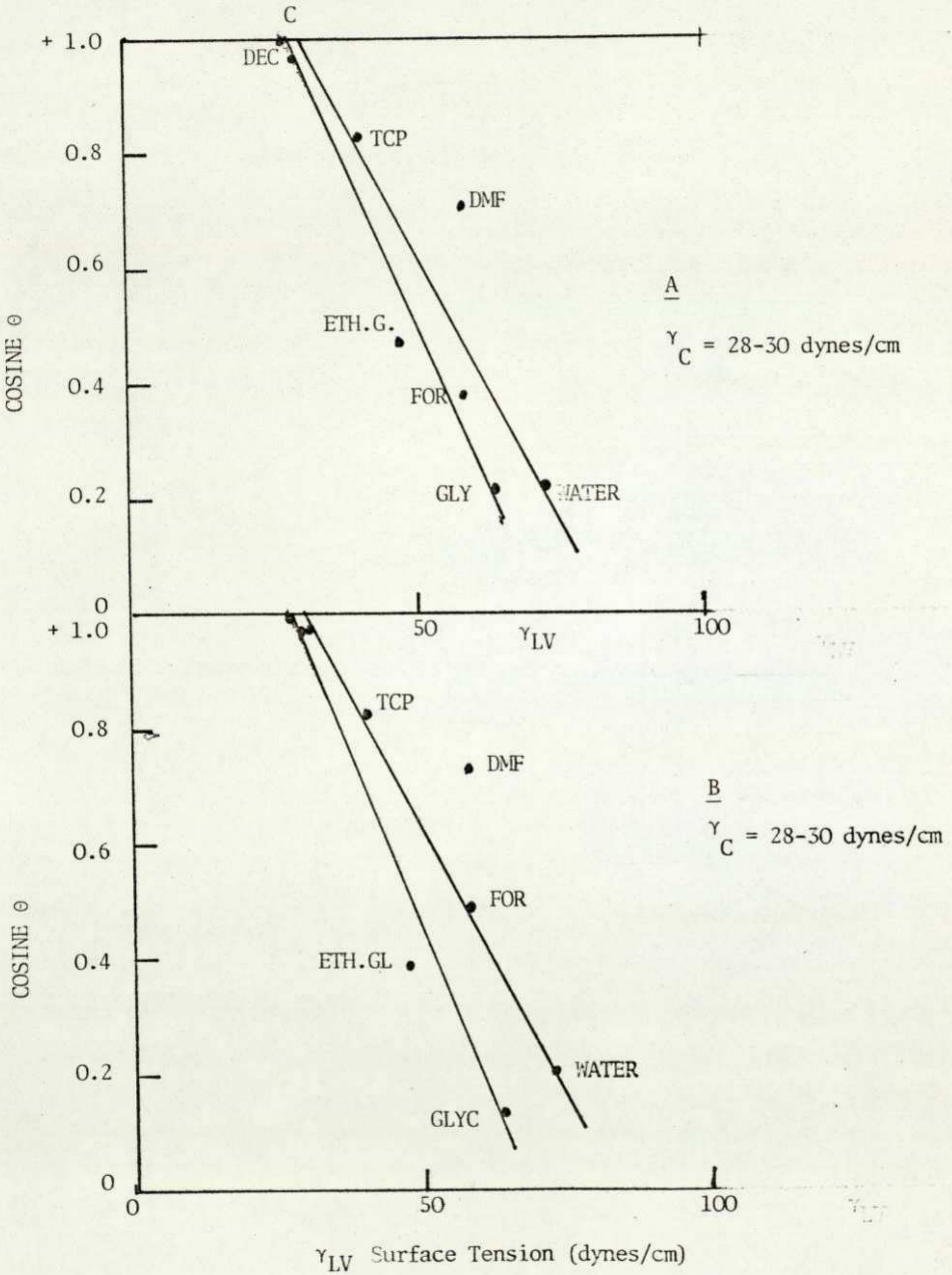


Figure 20. Cosine of Contact Angles vs. γ_{LV} for Various liquids on

A. Top side of polybutylmethacrylate Paint

B. Underside of polybutylmethacrylate Paint After Breaking the joints

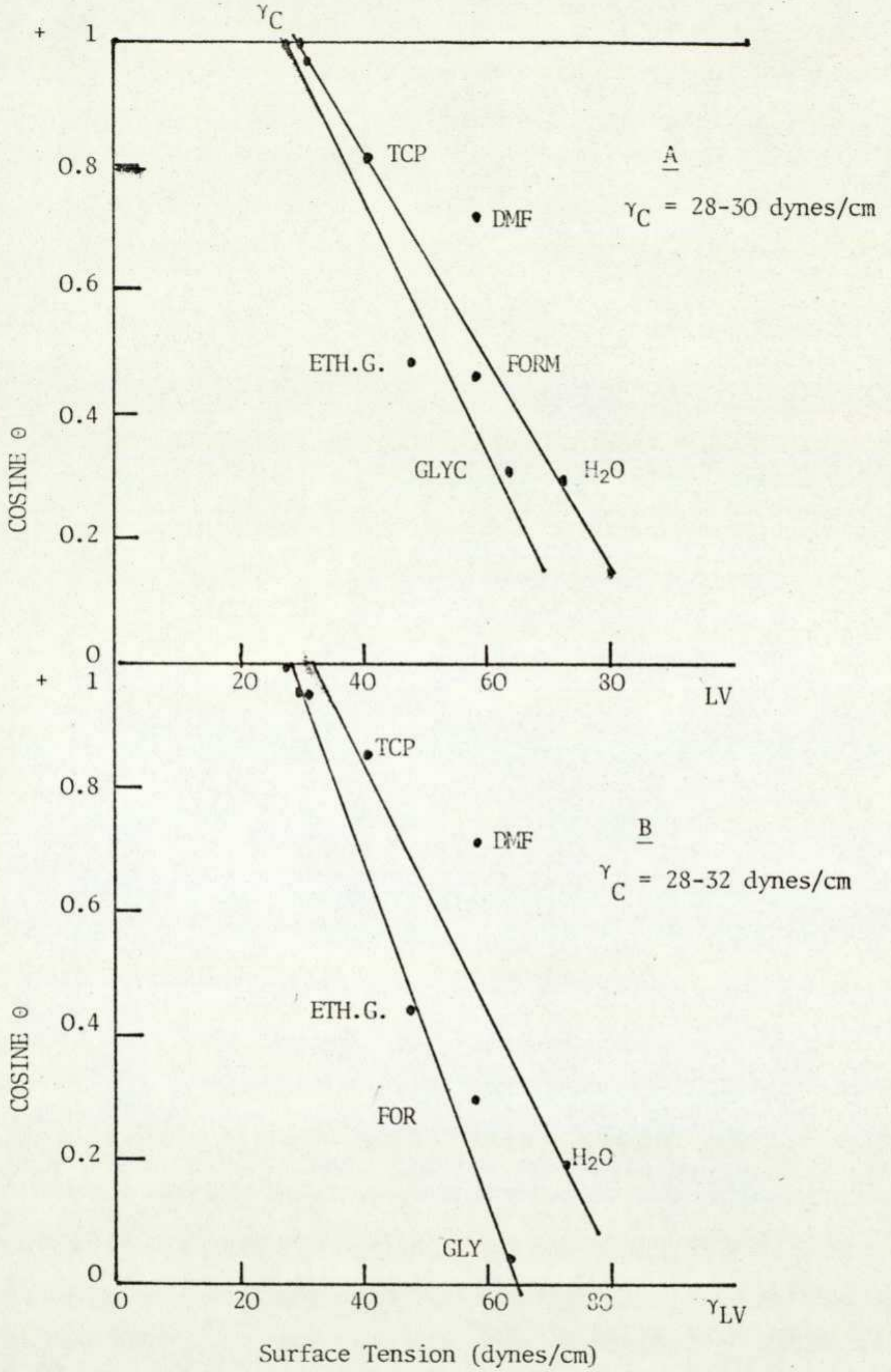


Figure 21. Cosine of Contact Angles vs. γ_{LV} for various liquids on
A. Topside of Paint based on Polymer (N5)
B. Underside of Paint based on Polymer (N5)

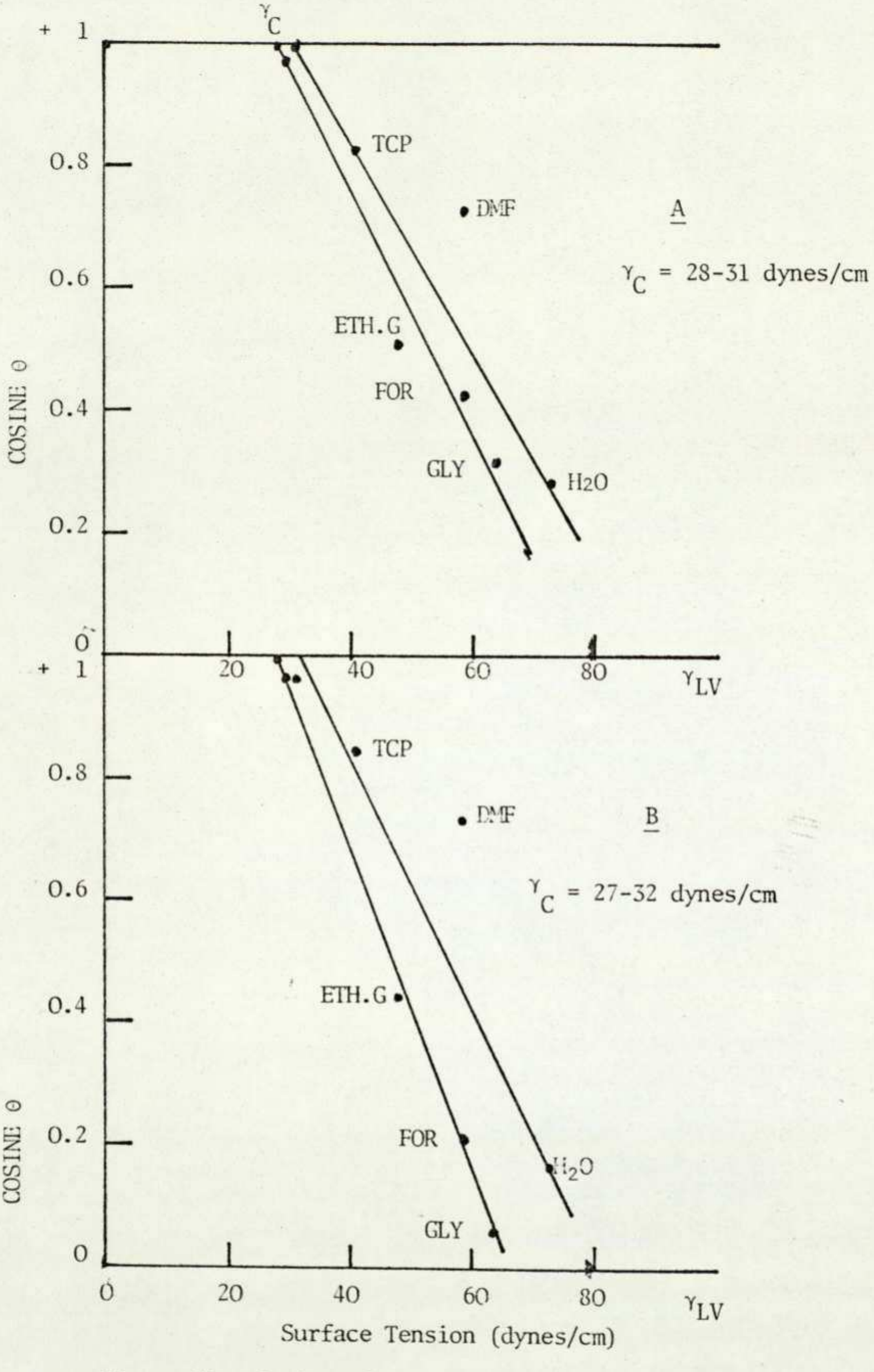


Figure 22. Cosine of Contact Angles vs. γ_{LV} for Various Liquids on
A. Topside of Paint Based on Polymer N18
B. Underside of Paint Based on Polymer N18.

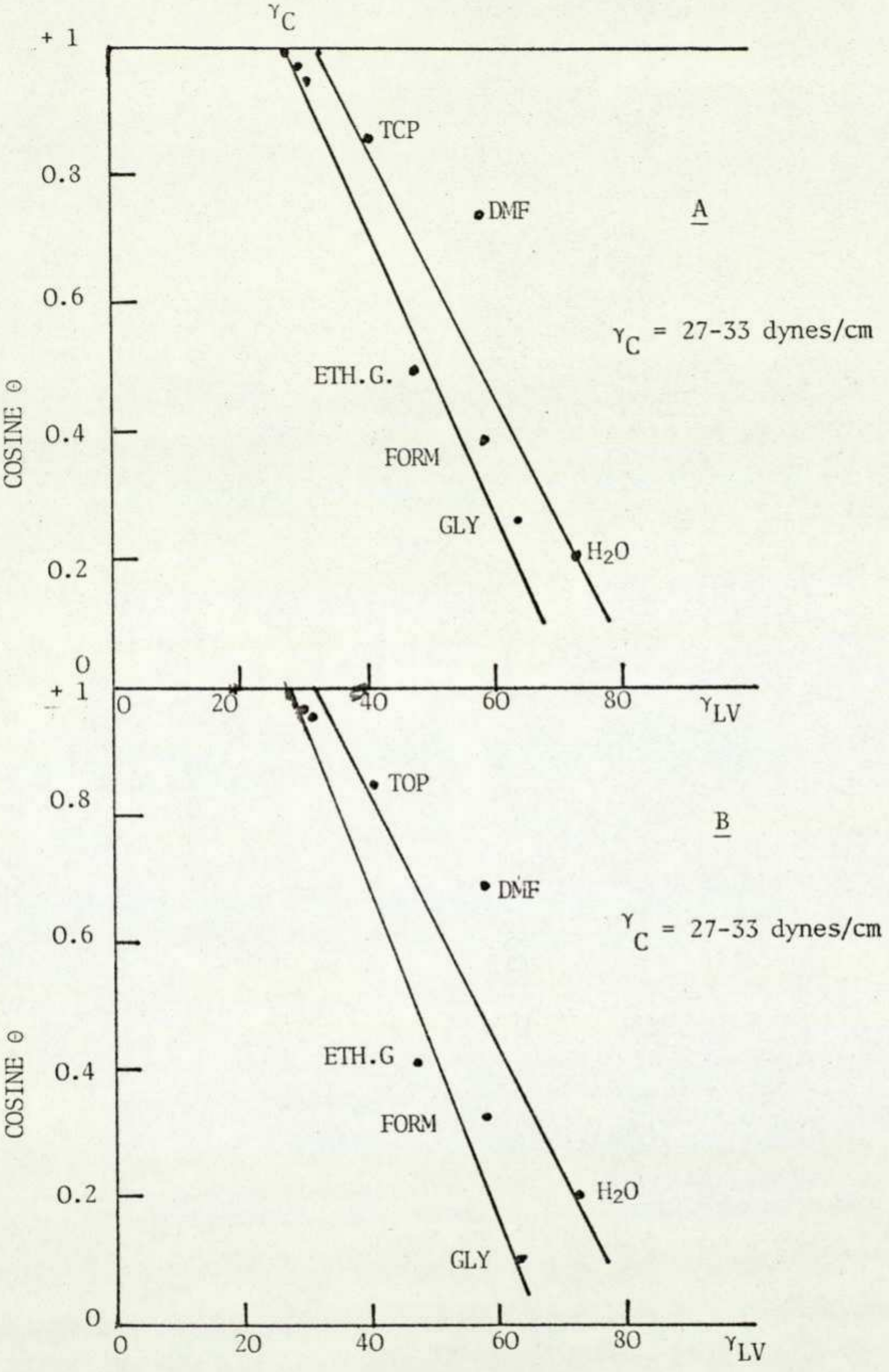


Figure 23. Cosine of Contact Angle vs. $_{LV}$ for Various Liquids on

A. Topside of Paint Based on Polymer N16
B. Underside of Paint Based on Polymer N16

3.18. Determination of the Dispersion $(\gamma_s{}^d)$ and the Polar (γ^p) Contribution to the Total Surface Free Energy of Paints by Kealble's Technique

3.18.1. Discussion

The computational approach to determining $\gamma_s{}^d$ and $\gamma_s{}^p$ for polymeric materials adopted by Kealble[135,140] and discussed in Section 2.8.3. was used for the calculations of these contributions to the surface energy of four paints.

A computer program was written for the solution of equation (53) using the calculated values of work of adhesion of paints and liquids used in the determination of γ_C i.e. Section 3.17. An example of such a calculation is given for paint N5, in Table 38.

The results are tabulated in Table 39 for the four paints before and after breaking the bonds.

The method has been under heavy criticism[268]. In addition the standard deviation in calculating $\gamma_s{}^d$ or $\gamma_s{}^p$ is very high.

Although there is an indication of higher values from polar components within the modified paints, the results have little significance in aiding the advancement of an explanation for adhesion improvement.

However, the effect of single liquids such as water on the interfacial free energy with the paints is illustrated.

Utilising the values of the dispersion and the polar components of the surface free energy of paints as given in Table 39, we can calculate the interfacial free energy between water and the paints and work of adhesion. Such calculations are shown in Table 40, accepting that $\gamma^d_{H_2O}$ = 21.8 dyne/cm; $\gamma^p_{H_2O}$ = dyne/cm as given by Fawkes[80,128].

The results in Table 40 suggest that there is a strong interaction between water and the modified paints (W_a top surface > W_a under surface) which is reduced for the underside of paints which were in contact with stearic acid. Thus perfect match as Good suggested (W_a is max, γ_{SL} is minimum), W_a is min. γ_{SL} is maximum).

