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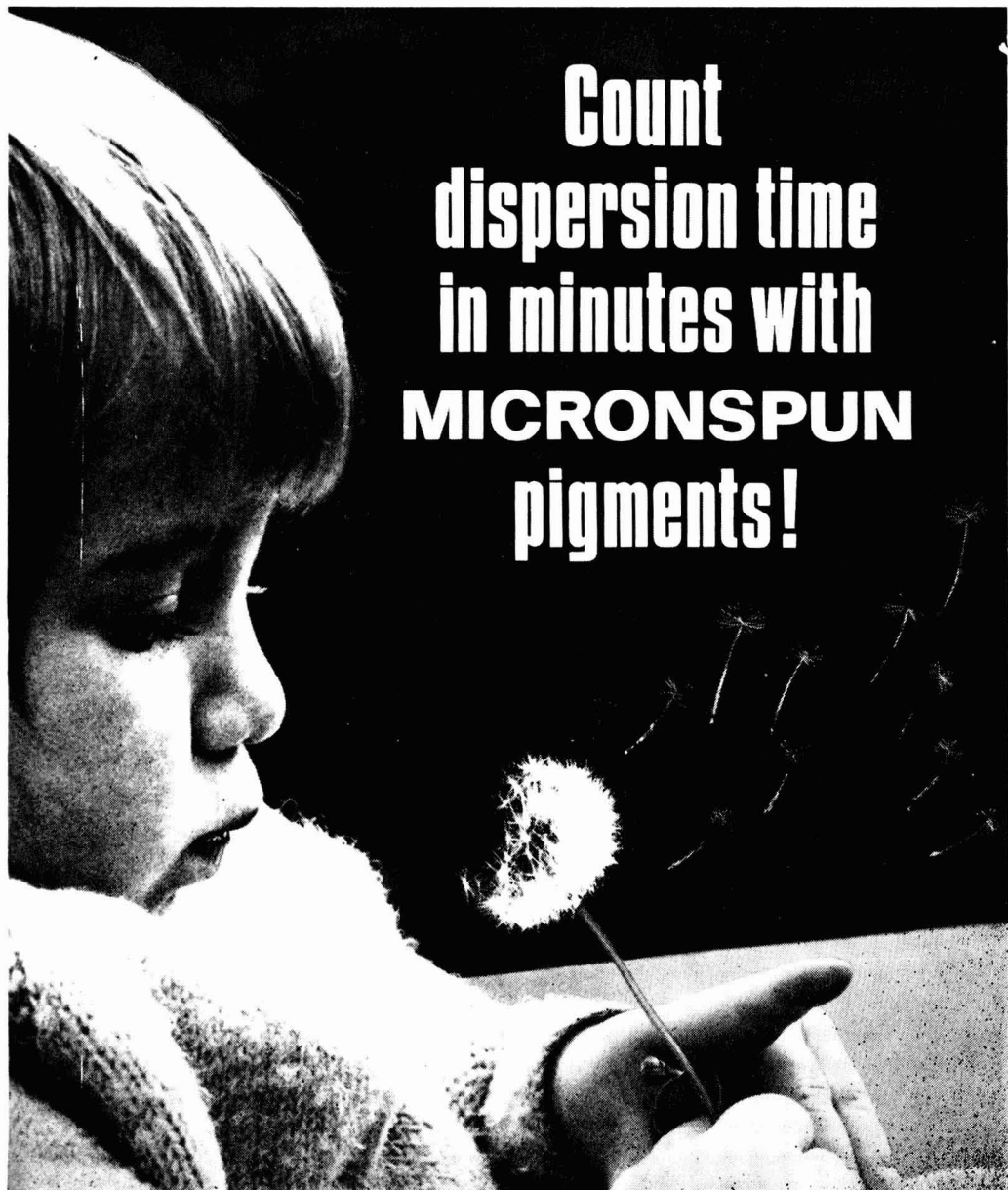
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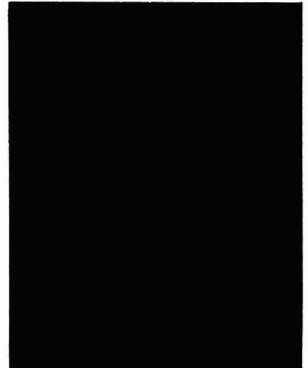
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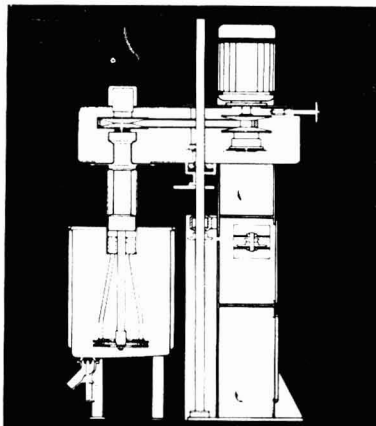
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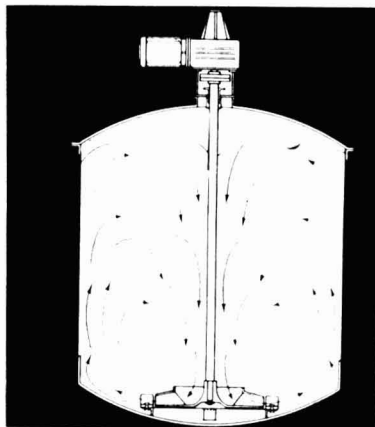
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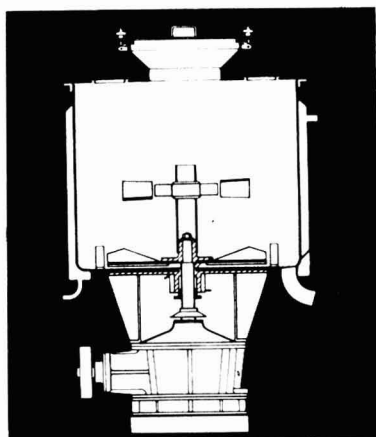
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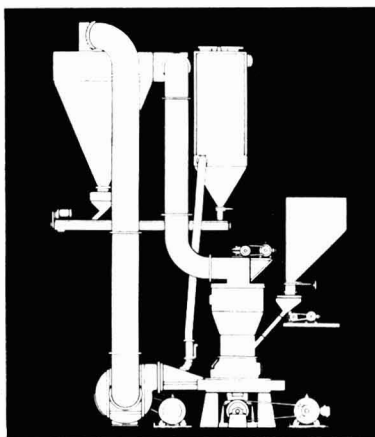
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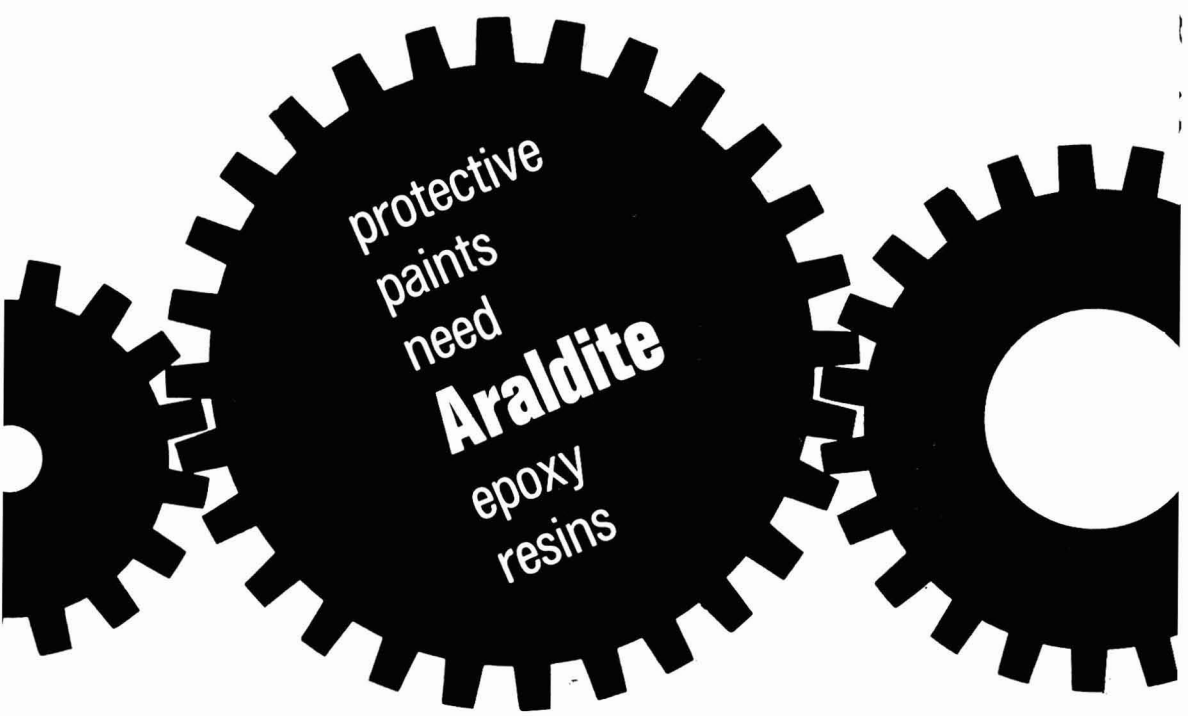
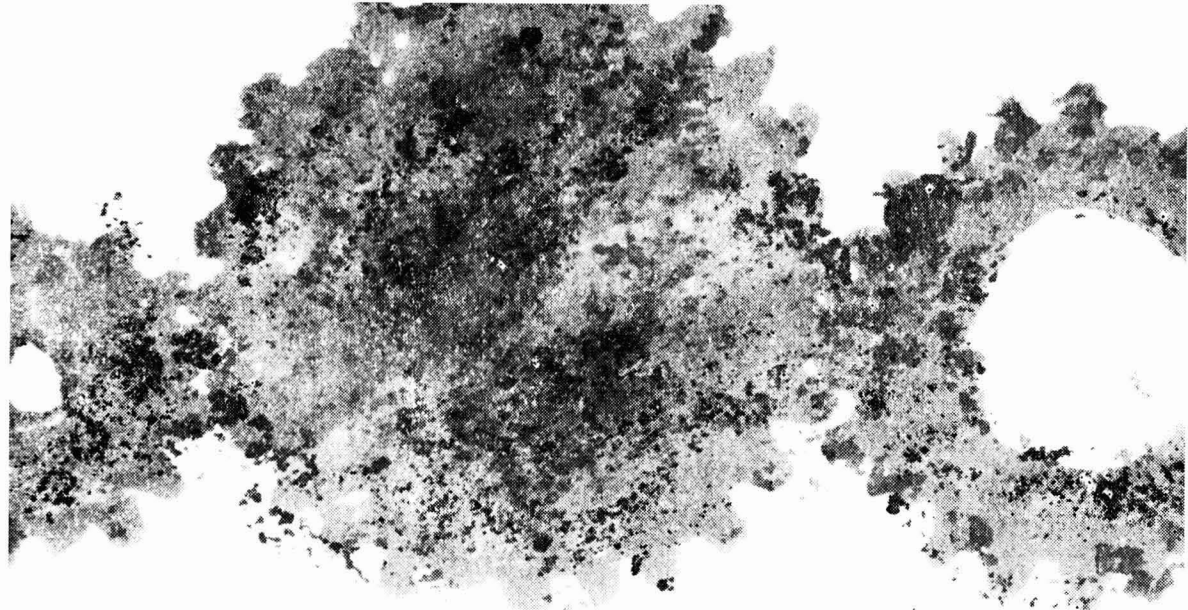
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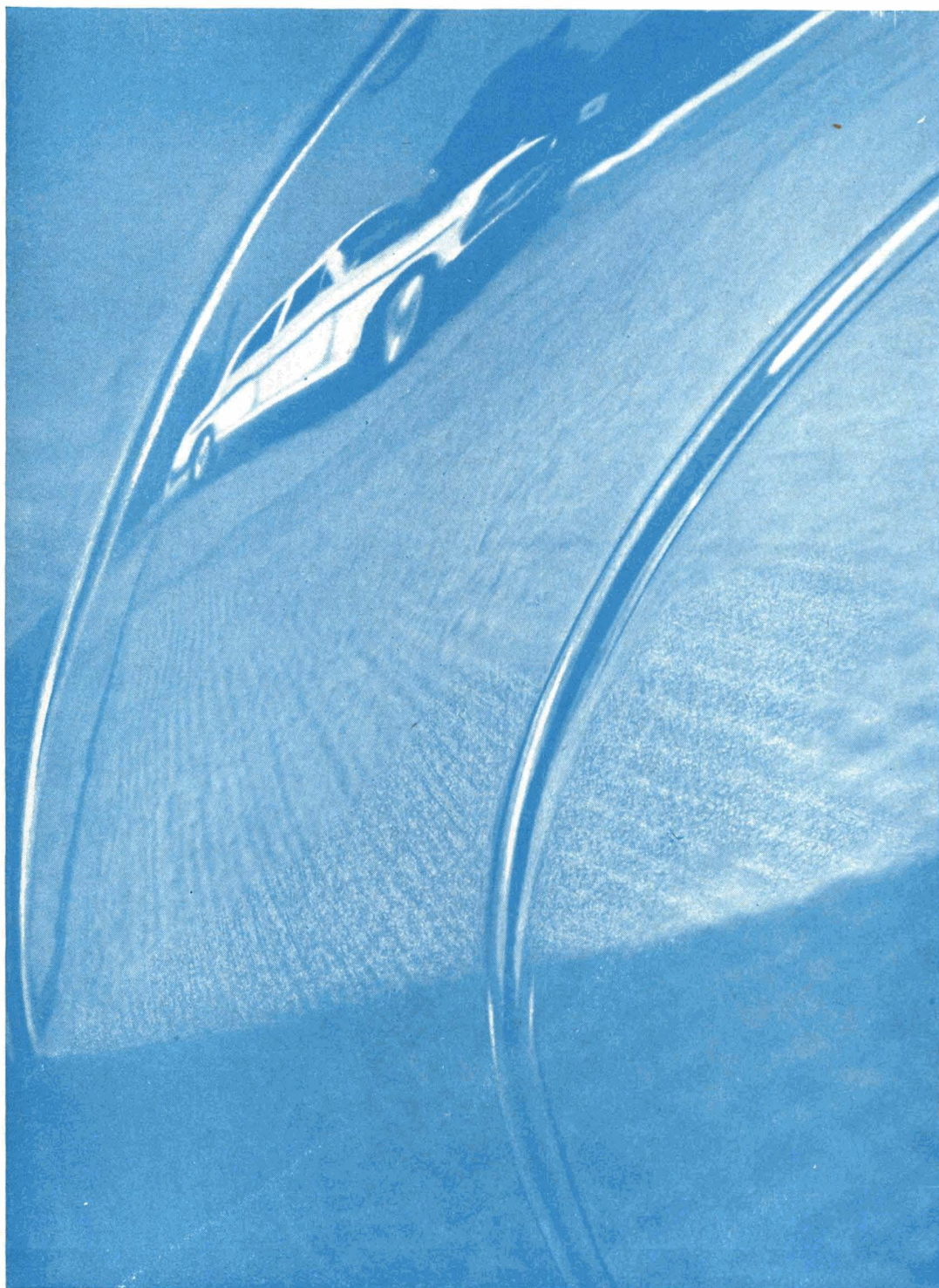
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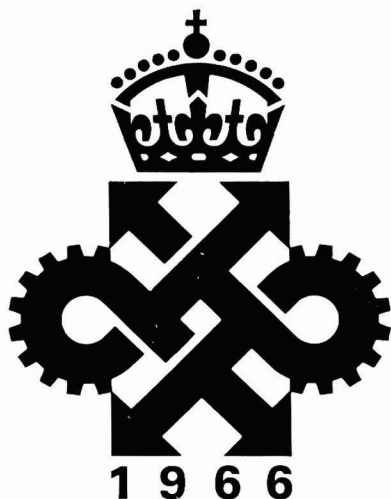
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CHEMISTS' ASSOCIATION

