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Papers from the Eastbourne Conference

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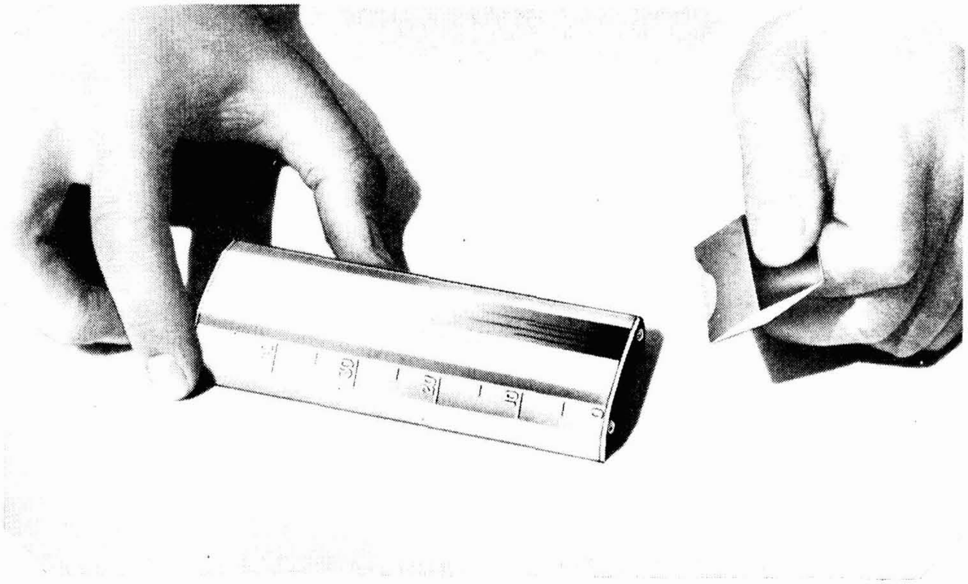

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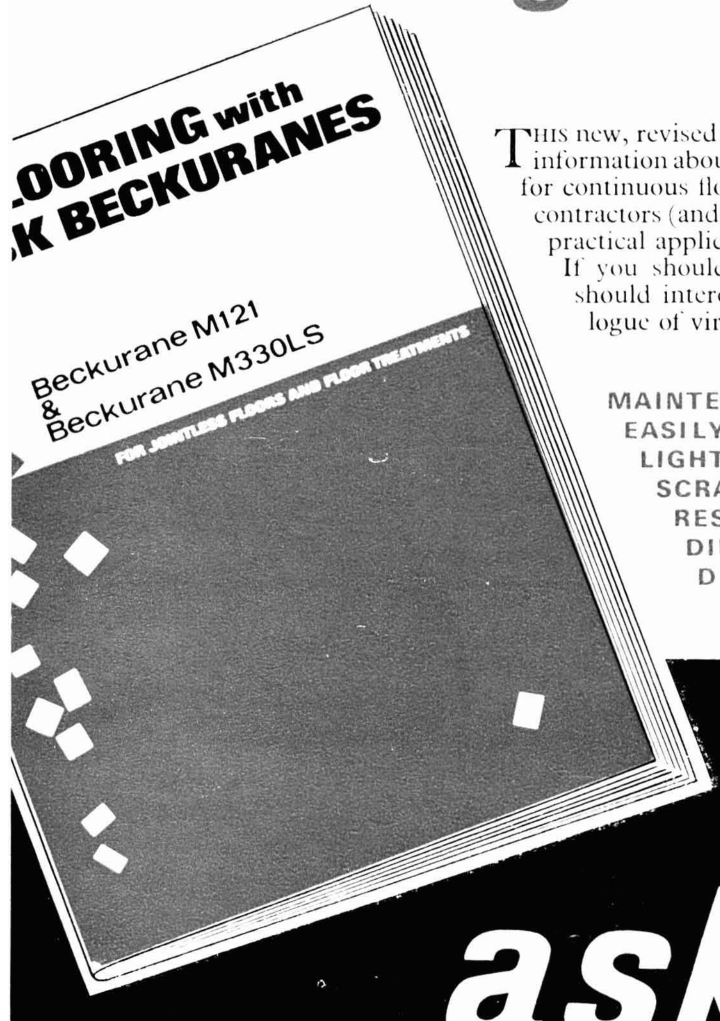

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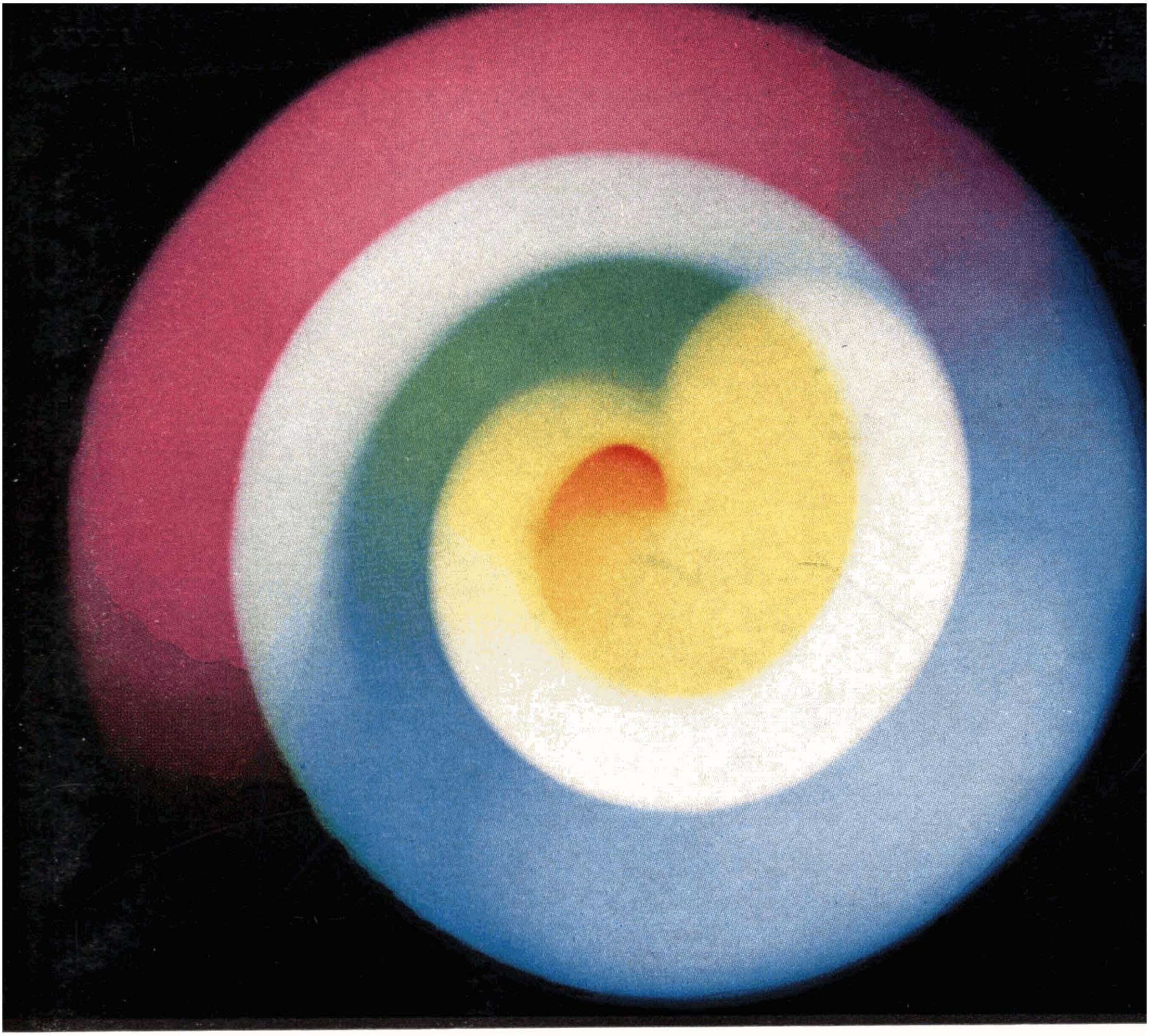

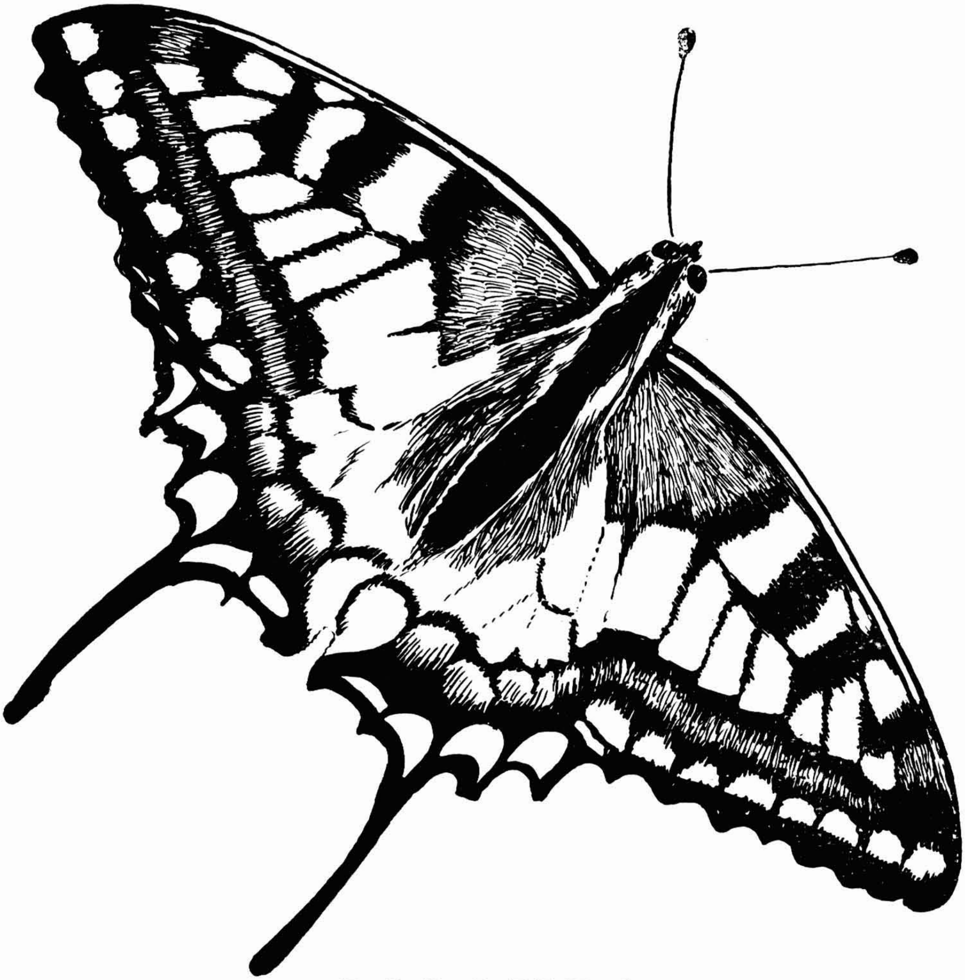

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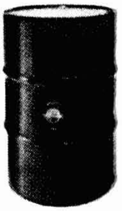

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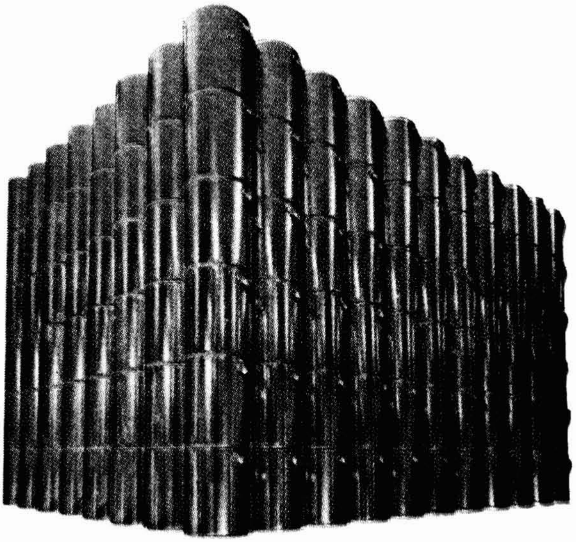

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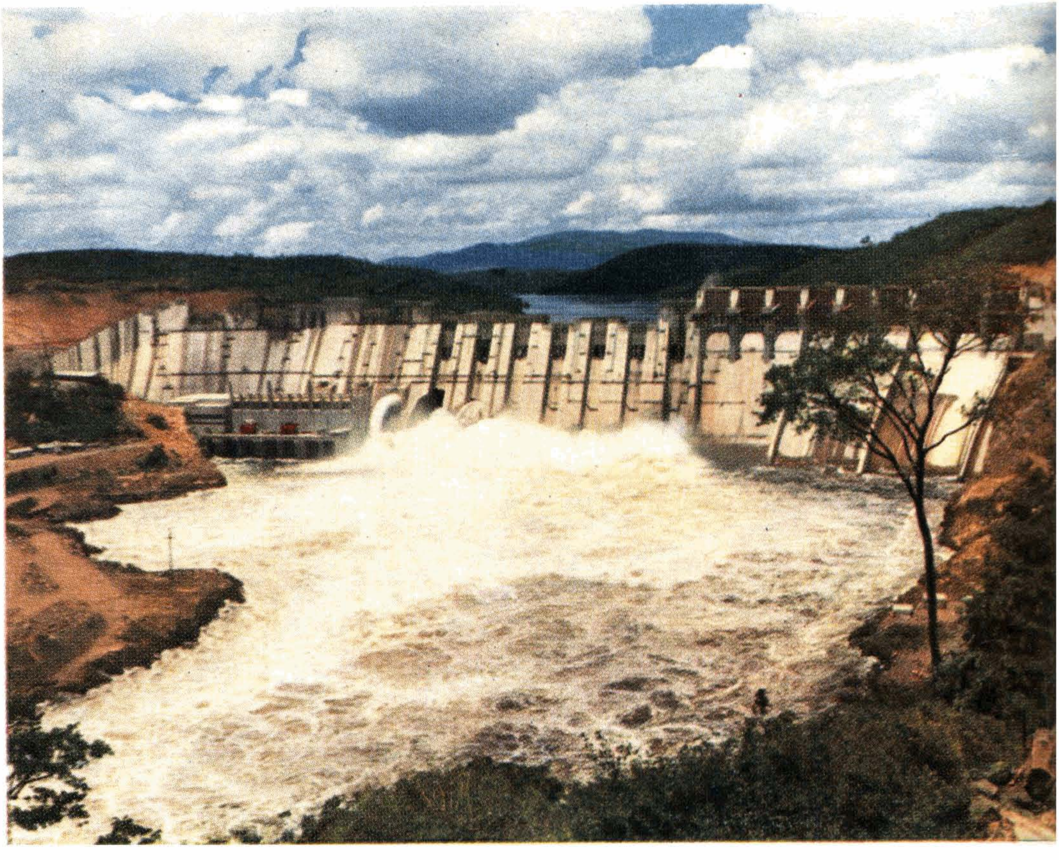

JOURNAL of the OIL AND COLOUR CHEMISTS' ASSOCIATION

Contents **Vol. 52 No. 9** **September 1969**

Transactions and communications

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Film formation and curing

Foreword

The 14th Biennial Conference of the Oil & Colour Chemists' Association was held at Eastbourne in the period 17-21 June 1969.

On this occasion, for the first time, our President was able to welcome the presidents of the principal European and US organisations connected with our technologies, namely Dr P. Castan of FATIPEC, Mr K. Christensen of the Federation of Scandinavian Paint & Varnish Technologists and Mr M. E. Schleicher of the Federation of Societies for Paint Technology. A unique occasion but one it is hoped which will not remain so.

The Technical Sessions, under the Chairmanship of Dr S. H. Bell (Paint Research Station), Dr J. Gaunt (Atomic Energy Authority) and Dr G. de W. Anderson (Paint Research Station), were all well attended and the discussion was active and informed.

The nine papers, three from overseas, covered a variety of concepts, techniques and materials and the authors are to be complimented on their papers and the presentation of their subject matter. The Chairman, at the end of each Session, summarised the matter presented and provided the thread linking the various topics with the Conference theme.

The Workshop Sessions again attracted more applications than the places available and the Convenors, Mr W. E. Moss (The futility of artificial weathering), Mr R. J. P. Nicklin (Surface preparation of steel) and Mr J. A. L. Hawkey (Colour), all reported lively and useful discussion. In all cases the Workshop Sessions had to be terminated while discussion and comment were vigorous and participants could well have said more. No doubt the topics were further debated during subsequent social gatherings. It seems fair to say that the open forum, where comment can be frank and controversial without the possible embarrassment of publication, is attractive to many participants.

"Forward Thinking" and the future pattern of Association activities are still under active review. It is possible that the format of the Conference will change with a new Honorary Research & Development Officer, and a new President and Council, and this is probably desirable for, with changing needs, all activities should be considered for change.

Dr S. H. Bell, Chairman of the first Session and President at the time of the 13th Conference, reiterated the statement he made at Scarborough about the need to "bridge the gap" between the academic and technological needs of our industries and said that the subject matter of the 14th Conference bid fair to contribute to this aim. If those who participated can concur with this belief the 14th Conference was a success but other requirements may supervene at future Conferences. There is little doubt that the Honorary Officers and Council have the "forward look" well in mind.

A. T. S. Rudram,
Hon. Research & Development Officer, 1963-1969.

J. Oil Col. Chem. Assoc. 1969, **52**, 814-829

Transactions and Communications

Keynote address: Physicochemical principles of film formation*

By A. R. H. Tawn

Cray Valley Products Ltd., St. Mary Cray, Kent,
and The Borough Polytechnic, London, SE1

Summary

In a brief introduction, the dimensions of the components of coatings are discussed in relation to film thickness and it is postulated that the polymer matrix itself should not be considered a continuum. Attention is then turned to convertible coatings in particular, and theories of polymer formation in terms of the functionality concept are outlined. Deviations from basic Flory statistics owing to unreal assumptions are discussed in some detail. The final sections deal with the complementary approach in which an ideal Gaussian network is first considered and the properties of real networks are discussed in terms of departures from the idealised structure. Particular attention is drawn to the formation of inhomogeneities in polymer matrices and to the ways in which they may influence film properties.

Key words

Binders—resins etc.
polymer

Processes primarily associated with manufacturing or synthesis
polymerisation

Discours-Thème
Principes physico-chimiques de la formation de feuil

Résumé

Dans une briève introduction, on discute les dimensions des constituants de revêtements filmogènes par rapport à l'épaisseur de feuil, et l'on propose que la matrice polymère, ellemême, ne doit pas être considérée un continu. Puis on fait attention en particulier, aux revêtements durcissables, et l'on établi les grandes lignes de quelques théories de formation polymère au point de vue du concept de fonctionnalité. On discute en quelque détail des déviations, dûes aux assomptions fausses, à partir des statistiques de base, dérivées pas Flory. Les dernières sections du discours se traitent de la technique complémentaire où, d'abord, l'on considère un idéal réseau Gaussien, et puis on discute les caractéristiques des réseaux réels en termes des écarts de la structure ideéalisée. On fait attention particulière à la formation des inhomogénéités dans les matrices polymères et à la manière de leur influence sur les propriétés de feuil.

Richtungsweisender Vortrag: Physikalisch-Chemische Prinzipien der Filmbildung

Zusammenfassung

In kurzen, einleitenden Worten werden die Dimensionen der Komponenten, aus denen Anstrichmittel bestehen, im Vergleich zur Filmdicke besprochen, und die Behauptung aufgestellt, dass die Polimermater selbst nicht als ein Kontinuum zu betrachten sei. Alsdann werden vor allem die härtbaren Anstrichmittel besprochen, und Theorien über die Polymerbildung in der Sprache des Funktionalitätskonzeptes skizziert. Ziemlich ins einzelne gehend werden Abweichungen von grundsätzlichen Flory-Statistiken, weil auf unwirklichen

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*Presented at the Eastbourne Conference, 18 June 1969.

Annahmen beruhend, besprochen. Die Abschnitte am Ende befassen sich mit der zusätzlichen Behandlungsmethode, in welcher zunächst eine ideale Gauss-Vernetzung betrachtet wird, und die wirklichen Vernetzungen besprochen werden, als ob sie von der idealisierten Struktur abwichen. Besonders wird die Aufmerksamkeit auf die Bildung von Ungleichartigkeiten in Polymermatern gelenkt, und wie dadurch die Filmeigenschaften beeinflusst werden können.

Физико-химические принципы образования пленок

Резюме

В кратком введении обсуждаются размеры компонентов покрытий по отношению к толщине пленок и постулируется что матрица самого полимера не должна рассматриваться как континуум. Затем в частности обращено внимание на обратимые покрытия и обсуждаются теории образования полимеров с точки зрения идеи функциональности. Рассматриваются довольно подробно отклонения от основной статистики Флори за счет нереальных предположений. Последняя часть статьи анализирует дополнительный подход, в котором сперва рассматривается идеальная гауссова сеть и затем обсуждаются свойства реальных сетей с точки зрения отклонений от идеализированной структуры. Особое внимание уделяется образованию неоднородностей в полимерных матрицах и их возможному влиянию на свойства пленок.

Introduction

Coatings technology, as it is to be understood throughout this Conference, is distinguished from other polymer technologies by a combination of two essential features. The first is the small thickness of the film relative to its area, and hence a high value of the surface:volume ratio. The second is the liquid-solid transition which must follow the application step—usually as rapidly as possible.

The relevance of film thickness—or rather thinness—is easily seen if one considers some typical dimensions. A typical film thickness might be 25 microns or 25×10^3 nm. The C-C bond is *ca* 0.15nm long, *i.e. ca* 170×10^3 C-C bonds placed end to end span a distance equal to the film thickness. Allowing for contraction due to bond angles, a single polymer chain can easily span the film thickness. Even when the polymer chains are highly coiled or when polymers of rather low molecular weight are considered, a number of molecules of the order of about a hundred is all that may be encountered between one surface of the film and the other. Typical particles of pigments and extenders range in diameter from *ca* 30nm to *ca* 3,000nm, *i.e.* the film thickness considered corresponds to only 8-800 particle diameters. These facts show that the building blocks of which the film is made are of a size which is certainly not so small that the film can be regarded as a continuum.

The concept of structure in films, particularly with regard to the size distribution and disposition of pigment particles, has been discussed by many workers. Discontinuities in the structures formed by the coalescence of emulsion particles have also been extensively studied for many years. In contrast, there has been a tendency to treat as a continuum the polymer matrix deposited from solution, because, notwithstanding the dimensions quoted above, little evidence of phase boundaries has been adduced until recently.

The liquid-solid transition may be achieved by various physical and chemical processes, and the most important permutations have been classified by Talen[1]. It will be sufficient here to emphasise that the objective of the coatings manufacturer is to satisfy ultimately those who will adjudge the coated object. These ultimate users are seldom concerned with how the coating came to be there or what it is made of, as long as it performs satisfactorily and is acceptable in cost. The formulator must therefore ask himself what purpose the coating is to serve, since it is upon this that all other considerations depend.

It may be noted that a rather rigid classification of coatings as convertible and non-convertible has been adopted for many years and from this have developed some rather fixed ideas about what each can do. The teaching of experience is that coherent films are seldom formed from materials having molecular weights below about 5,000 and that, for good mechanical properties and acceptable solvent resistance, many times this figure is commonly needed. One is accustomed to the compromises that must be reached between viscosity, application solids, film weight and mechanical strength in non-convertible coatings. The extra formulating dimension afforded by the convertible coating permits facile avoidance of such compromises. This, however, does not necessarily imply that non-convertible coatings cannot in principle achieve the results commonly associated with cross-linked systems. Such a view was forcibly presented by Reiser[2] in a paper read to the London Section of OCCA in 1963 but unfortunately not published *in extenso*. Some convincing arguments for the use of secondary bonding as the primary source of film cohesion in preference to the covalent cross-links of convertible coatings were presented, and it is interesting to note that recent studies of polymer-solvent interaction suggest that it should be possible to take advantage of oriented adsorption effects at the substrate surface, and even the graded deposition of different species in layers as film formation proceeds.

Gaylord has pointed out the danger of supposing that a polymer having desirable properties in one form, in bulk for example, will necessarily display the same advantages in an adherent film, but it is nonetheless tempting to regard the properties of some highly crystalline polymers, widely used in bulk, as closely approaching those of the ideal film-former for many purposes. The problem, of course, is that of solubility: crystallinity is associated with poor solubility, so polymers like the nylons can only be handled as solutions in a few specialised applications such as wire coating, where powerful and generally unattractive solvents can be tolerated. Some progress has been made in the use of dispersions and powder-coating techniques, but the possibility of depositing an oriented crystalline film from solution, or even of forming such a film *in situ* from materials of low molecular weight, remains an attractive speculation.

At the time of writing, however, it must be recognised that most high performance coatings are based on systems in which the liquid-solid transition is effected by a process of chemical cross-linking. The present Conference is concerned almost exclusively with this method of film formation and the remainder of this paper will therefore be devoted to it.

Polymerisation and the conversion step

The cross-linking process of the conversion step results in the formation of a three-dimensional polymer network of indefinitely high molecular weight in which the species initially present have, to all intents and purposes, lost their individuality. The properties of this network depend, in the first place, on the density of the cross-links, the nature of the chains between the cross-links, and the number and nature of any functional groups remaining unreacted. The network may, moreover, be more or less swollen by the presence of materials of relatively low molecular weight. The problem of designing a film of specified performance is thus, from the polymer viewpoint, a matter of finding the means to produce a particular network structure in a time determined by the curing conditions which are acceptable in the circumstances. This, of course, presupposes a knowledge of the relationship between structure and performance, a far from simple matter which has been discussed by the author elsewhere.[14] The present discussion will be restricted to polymer formation.

Polymer networks may be formed either by the direct interaction of polyfunctional monomers or by the cross-linking of pre-formed, linear or branched, open-chain macromolecules. An intermediate situation occurs when macromolecules are cross-linked through the agency of monomeric co-reactants. Direct polymerisation of monomers to give films is limited to one or two processes which, as yet, are little developed, such as glow discharge[3] and surface photopolymerisation[4]. It may also be found applicable to certain other radiation-induced polymerisation procedures such as electron beam polymerisation *in vacuo*. With the notable exception of linseed oil and its near relatives, now little used alone, the materials applied as wet films are already more or less polymeric, and the curing reaction may be either a continuation of that used in their formation or some further reaction imposed at the conversion stage. It is necessary, therefore, to give some consideration to the formation of open-chain polymers before the synthesis of network structures can be discussed sensibly.

Modern views of polymer formation originated in the concept of functionality, variously attributed to Kienle and Carothers. A discussion of these early ideas and an elementary introduction to functionality theory have been given recently by the present writer[5]. The greater part of current theory is based on Flory's statistical approach to molecular weight distribution, developed for linear polycondensates[6] and extended to branching systems[7]. Valuable reviews which treat the subject in depth are those of Flory[8], Howard[9] and Dusek and Prins[10]. A most useful discussion of recent work, of particular relevance to coatings, is that of Funke[11]. In view of the ready availability of information on basic polymerisation theory, the present discussion will merely highlight certain features which, in the author's experience, have tended to cause difficulty and to lead to misconceptions.

It is important to realise that Flory, like Kienle and Carothers before him, made certain simplifying assumptions which lead to idealised relationships, seldom if ever strictly applicable to real systems. Even today, theories which avoid these assumptions and seek to describe real systems are incompletely developed.

Foremost among the simplifying assumptions is that of equal reactivity of all functional groups of a given kind present in the system, and the corollary that reaction rate constants are independent of degree of polymerisation. This, with the further assumption that intramolecular reaction (ring formation) does not occur, leads to the familiar picture of random intermolecular reaction which gives rise to a "most probable" distribution of species.

It is tempting to suppose that the erstwhile tendency to treat a polymer matrix as a continuum arose through this treatment of polymer formation as a random process. Thus, it is argued that, if the whole macromolecular assemblage has a random structure, no finite volume element can be expected to differ appreciably from any other. The argument is plausibly extended to cross-linked structures, when there emerges the convenient picture of the Gaussian network having a random distribution of chain lengths between cross-links. Now a Gaussian distribution is defined by two parameters, the mean and the standard deviation, so it is not much more difficult to treat theoretically than is a single species. It has formed the basis of extensive theoretical work on the physical properties of gels, and on elasticity in particular. Hence, there is considerable temptation to over-simplify and to forget about inherent assumptions which may be invalid. In reality, of course, departures from Flory's most probable distribution are common even among linear polymers, whilst the ideal Gaussian network is seldom if ever realised.

Linear polymerisation statistics

Even when the basic assumptions are borne in mind, there are other factors which may cause deviations from what may be termed ideal behaviour. It will be recalled that Flory's original distribution functions were derived for linear polycondensates and that, given his assumptions, it was a simple matter to show that the distribution of species, the most probable distribution, depends only on the proportions of ultimate structural units present and on the degree of reaction. Typically, a system comprising equimolar proportions of adipic acid and ethylene glycol at degree of reaction p, has a number distribution function $n_x = p^{x-1}(1 - p)$, a number average degree of polymerisation $\bar{x}_n = 1/(1 - p)$, and a weight average degree of polymerisation $\bar{x}_w = (1 + p)/(1 - p)$, whether prepared by condensation of adipic acid with ethylene glycol, by hydrolysis of a polymer of more advanced degree of reaction, or by ester interchange between a higher and a lower polymer. These results, relating to the most probable distribution, will only be valid, however, if the system at degree of reaction p is in equilibrium. This is most clearly apparent if one considers the polymer formed by ester interchange. Here the only process occurring is one of redistribution: p and $\bar{x}_n$ remain constant, but the value of $\bar{x}_w$ exceeds $(1 + p)/(1 - p)$ at all stages prior to the attainment of equilibrium, and only at equilibrium is n_x given by $p^{x-1}(1 - p)$.

It is intuitively obvious that such an argument will be extensible to branching systems and that many varnish cooking procedures of limited duration will be liable to give non-equilibrium products. The futility of the old arguments concerning the identity or otherwise of a monoglyceride processed alkyd with its fatty acid processed analogue is readily appreciated. The theory predicts that they will be identical only if interchange processes occur with sufficient readiness for the thermodynamic equilibrium state to be attained before the reaction is quenched. It may also be noted that systems which have not reached equilibrium will be thermodynamically unstable. They may remain metastable for years in the absence of a reaction which can proceed under the conditions of storage, but will inevitably go towards the equilibrium state if such a reaction is facilitated, for example, by heat or catalysis. Such matters are more readily appreciated if one considers the alternative approach to distribution functions, based on reaction kinetics and developed by Stockmayer[12]. Here, account is taken of both polycondensation and hydrolysis rate constants and the treatment leads to the same relationships as Flory's *under equilibrium conditions.*

Although derived in the first place for polycondensation, certain of Flory's basic relationships can be extended in certain circumstances to addition polymers[8]. It is necessary to recognise, however, the fundamental distinctions between the two mechanisms. At its simplest, addition polymerisation comprises the three reactions of initiation, propagation and termination. Termination may occur by combination or by disproportionation. Rate of reaction depends on the concentrations of initiating species and monomer. If chain transfer occurs, solvent concentration also becomes important. Making the usual assumption that a steady concentration of free radicals is rapidly attained, one can derive a distribution function for the polymer being formed within an infinitesimally small interval during which conditions, such as monomer concentration, can be defined and considered constant. But monomer concentration is changing throughout conversion, so over a wide conversion range the product will comprise the summation of all such increments, each having a most probable distribution about an average which changes with conversion. Flory[8] has shown that, when nearly all molecules are terminated by chain transfer, the instantaneous expression for $\bar{x}_n$ takes the same form as in linear polycondensation, *i.e.* $1/(1 - p)$; when termination occurs by combination the instantaneous value for $\bar{x}_n$ is given by $2/(1 - p)$. In the more common situation in which both termination processes occur, even the instantaneous value results from the superimposition of two expressions and the difficulty of predicting distributions in the still more complex situation where steady state conditions cannot be assumed, in electron beam curing for example, can well be imagined.

Mention may finally be made of the linear polymer produced by simultaneous growth of all chains under conditions affording equal opportunities for all, and where there is no spontaneous termination step. An example is the polymerisation of ethylene oxide in presence of an alcohol. Here the polymer can be shown[8, 15] to have a very narrow distribution of molecular weights—the Poisson distribution—quite different from the most probable distribution for polycondensates.

It is tempting to conclude that, largely as a result of the prominence of polycondensates as components of coatings systems until comparatively recently, too much attention has been paid by coatings technologists to polycondensation theory at the expense of other mechanisms which require different, or at least modified, treatment. There are ample indications in the literature, moreover, that there has been insufficient awareness of the deviations from ideality which are liable to occur in real systems.

Formation of polymer networks

The theory in branching and gelation in polyfunctional condensation as originally developed by Flory, again assumes equal reactivity of functions and absence of ring formation. A branching coefficient α is defined as the probability that a given branch point is joined directly or via a linear chain to another branch point. Gelation is considered to occur when α exceeds a critical value given by $\alpha_c = 1/(f - 1)$, where f is the functionality of the branch point.

A probabilistic argument leads to an expression relating p and α for the system under consideration, and either can be used to express the size distribution of species present up to the gel point, the degree of reaction at which gelation occurs, the fraction of gel present at any higher degree of reaction, the distribution of species in the sol fraction coexistent with the gel, the cross-link density of the gel, and the fraction of unreacted functions attached to the gel. It is shown that as p and α increase, the degree of branching increases and the molecular weight distribution broadens until $\bar{x}_w$ becomes infinite at α_c and gel suddenly appears while $\bar{x}_n$ is still finite. After the gel point, the gel fraction increases rapidly while the distribution of the coexistent gel fraction undergoes retroversion as larger species are progressively incorporated in the gel. Plots of the weight fraction of x-mers are always asymptotic to zero at large values of x, *i.e. very* large, *almost* infinite species never account for more than an extremely small fraction of the total.

The theory can be readily extended to the formation of gel networks by the cross-linking of pre-formed polymer chains. Provided all chain segments have equal probability of being cross-linked, the picture is much the same; the polyfunctional polymer merely takes the place of the branch unit of the polyfunctional monomer system and has a functionality equal to the number of segments; $f =$ degree of polymerisation of the polymer (x) and $\alpha_c = 1/(x - 1) \simeq 1/x$ for large x. This leads to the well-known principle that, the greater the degree of polymerisation of the reactive polymer, the smaller the extent of the cross-linking reaction needed to produce an infinite network. When all chain segments are not cross-linkable, the simple theory can still be retained by introducing a factor expressing the fraction that are, provided equal reactivity can still be presumed.