This difference is probably due to the appearance of some of the polar component of free energy of water at the interface as a free energy which cannot interact with the nonpolar component of the adsorbed stearic acid on the modified paint surfaces; the polar component is already reacted with the paints during application.

TABLE 38

CALCULATION OF γ_S^d and γ_S^p FOR PAINT (N5) FOR TOP SURFACE AND UNDERSIDE OF PAINT FILM AFTER JOINT FAILURE

No.	Liquid	γ	γ_L^d	γ_L^p	TOPSIDE		UNDERSIDE		i/j	TOP SURFACE			UNDERSIDE		
					cos θ	W_A	cos θ	W_A	combination	γ_s^d	γ_s^p	γ_s	γ_s^d	γ_s^p	γ_s
1.	Water	72.8	21.8	51	.295	94.3	.192	86.8	1-2	7.56	23.13	30.69	.42	31.92	32.34
2.	Glycerol	63.4	37	26.4	.307	82.9	.041	66	1-3	15.86	16.04	31.90	11.20	15.12	26.32
3.	Formamide	58.2	39.5	18.7	.455	84.7	.3	75.7	1-4	6.65	24.21	30.86	9.95	16.09	26.04
4.	Ethylene glycol	47.7	28.6	19.0	.478	70.5	.441	68.74	1-5	27.69	10.02	37.71	30.76	6.02	36.78
5.	Tricresyl phosphate	40.9	39.2	1.7	.812	74.1	.854	75.8	1-6	29.20	9.42	38.62	28.52	6.68	35.20
6.	O-xylene	30.1	30.1	0	.97	59.3	.947	58.6	1-7	29.39	9.35	38.74	28.32	6.75	35.07
7.	Decaline	29.9	29.9	0	.991	59.5	.946	58.2	1-8	27.35	10.12	37.47	27.49	7.01	34.50
8.	Hexadecane	27.6	27.6	0	.992	54.97	.995	55.1	2-5	31.64	1.98	33.62	39.18	.97	40.15
									2-6	29.20	2.79	31.99	28.52	.01	28.53
									2-7	29.59	2.65	32.24	28.31	.02	28.33
									2-8	27.37	3.52	30.89	27.50	.05	27.55
									3-5	30.97	2.93	33.90	36.86	.00	36.86
									3-6	29.21	3.76	32.97	28.53	.98	29.51
									3-7	29.58	3.56	33.14	28.31	1.04	29.35
									3-8	27.40	4.81	32.21	27.54	1.28	28.82
									4-5	32.45	1.23	33.68	35.12	.38	35.50
									4-6	29.20	2.12	31.32	28.52	1.78	30.30
									4-7	29.60	1.99	31.59	28.32	1.84	30.16
									4-8	27.36	2.79	30.15	27.51	2.11	29.62
									Total	497.27 = n = 19	136.42	633.69	500.88	100.05	600.93
										26.17	7.18	33.35 ±3.6	26.36	5.26	31.62±4.06

TABLE 39

CALCULATED DISPERSION (γ_s^d) AND POLAR (γ_s^d) CONTRIBUTIONS TO PAINT SURFACE ENERGIES ($\gamma_s^d + \gamma_s^p$) IN UNITS OF DYNES/CM.

PAINT FILM TOP SURFACE						UNDERSIDE OF PAINT FILM AFTER DETACHMENT FROM CONTAMINATED SUBSTRATE			
Ref. No.	Paint (1:1 pigmentation based on:-	(γ_s^d)	(γ_m^p)	$(\gamma_s)_m$	$\pm\ \delta_m$	$(\gamma_s^d)_m$	$(\gamma_s^p)_m$	$(\gamma_s)_m$	$\pm\ \delta_m$
N8	n-Butylmethacrylate	26.72	5.44	32.16	3.1	26.72	5.66	32.34	3.15
N18	" + 5% VMI	26.54	6.69	33.24	4.3	26.48	4.72	31.21	2.79
N5	+ + 5% DMAEM	26.17	7.18	33.35	3.6	26.36	5.26	31.62	4.00
N16	" + 1% AA	26.45	6.37	32.81	3.2	26.70	5.00	31.70	3.7
	stearic acid contaminated aluminium	22.92	.74	23.67	4.67	-	-	-	-

TABLE 40

EFFECT OF WATER

CALCULATED INTERFACIAL FREE ENERGIES BETWEEN WATER AND PAINTS

$$\gamma_{W/P} = \gamma_W + \gamma_P - 2 \left(\sqrt{\gamma_W{}^d \;\; \gamma_P{}^d} + \sqrt{\gamma_W{}^p \;\; - \gamma_P{}^p} \right)$$

$$W_A = 2 \left[(\gamma_s{}^d \; \gamma_w{}^d)^{\frac{1}{2}} + (\gamma_s{}^p \; \gamma_w{}^p)^{\frac{1}{2}} \right]$$

PAINT REF.	PAINT FILM TOP SURFACE		UNDERSIDE OF PAINT FILM AFTER DETACHMENT	
	γ W/P	W_A	γ W/P	W_A
Stearic acid contaminated Al	39.48		-	
N8	23.4	81.56	22.92	82.23
N18	20.9	85.04	24.92	79.07
N5	20.1	86.02	23.70	80.68
N16	21.5	84.06	24.31	80.18

3.19. Infra-Red Spectroscopy

This section deals with the study of the potentiality of infra-red spectroscopy as a technique for establishing the possibility of interaction of the contaminant with polymers.

Although this method was found to be inadequate, it is necessary however to discuss the obstacles and the outcome of such a method.

Initially an appropriate choice of absorption bands of stearic acid from the infra-red spectrum, Figure 24, and of polymers was made.

The carbonyl stretching vibration at 1700 cm^{-1} for the acid, and the ester band at 1739 cm^{-1} for the polymer were chosen.

10% Solution in toluene of polybutylmethacrylate (N8), of copolymer containing 5% 1-vinyl-2-methylimidazole and those with up to 12% stearic acid were left for 24 hours at room temperature to allow for the reaction to take place.

Films were cast on sodium chloride plates and were dried in a vacuum hot plate at 60^{o}C. Film thickness was regulated until the absorbance band of the ester group was at 0.7 absorbance, which insured that the absorbtivity value was constant regardless of the amount of polymer used.

A linear relationship between optical density and concentration at a constant cell thickness should be obtained if a system conforms to Lambert-Beer's law. The latter and its use in analysis is comprehensively discussed elsewhere[269].

In this work, measurements of the change in the peak absorption intensities from appropriate base lines of the two bands were made. Their ratio was plotted against the concentration of the acid.

This technique is quite widely used in studying reactions.

Danilov[270] et.al. used the intensity of OH group of stearic acid at 3500 cm^{-1} to provide an accurate, fast and safe method for determining the specific interaction between the molecules of the acids and resins, using the acid value and taking the reaction of stearic acid with linseed oil, alkyd resins and maleic resin as a model.

In these experiments, the quantitative technique adopted was not reproducible. Variations in the intensity of the bands of the same sample occurred, which were due to the inhomogeneity and crystallinity of the contaminant on the surface of the polymer film after removal of the solvent.

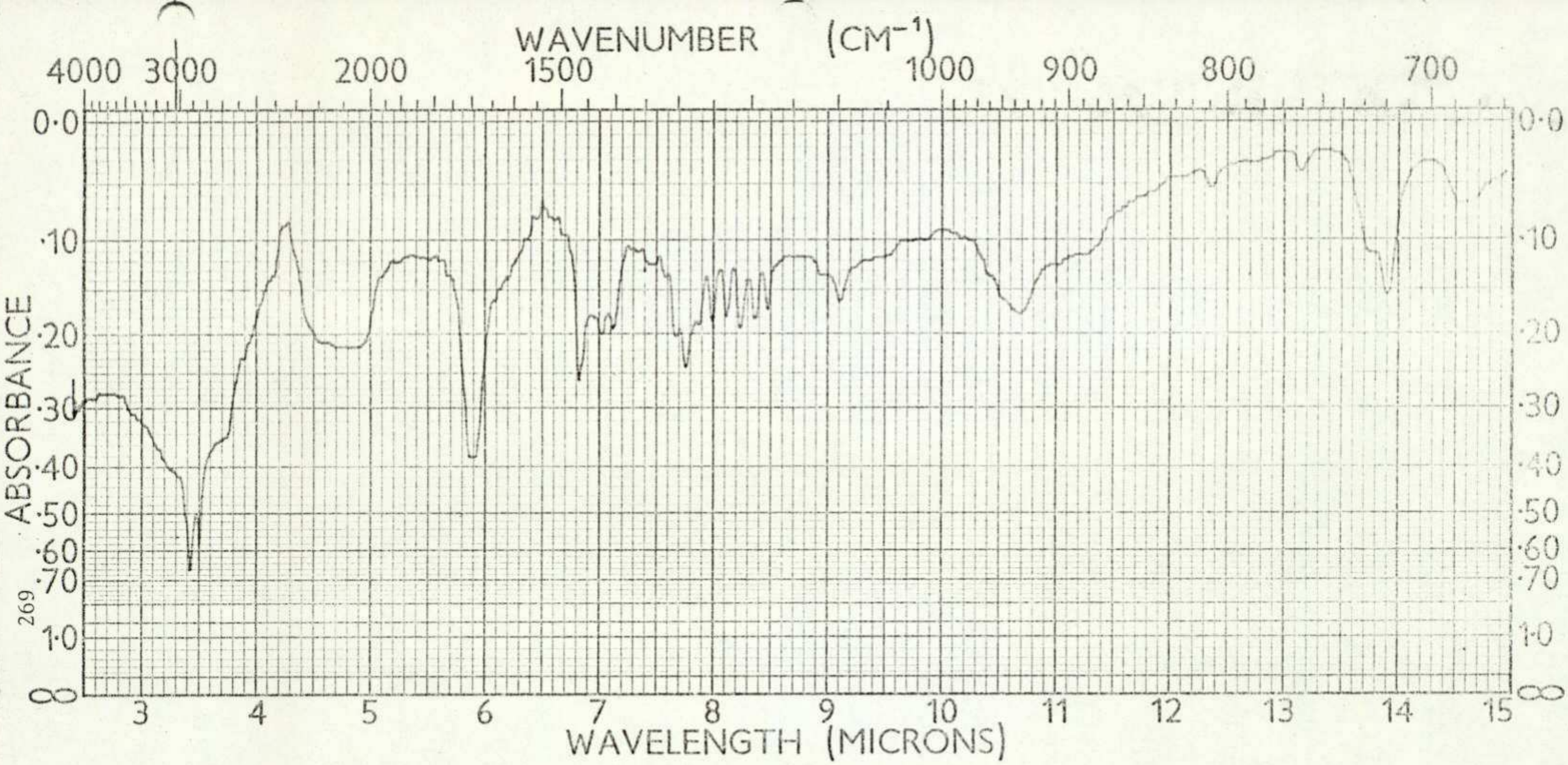
For this reason it was anticipated that the monomeric form of the modifiers could be more suitable. However, a comparison of their spectra, see Figure 25, with that of the acid showed limited choice of suitable bands.

Another approach was to search for the appearance of new bands particularly of NH link, that is the nitrogen of a modifier and the hydrogen of stearic acid. The monomer 1-vinyl-2-methyl-imidazole was chosen as a model, see Figure 25.

The infra-red spectra of a mixture of equimolar quantities of stearic acid and the monomer obtained from films of various thicknesses or a KBr dis (see Figures 26, 27, 28) showed a decrease or increase in the intensity at 1350 cm^{-1} associated with N-H vibrations. This was attributed to variations in concentrations of

(1V2MI) or stearic acid in the sample contained between two plates affected by crystallization of the acid.

To sum up, the formation of new compounds in this case was better understood from the analysis of the melting point/ concentration diagram (see Section 3.12).



SAMPLE Stearic Acid

Figure 24.

ORIGIN

PHASE KBr Disc

SOLVENT

CONC.

CELL PATH

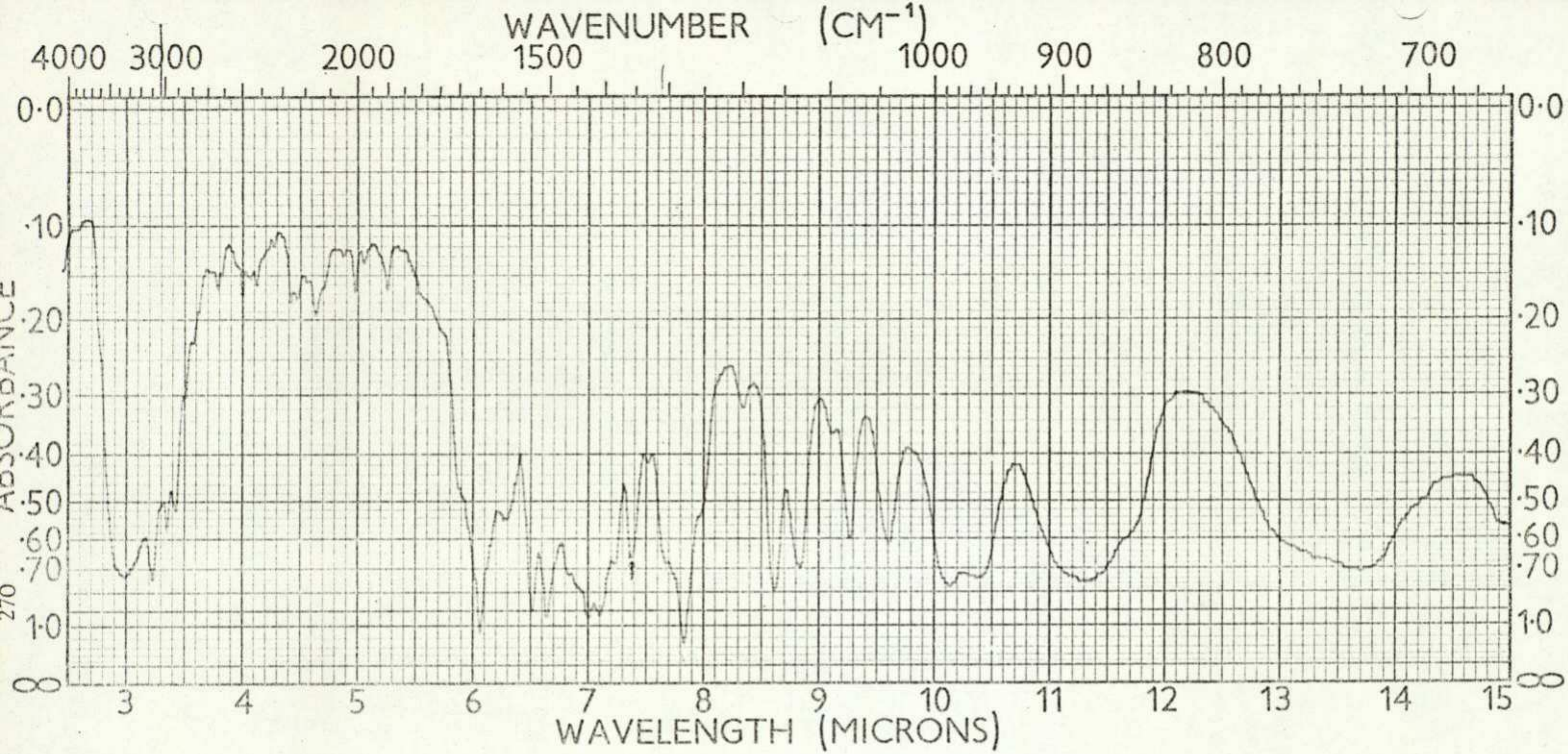
REFERENCE

SCAN SPEED 12 min. SLIT N

OPERATOR DATE

REMARKS

NO.



SAMPLE

1-Vinyl-2-methylimidazole, monomer

Figure 25.

ORIGIN

PHASE Thin film between two plates

SOLVENT None

CONC.

CELL PATH

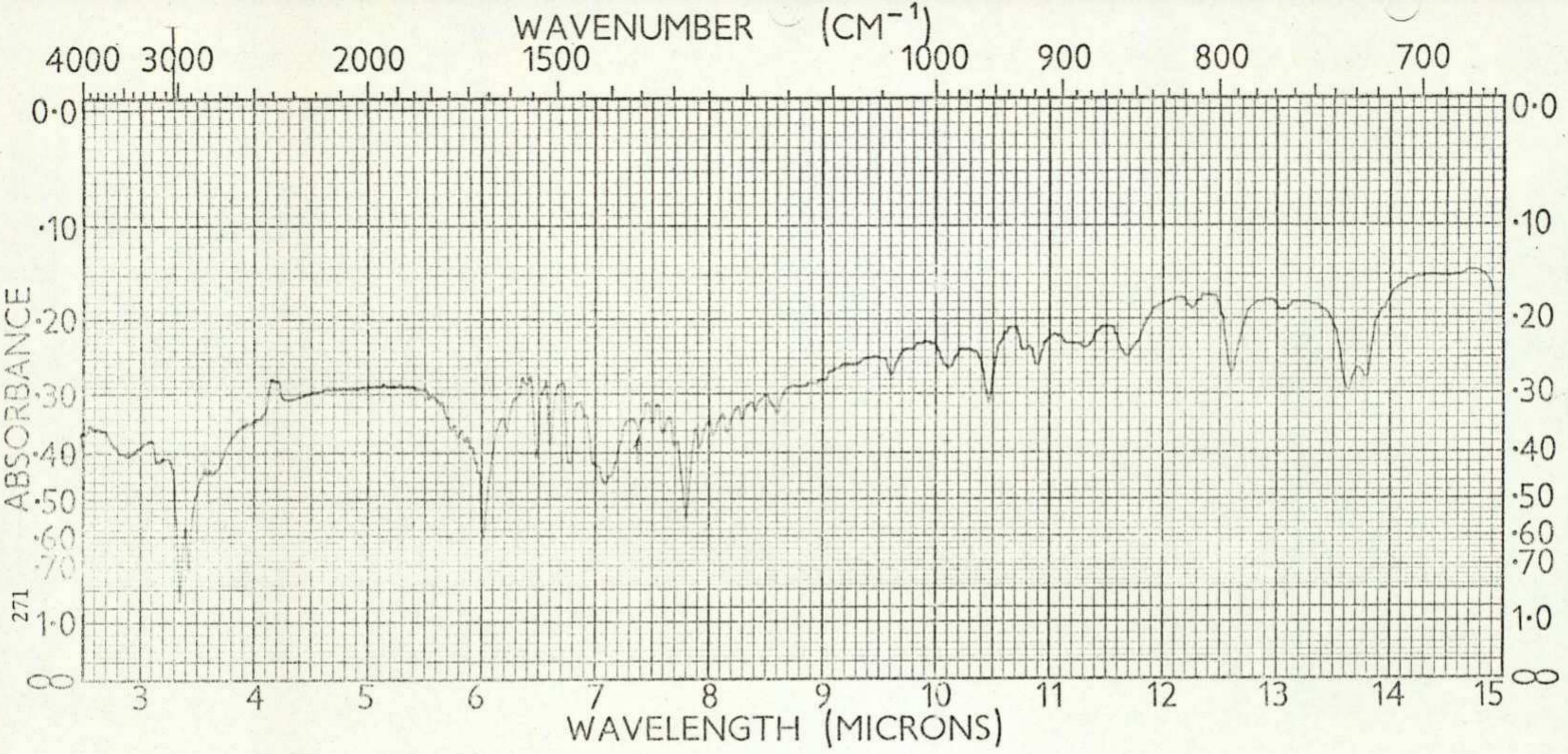
REFERENCE

SCAN SPEED 12 min. SLIT N.