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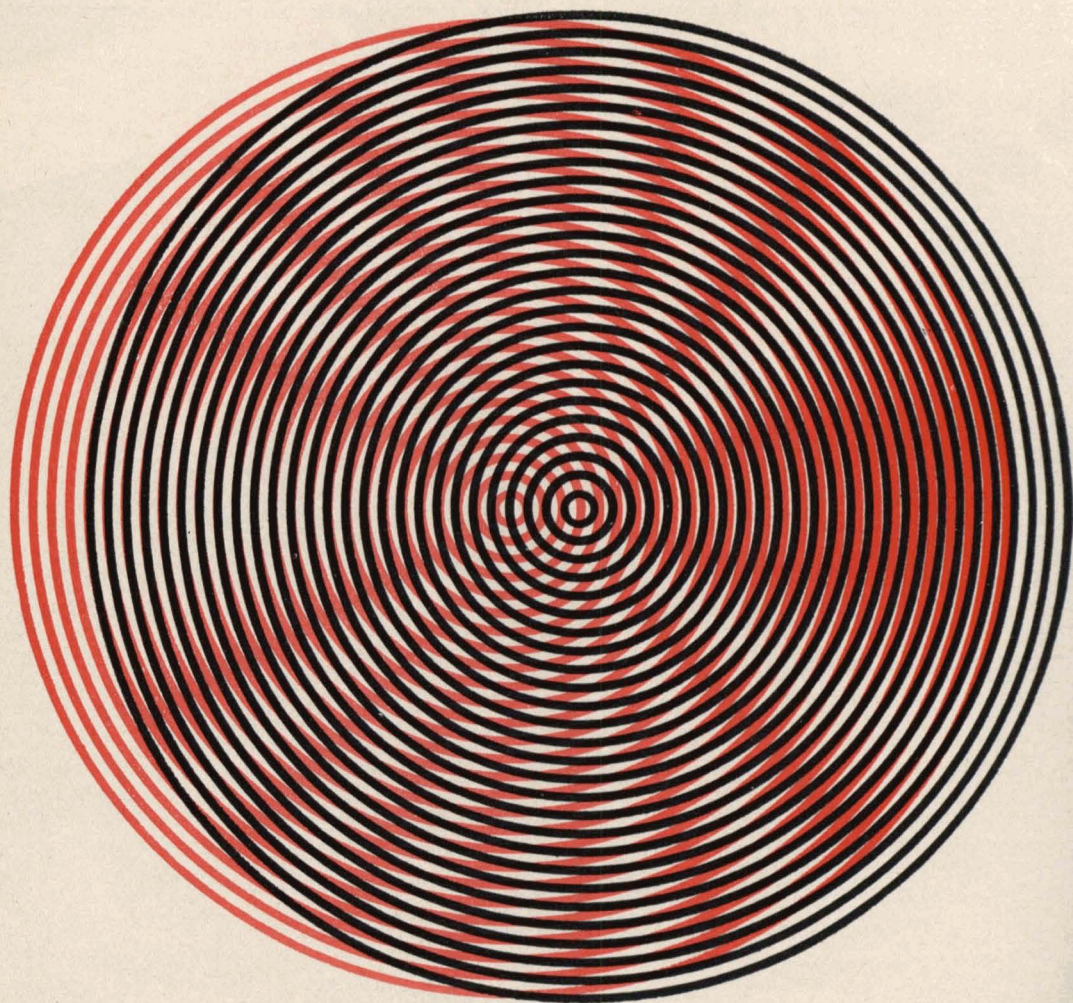
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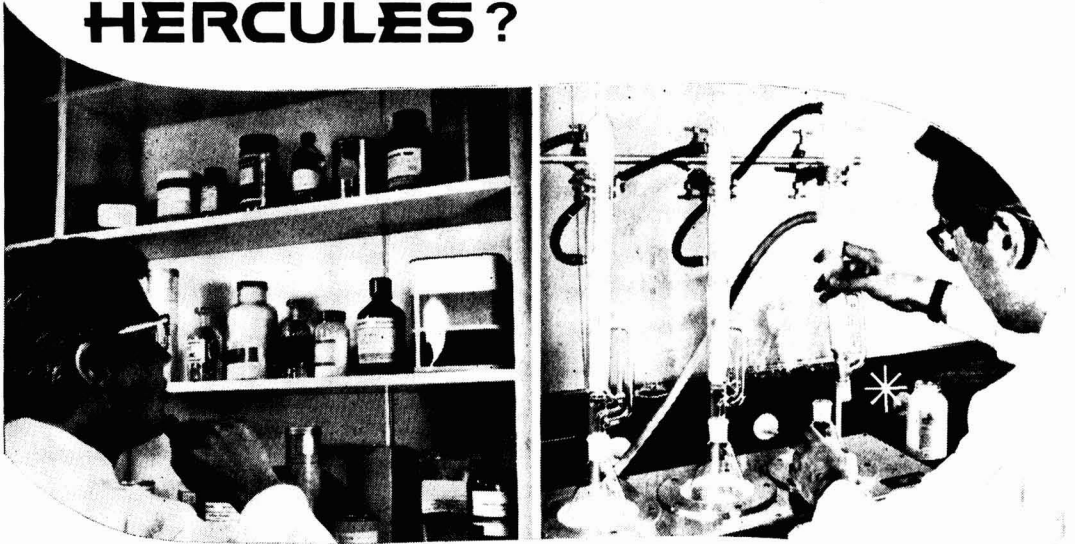
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Air drying alkyd paints

The effect of incorporation of involatile monomers on film properties

By K. E. J. Barrett and R. Lambourne

Research Department, Imperial Chemical Industries Ltd., Paints Division, Slough, Bucks

Summary

The effect of the addition of involatile polymerisable monomers to autoxidisable paint compositions has been studied. It has been established that monomer additions substantially modify the film properties and drying characteristics of paint media such as alkyds giving an additional degree of freedom in paint formulation. Long chain alkyl monofunctional acrylic esters such as lauryl methacrylate improve the through drying of films (at 25°C) compared with the unmodified alkyd but soften or plasticise the film. Polyfunctional monomers such as ethylene glycol dimethacrylate improve through drying of alkyds and harden the films compared with the unmodified alkyd. It has been demonstrated that adequately through-dried films can be prepared without using toxic lead drier. The effect of changes in alkyd structure (*viz* nature of oil and oil length) on the drying and film properties of paints based on alkyd-monomer mixtures has been studied and data on drying rate, film hardness and durability collected.

Peintures aux alkydes séchant à l'air

L'effet exercé par des monomères non volatils sur les propriétés de feuil

Résumé

On a étudié l'effet des monomères non volatils polymérisables ajoutés aux peintures autoxydables. On a établi que des additions de monomères modifient sensiblement les propriétés de feuil et de séchage des liants tels que résines alkydes. Ces additions donnent une autre possibilité en ce qui concerne la mise au point de formules de peinture. Esters des alcoyles monofonctionnels de chaîne longue et de l'acide méthacrylique, par exemple, méthacrylate de lauryle, augmentent le séchage à cœur des feuil (à 25°C) par comparaison à l'alkyde non modifiée, mais en même temps ils amollient ou plastifient le feuil. Monomères polyfonctionnels tels que diméthacrylate d'éthylène glycol augmentent le séchage à cœur d'alkydes et durcissent les feuil par comparaison à l'alkyde non modifiée. On a démontré que des feuil suffisamment séchés à cœur peuvent se produire sans l'intervention de siccatif toxique de plomb. On a étudié l'effet des variations de la composition de l'alkyde (notamment la nature de l'huile et la longueur en huile) sur les propriétés de séchage et de feuil des peintures à base des mélanges alkydes/monomères. Les données sur vitesse de séchage, dureté de feuil et durabilité sont mentionnées.

Lufttrocknende Alkydharzlacke

Beeinflussung der Filmeigenschaften durch Einverleibung nichtflüchtiger Monomere

Zusammenfassung

Es wurde untersucht, welchen Einfluss Zusätze von nichtflüchtigen, polymerisierbaren Monomeren auf autoxidierbare Anstrichmittel haben. Dabei wurde festgestellt, dass Zugaben von Monomeren die Eigenschaften des Filmes, sowie die Charakteristika der Trocknung

von Anstrichbindemitteln, wie z.B. von Alkydharzen, wesentlich modifizieren und zusätzlich grössere Beweglichkeit in der Formulierung von Anstrichfarben ermöglichen. Langkettige alkyl- monofunktionelle Akrylester, wie z.B. Lauryl- Methakrylsäureester verbessern die Trocknung von Filmen (bei 25°C), verglichen mit unmodifizierten Alkydharzen, machen sie jedoch weicher oder plastifizieren sie. Polyfunktionelle Monomere, wie z.B. Äthylenglykoldimethakrylsäureester verbessern die Durchtrocknungseigenschaften von Alkydharzen und die Filmhärte im Vergleich mit unmodifizierten Alkydharzen. Es wurde auch nachgewiesen, dass gut durchtrocknende Filme ohne den Einsatz giftiger Bleisikkative hergestellt werden können. Die Auswirkung von Änderungen im Aufbau des Alkydharzes (in anderen Worten : Art des Öls und Ölgehalt) auf Trocknung und Filmeigenschaften von auf Alkydharz-Monomermischungen basierenden Anstrichmitteln wurde geprüft, und Zahlenwerte hinsichtlich Trocknung, Filmhärte und Haltbarkeit wurden gesammelt.

Сушка на воздухе алкидных красок

Влияние включения нелетучих мономеров на свойства пленок

Резюме

Изучалось влияние добавления нелетучих полимеризуемых мономеров к авто-окисляющимся красочным составам. Установлено, что добавление мономеров материально изменяет пленочные свойства и характеристики сушения красочных сред, как например алкидные смолы дающие добавочную степень свободы в процессе формулировки красок. Длинно-цепные алкиловые монофункциональные акриловые жиры, как например лауриловый метакрилам, улучшают сквозную сушку пленок (при 25°C) по сравнению с неизменным алкидом, но пленки становятся мягкими и пластичными. Полифункциональные мономеры, как например этилин гликол диметакрилам, улучшают сквозную сушку алкидов и затвердевают пленки по сравнению с неизменным алкидом. Показана возможность удовлетворительной сквозной сушки пленок без использования токсических свинцовых высушивающих средств. Изучалось также влияние изменений структуры алкидов (т.е. сорт масла и содержание смолы в масле) на высыхающие и пленочные свойства красок изготовленных из алкидо-мономеровых смесей; также собраны данные о скорости сушки, твердости пленок и их прочности.

Introduction

Alkyd resins have been used in the paint industry for over 30 years and during this time a considerable amount of experimental work has been carried out on their mechanism of drying and film properties. Many attempts have been made to overcome their deficiencies for particular purposes and generally to improve and broaden their fields of application. One of the major problems in air drying media is to obtain the correct balance of drying properties such that "through-drying" occurs shortly after a surface skin has formed so that the possibility of mechanical damage in the early life of the film is minimised. On the other hand surface drying should not be so rapid that shrivelling or frosting occurs. Current formulation practice attempts to solve this problem by the careful selection of "autoxidative" and "through" driers.

The processes of styrenation, methacrylation, etc., of alkyds are attempts to improve the drying properties (i.e. rate of drying and hardening) by increasing the molecular complexity of the resin in order to increase "lacquer-type" drying. These processes achieved what they set out to do to some extent but the products suffer from some of the disadvantages of lacquers, that they are more viscous than their parent alkyds and require to be used at lower solids. They also frequently give rise to recoating problems.

The possibility of copolymerising simple monomers such as acrylate or methacrylate esters with an alkyd during the film-forming (autoxidative) stage

of drying has hitherto received scant attention, yet such a process could have certain advantages over the conventional film forming processes. For example, the monomer would act as a solvent for the alkyd resin and thus enable the formulation of "high solids" compositions. The polymerisation process in the bulk of the film should occur in the absence of the toxic lead drier and film properties could be varied by selection of monomer or monomer mixtures so that a film may be softened or hardened. The limitation that film application imposes is, of course, that the polymerisable monomer should be to all intents and purposes involatile. Thus polymerisable monomers that are high boiling would appear to be the only monomers that can be used in practice. Lauryl methacrylate, lauryl acrylate and ethylene glycol dimethacrylate are commercially available examples of such "involatile" monomers and were used for the bulk of the experiments described in this paper.

Initially work was concerned with examining the effect of the addition of high boiling (i.e. essentially involatile) monomers to long oil linseed and soya alkyds (designated alkyds *A* and *B* in the experimental section) and to an autoxidisable styrene-butadiene copolymer (Buton 100, supplied by the Esso Petroleum Co.). The effect of the addition of lauryl methacrylate to Buton 100 (dried with 0.12 per cent cobalt as naphthenate) was quite striking. Buton 100 in thick films dries rapidly at its surface to give a brittle layer with a liquid underlayer. The addition of lauryl methacrylate (20 per cent by wt.) gave a composition which formed a film with a hard surface but with a gelled, rubbery underlayer. Similarly with the two alkyds selected it was demonstrated that improved through-drying could be achieved, although it was clear that undesirable softening of the alkyd film occurs when a plasticizing monomer is used in a comparatively soft, long oil alkyd film. The effect on through-drying was demonstrated with a range of monomers including lauryl acrylate, *N*-butyl acrylamide, di-2-ethylhexyl fumarate and di-2-ethylhexyl itaconate; butane 1,4 di-acrylate and butane 1,4 dimethacrylate; also with unsaturated oligoesters such as "Nuron" resin (a linear polyester with methacrylate end groups).

There appeared to be two obvious areas in which to work in order to obtain modified alkyd compositions with technologically useful properties. The first was to select a monomer that would harden (or at least not soften) the films obtained from a long oil alkyd paint, whilst giving improved through-drying. The second was to use a plasticising monomer with an alkyd that forms films that are too hard or inflexible for use in decorative paints. The first route was limited by the scarcity of commercially available monomers that should be capable of hardening an air dried film. For example, monomers that are sufficiently involatile to be retained in the drying paint film usually contain long alkyl chains and hence are inherently plasticising molecules. The only commercially available monomer that seemed likely to harden a film was ethylene glycol dimethacrylate and the hardening of long oil alkyds by the incorporation of this monomer was subsequently demonstrated. Considerably more effort was concentrated on the use of plasticising monomers with a range of alkyds varying in oil length and in the nature of the oil from which they were prepared. Thus alkyds ranging in oil length from 69 per cent to 43 per cent and based upon linseed, soya and dehydrated castor oils were examined and the effects of the addition of lauryl methacrylate at various concentrations studied.

Part of the work described in this paper forms the subject of a pending patent application (BPA 38225/63).

Experimental

Materials for film evaluations

Alkyd resins : A range of alkyd resins covering variations in oil length and the nature of the oil was selected for evaluation largely with lauryl methacrylate additions. Their composition and analytical constants are shown in Table 1. The alkyls were prepared by the conventional "solvent" process.

Table 1

Alkyd	Oil length %	Type	Acid value (mg KOH/g)	Viscosity (sec. body- tube at 25°C)	Solids %
<i>A</i>	69	Linseed/PE	12.5	5.5	75.0
<i>B</i>	68	Soya/PE	10.0	12.5	75.0
<i>C</i>	62	Linseed/PE	3.8	11.5	62.0
<i>D</i>	62	Soya/PE	8.2	5.5	63.5
<i>E</i>	54	Linseed/glycerol	4.8	7.5	56.0
<i>F</i>	43	DCO/glycerol	22.2	11.0	51.8
<i>G</i>	43	Soya/glycerol	11.5	26.5	64.4

Paints : The paints tested were based on rutile titanium dioxide (Rutiox R-CR, ex British Titan Products Limited) and the pigment volume of the dried films was kept constant at 12.5 per cent throughout the experiments.

Monomers : The majority of the experiments were carried out using lauryl methacrylate, but additional experiments were carried out with lauryl acrylate and ethylene glycol dimethacrylate and a few with other monomers.

Lauryl methacrylate (ex I.C.I. Ltd. Mond Division) was dried with anhydrous sodium sulphate and passed through a column of activated alumina (Type "O", Peter Spence and Co. Limited) to remove the phenolic stabiliser. Before the monomer was used in the film forming compositions the absence of inhibitory material was demonstrated by the bulk oxidation of the monomer in the presence of an autoxidisable substrate. Thus alkali refined linseed oil (10g), lauryl methacrylate (5g) and cobalt octoate (0.05g) were oxidised in oxygen at 25°C in a modified Warburg apparatus and the induction period for the oxidation measured. The monomer was considered satisfactory for use if the induction period was less than two hours. The inhibitor free product was stored prior to use at -5°C in a refrigerator. A similar procedure was adopted for the other monomers.

Unless otherwise stated the proportion of the monomer which was added in any composition is the weight percentage replacement of resin solids.

Driers : The naphthenates of cobalt, calcium or lead (as available commercially in solution in hydrocarbon) were used unless otherwise indicated. The drier compositions were chosen to give adequate set times without particular regard to through-drying, since it was hoped that monomer containing compositions

would exhibit adequate through-drying in the absence of, or with low concentrations of, lead. The metal concentrations are expressed on the oil contents of the paints throughout the experiments, except that the drier concentrations were kept constant when the resin was replaced with monomer.

Anti-skinning agent : In most cases dipentene (4 per cent of total resin composition) was incorporated to prevent skinning of the paints on storage.

Testing of storage stability and film properties

Storage stability : The can stability of the paints was assessed by examining samples kept in half-filled $\frac{1}{4}$ pint cans at 25°C and 40°C at monthly intervals. Skinning, thickening and settlement were noted.

Drying times : The drying times of the paints at 25°C and at 7-10°C (50 per cent RH) were measured by means of a Beck-Koller Drying Time Recorder. Two points were noted, the "set point" (SP) where the paint failed to flow back behind the needle and the "through-dry point" (TD) where the needle ceased to tear the film. The films were prepared with a 0.004 in. spreader. The drying times were recorded to the nearest 0.25 hour.

Yellowing in the dark : The yellowing of paints kept in the dark was measured on the General Electric Recording Spectrophotometer. The reflectances were measured at 420m μ (blue) and 680m μ (red) wavelengths and the ratio of reflectances blue/red recorded as a measure of yellowing. For a standard white the ratio is unity and yellowing is indicated by a decrease in the value of the ratio.

Hardness : Hardness measurements were carried out with the Wallace Micro-indentation Hardness Tester using a $\frac{1}{16}$ in ball-ended needle and a 15g load. The indentation and recovery I/R were recorded in units of 10⁻⁵ in. The measurements were made at 25°C in a constant temperature room. For clarity, indentation hardness only was plotted (Figs. 9-15).

Durability : Accelerated weathering and natural weathering was carried out on paints applied as single coats (by spinning) to 6 in \times 4 in "Alocromed" aluminium panels. They were subjected to the Marr (carbon) arc cycle for periods up to 1000 hours (84 cycles ; one cycle consisting of 12 hours UV irradiation concurrent with ten hours water spray and a two-hour drying period), or exposed at 45° in racks facing South. The panels were withdrawn periodically for measurements of gloss.