It seems likely that the condition of equal reactivity of all functional groups may be fulfilled in many homopolymers and many random copolymers, of the kind encountered in thermosetting acrylics for example. It is clear, however, that this will not always be the case: the fraction of chain units which are cross-linkable may well vary with the molecular weight of the original macromolecules and their distribution may not be random over those molecules. When the parent, open-chain, polymer is produced by copolymerisation, the situation will clearly depend on the proportions in which the monomers are employed and on their reactivity ratios. An obvious case of non-random distribution of functional groups occurs in the styrene-maleic copolymers, where there is a strong tendency for styrene and maleic units to alternate and where, moreover, the carboxyl groups occur in pairs.

Unequal reactivity and ring formation

Deviations from the cross-linking patterns predicted by the basic Flory theory and the generalised treatment of Stockmayer[13] must be expected if, as is usual, the system deviates from the assumed conditions of equal reactivity of functions and absence of ring formation. The simple alkyd based on phthalic anhydride and glycerol is an obvious case in point. The primary and secondary hydroxyls of glycerol are known to exhibit unequal reactivity, and evidence has been adduced that each behaves differently towards the carboxyl groups of fatty and phthalic acids. Whatever may be said about the situation of high degrees of reaction, the use of phthalic anhydride means that the initial formation of the phthalic half-ester will occur at a much higher rate than the esterification of the second phthalic carboxyl, and by a different mechanism. There is also evidence for the occurrence of ring formation in this system: gelation occurs less readily than when isophthalic acid is used, pointing to an apparent difference in functionality reconcilable with the greater ease of ring closure in the orthophthalic system.

Extension of branching coefficient theory to systems containing groups of unequal reactivity is not difficult in principle. It is only necessary to introduce a factor expressing the lower reactivity of one group which can be identified with its lower probability of reaction. This, however, requires a knowledge of the relevant reaction rate constants, which are not always readily accessible. It is not always appreciated how different such rate constants can be. For example, the ratios of the esterification rate constants of methanol and ethanol with a variety of aliphatic acids are in the region of 4-8; for methanol and isobutanol they are in the region of 50-90. The ratio of reactivities of the primary and secondary hydroxyls of glycerol appears to lie somewhere between 2 and 5.

The general theoretical solution has been given by Case[16] whose paper makes it clear that the main problem is that of deducing α_c when a variety of reactants is present, together with the labour of solving the resultant equations when computer facilities are not available. The subsequent treatment of Jonason[17], which has received a certain adulation among alkyd chemists, really adds little to Case's solution and has in fact been severely criticised by Lilley[18]. The general result of using an unsymmetrical reactant is to increase the degree of reaction needed to cause gelation; the higher the degree of asymmetry, the higher the degree of reaction at gelation. The only significant departure from this conclusion occurs with an anhydride, the second (liberated) carboxyl of which reacts more than half as fast as the anhydride.

Application of these ideas to the gelation of addition polymers requires an awareness of, and careful attention to, reaction mechanism and the changes in the reactivity in one double bond which can result from the reaction of another present in the molecule. Two extreme cases can be identified in dienes, (a) when the two double bonds are substantially independent as in 2,11-dodecadiene, and (b) when the reaction of one greatly affects the behaviour of the other as in conjugated systems. Each of these systems can be further classified according to whether or not the two double bonds initially have equal reactivity. Except for the rare cases in which polymerisation of the first double bond leaves the other substantially unreactive, monomers of all these types can lead to branching and cross-linking, but the course of the reaction and the degree of reaction needed for gelation can vary widely. On the one hand, is a monomer like glycol dimethacrylate with a pair of initially identical double bonds which behave independently. Such a monomer may be expected to polymerise in a random manner. On the other hand, is a monomer like chloroprene with unsymmetrical double bonds which are strongly interdependent. Here polymerisation can readily be made to occur in two stages: an isolable and stable linear polymer results from polymerisation through one double bond leaving a second available for a subsequent cross-linking reaction. Intermediate examples are provided by divinyl benzene (symmetrical) and isopropenyl styrene (unsymmetrical), in neither of which do the double bonds behave with complete independence. Sequential reactions differ from random reactions in the degree of reaction needed to yield cross-linked structures, and it is easy to see that, in such situations, markedly different distributions of cross-links may occur. An indication of the level of sophistication needed to treat such systems theoretically is provided by linseed oil which is composed of mixed triglyceride molecules comprising saturated, monoene, diene and triene fatty acids, not necessarily distributed at random. The behaviour of the double bonds in one fatty chain may be independent of the behaviour of those in another, but where more than one double bond is present in a given chain, there is ample evidence of mutual influence, as witness the great difference in rates of oxygen uptake per double bond by oleic, linoleic and linolenic acids. Added to this, is the profusion of chain transfer and other reactions believed to occur during the polymerisation or autoxidation of oils. Such complications and such multiplicity of unknowns make it unlikely that the cross-link pattern of an air-dried oil or alkyd will be predictable in the forseeable future. If one is trying to design a particular network structure, the use of drying oil systems is clearly to be avoided, but this is not to say that means may not be found for characterising the structure once it has been formed.

Intramolecular reaction or ring formation is a problem which, like unequal reactivity, can be treated theoretically, though the approach is somewhat less simple and the mathematics much more abstruse. Long before the theory was developed, it had been realised that ring formation would be favoured by dilution of the system during reaction since intermolecular reaction becomes less probable as concentration falls whereas intramolecular reaction does not. It was also realised that intramolecular reaction would increase the degree of reaction needed for gelation, since each ring formed would consume two functional groups without any increase in molecular weight. Stockmayer and Weil[19], in 1945, demonstrated the effect experimentally in the polyesterification of adipic acid with pentaerythritol and showed that a series of results extrapolated to infinite concentration gave a gel point which agreed to three significant figures with Flory's prediction for no ring formation. It is interesting to note that the concentration referred to here is the concentration of functional groups, non-reactive parts of the molecules being considered as diluent.

The theoretical solution for the case of a bifunctional reaction was propounded by Jacobson and Stockmayer[20] and a brief discussion of this and its extension to polyfunctional systems by Harris[21] and Kilb[22] has been given elsewhere by the author[5]. It will suffice here to observe that, whilst theory accords with experiment in many cases, some puzzling discrepancies still remain. The most recent and apparently satisfactory approach is that of Gordon[23] who uses Good's theory of cascade processes to plot the course of a polyfunctional reaction. This is a powerful method which seems to take satisfactory account of ring formation and unequal reactivity of functions. It also deals adequately with the cross-linking of existing chains and can be extended to polyaddition reactions. Substantial agreement between theory and experiment has been observed for such diverse reactions as those between phosphorus oxychloride and the phosphorous pentoxide lattice, urea and formaldehyde, adipic acid and trimethylol propane, and adipic acid and pentaerythritol.

Polymer network structures

It has already been stated that the Gaussian network has proved to be a convenient model for the development of theories relating cross-link density to physical properties. The approach here is complementary to that so far considered: instead of trying to predict formation of a particular network structure from the nature of the building blocks and their reactions, the behaviour of an idealised network is first deduced theoretically and an attempt is made to reconcile deviations from that behaviour with deviations from the ideal structure. In this presentation, crystalline structures will not be considered, since it is non-crystalline materials which form the main basis of present-day coatings technology. It is to be noted that the term "non-crystalline" is preferable to "amorphous" because one should not overlook the possibility, already indicated, that non-crystalline polymers may contain more local ordering or heterogeneity than is suggested by the familiar felt-like pattern of randomly disposed, randomly coiled and randomly cross-linked chains.

More than one basic type of network structure can readily be envisaged, depending in the first place on the functionality of the branch unit; but how many more depends on what one chooses to define as the branch unit. Unless

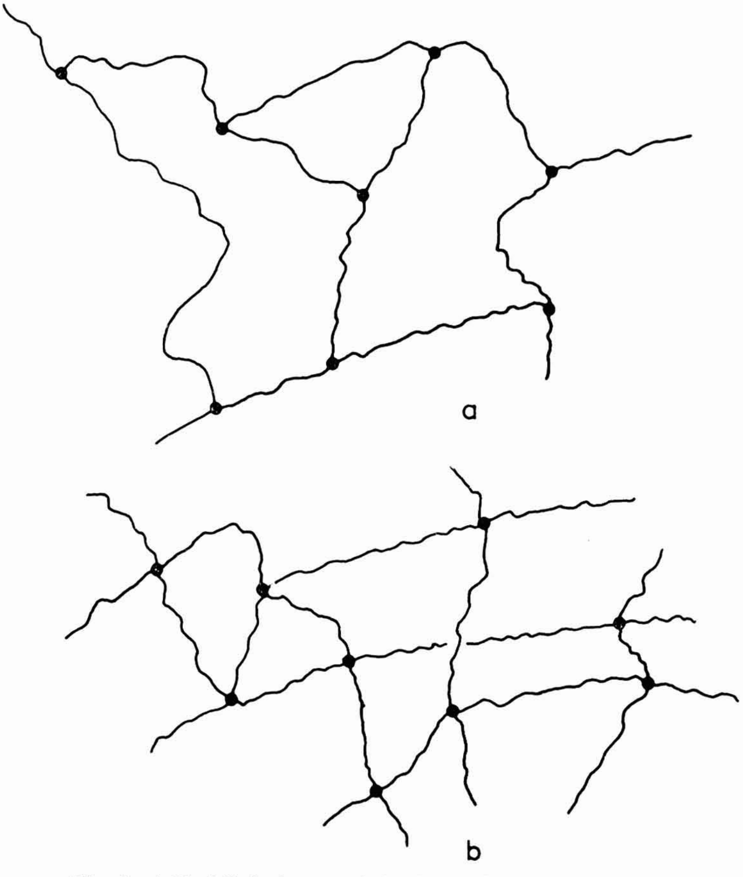

Fig. 1 a) End-linked network b) Cross-linked network branch units of functionality at least three are present, no network will be formed at all. Tri- and tetra-functional branch units lead to networks of the types represented by Figs. 1a and 1b respectively. The former is sometimes called an end-linked structure to distinguish it from the latter, termed cross-linked.

Now consider the structure resulting from reaction of a hexafunctional compound like mannitol or dipentaerythritol (assuming all functions to be equally reactive in intermolecular reaction). Considering the polyol molecule to be the branch unit, one may depict the structure as in Fig. 2a. Looking further into the structure, however, the mannitol and dipentaerythritol based polymers are seen to differ. The mannitol molecule may itself be represented as a series of trifunctional units (Fig. 2b) which would lead to an end-linked network, whilst dipentaerythritol is seen to comprise a union of two tetrafunctional units (Fig. 2c) from which the cross-linked network of Fig. 1b would

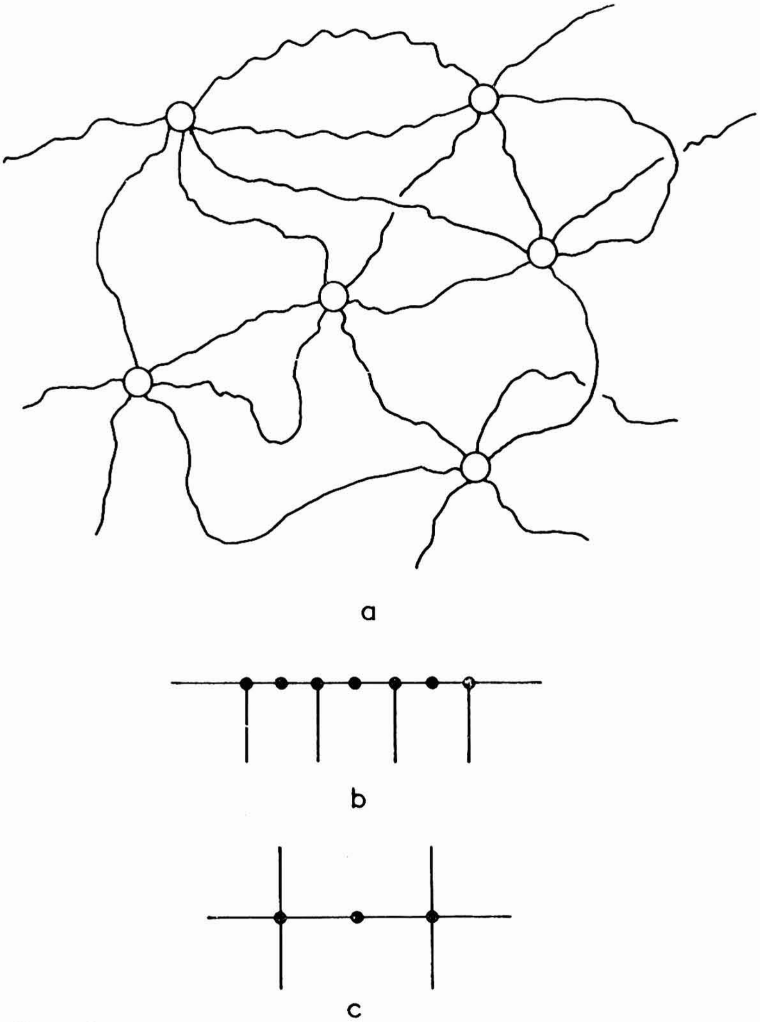

Fig. 2 Theoretical structures of: a) hexamethylene molecule, b) Mannitol molecule, c) Pentaerythritol molecule

result. Thus, unless elements of greater valency than four are present, all networks can be represented as being of type 1a or type 1b or a combination of the two. It may be noted that this necessitates a revision of one's ideas about what constitutes the chains between branch points and hence a modified concept of chain length distribution.

Most of the theoretical work on relating network properties to structures has been done by workers interested in rubbery elasticity who have adopted the type 1b cross-linked structure as an idealised model of vulcanised rubber. Such a model, infinite in extent (i.e. having no free chain ends), and composed of freely orienting chains of random length distribution, is the ideal Gaussian network from which the theoretical approach starts. Since the purpose of this paper is to present concepts rather than detail, the reader is referred to the standard works[8, 10, 24] for an account of such theories. Attention will, instead, be focussed on the ways in which real systems deviate from the idealised picture; it is in this direction that further work is needed if results of value in coatings technology are to be obtained.

Departures from network ideality

Following Dusek and Prins[10], three types of dry network may be depicted, in which the disposition of cross-links may be more or less ordered. In the first, the polymer chains are unstrained and exhibit what may be called their natural degree of coiling. In the second, the chains are more highly coiled ("supercoiled") and the network is compressed. One may imagine such a structure being formed if cross-linking occurred in presence of a diluent and the diluent were subsequently evaporated causing the network to contract. The third type of network would be composed of chains less highly coiled than "normal." Such an expanded network could arise if a normal network were swollen with a liquid monomer which was later polymerised to fix the expanded network in a composite structure.

Deviation from random disposition of cross-links in any of these types of network may arise either through deviations from randomness in the system prior to cross-linking (pre-existing order) being carried forward into the network, or through the occurrence of a cross-linking process which is not itself random. Either may lead to inhomogeneous cross-link distribution in a single phase system or to actual phase separation in the polymer.

An indication has already been given of some ways in which pre-existing order may arise through the non-random formation of open-chain polymers. Whether or not the chain lengths and functional groups of the open-chain polymers are randomly distributed, the disposition in space of the polymer molecules and their segments at the moment of cross-linking may be more or less ordered as a result of secondary forces. Such ordering, which is known to occur both in solution and in bulk, can clearly affect the disposition of the functional groups active in cross-linking and hence the distribution of cross-links.

Extreme examples of ordering through secondary forces occur in solutions of block copolymers. Such a block copolymer would be one of polystyrene and polyoxyethylene in which a long sequence of styrene units is joined to a long series of oxyethylene units. Each half of the block tends to behave like the corresponding homopolymer. Thus, in a good solvent for polystyrene, the polystyrene chains are extended from micelles having polyoxyethylene cores, whilst the reverse occurs in a good solvent for polyoxyethylene. Clearly, different network structures would result if cross-linking could be induced in the two solutions, by gamma irradiation for example. By building functional groups into one or both chains, capable of reaction under more conventional conditions, an obvious route to a structured film is revealed.

Turning to network defects which can arise in the cross-linking process itself, intramolecular loops or rings of the kind already discussed are illustrated in Fig. 3a. Chain entanglements are shown in Fig. 3b. Such entanglements will act as permanent cross-links if they cannot be dispersed in the time span of a deformation process. Separation of an entanglement is clearly impossible if it is tied into the system by permanent cross-links. The other type of network

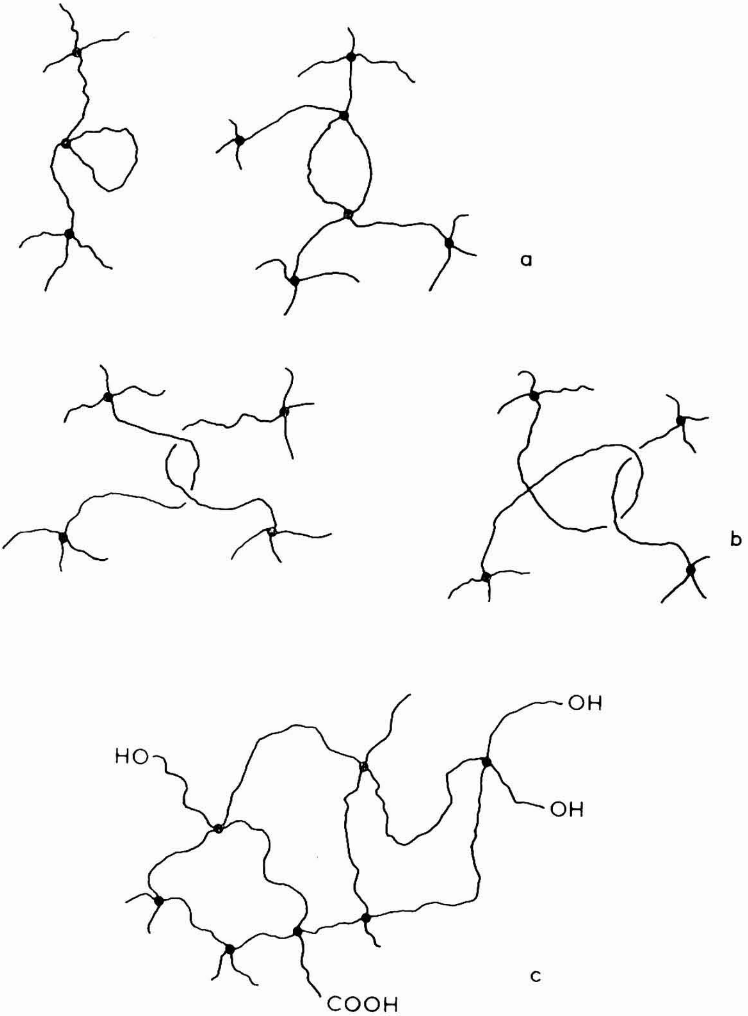

Fig. 3. Network defects: (a) intramolecular loops, (b) chain entanglements, (c) unreacted chain ends

defect, so called only because its existence is contrary to the idealised Gaussian picture, is the unreacted chain end, examples of which are illustrated in Fig. 3c. These are important in elasticity theory because they imply the existence of dangling chains which are not part of the elastically effective network.

The effect of these three types of network defect is extremely difficult to predict when, as is usual, no clear picture of the arrangement of chains is to hand. In general, it is to be expected that the number of such defects and their effect on elastic properties will be minimised by cross-linking primary chains which are long, by carrying the reaction to a high degree in bulk or in concentrated solution, and by creating high cross-link densities. It is at this point that caution is needed in interpreting the results of the theoreticians. The term network defect itself suggests some sort of inferiority in the structure. In fact it merely implies a departure from an idealised structure which has predictable elastic behaviour. It does not necessarily follow that such "defects" affect the properties of coatings adversely; whether they do or not is as yet unknown, and clearly what holds for one property may not hold for another. Ring formation, for example, has been turned to advantage in producing from the alkyd kettle products believed to have high chain length, limited branching, and narrow molecular weight distribution at high degrees of reaction, which dry appreciably faster than conventional alkyds.

Inhomogeneous networks

The cross-linking process can clearly lead to aggregation of network elements and hence to significant variation in the density of cross-links or inter-link segments. A typical inhomogeneous network is shown in Fig. 4.

It has already been seen that cross-linking leads to a size distribution of chains between the cross-links which is broadened when there are great differences in reactivity between the participating functional groups. The more reactive functional group may be expected to be exhausted more rapidly and, if this group is attached to the polyfunctional unit, short chains are formed early in the reaction and long chains later. This leads to an assemblage of densely cross-linked zones separated by areas of low cross-link density. In such a situation free energies of mixing between the zones may become such that phase separation occurs and the gel becomes physically heterogeneous. Such phase separation is generally considered undesirable in coatings because of its association with poor gloss, but it is worth thinking about the great advances now being made in the study of polymer composites. In the modification of rubbers with plastics or of plastics with rubbers, considerable and often valuable changes in properties can be achieved by introducing a second polymeric phase. There seems to be no *a priori* reason why advantage should not be taken of the idea in coatings formulation[14].

Inhomogeneous cross-linking may be particularly readily induced by dilution of the system though, of course, this frequently has technological and economic disadvantages. In the dilute solution, the concentration of polymer segments within an individual polymer coil may be many times greater than the average for the whole system. This leads to a relatively high probability of reaction within the coil leading to regions of high cross-link density. Since polymer-

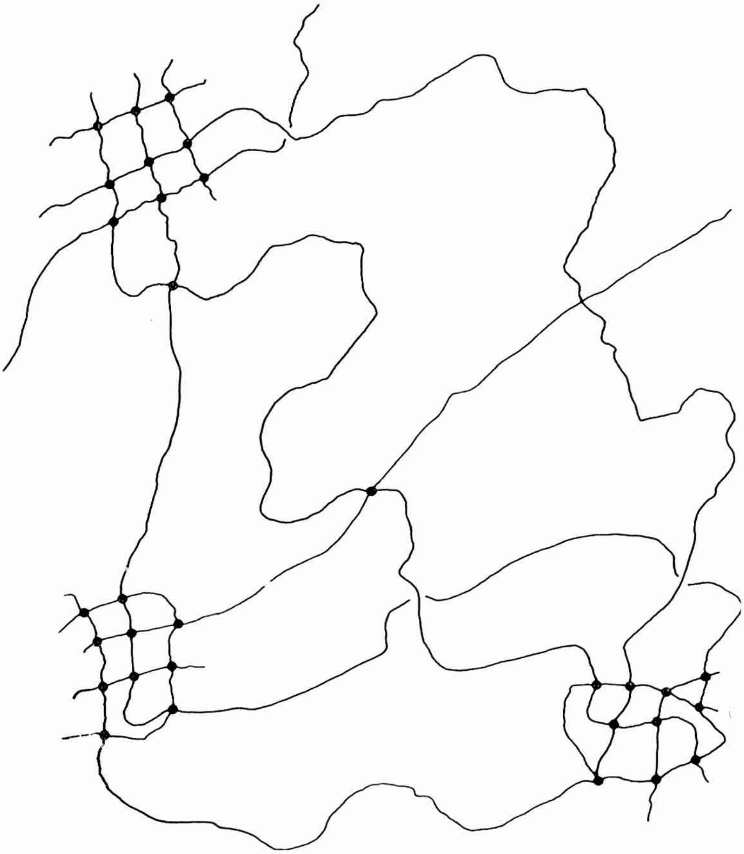

Fig. 4. Inhomogeneous polymer network

solvent interaction affects coil expansion, the nature of the solvent as well as the concentration can affect the cross-link density pattern.

Alkyds processed conventionally to a point just short of gelation appear to contain a dispersed microgel phase. A gelation mechanism comprising formation of such microgel particles and a gradual increase in their number followed by phase inversion has been proposed by Bobalek *et al*[25]. This idea has been pursued by Solomon and Hopwood[26] who have demonstrated the presence of microgel by means of electron microscopy and have related film-forming properties to microgel content.

Finally, it may be noted that cross-linking in presence of a solvent can so affect polymer-solvent interaction that the activity of the solvent within the network may become equal to that of the pure solvent. In this event, syneresis occurs; pure solvent separates and the gel contracts. Should this take place progressively during the cross-linking process, a highly complex network must be expected as cross-links will be introduced at different degrees of swelling. This phenomenon is not uncommon in coatings systems in which, incidentally, unreactive polymer species can play the role of solvent, and continued cross-linking beyond incipient phase separation leads to shrinkage of the network phase. The work of Funke[11, 27] is of the greatest interest in this connection. It has led him to postulate the formation of "networks of networks" which may be porous in the dry or swollen state or in both states, depending on their structure.

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Coatings systems utilising non-equimolar styrene-maleic anhydride copolymers of uniform composition*

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Summary

Styrene and maleic anhydride exhibit such a strong tendency to form a 1:1 alternating copolymer by free radical copolymerisation, that in the literature polymer chemists and technologists have discussed this interpolymer as if it were the only product that can be obtained. However, techniques are known for synthesising copolymers of any combination of these monomers having less than 50 mole per cent maleic anhydride. In addition, the molecular weight can be varied from very low to very high. Analytical data are presented to show how these materials are characterised as to composition, molecular weight, functionality, solubility, compatibility and chemical reactivity. Fractionation studies reveal the degree of composition and molecular weight homogeneity obtained by a given polymerisation method.

Specific low molecular weight resins were investigated for application in solvent borne thermosetting and air-drying coatings. Baked films cured with epoxy resins, amine resins, polyols, etc were tested in the development of a stain resistant, gloss appliance enamel. Among possible air drying vehicles, particular attention was given to invert styrenated alkyds derived from cooking the polymeric polyanhydride copolymer with a polyol and unsaturated oil or fatty acids. Some water thinnable coatings were also synthesised. Thermosetting laminates and styrene-polyester-type curable systems were additional applications studied.

Key words

Types and classes of coating
gloss finish
thermosetting finish

Solvents
acetone
butanol
methyl isobutyl ketone
toluene
xylene

Binders (resins etc)
amine resin
copolymer resin
epoxy resin
maleic resin
styrene resin

Systèmes de revêtements à base des copolymères de styrène et de l'anhydride maléique en proportions non-équimolaires et de composition uniforme

Résumé

Stryrène et l'anhydride maléique démontrent une tendance si forte à former, par copolymérisation aux radicaux libres, un 1:1 copolymère alternant, que dans la littérature les chimistes et technologistes qui s'occupent des polymères, ont discutés cet interpolymère comme s'il est le seul composé qu'on peut produire par cette réaction. Cependant, des techniques existent également pour synthésiser des copolymères de n'importe quoi combinaison de ces monomères à moins de 50 pour cent molaire d'anhydride maléique. En outre on peut faire varier le poids moléculaire de très bas jusqu'a très haut. On présente des données analy-

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tiques qui témoignent les caractéristiques à l'égard de composition, poids moléculaire, fonctionnalité, solubilité, compatabilité, et réactivité chimique. Des études de fractionnement révèlent le degré de l'homogenéité de composition et de poids moléculaire du produit obtenu par une méthode particulière de polymérisation.

On a investigé certaines résines de bas poids moléculaire au point de vue de leur utilisation, en solvants organiques, en tant que revêtements thermo-durcissables ou séchant à l'air. Au cours de la mise au point d'une peinture-émail brillant et anti-tache pour appareils ménagers, on a épreuvé des feuils séchés au four et durcis par des résines époxydes, des résines aminées et des polyols, etc. Parmis les liants possibles séchant à l'air, on avait des attentions particulières pour des résines alkydes styrénées inverties préparées par la cuisson du polyanhydride copolymère avec du polyol et de l'huile ou de l'acide gras non-saturé. On a également synthésisé des revêtements diluable à l'eau. En plus on a étudié des systèmes de stratifiés plastiques thermodurcissables et des systèmes durcissables du type styrène-polyester.

Anstrichsysteme enthaltend Ungleichmolare Styrol-Maleinsäureanhydrid Mischpolymere Gleichartiger Zusammensetzung

Zusammenfassung

Die Neigung von Styrol und Maleinsäureanhydrid 1:1 alternierende Mischpolymere durch freie Radikall-Mischpolymerisation zu bilden ist so stark, dass Polymerchemiker und Technologen dieses Interpolymer in der Literatur so besprochen haben, als ob nur dies allein erhalten werden könne. Indessen sind Methoden bekannt, Mischpolymeren, die weniger als 50 Maleinsäureanhydrid enthalten, aus einer beliebigen Kombination dieser Monomeren herzustellen. Ausserdem kann das Molekulargewicht von sehr niedrig zu sehr hoch variiert werden. Analytische Werte werden vorgelegt, um aufzuzeigen, was für diese Produkte hinsichtlich Zusammensetzung, Molekulargewicht, Funktion, Löslichkeit, Verträglichkeit und chemischen Reaktionsvermögens charakteristisch ist. Fraktionierungsstudien bringen die Proportionen und die Homogenität des Molekulargewichts für eine feststehende Polymerisierungsmethode zu Tage.

Harze mit spezifisch niedrigen Molekulargewichten wurden auf ihre Eignung als wärmehärtbare und lufttrocknende Anstrichstoffe auf Lösungsmittelbasis untersucht.

Ofentrocknende, mit Epoxidharzen, Aminoharzen, Polyalkoholen usw. vernetzte Filme werden auf ihre Eignung als fleckenfeste Glanzemaillen für Haushaltgeräte geprüft. Unter den möglichen lufttrocknenden Bindemitteln wurde besondere Beachtung den invers styrolisierten Alkydharzen, die durch Kochen des polymeren Polyanhydrid-Mischpolymers mit Polyalkohol und ungesättigtem Öl oder Fettsäuren erhalten wurden, geschenkt. Ebenfalls wurden einige mit Wasser verdünnbare Anstrichmittel synthetisch dargestellt. Zusätzlich wurden Anwendungsmöglichkeiten für wärmehärtbare Lamellengefüge und vernetzbare Styrol-Polyestertyp-Systeme geprüft.

Системы покрытий применяющие неэквимолярные стирено-малеиновые ангидридные сополимеры однородного состава

Резюме

Стиреновые и малеиновые ангидриды проявляют настолько сильную тенденцию к образованию переменного сополимера в отношении 1 : 1 путем свободной радикальной сополимеризации, что в литературе полимерные химики и технологи рассматривали этот сополимер точно он является единственным возможным продуктом. Однако известны технические приемы для синтезирования сополимеров состоящих из любой комбинации этих мономеров, включающих менее 50-ти молей процентов малеинового ангидрида. Кроме того молекулярный вес может быть изменен от весьма низких до весьма высоких значений. Прилагаются аналитические данные дающие характеризацию этих материалов с точки зрения состава, молекулярного веса, функциональности, растворимости, совместимости и химической реактивности. Исследование фракционирования обнаруживает степень однородности состава и молекулярного веса полученной данным методом полимеризации.

Изучались специфические смолы низкого молекулярного веса для применения в растворенных, термореактивных, высыхающих на воздухе покрытиях. Высушенные пленки, термообработанные с эпоксидными и аминовыми смолами, полиолами и т. д., испытывались при развитии глянцевитой эмали стойкой против загрязнения. Среди возможных высыхающих на воздухе растворителей, особое внимание было уделено инвертированным стиреновым алкидам, полученным путем варки полимерного полиангидридного сополимера с полиолом и ненасыщенными масловыми или жирными кислотами. Синтезировались также некоторые покрытия разбавляемые в воде. В качестве добавочных применений, изучались также термореактивные слои и высыхающие системы стирено-полиэфирного типа.

Introduction

In 1965 the authors, together with several colleagues, published three papers in the *Official Digest*[1,2,3] detailing the use of homogeneous non-equimolar styrene-maleic anhydride copolymers in thermosetting coatings, invert styrenated alkyds (formed by alkyd formation on a polystyrene backbone) and electrical laminates. The present contribution is offered as a partial review of this earlier work, but will include a more extensive elucidation of the nature of the copolymers and their properties, with some further developments in coatings applications.

Copolymerisation

Most polymer chemists are familiar with the strong tendency for styrene (S) and maleic anhydride (MA) to form an alternating copolymer, so much so that this interpolymer has often been reported in the literature to be the only obtainable product. From published reactivity ratios summarised in Table 1 it is evident that the maleic free radical on the end of a growing chain never reacts with maleic monomers ($r_2 = 0$), and a chain with a styrene radical on the end will seldom react with styrene monomer unless a very high concentration of styrene is present. This is illustrated in Fig. 1, which is a plot of instantaneous monomer-polymer composition for high styrene-maleic anhydride ratios[2]. The plotted points are based upon analysis of monomer and copolymer present in

Table 1

Reactivity ratios[4] of styrene (M_1) with maleic and fumaric monomers (M_2)

r_1	M_2	r_2	T, °C
0.01	Maleic anhydride	0	60
0.042±0.008	Maleic anhydride	0	80
0.02	Maleic anhydride	0	60
0.097±0.002	Maleic anhydride	0±0.002	50
0.040	Maleic anhydride	0.015	50
0.019	Maleic anhydride	0	50
0.18±0.1	Ethyl acid fumarate	0.25±0.10	60
0.13±0.01	Ethyl acid maleate	0.035±0.01	60

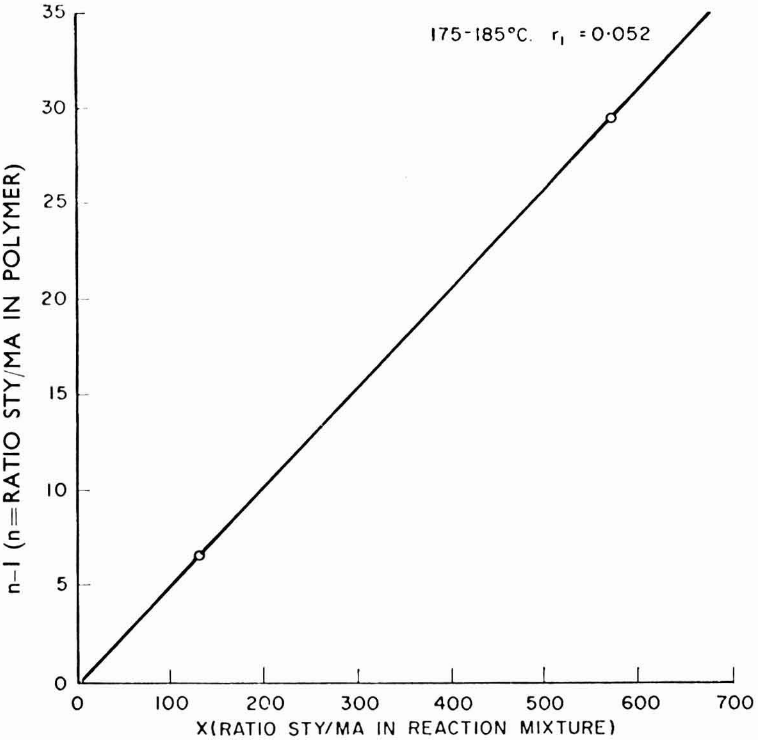
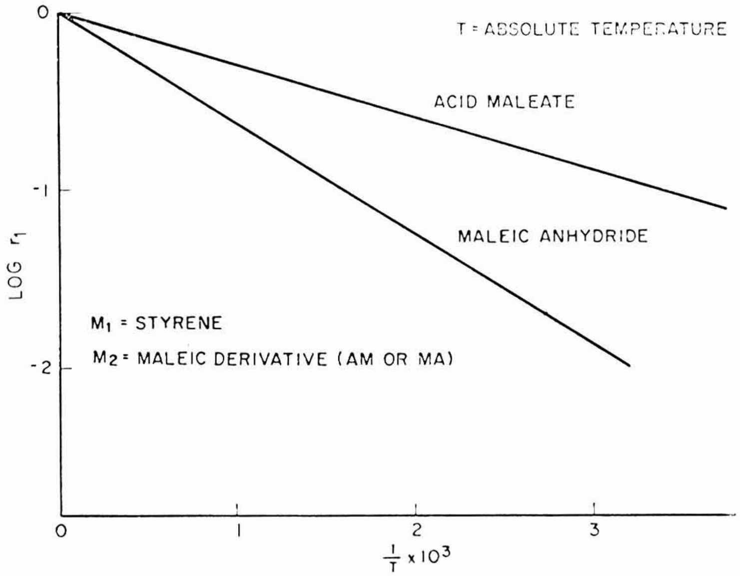


Fig. 1. Instantaneous monomer-polymer ratios for different reaction mixtures

a coil or single loop reactor with a pump to circulate the contents, operated with continuous monomer feed and monomer-polymer displacement until steady state conditions were achieved[5,24]. The slope of the line should be a measure of r_1 which was determined to be 0.052 for the reaction temperature 175-185°C. The higher value of r_1 is due primarily to the high temperature. Fig. 2 shows the effect of temperature on r_1 for maleic copolymers with styrene.