OPERATOR DATE

REMARKS

NO.



SAMPLE

1-Vinyl-2-methylimidazole
monomer/stearic acid at
equimolar ratio

Figure 26.

ORIGIN

PHASE Film between two plates

SOLVENT None

CONC.

CELL PATH

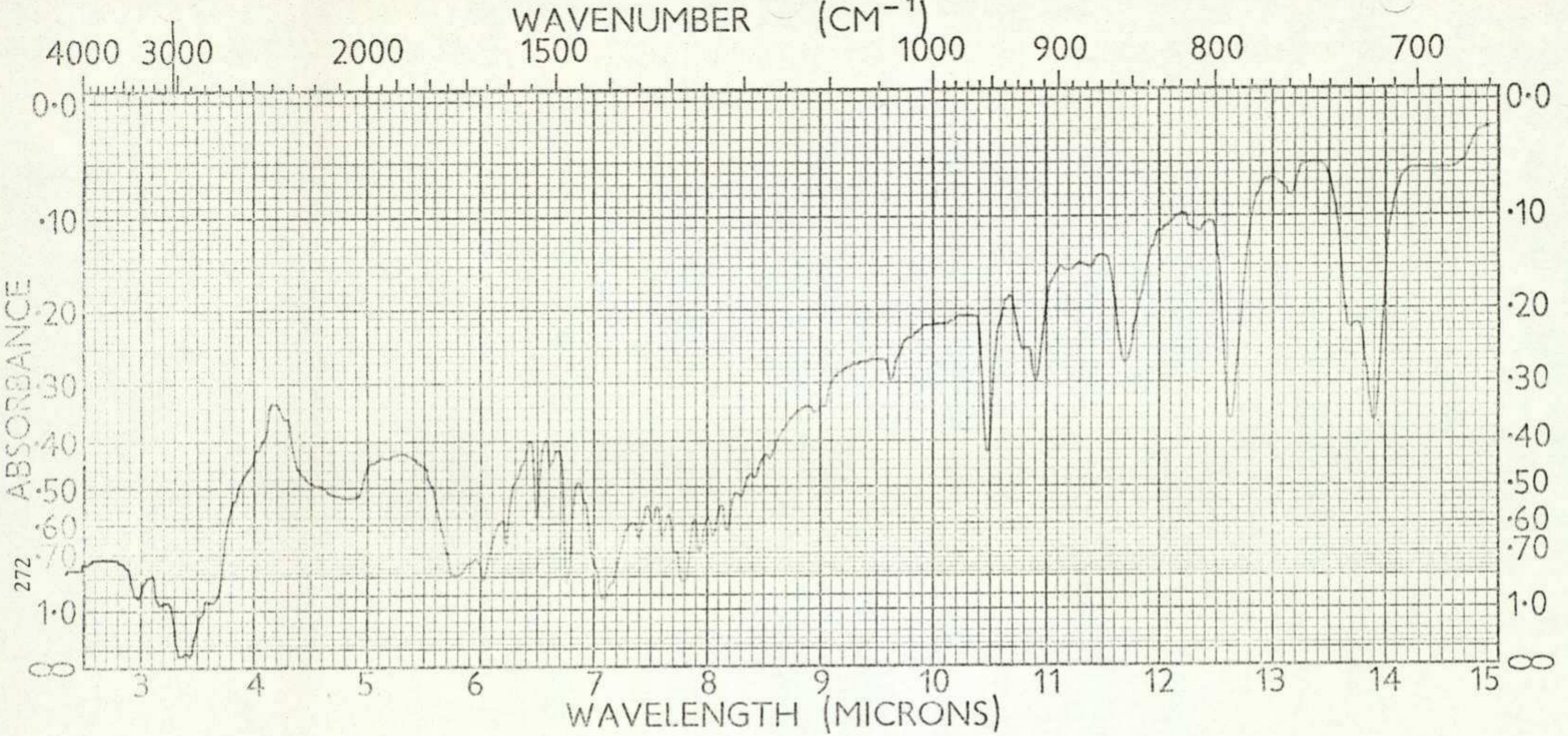
REFERENCE

SCAN SPEED 12 min. SLIT N

OPERATOR DATE

REMARKS

NO.



SAMPLE

1-Vinyl-2-methylimidazole monomer/stearic acid at equimolar ratio

Figure 27.

ORIGIN

PHASE KBr Disc

SOLVENT None

CONC.

CELL PATH

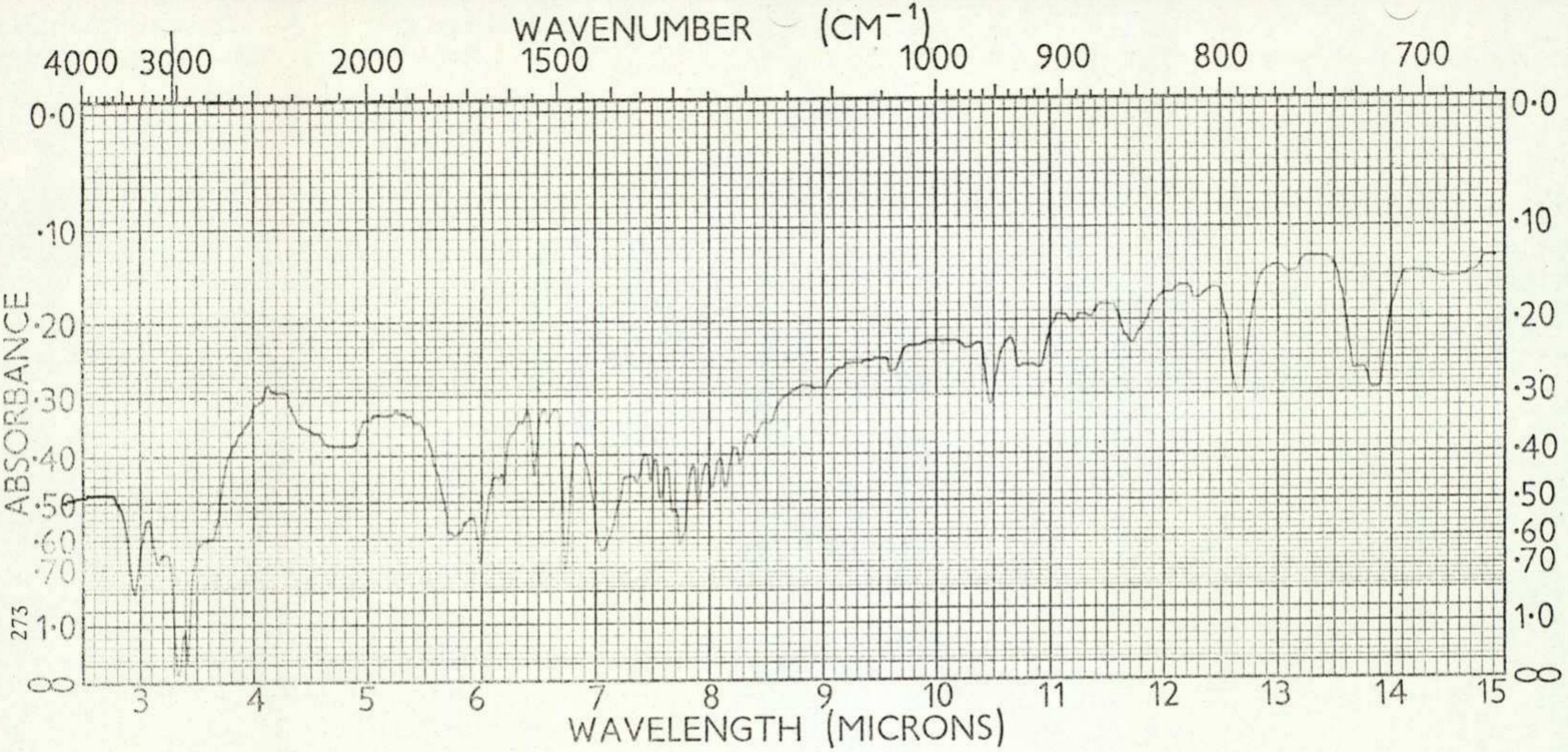
REFERENCE

SCAN SPEED 12 min. SLIT N

OPERATOR DATE

REMARKS

NO.



SAMPLE

1-Vinyl-2-methylimidazole monomer/stearic acid at equimolar ratio.

Figure 28.

ORIGIN

PHASE KBr Disc

SOLVENT

CONC.

CELL PATH

REFERENCE

SCAN SPEED 12 min SLIT N

OPERATOR DATE

REMARKS Second Trial

NO.

CHAPTER FOUR

THERMOSETTING ACRYLIC RESINS

4. Thermosetting Acrylic Resins

4.1. Review of Existing Knowledge

Although discoveries of thermosetting acrylic resins was made earlier by Strain (1939)[271], it was not until the late 1950's that several types of organic soluble and water soluble resins for industrial finishes were introduced[272-277].

Vogel et al[278,279] gave further impetus to the development of thermosetting acrylics. These are designated as those resins which react on heating, becoming highly insoluble and which, in one way or another, contain derivatives of acrylic or methacrylic acid.

These resins as a result of there being only carbon-to-carbon linkages in the polymer chain are acknowledged to have improved properties because of the high bond strengths throughout the chain lengths (unobtainable previously with thermoplastics) in the areas of:-

surface hardness and hardness associated with toughness, and ease of fabrication,
durability
resistance to grease, detergents and stains
high gloss, excellent colour retention and good flexibility.
Adhesion to chemically treated metals
high temperature service.

They find important applications in coil coatings, can coatings and automotive and home appliance finishes.

Comprehensive reviews of the chemistry of polymerisation and cross-linking of the various types of thermosetting acrylics whether commercial or not have been given by Piggott[280], Robinson and Winter[281], Taylor and Price[282] and Taylor and Foster[283].

Piggott[280] made a particular reference to four systems which have been exploited commercially, to the possible chemical reactions which take place on curing, and to a comparison with alkyd/amino resins.

This family of polymers essentially possess two chemical characteristics in that there is present a resinous "backbone" built up by vinyl addition polymerisation, and that along this backbone there are dormant pendant chemical groups which are capable of further reaction to give a highly cross-linked polymer network.

The polymers fall into two main classes:-

Class 1 "Self-Reactive" Acrylic Polymers.

In this class, the pendant chemical groups will react to form a highly cross-linked polymer network by the application of heat above a certain threshold temperature and sometimes in the presence of trace of a catalyst.

Representation of the chemical features of this class was given[280] with the co-reactive groups, and relevant examples are reported in the literature[284-286].

Class 2 "Potentially-Reactive" Acrylic Polymers

This class differs from the first in that an addition of a further compound is required to achieve the cross-linking of the polymer chains because the pendant chemical groups are not in themselves capable of reacting.

Piggott[280] provided Table 41 to illustrate four systems which have been exploited commercially. A schematic representation of a typical cross-link reaction mechanism of each system is given in the appropriate diagram.

TABLE 41

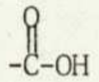
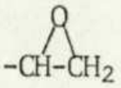
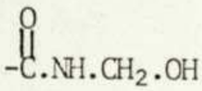
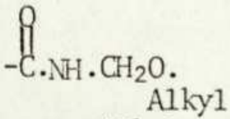
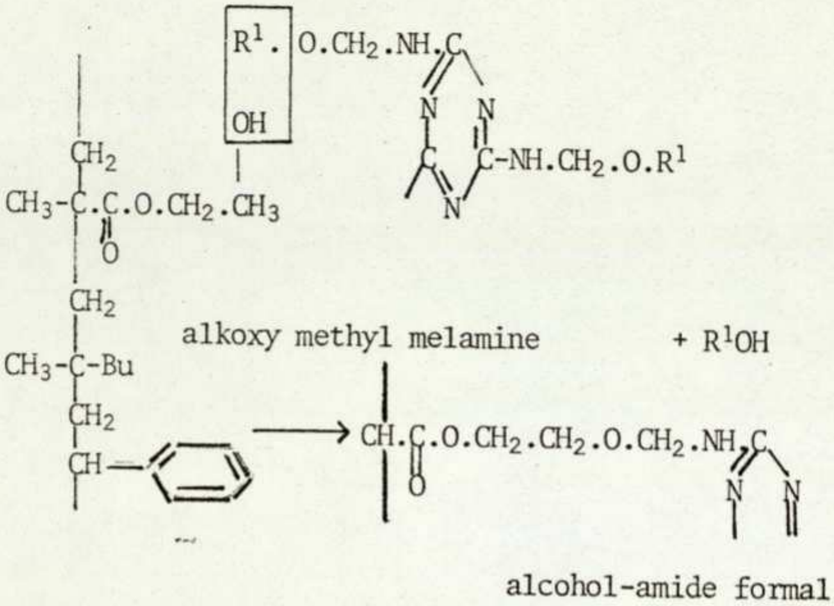
System	Pendant Group	Monomer type	Cross-linking products	Catalyst
A	$-CH_2-OH$ hydroxyl	Hydroxy alkyl methacrylate	Alkoxy aminoplast	Acidic
B	 $-\overset{\overset{O}{\|}}{C}-OH$ carboxyl	Acrylic or methacrylic acid	Epoxy resin	Basic
C	 epoxy	Glycidyl methacrylate	Carboxylic polymers	Acidic or basic
D	 $-\overset{\overset{O}{\|}}{C}.NH.CH_2.OH$  $-\overset{\overset{O}{\|}}{C}.NH.CH_2O.Alkyl$ Alkyl methylol	Methylol acrylamide (etherified)	Epoxy resins Alkoxy aminoplasts Carboxyl containing polymers	Acidic or basic

DIAGRAM I

System A: Hydroxyl Containing Polymer Cross-Linked with Amino Formaldehyde Resin



The alkoxy methyl melamine can be hexa functional with regard to cross-linking of the polymer chains.

Here the hydroxyl groups were introduced along the chain of a copolymer consisting of styrene and n-butylmethacrylate at 3:1 mole ratio, by the use of 25 moles % hydroxy ethyl methacrylate. These ratios resulted in best overall compromise of film properties. The cross-linking was achieved by heat curing.

Other hydroxyl groups can originate from such monomers as hydroxy ethyl or propyl acrylates or methacrylates.

The reaction rate can be controlled by the strength and concentration of the acid catalyst and by the degree of butylation or methylation of the melamine formaldehyde condensate.

Similar amino resins are the methylolated or butylated dimethoxy methyl urea, trimethylol melamine, glycidyl groups containing monomers like glycidyl methacrylate.

System B:

The reaction between a carboxyl containing polymer, where the carboxyl groups are derived from acrylic or methacrylic acid, itaconic acid or maleic anhydride and epoxy resin[287]. The reaction can be catalysed by base, such as trimethyl lauryl ammonium hydroxide or hydroxy ethyl trimethyl ammonium bicarbonate. To reduce the possibility of premature gellation, these catalysts are added to the paint just before application.

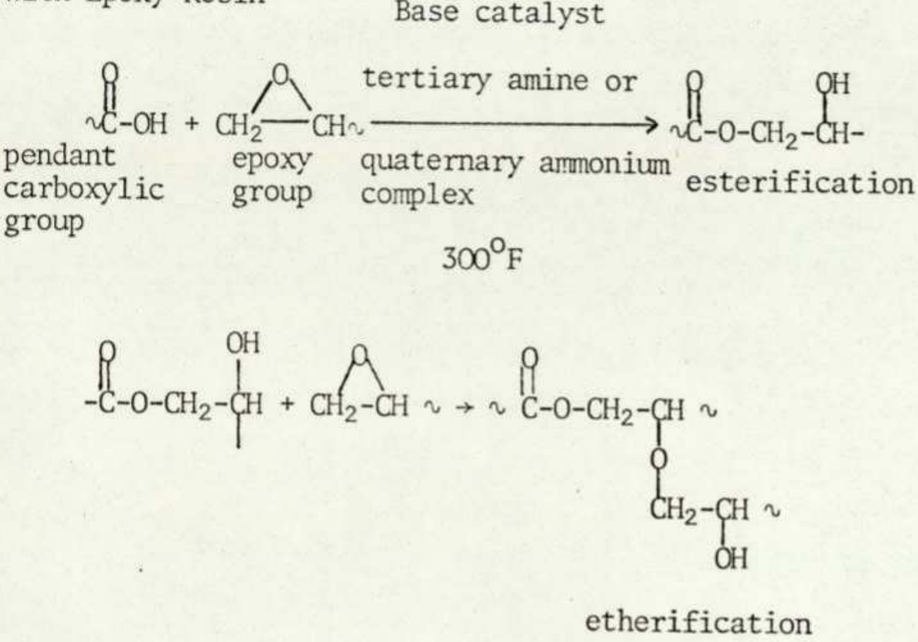
The majority of the work on this system has been confined to copolymer systems consisting of 72% vinyl toluene, 20% ethylacrylate and 8% acrylic acid.