Determination of lauryl acetate and lauryl methacrylate in oxidised alkyd paint films

Materials : *n*-Dodecyl (lauryl) acetate was prepared by the acetylation (acetic anhydride, AR) of *n*-dodecanol (British Drug Houses Batch 761500). The b.p. was 160-162°C/20 mm (150-151°C/15 mm)⁵ and refractive index, n_D^{25} was 1.4308 ($n_D^{23.2}$ 1.4279)⁵. Analysis by the Pye Argon gas-liquid chromatograph at 130°C gave a main peak (81 per cent) at a retention time of 12.5 min. with subsidiary peaks (5 per cent, 14 per cent) at 6.25 and 27.5 min. respectively.

n-Octyl acetate was similarly prepared from *n*-octyl alcohol (L.Light, 95 per cent). The b.p. was 98-99°C/15 mm (102°C/18 mm)⁵ and refractive index

n_D^{25} was 1.4155 (n_D^{25} 1.4157)⁵. Gas-liquid chromatographic analysis at 130°C gave a main peak (97 per cent) at a retention time of 3.75 min. with a smaller peak (3 per cent) at 6 min.

Diethyl succinate (L.Light, 99 per cent) was distilled before use (b.p. 70°C/1 mm ; 85-86°C/6 mm)⁶. Gas-liquid chromatographic analysis of the distilled material at 130°C gave a single peak at a retention time of 17 min.

Lauryl methacrylate (I.C.I. Limited, Mond Division) contained "Topanol A", (0.1 per cent) as stabiliser. Before use, the stabiliser was removed by passage of the dry (anhydrous sodium sulphate) monomer through activated alumina (Type "O", Peter Spence Ltd.). Absence of inhibitory material was confirmed by the bulk oxidation of the monomer in the presence of an autoxidisable substrate.

Analysis : Analyses were carried out with the Pye Argon Chromatograph by means of a column packed with polyethylene glycol adipate (20 per cent on Celite). The lauryl acetate content of film extracts in petrol-ether was determined at 120°C using n-octyl acetate (50 per cent by wt.) as reference compound. Relative peak areas obtained (by triangulation) were converted to lauryl acetate content by means of a calibration curve of determined peak area ratios versus known lauryl acetate concentrations. The following calibration was used :—

Peak area ratios	$\frac{\text{lauryl acetate}}{\text{n-octyl acetate}}$	0.19	0.30	0.42	0.50	0.64	0.78
Percentage	lauryl acetate	11.3	19.8	25.5	30.1	40.2	47.2

The lauryl methacrylate content of film extracts were similarly determined with diethyl succinate (50 per cent by wt.) as reference compound at 130°C. The following calibration was used :—

Peak area ratios	$\frac{\text{lauryl methacrylate}}{\text{diethyl succinate}}$	0.20	0.32	0.41	0.53	0.56	0.59
Percentage lauryl methacrylate		9.9	15.3	23.9	32.3	40.6	51.0

The following paint composition was used :—

Linseed alkyd millbase, based on Alkyd A	90.0 g.
Lauryl acetate (or lauryl methacrylate)	10.0 g.
Cobalt octoate (10.5 per cent Co in white spirit)	0.48 g.

Films of these compositions were prepared (0.004 in block spreader) on glass panels (12 in × 4 in), dried and stored at 25°C until required. The detached paint films (ca 2 g of film) were extracted for six hours with light petrol (b.p. 40-60°C) in Soxhlet apparatus with the addition of a few crystals of hydroquinone. The bulk of the petrol was removed by distillation under reduced pressure. The residue was weighed and an equal weight of reference compound was added for the gas-liquid chromatographic analysis.

The recovery of lauryl acetate (19 per cent) and lauryl methacrylate (18 per cent) from a liquid, pigmented linseed-oil-based alkyd (Alkyd A) was checked by gas-liquid chromatographic analysis. Essentially quantitative recoveries (18 per cent for both samples) were obtained.

The following recoveries of lauryl acetate and lauryl methacrylate were obtained from dry linseed-oil-based alkyd paint films after storage at 25°C. (Table 2).

Table 2

Storage time (hour)	24	48	72	120	144	168
Lauryl acetate recovered (%)	94.4	86.5	—	53.8	—	38.0
Lauryl methacrylate recovered (%)	41.0	23.0	11.3	—	0	0

These results are illustrated in Fig. 1.

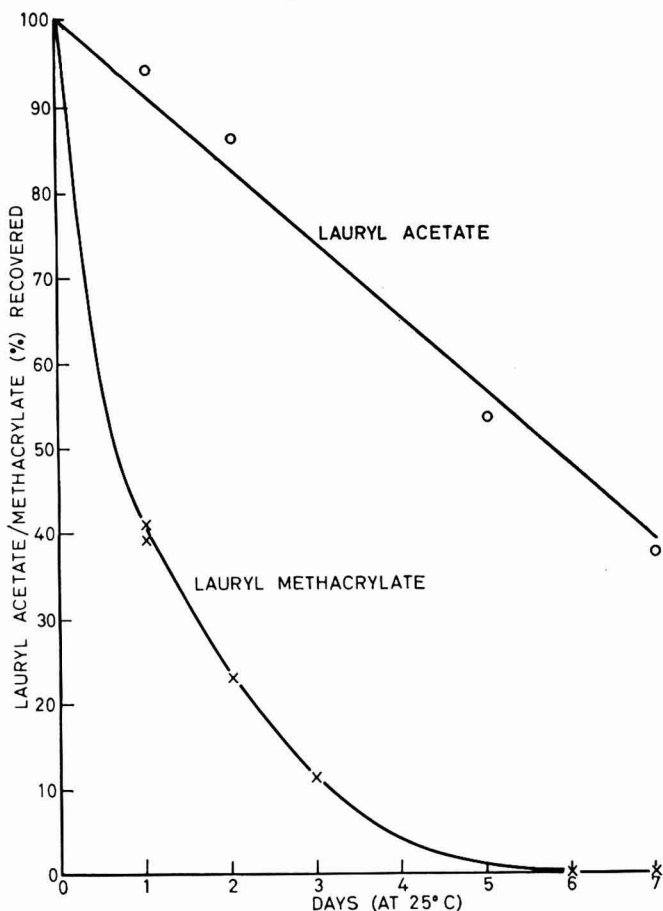
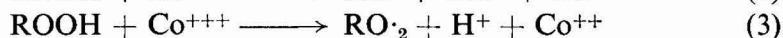
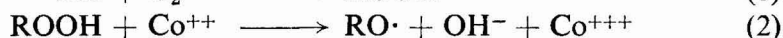


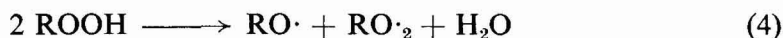
Fig. 1

Discussion and results

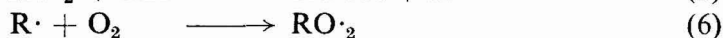
It is well known that drying oils, such as linseed oil, autoxidise at room temperature in the presence of a redox metal catalyst, e.g. cobalt naphthenate. The hydroperoxides initially formed undergo scission in the presence of the cobalt and polymeric products can be formed. The system, unsaturated ester/cobalt ion/oxygen thus has the capability of generating radicals that may initiate the polymerisation of an ethylenically unsaturated polymerisable monomer. The reaction sequence can be summarised :—



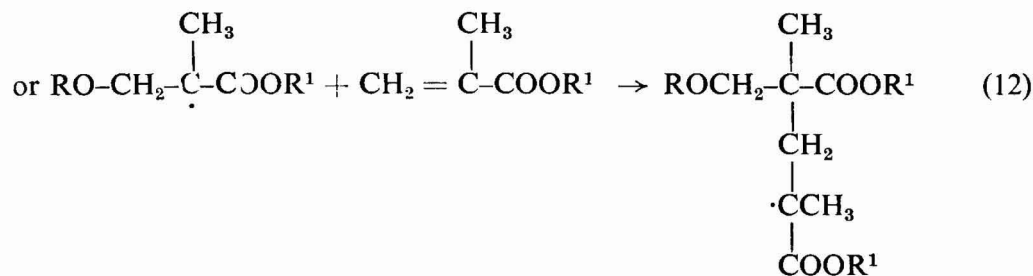
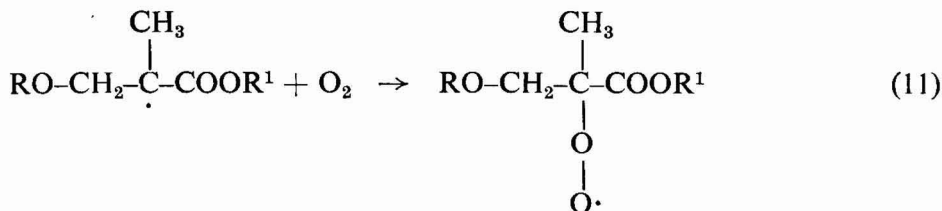
Reactions (2) and (3) may be considered together



The subsequent reactions are responsible for the regeneration of hydroperoxide and the formation of stable non-radical products :—



If a polymerisable monomer is introduced into the autoxidising oil, alternative reactions are possible, *viz.*



There is a considerable body of experimental evidence to suggest which reactions are likely to be favoured when an acrylic monomer is mixed with a free radical generator and autoxidised. Mayo¹ has shown that when methyl methacrylate is autoxidised in the presence of azobisisobutyronitrile as initiator, the products of autoxidation are methyl pyruvate and methyl methacrylate polyperoxide. The formation of the polyperoxide is slower than the rate of polymerisation of methyl methacrylate under similar conditions but in the absence of oxygen.

Thus, in the liquid film of an autoxidisable alkyd, where dissolved oxygen is abundant, reaction (11) might preponderate, giving peroxide crosslinks, with some degradation of the monomer to the pyruvate occurring as a side reaction. When gelation of the film or skinning of the surface layers has taken place, dissolved oxygen should be rapidly used up and the oxidation should be controlled by diffusion of oxygen into the system and reactions of type (12) should preponderate. Mayo² suggests that this is not so and that there is always oxygen available to give peroxy radicals. This conflicts with experimental work carried out at the Paint Research Station on "linoxyn" gels when it was found that a substantial amount of C-C in addition to C-O-C linked polymer was formed in the bulk of the gel³. It would appear, therefore, that the addition of involatile monomers such as lauryl acrylate or methacrylate should affect the drying of alkyd films. Furthermore, it is probable that they would improve the "through-drying" of an alkyd which normally required the addition of a "through-drier" such as lead naphthenate.

Storage stability

Of the paints containing lauryl methacrylate only those based on the long oil linseed alkyd (alkyd *A*) exhibited slight thickening within four months at 40°C. No significant changes in viscosity of the remaining paints were observed during this period. At 25°C, slight skinning occurred in the cases of paints based on alkyds *A*, *C* and *E* (all linseed alkyds) after 12 months storage. Settlement of pigment occurred after one-two months in all cases but the pigment could be readily redispersed on stirring.

Compositions containing ethylene glycol dimethacrylate were much less stable. A paint containing 10 per cent glycol dimethacrylate had doubled its viscosity after one week and had gelled after two weeks' storage.

Drying times

The drying times of alkyd paints containing (in most cases) two levels of monomer at 25°C and 10°C are set out in Table 3 (see also Figs. 2 and 3). The measurements made by means of the Beck Koller Drying Time Recorder show that at 10°C and to a lesser extent at 25°C addition of monomer increases the time for an alkyd to reach the set point. At 10°C there is a similar increase in the time to through-dry. At 25°C the time to through-dry decreases with increase in monomer content in the case of paints based on alkyds *A*, *B*, *D*, *E* and *G*. It might be expected that the DCO alkyd (*F*) would exhibit poor drying particularly in the presence of added monomer but it is difficult to understand why the 62 per cent linseed alkyd (*C*) should behave differently from the 69 per cent and 54

Table 3

Drying times of paints with and without the addition of lauryl methacrylate at 25°C and 10°C

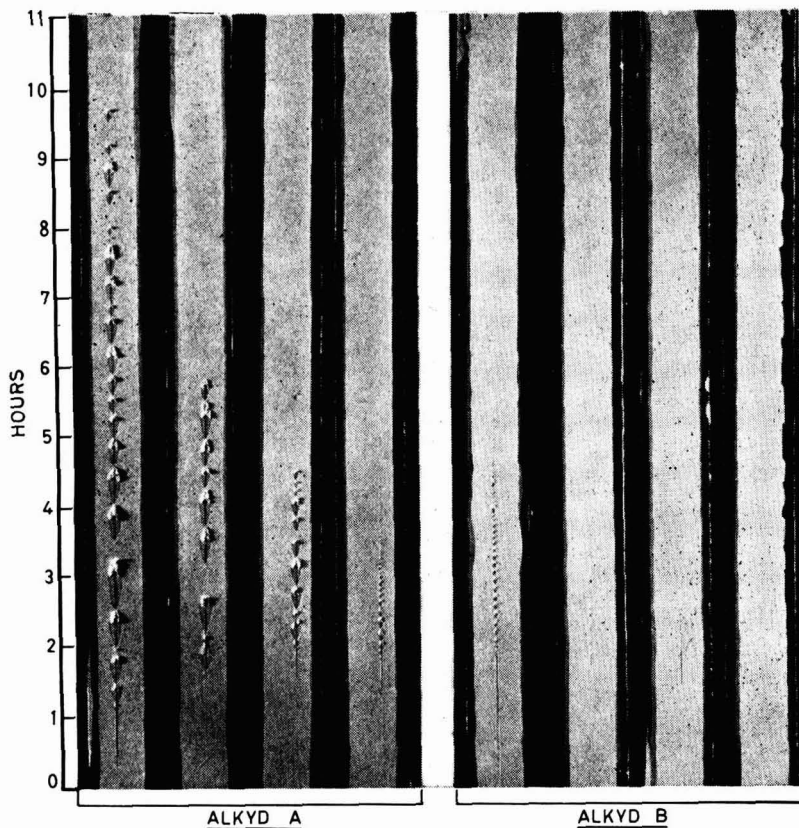
Paint based on		BK drying times (hour)			
		at 25°C		at 10°C	
Alkyd	Monomer (%)	SP	TD	SP	TD
<i>A</i>	0	1.0	6.0	2.0	10.0
	10	1.5	4.75	5.5	11.0
<i>B</i>	0	1.0	6.0	2.0	10.0
	10	2.0	3.0	9.5	13.5
<i>C</i>	0	0.75	5.5	0.5	4.75
	5	0.75	3.0	0.5	5.0
	10	1.0	5.5	0.75	7.75
<i>D</i>	0	1.25	6.75	0.75	9.0
	5	1.5	6.5	1.25	9.25
	10	1.5	2.5	6.0	9.0
<i>E</i>	0	0.5	6.25	0.2	5.5
	5	0.75	5.0	0.5	5.75
	10	1.0	4.5	3.75	6.0
<i>F</i>	0	0.1	12.25	—	>22
	5	0.1	13.25	—	>22
	10	0.1	14.5	—	>22
<i>G</i>	0	0	13.25	0	13.0
	5	0	11.5	0	>22
	10	0	8.75	0	18.5

The paints based on alkyds *F* and *G* showed short 'flow-back' or set up times but failed to dry to touch satisfactorily at 25°C or at 10°C.

per cent linseed alkyds (*A* and *E*). However, the general pattern of drying times indicates that retardation of drying to the set point occurs with monomer addition and at room temperature through-drying occurs more rapidly.

The drying characteristics of alkyds *F* and *G* require special comment. The non-volatile resin viscosity in these cases was significantly higher than in the longer oil length alkyds and the "set points" (defined in the experimental section) were short due to solvent evaporation and lacquer-type dry. Examination of the films by the finger touch method of estimating drying time indicated that the films had tacky surfaces long after the B.K. Recorder would have indicated that they were "set" or "through-dry." No further work was done on paints based upon these resins.