In order to produce a copolymer containing, say, 15 mole per cent MA, the ratio, n, of polymerised S to MA is 85/15 or 5.67 and $n - 1 = 4.67$. Using the curve in Fig. 1 the corresponding value of x, the ratio of S to MA monomer, is 90, which means that the monomer composition must be maintained at 1.1 mole per cent MA during the polymerisation in order to produce the 15 per cent copolymer. Obviously, any deviation in the monomer composition will produce a proportionate change in copolymer composition.

Various techniques have been described[5-11,24] for making non-equimolar styrene-maleic anhydride copolymers, but not all of the methods can be relied upon consistently to produce homogeneous copolymers having a narrow composition distribution. Gross inhomogeneity can be detected by cloudiness or haze in a cast or pressed film. Solubility tests can also reveal poor composition homogeneity. More elegant techniques are fractionation, gel permeation, chromatography, light scattering and ultracentrifugation[12].



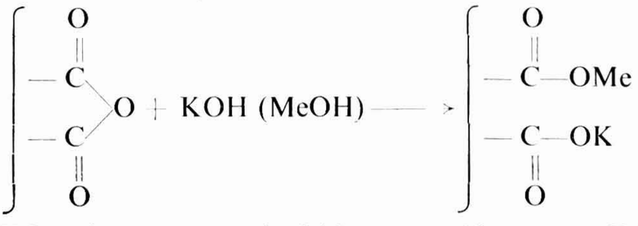
$$r_1 = \frac{k_{11}}{k_{12}} \qquad r_2 = \frac{k_{22}}{k_{21}}$$

$$r_2 \simeq O$$

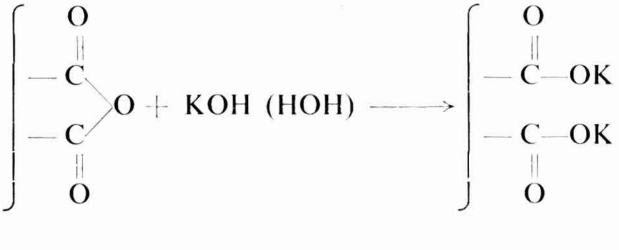
Fig. 2. Relation between r_1 and temperature

Fractionation by composition and molecular weight

Before discussing the topic of polymer distribution, the technique used for determining composition in styrene-maleic copolymers should be reviewed. The most accurate way to analyse for maleic anhydride content of a copolymer is by simple base titration in pyridine, which will dissolve the entire range of copolymer compositions and gives a sharp endpoint with thymol blue (pyridine solution). For best results, the pyridine should be dried (for example, with Drierite). The standard reagent is 0.1N KOH in anhydrous methanol. With this reagent the stoichiometry is 1:1,



that is, one KOH titrates one anhydride group. If aqueous KOH is used the reaction requires two moles of KOH to titrate one anhydride group.



By titrating a sample of polymer with methanolic KOH and then with aqueous KOH, it is possible to differentiate between maleic anhydride and maleic acid in a sample.

Half-esters can be titrated with either reagent, but the titration must be done quickly since the end point fades due to hydrolysis. The double titration above also permits analysis of a sample for both half-ester and anhydride content.

Fractionation is probably the most fundamental way to investigate a polymer and, in the case of a copolymer, fractionation will generally involve both molecular weight and composition separation. Litmanovich and Topchiev[13] have shown that, in fractionation, a polymer of length r and composition α is distributed according to the equation

$$v'_{r,\ \alpha}/v_{r,\ \alpha} = \exp\left[r(\sigma + K\alpha)\right] \tag{1}$$

where v' and v are the volume fractions in the concentrated and dilute phases. Fractionation by composition is dependent on the size of K, which they give as

$$K = (v' - v)\ (\chi_A - \chi_B) \tag{2}$$

where χ_A and χ_B are the interaction parameters of the solvent with links A and B. Then the larger the value of K, the more sensitive is the fractionation to the composition α.

The solubility parameter, δ, of the solvent relative to the δ of the individual links is a gross measure of the interaction parameters χ_A and χ_B. In most fractionations where there is a solvent and a non-solvent (as distinct from those fractionations made by cooling a solvent), the solubility parameter, and hence K, changes during the fractionation.

Litmanovich and Topchiev[13] calculate the effect of K on the distribution curves of copolymers, but maintain a *constant* K in any given fractionation. This is quite different from the situation where K changes during the fractionation. This latter corresponds to the fractionation of S/MMA by Kudryavtseva, Litmanovich, *et al.*[14]. They fractionated this copolymer in two solvent/non-solvent systems and obtained two strikingly different distributions.

In one of our earlier publications[2] the fractionation of a 12.0 per cent MA copolymer having a solution viscosity (10 per cent in methyl ethyl ketone (MEK)) of 0.820cps at 25°C was described. The sample (30g) was dissolved in toluene (270g) and precipitated with Skellysolve, bp 96-99°C. Table 2 summarises the results along with similar data for a 10.25 per cent MA sample of 1.42cps and a 5.89 per cent MA copolymer having 1.27cps solution viscosity. These copolymers were all made by a continuous polymerisation process as described in ref. (6). Inspection of the maleic anhydride content and the solution viscosity of the fractions indicates that the copolymers were fractionated by both composition and molecular weight.

Since the solubility parameter, δ, of the solvent pair decreased as fractionation proceeded, the higher maleic copolymers came down first. These copolymer samples were relatively uniform in composition, the maleic anhydride per cent falling in a range of less than about 5 per cent for roughly 90 per cent of the sample.

By contrast, a cloudy copolymer sample obtained under non-steady-state conditions in a continuous coil copolymerisation was fractionated and, in this

Table 2

Fractionation of copolymer dissolved in toluene using "Skellysolve"

Sample I 12.0% MA; 0.820cps 30g Sample; 0.5% Volatiles 270g Toluene

Fraction	"Skellysolve," ml	Weight, g	% MA	Visc, cps
1	330	6.25	13.4	1.09
2	390	7.62	12.3	0.951
3	450	2.26	11.6	0.858
4	510	1.73	11.3	—
5	690	2.78	11.0	0.778
6	1100	1.22	10.6	—
7	Residue	6.44	11.2	0.564
		28.30		

Sample II 10.25% MA; 1.42cps 50g Sample; 2.1% Volatiles 250g Toluene

Fraction	"Skellysolve," ml	Weight, g	% MA	Visc, cps
1	175	10.90	10.90	1.86
2	25	16.65	10.9	1.70
3	50	10.62	10.1	1.42
4	150	5.80	8.75	1.08
5	500	1.34	7.71	—
6	Residue	1.98	16.6	—
		47.29		

Sample III 5.89% MA; 1.27cps 50g Sample; 0.6% Volatiles 250g Toluene

Fraction	"Skellysolve," ml	Weight, g	% MA	Visc, cps
1	275	14.56	5.87	2.30
2	25	14.57	5.52	1.98
3	50	9.82	4.72	1.58
4	150	3.61	4.14	1.20
5	500	2.32	3.22	0.846
6	Residue	2.37	8.92	0.594
		47.25		

instance (Table 2A), a considerably wider range of maleic anhydride compositions was obtained in the fractions.

Table 2A

Sample IV 10.01% MA; 1.48 cps 50 g Sample 300g Toluene

Fraction	"Skellysolve," ml	Weight, g	% MA	Visc, cps
1	150	3.25	16.3	2.09
2	50	23.30	13.3	1.83
3	50	3.37	7.59	1.43
4	100	8.10	6.21	1.25
5	200	4.05	3.91	1.03
6	600	3.40	3.28	0.843
7	Residue	3.08	9.90	0.558
		48.55		

For copolymers of higher maleic anhydride content, methyl isobutyl ketone (MIBK) was used for the solvent. Fig. 3 shows the results of fractionating two copolymer samples prepared by different polymerisation methods. Sample V was made by the continuous technique[6] and Sample VI by the batch method of reference 9. In this instance the batch method did not produce as homogeneous a product as the continuous method.

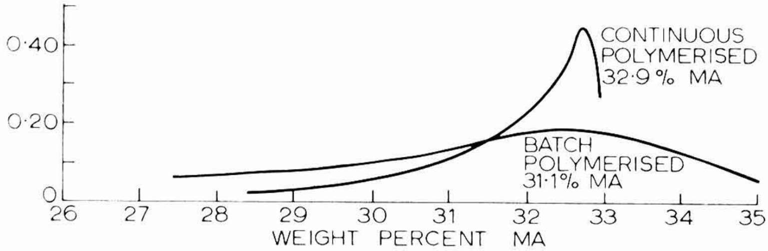


Fig. 3. Fractionation of two samples prepared by different polymerisation methods

Fig. 4 shows the cumulative composition distributions of three S/MA copolymers prepared by different procedures. All three were made starting with methyl acid maleate (MAM), which was converted to MA during or after polymerisation.

(1) In this case, the styrene and catalyst were fed to a solution of MAM. The average per cent MA was 12.5, but there was a sizeable amount of high-maleic copolymer as well as polystyrene in the sample.

(2) Catalyst, styrene, and MAM were fed slowly to heated solvent. The polymer contained 15.0 per cent MA with a very narrow range of composition.

(3) Catalyst, styrene, MAM, and MA were fed together to heated solvent. The average per cent MA was 14.8, but the composition distribution is broader than case 2.

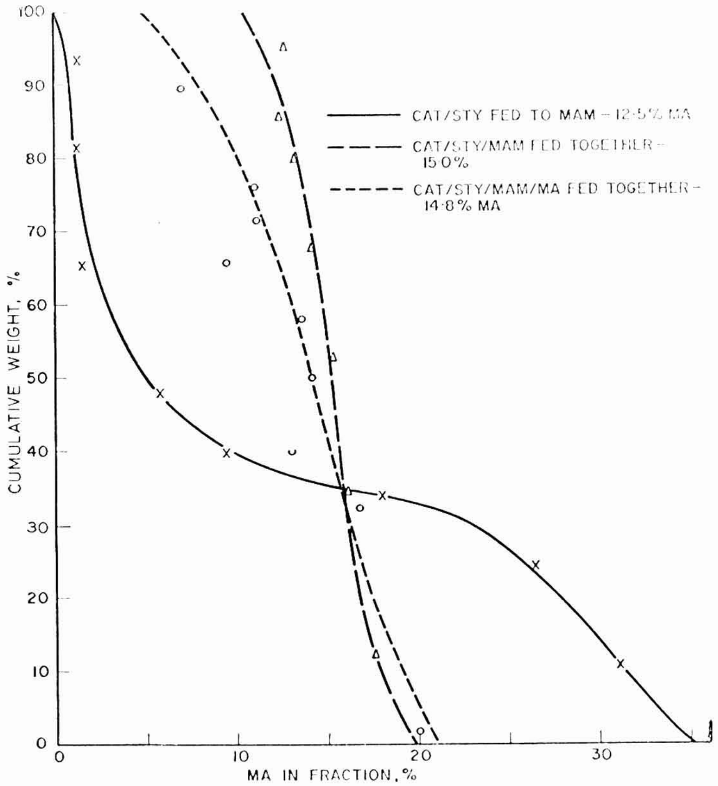


Fig. 4. Cumulative composition distributions of three S/MA copolymers

In another fractionation experiment, a polymer (made by the continuous polymerisation process[6]) containing about 10 per cent MA of moderate molecular weight was chosen. It was hydrolysed to the maleic acid (MA_2) form since it was felt that this would produce a cleaner fractionation. The polymer was dissolved in tetrahydrofuran (THF) and an equivalent amount of aqueous NaOH was added. The polymer salt was precipitated in water containing HCl and dried. It was then redissolved in THF, centrifuged to remove NaCl, reprecipitated in water containing a small amount of HCl, and dried.

This sample was fractionated in the first three different solvent systems shown in Table 3. Notice that in each system the solvent is more volatile than the non-solvent. The solvent was pumped off slowly (while holding the solution at constant temperature) until the solution was sufficiently turbid. The fraction was then allowed to settle and was withdrawn.

The fractions were dried at 40°C to preserve the MA_2 intact for titration. Then each fraction was heated for one hour at 180°C under vacuum to regenerate MA and cooled under vacuum. Intrinsic viscosities were determined in MEK at

Table 3

Solvent systems for fractionating S/MA

Solvent	Non-solvent	Initial Conditions
THF $\delta = 9.32$	HOH $\delta = 23.47$	~100g polymer 4000g THF 700g HOH
THF $\delta = 9.32$	α-pinene $\delta \leqslant 8.5$	~100g polymer 2000g THF 2800g α-pinene
acetone $\delta = 9.76$ av.	*t*-butanol $\delta = 10.47$ av.	~100g polymer 4300ml acetone 1350ml *t*-butanol
THF $\delta = 9.32$	HOH $\delta = 23.47$	100g polymer 4260g THF 950g HOH

25.1°C in dilution viscometers. Some $\overline{M}_n$ were measured in MEK using a Mechrolab automatic membrane osmometer; others were determined in toluene using a Hallikainen automatic membrane osmometer.

A surprising result emerged from the fractionation in acetone/*t*-BuOH. Ordinarily it is difficult to force *t*-BuOH to react with maleic anhydride in a copolymer, so it was felt there would be little reaction with maleic acid. However, the long exposure of the polymer to the solvent apparently did produce reaction which caused poor titration results. Therefore, this series was titrated for MA after heat *in vacuo* to convert MA_2 to MA, however the results were then reconverted to MA_2. It should be borne in mind that the other fractions were titrated while in the MA_2 form, but that $[\eta]$ and $\overline{M}_n$ were determined only on samples that had been heated and were in the MA form.

Fig. 5 shows the cumulative weight average per cent vs. per cent MA_2 for the three fractionations. Fig. 6 shows the differential curves. The following conclusions can be drawn.

(1) In the fractionation in THF/HOH, δ increases as fractionation proceeds (THF is removed) so fractions with higher MA_2 should come down last. This was the case. The distribution curve indicates that there may be a sizeable high MA_2 portion in the sample.

(2) In the fractionation in THF/α-pinene, δ decreases as fractionation proceeds (THF is removed), so fractions with higher MA_2 should come down *first*. This also was the case. The peak in the distribution curve comes between 9 and 10 per cent MA_2, but the curve shows sizeable low and high MA_2 tails.

(3) In the fractionation in acetone/*t*-BuOH, δ increases slightly during fractionation (acetone is removed), so samples higher in MA_2 should come down last. It was hoped that all fractions would have nearly the same composition. The change in δ is enhanced in part by the greater H-bonding capacity of the *t*-BuOH, otherwise there might have been even less spread in the composition. Nevertheless the bulk of the polymer falls between 9 and 10 per cent MA_2 with very little high or low tail.

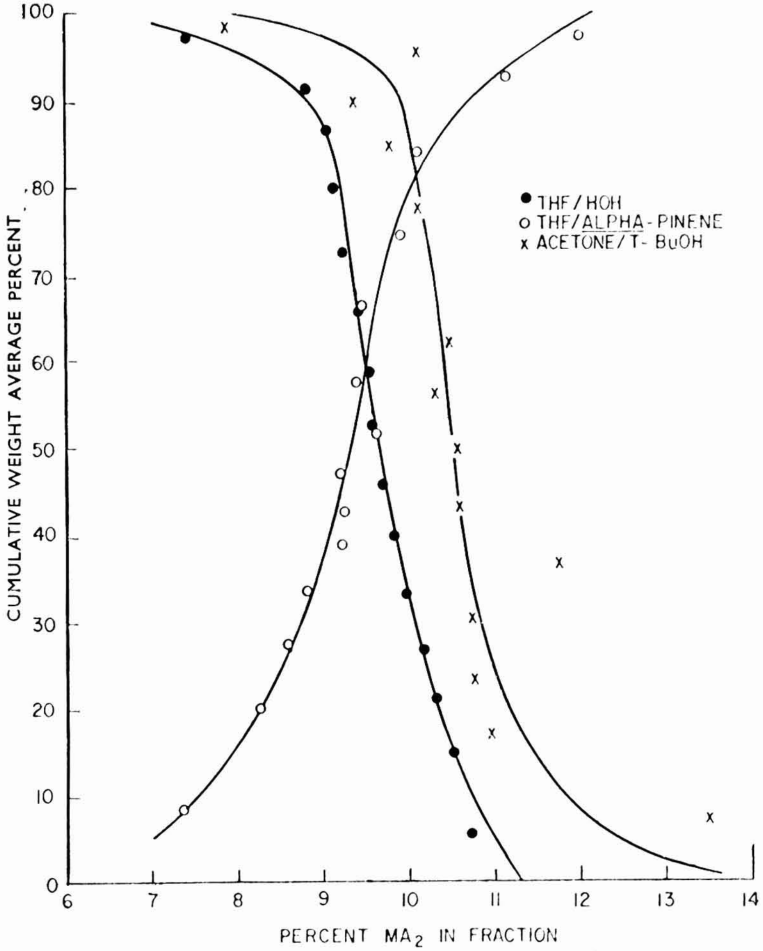


Fig. 5. Fractionation of S/MA copolymer with three solvent/non-solvent mixtures

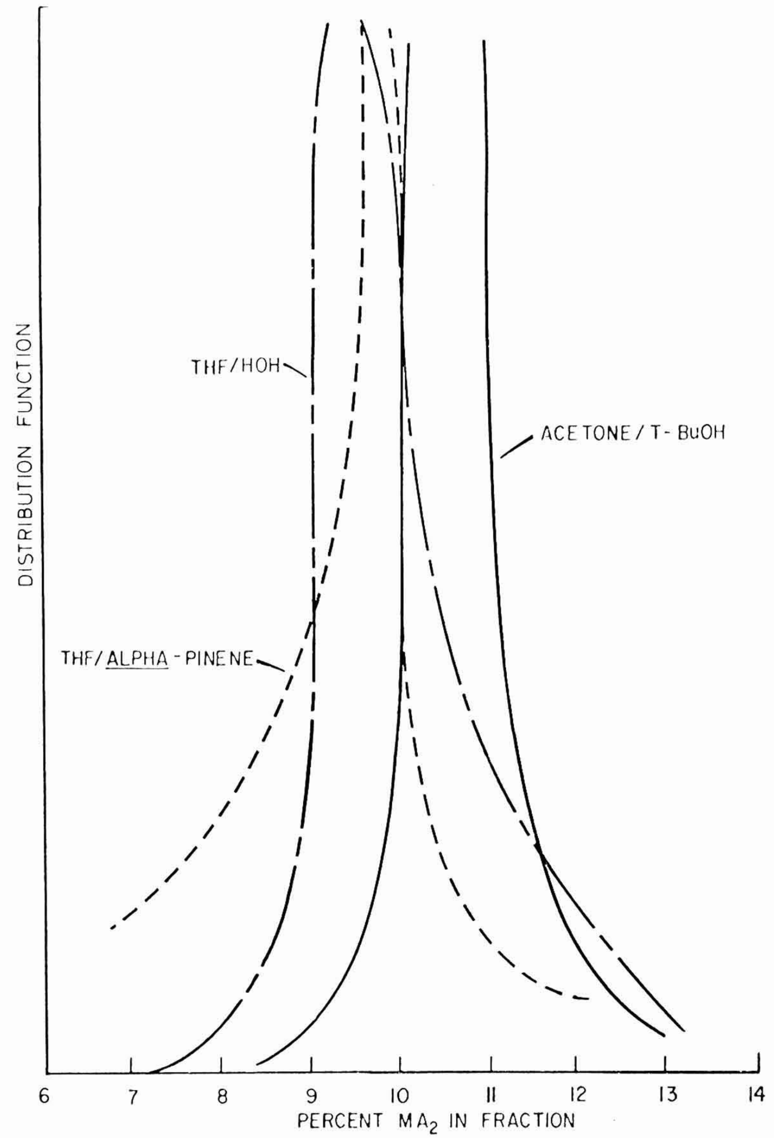


Fig. 6. Differential curves for fractionation of S/MA copolymer with three solvent/non-solvent mixtures

Considering all three distribution curves, most of the copolymer sample seems to fall within about a 2 per cent composition range: 8.5 to 10.5 per cent MA_2.

A low molecular weight sample having the same MA composition as the higher molecular weight sample was also fractionated. The procedure was the same, except that only one solvent system was used (foot of table 3).

Fig. 7 shows the molecular weight *vs* intrinsic viscosity for all fractions from both polymer samples. They produce one line covering $[\eta]$ from 0.07 to 0.7

dlg^{-1} although the MA compositions ranged from 7 to 13 per cent MA. Hence it seems safe to conclude that the intrinsic viscosity of S/MA in MEK is not materially affected by the per cent MA in the range of about 5-15 per cent. This is quite useful from a practical standpoint.

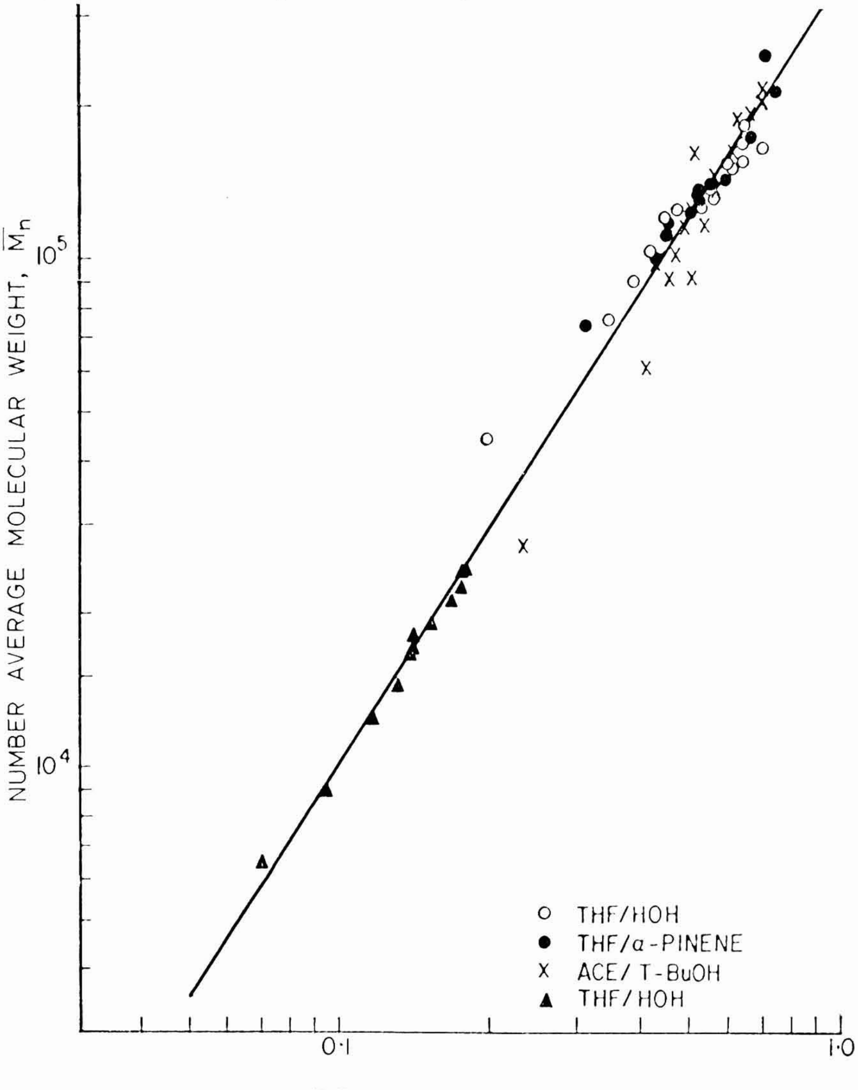


Fig. 7. Molecular weight vs intrinsic viscosity for all fractions

A least squares fit of these points gives the equations:

$$\ln \overline{M}_n = 12.781 + 1.534 \ln [\eta] \quad (3)$$

$$[\eta] = 2.42 \times 10^{-4} (\overline{M}_n)^{0.652} \quad (4)$$

Equation (4) shows that in this range of MA the chains are not too uncoiled in MEK.

As a comparison, Fig. 8 is a plot of $\overline{M}_n$ *vs* 10 per cent solution viscosity in MEK for some of the fractions.

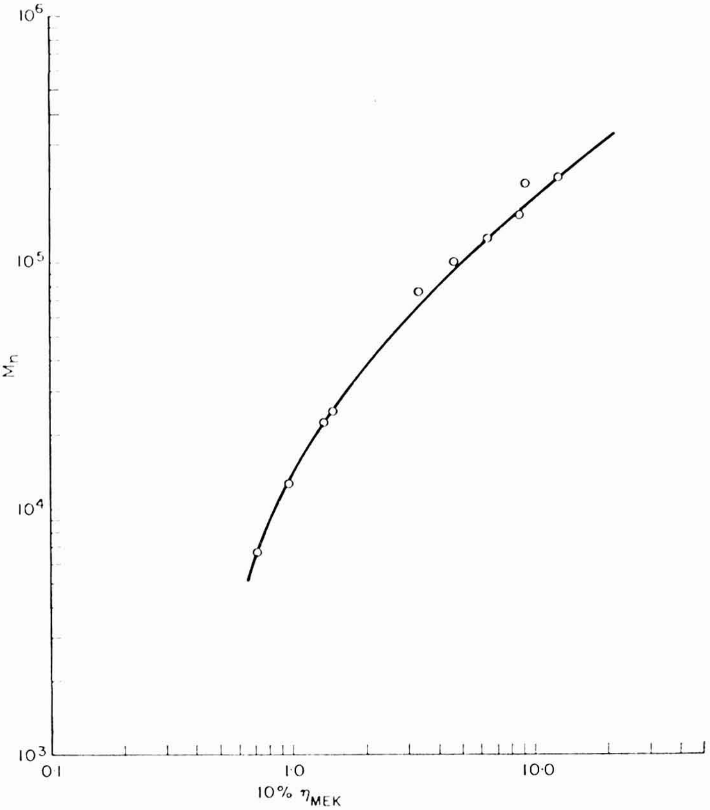


Fig. 8. $\overline{M}_n$ **vs 10 per cent solution viscosity in MEK**

Some of the osmotic pressure data from molecular weight determinations were used to estimate the Flory interaction parameter, χ.

Table 4

Flory interaction parameter in MEK

Fraction	$\overline{M}_n$	Slope of π/c *vs. c*	% MA$_2$	$\frac{1}{2}-\chi$
3	155,000	0.0028	9.06	0.00046
9	132,000	0.0092	9.67	0.00150
12	104,000	0.0088	10.19	0.00144
III	175,000	0.0096	10.08	0.00157
XIV	64,400	0.0139	7.36	0.00227

Table 4 shows that since $(1/2 - \chi)$ is very small there is little interaction between MEK and the polymers in this range of maleic anhydride composition.

Properties of whole copolymers

Since it is not usually convenient to fractionate samples, it was desirable to determine the relation between molecular weight and intrinsic or solution viscosity for unfractionated samples.

Ten samples of S/MA were chosen containing between 8 and 11 per cent MA and having a range of 10 per cent solution viscosity in MEK. These were carefully ground and then devolatilised for one hour under vacuum at 180°C. This removed all volatiles and converted any maleic acid to MA. The intrinsic and 10 per cent solution viscosities in MEK were then determined. $\bar{M}_n$ in toluene was measured using a Hallikainen automatic membrane osmometer. Gel permeation chromatography (GPC) curves were run on each sample in THF, and $\bar{M}_n$ and $\bar{M}_w$ were calculated using the osmotic $\bar{M}_n$ as a calibration. The $\bar{M}_w$ from GPC are plotted in Fig. 9.

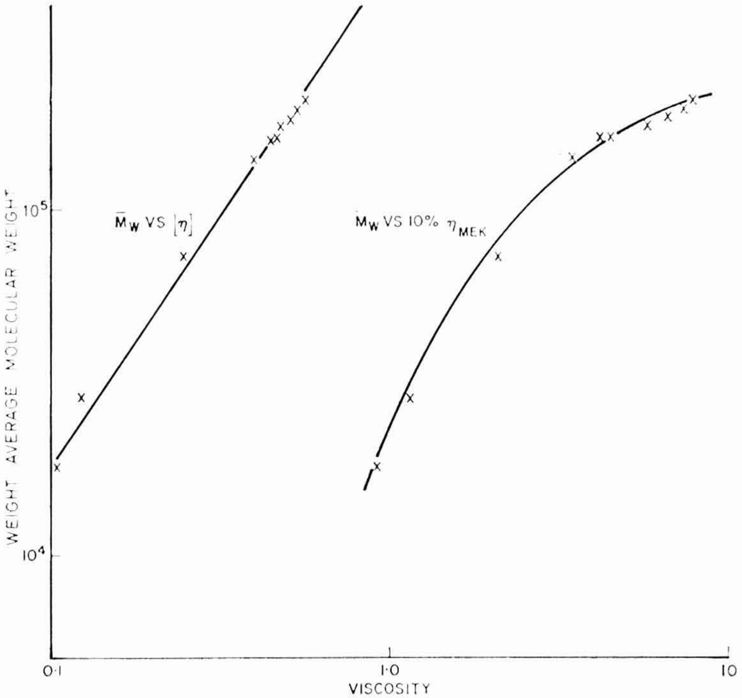


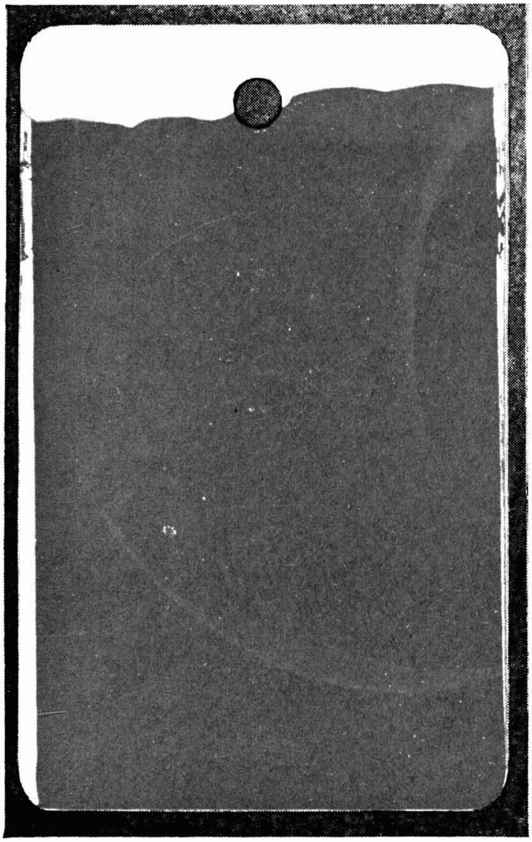
Fig. 9. $\bar{M}_w$ vs viscosity from gel permeation chromatographic determinations

Since viscosity is more a measure of $\bar{M}_w$ than $\bar{M}_n$, one would expect the $\bar{M}_w$ of all the samples to correlate with $[\eta]$. The least squares equation is :

$$\bar{M}_w = 4.98 \times 10^5 [\eta]^{1.426} \tag{5}$$

or

$$[\eta] = 2.01 \times 10^{-6}(\bar{M}_w)^{0.702} \tag{6}$$



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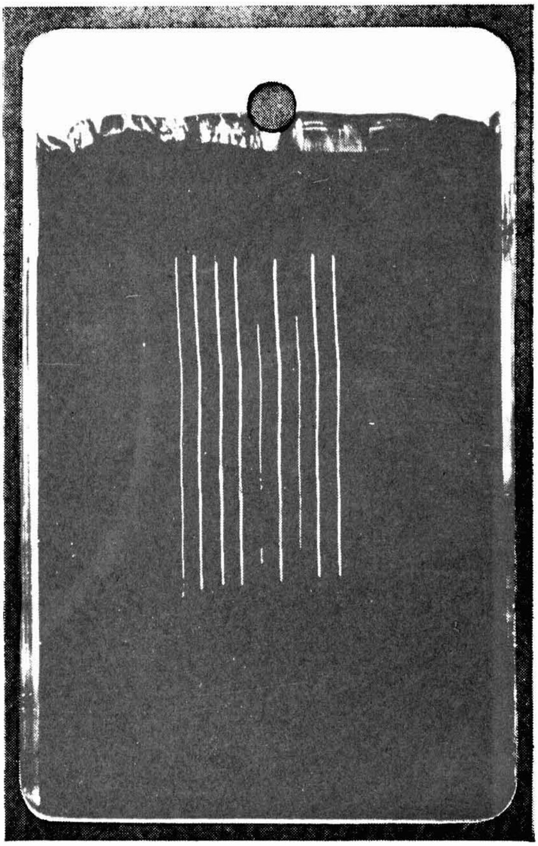

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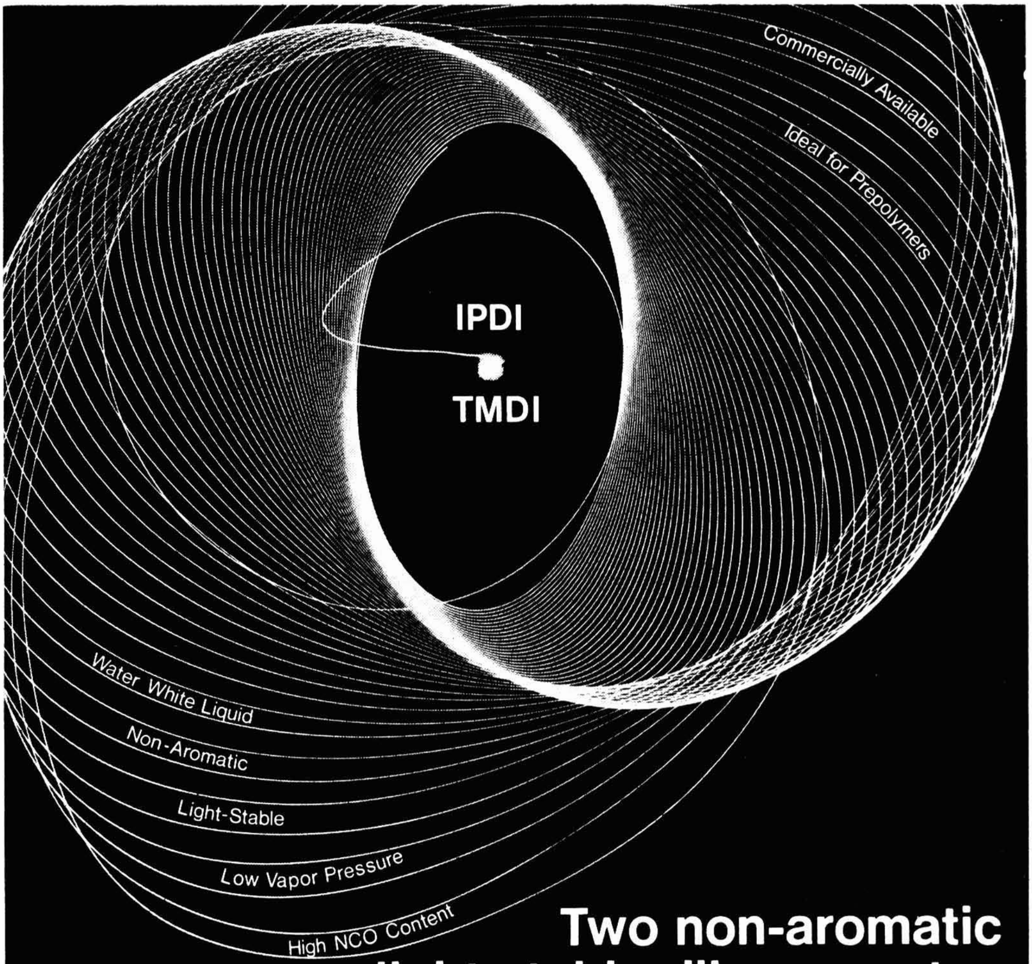

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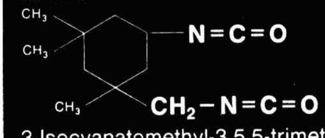

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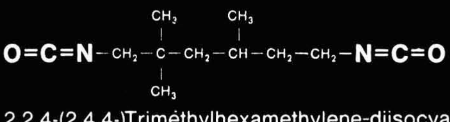

$$O{=}C{=}N{-}CH_2{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_2{-}\overset{CH_3}{CH}{-}CH_2{-}CH_2{-}N{=}C{=}O$$

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Since the 10 per cent solution viscosity is so easy to measure, the curves for 10 per cent η_{MEK} *vs* molecular weight are also plotted in Fig. 9. Because the distribution of samples may vary, it is better to use η_i as a measure of $\overline{M}_w$.