This system is not as good as System A, because it leads to the formation of a relatively weak ester linkage which is readily attacked by chemical reagents, the cross-linking factor is low and solvent resistance is not high.

DIAGRAM II

System B: The Reaction Between a Carboxyl Containing Polymer and Epoxy Resin

With Epoxy Resin



System C:

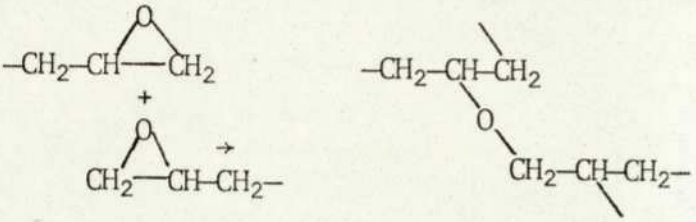
This system is based on the use of a glycidyl-containing monomer with possible inclusion of hydroxyl groups on the polymer chain. In addition a small amount of acrylic or methacrylic acid, or in one particular case, the inclusion of a polymerisable amine which results in a polymer containing oxirane groups and amino groups as the pendant cross-linking sites[290] appear to be general. The polymer of this system is generally self-cross-linking. However, amino-formaldehyde or epoxy resins are recommended to afford improvement in certain properties such as flexibility adhesion or corrosion resistance.

Diagram III illustrates the types of chemical reaction for this system. Disadvantages are, the cost of the epoxide monomer and the poor stability of the glycidyl group towards further reaction at normal temperatures in the presence of acids, amino groups or other trace materials.

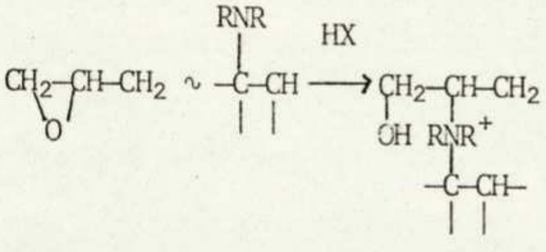
DIAGRAM III

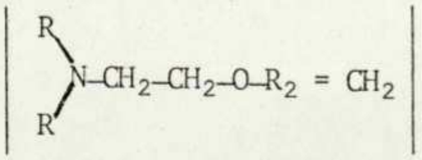
System C: Use of a Glydidyl Containing Monomer as the Potential Cross-Linking Material

With Glycidyl or Epoxy Groups



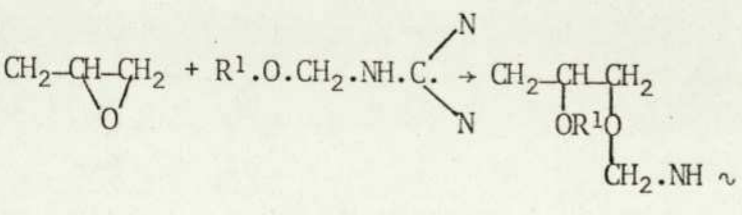
With Amino Groups





e.g. β-diethylaminoethyl methacrylate

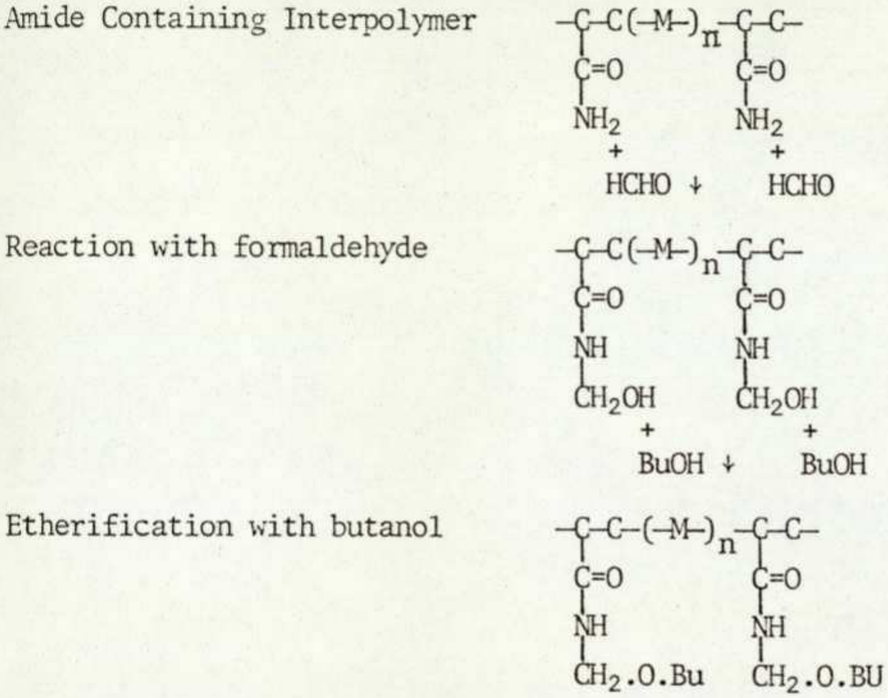
With Amino-formaldehyde Resins



System D:

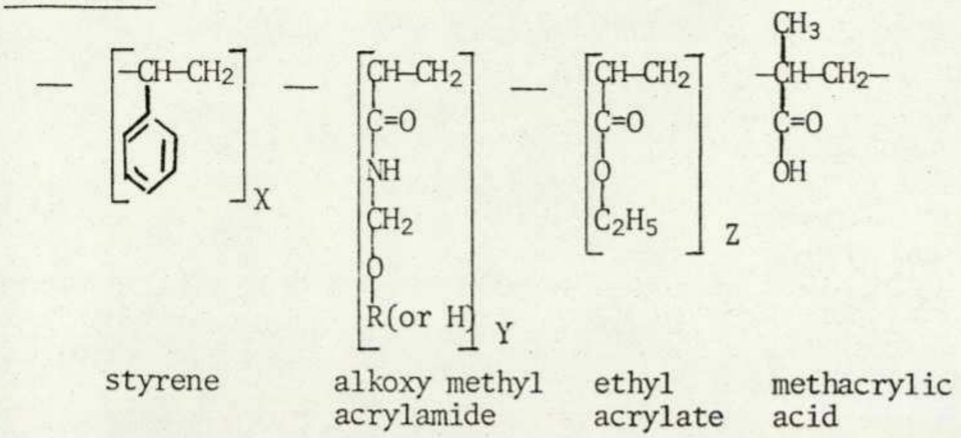
The reaction of a long chain interpolymer containing pendant amide group with formaldehyde yields products containing pendant methylol and butoxy methyl groups[289]. Acrylamide or methacrylamide monomers are normally used to introduce the amide groups into the polymer. This is shown in Diagram IV.

DIAGRAM IV



As the etherification of the methylol groups with butyl alcohol proceeds under acidic conditions as also the final cure of the resins, a small proportion of carboxylic groups are introduced into the polymer by use of methacrylic acid. The functional groups that are present in a typical styrene, ethyl acrylate, acrylamide interpolymer, as shown in V. The numbers of each monomer unit and their arrangement, of course, depends on the charge and the course of the polymerisation.

DIAGRAM V



The products on application to a surface and baking at temperatures of 320-350°F, cure to yield highly cross-linked, chemically resistant films.

As these resins are compatible and cross-link with many other systems, a wide range of formulations is given to the paint maker.

The types of chemical reactions which take place on "curing" the resin of a methylol containing copolymer are illustrated in Diagram VI.

DIAGRAM VI

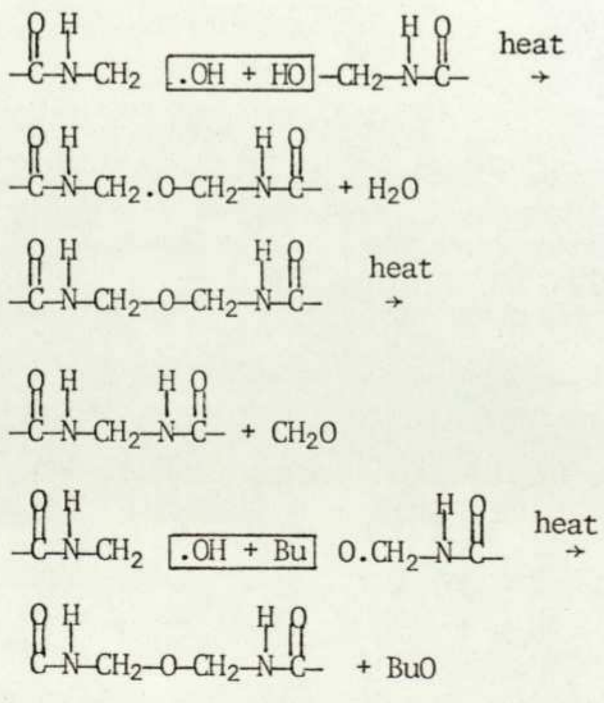
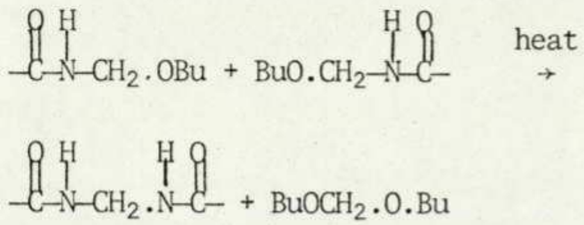


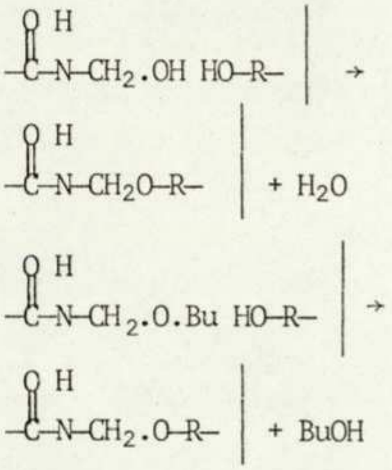
Diagram VI (cont.)



$$-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-CH_2.OBu + BuO.CH_2-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}- \xrightarrow{\text{heat}}$$

$$-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-CH_2.\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}- + BuOCH_2.O.Bu$$

With hydroxyl containing resins such as an alkyd resin, epoxy resin or several other resinous polyols, co-reaction is possible.



$$-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-CH_2.OH\ HO-R- \Big| \rightarrow$$

$$-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-CH_2O-R- \Big| + H_2O$$

$$-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-CH_2.O.Bu\ HO-R- \Big| \rightarrow$$

$$-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-CH_2.O-R- \Big| + BuOH$$

Related equations can be written for the co-reaction of amide, amine, phenolic, urea and melamine resins.

The variety of chemical reactions which this system can undergo and the "strong" nature of the bonds formed sets this particular system apart from the thermosetting acrylic "family" of polymers. It can be said that here there is a similar system to the already well established amino-formaldehyde resins, only in this case a great many varieties of synthetic "amino-containing" polymers can be prepared to give products of widely differing chemical and physical properties.

Robinson and Winter[281] gave a brief review of various types of thermosetting acrylic resins and described certain aspects of the development of the resins, particularly those of the acrylamide type with low-temperature curing properties. The way in which the temperature was lowered was by the use of highly functional cross-linking materials such as aminoplasts and alkyds in association with functional thermosetting acrylic resin.

Taylor and Price[282] were concerned with the performance of new systems of thermosetting acrylic resins in paints and with the design philosophy of vehicles for use in the automobile and Industrial Finishing field.

The basis of thermosetting acrylic resin design was discussed in terms of (1) comonomer composition, (2) level of monomers contributing to film hardness (3) nature of the hydroxy functional monomer and (4) curing of the hydroxy functional copolymers.

(1) Comonomer Composition

The typical monomers which may be present in a thermosetting acrylic resin are shown in Table 42. A common combination of monomers for the copolymer is styrene with the alkyl acrylates. The effect of varying their ratio is that as the styrene level increases, the cost falls, hardness increases, chemical resistance increases and amino resin compatibility decreases. As the acrylate level increases flexibility increases and exterior durability increases within limits. This seems to be a pattern that applies whatever the cross-linking monomers or groups employed, be they hydroxyl, acrylamide, carboxyl etc., though naturally the optimum ratios will vary from system to system.

(2) The level of monomers reflects on:

(a) Durability (b) exterior durability prediction and (c) compatibility.

In durability terms, it is known that very high styrene levels give excellent chemical resistance and such systems have applications in domestic appliance finishes. They have however, poor exterior durability due to the vunerability of the styrene tertiary carbon atom to peroxidation and to the high U.V. absorption of aromatic compounds. It is to be expected therefore that durability would increase progressively as the styrene level falls and the flexibilising monomer increases. However, an optimum level exists for the proportion of monomer contributing hardness to the copolymer.

A diagram showing the effect of hard monomer on gloss retention after weathering for copolymers of MMA/EA/AM, styrene/butylmethacrylate styrene/ethylacrylate and vinyl toluene/ethylacrylate with copolymerised acrylamide and cross-linked with a urea formaldehyde resin was given by Graham et al[291]. The optimum level for maximum durability were 20, 30 and 53% for vinyl toluene, styrene and methylmethacrylate respectively.

It was concluded by Taylor and Price[282] that it is the level of hardening monomer which determines the maximum durability of the copolymer and by using a triangular co-ordinate plot, the maximum durability composition may be predicted from the individual optimum levels. Factors other than 'hard' monomer can affect durability particularly the level of carboxylic acid, the higher level of which can cause a considerable reduction in gloss retention.

Compatibility problems are only associated with the hydroxyl

TABLE 42

TYPICAL MONOMERS WHICH MAY BE PRESENT IN A THERMOSETTING ACRYLIC RESIN

Monomer	Contribution
Methylmethacrylate Styrene Vinyl toluene Acrylonitrile	Hardness
Ethyl Butyl 2-Ethylhexyl Acrylates and methacrylates Butyl maleate	Flexibility
Acrylamide Butoxymethyl-acrylamide Hydroxy alkyl-acrylates Glycidylacrylates Acrylic acid	Cross-linkages
Acrylic acid Methacrylic acid Maleic anhydride	Cure acceleration

functional acrylics for domestic appliance finishes where the high styrene level gives compatibility problems with malamine.

(3) The nature of the hydroxy functional monomer

This monomer is introduced in the acrylic polymer by copolymerising an hydroxalkyl acrylate or methacrylate with the monomers.

It was claimed[292] that secondary hydroxyl groups as in 2-hydroxy propyl acrylate are preferred to primary hydroxyl groups as in 2-hydroxyehtylacrylate in terms of better initial glass and can stability of paints. The work of Taylor and Price[282] on the comparison of hydroxyehtyl and hydroxypropyl acrylates and methacrylates has not revealed any significant differences between the comonomers, which are not explicable in terms of the chain stiffening effects of methyl group on the α carbon atom. It was interpreted[282] that it is more likely that the introduction of carboxyl groups into the 2-hydroxypropylacrylate resins described in the patent[292] produced the effects on gloss as this is intimately associated with better pigments wetting with resins containing -COOH groups.

(4) Curing of the hydroxy functional copolymers.

The two component hydroxy functional acrylic/melamine systems can cure in 30 minutes at 120°C and acid catalysis is necessary. Recent work[293,294] has shown that the carboxyl function is indeed catalytic, very little cross-linking taking place between carboxyl groups and the methylol group of the amino resin.

Taylor and Foster[283] gave an account of the practical and theoretical considerations of the use of thermosetting acrylic resins containing hydroxy acrylates and cross-linked with etherified amino melamine resins used in the automobile industry, particularly for the formulations of metallic finishes.

It was concluded[283] that the performance of hydroxylated acrylic/melamine resin in reflow enamels is dependent upon several inter-related factors including the chemical constitution of the resins, co-monomer composition type and level of pigmentation and the ratio of acrylic/melamine resins (cross-linking mechamisms) in the paint. They also showed that it is possible to formulate a resin having the required speed of cure to give satisfactory sanding reflow and over-spray acceptance properties for repair-in-process operations and at the same time to be resistant to cold checking under severe conditions, in thick films. The weathering properties were shown to be extremely satisfactory.

The recommended acrylic:melamine ratio for hydroxy acrylic resin is often 70:30 based on solid resins. This gives the optimum balance between hardness, flexibility and chemical resistance. The effect of varying this ratio was investigated by Taylor and Foster[283] and the results indicated that reflow and overspray acceptance were favoured by a low acrylic:melamine ratio and that sandability was favoured by a high acrylic-melamine ratio.

A further investigation by Robinson and Winter[281] involved the use of different levels of melamine resin in blend with a copolymer of the optimum carboxyl/hydroxyl content. A plot of 1% inextractable against % melamine content showed that increasing cure with increasing melamine formaldehyde content was obtained. This effect is a true inter-cross-linking effect, but, at high levels of melamine/formaldehyde resin, is also strongly related to the increasing proportion of self-cross linkable component. The choice of malamine level was decided upon as a result of the characteristion of film performance data which results in a 30 per cent melamine level was thought to offer optimum performance especially when the properties of mar resistance and polishability were considered.