The increase in time to set is consistent with the hypothesis that the molecular weight of the involatile resin mixture decreased with the addition of the monomer and that an increase in reaction time was necessary to reach the degree of cross-linking required for gelation. The formation of the relatively stable peroxy-methacrylate radical (favoured by the ready availability of oxygen) could also



CONCN. OF LAURYL METHACRYLATE (%)	0	2.5	5.0	10.0		0	2.5	5.0	10.0
CONCENTRATION (%)	0.12% Co + 0.6% Ca throughout								

Fig. 2

contribute to the retardation of the crosslinking reaction. When gel formation has occurred (i.e. at the set point) the availability of oxygen will decrease and ultimately the rate of oxidation will be governed by the rate at which oxygen can diffuse into the film. Under the latter conditions the polymerisation of the monomer should be favoured and crosslinks will result to a large extent by the initiation of polymerisation by the decomposition of hydroperoxides attached to the alkyd (10) and termination similarly on alkyd that has undergone autoxidation. Thus an alkyd modified by the addition of an involatile monomer should differ considerably from an alkyd modified by methacrylation or styrenation in the conventional way, using a separate initiator such as benzoyl peroxide or ditertiary butyl peroxide. In the latter case the polymer (formed before film formation has taken place) would not contribute to crosslinking and would be present essentially as a high molecular weight diluent that improves drying of the resin by imparting lacquer-type drying. In the case of the co-

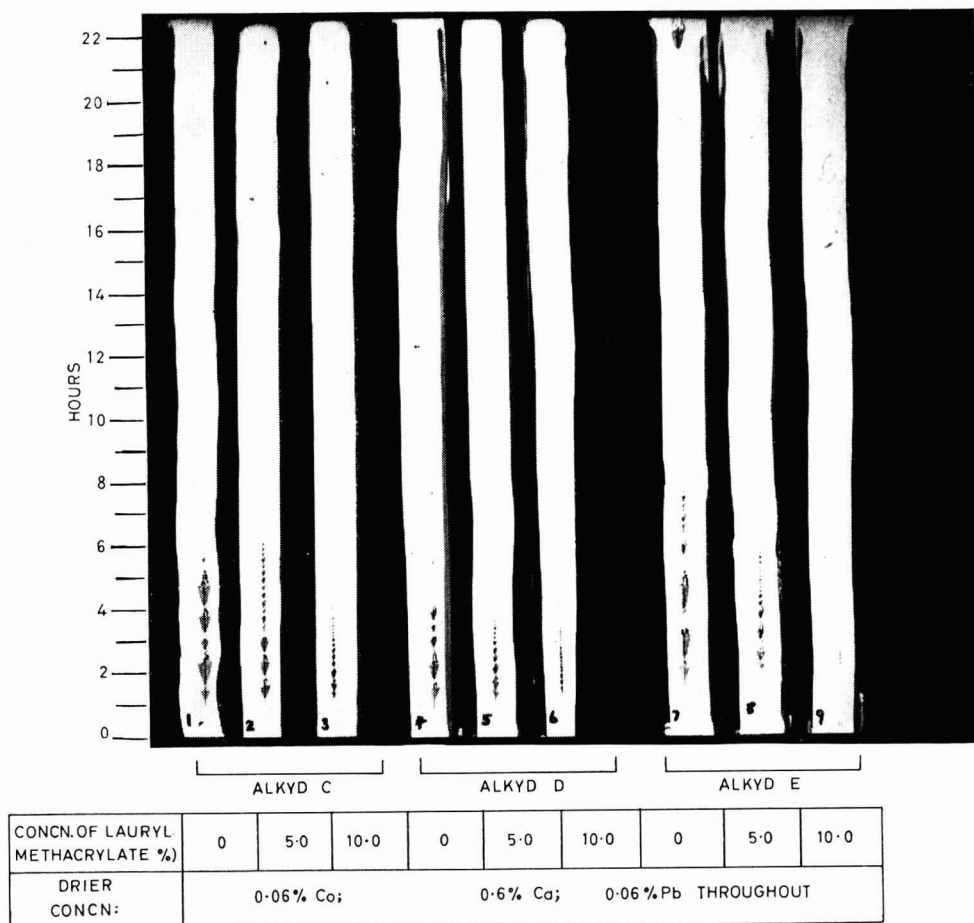


Fig. 3.

oxidised alkyd-monomer mixture, low molecular weight or short crosslinks should result and these would contain C-C links, peroxy and ether links.

Table 4 shows the effect of the addition of a difunctional monomer, ethylene glycol dimethacrylate to the long oil soya and linseed alkyds. The improvement in through-drying is quite marked and in this case rapid drying was accompanied by instability in the can. Whereas compositions containing lauryl methacrylate exhibited no change in viscosity over 12 months, compositions containing ethylene glycol dimethacrylate had doubled their viscosity on storage for one week.

Drying time alone, however, judged by the appearance of the Beck-Koller trace is not necessarily an adequate guide to the drying characteristics of the film. For example the addition of an unreactive, involatile plasticiser, such as lauryl acetate, produced an effect superficially similar to the addition of a reactive monomer. Since both materials could plasticise a crosslinked film, it was necessary to demonstrate that the differences in physical properties observed

Table 4
Drying times of paints incorporating ethylene glycol dimethacrylate

Paint based on		Driers	BK drying times (hour) at 25°C	
Alkyd	Monomer (%)		SP	TD
<i>A</i>	0	0.12% Co 0.6 % Ca	1.0	10.0
<i>A</i>	2.5	0.12% Co	1.0	5.0
<i>A</i>	10.0	0.6 % Ca	1.0	2.0
<i>B</i>	0	0.12% Co 0.6 % Ca	0.5	6.5
<i>B</i>	2.5	0.12% Co	1.0	5.0
<i>B</i>	10.0	0.6 % Ca	1.5	2.0

on adding a reactive "involatile" monomer were not purely the result of its plasticising effect. Hardness measurements showed that a film containing lauryl acetate hardened more rapidly with time than did the film containing lauryl methacrylate. This supports the view that the reactive monomer provides a more permanent plasticising effect by polymerising in the film. Confirmation of this was obtained by determining the rate of disappearance of lauryl acetate and lauryl methacrylate by a gas-liquid chromatographic technique on ageing paint films containing these materials, over a period of eight days. The results of these experiments are shown in Fig. 1. The lauryl methacrylate curve follows an exponential (approximately first order) decay whilst with lauryl acetate the disappearance is largely linear with respect to time. This supports the view that acetate disappears by a (linear) evaporation process from the film whilst the methacrylate is consumed by chemical reaction.

Yellowing in the dark

The yellowing of paint films kept in the dark for periods up to four months is shown in Figs. 4 to 8. With the long oil alkyd paints the addition of the lauryl methacrylate had little effect on the yellowing of the films. The linseed paints (*A*) (Fig. 4) were initially yellower than the soya (*B*) (Fig. 5) and yellowed more than soya during the period of test. Slightly larger differences were observed between the monomer-free and monomer containing compositions based on alkyds *C*, *D* and *E* (Figs. 6 to 8). Generally, the monomer containing paints yellowed less than the monomer-free paints. The worst alkyd for yellowing was the 54 per cent linseed alkyd (*E*) (Fig. 8) and it was with this alkyd that the largest improvement in yellowing was observed.

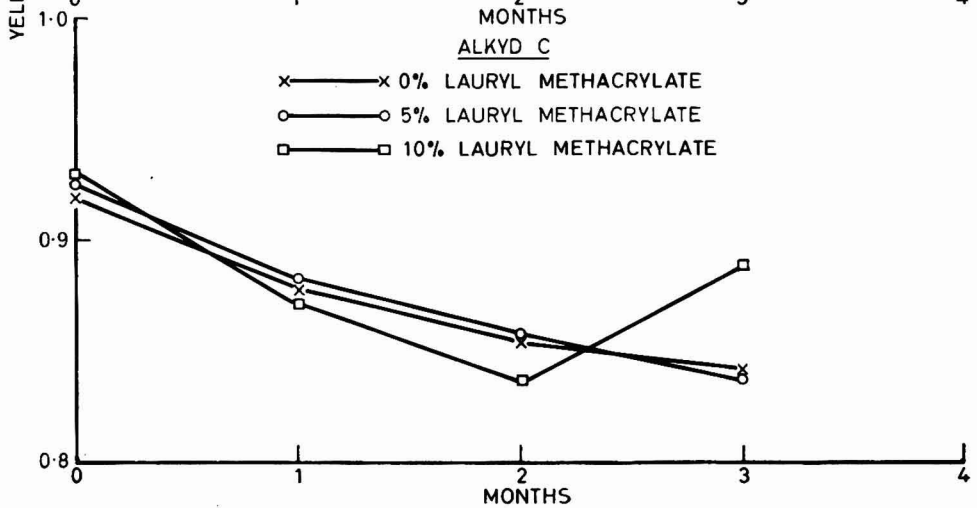
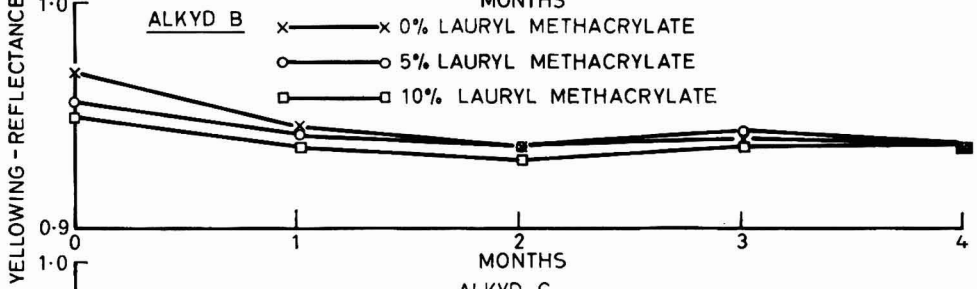
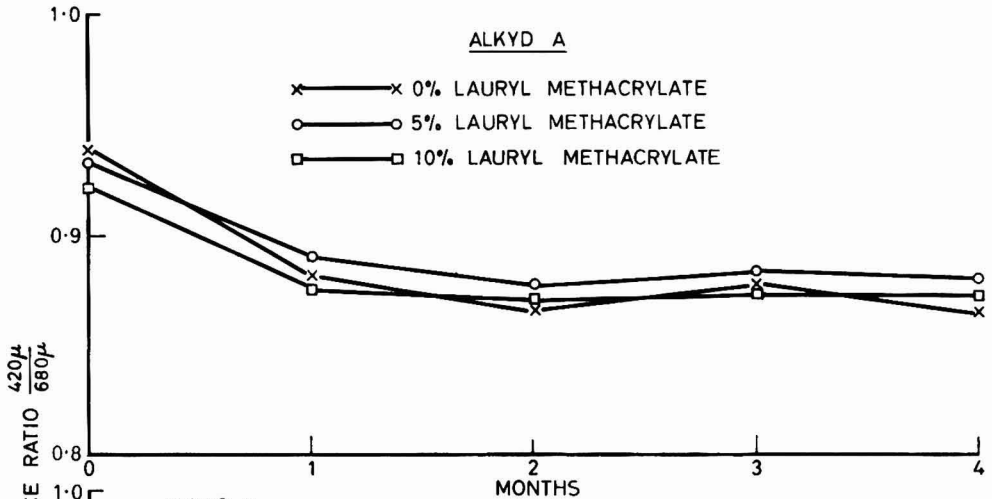


Fig. 4. (top)

Fig. 5. (middle)

Fig. 6. (bottom)

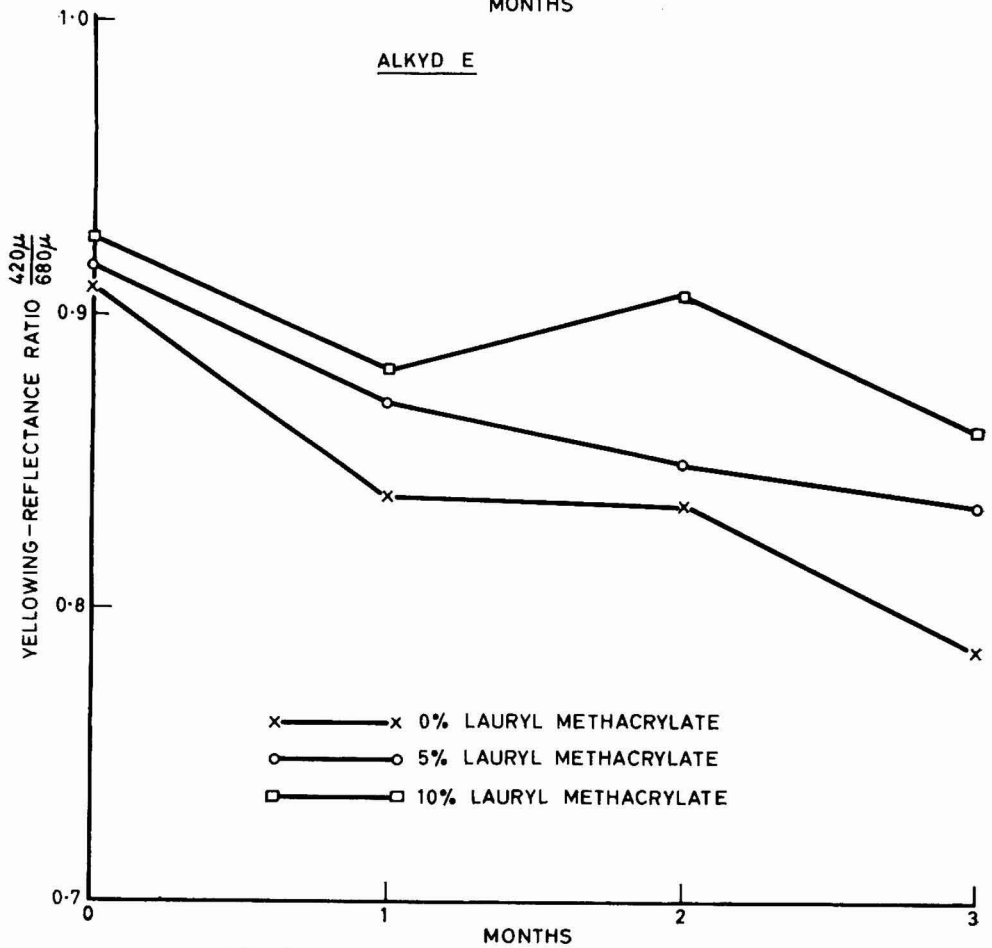
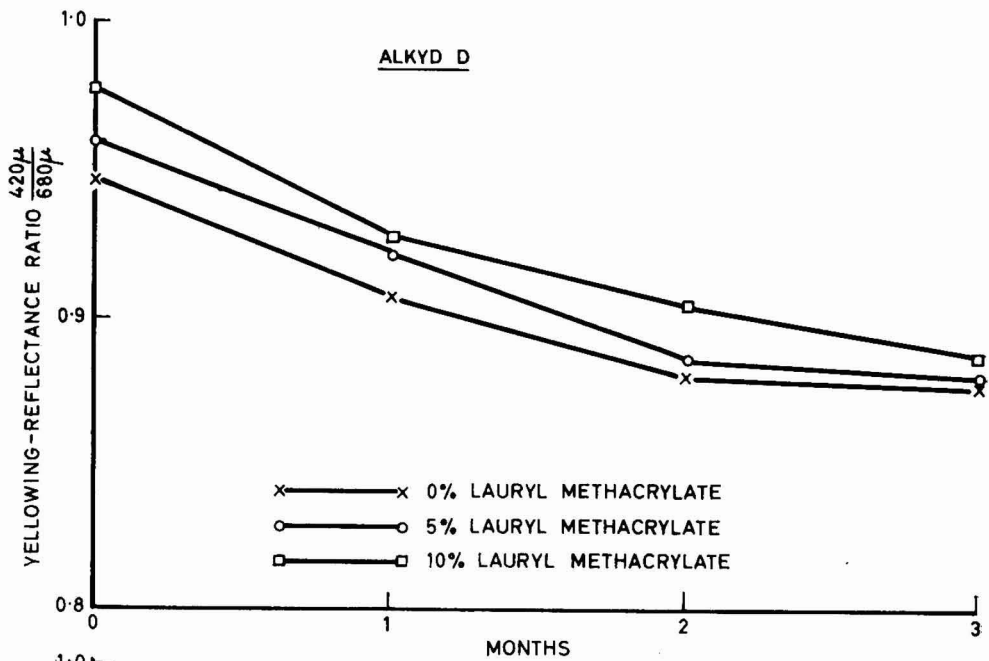


Fig. 7. (top)

Fig. 8. (bottom)

Film hardness

The results of hardness measurements on dried films aged at 25°C are shown in Figs. 9 to 15. With the long oil alkyds *A* and *B* the results were somewhat scattered and no attempt was made to draw continuous curves through the experimental points obtained. The plasticising effect of lauryl methacrylate additions to these alkyds was clearly demonstrated (Figs. 9 and 10). With alkyd *C* (Fig. 11) the plasticising effect was also apparent in the early life of the film but the ultimate film hardness was much less affected by the lauryl methacrylate and there was not a significant difference between the films containing 0, 5 and 10 per cent lauryl methacrylate after about 30 days aging. With alkyd *D* (Fig. 12) and particularly with alkyd *E* (Fig. 13) the plasticising effect of the monomer is again amply demonstrated. The effect of adding 10 per cent lauryl methacrylate to the paint based on the 54 per cent linseed alkyd (*E*) was to change its hardness such that it resembled the long oil soya alkyd paint (*B*).

Increase in film hardness of the long oil alkyds *A* and *B* (Figs. 14 and 15) was achieved by the addition of ethylene glycol dimethacrylate, a result that is indicative of the increase in crosslinking derived from the use of the bifunctional monomer. The effect of polyfunctional monomers on the hardness of air dried alkyd films has been reported recently⁴ and similar effects were obtained. Very little work was carried out with polyfunctional monomers since a simple solution to the problem of stabilising the paints was not available.

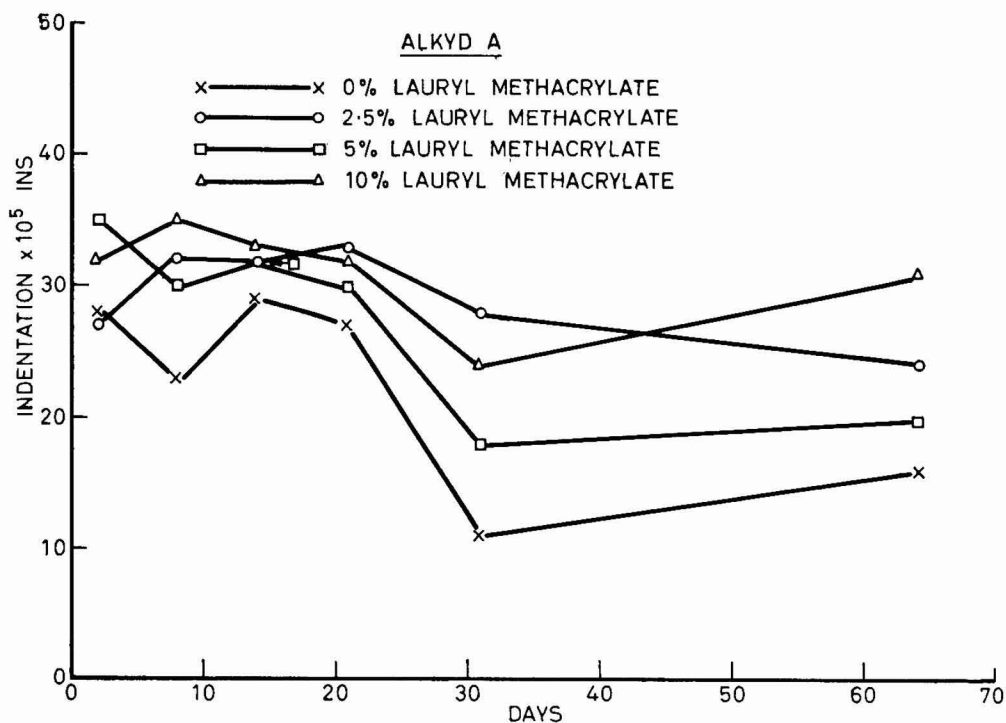


Fig. 9.