Fig. 10 shows the intrinsic viscosities of unfractionated, equimolar S/MA copolymers (48 per cent MA) *vs* $\overline{M}_w$ by light scattering. The range of $\overline{M}_w$ is 20,000 to 5×10^6. The equation of the line is

$$\overline{M}_w = 473{,}000\, [\eta_i]^{1.380} \tag{7}$$

$$[\eta_i] = 0.7704 \times 10^{-4}\, (\overline{M}_w)^{0.725} \tag{8}$$

Equation (8) compared with equation (6) shows that the equimolar copolymers are somewhat more expanded in MEK, as could be expected.

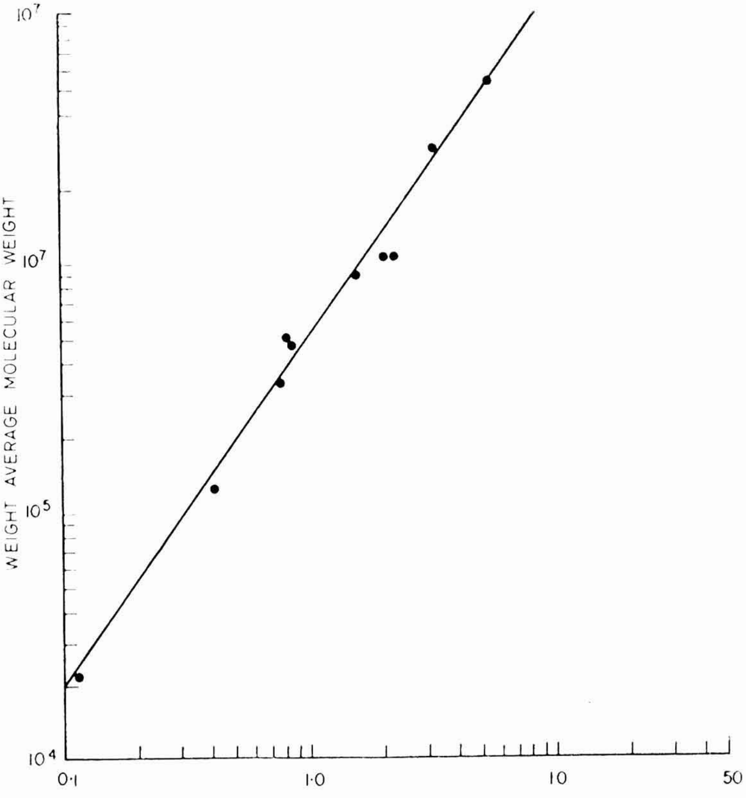


Fig. 10. $\overline{M}_w$ **vs intrinsic viscosity from light scattering determinations**

Another series of samples was chosen containing from 0 to 33 per cent maleic anhydride and with a constant solution viscosity of about 4cps. These samples were analysed for molecular weight by both osmometry and GPC as shown in Table 5. Additional data on thermal gravimetric analysis, solubility parameter, glass transition temperature by torsion pendulum and a differential thermal analysis maximum endotherm are given in Tables 6 and 7.

Table 5

Molecular weight of whole polymer samples

% MA	0	5	18	25	33
$\overline{M}_n$ (High Speed Osmometry) x 10^{-3} ..	87.5	82.0	75.4	79.6	75.2
$\overline{M}_n$ (GPC) x 10^{-3}	90.4	82.0	84.0	79.6	65.1
$\overline{M}_w$ (GPC) x 10^{-3}	195.1	175.2	184.3	177.6	146.4
$\overline{M}_w/\overline{M}_n$ (GPC)	2.16	2.14	2.20	2.26	2.25
η(10% in MEK, cps)	4.06	3.92	4.07	3.96	4.19

Table 6

Thermo-gravimetric analysis at 10°C/min. of 4cps copolymer, °C

% MA	0	5	18	25	33
% Weight Loss					
1	295	275	302	301	294
2	308	289	312	310	308
5	330	312	333	327	325
10	345	328	347	342	338

Table 7

Solubility parameter, glass transition, DTA max. endotherm

% MA	0	5	18	25	33	48
Sol. Parameter (δ)	9.188	9.314	9.729	9.874	9.907	
Glass Temp. °C (Torsion Pendulum)		106			155	
DTA Max. Endotherm, °C	95	111	131	133	153	160
% Volatile	0.20	0.45		0.65		0.82

Direct solubility tests (see Table 8) show that the S/MA copolymers have higher solubility parameter (δ) values than polystyrene. The S/MA copolymers are less soluble than polystyrene in non-hydrogen-bonded low δ solvents.

The relationship is less clear with moderately hydrogen-bonded solvents, and acetone, pyridine and dimethyl formamide were the only highly hydrogen-bonded solvents that dissolved the polymers to any degree. Polystyrene and a styrene-acrylonitrile (VCN) copolymer were used as guides because their δ values were available.

Intrinsic viscosity was employed to accurately determine the δ for an S/MA copolymer having the following analysis: 15.1 weight per cent MA, 10 per cent solution viscosity in MEK at 25°C equal to 5.16 cps. The maximum intrinsic viscosity, as shown in Fig. 11, occurs at a $\delta = 9.7$.

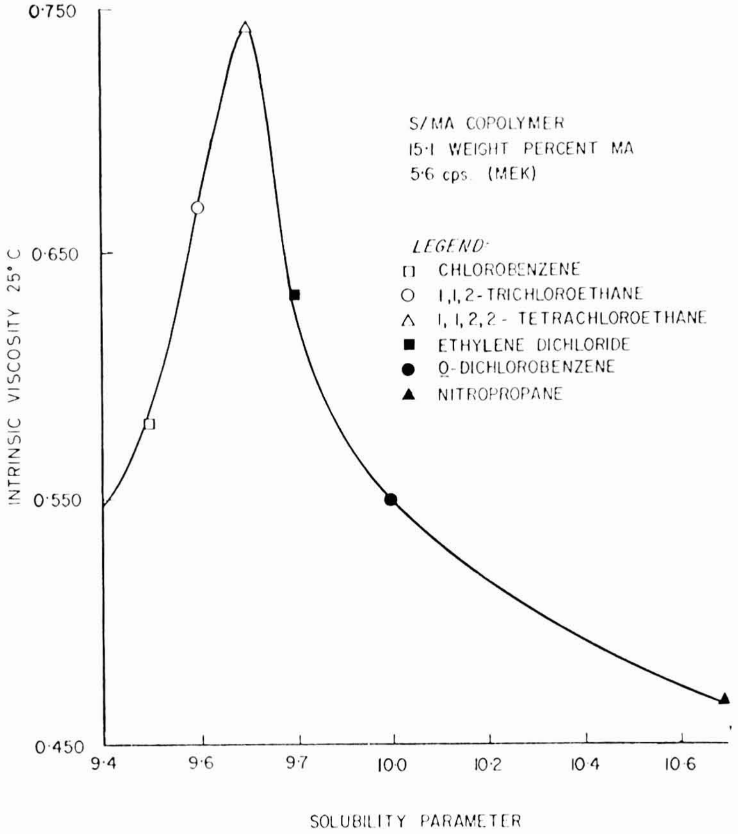


Fig. 11. Determination of solubility parameter by means of intrinsic viscosity

Turbidity titration shows the differences in δ of S/MA copolymers and compares them to the known δ for polystyrene and a styrene/VCN copolymer. Molecular weight differences between the polymers probably cause some error, and a non-hydrogen-bonded solvent would be preferred over MEK. From Table 9, the tolerance for low-δ n-pentane or n-heptane decreases as the MA content increases. High-δ non-solvents such as methanol and ethanol have the reverse effect with increasing MA content resulting in increased alcohol tolerance.

The literature value for the δ of polystyrene is 9.1 in agreement with the cloud point data in Table 9 for polystyrene. As the MA content of a S/MA copolymer increases so does the δ. For the 15 per cent MA copolymer the δ observed from the intrinsic viscosity method also agrees with the cloud point method. However, the literature value for styrene/VCN is in very poor agreement with the cloud point data.

Table 8
Polymer solubility in various solvents

Solvents δ	Class	Composition	Poly-styrene	% MA 5.37	10.5	15.2	21.0	32.0	Styrene/ VCN
7.1	1	*n*-pentane	I	I	I	I	I	I	I
7.4	1	*n*-heptane	I	I	I	I	I	I	I
7.6	1	VM & P	I	I	I	I	I	I	I
7.8	1	methylcyclohexane	sls	vsls	I	I	I	I	I
8.2	1	cyclohexane	S	sls	I	I	I	I	I
8.5	1	SC 150	S	S	sls	sls	I	I	vsls
8.9	1	toluene	S	S	S	S	sls	I	sls
9.3	1	styrene	S	S	S	S	S	I	S
9.5	1	chlorobenzene	S	S	S	S	S	sls	S
9.5	1	"Tetralin"	S	S	S	S	sls	I	sls
10.0	1	*o*-dichlorobenzene	S	S	S	S	S	vsls	S
10.4	1	1, 2-dibromoethane	S	S	S	S	S	S	S
10.6	1	α-bromonaphthalene	S	S	S	S	I	I	S
10.7	1	nitropropane	S	S	S	S	S	S	S
11.1	1	nitroethane	vsls	S	S	S	S	S	S
12.7	1	nitromethane	I	vsls	vsls	vsls	sls	S	S (cloudy)
7.4	2	diethylether	sls	sls	sls	I	I	I	vsls
7.8	2	diisobutyl ketone	sls	sls	sls	I	I	I	vsls
8.4	2	methyl isobutyl ketone	S	S	S	S	S	S	S
8.5	2	butyl acetate	S	S	S	S	S	S	S
8.9	2	butyl carbitol	vsls	sls	sls	sls	sls	I	vsls
9.1	2	ethyl acetate	S	S	S	S	S	S	S
9.3	2	methyl ethyl ketone	S	S	S	S	S	S	S
9.3	2	dibutyl phthalate	vsls	sls	sls	sls	sls	I	v^{2}sls
9.9	2	dioxane	S	S	S	S	S	S	S
9.9	2	cyclohexane	S	S	S	S	S	S	S
10.4	2	cyclopentanone	S	S	S	S	S	S	S
10.7	2	dimethyl phthalate	S	S	S	S	sls	I	S
10.8	2	methyl "Cellosolve"	I	I	sls	S	S	S	S
13.3	2	1, 2-propylene carbonate	I	I	vsls	S	S	S	S
13.3	2	propiolactone	I	vsls	cloudy	S	S	S	S
14.7	2	ethylene carbonate	I	I	I	I	sls	S	sls
15.5	2	4-butyrolactone	S	S	S	S	S	S	S
9.5	3	2-ethyl-hexanol	I	I	I	I	I	I	I
10.0	3	4-methyl-2-pentanol	I	I	I	I	I	I	I
10.0	3	acetone	sls	sls	almost S	S	S	S	S
10.5	3	2-ethyl-1-butanol	I	I	I	I	I	I	I
10.7	3	pyridine	S	S	S	S	S	S	S
10.8	3	*sec*-butanol	I	I	I	I	I	I	I
11.4	3	*n*-butanol	I	I	I	I	I	I	I
11.9	3	*n*-propanol	I	I	I	I	I	I	I
12.1	3	N, N-dimethylformamide	S	S	S	S	S	S	S
12.7	3	ethanol	I	I	I	I	I	I	I
14.5	3	methanol	I	I	I	I	I	vsls	I

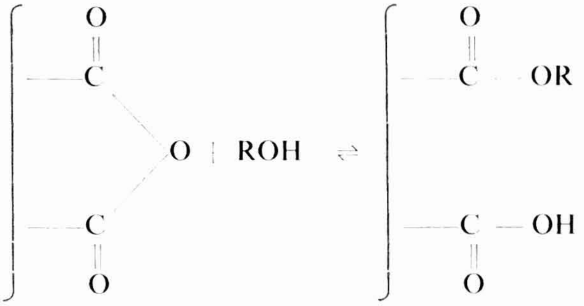
Class 1–poorly hydrogen-bonded 2–moderately hydrogen-bonded 3–highly hydrogen-bonded

Solubility

vsls — very slightly soluble—sl fusing of granules and granules turned sl opaque.
sls — slightly soluble—fused granules but not dissolving.
S — soluble—clear solution.
Almost S — almost soluble—cloudy solution.
I — insoluble—granules not fused.

Chemical reaction with alcohols

An outstanding characteristic of S/MA copolymers is that their properties can be modified so readily by chemical reaction of the MA. One of the most important of these reactions is with alcohols to generate half esters:



or symbolically,

$$\mathrm{MA} + \mathrm{ROH} \rightleftharpoons \mathrm{MHE}$$

Table 9

Solubility parameters by turbidity titration

Polymer Properties			Vol (ml)-Cloud Point				(δ)-(calculated)	
			Lower Cloud Point		Upper Cloud Point			
wt % MA	10% Visc MEK cps	Known (δ)	n-Pent	n-Hept	EtOH	MeOH	MeOH & n-Pent	MeOH & n-Hept
Polystyrene	17	9.1	54.3	65.8	11.8	10.2	9.15	9.18
5.37	6.93	—	57.5	62.7	18.0	15.5	9.28	9.34
10.5	8.66	—	48.6	51.0	21.0	18.2	9.40	9.46
15.2	3.74	9.7*	50.0	51.2	31.0	30.2	9.65	9.73
21.0	4.08	—	40.2	39.7	36.2	37.0	9.83	9.90
32.0	3.39	—	30.0	29.3	38.2	40.7	9.96	10.03
Styrene-VCN	12.6	11.0	33.5	32.5	—	47.7	10.04	10.11

*Solubility parameter determined on a similar S/MA copolymer by the intrinsic viscosity method. See Fig. 7.

The product and reactants exist in equilibrium, and the reaction readily reverses because:

(a) it is pure addition—no small molecule is eliminated,

(b) one of the reactants is the easily regenerated anhydride ring.

The stoichiometry of the reaction is

$$\mathrm{MA} + \mathrm{ROH} \underset{k'}{\overset{k}{\rightleftharpoons}} \mathrm{MHE} \qquad (9)$$

$$(a - x) \quad (b - x) \qquad x$$

a = initial concentration of anhydride

b = initial concentration of alcohol

x = concentration of half ester at time t

c = concentration of some added acid catalyst

The complete differential rate equation is

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_1c(a - x)(b - x) + k_2x(a - x)(b - x) + k_3(a - x)(b - x) - k_1'cx - k_2'x^2 - k_3'x \qquad (10)$$

k_1 = rate constant for the externally catalysed reaction

k_2 = rate constant for the reaction catalysed by the acid product

k_3 = rate constant for the uncatalysed reaction

k_i' = corresponding rate constants for the reverse reaction

K_{eq} = equilibrium constant = k_i/k_i'

The rates of reaction of S/MA with several model alcohols have been investigated, and the results show that all three forward and reverse mechanisms must be considered, even when catalysts are used. As might be expected, the order of reactivity of alcohols is: primary $>$ benzylic $>$ polyglycol $\gg$ secondary. The equilibrium constants are in the order primary $>$ benzylic $\sim$ polyglycol $\sim$ secondary.

Thermosetting coatings

Styrene-maleic anhydride copolymers containing less than 20 mole per cent MA are soluble in aromatic solvents as are copolymers containing up to 50 mole per cent maleic half ester. Xylene-based thermosetting coatings, wherein the anhydride or acid copolymers are cured with various epoxy resins, amine resins, and glycols have been discussed[1, 8, 15, 16, 17]. Table 10 gives a formulation developed for a gloss appliance enamel and the physical properties of the cured coating. The resin employed was a styrene/octyl acid maleate copolymer having a solution viscosity of 1.5 cps (10 per cent in MEK). A lower molecular weight resin "styrene-maleic half ester copolymer" designated S/MA 3840A has recently been introduced commercially[18] in the United States.

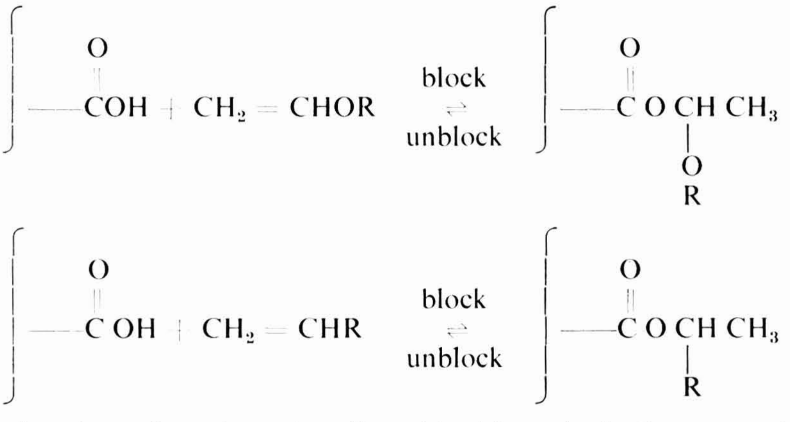
Although the above-mentioned systems have satisfactory one-package shelf life for most industrial coatings applications, it is desirable to find means for achieving greater stability. One way of accomplishing this end result has been discovered for carboxyl-epoxy reactions, and that is chemically to block the carboxyl group.

Table 10

	Weight %
Styrene-Octyl Acid Maleate (75/25)	21.6
DER ®337 Epoxy Resin[a]	5.4
Titanox® RANC TiO_2[b]	25.0
Ethylene Glycol Methyl Ether	4.9
Cellosolve® Acetate[c]	7.2
Butanol	5.8
Penola® 150[d]	2.2
Xylene	24.8
Resimene® 882 Butylated Melamine[e]	30
Viscosity (KU)	65-70
Baked on Bonderite 1000 for 30 minutes at 350 F (177 C)	
Front impact (in-lb)	24
Conical mandrel (Apex = 0)	Fail 0-1.5in
Knoop hardness	39
Gloss, 60° C	98
Tide, 1%, 160 F 200hr, ASTM	OK
Salt Spray, 5% 100° F, 10 days	OK
Common Stains	OK

(a) The Dow Chemical Company
(b) Titanium Pigments Corp.
(c) Union Carbide Chemicals Co.
(d) Humble Oil and Refining Co.
(e) Monsanto Company

This can be done by forming a thermally unstable ester[19], for example,

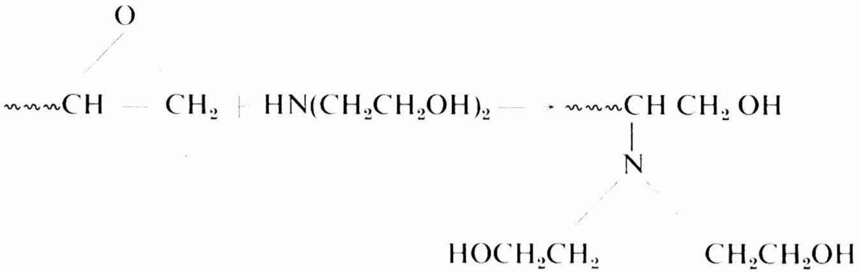


$$\left\{-\overset{\overset{\displaystyle O}{\|}}{C}OH + CH_2=CHOR\right\} \underset{\text{unblock}}{\overset{\text{block}}{\rightleftharpoons}} \left\{-\overset{\overset{\displaystyle O}{\|}}{C}O\underset{\underset{\displaystyle R}{\overset{|}{O}}}{CH}CH_3\right\}$$

$$\left\{-\overset{\overset{\displaystyle O}{\|}}{C}OH + CH_2=CHR\right\} \underset{\text{unblock}}{\overset{\text{block}}{\rightleftharpoons}} \left\{-\overset{\overset{\displaystyle O}{\|}}{C}O\underset{\underset{\displaystyle R}{|}}{CH}CH_3\right\}$$

by reacting the polymeric carboxylic acid with a vinyl ether or a vinylidene hydrocarbon such as isobutylene. A styrene-octyl acid maleate copolymer was esterified at 60°C in 48 hours separately with two moles per carboxyl of either ethyl vinyl ether or isobutylene, using a trace of acid catalyst. In a wet enamel such as in Table 10, the stability on ageing at 60°C was increased by a factor of three with the vinyl ether and by a factor of at least two with isobutylene. Nevertheless, films were curable when subjected to the thermosetting reaction conditions. Freshly applied films showed less sagging and solvent bleeding than the unmodified resin.

Another route to shelf stability is possible by modification of the epoxy resin. Reaction with an alkanolamine such as diethanolamine



produces a reactive polyol that will give a stable enamel but which will co-react with the carboxylic resin at baking temperatures[20]. This system is useful for solvent-borne coatings, but is particularly suited to aqueous systems because the alkanolamine adduct of a liquid epoxy resin is water soluble. For example, a 51 weight per cent 2-[2-(2-butoxyethoxy)ethoxy] ethyl maleate-styrene copolymer was dissolved in aqueous ammonia at 31 per cent solids, and to 100g of this solution was added 38g of a 60 per cent aqueous solution of the adduct of DER®332 liquid epoxy resin with diethanolamine.

The adduct was prepared by heating 18g of diethanolamine and 10g of DER 332 to an exotherm reaction at about 150°C and following with two more 10g portions of DER 332 after about 15min intervals.

A primer formulation was made by adding a pigment paste to the copolymer-epoxy adduct mixture. The resulting blend was found to have indefinite shelf stability; and, upon curing at 175°C for 30min and topcoating with a melamine alkyd, the primer exhibited equally satisfactory performance as compared with an unmodified DER 332 primer which required emulsification of the epoxy resin with a surfactant and which set up in 4 weeks at 75°F.

Invert styrenated alkyds

The reaction of a low molecular weight resinous styrene-maleic anhydride copolymer with a polyol and fatty acid is the inverse of the normal styrenation procedure. Details of preparation and comparison with the conventional procedure were published earlier[2]. As previously noted, there is a basic difference in formulation composition between the two methods which results in greater styrene content for equivalent oil length (Fig. 12). In the invert system, all of the styrene is bound at the start, resulting in better mineral spirits compatibility and final film solvent resistance. Alkali resistance was also found to be superior.

By maleinising the fatty acid before esterification and diluting with a co-solvent, a functional water-reducible binder could be synthesised. This vehicle has been tested in an air-dry gloss enamel formulation. The resin used was a styrene/α-methyl styrene/maleic anhydride terpolymer of 50/35/15 weight per

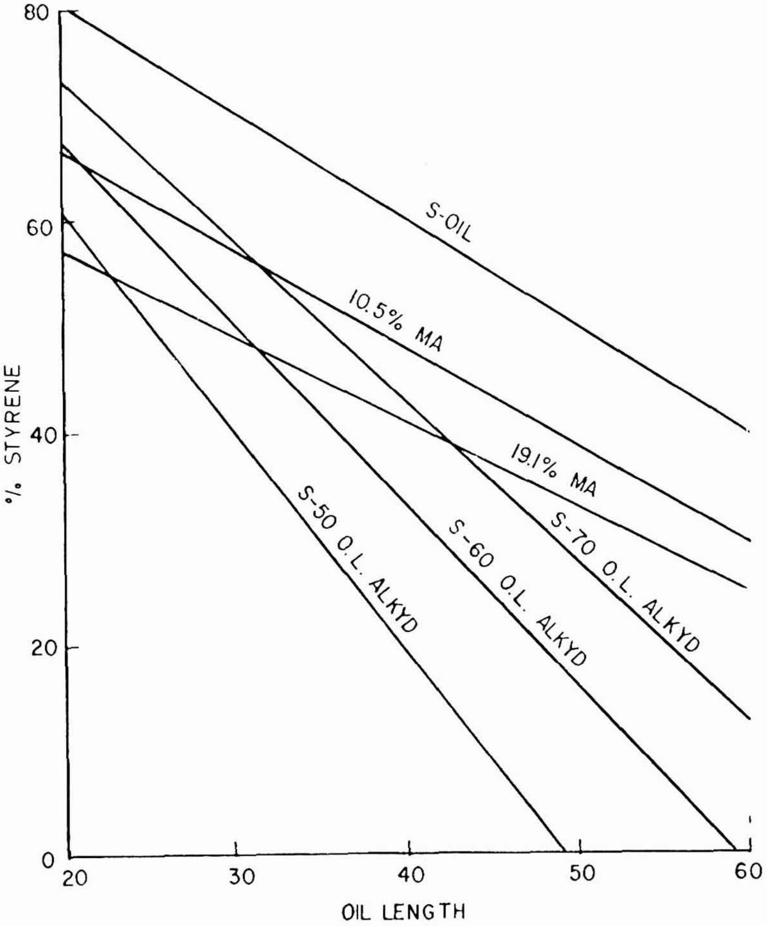


Fig. 12. Styrene content related to oil length for various polymers

cent composition having a viscosity of 0.677cps and a number average molecular weight of 1420. At the start, 129g of DCO fatty acids was maleinised with 15.1g of maleic anhydride using 0.2g of iodine as catalyst and 3g of toluene. Then 100g of the resin and 28.6g of glycerol were added and cooked to an acid number of 44.5. The cook was dissolved in 119g of Dowanol ®EB, ethylene glycol monobutyl ether, neutralised with concentrated ammonia and diluted with water to 43.6 per cent solids.

As shown in Table 11 the invert alkyd was compared with a maleinised ester of RJ-100 (Monsanto Company) in a low PVC gloss enamel formulation. Paint film properties are also listed in Table 11. The invert alkyd was very fast drying and quickly developed good water, alkali and scrub resistance. Gloss and colour were about equivalent to the RJ-100 ester but the film was less flexible.

Table 11
Air dry gloss paint

	Invert alkyd	RJ-100 ester
Pigment grind		
Invert alkyd (43.6%)	128	—
RJ-100 ester (35%)(a)	—	180
TiO_2-R-900	350	280
Dowanol® EB(b)	65	3
Water	—	26
Polyglycol P-1200	7.0	5.6
Let Down		
Resin	254	200
Water	64	—
Cobalt Cyclodex (6%)(c)	2.76	2.2
Viscosity (KU)	112	very high
Drying 20hr		
Tack-free	yes (75min)	no
Print-free	yes	no
Hand Scrub (Cycles)		
24hr	1320	265
7 day	>500	>500
21 day	>500	>500
Flexibility bend test		
21 day	cracked	OK
60° Gloss		
20hr	77	77
21 day	75	73
Yellowness index		
5 day	0.31	0.30
65 day exposed	0.67	0.50
65 day dark	0.98	0.79
Spot tests		
Water	vsl spotting	vsl spotting
0.5% NaOH	sl discolor	sl discolor
Washability—100 cycles on Gardner		
7 day		
Appearance	OK	OK
% Gloss retained	69	79
Stain removal	OK	Lipstick
21 day		
Appearance	OK	OK
% Gloss retained	84	92
Stain removal	OK	OK

(a) Monsanto Company
(b) The Dow Chemical Company
(c) Nuodex Products Co., Division of Heyden Newport Chemical Co.

Thermosetting laminates

The cure chemistry of styrene-maleic anhydride copolymers can be employed for preparing pre-impregnated laminates of paper or glass as used in electrical applications. Epoxy resins were found[3] to give the strongest glass-reinforced laminates, but some polyols also produced strong and hard products. The choice of an aromatic polyol[21, 22] as the curing agent has the advantage of better compatibility with the styrene-maleic resin. Table 12 lists some properties of glass laminates prepared by impregnating style 181 glass cloth having a Volan A finish with a 60 per cent acetone solution of a styrene/10.2 per cent MA copolymer and the indicated amount of an aromatic polyol curing agent plus a small amount of DMP-30 tri-(dimethyl amino methyl) phenol curing agent. After air-drying to remove acetone, the cloth contained 42-45 per cent resin. Twelve plies were stacked and cured in a compression press at 350°F for 30 minutes and then tested.

Styrene-diluted 100 per cent solids thermosetting systems

It has been found possible to formulate liquid systems based on S/MA resins[23] which cure to form products that are similar to thermoset polyester resins. By dissolving the S/MA resin in a mixture of styrene and maleic anhydride monomer and adding a crosslinking agent, a heat-cured product can be obtained which resembles the thermoset product resulting from the simple addition reaction of crosslinking agent and copolymer. For example, a laminate was prepared from 62.4 weight per cent styrene monomer, 2.9 per cent maleic anhydride monomer and 34.7 per cent of a styrene/10 per cent maleic anhydride copolymer having a 10 per cent solution viscosity in MEK of about 1.5cps at 25°C. On the basis of 100 parts of this solution, 3.76 parts propylene glycol were added followed by 1.0 part benzoyl peroxide and 0.2 part cobalt naphthenate. A 12-ply glass laminate was made by impregnating glass cloth with the resin solution and allowing the laminate to set for 24 hours at room temperature followed by heating at 130°C for one hour. A pressure of 40 pounds per square inch was then applied and the product held at 130°C for an additional 24 hours. The resulting laminate was $\frac{1}{8}$in thick, had a good appearance and excellent physical properties. The flexural strength was 54,000psi at room temperature and 49,000psi at 160°F.

Table 12

Aromatic Polyol	Weight % Polyol	% Weight gain (2hr water boil)	Tensile str (psi)/ Modulus × 10^{-6} (psi)
			75°F
Dihydroxy methyl diphenyl oxide ..	16.46	0.14	55,000/2.24
Oxy-bis-benzyl alcohol	16.42	0.181	56,000/2.06
Styrene/20% allyl alcohol copolymer (RJ-100)	23.9	—	64,900

Conclusions

Advances in polymerisation technology have made practical the production of styrene-maleic anhydride copolymers containing from nearly zero MA up to the well-known equimolar composition. Copolymerisation of styrene with MA requires precise process control to yield non-equimolar compositions of uniform composition. The polar character of the anhydride groups produces sizeable effects on copolymer properties such as solubility parameter. Differences in composition distribution which can result from some methods of synthesis should be avoided in order to achieve consistent behaviour in coatings applications when solubility and reactivity are important.

Fractionation has been shown to separate this type of copolymer by both composition and molecular weight. The fractions as well as whole polymers have been characterised by molecular weight, viscosity, solubility and some additional properties.

The reversible reaction of copolymeric anhydride groups with alcohols has been described as a reversible reaction and an order of reactivity by alcohol type has been set down.

In thermosetting coatings employing maleic half ester copolymers, the acidic groups can be blocked by a vinyl addition reaction to improve shelf life of one-pack systems. Alternatively, an epoxy curing resin can be modified with an ethanolamine to produce an adduct that is shelf stable as well as water soluble.

Maleinised alkyd-type resins have been prepared and tested for use in air-drying water-based gloss paint.

The anhydride copolymers have been cured with aromatic polyols in thermoset electrical laminates and have been employed in 100 per cent reactive liquid casting or coatings systems by dissolution in styrene monomer together with a polyol and additional maleic anhydride.

Greater understanding of the preparation and properties of non-equimolar styrene-maleic anhydride resins should open the way to utilisation of these versatile copolymers in a number of coatings applications.

Acknowledgments

The authors appreciate the permission of The Dow Chemical Company to publish this paper. Numerous colleagues and service laboratory personnel have been involved in various portions of the synthesis, characterisation and application studies involved. We particularly wish to cite Dr C. E. Lyons, Dr L. H. Lee, W. A. Henson, W. E. Alexander, D. R. Spiekerman, E. G. Larson and W. E. O'Connor for their contributions.