Similar findings were obtained by Taylor and Price[282], who showed that by varying the acrylic/maleamine ratio does not affect the rate of cure significantly but it does affect the degree of cure obtainable. The mechanical and chemical properties required are the determined factor in chosing the optimum ratio for a given acrylic copolymer, e.g. 70:30 ratio of acrylic to amino resin is near optimum for commercially available thermosetting acrylics of DYNOCRYL H-260 XB series which is the new designation for what was previously EPOK D-2101.

Differences between the various commercial amino resins on the rate of cure of i.e. DYNOCRYL H-260 Xb at 120°C, as reported[282] are not large. However, as the temperature decreases to 100°C bigger differences are discernible.

A comparison was made by Taylor and Foster[283] between a conventional hydroxy acrylic resin such as DYNOACRYL-H-2102 or EPOK D2102 and a reflow thermosetting acrylic resin. In their experiments, the acrylic:malamine ratios were varied between 6:40 and 80:20. The initial bake in all cases was 22 minutes at 100°C. From the curing curves obtained with reflow resin, initial thermoplasticity i.e. slow curing rate was obtained with the low acrylic: melamine ratio, while the high acrylic:melamine ratio gave a much faster initial cure. The hardest ultimate film was obtained at the recommended ratio of 70:30.

Similar observations may be made in the case of EPOK D 2102 or (DYNOCRYL), but it was obvious that more cross-linking had taken place in each case after the inital bake. There was no great difference in film hardness between resin or model resin B and D2102 at the 70:30 ratio after original bake of e.g. 20 minutes at 140°C.

Taylor and Foster[295] studied the surface properties and appearance of paint films based on thermosetting acrylic resins in terms of oven flow, mar resistance, i.e. as related to the surface hardness of a paint film and weathering characteristics. Reflow of a paint film during a double stoving cycle was discussed and an attempt was made to explain certain anomalies in the behaviour of three-component films, by consideration of the rate of cure and of the mutual compatibility of the reactive components of the binder.

Ovenflow was examined by following the viscosity changes during the baking cycle of a thermosetting resin film and graphs were constructed for illustrating the difference in viscosity changes between reflow and conventional acrylic/melamine blends.

The surface appearance is usually described in terms of a number of visual characteristics such as gloss colour, texture, uniformity and the presence of foreign matter. In the case of surface coatings these properties are influenced by various factors including the pigments, resins, solvents and additives used and by environmental effects resulting from weathering, heat and abrasion.

Using the optimum acrylic:malamine ratio of 7:3 gave the best all-round properties.

4.2. Experimental

4.2.1. Preparation of Polymers

For this work, a thermoset acrylic polymer of the hydroxyl type was used. The standard polymer was prepared by the addition polymerisation of styrene, n-butylmethacrylate, hydroxy ethyl methacrylate and acrylic acid in xylene:butanol (1:1 w/w). A resin with a higher acid content and that modified with 5% molar 1-viny-2-methyl imidazole were also prepared by the same method. The application of other modifiers was not attempted.

Polymerisation was carried out in a three-necked flask fitted with a stirrer, thermometer, nitrogen inlet and a condenser. The components, solvent and (0.5% by weight on monomers) - azobis isobutyronitrile as initiator were added to the flask and it was heated on a water bath to a temperature of 80-90°C. Further initiator at eight-hour intervals was added until > 99% degree of polymerisation was reached.

The formulations used and characteristics of the resin are recorded in Table 43 and Table 44 respectively.

TABLE 43

FORMULATIONS OF RESINS

Reference Number	T_1(a)		T_2		T_4	
Monomers	% mole	% By weight	% mole	% By weight	% mole	% By weight
Styrene	52.5	47.3	50	45.82	50	45.10
n-Butylmethacrylate(*)	17.5	21.5	16.7	20.9	16.7	20.50
2-Hydroxy ethyl methacrylate	25.0	28.1	23.8	27.3	23.8	26.9
Acrylic Acid	5.0	3.1	9.5	6.0	4.75	3.0
1-Vinyl-2-methyl imidazole(*)	-	-	-	-	4.75	4.5
Xylene:Butanol (1:1 w/w)	-	50	-	50	-	50
initiator % on wt. of monomers	-	.85	-	0.75	-	0.76
Period of reactions, hours	≈ 50 h		≈ 40 h		= 50 h	

* Re distilled before use

TABLE 44

CHARACTERISTICS OF SYNTHESIZED POLYMERS

Ref. No.	Compositions	Acid Value, mg KOH/gramm of resin		M_w	M_n	D
		Theoretical	Experimental			
T (a)*	B.M.A. + Styrene + Hydroxy ethyl methacrylate + Acrylic Acid (STANDARD)	24.3	27.5	112920	21953	5.41
T_2	"	46.9	47.2	147484	36266	4.067
T_4	" + 1-Vinyl-2-methyl imidazole	23.3	23.0	21980	10880	2.02
C D2101 (+)			11-16			
C D2102			11-16			
C D2103			18-24			

* Theoretical hydroxyl content 122
Experimental " 124
Extensibility 7%
Extension at break of free film 1%

\+ BP Chemicals (UK) Ltd.
EPOK Surface Coating Resins, Technigram E161, 1971

Fractionation of resins T_{1_a} and T_2 for the high, medium and low molecular weight species, by Gel Permeation Chromatography, revealed the composition to be as given in Table 45.

TABLE 45

COMPOSITION OF RESINS

Resin Ref.	Molecular Weight Fraction	Composition; % By Weight			
		Styrene	n-butyl-methacrylate	HEMA	AA
T_{1-a}	1. High	45	20	30	5
	2. Medium	48	29	20	3
	3. Low	31	29	35	5
Average		41.3	26	28.3	3.1
T_2	1. High	47	20	27	6
	2. Medium	52	20	22	6
	3. Low	34	12	34	20
Average		44.3	17.3	27.7	10.6

The percentage of average values of each component present in the final resin is in good agreement with the percentage of starting monomers.

Three commercially available thermosetting acrylic resins designated here as C_1, C_2 and C_3 of the hydroxyl type were also included in this work to establish that resin T_{1_a} was fully upto commercial standards, to compare adhesion performances and to ascertain any advatantages obtained from the laboratory prepared resins.

The composition of these resins C_1 C_2 C_3 are the subject of a licensing agreement, and therefore could not be disclosed. However, a comparison carried out by the supplier between the polymer composition of $T1_a$ and their resin revealed that the compositions are very close.

In addition, the infra red spectra of these resin indicated the presence of styrene, butyl acrylate and hydroxyl compound. Styrene was readily recognised from the aromatic substitution bands at 700 and 760 cm^{-1} with confirmation from other bands e.g. at 1600 cm^{-1}.

The spectra of known copolymer of 45/55 styrene/butylacrylate as a reference showed that the commercial resin contained at least 50% styrene.

Detailed spectra of the commercial resin obtained on Perkin Elmer 177 showed a doublet at 2940 and 2960 cm^{-1} which is present in a reference spectra of 2-ethylhexylacrylate.

Butylacrylate showed several characteristic bands namely at 840, 1021 and 1065 cm^{-1}.

Hydroxyl containing monomer was shown by the band at 3525 cm^{-1}.

It was concluded that the commercial resin is suitable for comparison.

4.2.2. Preparation of Paints and Films

The resins were pigmented by ball milling with rutile titanium dioxide (RCR), at 0.75:1 pigment/binder ratio. For the amino-resin cured systems butylated or fully methylated melamine resin was added and ball-milled sufficiently to give adequate mixing.

All paints were finally thinned to a viscosity of 4 poise at 25°C with 1:1 by weight xylene/butanol. Procedures of surface preparation of panels, contamination and adhesion testing were the same as those described in Chapter 3.

Five paints based on each laboratory prepared acrylic resin were made, the additives being as follows:-

System (1). Resin without cross-linking agent.

(2). Resin with 1% on total resin solids of p-toluene sulphonic acid, (ptSa).

(3). Resin with 30% butylated malamine-formaldehyde resin, Beetle BE615(*).

(4). Resin with 20% methylated melamine-formaldehyde resin, Beetle BE670(+).

(5). Resin with 20% BE670 + 1% (ptSa).

Paints based on commercial resins were also made with the addition of butylated malamine resin only (as system 3).

(*)(+) Trade name of amino resin manufactured by British Industrial Plastics Ltd., with the following properties.

Ref.	% non volatile	Solvent	Maximum Acid Value	Notes
BE 615	58 - 62	n-Butanol	11.5 - 20.5	n-butylated resin
BE 670	93 - 97	none	0.2	Hexamethoxy-methyl melamine

4.2.2.(i) Results and Discussion

The results of the measurements of adhesion of paint films of the five systems applied to contaminated and uncontaminated aluminium after stoving for ½ hour at $80^{o}C$ and $120^{o}C$ are recorded in Tables 46 and 47 respectively.

The results at both temperatures show that the adhesion of paints based on resins T_{1a}, T_2 and T_4 to both clean and contaminated aluminium was excellent in the absence of amino-resin component. With the standard resin T_{1a}, paints showed very poor adhesion to contaminated aluminium when using either a butylated or methylated melamine formaldehyde resins as curing agent. This was true not only with the laboratory prepared acrylic resins but also with the commercial resins examined. The adhesion of these systems to contaminated aluminium was improved however, by using an acrylic resin of higher free acid content cured at $80^{o}C$ and in addition at $120^{o}C$ with system 4. Particularly good adhesion was obtained with the acrylic resin modified with 1-vinyl-2-methyl imidazole, i.e. T_4.

TABLE 46

ADHESION OF ACRYLIC RESIN PAINTS TO CONTAMINATED ALUMINIUM AFTER STOVING AT 80^{o}C AND 120^{o}C/½ HOUR

	Joint Strength, N/m^2 x 10^{-4} / % Area of Adhesion Failure										
		1		2		3		4		5	
	System	No cross-linking agent		1% ptSa		30% Butylated m/f resin		20% Methylated m/f resin		20% Methylated m/f resin + 1% ptSa	
Temp.	Paint Ref. No.	Mean value	Standard Devn. (*)	Mean Value	Standard Devn.	Mean Value	Standard Devn.	Mean Value	Standard Devn.	Mean Value	Standard Devn.
80^{o}C	PT_{1_a}	1963/5	166	2830/0	328	797/100	64	992/100	84	565/100	44
	PT_2	2920/0	236	2869/0	296	1360/60	104	2674/0	93	979/100	61.6
120^{o}C	PT_{1_a}	2433/0	190	2730/0	250	370/100	29	782/100	96	862/100	100
	PT_2	2770/0	199	3014/0	193	602/100	41	2900/0	322	952/100	95
	PT_3	2236/5	170	2944/0	123	1907/70	126.5	1609/70	92	2842/0	220
120^{o}C	C_1					720/100					
	C_2					620/100					
	C_3					535/100					

(*) Number of observations is between six to ten.

TABLE 47

ADHESION OF ACRYLIC RESIN PAINTS TO CLEAN ALUMINIUM AFTER STOVING AT 80°C AND 120°C / ½ HOUR

Temp.		Joint Strength, N/m^2 x 10^{-4} / % Area of Adhesion Failure (*)									
		1		2		3		4		5	
		No cross-linking agent		1% ptSa		30% Butylated m/f resin		20% Methylated m/f resin		20% methylated m/f resin	
	Paint Ref. No.	Mean Value	Standard Devn.	Mean Value	Standard Devn.	Mean Value	Standard Devn.	Mean Value	Standard Devn.	Mean Value	Standard Devn.
80	PT_{1a}	2837	250	3168	87	2708	131	2690	161	4015	80
	PT_2	2925	128	3198	196	2991	209	3034	177.8	3727	328
120	$PT_{1}a$	2516	188	3043	100	3568	281	3498	216	2892	220
	PT_2	2401	232	2916	109	3280	238	3180	215	2688	112
	PT_4	2990	116	3247	151	2988	144	3122	305	3166	118
120	C_1					3140					
	C_2					2816					
	C_3					2680	298				

(*) % area of adhesion failure is zero in all cases

(+) Number of observation is between six to ten.

4.2.3. Determination of Degree of Cross-Linking in Stoved Acrylic Resin Films

4.2.3.(i) Method, Results and Discussion

The degree of cross-linking of the various resins described in Tables 43 and 44, after stoving at 120°C for ½ hour, with and without various curing agents, was obtained by determining the amount of material not extracted from the clear films after refluxing with methyl ethyl ketone in a soxhlet apparatus.

Similar determinations were carried out for the standard and higher acid content resins after stoving at 80°C and 150°C.

The results of these determinations are summarised in Table 48.

TABLE 48

% MEK INEXTRACTABLE AFTER STOVING AT 120°C FOR ½ HOUR

Stoving Temp. and Time	System	1	2	3	4	5
	Ref.	No cross-linking agent	1% PTSA	30% Butylated M/F resin	20% Methylated M/F resin	20% Methylated M/F resin + 1% ptsa
80°C/½ hr.	T_{1a}	0	59.5	45	0	92
"	T_2	0	52	58	15	93
120°C/½ hr.	T_{1-a}	0	92	100	90	99
"	T_2	0	91	100	88	98
"	T_4	32	34	97	81.5	90
150°C/½ hr.	T_{1a}	0	100	100	97	100
"	T_2	42	100	100	100	100

System 1

The results indicate that no cross-linking of the standard resin (T_{1_a}) occurred on stoving in the range 80-150°C in the absence of catalyst or curing agent. With resins T_4 and T_2 some self-curing propensity, i.e. without any added catalyst, is evident at stoving temperatures of 120 and 150°C respectively.

System 2

In the presence of 1% p-toluene sulphonic acid, however high MEK inextractable contents were obtained, resin T_{1_a} showing apparently complete cure at 150°C. The high degree of cross-linking obtained with the acid catalyst alone showed the "self-reactive" nature of this resin.

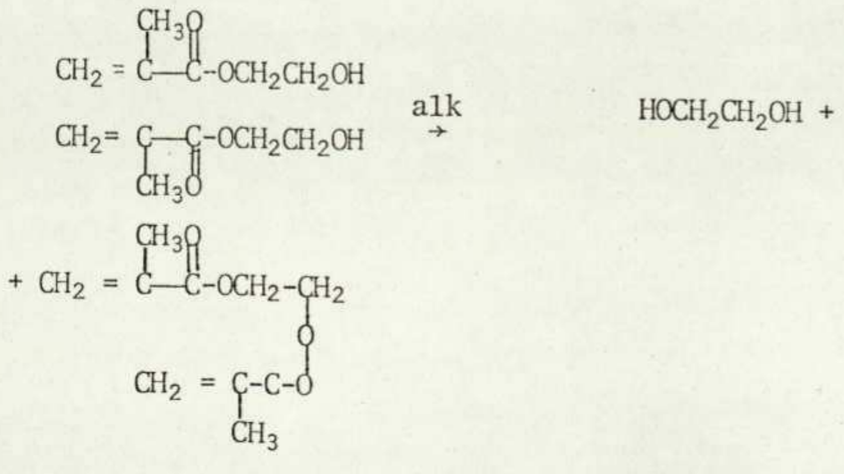
The effectiveness of added catalyst, however, was reduced with resin T_4 due to the basic nature of this resin, arising from the imidazole ring.

The mechanism of cure of the standard resin system with acid catalyst was investigated. The possible curing mechanisms are:

(1) Simple esterification between free -OH and -COOH groups, i.e.

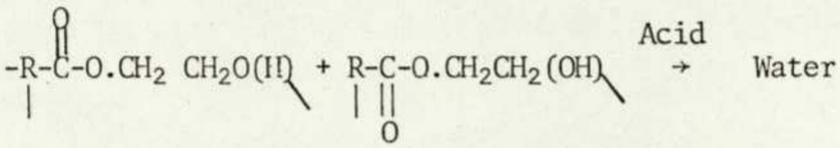
$$R \sim OH + R'\text{-}COOH$$

(2) Disproportionation of the hydroxyethylmethacrylate component with loss of ethylene glycol or butyl alcohol, i.e.,



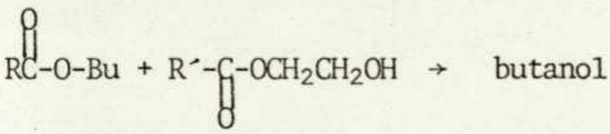
$$\begin{matrix} CH_2=C(CH_3)-C(=O)\text{-}OCH_2CH_2OH \\ CH_2=C(CH_3)-C(=O)\text{-}OCH_2CH_2OH \end{matrix} \xrightarrow{alk} HOCH_2CH_2OH + CH_2=C(CH_3)-C(=O)\text{-}OCH_2\text{-}CH_2\text{-}O\text{-}C\text{-}C(CH_3)=CH_2$$

3. Etherification of -OH groups.



$$-\underset{|}{R}-\overset{O}{\overset{\|}{C}}-O.CH_2\ CH_2O(H) + \underset{|}{R}-\underset{\underset{O}{\|}}{C}-O.CH_2CH_2(OH) \xrightarrow{Acid} Water$$

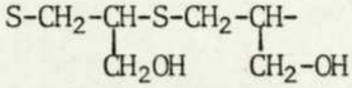
To eliminate simple esterification during curing, an acid free copolymer was prepared from styrene, hydroxy ethyl methacrylate and n-butylmethacrylate in toluene and clear films were stoved at 120°C/½ hour with 1% ptSa. Mehtyl ethyl ketone inextractable content was again high (92%) indicating extensive cross-linking in the absence of -COOH groups.

i.e. 

$$R\overset{O}{\overset{\|}{C}}-O-Bu + R'-\underset{\underset{O}{\|}}{C}-OCH_2CH_2OH \rightarrow butanol$$

In a large scale experiment with this copolymer a small amount of butanol ≈ 3% was detected by G.L.C. in the volatile products obtained at 120°C. This suggests that although some disproportionation occurred via butyl alcohol loss, as in reaction 2, it was not the main cross-linking reaction.