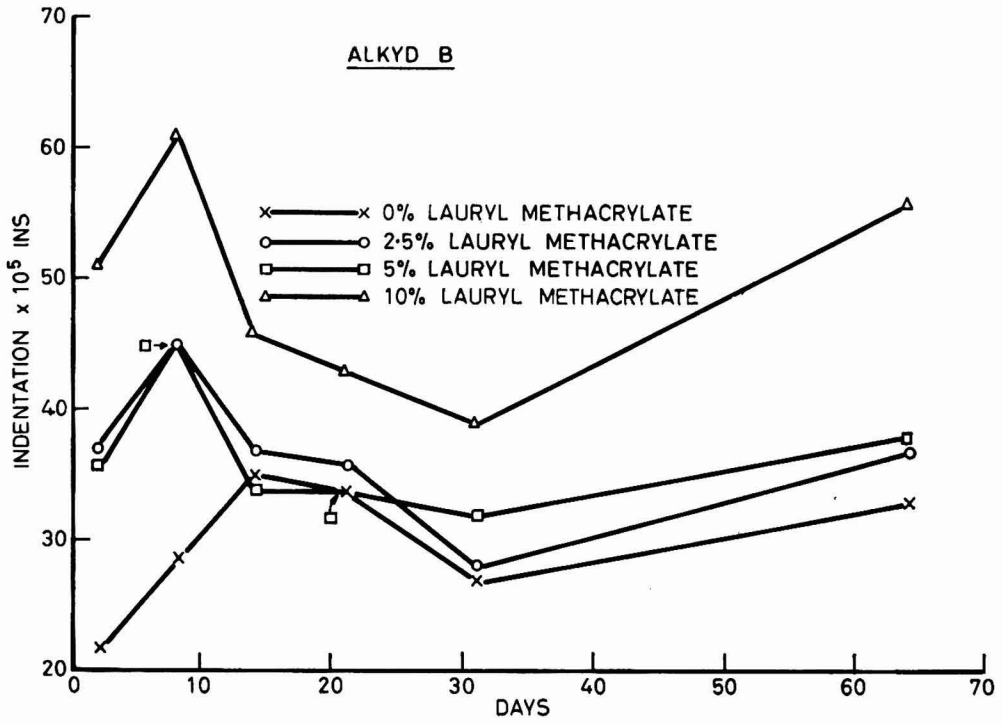


Fig. 10.

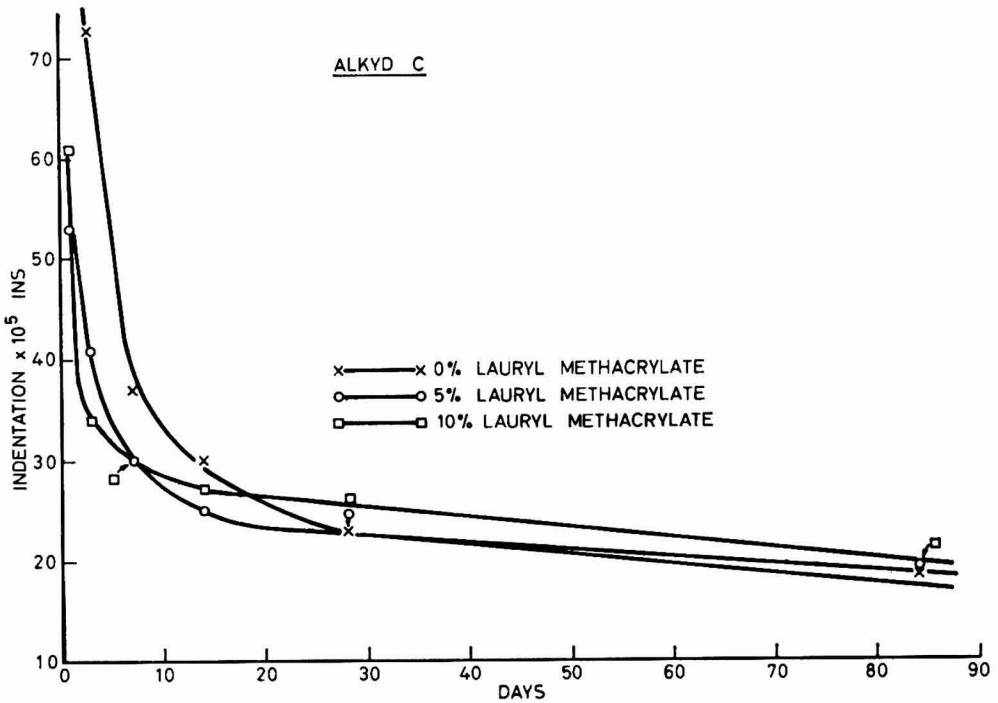


Fig. 11.

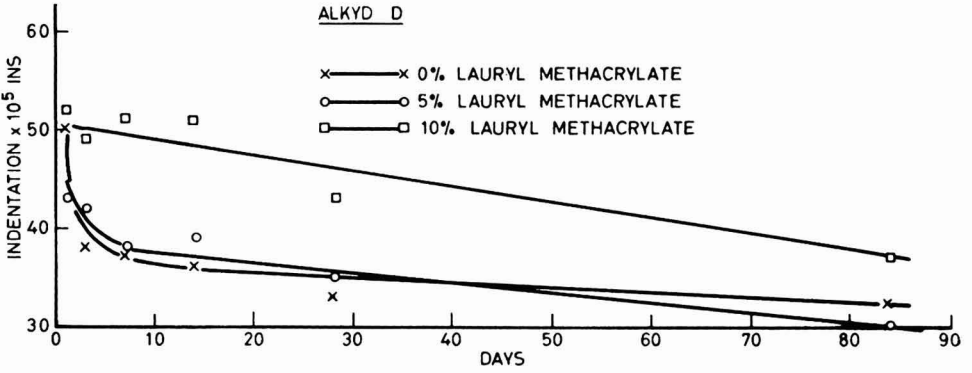


Fig. 12.

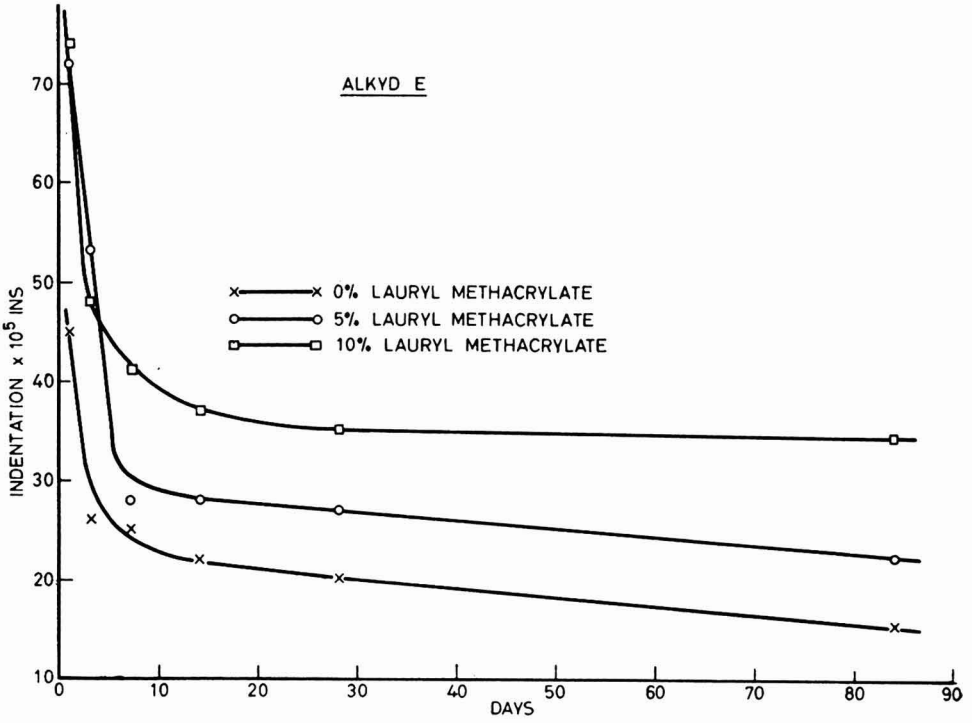


Fig. 13.

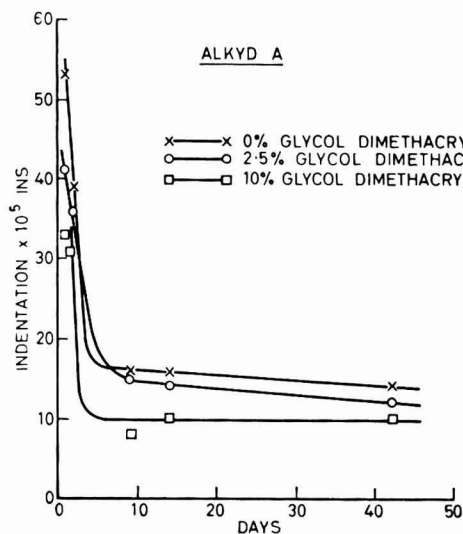


Fig. 14. (left)

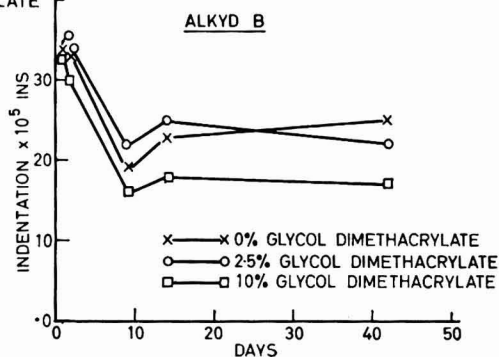


Fig. 15. (right)

Durability

A comparison of the gloss retention of paints subjected to accelerated weathering is set out in Tables 5 and 6. The addition of 10 per cent lauryl methacrylate to the long-oil alkyds *A* and *B* did not appear to affect gloss retention adversely.

Table 5

Durability. Accelerated weathering of paints with and without the addition of lauryl methacrylate—A comparison of linseed and soya based long oil alkyds

Paint based upon alkyd	Driers, Percentage metal on oil	Monomer (%)	Initial gloss (%)	Percentage gloss after		
				90 hours	500 hours	1,000 hours
<i>A</i>	0.12 Co ; 0.6 Ca	0	95	73	53	18
	0.12 Co ; 0.6 Ca	10	92	65	44	16
<i>B</i>	0.12 Co ; 0.6 Ca	0	95	63	57	33
	0.12 Co ; 0.6 Ca	10	94	68	52	27

Table 6

Durability. A comparison of long and medium oil length alkyds, the latter plasticised with lauryl methacrylate to simulate the film properties of the former

Paint based upon alkyd	Driers, Percentage metal on oil	Monomer (%)	Initial gloss (%)	Percentage gloss after		
				90 hours	500 hours	1,000 hours
<i>B</i>	0.06 Co ; 0.6 Ca 0.6 Pb.	0	91	66	33	17
<i>E</i>	0.06 Co ; 0.6 Ca 0.6 Pb.	10	92	82	56	36

Table 6 compares the gloss retention on accelerated weathering of paint films having similar physical properties e.g. hardness, flexibility. The "plasticised" medium oil length linseed alkyd (*E*) exhibits slightly better gloss retention than the unmodified long oil alkyd (*B*) but it is probable that both compositions would have retained their gloss better in the absence of lead and only the monomer containing paint would have through-dried adequately.

Table 7
Durability. Natural weathering of paints containing lauryl methacrylate

Paint based upon alkyd	Driers, percentage metal on oil	Monomer (%)	Initial gloss (%)	Washed/unwashed gloss percentage after	
				16 weeks	32 weeks
<i>A</i>	0.12 Co 0.6 Ca	0	95	86/49	70/32
	0.12 Co 0.6 Ca	5	94	99/52	73/27
	0.12 Co 0.6 Ca	10	93	82/38	68/29
	0.12 Co 0.6 Ca				
<i>B</i>	0.12 Co 0.6 Ca	0	95	87/51	74/27
	0.12 Co 0.6 Ca	5	94	82/50	74/31
	0.12 Co 0.6 Ca	10	97	66/48	75/27
	0.12 Co 0.6 Ca				
<i>C</i>	0.06 Co 0.6 Ca	0	98	85/48	56/21
	0.6 Pb				
	0.06 Co 0.6 Ca	5	97	77/45	48/18
	0.6 Pb				
	0.06 Co 0.6 Ca	10	97	56/35	40/10
	0.6 Pb				
<i>D</i>	0.06 Co 0.6 Ca	0	97	67/40	45/22
	0.6 Pb				
	0.06 Co 0.6 Ca	5	98	60/30	36/13
	0.6 Pb				
	0.06 Co 0.6 Ca	10	95	42/18	30/6
	0.6 Pb				
<i>E</i>	0.06 Co 0.6 Ca	0	93	52/35	51/24
	0.6 Pb				
	0.06 Co 0.6 Ca	5	88	68/40	52/17
	0.6 Pb				
	0.06 Co 0.6 Ca	10	92	55/42	41/14
	0.6 Pb				

The gloss retention of paint films weathered naturally has been studied only over short periods but the effects of lauryl methacrylate addition are clearly shown.

The gloss retention of paints based on the long oil alkyds (*A* and *B*) (Table 7) was better than that of alkyds *C* to *E*. In the case of alkyds *A* and *B* the addition of the monomer had little effect on gloss retention and dirt pick-up after 32 weeks but it should be borne in mind that under conditions of exterior painting, dirt pick-up could be excessive during the early life of these films when they are soft and thermoplastic. With alkyds *C* to *E* the addition of lauryl methacrylate had a deleterious effect on gloss retention and dirt retention, loss of gloss increasing with monomer concentration.

Conclusions

It has been demonstrated that substantially involatile polymerisable monomers can modify the drying behaviour of alkyd paints and other autoxidisable media. Long chain monofunctional acrylic esters such as lauryl methacrylate or lauryl acrylate soften or plasticise the films from alkyd compositions in which they are incorporated, retard the setting of the film but markedly decrease the time taken for the film to through-dry at 25°C. The compositions exhibit good can stability. With suitably designed alkyds which unmodified would yield rapid drying but brittle films for decorative purposes, the use of plasticising monomers such as lauryl methacrylate can yield decorative films of satisfactory film properties and improved through-drying time.

Polyfunctional monomers, e.g. ethylene glycol dimethacrylate, do not significantly change the time taken for a long oil alkyd composition to set but decrease the time for the film to through-dry. The resulting films are harder and more brittle than those from the unmodified alkyds. Practical difficulties were encountered in stabilising compositions containing polyfunctional monomers. Polyfunctional monomers appear to be technologically more attractive for use in autoxidative surface coatings since they are not inherently plasticising monomers as are the simple alkyd methacrylates or acrylates that are commercially available.

Acknowledgments

The authors wish to thank Mr. N. R. Garrard, Mr. R. J. K. Blewett, Mr. B. W. Cooper, Mr. P. J. Smith and Mr. J. S. Roberts for experimental assistance in the work described in this paper.

[Received 9 February 1966.]

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An investigation into the effects of painting over millscale

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Summary

A particularly serious type of paint failure is that in which large areas of paint flake from the surface within a few months of painting. The Paint Research Station and the British Iron and Steel Research Association have carried out a joint investigation into certain aspects of this problem. This type of failure is likely to be caused by comparatively short periods of weathering in an aggressive atmosphere before painting. A similar type of failure can occur if paint is applied over a millscale-free rusted surface. However, these failures are unlikely to occur as quickly as those caused by millscale flaking.

Usually, with the standard methods generally available, it is not possible to distinguish with any certainty between rust and weathered millscale under a paint film.

Une investigation des effets de l'application de peinture au dessus d'écaillés de laminage

Résumé

Un type, notamment grave, de défaut de peinture est l'écaillage à partir de la surface des grandes étendues de peinture après quelques mois de l'application de la peinture. La Paint Research Station et La British Iron and Steel Research Association ont effectué une investigation collective sur certains aspects du problème. Cette espèce de défaut peut suivre l'exposition du subjectile à une atmosphère agressive pendant des périodes assez courtes de vieillissement. Une défaut assimilée peut se produire lorsqu'on applique la peinture à une surface rouillée, mais libre d'écaillés de laminage. Cependant, il n'y a pas de probabilité que ces défauts se produisent aussi rapidement que celles provoquées par écaillés de laminage.

Usuellement, il n'est pas possible de distinguer certainement, par des méthodes normaux généralement disponibles, entre la rouille et les écaillés de laminage au dessous d'un feuil de peinture.

Eine Untersuchung der durch Aufbringen von Anstrichen auf Walzhaut hervorgerufenen Wirkungen

Zusammenfassung

Das Abblättern grosser Teile eines Anstrichfilms von seiner Grundfläche innerhalb weniger Monate nach seiner Aufbringung ist ein besonders ernst zu nehmender Anstrichfehler. Die Paint Research Station und die British Iron and Steel Research Association haben gemeinsam verschiedene Seiten dieses Problems untersucht. Diese Art Fehler wird wahrscheinlich durch verhältnismässig kurze Bewitterungsperioden vor dem Anstreichen in korrosiver Atmosphäre verursacht. Ein Fehler ähnlicher Art kann auch vorkommen, wenn eine verrostete, aber walzhautfreie Oberfläche angestrichen wird. Es ist jedoch unwahrscheinlich, dass derartige Fehler so schnell auftreten wie die durch Abblättern der Walzhaut verursachten.