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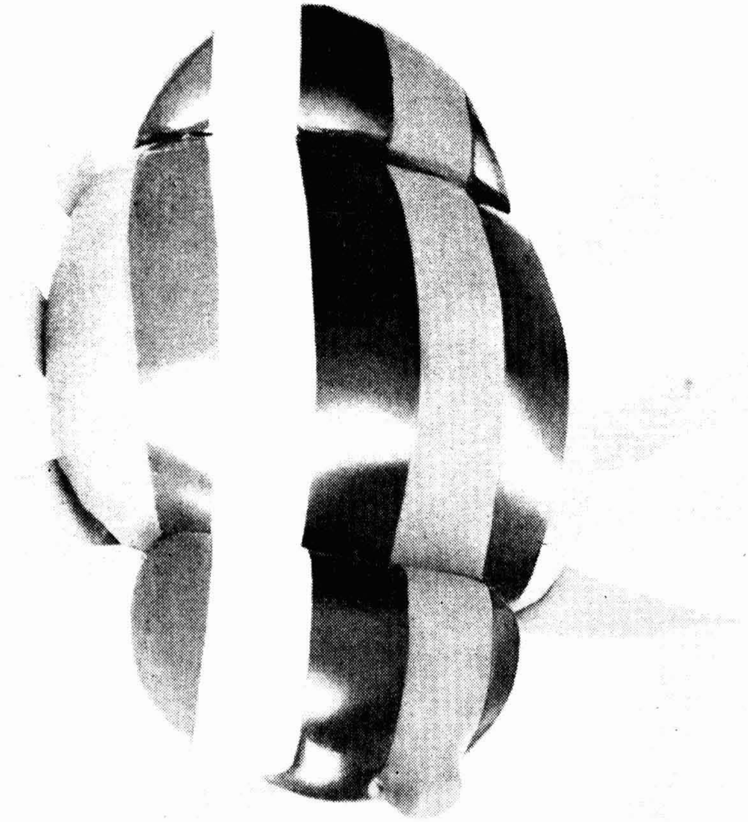

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Discussion at the Eastbourne Conference

DR L. A. O'NEILL said that the paper had described materials called invert styrenated alkyds, but with the same products one could also make invert unsaturated polyesters, which were normally polyglycol maleates copolymerised with styrene. Had the products been considered in the field of the unsaturated polyesters, perhaps for wood finishing?

Also, mention had been made of some water soluble fatty acid products which could be developed. Had these been examined for use in electro-coating?

He congratulated Mr Zimmerman on the gel-permeation chromatography. The results and agreements were excellent, bearing in mind the difficulties in dealing with copolymers of heterogeneous composition.

MR R. L. ZIMMERMAN said, in answer to the first question, that, in order to have a fluid coating for application, styrene monomer had been used as a diluent with these copolymers and with a polyol. In this case it was not an unsaturated polyester; it was a simple polyol such as 1:4 butane diol, and the system with maleic anhydride monomer in it would form a 100 per cent solid type coating. In order to get an application by other than powder coating or similar types of application, one would have to use styrene monomer, and then the styrene monomer must be co-reacted with the system. He and his co-workers had made no attempt to prepare an unsaturated maleic type polyester as a hydroxy polyester and to use that as a cross-linking agent. In answer to the second question, they had not investigated electro-coating application of these water dilutable systems. However, he would predict that the system would perform similarly to the maleinised RJ-100 ester mentioned in the paper.

DR O'NEILL remarked that the paper suggested that one could titrate the two carboxyls of maleic anhydride under aqueous conditions. Could that be done readily? It was not normally easy to titrate two carboxyls of maleic acid.

MR ZIMMERMAN replied that there was a considerable difference in the pK values for maleic acid. The first acid was a strong acid, with a pK value of about 3. The second one was much weaker and should be distinguishable in a titration. With maleic anhydride and maleic acid itself one could actually see the inflection point in a conductiometric titration.

DR O'NEILL agreed that it was usually distinguishable, but not that it allowed for accurate measurement.

MR ZIMMERMAN felt that this was probably correct, and that the effect would be even less accurate for the polymeric form. The polymeric diacids were titrated in the sense of titrating for the composition, not by a pH type titration, but working to a specific end-point of thymol blue, which was simply an analysis of one carboxyl group of all the carboxyl groups that were titratable, rather than distinguishing between the two. It was possible to distinguish between the anhydride and acid forms by a double titration. First one titrated in pyridine with methanolic KOH, and then one titrated again in the presence of water. From this titration the composition could be calculated in terms of anhydride and diacid related to copolymer composition.

MR R. W. HALL congratulated Mr Zimmerman and his colleagues on the very elegant polymerisation technique for manufacturing these copolymers. This was one of the few techniques which, on a larger scale of production, could be used to determine fairly basic copolymerisation parameters which related to copolymer composition.

He asked what the present status of these materials in the coating field was, and if the policy of the Dow Company was to make the copolymers available to industry for subsequent modification, or to manufacture the half-esters and other modifications themselves.

On the GPC work, could Mr Zimmerman indicate what the column packing was in the fractionation of the acid copolymers?

His third point related to the structure of the half esters which were prepared. Had any comparison been made of materials by three different groups: first, the half esters made by the continuous polymerisation technique, secondly, half esters made by directly copolymerising styrene with a half maleate, and thirdly, copolymerisation of styrene with the diester, and then partial hydrolysis back to half ester again. These should give three quite different types of copolymer backbone structure.

MR ZIMMERMAN, replying to the first question, said that the potential was there in terms of commercial production only if a business developed in terms of volume, and styrene maleic anhydride polymers were not at this stage a significant world-wide business in terms of chemical companies producing such copolymers. It would be the broad field of coating chemists who would determine ultimately whether there was truly a market.

In answer to the second question, the column packing was identical to the columns used in gel permeation chromatography with polystyrene, and tetrahydrofuran was the solvent. Some care, of course, had to be exercised in taking a polymer of this type and running it in a gel permeation separation.

The third question was well put and would make an interesting study. The styrene and maleic anhydride, copolymerised and then reacted with the alcohol to the half ester form, had been compared that with a polymer prepared by polymerising styrene and the maleic half ester. On a coatings basis roughly the same result was obtained. A specific gloss appliance enamel had been used, containing the half ester copolymer, and then on another occasion containing the copolymer made by continuous polymerisation of styrene maleic anhydride and esterification. The result in terms of the coating performance was to all intents identical.

He pointed out that the half ester formation of these copolymers was an equilibrium reaction, and when one prepared a copolymer of the half ester, introducing the alcohol at elevated temperature in the system, the half ester would revert partially back to the anhydride in the equilibrium, depending upon the temperature and the equilibrium constant of the particular alcohol. So it was not possible to maintain an absolutely clean reaction of the half ester in copolymerisation.

MR C. BARKER asked whether there was any data on the thermal stability of the backbone change stability of these copolymers.

Solomon, in Australia, had done some interesting work on making methacrylic acid copolymers and then cooking them into alkyd resins or polyesters rather like the invert alkyds Mr Zimmerman had described. One of the problems was the depolymerisation of the polymethacrylate, but this was known to be a system which did depolymerise relatively easily at temperatures used in alkyd cooking. Methacrylates clearly depolymerised and evaporated. He wondered how stable the styrene/maleic anhydride was at these sort of ratios and therefore what the implication was of cooking at temperatures of the order of 220°C minimum in bulk, where the time cycles might be quite long. This would be important if the products were developed commercially.

MR ZIMMERMAN stated that Dr Dennis and Dr Moore had recently done a study by differential thermal analysis and weight analysis of the elevated temperature stability of some of the copolymers, and in the range of the low maleic content, the range of the 10-20 per cent maleic anhydride that was being discussed, they were relatively stable at temperatures up to 250°C and possibly approaching 300°C for the order of a few hours. At the same time this might explain the low functionality in cooking to as high an extent as had been achieved. The maleic anhydride in the copolymer did decarboxylate. Whether or not that led to chain degradation was not certain. However, it was an open question whether the polymer in the final alkyd after cooking was strictly the same composition as it was initially, because at those temperatures some decarboxylation could be expected to take place.

MR BARKER said he had found that it didn't matter from the practical point of view whether the polymer had degraded if there was a useful end result, but it might lead to an equilibrium concentration of methyl methacrylate monomer. In Mr Zimmerman's work it might produce styrene, leading to instability problems.

MR ZIMMERMAN replied that specifically these copolymers would not depolymerise; they degraded by evolution of CO_2, as far as could be seen from thermal analysis of the copolymers.

MR A. F. WILSON asked whether the half ester formation was a catalysed or uncatalysed reaction.

MR ZIMMERMAN said that in most of the work a catalyst had been used. As the reaction rate constants were not good, especially in the copolymers, a weak phosphoric acid ester had been used.

MR F. ARMITAGE brought up two points. The first was about the invert alkyd resin. He presumed that it was almost impossible to reproduce by Mr Zimmerman's method an existing styrenated alkyd resin, even though the copolymerisation of the styrene with the alkyd resin would be through a maleic anhydride incorporated into the alkyd. This didn't mean to say that a new type of alkyd resin might not have its own special uses.

The second point was that over the past five or ten years styrenated alkyds had been complemented by vinyl toluenated alkyds and by monomer modified alkyds containing acrylonitrile and methyl methacrylate as well as styrene. Had Mr Zimmerman studied the reaction of mixed monomers with maleic anhydride?

MR ZIMMERMAN pointed out that there was a plot in the data, attempting to compare the styrenated alkyd and an invert styrenated alkyd, and the difficulty was the difference of formulation, as, in the system used, phthalic anhydride was replaced with styrene. It was difficult to know whether to compare them at the same oil length, at the same styrene content, at the same air dried temperature, or to decide what should be the basis for comparison. He felt one could synthesise a comparable coating or composition if phthalic anhydride as well as the polyanhydride was introduced in the invert system.

MR ARMITAGE thought that this might be a matter for dispute, because of the way that polymerisation took place.

MR ZIMMERMAN replied that if it was wished to compare the two systems with the same composition, and thus prepared one one way and the other the other way, it was quite possible that one could design such a system. The design of a specific system might take a coating chemist in quite different directions. It would be dependent upon what his design characteristics were in the alkyd or coating required. And therefore the comparison would probably end up being rather theoretical, at least in the end result.

As regards the question of using other monomers, some copolymers had been prepared, from mixtures of styrene, butylacrylate, maleic anhydride, and various acrylates. However these copolymers did not have the resistance properties in terms of a thermosetting appliance enamel. So the simple half ester forms had been retained from both an economic and a performance argument.

The alkyd systems described in the paper were tripolymers; they included α-methyl styrene with styrene and maleic anhydride, which was out of the simple expedient of getting lower molecular weight in a rather convenient way.

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Functional groups in butylated melamine-formaldehyde resins and their influence on the curing behaviour of these resins in combination with alkyd resins*

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Summary

Commercially available butylated melamine-formaldehyde (MF)-resins of different "reactivity" were analysed for nitrogen content and formaldehyde content. The content of methylol groups was determined by a new method, using dimedone as a reagent. The amount of —NH groups was estimated spectroscopically by measuring the absorption at 1480nm.

On the basis of these analytical data, information could be gained about the amounts present of the following groups:

(a) the sum of —OCH_2OH ("free formaldehyde") and —NCH_2OH.

(b) —NH.

(c) —NCH_2OR.

It was now postulated that "reactivity" increases with decreasing amount of —NCH_2OR groups present.

Four alkyd resins were prepared from isophthalic acid, lauric acid and trimethylolpropane in such a way that variations in hydroxyl value and average molecular weight were obtained. Mixtures of these alkyd resins with selected butylated MF-resins were applied to aluminium plates of 120cm length. The coated plates were baked in a "gradient cure block", maintaining a temperature gradient of 20-200°C along the length of each plate. The König pendulum hardness of the baked coatings was determined, and graphs of pendulum hardness versus baking temperature were obtained. By solvent extraction experiments and by comparing stress-strain curves of pre-swollen films, additional information was obtained.

The curing behaviour of the butylated MF-resins of different "reactivity" could be related to the number of —NCH_2OR groups present.

Key words

Binders (resins etc.)
alkyd resin
melamine formaldehyde resin

Processes and methods primarily associated with:
analysis, measurement and testing
colorimetry
functional group analysis
hardness test
infra-red spectroscopy
Kjeldahl method

manufacture or synthesis
condensation
polymerisation

Groupements fonctionnels d'éthers butyliques des mélamine-formol et leur influence sur la durcissabilité de ces résines en combinaison aux résines alkydes

Résumé

On a dosé la teneur en azote et en formaldéhyde des éthers butyliques de mélamine-formol, ayant des "réactivites" diverses, qui se trouvent en commerce. La teneur en groupements méthylols était dosée au moyens d'une nouvelle méthode, en utilisant dimédone en tant que

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réactif. La quantité de groupements $-NH$ était dosée spéctroscopiquement par l'absorption à 1,480nm. Grâce à ces données analytiques on peut obtenir une connaissance de la quantité des groupements suivants qui se présentent:

(a) La somme totale de $-OCH_2OH$ ("formaldéhyde libre") et de NCH_2OH.
(b) $-NH$.
(c) $-NCH_2OR$.

Dans la suite on a suggéré que la "réactivite" s'augmente selon la diminution de la quantité de groupements $-NCH_2OR$.

On a préparé quatre résines alkydes à partir des acides isophtalique, laurique, et du triméthylolpropane dans une telle manière que des variations en l'indice d'hydroxyle et le moyen poids moléculaire étaient obtenues.

Des mélanges de ces résine alkydes avec certaines résines MF sous forme d'éthers butyriques étaient appliqués aux plaques d'aluminium à 120cm de longueur. Les plaques si-revêtues étaient cuites dans un bloc de Maquenne où l'on maintient un gradient de température à 20 de 200°C le long de chaque plaque. La dureté des revêtements cuits a été déterminée et l'on a obtenue des courbes de dureté contre température de cuisson. On a obtenu des données supplémentales au moyens des expériences à extraction par solvant et par la détermination de la résistance à la traction de feuils pré-gonflés.

La durcissabilité des éthers butyriques de résines MF ayant de diverse "réactivite" peut être mise en rapport au nombre de groupements $-NCH_2OR$.

Funktionelle Gruppen in Butanolverätherten Melamin-Formaldehydharzen und ihr Einfluss auf das Härtungsverhalten dieser Harze in Kombination mit Alkydharzen

Zusammenfassung

Im Handel erhältliche butanolverätherte Melamin-Formaldehyd (MF) Harze verschiedener "Reaktivität" wurden auf ihren Stickstoff- und Formaldehydgehalt hin analysiert, Der Gehalt an Methylolgruppen wurde mit Hilfe einer neuen Methode unter Benutzung von Dimedon als Reagenz bestimmt. Der Gehalt an $-NH$ Gruppen wurde spektroskopisch durch Messung der Absorption bei 1480nm festgestellt. Auf diese analytischen Resultate gestützt, konnte Information über die in den folgenden Gruppen anwesenden Mengen gewonnen werden:

(a) Die Summe von $-OCH_2OH$ ("freies Formaldehyd") und $-NCH_2OH$.
(b) $-NH$.
(c) $-NCH_2OR$.

Es wurde nunmehr behauptet, dass sich "Reaktivität" mit abnehmenden Mengen von vorhandenen $-NCH_2OR$ Gruppen erhöht.

Vier Alkydharze wurden aus Isophthalsäure, Laurinsäure und Trimethylolpropan in der Weise hergestellt, dass Varianten in der Hydroxylzahl und im Molekulargewicht erhalten wurden.

Mischungen dieser Alkydharze mit ausgewählten butanolverätherten MF-Harzen wurden auf 120cm lange Aluminiumbleche aufgetragen. Die lackierten Tafeln wurden in einem "graduierten Gel Block" unter Aufrechterhaltung längs jeder Tafel eines Temperaturgradients von 20 bis 200°C ofengetrocknet. Die Härte der ofengetrockneten Anstriche wurde gemessen, und es wurden Diagramme für Härte bei verschiedenen Trocknungstemperaturen erhalten. Zusätzliche Information konnte durch Extraktionsversuche mit Lösungsmitteln und Messung der Zerreissfestigkeit vorgequollener Filme gewonnen werden.

Das Verhalten der butanolverätherten MF- Harze verschiedener "Reaktivität" konnte mit der Anzahl der anwesenden $-NCH_2OR$ Gruppen in Beziehung gebracht werden.

Функциональные группы в бутиловых меламино-формальдегидных смолах и их влияние на сушку этих смол в соединении с алкидными смолами

Резюме

Коммерчески доступные бутиловые меламино-формальдегидные смолы различной «реактивности» анализировались на содержание азота и формальдегида. Содержание метилольных групп определялось новым методом, применяя димедон в качестве реагента. Количество групп — NH определялось спектроскопически, путем измерения поглощения при 1480 нано м. На основании этих аналитических данных получены сведения о наличии количества следующих групп:

(а) сумма — OCH_2OH («свободного формальдегида») и — NCH_2OH.

(б) NH.

(в) NCH_2OR.

На основании этого было постулировано что «реактивность» увеличивается с уменьшением количества наличия групп — NCH_2OR.

Приготовлялись четыре алкидные смолы из изофталевой кислоты, лауриновой кислоты и триметилолпропана, таким образом чтобы получить вариации гидроксильного значения и среднего молекулярного веса.

Смеси этих алкидных смол с избранными бутиловыми меламино-формальдегидными смолами, налагались на алюминиевые пластинки длиной в 120 см. Покрытые пластинки просушивались в «градуированном гелевом блоке», сохраняя температурный градиент в 20-200° С вдоль длины каждой пластинки. Твердость высушенных покрытий измерялась и были получены графики зависимости между твердостью и температурой сушки. Добавочные сведения были получены путем селективной экстракции растворителями и путем измерения разрывной прочности предварительно набухших пленок.

Поведение при сушке бутиловых меламино-формальдегидных смол различной «реактивности» могло быть отнесено к числу наличных групп — NCH_2OR.

Introduction

Two-component alkyd-melamine resin systems have now been in use for surface coatings for almost 30 years. During this period, the chemistry of these systems has been the subject of a vast amount of literature. The thermal degradation and curing of butylated melamine resins has been investigated by means of infra-red spectroscopy[1, 2, 3] and thermogravimetric analysis[3]. The curing of alkyd-butylated melamine resin systems has been dealt with by Wohnsiedler[4] and by Seidler and Graetz[5]. From the experiments of these authors it became evident that the alkyd resin not only exerted a plasticising action but was also incorporated into the network by reaction of hydroxyl groups present. A similar view had been expressed in 1951 by Parker[6]. Further work on this subject was carried out by Fry,[7] by Vogelzang and Oosterhof[8], and by Augustsson[9] who was mainly interested in the possible use of several acids as curing catalysts. Both self-condensation of the melamine resin, and condensation of the melamine resin with the hydroxyl groups of the alkyd resin, appeared to be catalysed by acid groups, e.g. those present in the alkyd resin. Vogelzang and Oosterhof concluded that under similar conditions "low reactive" melamine resins show a lower extent of self-condensation than "high reactive" resins, at about the same extent of co-condensation with the alkyd resin.

Much work has been done on the curing reactions of hexakis(methoxymethyl)-melamine (HMMM) which can be regarded as a completely etherified monomeric melamine resin. Saxon and Daniel[10] studied the reactions of HMMM with acrylic acid-acrylic ester copolymers, whilst Saxon and Lestienne[11] assessed cure of HMMM alone and in blends with acrylic polymers, containing either carboxylic acid groups or hydroxyl groups. Self-condensation of HMMM appears to occur in the presence of strong acid catalysts only, whereas in the presence of weak acid catalysts such as phthalic anhydride, only reaction with hydroxyl and carboxylic acid groups occurs.

When HMMM-acrylic resin blends are cured, self-condensation of HMMM proceeds at a much slower rate than reaction of HMMM with functional groups of the acrylic resin. Further work on the curing of HMMM with acrylic resins as well as with alkyd resins was carried out by Brett[12] and by Koral[13, 14]. They concluded that, in the absence of a strong acid catalyst, co-condensation of HMMM with polymers containing carboxylic acid groups proceeds at a faster rate than phthalic acid catalysed co-condensation with polymers containing hydroxyl groups. In the presence of a strong acid catalyst the co-condensation with hydroxyl groups is many times faster than self-condensation.

From this work, a rather clear picture of the reactions of the $-NCH_2OR$ group was obtained, but it is well-known that butylated melamine resins also contain $-NCH_2OH$ groups[15] and/or $-NH$ groups. It is also well-known that "reactivity" of butylated melamine resins increases with decreasing formaldehyde to melamine ratio and with decreasing degree of etherification[6, 16, 17]. Generally a high "reactivity" of the melamine resin has the following effects:

(a) high viscosity,
(b) rapid cure,
(c) low white spirit tolerance.

"Rapid cure" means:

(a) higher hardness at equal stoving temperature,
(b) lower stoving temperature necessary for obtaining equal hardness,
(c) less melamine resin necessary for obtaining equal hardness.

This qualitative picture does not suffice to explain and predict the curing behaviour of an arbitrarily chosen alkyd-melamine resin combination.

In order to make a study of this problem, it is in the first place necessary to relate "reactivity" to the relative amounts of different functional groups present.

In this paper, the analysis of a series of commercial butylated melamine-formaldehyde resins (henceforward referred to as "MF-resins") is described.

MF-resins, differing in content of functional groups, were selected and their cure with alkyd resins of different hydroxyl value and average molecular weight was investigated.

Analysis of MF-resins

Evaporation of the organic solvent from a commercial MF-resin, as well as any analysis carried out in an acid medium, leads to changes in the nature and content of functional groups. For this reason, it was thought most convenient to relate analytical data to the melamine content and not to the "solids content" of the resin, and to use analytical methods which did not involve removal of solvent or the use of acid reagents, for the determination of functional groups.

Melamine content was calculated from a nitrogen determination according to Kjeldahl. A method, described by Knappe and Peteri[18], for the determination of melamine by direct titration with perchloric acid in anhydrous acetic acid appeared to be unreliable, since it could be shown that the results were dependent on titration speed. Good results were obtained only for melamine itself.

Formaldehyde content was determined by hydrolysis of the resin with phosphoric acid at elevated temperatures, followed by reaction of the evolved formaldehyde with aqueous hydroxylammonium chloride and colorimetric titration of hydrochloric acid formed with sodium hydroxide.

This method, evaluated by "Nederlandse Staatsmijnen DSM", proved to be at least as accurate but much less tiresome than the "chromotropic acid method", recommended by Morath and Woods[19]. Functional group analysis comprised analysis for content of $-CH_2OH$ groups and of $-NH$ groups. No suitable method for the determination of $-NCH_2OR$ groups which did not involve removal of solvent could be devised. The methods used for $-CH_2OH$ and $-NH$ groups will now be described in more detail.

Determination of methylol groups

Many methods have been described for the determination of methylol groups in aqueous media. The methods for determining methylol groups in organic solvents are not so numerous. One method, described in the literature[19], involves methylation with HCl-containing methanol, followed by determination of water formed by the standard Karl Fischer method. It is also necessary to determine the water content of the original sample. This method is very liable to give erroneous results. According to Miyauchi[20], it is possible to conduct the iodimetric titration of methylol groups in dioxan as a solvent. The present author was not, however, able to obtain good solubility in this manner, and based his determination of methylol groups on the well-known reaction of formaldehyde with dimedone (5.5-dimethyldihydroresorcinol)[21].

Two moles of this compound condense with one mole of formaldehyde to form methylenebismethone. Dimedone, as well as methylenebismethone, is a monovalent acid. So, for each mole of formaldehyde reacted, one equivalent of alkali is formed.

When applying this method to solutions of formaldehyde in *n*-butanol, it appeared necessary to heat the solution to temperatures in excess of 60°C in order to obtain reaction of formaldehyde at a measurable rate. At 80°C, complete reaction was obtained within 20 minutes. The reagent was added as a neutralised solution and the alkali formed was back-titrated continuously with a solution of HCl in methanol. Reproducible results were obtained on solutions of known formaldehyde content. It may be concluded from these experiments that formaldehyde is much more tenaciously held by butanol than by water. The same procedure was now applied to solutions or dispersions in butanol of compounds containing formaldehyde in the form of $-NCH_2OH$, $-OCH_2OH$ or $-NCH_2OR$ groups.

The following compounds were tested: dimethylolurea (DMU), hexamethylolmelamine (HMM), hexakis(methoxymethyl)melamine (HMMM), hexakis(butoxymethyl)melamine (HBMM), (prepared from HMMM by transetherification at 100°C in the presence of phthalic acid as a catalyst, using *n*-heptane for azeotropic removal of methanol formed), tris(ethoxymethyl)-melamine (TEMM)[22], and dibutylformal. Results are summarised in Table 1. Iodimetrically determined $-CH_2OH$ contents and CH_2O contents, determined by phosphoric acid hydrolysis, are also given. For comparison, results for a solution of CH_2O in butanol and for CH_2O-free butanol are added.

Table 1

Determination of $-CH_2OH$ content of some model compounds

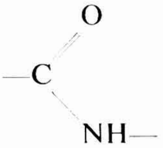
Model compound	Functional groups	Titration		$-CH_2OH$ content (as CH_2O)			CH_2O content
		temperature °C	time min	found %w	theoretical %w	iodimetric %w	%w
DMU	$-NCH_2OH$	80	30	47.5 48.0 47.9 48.3	50.0	48.3 48.4	48.6 (theor. 50.0)
HMM	$-NCH_2OH$	80	45	48.4 48.4	55.6	29.0 29.9	48.0 (theor. 55.6)
HMMM	$-NCH_2OCH_3$	80 100	15 240	0.36 2.30	0	—	45.8 (theor. 46.2)
HBMM	$-NCH_2OC_4H_9$	80	120	0.07	0	—	—
TEMM	$-NH$ $-NCH_2OC_2H_5$	80	30	0.04 0.10	0	—	30.1 (theor. 30.0)
dibutylformal	$-OCH_2OC_4H_9$	80	10	0.53	0	—	—
CH_2O in butanol	$-OCH_2OH$	80	20	8.9 9.0		10.88 10.99	9.45 9.51
butanol	—	100	240	2.0	0	—	—

From the results of Table 1 we may conclude that at 80°C —NCH_2OR groups and —OCH_2OR groups remain unattacked, whereas formaldehyde is split off from —NCH_2OH groups as well as from —OCH_2OH groups.

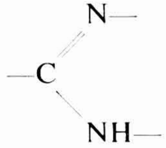
It is very probable that, under these circumstances, no decomposition will occur of butylated methylol groups, methylene bridges (—NCH_2N—), and dimethylolether bridges (—NCH_2OCH_2N—), which may be present in the MF-resin. So it is in this way possible to determine the amount of formaldehyde present as aminomethylol groups (—NCH_2OH) and as "free formaldehyde" (mainly $C_4H_9OCH_2OH$). It will be very difficult to distinguish between these two kinds of methylol groups. It will depend on the relative reactivities and amounts present of butanol and NH— groups available for reaction which kind of methylol group prevails. In order to impede condensation reactions in NH-containing MF-resins during analysis, all analyses are carried out in dilute solution (1g resin/100ml butanol).

Estimation of NH-groups

It was found that substances containing the entity



or



within their structure showed near infra-red absorption at a wavelength of 1480nm. When no N—H bonds were present, no absorption occurred at this wavelength. The OH absorption in this spectral region shows a maximum at 1420nm. The measured extinction values at 1480nm for a number of MF-resins were directly proportional to resin concentration within a suitable concentration range. Attempts, however, to use bis(butoxymethyl)urea (BBMU)[23] as a reference material failed because of serious deviations from Beer's law at low concentrations in choloroform. Therefore, solutions of TEMM[22], a substance which is not easily purified and characterised, had to be used for calibration.

This substance was characterised by determination of nitrogen content, formaldehyde content, methylol content (see Table 1) and ethoxyl content. No evidence was found for the presence of NH_2 groups in commercial MF-resins.

Results

Twelve commercially available MF-resins were analysed for nitrogen content, CH_2O content, content of CH_2OH groups and content of NH groups. The resins are coded A_1, A_2, A_3, A_4, B_1, B_2, B_3, B_4, C, D, E and F. Resins designated by the same letter were obtained from the same manufacturer. Series A and B are arranged in order of increasing reactivity as stated by the respective manufacturers. Resins C, D, E and F were said to be extremely highly reactive.

In Fig. 1 an example is given of the relation between concentration and near-infra-red extinction at 1480nm for solutions in chloroform of resin D and reference material TEMM. The extinction of the other resins was measured at one concentration only.

The results are summarised in Table 2.

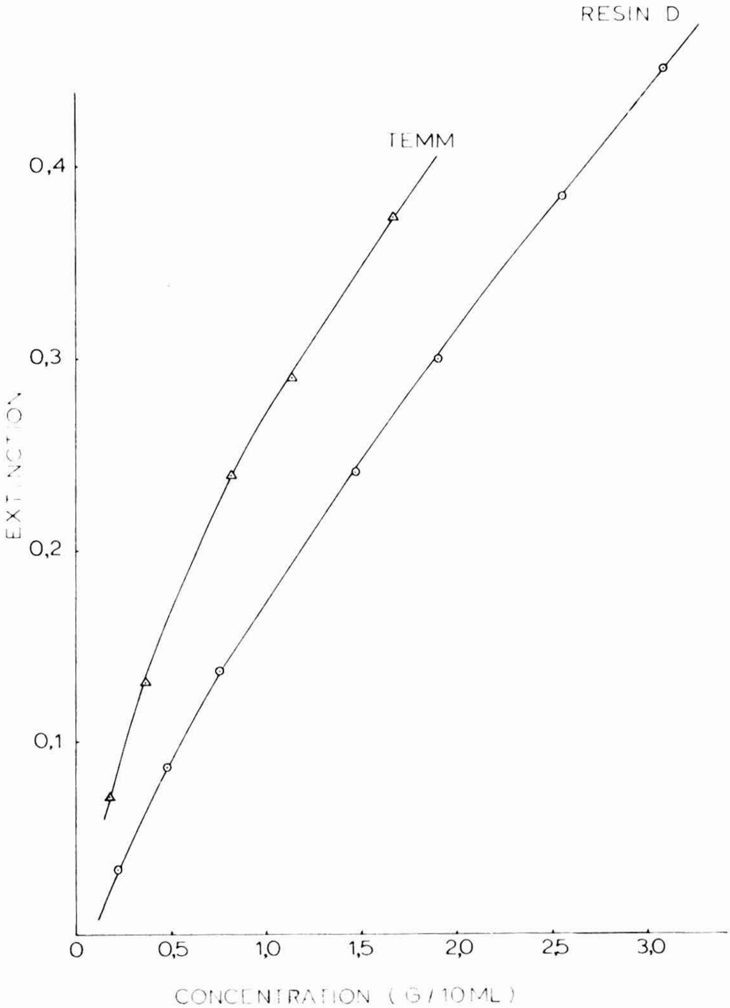


Fig. 1. Extinction of solutions in chloroform of TEMM and Resin D, at wavelength 1480nm cell thickness 1cm

Weight percentages of nitrogen, formaldehyde, and formaldehyde present in the form of —CH_2OH groups, calculated on weight of butanol-containing resin, as obtained from the manufacturer, are summarised in Table 3.

Furthermore, this table contains the percentage "solids content," as determined by determination of weight loss after 48hr drying *in vacuo*. The methylol content of the material remaining after drying was also determined. This methylol content, calculated as weight percentage CH_2O on the weight of the original solvent-containing resin, is also given in Table 3.

From the results, summarised in Table 3, the molar ratio of formaldehyde to melamine (F/M) for each MF-resin was calculated. In the same way the

Table 2

Extinctions at 1480nm of solutions in chloroform of MF-resins. Cell thickness 1cm

MF-resin	Concentration (g/10ml)	Extinction
A_1	4.738	0.103
A_2	3.239	0.076
A_3	3.152	0.217
A_4	2.996	0.335
B_1	3.472	0.082
B_2	3.431	0.125
B_3	3.530	0.166
B_4	3.712	0.160
C	3.031	0.467
D	1.661	0.373
E	3.625	0.359
F	3.455	0.182

Table 3

Nitrogen-content, formaldehyde content, "solids content," and content of methylol groups, before and after drying in vacuo

MF-resin	Nitrogen %w	Formaldehyde %w	Methylol %w CH_2O	Solids %w	Methylol content of solids %w CH_2O
A_1	14.7	34.9	12.6	79.6	8.7
A_2	12.7	30.0	13.0	69.4	9.6
A_3	15.8	29.8	10.3	73.6	8.6
A_4	16.8	26.2	5.7	75.9	4.5
B_1	15.5	32.4	4.2	84.0	2.0
B_2	13.2	26.1	7.0	66.7	3.5
B_3	17.2	35.6	10.3	84.5	7.0
B_4	17.2	36.3	14.7	78.0	12.6
C	17.4	18.4	2.1	62.7	1.3
D	15.4	15.7	3.0	54.8	1.8
E	15.6	25.7	7.5	73.0	7.2
F	12.8	24.8	10.3	61.0	9.3

ratio CH_2OH/M was calculated. The number of $-NH$ groups per mole of melamine (NH/M) was calculated from the results of Tables 2 and 3. If we assume that no solvent butanol is left after drying *in vacuo*, the remaining methylol content must be present either as CH_2O, tenaciously held by the MF-resin, and/or as $-NCH_2OH$ groups.

As a simplification, this methylol content may be regarded as being entirely due to the presence of $-NCH_2OH$ groups in the original resin and may be enumerated $-NCH_2OH/M$.

The calculated values of F/M, CH_2OH/M, NCH_2OH/M, NH/M and $F/M - CH_2OH/M$, the latter representing the number of moles of formaldehyde per mole of melamine, present as butylated methylol groups plus bridges —NCH_2N— and/or —NCH_2OCH_2N—, are summarised in Table 4.

Table 4

Moles of formaldehyde and numbers of groups —CH_2OH, —NCH_2OH, —NH, per mole of melamine

MF-resin	F/M	CH_2OH/M	NCH_2OH/M	NH/M	$F/M - CH_2OH/M$
A_1	6.6	2.4	1.7	0.25	4.2
A_2	6.6	2.9	2.1	0.31	3.7
A_3	5.3	1.8	1.5	1.2	3.5
A_4	4.4	1.0	0.8	2.0	3.4
B_1	5.8	0.8	0.4	0.26	5.0
B_2	5.5	1.5	0.8	0.55	4.0
B_3	5.8	1.7	1.1	0.67	4.1
B_4	5.9	2.4	2.0	0.70	3.5
C	3.0	0.3	0.2	2.8	2.7
D	2.9	0.6	0.3	3.0	2.3
E	4.6	1.4	1.3	2.0	3.2
F	5.3	2.3	2.0	1.0	3.0

An attempt may be made to calculate the relative amounts of —NCH_2OR groups, —NCH_2OCH_2N— bridges and —NCH_2N— bridges present per mole of melamine from the data in Table 3.

If: number of —NCH_2OCH_2N— bridges per mole of melamine = x
number of —NCH_2N— bridges per mole of melamine .. = y
weight percentage solids .. .. = S
weight percentage nitrogen .. .. = N
weight percentage formaldehyde .. .. = F
weight percentage loss of methylol-formaldehyde on drying = F'

we find the following relations:

(1) $130x = 56(F/M - CH_2OH/M) - 84\,(S - 3N/2 - F + F')\,N^{-1}$
in case only —NCH_2OCH_2N— bridges are present and

(2) $74y = 56(F/M - CH_2OH/M) - 84\,(S - 3N/2 - F + F')N^{-1}$,
in case only —NCH_2N— bridges are present.

For the cases (1) and (2) the amount of —NCH_2OR groups per mole of melamine may then be calculated according to

—$NCH_2OR/M = F/M - CH_2OH/M - 2x$, or

—$NCH_2OR/M = F/M - CH_2OH/M - y$, respectively.