Etherification is unlikely to occur since a styrene/allyl alcohol copolymer (RJ 100), $S-CH_2-\underset{\underset{CH_2OH}{|}}{CH}-S-CH_2-\underset{\underset{CH_2-OH}{|}}{CH}-$ on heating with 1% ptSa produced no cross-linked material.



The most likely curing mechanism with the acrylic resin is therefore disproportionation with loss of ethylene glycol from the hydroxy ethyl methacrylate component to form a diester of methacrylic acid in situ.

This system could have a practical advantage since in the presence of 1% ptSa a completely cross-linked film was obtained on stoving at 120°C (see Table 48), and in addition, the adhesion of these films without amino resin present was also very good indeed. (see Table 46). There have not been any reported information on this type of cross-linking, and it will be very interesting to evaluate its performance as an OH self reactive resin under various environmental conditions.

Systems 3, 4 and 5

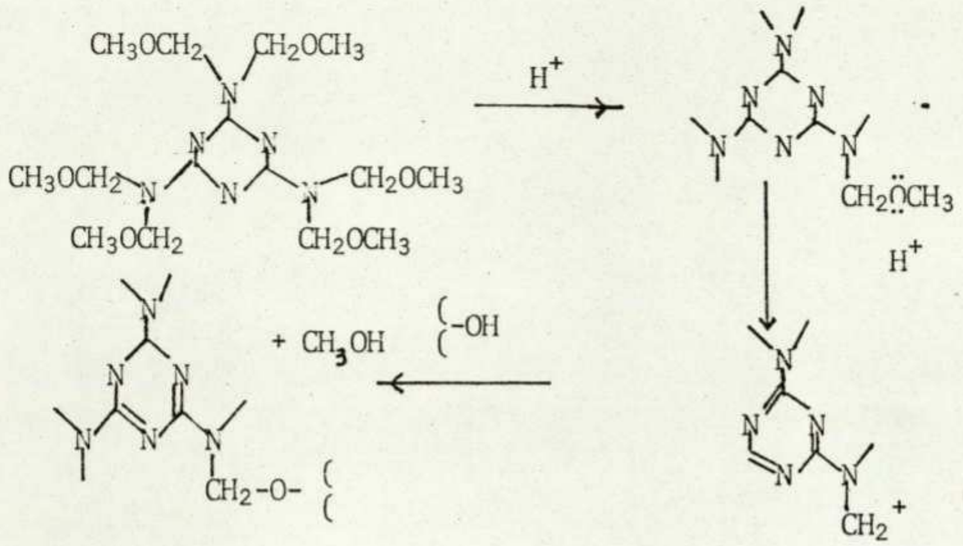
In the presence of a butylated melamine-formaldehyde resin, high levels of MEK unextractable material were obtained after stoving at 120 and 150°C. However, low temperature of 80°C was insufficient to accelerate the anticipated reaction.

The methylated melamine formaldehyde resin was more efficient in the presence of the acid catalyst, this being particularly marked at 80°C.

The more complex mechanism of cure, of hydroxylated acrylics with amino resins, the properties of resin and performance have received considerable attention by researchers in this field.

The curing mechanism of these systems is the same as that given in system A, reviewed by Piggott[280] and Taylor and Price[282] in the introduction.

In addition, the possible mechanism for the cross-linking of hexamethoxy methyl melamine (HMMM) with hydroxyl functional acrylic polymers, using 1% ptSa as a catalyst, was given by Nyquist[296] and is illustrated on the next page. A series of resins pigmented with T_1O_2 based on styrene, butylacrylate, hydroxy alkyl acrylates and acrylic acid were evaluated in terms of adhesion to steel, gloss,



impact resistance, flexibility, hardness, salt spray resistance and MEK resistance. Optimum properties for coating were obtained with coating containing 10% by weight of hydroxy ethyl acrylate (HEA) on total weight of monomers using HMMM at molar ratio of 1:2 to HEA.

The curing mechanism could thus result from an esterification reaction as well as etherification when melamine resin is used in the presence of an acid catalyst.

In cases where the acrylic resins can contain both carboxyl and hydroxyl groups[297] and as such it can be regarded as taking the place of non-drying alkyds in alkyd/melamine systems, Robinson and Winter[281] evaluated the effect of the content of these groups and, in addition, the effect of different melamine contents on the degree of cure and film performance of enamels derived from them.

A series of resins of different hydroxyl and carboxyl contents was cured at 120°C in the presence of 30 percent melamine formaldehyde resin and the percentage of inextractable contents were plotted against the hydroxyl value. This relationship revealed that a copolymer containing high levels of carboxyl groups but low levels of hydroxyl groups does not cure at all well with the melamine resin and it is only at a hydroxyl number of around 25 that adequate levels of cure were obtained i.e. 80%, 75% and 70% cure at acid values of 50, 35 and 70 respectively. However, the extractability results obtained showed that where the acid level was very low, then, even though high levels of hydroxyl content were present, low degrees of cure were obtained. This suggested that the carboxyl group has at least a dual function in that it can act as a catalyst for the hydroxyl/aminoplast reaction as well as taking part in cross-linking reaction directly.

The second conclusion was that an increase in performance regarding water resistance with a lowering of acid number at the same hydroxyl content and there is no improvement to be gained by increasing the acid number beyond a level of acid value of 50½ Similarly there is little to be gained from increasing the hydroxyl number above a certain level since this does not result in any further significant increase in inextractables. This was related to reactivity ratio consideration and it was envisaged that copolymer molecules exist which do not contain any cross-linking active centres.

The findings of Akay et al[298], 1973, bears an interesting effect on the present work. He studied the dynamic mechanical properties of thermosetting acrylic coatings for appliance finishes of the hydroxyl type, cross-linked with hexamethoxymethyl melamine and over a wide temperature range. The results, which were correlated with conventional physical test results, showed that the effects of varying acrylic copolymer composition, level of cross-linking agent and level and type of pigment influenced the glass transition temperature.

Composition of a typical resin preparation is 40% styrene 40% ethylacrylate, 17% hydroxyethylacrylate and 3% methacrylic acid.

With this type of resin, the extent of the reaction of hydroxyl sites in the copolymer with (HMMM) in the presence of p-toluene sulphonic acid will determine the level of cross-linking of the cured coating $2 \times 10^9 - 10^1$.

At a constant quantity of (HMMM), increasing OH content leads to cured films with increasing hardness (modulus at 100°C, $E = 2 \times 10^9 - 10^{10}$ dyne.cm^{-2} as HEA 7.2% - 16.8%.

Effect of cross-linking agent (HMMM) on the dynamic mechanical properties was also investigated by Akay[298] with a copolymer containing 17% hydroxyethyl acrylate compound with HMMM in weight ratio of 95/5, 90/10, 80/20 and 70/30. It was found that for unpigmented films, increasing the HMMM concentration from 5% to 30% brought about an increase in glass transition temperature of about 45°C. At temperatures above 50°C there was also a pronounced increase in the elastic moduli.

For pigmented film with T_1O_2 a similar behaviour was observed. There was an increase in the Tg from 70°C to 90°C with increasing HMMM content and the value of the elastic modulus increased at any given temperature. At low temperatures, the elastic modulus for the pigmented material is greater than that for the clear film owing to the resin forcing effect of filler.

It was concluded that increases in cross-link density, whether brought about by modification of the copolymer or by increased concentration of cross-linking agent, have the effect of raising the glass transition temperature and lowering the damping capability of the cured resin system. The derived paints exhibit increased hardness and reduced flexibility and impact resistance as consequences of the changes in resin structure.

4.2.4. Assessment of film shrinkage

Paint films of resins T_1a, T_2 and T_4 with and without curing agents added (i.e. systems 1-5) were applied to microscope slides and were held under vacuum at room temperature until no further weight loss occurred. The films were then cured at 120°C for ½ hour and the losses in weight of condensation products, i.e. water, butanol or methanol were determined as a measure of shrinkage of paint films.

The results are recorded in Table 49.

TABLE 49

% SHRINKAGE ON THE WEIGHT OF UNCURED SOLVENT FREE PAINT FILM

SYSTEM	1	2	3	4	5
Ref. No.	No cross-linking agent	1% PTSA	30% Butylated M/F resin	20% Methylated M/F resin	20% Methylated M/F resin + 1% PTSA
PT_{1-a}	7.5	8.54	11.25	9.11	10.8
PT_{-2}	6.4	6.42	9.13	7.44	8.95
PT_{-4}	11.7	10.5	14.1	10.6	10.3

4.2.5. The relationship between adhesion/degree of cross-linking and shrinkage of paint films at 120°C

The trends in adhesion of paints, degree of cross-linking and shrinkage of acrylic resins T_{1_a}, T_2 and T_4 found after stoving at 120°C are summarised in Table 50.

TABLE 50

ADHESION/DEGREE OF CROSS-LINKING/SHRINKAGE RELATIONSHIP OF PAINT FILMS

Ref. No.	Trend of increasing adhesion to contaminated aluminium	Trend of decreasing degree of cross-linking	Trend of decreasing shrinkage
PT_{1-a}	$3 < (5 \sim 4) \ll 1 \sim 2$	$3 > 5 > 4 > 2 \gg 1$	$3 > 5 > 4 > 2 > 1$
PT_2	$3 < 5 \ll 4 \sim 2 \sim 1$	$3 \sim 5 > 4 \gg 2 \gg 1$	$3 > 5 > 4 > 2 \sim 1$
PT_4	$4 < 3 < 1 < 5 \sim 2$	$3 > 4 \sim 5 > 1 \approx 2$	$3 > 1 > 4 \sim 5 \sim 2$

It is noted from these trends that with acrylic resins T_{1_a} and T_2 poor adhesion to contaminated aluminium was associated with a high level of cross-linking and more shrinkage in the film. With acrylic resin T_4, however, this relationship was not quite so clear cut.

The poor adhesion of films which cure rapidly to produce extensive cross-linking can be affected by the reduced mobility of the polymer chains and consequent inability to displace the contaminant effectively. Increased internal stresses due to more shrinkage in the highly cross-linked film could however, also be a factor involved. Thus, from the weight loss studies during stoving, system 3 (i.e. with butylated malamine formaldehyde resin) would be expected to undergo most film shrinkage (evolution of butanol) and this system also showed generally poor adhesion throughout.

4.2.6. Adhesion of thermosetting acrylic paints cross-linked with butylated M/F resin at 120°C to stearic acid contaminated and uncontaminated galvanised steel and tin plate

Experimental

Galvanised steel sheets obtained from Senmor Metals Ltd., were mild steel which were dipped in zink at 450°C, i.e. zink/steel alloy layer is formed followed by zink coating.

These were cut out to 6 x 4" panels, washed with Teepole and water, dried and degreased in ICI degreasing plant for 2 minutes in Trichloroethylene. These were contaminated in the normal way. A similar procedure was used for the preparation of tinplate panels.

The panels were coated with paints, by the spinning technique, stoved at 120°C for ½ hour and adhesion measurements were made.

The results are summarised in Table 51. All paints exhibited excellent adhesion to uncontaminated steel or tinplate. However, the superiority of resin paint containing 1-vinyl-2-methylimidazole is again demonstrated in this type of paint system, when applied to contaminated surfaces.

TABLE 51

ADHESION OF THERMOSETTING ACRYLIC PAINTS CROSS-LINKED WITH BUTYLATED M/F RESIN AT 120^{o}C TO STEEL AND TINPLATE

Ref.	Polymer Type	Joint strength N/m^2 x 10^{-4}			
		Galvanised steel		Tinplate	
		contaminated	uncontaminated	contaminated	uncontaminated
T_a	Standard	784±75$^{(*)}$	2545±178	1086±74	2756±250
T	Extra acid	1037±77.2	2573±277	1034±119	2752±160
T	Imidazole modified	1176±121	2547±176	2283±259	3072±152

(*) Standard deviation from six to eight observations.

In all cases, % area of adhesion failure is 100% for T_{1_a} and T_2 and 95% for T_4.

CHAPTER FIVE

EMULSION PAINTS

5. EMULSION POLYMER PAINTS

5.1. Introduction

Chemical modification of thermoplastic and thermosetting acrylic polymer chains with carboxyl and certain N-containing groups had been shown in Chapters 3 and 4 to improve the adhesion of solvent thinned acrylic paints, particularly to contaminated surfaces. This investigation was therefore extended into the acrylic emulsion field to see whether similar chemical modification would improve the adhesion of emulsion paints to selected substrates known to give occasional failures in practice. Particular attention was directed towards the problem of repainting old alkyd paint surfaces under both dry and wet conditions, and to the application of these polymers as wood primers.

5.2. Definition

An emulsion is an intimate mixture of two liquids, one of which is the disperse phase which is distributed in large or small particles (globules) throughout the other liquid - the continuous phase. Different classes of substances forming the two phases are realised. Thus polar or hydrophilic substances when mixed with non-polar or hydrophobic types form emulsions.

An oil-in-water emulsion is obtained when the disperse phase is a non-polar and the continuous phase is water. When the latter is dispersed in a hydrophobic phase, a water-in-oil emulsion is obtained.

An emulsion is a metastable system, and contains monomer, water, an emulsifying agent and a catalyst. The stability of such a system is determined by the size of the dispersed globules, by the difference in density between the two phases and by the proportion of large globules to small; large globules serve as coagulation centres for the others. Thus mono disperse emulsions are stabler than poly-disperse emulsions.

5.3. The Mechanism of Emulsion Polymerisation

In 1947 Harkins[299] proposed a qualitative general theory on the mechanism of emulsion polymerisatin, which was placed on a quantitative basis by Smith and Ewart[300] in 1948, and was comprehensively described by van der Hoff[301].

When a small amount of soap (surfactant or emulsifying agent) is dissolved in water, ionization occurs and spherical micelles are formed. At a higher concentration of surfactant however, lamellar micelles are obtained.

Emulsifying agents are compounds containing both a hydrophobic group and hydrophilic groups, and are classified as anionic, cationic and non-ionic.

The micelles are aggregates of molecules in which the interior consists of the hydrophobic part of the molecule, the surface being formed by the hydrophilic part. Normally there are about 10^{18} micelles per cubic centimetre, and Harkins and Debye[299] offered evidence for single double layers of soap which consist of 20 to 300 as small soap micelles.

Since in an emulsion system there is insufficient soap to solubilise all the oil or monomer, each emulsion droplet is surrounded by a monomolecular layer of soap molecules oriented with their hydrocarbon chain toward the monomer and their ionic-polar group toward the water. Thus the system will comprise:

(1) monomer droplets

(2) miccellar solubilised monomer or soap micelles swollen by monomer to form a solution in the hydrocarbon interior, i.e. Debye-Harkins micelles.

(3) the excess monomer dissolved in water.

Polymerisation could occur in the three systema and also at the interface.

The initiation reaction step of polymerisation

~~The orientation and polarization action of the~~ emulsifying agent would decrease the value of the energy of activation and hence increases the rate of polymerisation by a factor of 10^6 for every 8000 calories reduction. The lowering of the energy of activation is the result of the reduction in the surface tension between monomer/and water produced by the accumulation of electrical charge in the phase interface making the globules repellent.

In this work anionic and nonionic emulsifyers were used. In the case of anionic emulsifyers the charge is produced by ionization of the hydrophilic group. In the case of nonionic emulsifyers, and as a mechanical screening of globules, a charged shell is formed by absorbing ions.

Alternatively, a charge may be acquired by the adsorption of surface active species from solution. Nonionic emulsifyers can be mixed with both positively-charged and negatively charged materials without coagulating the polymer dispersion.

The fact that the energy of activation is lower locates the micelle as the principal locus of initiation. The initiating radical originating in the water phase from the water soluble catalyst will diffuse into the solubilised miccellar monomer to produce a polymer particle nucleus.

For this work a water soluble initiator, i.e. ammonium persulphate was used. This decomposes to sulphate ion-radicals and hydroxyl radical as follows:

$$S_2O_8{}^{2-} \rightarrow 2\ SO_4^{-}$$

$$SO_4^{-} + H_2O \rightarrow OH^{\cdot} + HSO_4^{-}$$

Since both types of radical are capable of initiating emulsion polymerisation, van der Hul and Vanderhoff[302] argued that the emulsion polymer must contain two types of end groups. The sulphate ion-radical would encounter a large potential energy barrier at the particle surface where as the hydroxyl ion would not. They then postulated and found that the surface of the latex particles are populated more densely with sulphate residues and the particle interiors tend to contain hydroxyl groups. Depending on the surface characteristics of the particle and the polarity of the initiating radical, it seems that[303] the polymerisation thus can take place both at the surface and in the interior of the particle.

In the propagation step, and once the polymer particle nucleus is formed,. the polymer can grow by the addition of the monomer molecules that exist in the micelle.

According to Harkin's theory, and in system that contains monomer in excess i.e. (true emulsion), the monomer droplets serve as a reservoir of monomer which diffuses through the aqueous phase into the internal hydrocarbon part of the micelles. The polymer particles or the active loci and almost all of the polymer is produced by polymerisation of this monomer in these particles. The driving force for diffusion is the maintenance of the monomer to polymer swelling ratio in the polymerising particle, i.e. the supply and absorption of monomer are sufficiently rapid to maintain the rate of monomer consumption.

As polymerisation proceeds, surfactant is adsorbed from the aqueous phase onto the new polymer-water interface, thus disturbing the equilibrium between molecularly dissolved surfactant and micellar surfactant. In order to restore the equilibrium, some of the micelles in which no polymer growth is taking place disintegrate. Many micelles disappear to form one polymer particle and the final latex usually contains about 10^{15} particles/cm^3 of water.