Mit den normalen, im allgemeinen verfügbaren Methoden ist es gewöhnlich unmöglich mit einiger Sicherheit zwischen unter einem Anstrichfilm befindlichem Rost und verwitterter Walzhaut zu unterscheiden.

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Исследование эффектов окрашивания по поверхности заводской окалины

Резюме

Знаком один особенно серьезный вид неисправности окрашивания, когда большие площади краски отслаиваются от поверхности в течении нескольких месяцев после окрашивания. Выполнено совместное исследование Исследовательской Станцией для Красок и Британским Обществом для Исследований Железа и Стали о некоторых аспектах этой проблемы. Неуспехи этого типа случаются иногда при выветривании в агрессивной атмосфере в сравнительно короткий промежуток времени перед окрашиванием. Подобный же тип разрушения встречается при скрашивании оржавленной поверхности при отсутствии заводской окалины. Однако эти случаи нормально случаются реже чем неуспехи причиненные отслаиванием заводской окалины.

Невозможно отличить с уверенностью, при применении доступных стандартных методов, ржавчину от выветренной заводской окалины под красочной пленкой.

Introduction

The advantages to be gained by applying paints to well-prepared steel surfaces have been clearly established. Paints applied to surfaces carrying rust and/or millscale nearly always have a performance inferior to those applied to blast-cleaned or pickled steel. However, the actual performances of paint coatings on poorly prepared surfaces vary considerably. Sometimes they last for a number of years, but there are situations where the coating flakes off within a few months or even weeks. This type of failure in which large areas of paint flake from the surface after a comparatively short time is particularly serious because complete repainting is often required.

A layer of rust and/or millscale is always attached to the underside of the paint flakes, showing that the failure is caused by lack of adhesion.

This lack of adhesion is between the steel and the rust or scale ; the paint usually adheres firmly to the scale. Such failures are usually attributed to poor surface preparation. However, they occur only occasionally, and the conditions necessary for their occurrence are not clearly understood. When investigating such failures it is important to be able to differentiate between millscale and rust, but this is not easy. They have similar structures and, whilst millscale with its high proportion of magnetite (Fe_3O_4) is magnetic, rusts may also have magnetic constituents. Rusts formed in air are usually hydrated oxides of the $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ type and are non-magnetic. However, under certain conditions $\gamma \text{Fe}_2\text{O}_3$ may be formed. This is one of a series of oxides similar to Fe_3O_4 and is magnetic. Thus a simple magnetic test will not necessarily serve to differentiate scale and rust under paint films.

As these problems were of interest both to BISRA and the Paint Research Station, a joint programme was formulated to investigate certain aspects of painting over millscale.

Aims of the programme

The programme was formulated with three main aims :

- (i) to reproduce the type of failure discussed above, i.e. widespread flaking,
- (ii) to investigate methods of differentiating between the rust and millscale attached to the paint flakes after failure, and
- (iii) to investigate the effects on paint performance of painting over surfaces prepared by weathering for different periods, and by blast-cleaning.

Methods of investigation

From previous investigations of failures by flaking it seemed probable that they were caused by the under-rusting of the millscale over which the paint was applied. However, there had been no clear proof that such failures could not occur on scale-free, rusted surfaces. Therefore, two types of surface were required for these tests—a weathered surface carrying rust and broken millscale, and a scale-free rusted surface. As the period of weathering seemed to be an important factor, two periods of weathering before painting were included—three months and six months. The rusted surface was produced by blast-cleaning an “as-rolled” steel plate “as-received,” then allowing it to weather for six months. For comparative purposes, paints were also applied to two other types of surface—(i) an “as-rolled” surface, i.e. one carrying unweathered millscale, and (ii) a blast-cleaned surface that had not been weathered. Thus five different surface conditions were included in the programme.

- (i) “As-rolled.”
- (ii) Gritblasted, not weathered.
- (iii) Weathered for three months.
- (iv) Gritblasted, weathered for six months.
- (v) Weathered for six months.

Two different sites were chosen for the tests: the PRS site at Hurst Castle and the roof of the BISRA laboratories at Battersea. The Battersea site is representative of industrial sites and Hurst Castle, being on the coast with little shelter, is a fairly aggressive marine environment.

To investigate whether inhibitive primers reduce the risk of the flaking type of failure, one set of specimens was painted with a three-coat system consisting of one coat of red lead type “C” (BS 2523 : 1954) and two coats of a long-oil alkyd pigmented with rutile titanium dioxide, whilst another set was painted with three coats of the alkyd paint.

As flaking failures only occasionally occur it seemed possible that painting under conditions of dampness might be the cause. Therefore, one other variable was included in the programme, and some of the specimens weathered for three months were placed in a controlled atmosphere room, so arranged that the specimens would remain moist for 24 hours. They were then painted whilst moist.

All the weathering was carried out at the site where the painted specimens were to be exposed. All painting was carried out in the laboratory.

Test procedure

Steel specimens 12 in \times 10 in \times $\frac{1}{8}$ in were supplied in the as-rolled condition. Some were weathered at the two sites, Battersea and Hurst Castle, for either three or six months, and returned to the laboratory. There they were brushed with a bristle brush to remove loose scale and rust. Although a wire brush would normally be used to remove rust, experience suggests that wire brushing is often not carried out thoroughly enough. Therefore, it was decided that

cleaning should be carried out with a bristle brush so as to produce the type of surface generally obtained in practice. The weathering and exposure after painting was at 45° to the horizontal, and the same specimen face was exposed to the front during weathering and after painting.

The blast-cleaned and as-rolled specimens were painted and then exposed, with those to be weathered for six months, in November 1961. The specimens to be weathered for three months were exposed in January 1962 and all weathered specimens were removed, painted and re-exposed in April 1962.

Test programme

The test programme is shown in Table 1. Similar groups of specimens were exposed at both Hurst Castle and Battersea. Duplicate specimens for each of the ten conditions were exposed, making a total of 40 painted specimens at the two sites. Two as-rolled specimens, unpainted, were also exposed at each site.

Table 1
Test programme

Specimen type	Weathering period before painting	Paint system	Period of exposure after painting (years)	Remarks
1	Nil	A	2½	Carrying unweathered millscale
2	Nil	B	2½	Carrying unweathered millscale
3	Nil	A	2½	Gritblasted
4	3 months	A	2	Broken scale and rust
5	3 months	B	2	Broken scale and rust
6	3 months	A	2	Painted under damp conditions
7	6 months	A	2	Broken scale and rust
8	6 months	B	2	Broken scale and rust
9	6 months	A	2	Gritblasted before weathering (i.e.) rusted but scale-free
10	6 months	B	2	Gritblasted before weathering (i.e.) rusted but scale-free

Total 20 specimens (two of each type)

A = three coats of long-oil alkyd

B = one coat of red lead and two coats of long-oil alkyd

Examination

The specimens were inspected periodically during the test, and approximately $2\frac{1}{2}$ years from the date of initial weathering they were all removed and returned to the laboratory for detailed examination. The examination was in three parts as follows :

- (i) visual examination.
- (ii) X-ray analysis of the corrosion products of selected specimens.
- (iii) microscopical examination of selected specimen sections.

Methods (ii) and (iii) were used to try to differentiate between rust and millscale under the paint film. The X-ray analysis was carried out by the standard Debye-Scherrer diffraction method using an 11.4 cm Phillips camera. The sections for microscopical examination were cut from the specimens and mounted in a synthetic resin. They were then polished and examined by standard methods.

Results

The results obtained are given under separate headings :

Breakdowns on specimens

A summary of the visual examination of the specimens is given below.

As-rolled, with approximately 100 per cent millscale : After $2\frac{1}{2}$ years' exposure the Hurst Castle specimens were still generally sound with slight blistering and rust-staining at the edges and suspension holes. The Battersea specimens were still sound (Fig. 1). There were signs that some rusting might be occurring under the paint films on the Hurst Castle specimens (Fig. 2).

Gritblasted, not weathered : These specimens were comparable, after $2\frac{1}{2}$ years' exposure, with the as-rolled specimens at both sites. The Hurst Castle specimens were blistering slightly at edges and suspension holes. These effects are shown in Figs. 3 and 4.

Weathered for three months : At Hurst Castle these specimens were sound for about two months, but after two to seven months' exposure they flaked badly and after two years' exposure very little paint was still adhering to the specimens. Those exposed at Battersea had not flaked, but were blistering badly, particularly on the backs of the specimens. This group, both at Hurst Castle and Battersea, gave the poorest performance (Fig. 5 and 6). Those painted under damp conditions performed in the same way as those painted under ambient conditions in the laboratory.

Gritblasted, then weathered for six months : Although one of the Hurst Castle specimens was in reasonable condition with only slight surface blistering, the others were poor, particularly on the reverse side, where the paint had lost adhesion to the steel and could be removed without difficulty. The Battersea specimens were covered in fine blisters, but there were no signs of flaking (Figs. 7 and 8).

Fig. 1.

Fig. 2.

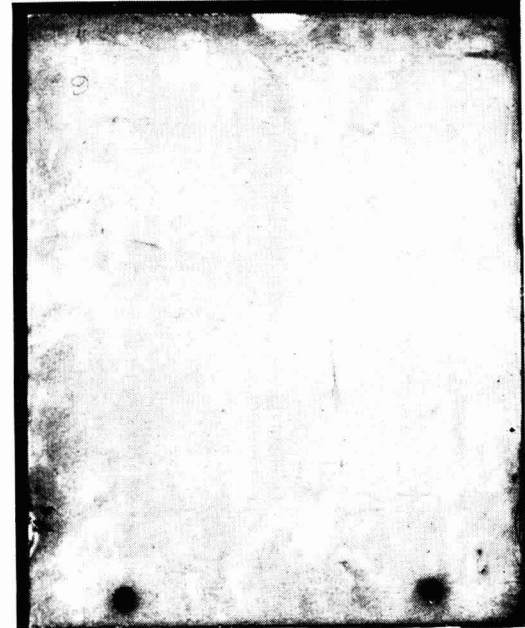
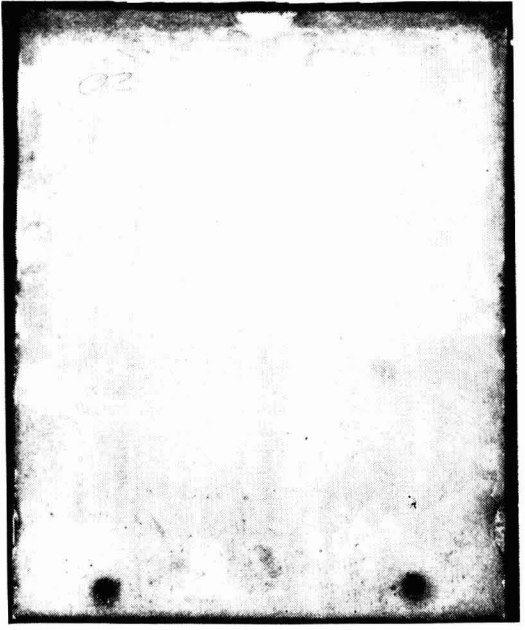
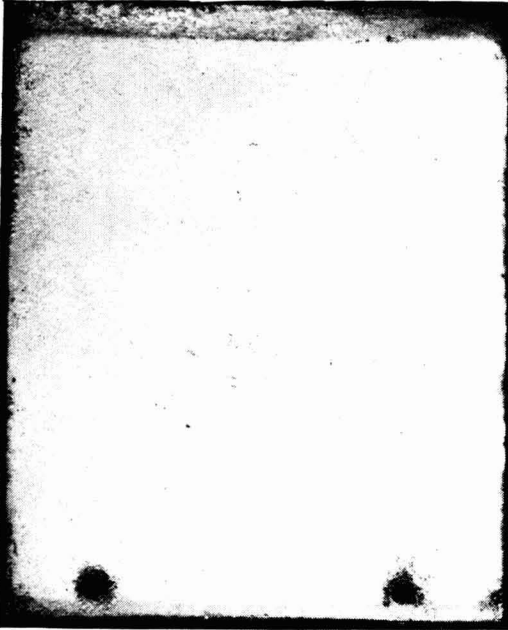


Fig. 3.

Fig. 4.

- Fig. 1. Battersea, As-rolled (100 per cent millscale), 2½ years' exposure
- Fig. 2. Hurst Castle, As-rolled (100 per cent millscale), 2½ years' exposure
- Fig. 3. Battersea, Gritblasted, 2½ years' exposure
- Fig. 4. Hurst Castle, Gritblasted, 2½ years' exposure

Fig. 5.

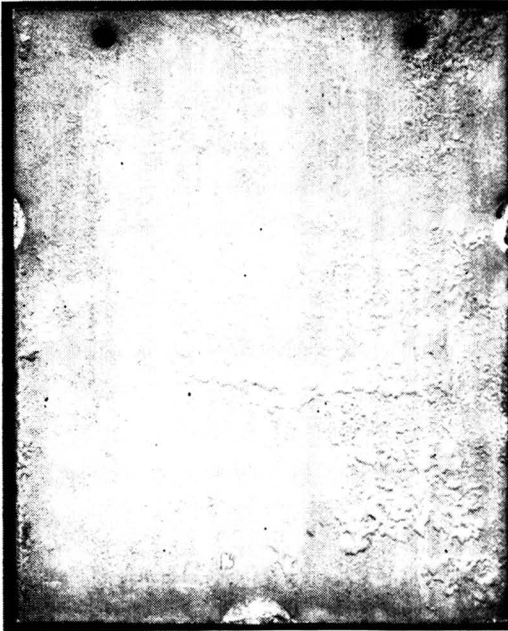


Fig. 6.

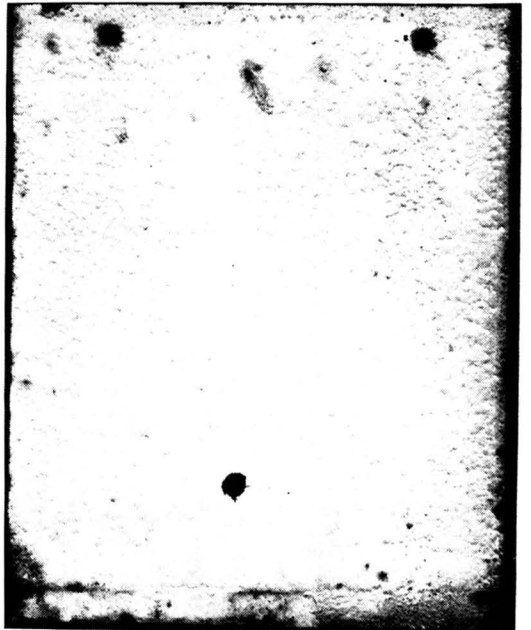


Fig. 7.

Fig. 8.

Fig. 5. Battersea, three months' weathering (rust and scale), two years' exposure
Fig. 6. Hurst Castle, three months' weathering (rust and scale), two years' exposure
Fig. 7. Battersea, six months' weathering (rust only), two years' exposure
Fig. 8. Hurst Castle, six months' weathering (rust only), two years' exposure

Weathered for six months : These specimens behaved in a similar manner to those weathered for three months at both sites. However, at Hurst Castle they were slightly superior, and although there was little adhesion between the paint and the steel, flaking had not occurred. The paint, after two years' exposure, was providing no protection, but the appearance was slightly better than the specimens weathered for three months as shown in Fig. 10. At Battersea the specimens were very similar to those weathered for three months (Fig. 9).

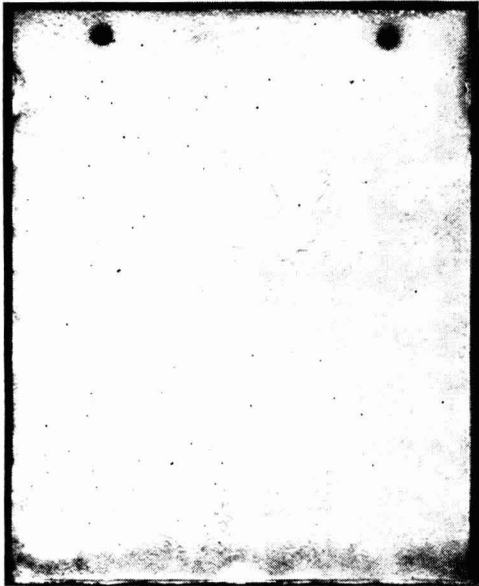


Fig. 9.



Fig. 10.

Fig. 9. Battersea, six months' weathering (rust and scale), two years' exposure

Fig. 10. Hurst Castle, six months' weathering (rust and scale), two years' exposure

Generally there was little difference in performance between the two types of paint system—one coat red lead + two of alkyd, and three coats of alkyd. Although there were marginal improvements in the earlier performance of the inhibitive system on the as-rolled and on the specimens weathered for three months, this was not evident after two years' exposure.

X-ray analysis

The purpose of the X-ray analysis was to determine whether this was a suitable method for distinguishing between rust and millscale under the paint film. Analyses were carried out on samples of the following types of specimen :

- (a) paint applied over a weathered surface of broken millscale and rust.
- (b) paint applied over rust with no millscale present.
- (c) weathered millscale.

On specimen (a), three samples were taken from the following positions :

- (i) at the steel surface.
- (ii) the underside of the paint flake.
- (iii) the loose corrosion product between the steel and the paint.

The results are given in Table 2.