The results of this calculation are shown in Table 5.

The data in Table 5 are rather arbitrary, since many assumptions were involved in deriving them. Nevertheless these data may provide a suitable basis for some qualitative considerations. So, it will be clear that values exceeding one for the number of bridges present are very improbable. This implies that in resins of the type A_1, A_3, B_1, B_3 and B_4, —NCH_2OCH_2N— bridges must be present.

Table 5

Numbers of —NCH_2OR groups, —NCH_2OCH_2N— bridges and —NCH_2N— bridges per mole of melamine

MF-resin	—NCH_2OCH_2N— only		—NCH_2N— only	
	—NCH_2OCH_2N—/M	—NCH_2OR/M	—NCH_2N—/M	—NCH_2OR/M
A_1	0.7	2.8	1.2	3.0
A_2	0.4	2.9	0.7	3.0
A_3	0.65	2.2	1.1	2.4
A_4	0.5	2.4	0.8	2.6
B_1	0.95	3.1	1.6	3.4
B_2	0.6	2.8	0.9	3.1
B_3	0.85	2.4	1.4	2.7
B_4	0.9	1.7	1.5	2.0
C	0.4	1.9	0.6	2.1
D	0.3	1.7	0.5	1.8
E	0.4	2.4	0.6	2.6
F	0.4	2.2	0.6	2.4

Resins of the types C and D, apparently prepared at very low F/M ratios (see Table 4), may contain —NCH_2N— bridges only. We now consider the figures, given in Table 5 in the third column from the left, as reasonably approximative values for —NCH_2OR/M. The least reliable figures in Table 4 are those given for the value of —NCH_2OH/M. The values of F/M —CH_2OH/M and, to a smaller extent, those of NH/M, are more reliable. For this reason, it is probably better to calculate —NCH_2OH/M, according to:

$$NCH_2OH/M = 6 - (F/M - CH_2OH/M) - NH/M.$$

Values of —NCH_2OR/M, —NCH_2OH/M, and —NH/M, based on these considerations, are summarised in Table 6.

Table 6

Numbers of groups —NCH_2OR, —NCH_2OH and —NH per mole of melamine

MF-resin	—NCH_2OR/M	—NCH_2OH/M	—NH/M
A_1	2.8	1.5	0.25
A_2	2.9	2.0	0.31
A_3	2.2	1.3	1.2
A_4	2.4	0.6	2.0
B_1	3.1	0.7	0.26
B_2	2.8	1.4	0.55
B_3	2.4	1.2	0.67
B_4	1.7	1.8	0.70
C	1.9	0.5	2.8
D	1.7	0.7	3.0
E	2.4	0.8	2.0
F	2.2	2.0	1.0

Discussion of results

From the data shown in Table 6, the conclusion may be drawn that "reactivity" shows a tendency to increase with a decrease in —NCH_2OR/M. This implies invariably that, provided the MF-resins have comparable degrees of condensation, "reactivity" tends to increase with increasing amounts present of —NH groups or —NCH_2OH groups or both. It must be borne in mind that the presence of —NCH_2OH groups has not been proven, but this does not affect the above conclusion. If only —NH groups were present, curing of alkyd-MF combinations below temperatures of 150°C would proceed mainly through self-condensation of the MF-resin, since reactions of the —NCH_2OR group with hydroxyl groups of the alkyd resin are not to be expected under these conditions[14]. If, however, mainly —NCH_2OH groups were present, co-condensation as well as self-condensation might occur. Co-condensation in this case would be favoured by a high hydroxyl value of the alkyd resin and a low content of —NH groups of the MF-resin. Thus, resins C and D will probably cure mainly by self-condensation, whereas F in addition has an opportunity for co-condensation. Resin B_1 will probably show the lowest overall degree of cure.

Alkyd resins

Degree of cure will be influenced by hydroxyl value as well as by molecular weight of the alkyd resins used. Four alkyd resins were prepared from isophthalic acid (IPA), trimethylolpropane (TMP), and lauric acid (LA). The resins are coded: H170, L170, H100, L100. The designation H means that the resin was formulated close to its gel point at acid value 10. The designation L means that the resin was further removed from its gel point than an H-resin at the same acid value. The numbers 170 and 100 stand for the hydroxyl values. All resins were cooked to acid value 10. In Table 7, the amounts of starting materials used in the preparation of each resin are given (in mg/g resin), together with the calculated p_A gel[24] for each resin.

Table 7

Composition and p_A gel of alkyd resins

alkyd resin	isophthalic acid mg/g resin	lauric acid mg/g resin	trimethylolpropane mg/g resin	p_A gel
H170	477.2	202.3	439.0	0.916
L170	439.4	246.6	428.3	0.943
H100	405.3	337.8	372.0	0.915
L100	372.5	376.2	362.8	0.943

Molecular weight distributions of the alkyd resins were determined by gel permeation chromatography on polystyrene gel, using tetrahydrofuran as eluting agent, and polyglycols for calibration. Results are shown in Figs. 2 and 3.

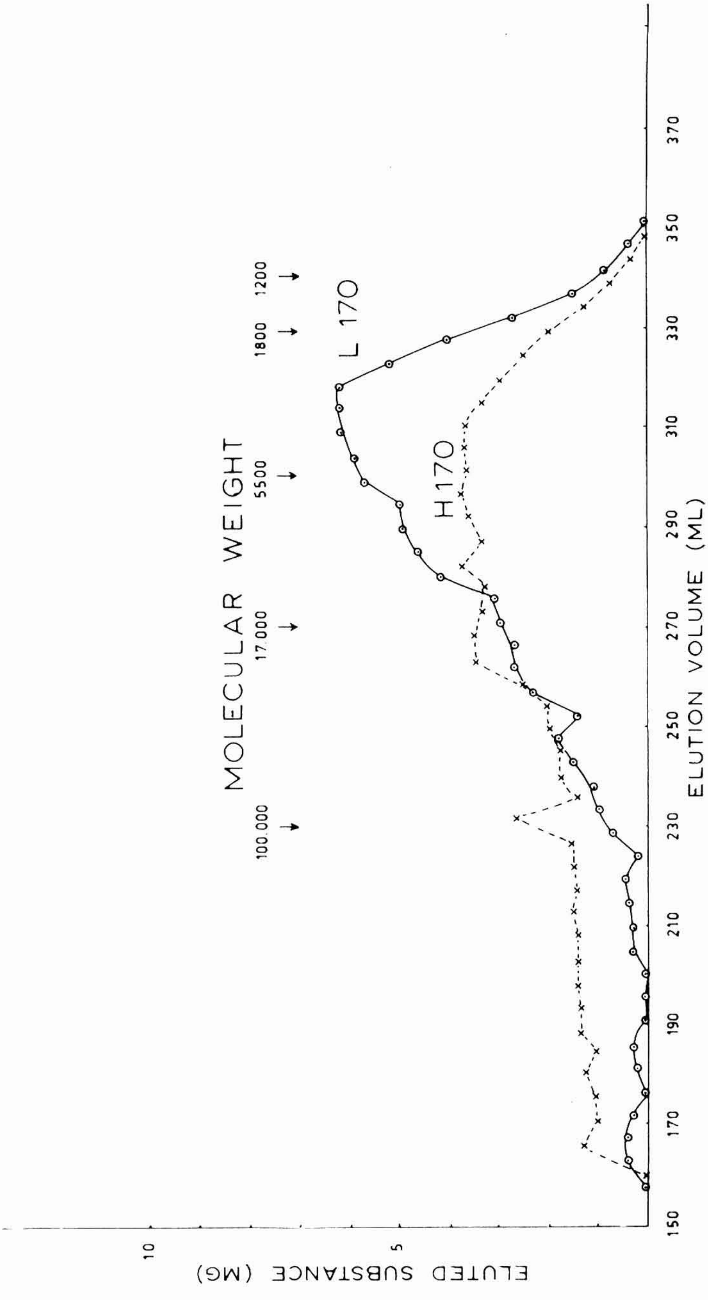


Fig. 2. Molecular weight distribution of alkyd resins H170 and L170

Cure of MF-resins and of alkyd-MF-resin combinations

Various methods have been devised for assessment of cure. Well-known methods include thermogravimetry, differential thermal analysis, infra-red spectroscopy, solvent-extraction, swelling by a solvent, and determination of modulus of elasticity or rigidity of swollen films. Swelling of supported films has been

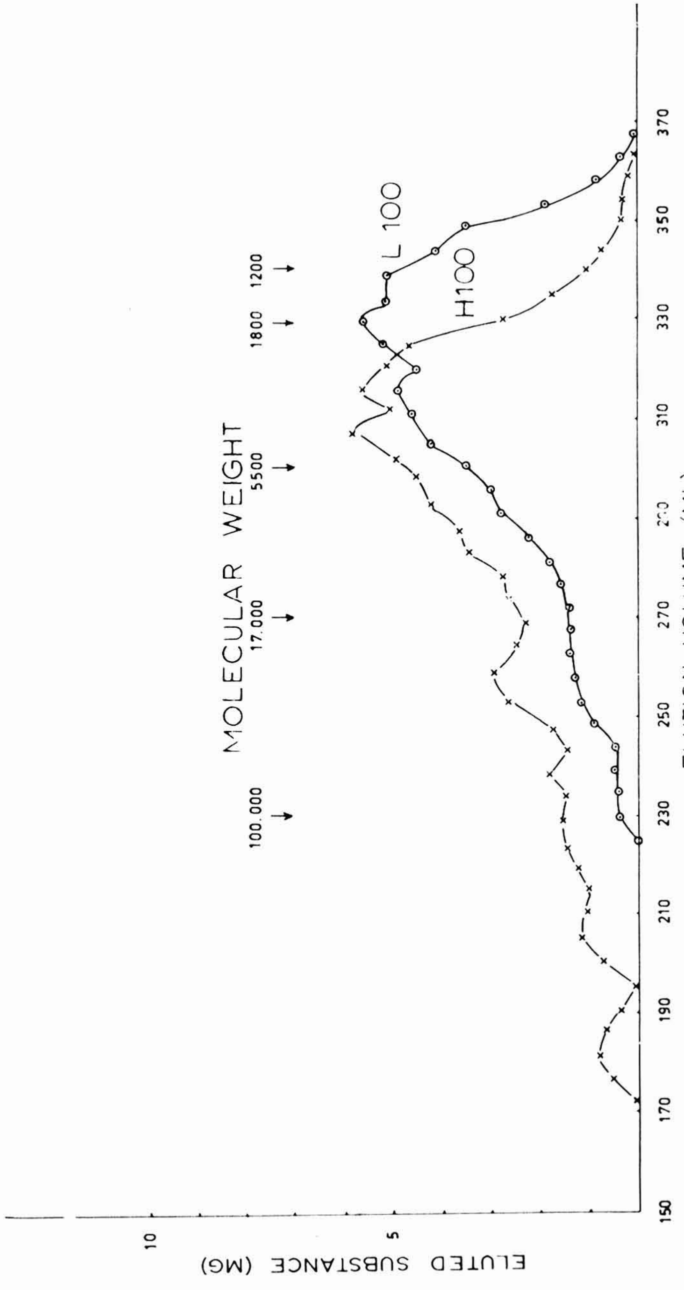


Fig. 3. Molecular weight distribution of alkyd resins H100 and L100

measured by Lewis[25] with an indentation tester. Cure of liquid materials has been followed by studying rigidity changes by means of torsional braid analysis[26]. Rigidity changes of thin supported films have been studied by Zorll by means of a torsional pendulum method. Results, obtained with a König pendulum hardness tester, were in good agreement with those obtained by the torsional pendulum method[27]. Japanese workers used the temperature dependence of damping of pendulum oscillations for assessing cure of acrylic resin-modified HMMM combinations[28]. The author decided to measure König pendulum hardness as a function of stoving temperature in order to compare curing performance of different alkyd-MF-resin systems.

König pendulum hardness is recorded as the period of time elapsed between two fixed boundary conditions for the amplitude of the pendulum.

The logarithmic decrement, defined as:

$$\Lambda = \ln \frac{A_n}{A_{n+1}}, \text{ where } \begin{array}{l} A = \text{amplitude,} \\ n = \text{amplitude number,} \end{array}$$

is inversely proportional to the number of oscillations which occur between these boundary conditions.

Cross-linking leads to a decrease in Λ, so the influence of stoving temperature on curing can be estimated by measuring König pendulum hardness as a function of stoving temperature. The limitations of this method are appreciated, but in this way it is possible to compare the influence of stoving temperature on curing of a large number of resin mixtures within a relatively short time.

Experimental methods

The MF-resin or alkyd-MF-resin mixture to be investigated is applied by means of a wire coater to an aluminium sheet of 0.1cm thickness, having a surface area of $120 \times 9\text{cm}^2$.

If necessary, the resin (mixture) is first diluted to the desired viscosity with a mixture of equal volumes of xylene and butanol. After a preliminary drying period of one hour at room temperature, the coated sheet is placed into a "gradient cure block." The essential part of this equipment is an aluminium block, having a surface area of about $120 \times 9\text{cm}^2$, which is maintained at a temperature gradient of 20-200°C along its length. The sheet is brought into direct contact with this block, removed after the desired stoving period and stored at 20°C and 65 per cent relative humidity.

The temperature gradient of the block is not exactly linear. The temperature is measured at 10cm intervals alongside the block. The corresponding points are marked on each sheet and film thickness, and König pendulum hardnesses are determined after storage for periods of 24hr, 48hr and 72hr respectively. König pendulum hardness is recorded as the time (in seconds) elapsed between amplitudes of 6° and 3°. For each sheet, plots of pendulum hardness *versus* stoving temperature are prepared.

Results

In Fig. 4 the influence of stoving temperature on König pendulum hardness of MF-resins A_1, A_4, B_1, B_2, B_4, D, E, F is illustrated. Stoving time was 15 minutes.

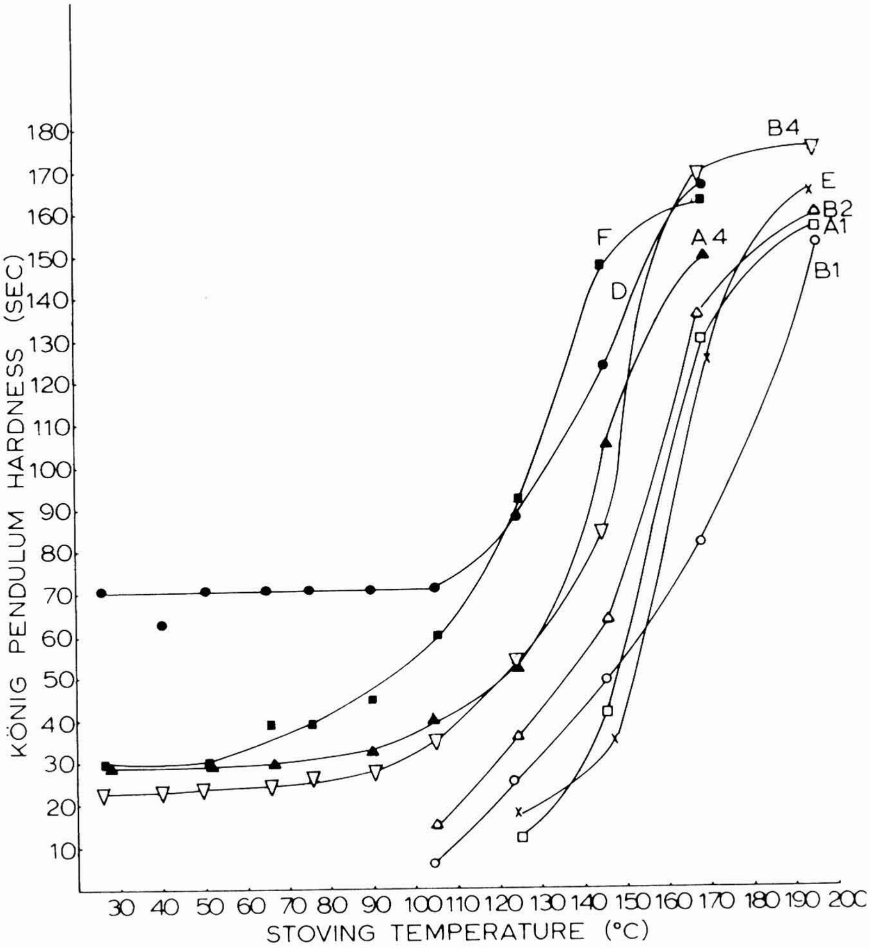


Fig. 4. König pendulum hardness v. stoving temperature. MF-resins, stoving time 15min

In Fig. 5 results are shown for the same MF-resins, to which 3 per cent by weight of monobutyl phthalate had been added as a catalyst. This amount of catalyst corresponds to the amount of carboxylic acid group present in the alkyd-MF-resin mixtures to be described in this section.

In Figs. 6, 7, 8 and 9 results are shown for mixtures of MF-resins B_1, B_2, B_4, D, F and HMMM with alkyd resins L100, H100, L170 and H170, respectively. The mixtures were prepared in such a way that the weight ratio of alkyd resin solids to melamine present in MF-resin amounted to 9:1 for each mixture. The resulting weight percentages of MF-resin in the mixture varied from 22 per cent (for resin D) to 30 per cent by weight (for resin A_1) calculated as solids. Stoving time was 30 minutes. Experiments at stoving periods of 15 minutes and 60 minutes were also carried out, but there were no important differences in the results, shown in Figs. 6, 7, 8 and 9. Experiments with the addition of 1.5

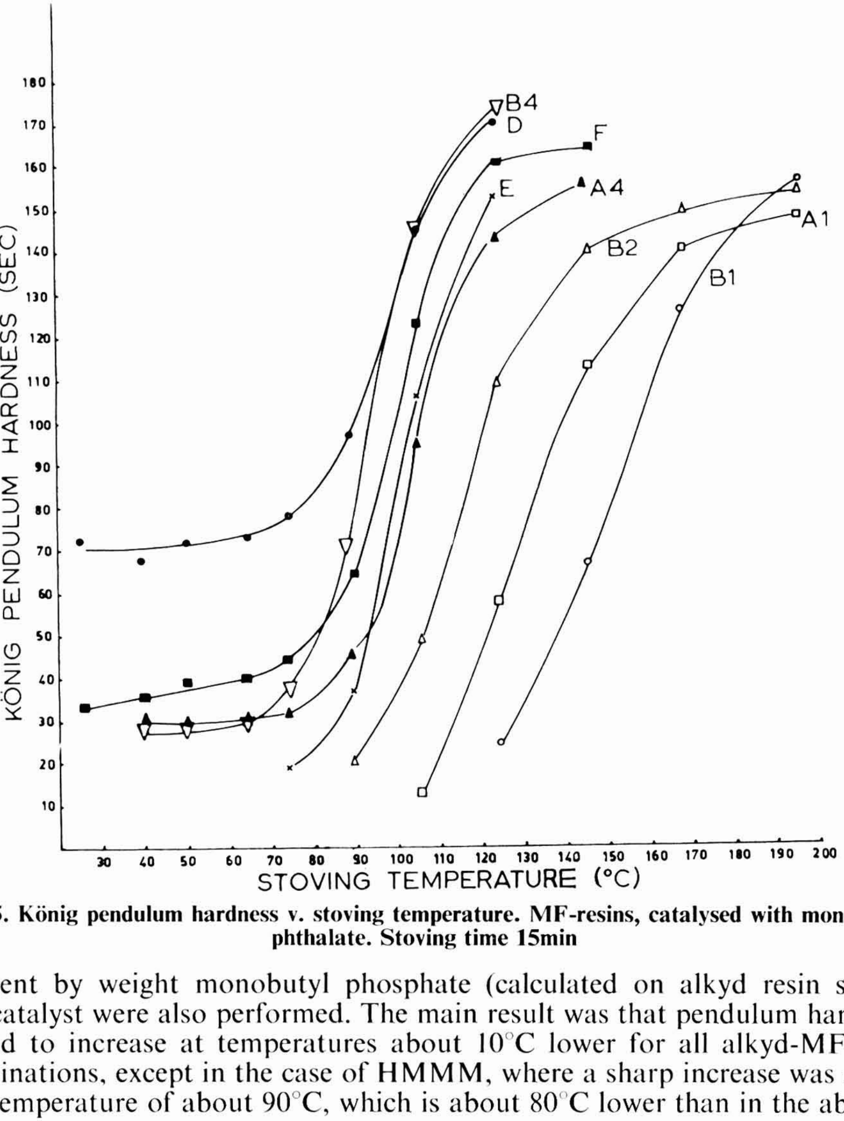


Fig. 5. König pendulum hardness v. stoving temperature. MF-resins, catalysed with monobutyl phthalate. Stoving time 15min

per cent by weight monobutyl phosphate (calculated on alkyd resin solids) as a catalyst were also performed. The main result was that pendulum hardness started to increase at temperatures about 10°C lower for all alkyd-MF-resin combinations, except in the case of HMMM, where a sharp increase was noted at a temperature of about 90°C, which is about 80°C lower than in the absence of a catalyst.

The measured film thickness varied from 25 μm to 40 μm. The largest difference between measured film thicknesses on one sheet was about 10 μm. A relation between stoving temperature and film thickness could not be ascertained.

Discussion of results

Pendulum hardness will be dependent on the following main factors:

1. hardness of the solvent-free resin,
2. amount of plasticiser present,
3. degree of curing.

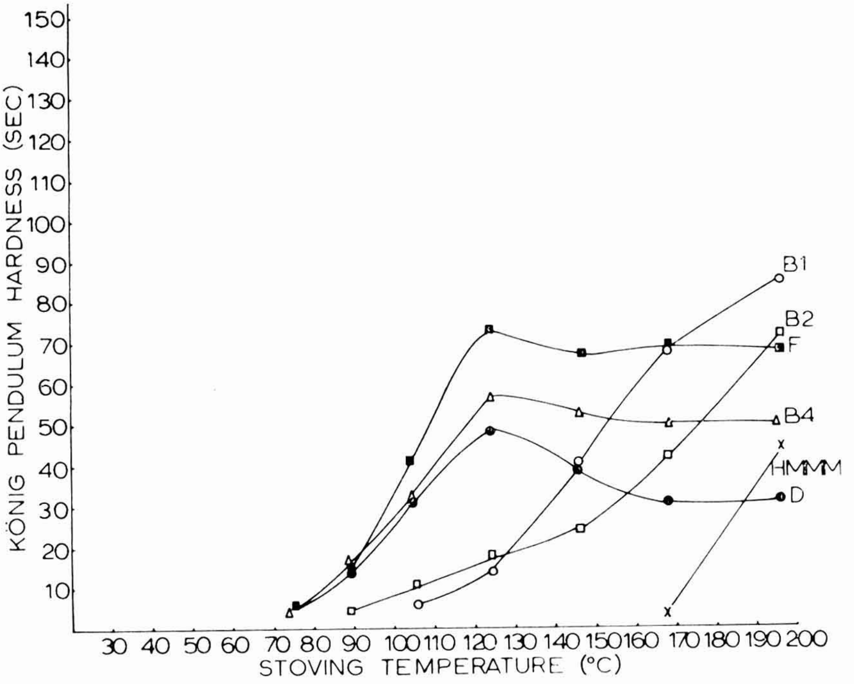


Fig. 6. König pendulum hardness v. stoving temperature. MF-resin-alkyd L100 combinations. Stoving time 30min

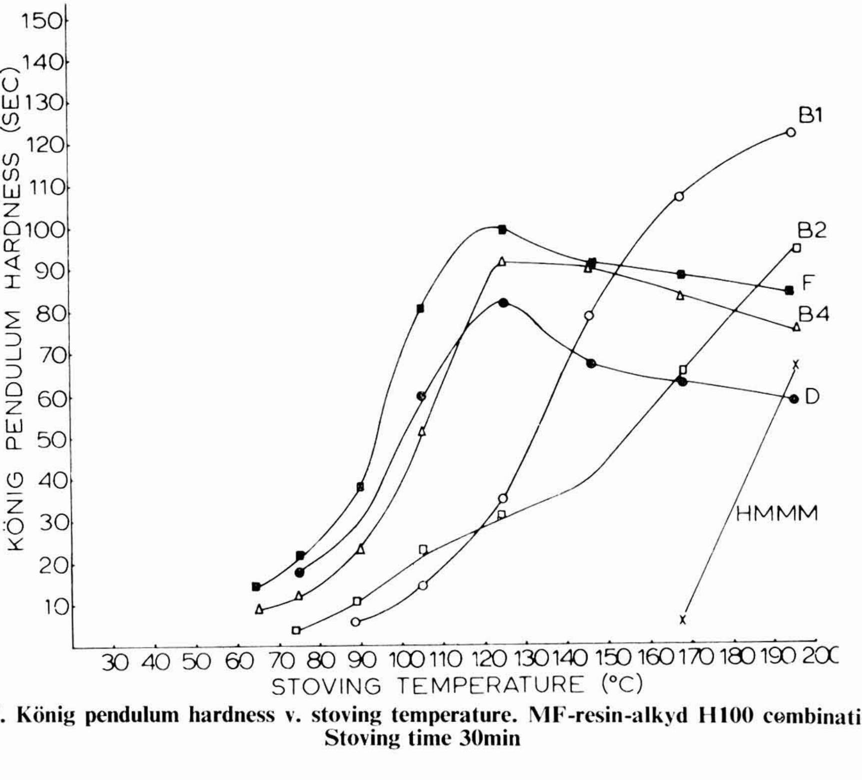


Fig. 7. König pendulum hardness v. stoving temperature. MF-resin-alkyd H100 combinations. Stoving time 30min

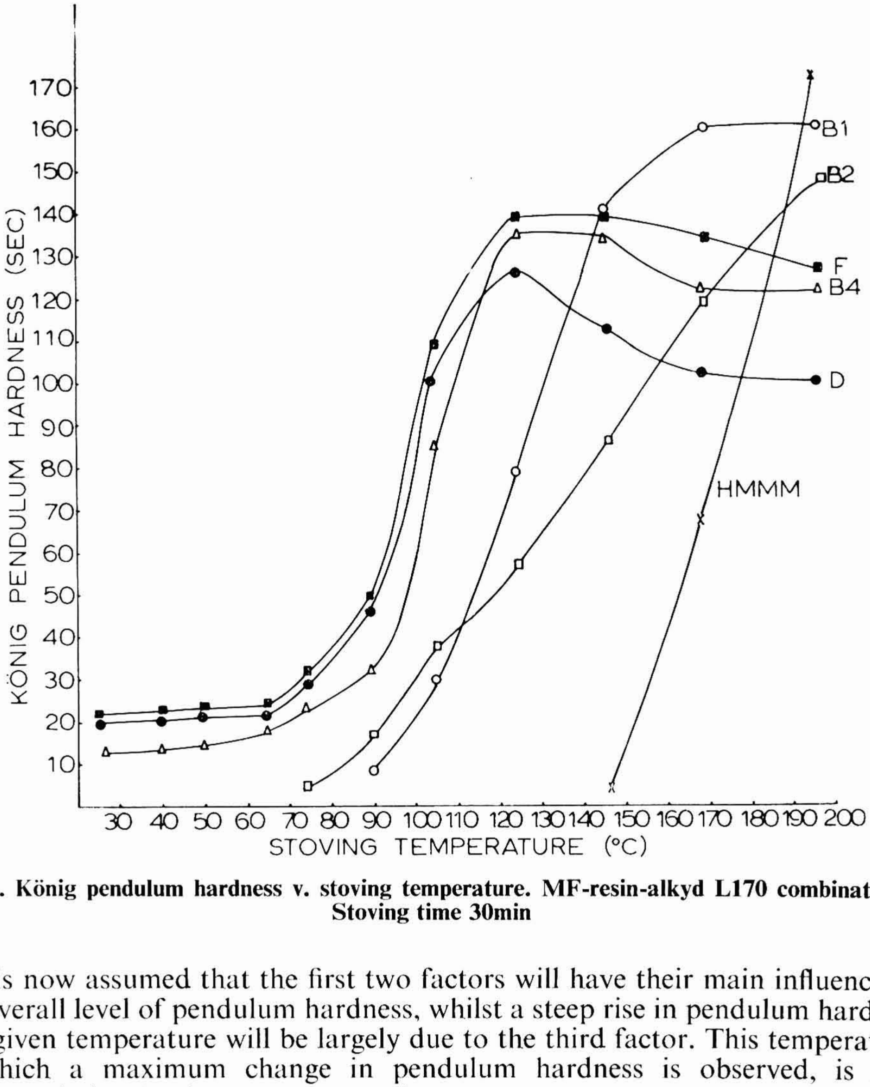


Fig. 8. König pendulum hardness v. stoving temperature. MF-resin-alkyd L170 combinations. Stoving time 30min

It is now assumed that the first two factors will have their main influence on the overall level of pendulum hardness, whilst a steep rise in pendulum hardness at a given temperature will be largely due to the third factor. This temperature, at which a maximum change in pendulum hardness is observed, is here designated the "curing temperature."

On comparing the results shown in Figs. 4 and 5, the catalytic effect of monobutyl phthalate is clearly demonstrated. The curing temperature is considerably lowered by the addition of monobutyl phthalate, especially in the case of resin D which should be particularly prone to self-condensation (see Table 6). The smallest effect is noted for resin B_1, which apparently does not contain sufficient —NH and/or —CH_2OH groups for rapid self-condensation. In Table 8, curing temperatures of monobutyl phthalate catalysed MF-resin are compared with the values of —NCH_2OR/M. The MF-resins are arranged in decreasing order of —NCH_2OR/M values. In the case of equal —NCH_2OR/M values, the resin with the lowest value of —NH/M + —CH_2OH/M is mentioned first.

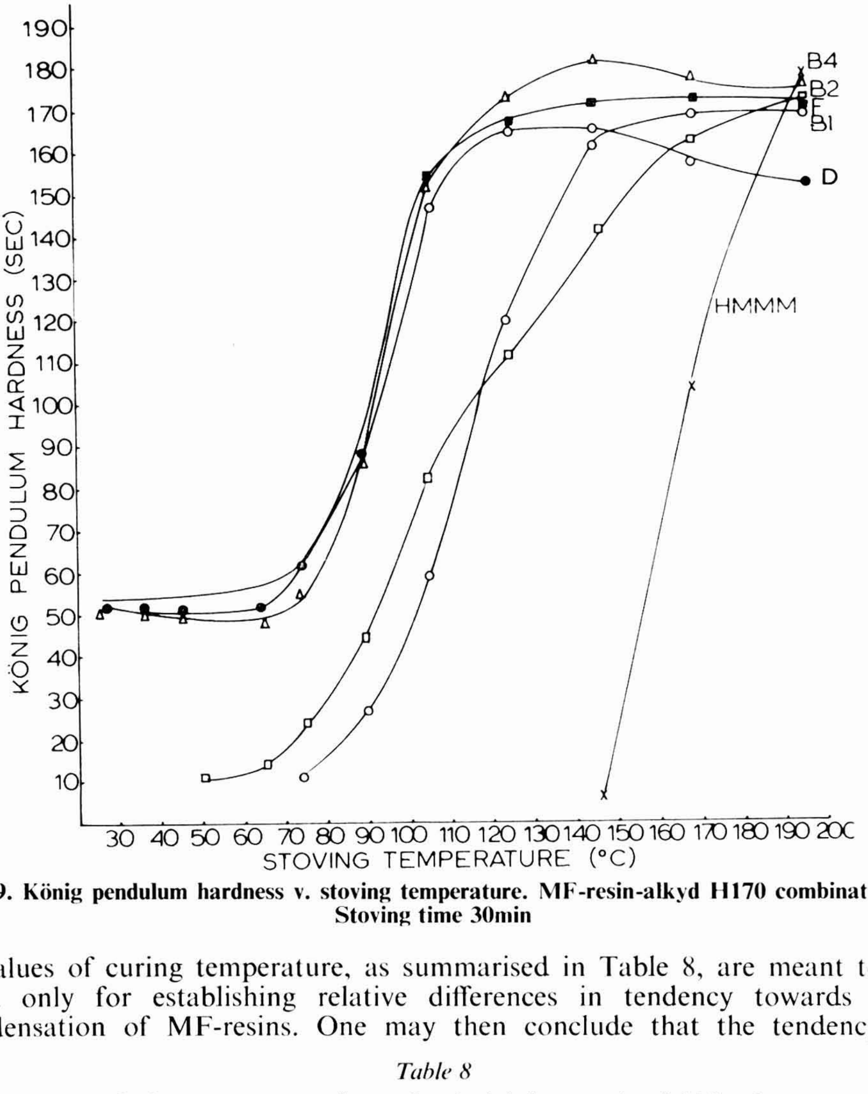


Fig. 9. König pendulum hardness v. stoving temperature. MF-resin-alkyd H170 combinations. Stoving time 30min

Values of curing temperature, as summarised in Table 8, are meant to be used only for establishing relative differences in tendency towards self-condensation of MF-resins. One may then conclude that the tendency of

Table 8

Curing temperature of monobutyl phthalate-catalysed MF-resins and number of groups —NCH$_2$OR present

MF-resin	Curing temperature (°C)	—NCH$_2$OR/M
B$_1$	155	3.1
A$_1$	130	2.8
B$_2$	115	2.8
A$_4$	105	2.4
E	105	2.4
F	100	2.2
B$_4$	95	1.7
D	95	1.7

MF-resins, catalysed by monobutyl phthalate, towards self-condensation is inversely proportional to the number of groups —NCH_2OR present. So, it may be stated that the MF-resins in Table 8 are arranged in order of increasing "reactivity."

The occurrence of a slight plasticising effect of monobutyl phthalate may be deduced from the absolute values of pendulum hardness obtained at high stoving temperature (see Figs. 5 and 6). This same plasticising effect was observed on using monobutyl phosphate in curing alkyd-MF-resin combinations.

The higher values of pendulum hardness of "more highly reactive" MF-resins are not necessarily due to increased curing, but may also be caused by the presence of only a small amount of plasticising —NCH_2OR groups.

It is to be expected that self-condensation of MF-resins plays an important part in the curing of alkyd-MF-resin combinations. The results shown in Figs. 6, 7, 8 and 9 confirm this point of view. There is no large influence of alkyd resin type on the relative order of curing temperatures of MF-resins.

Combinations of alkyd resins with HMMM, which can cure only by reaction of OH groups of the alkyd resin with —NCH_2OR groups of HMMM show much higher curing temperatures than combinations of alkyd resins with other MF-resins. The curing temperature of alkyd-HMMM combinations is more dependent on OH value than on molecular weight of the alkyd. This difference may also be caused by the large influence of alkyd resin type on the absolute values of pendulum hardness, due to differences in the isophthalic acid/lauric acid weight ratio. Generally, alkyd resin type has a much greater influence on pendulum hardness than MF-resin type, but this does not prove that faster cure is obtained with alkyds of higher OH value and/or molecular weight. An important contribution of co-condensation to pendulum hardness is to be expected for those MF-resins which have a relatively high ratio of —NCH_2OH/M to —NH/M (see Table 6). This effect should be most conspicuous for MF-resins having little opportunity for self-condensation. These views are verified by the results in Figs. 6, 7, 8 and 9, in comparison with those of Fig. 5, but, again, this effect may also be due to differences in plasticising character of the alkyd resins for the different MF-resins.