After between 10 and 20 percent conversion no more micelles exist since most of the surfactant is adsorbed on the polymer particles, and no more polymer particles are formed. Thus the polymerisation is maintained by the rate of diffusion of monomer to the growing particle which is high enough because of osmotic forces to supply the extra monomer required for the equilibrium swelling of the particle.

After about 70% conversion, all the remaining monomer is absorbed in the particles and no more monomer droplets remain.

In systems where soap is in excess, all the monomer is contained in micelles and the active nuclei grow into polymers by exhaustion of monomer present in the micelles. The expected degree of polymerisation of the polymer would be low and the polymer exists in very small dispersed particles in the aqueous phase by the adsorption of soap.

Factors involved in emulsion polymerisation are: emulsifyers, catalysts, method of monomer addition, temperature, agitation, effect of pH, effect of salts, mechanical stability of polymer dispersion, activation by reducing agents. These factors are comprehensively discussed by Riddle[163].

5.4. Advantages of Emulsion Polymerisation

The development of the emulsion polymerisation technique for the production of polymers Latices[304] has provided a means of obtaining a well-defined system.

In comparison with other methods of polymerisation emulsion polymerisation is one of the most useful industrial methods with many advantages that more than outweigh the disadvantages.

The principal reasons are:

(1) the economy and safety of water as a polymerisation medium. The absence of organic solvents

(2) the ease of temperature control. The heat liberated during polymerisation is easily dissipated by transfer to the aqueous dispersing medium, and a high degree of control is achieved.

(3) The rate of polymerisation is much faster than in mass or solution polymerisation.

(4) The emulsion may be handled easily because the viscosity is much lower in contrast to the extremely viscous solution of the same polymer in an organic solvent.

(5) Greater uniformity of end product.

(6) Ease of isolation of solid polymer.

(7) The emulsion process is easily interrupted at any stage of the polymerisation thus facilitating the addition of other materials reactive or nonreactive for subsequent modification of the properties of the polymer.

5.5. Formation and Performance of Emulsion Films

In a review of the mechanism of latex film formation[305], it was concluded that initially, the particles move about freely with characteristic Brownian movement. As water evaporates, their motion naturally becomes more restricted and eventually the water-air interfacial tension forces bind them together in a packed array, with their double layers hindering further approach. Continued evaporation of water exerts a force to overcome this repulsion, the double layers then being ruptured and polymer-polymer contact established. The polymer-water interfacial tension is then brought into play, reinforcing and completing the water-air interfacial tension.

If the combined forces are sufficient to deform the polymer spheres, they form a continuous film. This film becomes more homogeneous on ageing and a further gradual coalescence occurs; the rate of which depends on the polymer structure, and during which any incompatible substance is exuded to the surface.

An ultra structure was found[305] of film of acrylic emulsions suggestive of a complex two-phase system. On the other hand, styrene/ butadiene emulsions revealed an ultra structure of packed emulsion particles. However, the multiphase character of acrylic and PV acetate emulsion films suggests a more complex mechanism of film formation than hitherto expected which cannot be fully explained within the current concept.

The requirements for a satisfactory performance of water-based polymer films are:

good adhesion to the appropriate surface
binding the right filler
flexible enough (not too flexible) at the temperature
at which it is to be used
resist alkali and oxidation by air
insoluble in water
colour retention on ageing.

The specific requirements can be met by other properties such as the rheological behaviour, particle size and particle size distribution, molecular weight and the presence and nature of other functional groups.

5.6. Emulsion Paints

From the middle 1930's emulsion paints were used in Germany and were based on polyvinylacetate emulsion stabilised with polyvinyl alcohol.

During the 1940's, acceptable paint emulsion were introduced into Canada and at about 1948 in the United Kingdom. However, an expansion of the range of emulsions which were available was made in about 1950.

Paint binders have been based on emulsion interpolymers of vinylchloride, vinylacetate, monocyclohexyl maleate and ethylene.

About 1953-54, copolymers for emulsion paint manufacture became available and included copolymers with dibutylmaleate and fumarate, various acrylic esters and in particular 2-ethyl-hexyl acrylate. A comprehensive list is presented[306]. Some of the most common monomers which are cheap enough to be used are:

Vinylacetate, acrylonitrile, styrene, vinylchloride
ethylacrylate, 2-ethyl-hexylacrylate, ethylene,
propylene and isobutene.

The application of water-based coatings was discussed[307] in broad terms including film formation, alkali-soluble polymers, gloss finishes, corrosion resistant finishes and cross-linking reactions. Many aspects of vinyl ester polymers and their applications including the preparation of monomers, polymerisation, plasticisation and cross-linking have also be reviewed by the same author[308].

Modified emulsions have been evolved[309] based on epoxy-polyamide system which yield the same high performance as the equivalent solvent based finishes in terms of chemical, solvent and mechanical resistance properties.

Organosilicone emulsions have been investigated[310] as air-dried or heat-cured systems, and were synthesized by grafting either methyl dichlorosilane or phenyldichlorosilane on the pendant chains of polyesters.

The cured films not only exhibited excellent corrosion and impract resistance, but in contrast to conventional emulsions, form films of high density and exceptional hardness.

Paints of improved properties[311] are obtained by incorporating proportion of low molecular weight fluoroacrylates which produce a fluorochemical surface after the coating has dried (thus lower critical surface energy) and presents a dirt repellent surface.

A new acrylic emulsion specifically developed[312] for use in exterior gloss paints has been claimed to show an outstanding balance of properties as high initial gloss,excellent gloss clarity and gloss retention, very good flow and good adhesion.

In the United States patents[313,314], modifications of aqueous addition polymer dispersion by the direct copolymerisation of special monomers, particularly ureido type was claimed. These were adopted for use as coatings and impregnating compositions and which were characterised by outstanding properties including improved adhesion to various substrates such as wood, textiles, paper, fabrics, plaster.

Homopolymers and copolymers of vinyl esters of an aliphatic acid, acrylic and methylacrylic acid esters, and mono and di ethylenically unsaturated hydrocarbons, e.g. styrene.

5.7. Experimental

Considerable difficulties were experienced in the preparation of acceptable acrylic copolymer emulsions modified with N-containing monomers. Thus with dimethylaminoethyl methacrylate as modifying monomer, no satisfactory emulsions could be produced. Using 1-vinyl-2-methyl imidazole as modifier for a methyl methacrylate/butyl acrylate system, polymerisation was either inhibited or unstable emulsions were produced. The only satisfactory polymer emulsion prepared was based on a butyl methacrylate/butyl acrylate copolymer system modified with 5% molar 1-vinyl-2-methyl imidazole. The evaluation and preparation of this type of emulsion together with a similar emulsion polymer modified with 5% acrylic acid is described below.

5.7.1. Preparation of Emulsion Polymers

A standard emulsion polymer was prepared from butyl methacrylate and butyl acrylate by heating the monomer mixture (85:15 by weight) on a water bath to 80°C in the presence of both anionic and non-ionic surfactants using ammonium persulphate as initiator. Emulsion polymers of the above type modified with 5% molar acrylic acid and 5% molar 1-vinyl-2-methyl imidazole were prepared by a similar technique.

Thus, the standard acrylic polymer emulsion E.10 was prepared in a three-necked flask fitted with a paddle stirrer, reflux condenser, thermometer and dropping funnel. Surfactants and distilled water were introduced into the reaction flask and heated to 75°C with vigorous stirring. The butyl acrylate and butyl methacrylate monomer mixture previously washed with 20% sodium chloride and 5% sodium hydroxide solution twice to remove the inhibitor, was placed in the dropping funnel and approximately 10% of the charge run into the solution of surfactants dropwise over one hour. 0.5g Ammonium persulphate dissolved in 2 - 3 mls distilled water was then added as initiator. The temperature was raised to 78-80°C, the remaining monomer mixture added dropwise over two hours and heating continued for a further one hour. Degree of polymerisation was determined by measuring the solids content of the emulsion, i.e. percentage residue on heating at 120^{o}C for ½ hour.

For the modified emulsion E.11 acrylic acid was included in the monomer charge after 10% of the butyl acrylate/butyl methacrylate mixture had been added.

With the imidazole modified emulsion E.6 1-vinyl-2-methyl imidazole, previously distilled, was included in the monomer charge after 50% of the butyl acrylate/butyl methacrylate mixture had been added.

The formulations used and characteristics of the emulsion polymers are recorded in Tables 52 and 53.

TABLE 52

ACRYLIC POLYMER EMULSION FORMULATIONS

Component	Polymer E.10		Polymer E.11		Polymer E.6	
	Mol(%)	Wt.(g)	Mol(%)	Wt.(g)	Mol(%)	wt.(g)
Butyl acrylate	16.3	15.0	15.6	14.6	15.6	14.4
Butyl methacrylate	83.7	85.0	79.6	82.9	79.6	81.8
Acrylic acid	-	-	4.8	2.5	-	-
1-vinyl-2-methyl imidazole	-	-	-	-	4.8	3.8
Sodium dioctyl + sulphosuccinate		4		4		4
Diethylene oxide/ fatty alcohol condensate*		2		2		2
Water		150		150		150

\+ Manoxol OT- * Lubrol W-

TABLE 53

ACRYLIC POLYMER EMULSION CHARACTERISTICS

Emulsion ref.	Type	Solids (%)	M_w*	M_n*	Dispersity (D)
E.10	Standard	40.2	1,730,600	289,300	6.0
E.11	Acrylic acid modified	40.7	1,010,800	138,200	7.3
E.6	1-vinyl-2-methyl imidazole modified	39.6	1,024,900	124,100	8.3

*M_n and M_w are number and weight average molecular weights calculated from G.P.C. data on the recovered polymers.

5.7.2. Preparation of paints and films for adhesion measurement

The emulsion polymers were pigmented with rutile titanium dioxide (tioxide R-HD4) at 2:1 pigment/binder ratio by the slow addition with stirring of a previously prepared pigment paste. The latter contained 210 g titanium dioxide (tioxide R-HD4), 112 g distilled water, 53.5 g of a 2% solution of a medium viscosity grade hydroxy ethyl cellulose (Natrosol 250 MR) as a protective colloid and thickening agent, and 10 g of 4% sodium hexametaphosphate solution as pigment dispersing agent. These were ground for 24 hours in a ball mill and a Hegman gauge reading of > 9 was obtained. The solids content of the past was 54.5%.

Emulsions E.10 and E.11 were brought to a pH > 9 by the addition of ammonia prior to pigmentation. The emulsion paint based on the acrylic acid modified polymer E.11 was rather unstable and small batches only were prepared as required.

The adhesion of the emulsion paints was determined to the following surfaces.

(i) Clean aluminium

Aluminium panels (15.2 x 10.2 cm) previously degreased with trichlorethylene and chemically cleaned by hydrofluoric acid/sulphochromate treatment were coated with the emulsion paints using a film spreader to give a dry film thickness of 20 - 25 μ. Films were aged at 25°C for one week before their adhesion was determined by the standard Hounsfield pull-off technique.

(ii) Adhesion of emulsion paints to alkyd paint film under dry conditions

Aluminium panels (15.2 x 10.2 cm) were coated with a proprietary alkyd gloss paint and the films (a) dried at 25°C for one week or (b) hardened by heating at 60°C for ten days. To simulate the effect of long term ageing, some of the alkyd films were artificially contaminated with stearic acid, which was applied from an 0.2% solution in isopropyl alcohol to give on evaporation a coverage of acid equivalent to 40 $\mu g/cm^2$. A short heating treatment finally ensured that an even coating of contaminant was obtained.

Emulsion paint films were applied to the alkyd painted surfaces with and without previous contamination, and the intercoat adhesion then assessed by the standard pull-off procedure.

(iii) Adhesion to hardened alkyd films under wet conditions

The series of emulsion paints applied to uncontaminated hardened alkyd paint films were aged for 7 days at 25°C and then totally immersed in water for 24 hours. Intercoat adhesion was determined immediately and after 24 hours drying period using a modified pull-off technique[252].

5.7.2. Results and Discussion

The results of adhesion measurements of acrylic emulsion paints to clean aluminium are recorded in Table 54.

TABLE 54

ADHESION OF EMULSION PAINTS OF 33% P.V.C. TO CLEAN ALUMINIUM

Paint ref.	Type of Polymer	Joint strength $N/m^2 \times 10^{-4}$/ % area of adhesion failure
PE 10/1	Standard	1507 ± 96.5/100
PE 11/1	Acrylic acid modified	2322 ± 74/60
PE 6/1	1-Vinyl-2-methyl imidazole modified	2331 ± 68/50

These results show improved adhesion to clean aluminium with paints based on both the acid and imidazole modified acrylic polymers - ref. PE 11/1 and PE 6/1.

The results of the intercoat adhesion of emulsion paints to alkyd paint films dried at 25°C and 60°C under dry conditions are given in Table 55.

TABLE 55

ADHESION OF ACRYLIC EMULSION PAINTS OF 33% PVC TO ALKYD FILMS

Paint Ref.	Joint Strength $N/m^2 \times 10^{-4}$ / % Area of intercoat adhesion Failure			
	Alkyd film dried at 25°C		Alkyd film hardened at 60°C	
	Uncontaminated	Contaminated	Uncontaminated	Contaminated
PE 10/1	1245 ± 97/80	1040 ± 90/100	1123 ± 138/100	822 ± 106/100
PE 11/1	1145 ± 41/100	780 ± 97/100	1664 ± 170/100	1393 ± 176/100
PE 6/1	1267 ± 171/0	1211 ±106/100	1312 ± 97/0	1131 ± 219/100

The above results show that the imidazole modified acrylic polymer paint (PE 6/1) was considerably better than the normal paint (PE 10/1) in terms of degree of intercoat adhesion failure to the uncontaminated alkyd films. To contaminated alkyd surfaces however only marginal improvements were noted with the imidazole modified system. Rather erratic results were obtained with the acid modified paint (PE 11/1), although improved adhesion characteristics were noted with the hardened alkyd paint as substrate.

The intercoat adhesion of emulsion paints to hardened alkyd film under wet conditions and drying conditions are summarised in Tables 56 and 57 respectively, and at 33% and 20% pigment volume concentration.

TABLE 56

ADHESION OF ACRYLIC EMULSION PAINTS OF 33% PVC TO ALKYD FILMS UNDER DRY AND WET CONDITIONS

Emulsion Ref.	Joint strength $N/m^2 \times 10^{-4}$ / % Area of Intercoat Adhesion Failure					
	Ageing under dry conditions (7 days)		After 24 hours water immersion		After water immersion and drying at $25^{\circ}C$ for 25 hours	
	Mean Value	Standard Devn.	Mean Value	Standard Devn.	Mean Value	Standard Devn.
E.10 (Standard)	1125/100	134	820/‡	81	1400/100	129
E.11 (Acid modified)	1670/100	165	1030/‡	190	1940/100	171
E.6 (Imidazole modified)	1310/0	79	970/0	83	1685/0	276

‡ Area of intercoat adhesion failure not assessed due to some cohesive failure of the fast curing adhesive used, in preparing the test pieces.

TABLE 57

ADHESION OF ACRYLIC EMULSION PAINTS OF 20% PVC TO ALKYD FILMS UNDER DRY AND WET CONDITIONS

Emulsion Ref.	Joint strength $N/m^2 \times 10^{-4}$ / % Area of Intercoat adhesion failure					
	Ageing under dry conditions(7 days)		After 24 hours water immersion		After water immersion and drying at $25^{\circ}C$ for 25 hours	
	Mean Value	Standard Devn.	Mean Value	Standard Devn.	Mean Value	Standard Devn.
E.10 (Standard)/2	895/100	97	445/100	37	650/100	218
E.6 (Imidazole Modified)	1995/70	81	1430/30	146	2495/40	114

The results indicate that the dry adhesion of paints based on both the acid and imidazole modified polymers was improved compared with the standard; the imidazole type showing, in addition, no intercoat adhesion failure.

It was significant that no intercoat adhesion failure occurred with the imidazole polymer paint under any of the conditions of test.

The results in Table 56 show that although intercoat adhesion was reduced on water soaking, adhesion loss was not so drastic as might have been expected. The modified polymer paints PE 11/1 and PE 6/1 maintained their higher level of adhesion after water soaking compared with the standard paint. Recovery of adhesion after 24 hours drying was remarkably good in all cases, the adhesion level being higher than that recorded initially. The modified polymer paints PE 11/1 and PE 6/1 were superior to the standard acrylic polymer paint PE 10/1 after drying out.

The results in Table 57 for paints of a lower pigment volume concentration show that the imidazole modified polymer paint PE 6/2 had superior initial intercoat adhesion compared with the standard paint, the adhesion, not being so drastically reduced on water soaking. After drying out, the adhesion recovery of the modified polymer was again remarkably good. The area of intercoat adhesion failure was less than the standard paint in all cases.

5.7.3. Evaluation of Acrylic Polymer Emulsion As Wood Primers

5.7.3.(i) Preparation of Wood Primers

1350 g Titanium dioxide (Tioxide R-HD4), 1380 g calcium carbonate (Queensgate QM/25), 695 g of a 2.5% solution of a medium viscosity grade hydroxyethylcellulose (Natrosol 250 MR)[315] as a protective colloid and thickening agent, 9 g of antifoam agent (Bevaloid), 63 g of 25% solution of an anionic surfactant (Tamol 731)[316] i.e. sodium salt of carboxylated polyelectrolyte as dispersing and stabilising agent, 18 g of a non-ionic surfactant (Triton X-102)[317], i.e. t-octylphenoxypolyethoxyethanol, and 225 g ethylene glycol were dispersed in a Cowles high speed mill at 4000 r.p.m. for one hour. The solids of the paste was 75%.

Paints as primers were prepared from portions of the above paste by the slow addition of the appropriate emulsion with stirring to give a pigmentation equivalent to 27% pigment volume concentration, i.e. 1.2:1 pigment binder ratio.