Table 2
Qualitative analyses of corrosion products under paint films

Sample	Position of sample	Main constituents
(a) Weathered millscale and rust	At steel surface	γ Fe ₂ O ₃ — Fe ₃ O ₄
(a) Weathered millscale and rust	Under paint film	γ Fe ₂ O ₃ — Fe ₃ O ₄
(a) Weathered millscale and rust	Between steel and paint	γ Fe ₂ O ₃ . H ₂ O, Fe ₂ O ₃ — Fe ₃ O ₄
(b) Scale-free rust	At steel surface	γ Fe ₂ O ₃ . H ₂ O, Fe ₂ O ₃ . H ₂ O γ Fe ₂ O ₃ — Fe ₃ O ₄
(c) Millscale	At steel surface	Fe ₃ O ₄

Microscopical examination

Sections of three specimens were studied :

- (a) painted over millscale.
- (b) painted over rust.
- (c) painted over broken millscale and rust.

On (a) the general form of the product would lead an experienced observer to conclude that it was millscale, but this type of section does not represent the practical conditions being investigated. Under these conditions millscale is weathered prior to painting so there is bound to be under-rusting. Sample C, rust plus scale, represents the practical problem and in this work the rust and millscale could not be distinguished with any certainty.

Discussion

The results can most conveniently be discussed by considering the original aims of the work.

Reproduction of general flaking

This type of failure was produced on the specimens weathered for three and six months at Hurst Castle within less than seven months of exposure after painting. Those weathered for three months failed completely within a year and those weathered for six months failed in a similar way over a longer period. At Hurst Castle the paints on specimens gritblasted, then weathered for six months, lost adhesion to the steel after 2½ years. At Battersea this type of

failure did not occur, although the weathered specimens were blistering after $2\frac{1}{2}$ years.

Two factors have to be considered when explaining these failures, the surface to which the paint was applied and the environment after painting. The environment of weathering affects the surface in two ways. Its aggressiveness determines the amount and condition of scale left after a period of weathering and also the type and amount of surface rust. The condition of the millscale is particularly important because if under-rusting has occurred to an appreciable extent before painting, then there is a likelihood that the adhesion between the scale and steel will be lost within a comparatively short time after painting. If this happens, then, clearly, the amount of millscale that has been left on the steel after weathering becomes important ; if large areas of millscale remain and under-rusting has occurred, large areas of paint are liable to flake off.

It is known that the amount and composition of rust left on steel varies with the local environment and the time of the year during which it formed. If the rust is of a type that is not strongly adherent then this rust promotes the flaking of the millscale and, even if all the millscale has been removed, the rust may, itself, cause flaking of areas of paint.

In these tests the weathering and exposure were carried out at the same sites, but this would not necessarily happen in practice. Steel may be allowed to weather during storage at one place and then be transported to the erection site later.

The environment to which the painted steel is exposed is also important, because severe conditions, particularly if they are damp, will promote the under-rusting of the scale with resultant flaking. Milder conditions may result in general blistering without overall flaking.

The results obtained can be explained on this basis. The environment at Hurst Castle is more aggressive than at Battersea, as demonstrated by the performance of steel painted after gritblasting. Where all the scale has been left on the steel, the performance has been good, although over a longer period flaking might occur. At Hurst Castle the shortest weathering period (three months) resulted in the removal of only a small amount of scale, but considerable under-rusting. The paint from these specimens flaked within six months. The longer period of weathering (six months) resulted in the removal of more scale, but the under-rusting of the remainder had started, so, although severe blistering and loss of adhesion occurred, the failure was generally less severe than on the specimens weathered for three months. The gritblasted and weathered specimens were representative of as-rolled steel allowed to weather long enough to remove all the scale. At Hurst Castle these specimens were sound for about 18 months, but after two years were blistering badly on the fronts, and generally there was little paint adhesion on the backs of the specimens ; the paint could be removed as flakes without difficulty. These specimens illustrate that rust alone can, if the environmental conditions are severe, cause flaking of large areas of paint, but that this requires a longer period of exposure than needed with millscale present.

The flaking type of failure did not occur at Battersea. This is probably due to a less aggressive environment, which resulted in a different pattern of scale

removal during weathering and less severe under-rusting after painting. The general pattern is similar to that on the Hurst Castle specimens, but much less severe.

In this investigation the initial scale was similar on all the specimens because they were the same thickness and had been rolled under the same conditions. However, on specimens rolled under different conditions the scales produced could have been different. Although scales consist of three oxide layers, namely ferrous oxide (FeO), magnetite (Fe₃O₄) and ferric oxide (Fe₂O₃), the amount and form of each varies with the rolling conditions. A full discussion of this aspect is outside the scope of the present paper, but certain points should be noted. The FeO layer is formed next to the steel and it is usually porous. The decomposition of this layer during weathering tends to undermine the rest of the scale by allowing under-rusting. Some scales have a more compact and more adherent layer of FeO than others, also some scales are thicker than others. Both these factors will affect the time required to remove a scale by weathering. Furthermore they will influence the amount of under-rusting of the scale not removed by weathering. Therefore some types of scale will be more prone to cause the flaking type of paint failure.

Differentiation of rust and scale under paint films

Both air-formed rust and scales are composed of oxides of iron which can be differentiated using X-ray diffraction techniques. Air-formed rusts usually consist mainly of FeO · OH, whereas scales are made up of FeO, Fe₂O₃ and Fe₃O₄. The X-ray lines of the hydrated and anhydrous oxides can be distinguished without difficulty.

The differentiation of rust and weathered millscale under a paint film presents a greater problem. Rusts formed under paint films may contain gamma iron oxide (γ Fe₂O₃), and it is difficult to distinguish between this oxide and magnetite (Fe₃O₄). Under some conditions magnetite may form part of the rust and it is then impossible to use this oxide as a means of distinguishing between rust and scale. Therefore, to be certain that millscale is present under the paint film, FeO must be identified.

It has been reported that millscale contains between 40 and 95 per cent of FeO¹. It might be expected, therefore, that this oxide could be identified without difficulty. However, this is not necessarily so because the FeO is formed next to the steel and may not be present to any marked extent in the scale attached to the paint flake. Furthermore it tends to decompose to magnetite during weathering. Fe₂O₃ is only present in small amounts in millscale, usually less than 10 per cent. Its identification may prove to be difficult in a mixture of rust and scale, as only about 1 or 2 per cent of the oxide may be present.

Therefore, it is not necessarily a straightforward matter to decide whether the corrosion product under the paint film contains millscale as well as rust. If FeO is identified then millscale is almost certainly present, but this oxide was not identified in this work and is unlikely to be on scales weathered for some months. However, if FeO is not detected it does not follow that scale was not present before painting. Mixtures of iron oxides are not easily interpreted because of line broadening and a general lack of sharpness of the

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lines. The strongest diffraction line for FeO is not similar to that of the other oxides, but it is similar to those of other substances that might appear in the sample from the paint, e.g. BaCrO₄ and ZnCrO₄. Therefore careful sampling is essential.

The microscopic examination of sections might, in the hands of an experienced investigator, prove to be a suitable method of distinguishing rust and scale. Although the different oxides can be identified on a section of unweathered scale, this is more difficult on weathered scale, for the scale is broken up and rust appears similar. If only a small amount of weathering has taken place then magnetite can, under some conditions, be distinguished from rust, but very careful techniques are required. This method must be considered as being rather uncertain.

Experienced observers may be able to differentiate rust and scale by colour. Scale tends to be bluish whereas rust is brownish in colour. However, the results from such a method are clearly open to variations in interpretation. If millscale is not detected there can be no certainty that it is not present, as rust, which interferes with the detection of millscale, will always be present on a weathered surface.

The position can be summed up as follows. If FeO is identified, and generally more than one diffraction line is required for this, millscale is present. However if it is not identified then there can be no certainty that it is not present unless all the product is FeO . OH. Considering the smallness of sample used for X-ray work, it is unlikely that all the corrosion product could be identified as rust.

The effect of surface preparation on paint performance

The results of this investigation confirm that the best results are obtained with a blast-cleaned surface. However, if millscale is not weathered it provides a good surface, but there is always the risk of under-rusting and subsequent failure, particularly in severe environments. In practice no precautions are taken to protect millscale, so it is clearly not advisable to paint over it. If the scale on the steel is to be removed by weathering then the period of weathering should be sufficient to ensure that all the scale is removed. Short periods of weathering are liable to produce a very poor surface for painting. The performance of paints applied to the rusty surface left after thorough weathering will depend upon the type of rust formed and the environment of exposure. In aggressive atmospheres such as that at Hurst Castle the rust will contain a relatively high proportion of salts and, as wire-brushing removes only about one-third of the total rust, serious breakdown including flaking may occur in a comparatively short time.

In certain industrial environments, rusts formed in the winter months may be particularly adherent to the steel, so that wire-brushing does not remove them. However, after a period of a few months' weathering, adhesion between the outer layer of rust and the adherent layer near the steel surface is lost and the outer rust falls off as large flakes. If this type of rust is painted over during the winter months, flaking may occur within six or seven months of painting.

Conclusions

As a result of this investigation the following conclusions can be drawn, although they may not be generally applicable.

1. The early flaking of paint films is liable to occur if steel is weathered for a limited period in an aggressive environment. This is because, although only a small amount of scale is removed, considerable under-rusting of the remainder may occur, and this rust flakes from the steel, carrying the paint with it.
2. If all the millscale is removed by weathering, this early flaking is unlikely to occur.
3. Paint flaking can occur, even if all the millscale is removed by weathering, because certain types of rust can lose their adhesion to the steel. However, this is not likely to happen until some months after exposure and will not usually be as widespread as that caused by scale flaking.
4. Rapid flaking is not reduced by using inhibitive primers.
5. Differentiation of rust and millscale under paint films is uncertain. If ferrous oxide (FeO) is identified, then millscale is present, but the converse does not hold. Only a very experienced investigator can distinguish between rust and scale if FeO is not identified, and often it is impossible to distinguish between them.

[Received 2 February 1966]

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The gas chromatographic determination of residual monomers in vinyl acetate polymer emulsions

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Summary

The determination of residual monomers in polyvinyl acetate or vinyl acetate co-polymer emulsions is an important analysis which has frequently been carried out in the past by time-consuming or imprecise methods. A gas chromatographic method, combining speed, sensitivity and accuracy, is described, and shown to be applicable to the determination of vinyl acetate, 2-ethylhexyl acrylate and n-butyl acrylate monomers in a sample by a single analysis. The method should, with suitable modifications, be readily applicable to many other polymer systems.

La détermination, par chromatographie en phase gazeuse, de monomères résiduels dans émulsions d'acétate de polyvinyle

Résumé

La détermination de monomères résiduels dans émulsions d'acétate de polyvinyle ou des copolymères d'acétate de vinyle, est une analyse importante qui a été souvent effectuée auparavant par moyen des méthodes prolongées ou inexactes. On décrit une méthode chromatographique en phase gazeuse, rapide, sensitive et exacte. On l'a démontrée propre à la détermination, grâce à une seule analyse, des monomères d'acétate de vinyle, acrylate de 2-éthylehexyl et acrylate de n-butyle dans la même échantillon. A la suite des modifications appropriées, la méthode doit s'adapter facilement aux beaucoup de systèmes polymériques.

Gaschromatographische/Bestimmung von monomeren Rückständen in Emulsionen polymerisierten Vinylazetates

Zusammenfassung

Die Bestimmung monomerer Rückstände in Emulsionen von Polyvinylazetat oder Vinylazetatmischpolymeren ist eine wichtige Analyse. Sie wurde bisher häufig im Wege zeitraubender oder ungenauer Methoden durchgeführt. Es wird eine gaschromatographische Methode beschrieben, die Geschwindigkeit, Empfindlichkeit und Genauigkeit in sich vereinigt. Ferner wird gezeigt, dass auf diese Weise die Bestimmung eines Vinylazetat, 2-Äthylhexylakrylat und n-Butylakrylatmonomer enthaltenden Musters in einer einzigen Analyse durchgeführt werden kann. Die Methode dürfte sich nach entsprechender Modifikation ohne weiteres auch für viele andere Polymerisatsysteme eignen.

Определение с помощью газовой хроматографии остаточных мономеров в эмульсиях винил ацетатного полимера

Резюме

Определение остаточных мономеров в эмульсиях поливинил ацетата или винил ацетатного кополимера составляет важный способ анализа, который в прошедшее время часто выполнялся медленными и неточными методами. Описывается газохроматографический метод, дающий скорость, чувствительность и точность, применяемый

для определения винил ацетатовых, 2-этилгексил акрилатовых и *n*-бутил акрилатовых мономеров в образце посредством единственного анализа. Этот метод, с соответствующими видоизменениями легко применим ко многим другим полимерным системам.

Introduction

Emulsion paint formulations are commonly based on co-polymers of vinyl acetate with plasticising co-monomers such as 2-ethylhexyl acrylate and *n*-butyl acrylate. Analytical methods for these monomers are desired by :

(a) The user of the emulsion, since the concentration of unpolymerised monomer after polymerisation must be kept low (usually less than 0.5 per cent at the most) to avoid effects on such properties of the emulsion as stability, volatility, compatibility with additives, etc.

(b) The emulsion manufacturer, who will wish to follow the course of the polymerisation to avoid unnecessarily long reaction times, and also to ensure maximum utilisation of the monomers. Furthermore, it is necessary to know the ratio of the residual monomers in emulsions to confirm that the ratio in which they have combined is that required for the particular polymer application.

Among methods described in the literature, bromine addition to the double bond of the monomer (usually vinyl acetate) has been most frequently used^{2, 7}. Polarography⁶, infrared spectroscopy³ and nuclear magnetic resonance spectroscopy¹ have also been used, but a gas chromatographic method was thought preferable because, although earlier methods using this technique^{4, 5, 8, 9} were open to various objections, it seemed to offer the flexibility needed.

Discussion

Initial attempts in this laboratory to analyse residual vinyl acetate in polyvinyl acetate emulsions were by bromine addition methods, but it rapidly became evident that to get accurate values it was advisable first to remove the monomer from the emulsion by a preliminary azeotropic distillation with methanol. This procedure was time-consuming and also liable to poor reproducibility of results because, although interference from polymer was avoided, complete recovery of monomer was not easily ensured, and in addition high blank values were frequently obtained. The analysis for vinyl acetate in the distillate was somewhat shortened by determining it gas chromatographically, but this did not remove all the objections of the method and a direct gas chromatographic procedure was sought.

Bromination techniques rightly have an established place in the analysis of monomer in vinyl acetate polymer emulsions, principally perhaps because of their inherent simplicity, but it was felt that a gas chromatographic method would be a suitable alternative in many cases and could offer certain advantages. Principal among these was the possibility of determining relatively high-boiling co-monomers such as *n*-butyl acrylate and 2-ethylhexyl acrylate as well as vinyl acetate monomer in a single analysis.

Gas chromatography has frequently been used for the determination of monomers in polymers and other similar analyses, and is capable of giving accurate values for components in low concentrations in relatively small samples. For analysing polymers, however, it suffers from several defects

which seriously limit its accuracy, namely inadequate or slow vaporisation of the volatile constituents, accumulation of involatile polymer in the preheater and column, and cracking of polymer at the rather high temperatures necessary in the preheater. In addition, introduction of a small (a few microlitres only), accurately measured sample of polymer into a chromatograph may be troublesome if good reproducibility is required. The method described herein attempts to minimise errors from these sources, without prejudice to the ease and rapidity of the determination.

To try to ensure complete vaporisation of monomers from the aqueous co-polymer emulsions a moderately high preheater temperature (about 150-175°C) was selected and a solvent chosen to dissolve or (less satisfactorily) to disperse the emulsion so that the monomers should be given as good a chance as possible of being rapidly carried away by the carrier gas stream from the involatile polymers. For the particular vinyl acetate polymers under study methanol and dimethylformamide were suitable, but the former was generally preferred because it is less toxic and can be purified more easily (by treatment with 2, 4-dinitrophenylhydrazine or careful distillation). For samples in which 2-ethylhexyl acrylate was to be determined dimethylformamide was not a suitable solvent for accurate work because of partial overlapping of monomer and solvent peaks on the chromatogram. Ethylene glycol monomethyl ether and similar solvents gave almost complete solution of the polymers, but on standing the solutions were liable to troublesome gelling. Use of a diluting solvent had two other significant advantages in that it enabled less polymer to be injected into the preheater during each determination and it permitted the use of ordinary Hamilton syringes for accurate sample injection, provided that they were cleaned immediately after use to prevent a film of polymer forming as the solvent evaporated. One difficulty in using a solvent arose because the solubility of the emulsions was rather low, and solvent to emulsion ratios of between 10 : 1 and 20 : 1 were necessary. This drawback was, however, overcome by using high sensitivity gas chromatographic detectors and amplifiers, but care was needed to reduce base-line fluctuations on the recorder, bleed of stationary phase and mains supply variations to low levels. The use of high purity solvents and internal standards was important. In some cases the methanol solution was almost clear, but usually it was slightly translucent. On rarer occasions emulsions could not be dissolved at all in the suggested quantities of solvent even after prolonged contact. It was found to be pointless attempting to use more than 20 volumes of solvent, and in these cases a suspension was analysed. It was not established how large the errors were from the latter method of proceeding, but special care was taken to obtain good mixing of solvent and polymer so as to reduce sampling errors as much as possible.

The use of a solvent does not appear to have been reported for vinyl acetate monomer analyses. Durrett⁴ overcame the difficulty of injecting polymers on to a chromatographic column by using a method in which light constituents were stripped off the heated sample by a carrier gas stream, condensed into a cold trap, and finally flashed on to the column by heating the trap. Haslam and Jeffs⁵ modified this to avoid depolymerisation by evacuating monomer from the polymer under reduced pressure. A completely different approach

was chosen by Porter and Johnson⁹, who used a specially designed preheater into which a glass capillary containing a small, accurately weighed sample of polymer could be introduced.