The results obtained at temperatures in the vicinity of 200°C indicate a general plasticising effect of the alkyd resin, especially in the case of highly reactive MF-resins. For low reactivity MF-resins however, pendulum hardness continues to rise with an increase in temperature, and values in excess of those reached in the absence of an alkyd resin are possible with alkyd resins of high OH value, exactly as is the case with HMMM.

This difference between MF-resins of high reactivity and of low reactivity can be explained by their different rates of self-condensation, self-condensation of highly reactive MF-resins being too fast to allow for sufficient co-condensation with the alkyd resin.

Additional experiments

An attempt was made to find confirmation for some of the opinions expressed in the preceding section by determination of percentage acetone-extractable material, modulus of elasticity of acetone-swollen films, and dependence of the logarithmic decrement Λ on temperature by means of a torsional pendulum method, for some selected alkyd-MF-resin combinations.

For this purpose, coatings on steel panels as well as free films were prepared.

First, the percentage extractable material of L170-D combinations (see Fig. 8), baked at 105°C, 130°C and 200°C respectively, was determined, in order to check the apparently small differences in curing of highly reactive MF-resins at temperatures between 100°C and 200°C. The acetone-extractable material at these temperatures appeared to have values of 15 per cent by weight, 15 per cent by weight and 20 per cent by weight (based on film weight) respectively. Pendulum hardness values were 127, 127 and 123 sec, respectively.

Next, percentages of extractable material in combinations of H170 with MF-resins B_1 (low reactivity) and F (high reactivity, high content of $—NCH_2OH$) were determined. Alkyd/MF weight ratios of 80/20 and 70/30, and baking temperatures of 110°C and 150°C, were chosen. Results are summarised in Table 9.

Table 9

Percentage extractable material and pendulum hardness of combinations of H170 with B_1 and F at 110°C and 150°C

MF-resin	Alkyd/MF (w/w)	Baking temperature (°C)	Pendulum hardness (sec)	Extractable material (%w)
B_1	80/20	110	86	23
	80/20	150	148	4
	70/30	110	91	15
	70/30	150	152	1
F	80/20	110	164	15
	80/20	150	159	8
	70/30	110	172	10
	70/30	150	167	3

The results of Table 9 show that at 110°C more cure is obtained with the high reactive resin, whereas at 150°C the low reactive MF-resin has the higher degree of cure. For the high reactive MF-resin these differences are not reflected in the pendulum hardness values. Apparently co-condensation has a greater influence on pendulum hardness than self-condensation.

Some further experiments were carried out to estimate the relative influences of several factors on pendulum hardness. Alkyd/MF combinations used, baking temperatures, and results, are summarised in Table 10. Pendulum hardness, percentage extractable material, modulus of elasticity of acetone-swollen films at 20°C, and the dependence of the logarithmic decrement Λ on temperature were determined. The modulus of elasticity in acetone E_{ac} is a measure for the mean molecular weight M_c of chains between cross-links. Changes in E_{ac} of one and the same material are thus indicative of changes in degree of cross-linking of this material. Plots of Λ *versus* temperature were used by Ohe et al.[28] to estimate relative degrees of cross-linking of similar materials. A maximum value of Λ occurs at the glass transition temperature T_g.

Table 10

Values of KP, Ex, E_{ac} T_g, and Λ_{max}, of alkyd-MF-resin combinations, cured under different conditions

Alkyd resin	MF-resin	Baking temperature (°C)	catalyst	KP (sec)	Ex (%w)	E_{ac} (gcm^{-2})	T_g (°C)	Λ max
H170	B_1	130	none	93	15	1.2	40	1.0
H100	B_1	200	none	114	5	18.5	55	0.6
L170	D	130	none	152	22	2.6	45	0.9
L170	D	200	none	132	18	24.3	50	0.8
H170	HMMM	130	monobutyl phosphate	131	3	24.5	80	1.3
H170	HMMM	200	none	191	7	2.2	40	1.1

Values of König pendulum hardness, KP, percentage extractable material, Ex, modulus of elasticity in acetone, E_{ac}, glass transition temperature, T_g, and maximum value of Λ, Λ_{max}, are summarised in Table 10. Baking time was 15 minutes.

The results in Table 10 illustrate the risks involved in comparing degrees of curing of widely differing resin combinations on the basis of one parameter only. According to values of Ex, high degrees of cure are obtained with H100/B_1 and H170/HMMM. However the presence or absence of a strong acid in H170/HMMM leads to large differences in KP, E_{ac} and T_g. The high values of E_{ac} and T_g observed in the presence of strong acid apparently are caused by self-condensation of HMMM. This same effect of self-condensation on E_{ac} and T_g may be noted for H100/B_1 and L170/D, cured at high temperatures, although in the latter case overall degree of cure, as indicated by Ex, is low, due to insufficient co-condensation.

The large difference between KP of H170/B_1 and L170/D is probably partly due to the high KP of the solvent free MF-resin D (see Fig. 5). The low KP value of H170/HMMM, catalysed by monobutyl phosphate, compared to that of the uncatalysed combination, may be the result of a plasticising effect of monobutyl phosphate. Generally KP values of monobutyl phosphate-catalysed combinations were abnormally low, but no such effect was observed for penetration hardness as measured with a Wallace indentation tester.

Conclusions

On the basis of the foregoing results, discussions and observations, the following conclusions are drawn.

1. The relative amounts of functional groups present in butylated MF-resins can be determined by analytical methods.
2. Relative rates of cure of butylated MF-resins are inversely proportional to the number of butylated aminomethylol groups present.
3. Butylated MF-resins, containing a high proportion of butylated aminomethylol groups, are more capable of co-condensation with alkyd resins than those containing a low proportion of butylated aminomethylol groups.

4. Co-condensation of completely etherified MF-resins with alkyd resins takes place at a measurable rate at temperatures in excess of 150°C. No self-condensation occurs.

The conclusions on curing are valid only for resin combinations which do not contain a strong acid catalyst, such as phosphoric acid.

Acknowledgments

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Discussion at the Eastbourne Conference

MR R. A. BRETT expressed interest in Dr van Zuylen's work, since it was largely complementary to work that had been carried out at the Paint Research Station on the reaction mechanism of alkyd melamines, both in solvent and water based systems. He agreed with Dr van Zuylen that true co-condensation of the components such as the alkyd with the melamine should be encouraged.

He asked if there was any information on the effect of the size and shape of the alkyl modifying group used to etherify the melamine resin on the reactivity of the resin.

DR J. VAN ZUYLEN replied that the resins investigated were all of the butylated type. Some experiments comparing hexamethoxymethyl melamine with hexamethoxybutyl melamine had been carried out, but only be comparing the temperatures at which volatile reaction products were evolved. Combinations of the two compounds with trimethylolpropane were cured and the temperature at which methanol or butanol was set free recorded. The main result of this had been that no difference in reactivity between etherified methylol groups owing to the nature of the alcohol group was noted.

MR J. WEAVER asked if it was intended to publish further data on the precision of the dimedone analytical determination itself, and if Dr van Zuylen thought it was worthy of co-operative testing between various laboratories.

DR VAN ZUYLEN was not sure about the publication of further data on the analytical method. This would depend on the interest of other industries for the method.

In answer to the second part of the question, there was some testing going on at Dutch State Mines. They were very interested because they were producers of melamine, and they gave a lot of information about the production of melamine resins. It was intended to compare the methylol determination by the dimedone method with the results from the butoxyl determination by the Ziesel method on the solvent-free resin, removing the solvent in vacuo at low temperature.

He added that he had used the dimedone method only as a semi-quantitative method, and did not think it was a very good quantitative method.

THE CHAIRMAN, DR S. H. BELL, suggested that Dr. Bult might have some comment on a co-operative testing scheme.

DR R. BULT said that the Verfinstituut TNO would have no objections to co-operative testing, and he would be very willing to discuss any proposal for inter-laboratory investigation.

DR L. A. O'NEILL remarked that Dr van Zuylen had quoted in the paper a gel permeation chromatogram of the alkyds used. Had he looked at any of the melamines by gel permeation chromatography, because the technique was quite useful for studying low molecular weight components, and might have shown differences between some of the main types.

Secondly, some commercial melamine/formaldehyde resins contained stabilisers such as amines. Had any of the products Dr van Zuylen examined contained such stabilisers and would they have affected the reactivity which he had studied?

DR VAN ZUYLEN said that gel permeation chromatography of melamines and ureas had been investigated at the Dutch Paint Research Institute, but no good interpretation of the results had yet been achieved.

As to the second question, he didn't know if amine stabilisers were present, but thought it possible.

MR A. R. H. TAWN complimented Dr van Zuylen on an excellent piece of work. It was particularly refreshing to find several different methods being applied comparatively in the assessment of cross-link density which, as had been seen, was not necessarily closely related to pendulum hardness.

Dr van Zuylen did not explicitly state that his modulus of elasticity was a measure of cross-link density, but it seemed that this was implied. He himself would utter a word of warning about interpreting modulus of elasticity too strictly in this way, because such interpretation depended on an assumption which, to his knowledge, had never been proved. The theoretical relationship between tensile stress and extension ratio assumed an equilibrium process of affine deformation of an incompressible Gaussian network composed of freely orienting chains. Under the usual non-equilibrium conditions of measurement, the empirical Mooney-Rivlin equation was commonly employed, and the assumption was made that the first Mooney-Rivlin constant was identifiable with the theoretical expression in terms of the number of chains per unit volume. Such comparing of coefficients between a theoretical and an empirical equation was always tempting but could be challenged in logic. Although experience had shown it to be safe to assume a monotonic relationship between cross-link density and modulus of elasticity, there was less than adequate justification for the actual calculation of cross-link density values from elasticity moduli as usually measured, particularly as cross-link density reached high values and the system could no longer be regarded as freely orienting. One was thus led to question whether this method should be regarded, as the author seemed to regard it, as the ultimate standard against which others might be judged.

Criticism could also be levelled at the use of percentage of sol, *i.e.* extractable matter, as an inverse measure of cross-link density. Again the relationship invariably appeared to be monotonic, but the actual calculation of the one from the other assumed that Flory cross-linking statistics applied. These too were idealised and seldom described closely the behaviour of real systems.

DR VAN ZUYLEN said that he had thought that the modulus of elasticity measured in acetone solution gave some idea about the mean length of chains between cross-links, and intended to use it in this sense only. He had only tried to correlate it with the relative degree of self-condensation. When there was a large difference between the results of pendulum hardness and modulus of elasticity, as in the work he had described, the unexpected high values of modulus of elasticity might be ascribed to a very high degree of cross-linking, but inhomogeneous cross-linking. Hence cross-linking might be high, but the percentage of extractable material would still also be high.

MR P. DE CARPENTIER asked if Dr van Zuylen had any additional information on how the ratio of self-condensation and co-condensation would be affected when secondary hydroxyl containing alkyds, as opposed to the primary hydroxyl containing ones, were used.

DR VAN ZUYLEN replied that no work had been done on this as yet. However, there was some interest in investigation of alkyds with secondary hydroxyl groups, so it might be useful to do this in the future.

MR C. BARKER congratulated Dr. van Zuylen on the detail into which he had gone in this problem.

His question was about the HMMM type of product. The manufacturers of the commercial types of hexakismethoxymethylmelamine resins had made great play of the long weight usage that was required of these, in ratio of alkyd to melamine, so that one might use weight ratios of 85:15. His experience had been that this was optimistic.

The point was, what proportion of the available reactivity of HMMM was involved in cross-linking, because it was a small, compact molecule, and, when cross-linking a long-medium molecular weight alkyd, a reasonable proportion could be expected to react. When used in conjunction with high molecular weight alkyds, or perhaps even with acrylic polvmers, with which it was compatible, however, the chances of realising the very high functionality must be rather low, owing to steric considerations.

DR VAN ZUYLEN agreed that it was dangerous to make calculations on the basis of functionalities, but, in normal practice, in cross-linking reactions of HMMM a functionality in the order of 2—3 could be expected depending on the circumstances. The higher the degree of cross-linking owing to the other components, the lower the functionality of HMMM. However, it was almost impossible to get a value of 3.

A point to be kept in mind was that in most commercial systems using HMMM, there was a strong acid catalyst present, and in this investigation no catalyst had been used, except in one experiment mentioned in Table 10. So it was difficult to say anything about commercial practice in this respect, because when a strong acid catalyst was present there was a lot of self-condensation of the HMMM, although the reaction with the hydroxyl groups of another component was much faster.

MR N. MACLEOD referred to Table 9 of the paper. Regarding resin F, it would appear that at the lower curing temperature the resin was co-condensing, and that a certain amount of alkyd must therefore be acting as a plasticiser. Had Dr van Zuylen examined the extractable material to see whether it was alkyd or melamine or mixture?

DR VAN ZUYLEN replied that this had not been done.

MR TAWN, commenting on Mr Macleod's question, felt that one should effectively ignore the very low figures for extractables in this case, as he didn't believe that they gave any index at all of the extent of reaction between the melamine and the alkyd resin, because there would always be some species present in the alkyd which contained no hydroxyl groups, as could be shown statistically. If there were species in the alkyd which contained no hydroxyl groups, then, on the current mechanism being presumed, those species would not react with the melamine, and would remain permanently in the soluble form. Hence there would always be a certain small percentage of permanently extractable material and what was effectively 100 per cent reaction between the melamine and the alkyd would still give up to about 4 per cent of extractable material.

DR VAN ZUYLEN agreed, saying that the determination of nitrogen contents of the extractables had not been carried out because it had been expected that little information about relative amounts of self-condensation or co-condensation would be obtained.

MR P. W. MUNN remarked that monobutyl phosphate and monobutyl phthalate had been used as catalysts. What influenced the selection of these two particular catalysts? Was it governed by the pH value, or was there some need for the use of the butyl radical?

DR VAN ZUYLEN said that the choice of monobutyl phthalate was based on several considerations. An acid catalyst containing acid groups of about the same nature as the alkyd resin should be used. The butyl radical gave an acid catalyst that was as compatible as possible with the melamine resins used. Attempts had been made to use the half ester of isophthalic acid, but it was impossible because they were not compatible with the resins investigated.

Monobutyl phosphate had been used in order to see the difference when self-condensation of HMMM occurred. Monobutyl phosphate was a catalyst of a completely different nature, being a very much stronger acid than monobutyl phthalate. When a catalyst of this type was present the etherified methanol groups took part in the reaction by the splitting off of the etherifying radical. This was not the case when acid catalysts of the phthalic acid type, or weaker, were used. In some cases when a weaker catalyst was used it was difficult to catalyse a reaction between the hydroxyl groups of the alkyd and the etherified methanol groups.

Next month's issue

The Honorary Editor has accepted the following papers from the Eastbourne Conference for publication, and these are expected to appear in the October issue.

"**Curing reactions in isocyanate-based surface coatings,**" *by C. Barker and A. Lowe*

"**Electron and ultra-violet curing of coatings,**" *by W. Deninger and M. Patheiger*

"**Process characteristics of electron beam curing,**" *by W. H. T. Davison*

Correspondence

SIR,—Very little attention has been paid to the permanent influence of various solvents used in film formation, the paper by Katz and Munk in *JOCCA* May 1969 has indicated that final film properties can be modified surprisingly by the choice of solvent.

Nitrocellulose lacquers are commonly formulated on combinations of esters, ketones, alcohols and hydrocarbons; the balance is usually subject to considerations of cost, viscosity control, evaporation rate and progressive dilution ratio. It is commonly assumed that, if these requirements are met, then the resultant film will be adequate. Indeed, the protagonists of ketones and of ester solvents have often regarded these groups as being fairly interchangeable.

The measurement of such properties as water vapour permeability and tensile strength are rarely carried out and it is most interesting to note the authors' arguments concerning film orientation.

The matter of solvent retention by resins has been commented on from time to time but, in practice, there has been little to guide the lacquer formulator, apart from a few vague guesses. The reasoning put forward in this paper will greatly stimulate deeper thought on the physical formation of films and I hope that further research will lead to a closer theoretical and practical control over this process.

May I ask Messrs. Katz and Munk how they assess the "goodness" of solvent mixtures, such as ether/ethanol? Do they mean that a lower viscosity solution indicates a "better" solvent?

With many resins a "better" solvent (measured by a more complete solution of lower viscosity) may be unduly retained by the drying film. This detracts from its "goodness" but I would expect orientation to proceed further here than where a more easily released solvent is used—because of the lower viscosity of the film at that stage. There may even be a case for using a weaker solvent mixture, which results in a film that is slightly less continuous. Alcohol is an imperfect solvent for ethyl cellulose, while toluene is more effective. Does the former lead to a three-dimensional structure at a lower concentration because the solute is not so completely in solution to start with? Can this, perhaps, be compared with the "seeding" of crystals from an aqueous electrolyte?

Yours faithfully,
W. F. Daggett.

3 Barn Close,
Littlehampton,
Sussex.

SIR,—There are in our opinion three properties which together would characterise the quality of a solvent mixture with respect to a given polymer resin.

(1) The reduction in viscosity, if equal parts of solvent and resin mixture are compared.

(2) The homogenity of the solution and its freedom from any opalescence.

(3) The homogenity of the mechanical properties of a film cast from this solution.

For instance, the pure ethanol solution of ethyl cellulose has a lower viscosity than the pure toluene solution, but the first solution is cloudy and leads to a brittle film while the second solution is clear and gives strong films.

The best solvent mixture is in this case ethanol:toluene at 30:70 volume per cent; this mixture gives clear solutions of lowest viscosity and the mechanical strength of the film cast from this solution is at its maximum. Thus, we should call that the "best" solvent mixture for ethyl cellulose.

We quite agree to Mr Daggett's remark that slower drying of the resin solution may help in obtaining more compact and structurally organised films.

Yours faithfully,
R. Katz, B. F. Munk.

Paint Research Association,
Technion Campus,
Haifa, Israel.

Reviews

REVIEWS IN MACROMOLECULAR CHEMISTRY. VOL. 3

EDITED BY G. B. BUTLER AND K. F. O'DRISCOLL. New York: Marcel Dekker Inc., 1968. pp. vii+449. Price $16.50.

This Journal was not privileged to review Volumes 1 and 2 of this series, though the present writer does have them in his possession. Readers who have hitherto only encountered Volume 1, may like to know that the series has now become the hard-cover edition of the Journal of Macromolecular Science, Part C2.

In saying that this is yet another review series in polymer science, it is to be understood that nothing derogatory is implied. The writer has on his bookshelves no less than six such series with titles comprising various permutations of "Advances," "Reviews," and "Progress" with "Macromolecular chemistry," "Polymer science" and "High polymers." Add to these the symposium volumes of *Journal of Polymer Science*, the symposium reports of the Plastics & Polymer Group of the S.C.I., and the bound volumes of IUPAC plenary lectures, all of which abound with review papers, then the numerous chapters in the annual reviews of both the S.C.I. and the Chemical Society, in *Chemical Reviews* and *Quarterly Reviews*, and one appreciates the difficulty today of keeping up with the review literature alone. The term "plethora" springs readily to mind but is perhaps an unfair one since, according to the O.E.D., it means "unhealthy repletion," and it is not suggested that the repletion is unhealthy—yet. But already it is becoming indigestible.

In reviewing this review, the writer considers that there is nothing wrong with its being one of a number, even one of a large number, provided its sponsors try not to overlap with their competitors. For the hard-pressed reader who has reached a certain level of competence, the review series undoubtedly provide the most economical means of keeping abreast of this rapidly advancing field. So Mr Marcel Dekker, more power to your elbow, but please try to get together with your competitors and share out the field in a sensible manner, otherwise we will have more reviews of the subject than we already have text books, and to no better purpose.

The reviews contained in this volume set a high standard though they do vary somewhat in breadth of topic and depth of treatment. As is essential in any such production, numerous references are provided, in general up to the year before publication.

The topics covered comprise phosphorus-containing resins, inorganic phosphorus polymers, phosphorylation of polymers, sulphur-containing polymers, polymer molecular weight distributions, heteroatom ring-containing polymers, molecular theories of rubber-like elasticity and polymer viscoelasticity, end-group studies using dye techniques, and free-radical spin labels for macromolecules. Few of these have been reviewed at all comprehensively elsewhere, and all are timely. The short paper on molecular weight distributions is concerned mainly with the kinetic formulation of the problem but, since nearly one-third of its six and a half pages is devoted to telling one so, it is hardly surprising that it does not get very far.

A. R. H. TAWN

MOLECULAR PHOTOCHEMISTRY

A new journal edited by A. A. LAMOLA and published by Marcel Dekker Inc. New York: Subscription price: Vol. 1 (4 numbers): $35.00. Vol. 1. No. 1. January 1969. pp. 155.

Learned societies, bedevilled by the rising cost of publication, should take heart with the appearance of yet another journal devoted essentially to original papers and published by a commercial house which has not been deterred by the highly specialised nature of the subject matter. There must be money in it. The publishers are careful to point out that contributions are published free of charge—decent of them.

The purpose of *Molecular Photochemistry* is "to foster discourse between photochemists and spectroscopists so that the symbiotic relationship which has grown up between their respective fields may be broadened." In order that this laudable aim may be achieved, it is stated that papers considered for publication will be concerned with photochemical reactions and mechanisms, structure-spectra-reactivity relationships, radiationless processes, electronic energy transfer, and molecular orbital calculations, the emphasis throughout being on the excited state. Short notes, letters and literature highlights are also to be published.

Looking through the first issue there is little which strikes one as being of direct interest to the coatings scientist, even taking the broadest view of his field. Papers on the photosensitised *cis-trans* isomerisation of dienes and the photoisomerism of beta-styryl naphthalene ring a faint bell, as do references to the photochemical behaviour of quinone methides and benzophenone. Many readers of *JOCCA* are likely to find *Molecular Photochemistry*, rightly or wrongly, on the extreme fringe of their interests; others will consider it way beyond them. These will undoubtedly elect to rely on the abstract services for any items of special relevance rather than invest money and reading time in the original. It may be recalled, nevertheless, that we have referred previously to the growing importance of photochemistry in the polymer and coatings fields. Those giving special attention to photochemical aspects, whether of polymerisation, film formation, degradation or reprography may feel that this journal should be read regularly, if only because no abstract can compete with the original in providing stimulus and inspiration.

A. R. H. TAWN

Information Received

(In case of difficulty regarding addresses, members and subscribers to the JOURNAL *should apply for details to Director & Secretary of the Association at the address shown on the front cover.)*

The opening of a British sales company, **U-E Chemicals (UK) Limited,** has recently been announced by **Unilever-Emery NV.** The new company, which forms an integral part of Unilever-Emery's Industrial Chemicals Division, will handle sales of all oleochemical derivatives in the UK.

Fishburn Printing Ink Company has recently introduced a new non-heatset web offset newspaper printing ink. The ink, *Newsking*, is said to be a dense blue-black, with smooth lay on the print, good marking resistance, fast setting, and excellent lithographic properties.

Other colours are available including the three process colours matched to offset equivalents of BS 4160.

It has recently been announced that a new company, **Tanaka Matthey KK,** has been formed as a joint venture between **Johnson, Matthey and Co. Limited** and **Tanaka Kikinzoku Kogyo KK,** the leading Japanese precious metals company.

The Japanese authorities have approved the formation of the company, which is to commence operating in Tokyo.

Farbwerke Hoechst AG has recently introduced a new range of metal complex pigments, claimed to have good light fastness, and weather and solvent resistance, under the trade name *Paliotol. Paliotol Yellow 4G*, a green-yellow pigment with very high colour strength, said to be suitable for hammer-effect and polychromatic finishes, *Paliotol Yellow 3R*, a reddish-yellow pigment for medium and pale shades, and *Paliotol Red 3G*, a full shade red suitable for combination with inorganic pigments, are now available.

Hoechst have also added *Heliogen Green GF*, a flocculation resistant phthalocyanine green, to the *Heliogen* range, and introduced *Fluorescent Red GG*, an organic fluorescent dye for use in polystyrene, polymethacrylates, and rigid pvc.

Speedwell Research Ltd. have announced that agreement has been reached with **Le Carbone (Great Britain) Ltd.** for Speedwell to have marketing rights in the United Kingdom and Eire for centrifugal pumps produced in graphite or carbon by **Societe Le Carbone Lorraine.**

The Le Carbone graphite pumps, which are said to have a world-wide reputation for excellence of design, quality of materials, and reliability, will be additional to Speedwell's *Ardua* range, and will have full technical support from Speedwell, backed by comprehensive co-operation from Le Carbone.

Ministry approval has been received for the range of *Series 51 Junction Boxes*, announce **Barton Conduits Limited.** In all, 4 patterns of one-way box, 14 patterns of two-way box, 17 patterns of three-way box, and 14 patterns of four-way box are available in this range.

A new booklet on the use of *Beckurane M121* and *Beckurane M330LS* polyurethanes for seamless flooring applications has recently been issued by **Beck Koller and Co. (England) Ltd.** The booklet, entitled "Flooring with BK Beckuranes" is available from Beck Koller on request.

The third in the series of brochures issued by **Perkin-Elmer Limited** on the use of the *PE Model 700 Infrared Grating Spectrophotometer* deals with applications in paint and coatings.

It has recently been announced that **Price's Chemicals Limited** has taken over from its associate company, **The British Oil and Cake Mills Limited,** the responsibility for marketing hardened castor oil, both in the UK and overseas. Price's have for some time manufactured these products on behalf of BOCM.

Storeys of Lancaster have introduced a training scheme by which young entrants to the company may obtain an honours degree in polymer science and technology.

Young men of 16 or 17 years of age, who have reached a satisfactory standard at GCE 'O' level, will be employed by Storeys as student technologists for two years, during which time they will study for GCE 'A' levels, or ONC, on a day release basis.

Successful candidates will then enter university or a polytechnic on a four-year sandwich course, the vacations and the third year of which would be spent with Storeys. During the part of the course spent in the university students' grants would be supplemented by ex-gratia payments.

A new plant for production of *Kronos* titanium dioxide pigments has recently been brought into operation by **Titangesellschaft MBH.** The plant, at Nordenham, at the mouth of the river Weser in West Germany, has a capacity of 36,000 metric tons per year, supplementing the 104,000 metric tons per year produced at Leverkusen.

Veba-Chemie AG is the new name of the German company which was called **Scholven-Chemie AG,** it has recently been announced.

The new company's main office and plant will be at Gelsenkirchen-Buer, and the former Scholven-Chemie plant at Ruhrol will be operating at Bottrop. Also included in the group will be **Veba-Chemie West GmbH,** at Gelsenkirchen-Buer (previously Hibernia Chemie GmbH) with plants in Herne and Wanne-Eickel, and **Veba-Chemie Nord GmbH,** at Hannover (previously Nord-Chemie GmbH) with plants at Embsen, Langelsheim, and Oer-Erkenschwick.

These changes are said to have been carried out in an attempt to amalgamate the chemical and technical development of the company.

Pinchin Johnson Paints has recently produced a loose-leaf brochure giving details of the properties, uses and application methods of its range of structural polyester resins. The brochure is divided into three sections, covering basic polyester resins, ready-mixed polyester resins, and the finishing of resin/glass laminates.

Copies are available from Pinchin Johnson Paints on request.

Irgalite Yellow BGW, an improved metaxylidide bis-arylamide yellow pigment, has recently been introduced by **Geigy (UK) Limited.** The new pigment is intended for use in letterpress and lithographic inks, and is claimed to have excellent dispersibility for these applications, and appreciably better gloss and transparency than conventional products of the same chemical type.

"Technical Publication No. 31," recently issued by **Joseph Crosfield and Sons Limited,** gives full details of the use of *Gasil* micronised silica gels as antiblocking agents in polyolefin films.

Honeywill and Stein Limited, a wholly-owned subsidiary of **BP Chemicals (UK) Limited,** has recently announced that it has been appointed sole UK agents for the distribution of glycols, glycol ethers, and other ethylene oxide derivatives manufactured by BP's French associates, **Naphtachimie SA.**

This follows the termination by mutual agreement of the arrangement by which Honeywill & Stein acted as UK distributors for ethylene oxide derivatives manufactured by **Union Carbide Ltd.**

BP Plastics has recently published a booklet giving a summary of the plastics materials marketed overseas by the company.

A new personnel selection service, specialising in technical and scientific staff for industry, has been announced by **Arnold Services,** of Warrington.

As the principal, Mr M. H. M. Arnold, and his associates are all qualified scientists and technologists, it is felt that the organisation is well equipped to provide such a service.

Notes and News

OCCA 22
27-30 APRIL 1970

Technical Exhibition

Choice of Olympia proves to be very popular

As announced in the August issue of the *Journal*, the Twenty-second Technical Exhibition will be held in the Empire Hall, Olympia from 27-30 April 1970.

Many companies, both from the UK and overseas, have already applied for space, thus clearly approving of the move to Olympia. Any company, therefore, wishing to exhibit is urged to apply to the Director and Secretary immediately at the address shown on the front cover.

The return to a Central London venue will, of course, be of benefit particularly to overseas visitors in that Olympia is easily accessible from hotels in the West End. The special extension underground service from Earls Court to Olympia will be operating at 10-15 minute intervals throughout the period of the Exhibition. The hours when the Exhibition will be open are given below:

Monday	27 April	15.30—18.30
Tuesday	28 April	09.30—18.30
Wednesday	29 April	09.30—18.30
Thursday	30 April	09.30—18.30

As usual, information leaflets in six languages are available free of charge and these will be distributed to paint companies overseas well before the Exhibition. Any company or individual requiring copies to send to colleagues overseas should apply to the Association's office.

Interpreters for French, German, Italian and Spanish visitors will be in attendance throughout the period of the Exhibition, and all overseas visitors are asked to sign the Visitors' Book at the Information Centre.

The Association has again made arrangements with Grand Metropolitan Hotels Limited for hotel accommodation for visitors to the Exhibition. A copy of the booking form will be enclosed in each copy of the *Official Guide* being sent overseas in the New Year but any person wishing to take advantage of this service should write to the Association's office.

Meeting of Council

The first Council meeting under the chairmanship of the newly-elected President, Mr A. S. Fraser, took place on Thursday 3 July at Wax Chandlers'. Hall, 24 members being present. A welcome was extended to the three new elective members, whose election had been reported at the AGM and to those others who were attending a Council meeting for the first time.

It was reported that, following the invitation of Council at its previous meeting in April, Dr W.W. Hughes had aggreed to present his paper as being on behalf of the Association at a plenary session of the next FATIPEC Congress at Montreux in 1970.

Agreement was reached on the capitation fee for the Journal which should be paid by the members of the Oil & Colour Chemists' Association Australia to OCCA for the three years 1970/1/2.

Council appointed its Committees for the session 1969/70. A list of these appeared in the August issue of the *Journal*. Details regarding OCCA representation on other organisations were also confirmed and the dates for the Council meetings for the forthcoming session agreed.

It was reported that, following the Extraordinary General Meeting held at Eastbourne on 20 June, at which the necessary amendments to the Memorandum to allow the registration of the Association as a charity had been approved, formal application had been made to the Charity Commission.

After discussion on the 1969 Conference, which was held at Eastbourne in June, it was generally agreed that the facilities at the Grand Hotel had been excellent and the Conference very successful. It was felt that the theme of the Conference, "Film formation and curing," had been well chosen, and that the quality of papers had maintained the standard set by previous Conferences. The Workshop Sessions had been well arranged, resulting in some stimulating discussion.

It was reported that arrangements were in hand for the Past Presidents' Dinner to be held on 1 October, after the Council Meeting on that day, in the Court Room at Wax Chandlers' Hall.

Members were informed that the Exhibition Committee had decided to go ahead with the arrangements for the Twenty-Second Technical Exhibition and the Invitation to Exhibit had been despatched to potential exhibitors at the end of June. The Exhibition would be held in the Empire Hall, Olympia, from 27-30 April 1970, and it was felt by the Committee that exhibitors and visitors would welcome the return to a Central London venue.

It was reported that the autumn issues of the *Journal* would contain the Conference papers and discussions thereon. All Sections were urged to forward papers which they had for publication, and short articles or information for inclusion in the Student Review Section.

Reports were circulated to Council on the activities of the Sections since the last meeting. Members were particularly pleased to learn that the Auckland Section was hoping to arrange to transfer to the Association's account in the UK the accrued surplus for two or three years which, for reasons of control on foreign currency in New Zealand, could not previously be transferred.

An international flow cup

The question of an international flow cup to measure the consistency of paint and paint-like materials has been under consideration for some time. When the International Standards Organization (ISO) Committee TC/35 set up a subcommittee, SC9, for general methods of test and sampling of paints and varnishes, the inaugural meeting in Wiesbaden in October 1965 proposed an ISO Standard for measurement of consistency by flow cup early in the agenda. Some progress towards preparing the ground had already been accomplished by the Harmonisation sub-committee of the European Paint and Printing Ink Manufacturers Association, who were considering a series of common paint test methods for Europe. However, the ISO sub-committee SC9, while it reached agreement on the procedures for the use of flow cups, was divided on a recommendation for a universal cup, the choice being between the Afnor, ASTM 1200, British Standard B and DIN type flow cups. The British delegation broke this *impasse* at the Paris meeting of sub-committee SC9 in October 1967 by suggesting the possibility of an improved design of flow cup, which would lead to a better apparatus for use in the particular range of consistencies where flow measurements were most useful to manufacturers and users alike. They were asked to undertake a study at the Paint Research Station at Teddington. The theoretical study, confirmed by practical experiments, has resulted in an improved design of flow cup.

The Paris meeting of ISO sub-committee SC9 also set up a task group under UK leadership to keep in touch with this study and, if promising, to institute co-operative trials and report to the Dublin meeting of SC9 in June 1969. The task group, which comprised representatives from Denmark, France, Germany, India, Italy, Netherlands, South Africa, Sweden, Switzerland, UK and USA, was able to review the theoretical aspects of cup design undertaken at the Paint Research Station, and to consider correspondence from Switzerland in support of the Oesterle cup and from the USA in support of a series of Sherwin Williams cups. The members of the task group were also able to carry out co-operative trials using ten identical cups made to a design suggested by the UK theoretical studies.

The results obtained from seven countries were reviewed by task group E of sub-committee SC9 meeting in Dublin in June 1969. Their study was made easier by the fact that task group M of sub-committee SC9 under the leadership of Denmark was studying measurement of viscosity of paint and paint-like materials at high rates of shear. This task group has made good progress in formulating an ISO proposal which will be available for assessing the consistency characteristics of the more viscous range of paints and paint-like materials, where their anomalous flow characteristics make it necessary to measure the effect of high rates of shear on flow properties in order to assess properly their application properties and control manufacture.