Wood primers were formulated on the standard emulsion polymer (E.10), the imidazole modified emulsion polymer (E.6) and for comparison purposes on a proprietary 100% acrylic emulsion recommended for this application (AC-34)[318]. Two commercially available emulsion type wood primers were also examined.

5.7.3.(ii) Application and Adhesion Assessments

One coat of each primer was brush applied to previously sanded normal perosity Baltic redwood sapwood panels (150 x 100 mm) and dried for seven days at 25°C and 60% relative humidity. The panels were then exposed under the following conditions:-

(a) Over water in a closed container at 25°C to give 100% R.H.

and

(b) In a humidity cabinet at 43°C to give 100% R.H. with moisture condensation.

Adhesion assessment was carried out by the cross-hatch test using a mutli-blade cross-hatch tool to DIN 53150 with 2mm spacing, after:-

(i) Ageing for 7 days at 25^oC and 60% R.H.

(ii) As (i) + 7 days ageing over water in a closed container at 25^oC.

(iii) As (i) + 48 hours drying at 25^oC and 60% R.H.

(iv) As (i) + 24 hours treatment in the humidity cabinet

(v) As (iv) + 72 hours drying at 25^oC and 60% R.H.

(vi) As (i) + 7 days treatment in the humidity cabinet.

(vii) As (vi) + 48 hours drying at 25^oC and 60% R.H.

The results obtained from these adhesion tests are given in Table 58, recorded as the area of adhesion failure expressed as a percentage by visual assessment.

From the adhesion results shown in Table 58 it is clear that the best overall performance was given by the wood primer (PR/E6) based on the imidazole modified polymer. This primer was considerably better than primer PR/E10 based on the standard copolymer emulsion, significantly better than paint C based on the proprietary acrylic emulsion and showed a marginal improvement over the two commercial paints tested.

TABLE 58

ADHESION OF WOOD PRIMERS OF 27% P.V.C.

(Expressed as % area of adhesion failure after cross-hatch test)

Paint Ref.	Type	7 days at 25°C and 60% RH	AGEING CONDITIONS					
			(a) 7 days 100% RH at 25°C		(b) 24 hrs 100% RH at 43°C		7 days 100% RH at 43°C	
			No drying	48 hrs. drying	No drying	72 hrs. drying	No drying	48 hrs. drying
		(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)
A	Commercial paint	5	5	0	10	5	25	5
B	Commercial paint	5	0	0	5	0	15	5
C	Proprietary emulsion (100% acrylic) AC-34	5	5	5	15	5	50	5
PR/E10	Standard emulsion	10	15	5	15	10	100	20
PR/E6	Imidazole modified emulsion	0	0	0	0	0	20	0

CHAPTER SIX

DISCUSSION AND CONCLUSIONS

DISCUSSION AND CONCLUSIONS

The effect on adhesion to model contaminated surfaces of modification of the skeleton of a thermoplastic acrylic polymer in a model paint has been investigated. The exercise also included modification of polymers in thermosetting and emulsion paints.

The chemical modification was carried out by the application of minor proportions of monomers containing carboxyl groups, tertiary nitrogen, or a combination of both, and silicone.

Thermoplastic acrylic polymer paints

Polymers based on poly n-butylmethacrylate modified with various monomers were fully characterised in terms of molecular weight and molecular weight distribution, features of the infra-red spectra, composition distribution, ultra-violet absorption spectra, densities and the bulk properties via the cohesive energy density.

Surface properties of dried paints and of broken bonds, (in terms of the chemical constitution characterised by the critical surface free energy) were also investigated.

The results of this investigation showed that the adhesion promoting property of carboxyl groups in polymer chains can improve the adhesion of thermoplastic acrylic paint to contaminated surfaces. The beneficial effect of nitrogen groups such as those in 1-viny-2-methylimidazole, dimethylaminoethylmethacrylate, triallylisocyanurate and allylrhodanine on the adhesion of such acrylic paints has also been demonstrated. Glycidyl groups and silane containing monomers showed similar effects.

These groups are also effective in maintaining good adhesion after artificial weathering.

Attempts were made to ascertain the mechanism of improved adhesion.

The data indicated that neither the differences in the chemical constitution of paint surfaces as characterised by the critical surface energy, nor the cohesive energy density (CED) parameters are the factors responsible for the improvement. In the latter case, the level of modification was too small to cause any significant changes in (CED).

There was, however, strong evidence that displacement of the contaminant e.g. stearic acid was produced, particularly by a copolymer of n-butylmethacrylate with 5% molar 1-vinyl-2-methyl imidazole. This evidence was provided by the behaviour of a water drop on the paint film after breaking the adhesive bond. The water drop was very unstable and the contact angle decreased as the absorbed stearic acid molecules turned over.

These findings led to the investigation of the possibilities of a chemical interaction.

Since the modification level of the base polymer was small, detection of such reactions would be difficult, the monomeric form of the modifiers was used.

In the case of polymers carrying a polar group (i.e. -COOH) along the polymer chain, it was shown that the formation of two compounds occurred at a molar ratio of 2.0 stearic acid / 1.0 acrylic acid and 1.0 stearic acid / 4.0 acrylic acid.

It has also been suggested that the improvement in adhesion achieved by the application of nitrogen containing monomers is attributed to and satisfactorily demonstrated by the formation of compounds between modifiers and contaminant. The mechanism of adhesion is therefore shown to be of a chemical bonding nature.

Thermosetting acrylic paints

A thermosetting acrylic polymer of the hydroxyl type was synthesized; it was modified by increasing the acid content and its structure was altered with a minor proportion of 1-vinyl-2-methylimidazole.

In these studies, improved adhesion to contaminated aluminium, galvanised steel and to tin-plate were observed.

Since the phenomenon of poor adhesion associated with the labroatory-prepared hydroxyl-containing thermosetting acrylics cured with butylated or methylated melamine-formaldehyde resins was also apparent with several commercial acrylic resins, the above modification affords a significant contribution towards overcoming this problem.

In addition, highly cross-linked films were obtained with hydroxyl and carboxyl-containing acrylic polymers using 1% p-toluene sulphonic acid as catalyst, and in the absence of the normal amino resin component. For this system the mechanism of the reaction was investigated and it was found that a disproportionation with loss of ehtylene glycol from the hydroxyethylmethacrylate component to form a diester of methacrylic acid <u>in situ</u>. The self-reactive character of this system has not been previously reported.

It was postulated that poor adhesion in some systems was associated with a high level of cross-linking. This may be due to a reduction in polymer chain mobility or stresses produced by excessive film shrinkage. This accords with the observed behaviour of paint films reported by Bullet[105].

Emulsion Polymers

Acrylic type emulsion polymers have been chemically modified by copolymerising with 5% molar acrylic acid or 5% molar 1-vinyl-2-methylimidazole. Paints based on these modified emulsions showed better adhesion to clean aluminium and to hardened alkyd gloss paint surfaces under dry conditions. A feature of the imidazole modified system was the improved and the reduction in intercoat adhesion failure, and the excellent recovery of adhesion after 24 hours drying following water immersion.

Improved intercoat adhesion was also noted with paint modified with acrylic acid applied to hardened alkyd surfaces.

Of a series of wood primers examined, a paint based on the imidazole modified polymer showed greatly improved adhesion over a control paint under dry and wet conditions, as assessed by cross-hatch testing. Results were rather better than two commercial primers examined.

CHAPTER SEVEN

POSSIBLE FUTURE WORK

POSSIBLE FUTURE WORK

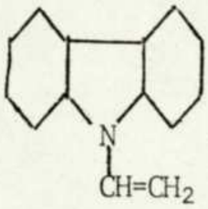
The present work has dealt with the aspect of the effect of chemical modification of polymer structure on adhesion to stearic acid-contaminated aluminium.

The objective of improving adhesion was successfully achieved by using certain nitrogen containing compounds and by the combination of these with carboxyl groups.

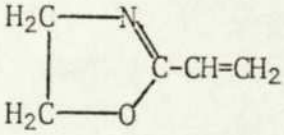
It is suggested that:-

(1) Other vinyl monomers containing nitrogen could be considered e.g.:

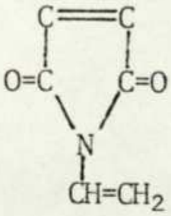
Vinylcarbazole



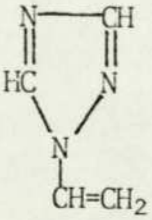
Vinyloxazoline



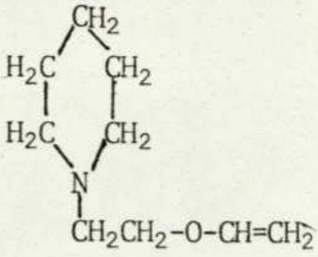
N-vinylsuccinimide



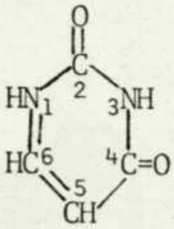
1,2,4 or 1,2,3 Vinyltriazole



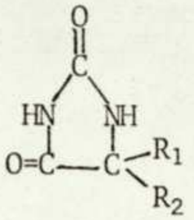
N-(β-Vinyloxyethyl)peperidine



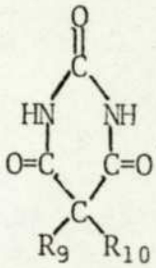
Uracil derivatives (allyl or vinyl)



Hydantoin and its derivatives
where R_1, R_2 are H, or CH_3



Barbituric acid and derivatives
where R_9 and R_{10} are the same or different and represents H, alkyl, alkenyl, phenyl

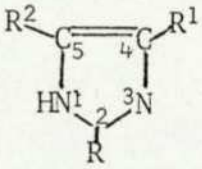


The hydrogen atoms attached to nitrogen are active and can be reacted with other functional groups.

(2) Studies can be extended to examine the long-term effects of the presence of modifiers in the polymer chain on adhesion under various service conditions. Achievement of good initial adhesion may not be as good an indicator of a good paint as the ability to maintain acceptable adhesion during the service life of its films. Possible deterioration of these compounds may occur over a long time and cease to be effective.

(3) Studies of the effect of changes in polymer structure in the mechanical properties of paints and their relation to adhesion in terms of flexibility, glass transition temperature and tensile strength can be made. These parameters are factors involved in explaining other mechanisms of adhesion phenomena.

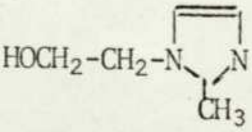
(4) The idea of the application of tertiary nitrogen-containing compounds or other derivatives can be fruitfully utilised into other alternative systems where adhesion failure occurs., e.g. polyesters and alky s. Different polymerisation techniques are envisaged and vary according to the type of resin required. For instance, derivatives of imidazoles can be reacted with appropriate chemical groups in other systems either directly or by the use of intermediates.



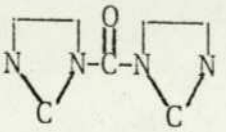
The comprehensive discussion of the imidazole chemistry given by Grimmett and others, the active hydrogen at the 1-position and the variety of the chemical groups which may be substituted at 2,4 and 5 positions, highlight the potential of these compounds.

Amongst these derivatives are:

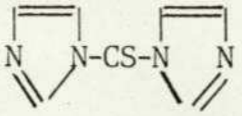
hydroxyethyl-2-methylimidazole



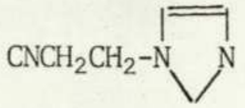
Carbonyldimidazole



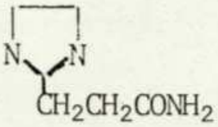
Thiocarbonyldimidazole



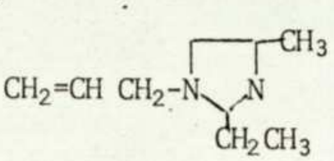
Cyanoethyl-2-methylimidazole



1-(2-Carbamylethyl)imidazole



1-Allyl-2-ethyl-4-methylimidazole

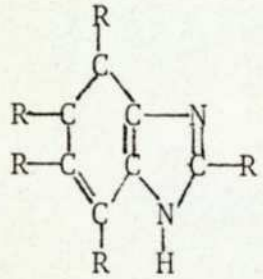


Here, the NH_2, C=O, OH, CS, CN are reactive

Benzimidazoles

Where R is halogen

hydrocarbon radical
(alkyl)



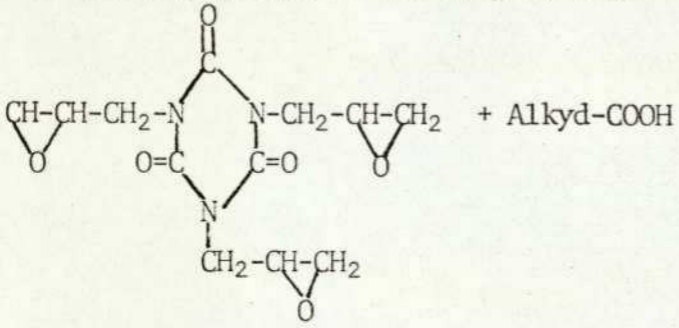
In considering alkyd resins which are basically condensation polymers of a diabasic acid, a monobasic acid and a polyol, i.e. phthalic anhydride (equivalent to dibasic acid), lauric acid, and glycerol produced by heating together to give a polyester with unreacted carboxyl and hydroxyl groups available for futher modification.

The application, say, of the hydroxy group of hydroxy ethyl-2-methylimidazole as a co-condensation compound for the alkyd resin gives a modified alkyd containing the tertiary nitrogen group. As an air-drying alkyd the drying process remains unchanged i.e. by the absorption of oxygen and subsequent reaction with the double bonds in the long chain of the hydrocarbon chain of the fatty acid.

The alkyd resin can also be modified with alkyloxy derivatives of imidazole, i.e.

$$\text{Alkyd-OH} + R'\text{-}CH_2CH_3 \rightarrow \text{Alkyd-O-O-}R'$$

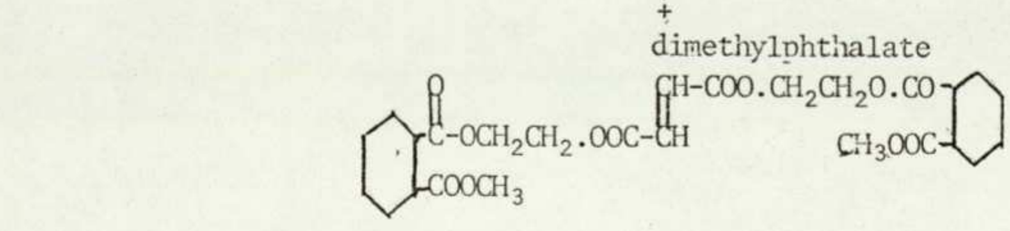
For stoving systems derivatives of isocyanurate, i.e. triglycidylisocyanurate can be used to modify the alkyd resin and using the carboxyl groups of the alkyd and the epoxide group



In polyester resins, which are the reaction products of polyhydric alcohols with polybasic acids, two types of polyesters can be obtained:

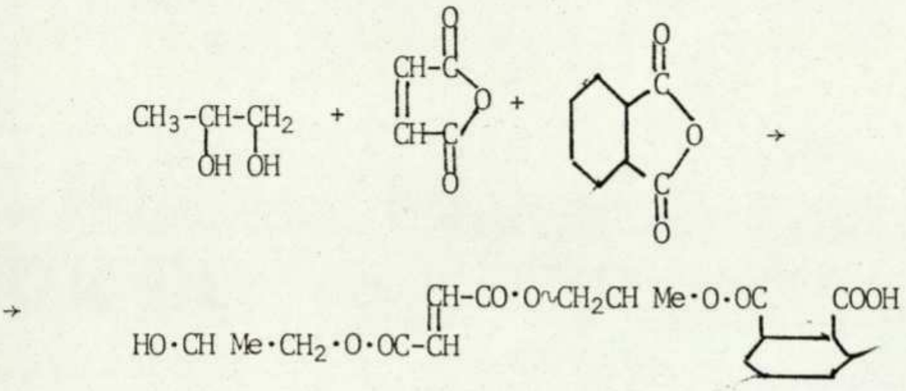
(a) Neutral polyester, an example is:

Propyleneglycol + diethylmaleate ⟶



(b) Unsaturated polyester, an example

Propylene glycol + maleic anhydride + phthalic anhydride →



The vinyl monomers used in this work may be added as solvents and reactive components for cross-linking reactions of polyester systems similar to the usual addition of styrene to these systems. The presence of vinyl monomers acts as stryene for ultra-violet curing systems.

(5) Other contaminants are likely to be present for example, cooking fat on exterior surfaces in a kitchen atmosphere, antifoam agents of the silicone oil which cause intercoat adhesion failure with thermosetting resin paint, and low molecular weight components and antioxidants migrating to the surface of polyolefines which present problems to printing ink manufacturers and the packaging industry.

The chemical nature of these contaminants influence the type of compounds that may be used to displace them. The mode of action is likely to be either by dissolving or dispersing surface contaminants by the application of water soluble versions of tertiary nitrogen containing polymers used as pretreatment washes or as primers.

Cooking fats contain in varying proportion, glycerides (esters) of certain unsaturated carboxylic acids. Silicon oils are long chain polymers usually of dimethyl or methyl phenyl siloxane units. These are incorporated into conventional air-drying or baking finishes and act as pigment grinding and dispersing aids, stops flotation, eliminates flow lines, silking, orange peel effects and pattern effects often found in enamels.

Water soluble versions of nitrogen containing polymers can be made from combination of acid and nitrogen containing monomers in a terpolymer system and with subsequent neutralisation with bases, i.e. ammonia or amines.

(6) Other nitrogen containing monomers of improved adhesion ability shown in thermoplastic polymers should be incorporated in the laboratory prepared thermosetting and emulsion polymers prepared for this work.

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