In view of this development, the task group on flow cups considered it a wise policy for ISO to recognise the use of flow cups *only* for paints of near Newtonian behaviour. This effectively limits their use to paints thinned for spraying, dipping and the like and of viscosity not greater than 1-1.5 poises. It has been most unfortunate that flow cups have assumed the role of viscometers, and it is hoped that this attempt to limit their use will help to prevent the misuse of these instruments. Not only is the flow property of one type of paint likely to be different from another, but the present trend in paint formulation is more and more toward built-in anomalous flow properties in order to enhance application characteristics and obtain thicker coatings. Such anomalous flow characteristics can only be properly assessed by measurement at controlled, and usually high, shear rates.

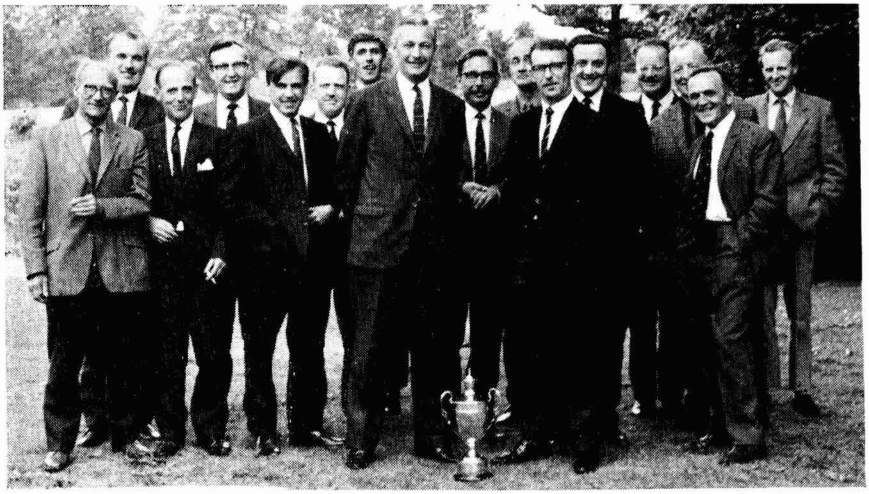
The ISO committee TC/35, at its plenary session in Dublin in June 1969, adopted the recommendation of its sub-committee SC9 and task group for flow cups, that a specification for one ISO flow cup based on the suggested design should be issued as a draft proposal, in the hope that such a cup will serve as an international referee standard, that it will gradually replace the existing national flow cups, and that its increasing use will help to eliminate the present misuse of flow cups. They fully appreciate that such a cup could not immediately and automatically replace existing national cups, but they are confident that over a short number of years the change-over could be effected and will lead ultimately to a better appreciation of the role and proper use of flow cups. The change-over can only be effected if proper publicity is given to the ISO proposal in all countries concerned. To encourage this publicity, it is intended that the work of the task group leading to the ISO recommendation, together with the theoretical considerations of the Paint Research Station on the optimum dimensions for the ISO cup, shall be published as a scientific paper.

A number of flow cups conforming to this specification will be available for distribution as widely as possible so that manufacturers and users of paint can familiarise themselves with the use of this cup. It is likely that suitable cups can be obtained from both French and UK sources.

A. N. MCK.

Editor's Note: It is hoped to publish the paper describing the work of the task group and the Paint Research Station in arriving at the ISO flow cup in the Journal *in the early part of 1970.*

Newcastle Section



The photograph shows some of the golfers who took part in the competition. (Left to right) R. Robinson, J. Bell, N. Buchanan, G. Carr, A. Wilson, A. Stockley, D. Ansbro, T. R. Peacock, H. Fuller, A. Wright, D. V. Smith, T. Meir, K. Hodgson, R. Lamb, L. Paine, M. Harvey

The British Titan Cup

The eighth annual tournament for the British Titan Cup was played for over Brancepeth Golf Course on Saturday 21 June 1969. The competition, a four ball, better ball, against bogey, was won jointly by Messrs. D. V. Smith and T. R. Peacock—one down.

Friendly matches were played during the afternoon to round off a very enjoyable day.

Scottish Section

Symposium 1970

"Dispersion in theory and practice" will be the theme of the Symposium to be held by the Scottish Section on 21-23 May 1970 in the new town of East Kilbride, near Glasgow.

The following speakers have agreed to contribute papers in their special fields of study:

W. M. Hess and M. D. Garret

(Columbian Carbon Co.) on "Some aspects of pigment dispersion with particular emphasis on carbon black."

Dr W. Carr (Geigy (UK) Ltd.) on "Dispersion in aqueous media."

K. Pond (Lorilleux & Bolton Ltd.) on "The influence of non-aqueous media on dispersions."

Dr R. Amberg (Kronos Titanium Pigments) on "Some aspects of dispersion in relation to titanium dioxide."

Dr W. Funke (Forschungsinstitut fur Pigmente und Lacke EV) on "The influence of interfacial activity in paint films on their properties."

Dr J. B. Slinger (ICI Paints) on "Dispersion machinery."

In addition to a discussion period after each lecture, Dr S. H. Bell, of the Paint Research Station, will summarise the papers as a whole and lead a more general discussion on the Friday afternoon. As well as the lecture programme, there will be a small exhibition by firms in the industry of the latest developments in dispersion technology. A social programme is also planned and will include functions for lady visitors.

It is proposed that the Annual General Meeting of the Association will be held on the evening of 21 May, followed by a dinner at the Bruce Hotel, East Kilbride.

The Symposium will be held in the Ballerup Hall—so called after East Kilbride's "twin town" in Denmark—a striking new building opened by Princess Margaret only last year. East Kilbride has a number of hotels graded up to international standard and accommodation will be reserved within a range of prices and standards.

The Symposium Secretary will be Mr I. R. McCallum, P. W. Hall Ltd., Woodilee Industrial Estate, Kirkintilloch, Glasgow.

Annual Golf Outing

The annual golf outing of the Scottish Section was held on Saturday 31 May, at the usual venue, Aberdour. A record turn-out of 44 members and friends—34 players and 10 non-combatants—had a most enjoyable day, the weather, catering and club-house facilities all being extremely good.

Prizes, both merit and "special," were presented and the Student Section members figured prominently in the former. Winner of the Whitaker Cup for returning the lowest nett score—55 (19 handicap)—was Gordon Watt, the runner-up being Alex Smith with a nett 60.

News of Members

Mr V. A. Moore, an Ordinary Member attached to the Thames Valley Section, has been appointed Sales Manager, Special Products, of Pinchin Johnson Paints. He was previously Group Technical Development Manager at Coventry.

Mr C. H. Morris, an Ordinary Member attached to the Midlands Section, and Chairman of the Section from 1966-68, has recently been appointed Marketing Manager of Resinous Chemicals Ltd. Mr Morris, who was previously Technical Service Manager of BIP Chemicals Ltd., will be responsible for the entire marketing group of Resinous Chemicals.

Mr G. Scott, an Ordinary Member attached to the Scottish Section, has been elected the first honorary member of the Scottish Association of Painting Craft Teachers. Already a Fellow of the Royal Society of Arts, and an Honorary Fellow of the Institute of British Decorators and Interior Designers, Mr Scott was awarded this honour in recognition of his work in stimulating interest in painting craft education.

Mr L. Moss, an Ordinary Member attached to the London Section, has been appointed to head U-E Chemicals (UK) Limited, the newly formed British subsidiary of Unilever-Emery NV.

Obituary

William Victor Lee 1902-1969

Members will be saddened to learn of the death, earlier this year, of Mr W. V. Lee, an Ordinary Member attached to the London Section for many years.

Mr Lee was educated at Thomas Street Central School, Limehouse, and the Borough Polytechnic, and was elected to Fellowship of the RIC in 1952. He achieved the unusual distinction of serving 50 years with the same company, joined BOCM Ltd. in 1917 as a laboratory assistant, and remaining with the company until his retirement in 1967, when he was group chief chemist and refinery adviser to the UK Oil Mills Administration of Unilever Ltd., of which group BOCM had become a part.

During his career, he was primarily responsible for the development of the phosphoric acid test as a standard method for determining the quality of raw linseed oil with respect to dissolved and visible impurities, and also simplified the method of determining aflatoxin in groundnut meals, effecting a great saving in time.

Mr Lee represented the Association on BSI Committees OSC12 and OSC24, and served on various committees of the SCI, IUPAC, the PRS, and the International Association of Seedcrushers.

He is survived by his wife, son and daughter, to whom the sympathy of Members is extended.

Programme Liaison Committee

This committee comprises representatives of each of the following societies:

Institution of the Rubber Industry
Oil and Colour Chemists' Association
Plastics Institute
Plastics and Polymer Group, Society of Chemical Industry
Society of Dyers and Colourists
Royal Institute of Chemistry

Major meetings or conferences on polymer or related subjects, and other functions planned by these societies, are given below and will be in London except where otherwise stated.

1969

10–12 September. Conference "Coloration of polymeric materials" at York (SDC)

15 September. Foundation lecture at Loughborough (IRI)

16–17 September. Conference "Advances in polymer blends and reinforcement" at Loughborough (IRI)

16–17 September. Symposium "Emulsion polymers" at Manchester (SCI)

24–25 September. Symposium "Recent advances in water-borne surface coatings" at Manchester (OCCA)

26 September. Conference "Help—sources of information and advice for the plastics industry" (PI)

23 October. Symposium "Management and training in the Midlands" (OCCA)

5 December. Conference "Diagnostic testing techniques" (PI)

1970

25 February. Conference "Sterilisable packages for foodstuffs" (SCI)

24 March. Conference "Product performance testing" at Bath (IRI)

31 March-3 April. Conference "Physical and structural lines of the yield, deformation and fracture of polymers" at Cambridge (IRI, PI, etc.)

5–11 April. AGM and associated symposia at Edinburgh (RIC)

8 April. AGM and dinner at Birmingham (IRI)

17 April. AGM and dinner at Nottingham (SDC)

27–30 April. Technical Exhibition (OCCA)

29–30 April and 1 May. PINTEC Plastics Institute national technical conference at Brighton (PI)

Easter. Symposium "Newer polymers" (SCI)

1970

21–23 May. AGM and symposium "Dispersion" in Scotland (OCCA)

29 May. Biennial dinner dance (OCCA)

29–30 September and 1 October. Conference "Advances in polymer science and technology" No. 3, Chemistry of liquid and thermoplastic copolymers (IRI PI/SCI/OCCA/SODAC)

1971

22–23 April. Industrial conference "Tyres" at Leamington Spa (IRI)

1972

15–18 May. International Rubber Conference at Brighton (IRI)

CIA Statistics

The Chemical Industries Association Limited has recently issued the "UK Chemical Industry: Statistics Handbook." This publication, which gives complete information on all aspects of the UK chemical industry, and compares these statistics with those from other UK industries, and also those from chemical industries of other countries, is available from the CIA, Alembic House, 93 Albert Embankment, London SE1, at a cost of £1 1s per copy, including postage.

Courses in surface coatings technology

The following courses in surface coatings technology will be held at the John Dalton College, Manchester, during the session 1969/70.

The City & Guilds Paint Technicians Certificate Parts I & II.

The Higher National Certificate Endorsement subject, " Chemical Technology with special reference to Polymers and Surface Coatings."

The Associateship of the Society of Dyers and Colourists (subject to sufficient enrolments).

Enrolment dates are as follows:

15, 16, 17 September during the periods 10-12 a.m., 2-4 p.m., and 6-8 p.m.

(Members of staff will be available for any discussion with potential students.)

The college lecture term commences 22 September 1969.

Decimalisation

The Chemical and Allied Products Industry Training Board has recently issued "Information Paper No. 3," entitled "Planning for decimalisation," giving full details of suggested preparations for the change-over in 1971. Copies are available from the ITB.

Seminar on zinc dust paints

The Zinc Development Association is to organise a seminar on the protection of steel with zinc dust paints at the Cafe Royal, London, from 25-26 September. The seminar is designed for engineers in the steel-using industries and others directly concerned with the prevention of corrosion, and delegates may register free of charge.

Programmes and full information are available from the ZDA, 34 Berkeley Square, London W1X 6AJ.

Register of Members

The following elections to membership have been approved by Council. The Section to which the new members are attached are given in italics.

Ordinary Members

CAWSTON, JOHN, LRIC, "Redenham," Bacons Mead, Denham, Uxbridge, Middlesex. (*Thames Valley*)

CROSBY, ATHOL GRAHAM, BSc, ANZIM, U.E.B. Research & Development Department, PO Box 11132, Auckland 5, New Zealand. (*Auckland*)

LAWSON, ALLAN STUART, DipChemEng, DipIndChem, 13 Bayview Road, Napier, Wellington, New Zealand. (*Wellington*)

MILLER, LOUIS, 10 Tizard Road, Auckland 10, New Zealand. (*Auckland*)

NAPPER, ROGER, BSc, GradRIC, Hardye's, 5 The Orchard, Chapman Lane, Flackwell Heath, Bucks. (*Thames Valley*)

ROBLEDO, SANTIAGO, MSc, ICO Pinturas SA, Apartado Aereo No. 2301, Barranquilla, Colombia S.A. (*Overseas*)

SIMPSON, WALLACE HARLEY, BSc, 48 Beechdale Crescent, Pakuranga, Auckland, New Zealand. (*Auckland*)

TANNAHILL, JOHN, LRIC, 37 Troubridge Avenue, Kilbarchan, Renfrewshire, Scotland. (*Scottish*)

TAYLOR, MAURICE DAVID, c/o Pinchin Johnson & Co. (NZ) Limited, PO Box 14-064, Kilbirnie, Wellington, New Zealand. (*Wellington*)

WEINBERG, GARY RICHARD, BSc, Box 1996, Wellington, New Zealand. (*Wellington*)

WINDRIDGE, MARTIN, 38 Lyndhurst Avenue, Hazel Grove, Stockport, Cheshire. (*Manchester*)

Associate Members

BRIDGEWOOD, ALAN, 12 Templar Gardens, Wetherby, Yorks. (*West Riding*)

Student Members

ANDREWS, RICHARD OWEN, 182 Moorgate Road, Rotherham, Yorkshire. (*West Riding*)

HEYWOOD, GEOFFREY PHILIP, Passmonds House, Rochdale. (*West Riding*)

JANES, ANTHONY, 5 Plantation Way, Baildon, Nr. Shipley, Yorkshire. (*West Riding*)

REED, KEITH EVAN, 16 Moorland Road, Cimla, Neath, Glamorgan. (*Bristol*)

YATE, M. J., Griffiths Bros. & Co., Well Lane, Wednesfield, Wolverhampton. (*Midlands*)

Forthcoming Events

Details are given of meetings in the United Kingdom up to the end of the month following publication, and in South Africa and the Commonwealth up to the end of the second month where available.

Tuesday 9 September

West Riding Section. "Industrial Training" by Mr H. DeLooze, Senior. Training Officer, and Mr L. Judson, Training Adviser for Yorkshire and Humberside, both from the Chemical and Allied Products Industrial Training Board, to be held at the Griffin Hotel, Boar Lane, Leeds 1, at 7.30 p.m.

Friday 12 September

Midlands Section. Ladies' Evening (21st Anniversary of the formation of the Midlands Section).

Saturday 13 September

Scottish Section, Student Group. "Antifouling Paints," by Mr I. R. McCallum of P. W. Hall Ltd. to be held at the St. Enoch Hotel, St. Enoch Square, Glasgow, at 10.00 a.m.

Wednesday 17 September

Manchester Section, Student Group. "Emulsion Polymerisation and Water Soluble Resins," by Mr B. C. Holdstock of the Paint Research Station, to be held at the Manchester Literary and Philosophical Society at 4.30 p.m.

London Section. Chairman's Evening, "Management, Men and Money," by J. E. Pooley, to be held at the New Engineering Block, University College, London WC1, at 6.30 p.m.

Friday 19 September

Midland Section. "Non-Stick and Anti-Corrosive Coatings," by Mr S. Wharrard of Loyne Ltd., to be held at the Chamber of Commerce House, 75 Harborne Rd., Birmingham 15, at 6.30 p.m.

Wednesday 24 & Thursday 25 September

Manchester Section. Symposium entitled "Recent Advances in Waterborne Coatings," at the University of Manchester Institute of Science and Technology.

Thursday 25 September

Trent Valley Branch. "The Determination of Particle Size and its Significance to the Paint Industry," by Dr R. J. Akers, to be held at the Loughborough University of Technology, Edward Herbert Building, at 6.30 p.m.

Thames Valley Section. "Application of Silicas and Silicates in the Paint and Printing Ink Industry," by Mr L. Muller-Fokken and Mr B. Stett of Degussa, to be held at The Manor Hotel, Datchet, Bucks, at 7.00 p.m.

Friday 26 September

Bristol Section. "Some Factors Affecting the Performance of Surface Coatings on Plastic Substrates," New Chairman's Address, by Mr J. R. Taylor, to be held at the Royal Hotel, at 7.15 p.m.

Irish Section. "Paint Formulation and Performance," by Mr Alan Hipwood of the Chemical Inspectorate, Woolwich, to be held in the Imperial Hotel, Cork, at 8.00 p.m., preceded by a Works Visit to Henry Ford & Sons Ltd., at 2.30 p.m.

Thursday 2 October

Bristol Section. "A Paint Manufacturer's view of Industrialised Building," by Mr T. Jones of John Hall & Sons (Bristol & London) Limited. Joint meeting with Birmingham Paint Varnish and Lacquer Club, to be held at the Imperial Hotel, Birmingham.

Newcastle Section. "Statistical Techniques in the Optimisation of Paint Formulation by Computer," by D. W. Brooker of Shell Research Limited, to be held at the Royal Turks Head Hotel, Grey Street, Newcastle on Tyne, at 6.30 p.m.

Monday 6 October

Hull Section. "Reactivity of Titanium Dioxide in Pigmented Vinyl Chloride/ Vinyl Acetate Copolymer Surface

Coatings," by Mr F. D. Robinson of Laporte Industries Limited, to be held at the Bullock Lecture Theatre, Hull University, at 7.00 p.m.

Thursday 9 October

Scottish Section. "Problems of Pigmentation of Thermosetting Acrylic Finishes," by Mr G. Willison of British Titan Products Limited, to be held in the St. Enoch Hotel, Glasgow, at 6.00 p.m.

Friday 10 October

Hull Section. Annual Dinner Dance at the Hotel Eden, Willerby.

Manchester Section. "Dispersymers," by Mr C. D. Cook of ICI Limited, to be held at the Manchester Literary and Philosophical Society at 6.30 p.m.

Saturday 11 October

Scottish Section—Student Group. Student Paint Project by Mr J. Devine of Craig Hubbock Limited, to be held at the "Wee Windaes Restaurant," 142 High Street, Edinburgh, at 10.30 a.m. followed by lunch and a skittles match.

Monday 13 October

London Section. Joint meeting with Society of Chemical Industry (Colloid and Surface Chemistry Group). "A Theory of Polymeric Dispersant Action," by E. J. Clayfield, to be held at 14 Belgrave Square, London SW1, at 6.00 p.m.

Tuesday 14 October

West Riding Section. "Future Developments in Paint," by Dr L. A. O'Neil of the Paint Research Station, to be held at the Griffin Hotel, Boar Lane, Leeds 1, at 7.30 p.m.

Saturday 18 October

Scottish Section—Student Group. Colour Systems.

Tuesday 21 October

London Section—Southern Branch. "Chemical Solvents for Paints," by Mr D. P. Sephon of Shell Research Limited, to be held at the Pendragon Hotel, Clarence Parade, Southsea, at 7.00 p.m.

Wednesday 22 October

Scottish Section—Eastern Branch. "Colour Measurements and Specifications," by Dr Latowski of Edinburgh University, to be held at the Carlton Hotel, Northbridge, Edinburgh 1, at 7.30 p.m.

Thursday 23 October

London Section. European Liaison Lecture. "Some Aspects of the Protection of Exterior Joinery," by R. Dooper of Verfinstituut TNO, to be held at the New Engineering Block, University College, London W1, at 6.30 p.m.

Midland Section. One-day Symposium "Management and Training in the Surface Coating Industry."

Friday 24 October

Irish Section. "Driers," by Mr J. H. W. Turner of Hardman & Holden Limited, to be held at the Clarence Hotel, Wellington Quay, Dublin, at 8.00 p.m.

Manchester Section. Annual Dinner Dance at Piccadilly Hotel, Piccadilly Plaza, Manchester 1.

Wednesday 29 October

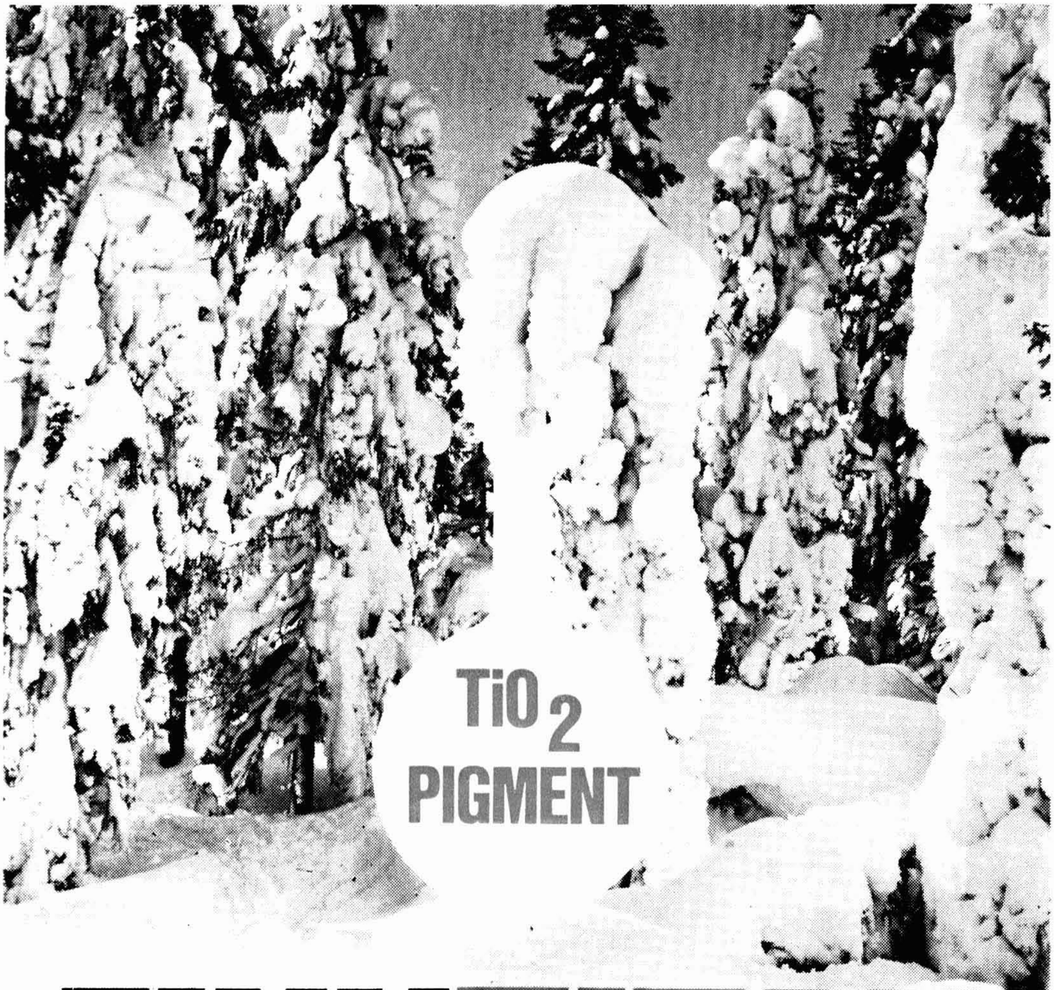
Thames Valley Section. "Glossy Emulsion Paints," by Mr J. Bax of Scott Bader & Co. Limited, to be held at the Manor Hotel, Datchet, Bucks, at 7.00 p.m.

Thursday 30 October

Midland Section—Trent Valley Branch. "The Influence of British Rail Modernisation on Paints and Painting," by F. D. Timmins, to be held at the British Rail School of Transport, London Road, Derby, at 6.30 p.m.

Friday 31 October

Bristol Section. "Packaging," by Mr F. P. Bull of E. S. & A. Robinson Limited, to be held at the Royal Hotel, Bristol, at 7.15 p.m.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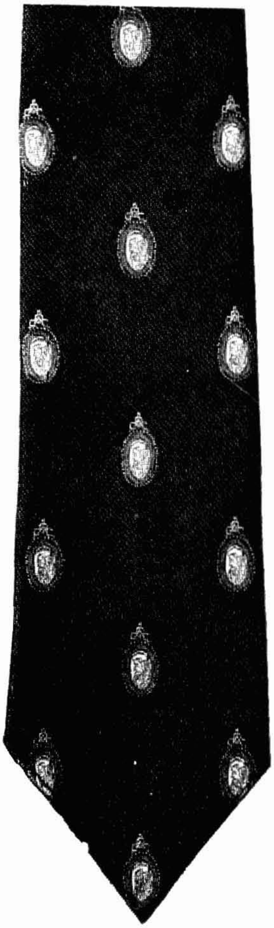

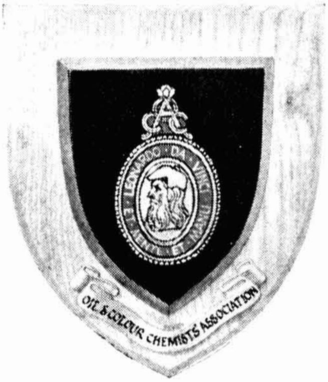

The tie is blue terylene, with the Association's insignia woven in red and gold silk.

The blazer badge has the insignia embroidered in silver and gold wire on a red and blue ground.

The plaque has the insignia hand-painted in red and gold on a blue ground.

The car badge has the insignia embossed in red and gold on a blue ground, the whole being covered in transparent polypropylene, with a thick chrome surround. Bar and grille fittings are available.

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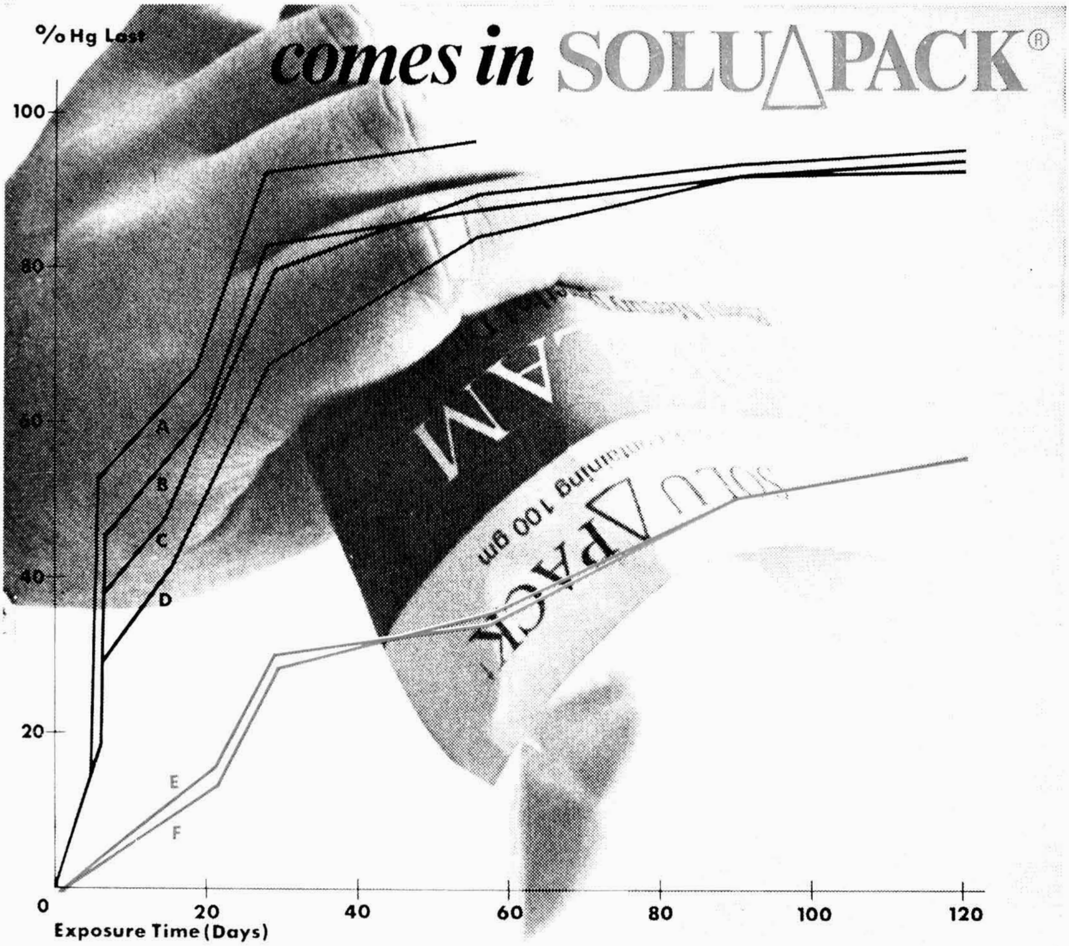

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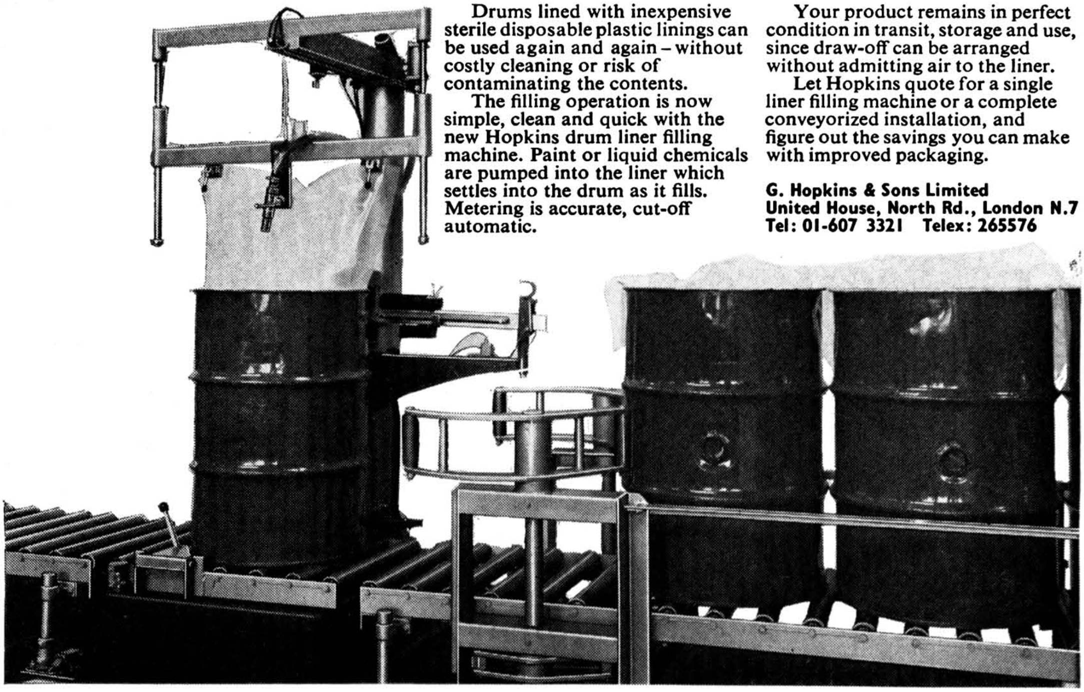
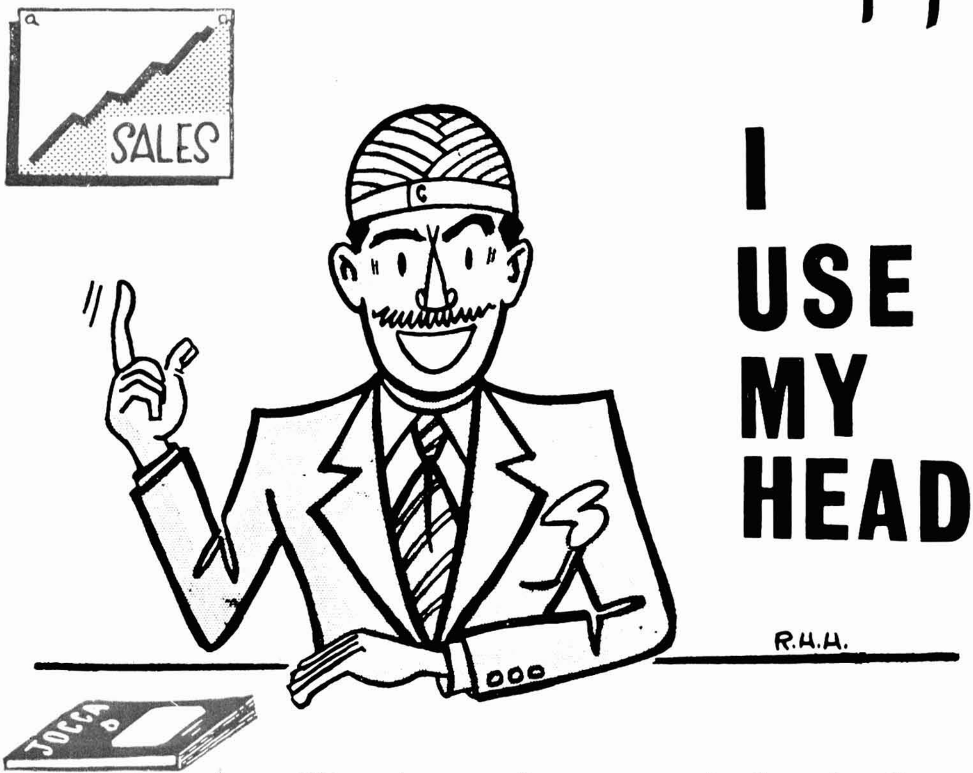


I'M NO FOOT-IN-THE-DOOR TYPE



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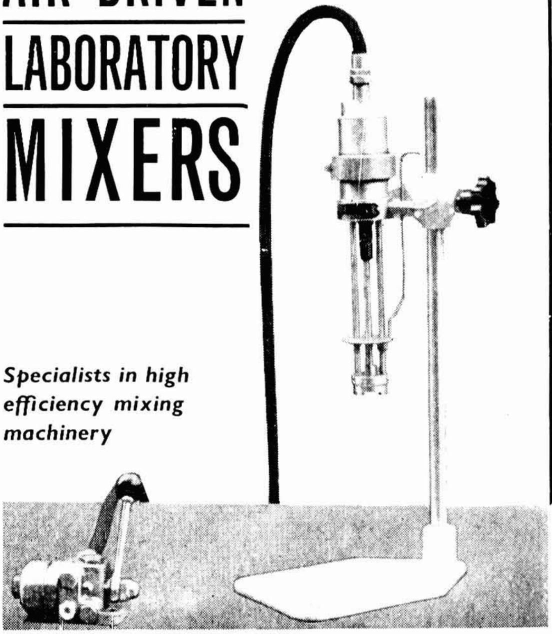

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