Implicit in the literature methods referred to above is the desire to prevent polymer from being carried into the chromatographic column. The approach to this particular problem adopted in this laboratory was to incorporate a disposable glass liner, containing a small plug of glass wool at one end and a lip for easy removal, into the injection port of the preheater as shown in Fig. 1. Because carrier gas passed through the liner good vaporisation occurred,

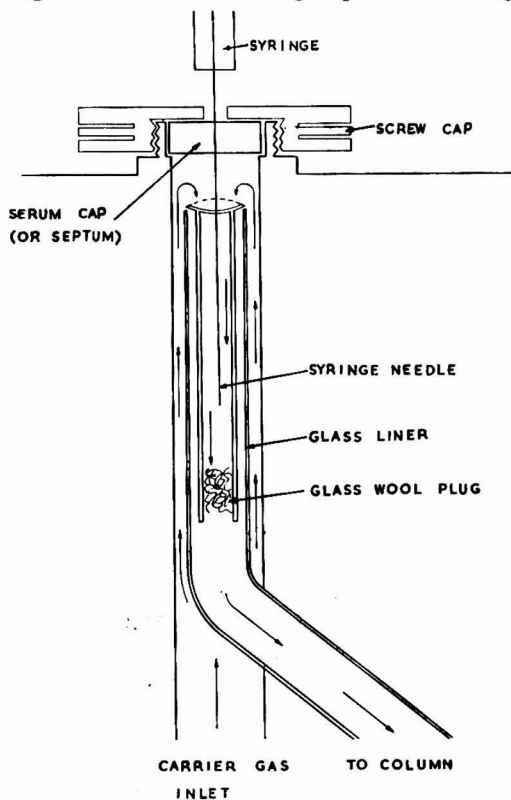


Fig. 1. Diagram of preheater with liner

a solution of the internal standard in methanol to ensure that peak heights for it and the component being determined were comparable.

The chromatographic conditions chosen for the analysis naturally varied with the required determination, but for most of the work a Perkin-Elmer F11 fitted with a temperature programming unit and twin-columns placed in parallel was used. It was important to use accurately matched columns for this work to eliminate the effects of stationary phase bleed. The columns were prepared by using equal weights of packing and approximately equal packing densities. They were then carefully "aged" to bleed off volatile components, first at low temperatures until bleed from the columns was negligible, and then at temperatures progressively 20°C higher until approximate matching was

and the glass wool plug helped to retain the unvolatilised polymer. Glass was a particularly favoured material for construction of the liners because it simplified fabrication, and meant that polymer was never in contact with hot metal surfaces. Nelson, Eggertsen and Holst⁸ preferred to insert a glass wool plug into an ordinary preheater for this purpose, and renewed it after every 2-3 analyses to avoid vaporisation from the residue of components which might be eluted during subsequent sample injections. The glass liners mentioned above could if necessary be replaced after each analysis, although in practice they were normally used for up to five determinations.

As a further safeguard against non-repeatability of sample injection an internal standard appropriate to the monomer being determined, e.g. n-octane for vinyl acetate, was added to the solution of emulsion. It was usual to use

obtained at a temperature somewhat above that needed for the analysis. Finally slight adjustment of the carrier gas rates was used to get good matching. For determinations samples were injected alternately to the two columns to eliminate as far as possible differences between them developing during use.

For the Perkin-Elmer F11 chromatograph a glass liner 3-4 in long and 0.1 in outside diameter was found suitable. Other materials of construction including stainless steel and copper were used, but offered no advantages for this particular application. Liners of the sort described are now commercially available.

The checks carried out on the procedure are described below. Typical GLC traces for a sample of polyvinyl acetate and a standard solution containing 100 ppm of three common co-monomers (vinyl acetate, n-butyl acrylate and 2-ethylhexyl acrylate) in methanol are shown in Figs. 2 and 3 respectively.

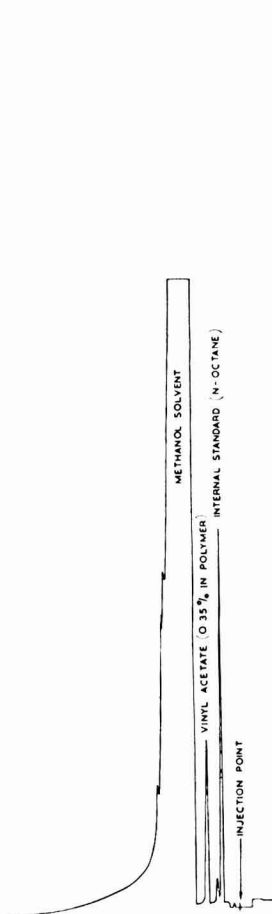


Fig. 2. Trace of polyvinyl acetate emulsion under the following conditions: approximately 7.5 per cent solution in methanol, column temperature 50°C, 3 μ l injection and 7 psig nitrogen inlet pressure

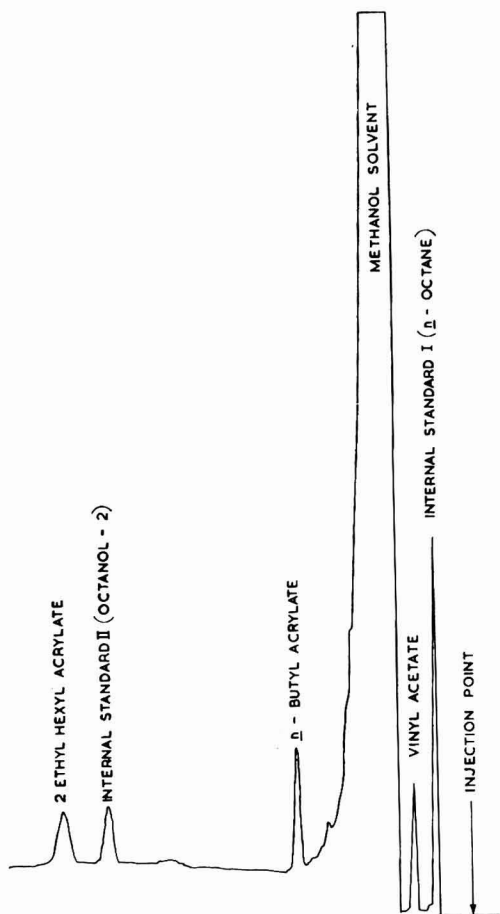


Fig. 3. GLC trace of 100 ppm solution of three typical monomers in methanol under the following conditions: temperature programmed at 50-110°C, 3 μ l injection and 7 psig inlet pressure

The sensitivity of the new method can be seen from the traces, which were obtained using an amplifier sensitivity (50×1) at which a steady baseline could be fairly easily obtained. Allowing for dilution of the emulsion with solvent the limits of detection for monomers were :

	<i>Percentage</i>		
Vinyl acetate	0.01
n-Butyl acrylate	0.01
2-Ethylhexyl acrylate	0.02

Experimental

Apparatus

Perkin-Elmer F11 chromatograph with twin-columns and flame ionisation detectors, and temperature programming facilities (or a similar apparatus).

1 mV Honeywell-Brown recorder.

10 μ l. Hamilton syringe.

Glass injection port liners as described above.

Two 6 ft \times $\frac{1}{8}$ in outside diameter nickel plated copper columns each packed with about 2.5 g 10 per cent Carbowax 1500 (Wilkins Instrument and Research Inc.) on 40-60 mesh acid-washed Chromosorb W, and carefully aged to ensure adequate matching.

Reagents

n-Octane : Phillips purified grade.

p-Cymene : BDH reagent grade of checked purity.

Octanol-2 : Koch-Light ; purity checked by infrared spectroscopy and gas chromatography.

Methanol : AR grade purified if necessary by fractionating using a 4 ft \times 1 in column packed with gauze rings, taking a 5-95 per cent heart-cut.

Dimethylformamide : BDH laboratory reagent.

Vinyl acetate, n-butyl acrylate and 2-ethylhexyl acrylate monomers of at least 99 per cent purity. The purity should be confirmed by gas chromatography on the column before use.

Calibration of the instrument

Make up separate internal standard solutions in purified methanol or dimethylformamide as appropriate as given in Table 1, or if preferred a single solution containing all the internal standards needed for the co-polymer under examination. Calibration methods are given below using methanol as solvent. Where dimethylformamide is used as solvent for the polymer emulsion it should also be used for preparing calibration curves.

Vinyl acetate : Weigh accurately approximately 1 g of pure vinyl acetate into a 100 ml volumetric flask and make up to the mark with purified methanol (or dimethylformamide if this is being used as polymer solvent). From this make up standards in three 100 ml volumetric flasks containing 2 ml, 4 ml and 6 ml one per cent w/v stock solution accurately measured with pipettes and exactly 5 ml of n-octane internal standard solution in each. Make-up to the mark with purified methanol. These solutions will correspond to 0.004 g,

0.008 g and 0.012 g respectively of vinyl acetate relative to 1 ml of internal standard solution.

Inject 3 μ l of each standard into the chromatograph under the conditions given below and plot a graph of weight of vinyl acetate/1 ml internal standard in the standard solution against the ratio of peak heights of vinyl acetate to internal standard. This should be a straight line plot passing through the origin. Using the graph the weight of vinyl acetate in a sample made from 1 g emulsion, 10 or 20 ml purified methanol and 1 ml internal standard solution may be found by measuring the ratio of peak heights of monomer to internal standard from a chromatographic trace.

2-Ethylhexyl acrylate : Obtain a calibration graph in the same manner, but using a 1 per cent w/v stock solution of 2-ethylhexyl acrylate in purified methanol. Transfer with pipettes 5 ml, 10 ml and 15 ml of this stock solution to three 100 ml volumetric flasks, add with a pipette 5 ml of octanol-2 internal standard solution, and make up to the mark with purified methanol. These solutions will contain 0.01 g, 0.02 g and 0.03 g 2-ethylhexyl acrylate per ml of internal standard solution respectively.

n-Butyl acrylate : Prepare a calibration graph in a manner similar to that given for 2-ethylhexyl acrylate, using the appropriate solvent and internal standard.

Method

Thoroughly mix the polymer emulsion and then weigh accurately approximately 1 g into a 25 ml round-bottomed test-tube and add with a pipette 10 ml of carefully purified methanol. Mix well using a glass rod to dissolve the polymer, but if this quantity of solvent is insufficient add with a pipette a further 10 ml and mix again. A clear or slightly cloudy solution should be obtained, but if the emulsion resists this treatment it should be made up similarly in an alternative solvent or analysed as a well-dispersed suspension in methanol. To the solution add, from a pipette, 1 ml of the appropriate internal standard solution shown in Table 1, and analyse the sample on the chromatograph using the conditions given below, and the temperature programming adjustments set to give the conditions specified in Table 1.

Table 1
Column conditions for temperature programmed runs

	Monomer to be determined		
	Vinyl acetate	n-Butyl acrylate	2-Ethylhexyl acrylate
Temperature of columns	50°C	50°C programmed to 85°C after 6 minutes	50°C programmed to 105°C after 20 minutes
Internal standard ..	0.4% w/w	2% w/w	2% w/w
Solution	n-Octane in methanol	p-Cymene in methanol	Octanol-2 in methanol

Gas chromatographic column conditions

Column temperature ..	50°C initially, temperature programmed appropriately.
Preheater temperature	Approximately 175°C.
Carrier gas	Nitrogen at approximately 7 psig inlet pressure to each column (equivalent to about 5 litre/hr to each).
Gas to flame detector	40 psig air, 20 psig hydrogen.
Amplifier sensitivity ..	50×1 normally.
Sample size	3 μl.

Place a glass liner in each injection port and allow them to come to the preheater temperature. Then inject, using a Hamilton syringe, 3 μl of the prepared emulsion polymer solution. Measure the peak heights of monomer and internal standard from the chromatogram, and using the calibration graph determine the weight of monomer in the sample. The concentration of monomer in the emulsion is then given by :

$$\text{Percentage monomer w/w} = \frac{\text{Weight of monomer in solution}}{\text{Weight of emulsion}} \times 100$$

Isothermal analysis

Table 2 gives conditions for the isothermal analysis of the individual co-monomers on the column. It should be emphasised that temperature-programming is to be preferred on the grounds of rapidity in samples where more than one co-monomer is to be determined. The repeatability of isothermal analysis was, however, slightly better and this method is also, of course, applicable to apparatus without temperature-programming facilities.

Table 2
Column conditions for isothermal GLC analysis

Co-monomer	Vinyl acetate	n-Butyl acrylate	2-Ethylhexyl acrylate
Column temperature ..	50°C	85°C	120°C
Preheater temperature ..	Approx. 150°C	Approx. 175°C	Approx. 175°C
Carrier gas	Nitrogen	Nitrogen	Nitrogen
Inlet pressure	7 psig	7 psig	7 psig
Sample solution ..	Approx. 2 g sample in DMF or methanol	Approx. 2 g sample in DMF or methanol	Approx. 2 g sample in methanol
Sample size	3 μl	3 μl	3 μl

Another advantage of the isothermal method was that a single chromatographic column only was necessary, thus avoiding the complication of preparing well-matched twin columns.

Tests of the GLC procedures

The stability of co-polymer solutions was investigated using 10 per cent w/v solutions of polyvinyl acetate emulsions in dimethylformamide and methanol. The isothermal column described above for analysing vinyl acetate monomer was used for the tests. The results (Table 3) indicated that the solutions could be kept for 24 hours with no apparent change; longer storage times were not, however, advisable as the solutions tended to gel. The two solvents appeared to give no significant difference in results. A smaller number of tests with emulsions containing other monomers gave similar results.

Table 3
Stability tests on emulsion solutions

Polymer	Monomer	Solvent	Percentage w/w monomer in polymer				
			5 min.	2 hr.	6 hr.	16 hr.	24 hr.
Pva I	VA	MeOH	0.27	—	0.26	—	0.26
Pva II	„	„	0.23	—	—	—	0.22
Pva III	„	„	0.15	0.15	—	0.15	0.15
Pva IV	„	„	0.07	0.07	—	0.07	0.07
Pva II	„	DMF	0.22	—	0.22	—	—
Pva V	„	„	0.40	—	—	—	0.40
Pva VI	„	„	0.21	0.21	—	0.21	0.22
Pva/nBuA I ..	nBA	MeOH	0.125	—	—	—	0.125
Pva/nBuA II ..	„	DMF	0.21	—	—	—	0.20
Pva/2EHA I ..	2EHA	MeOH	0.205	—	—	—	0.20

VA = vinyl acetate, nBA = n-butyl acrylate, 2EHA = 2-ethylhexyl acrylate.

A further series of tests using a range of concentrations of two polyvinyl acetate samples in methanol and dimethylformamide showed that, providing the polymer emulsion was adequately dissolved, the actual quantity of solvent used did not affect the reliability of the determination. Results are shown in Table 4.

No similar systematic study was made for 2-ethylhexyl acrylate or n-butyl acrylate in copolymers, but repeat determinations using different weights of emulsion in 10 ml solvent gave results agreeing within better than ± 0.01 per cent and no evidence for a concentration effect was noticed.

Table 4
The effect of emulsion concentration on monomer determinations

Solvent	Concentration of emulsion (g/10 ml)	Percentage w/w vinyl acetate found in sample
Methanol	1.21	0.124
	1.37	0.128, 0.124
	1.92	0.120
	2.33	0.121
	3.47	0.127
		<i>Mean 0.125</i>
DMF	1.10	0.154
	2.41	0.152, 0.155
	3.45	0.151
		<i>Mean 0.153</i>

As an additional check on the method, analyses were carried out on a large number of polymer samples to which the three co-monomers had been added. Most of these analyses were carried out by using the isothermal method of analysis (Table 5), but in a few checks using the temperature-programmed procedure essentially similar recoveries were obtained. The mean percentage recoveries of monomers in these experiments and the standard deviations were :

	<i>Mean percentage recovery</i>	<i>Standard deviation</i>
Vinyl acetate	98.4	1.8
2-Ethylhexyl acrylate	97.4	5.1
n-Butyl acrylate	100.3	2.8

Thus very good recoveries of vinyl acetate were obtained. Those for 2-ethylhexyl acrylate were not so good, but at the concentrations normally present in the emulsions the error was thought to be acceptable.

The doping experiments above suggested that the nature of the solvent had no effect, but this was further confirmed for two samples of polyvinyl acetate emulsion which gave results of 0.22 and 0.152 per cent w/w vinyl acetate monomer using dimethylformamide and 0.23 and 0.148 per cent w/w respectively using methanol.

Table 5
Recovery of added monomers by the GLC method

Polymer	Monomer	Solvent	Percentage w/w monomer added	Percentage w/w monomer recovered	Percentage recovery
PVA ..	VA	MeOH	.093	.094	101
" ..	"	"	.125	.120	96
" ..	"	"	.312	.303	97
" ..	"	"	.439	.440	100
" ..	"	DMF	.053	.052	98
" ..	"	"	.159	.152	96
PVA/2EHA	"	MeOH	.125	.126	101
"	"	"	.250	.248	99
PVA/2EHA	"	DMF	.106	.104	98
"	"	"	.212	.207	98
"	2EHA	MeOH	.15	.14	93
"	"	"	.44	.45	102
"	"	"	.54	.52 ; .48	96, 92
"	"	"	.54	.51 ; .50	94, 93
"	"	"	.88	.885	101
PVA ..	2EHA	"	.22	.235	107
"	"	"	.66	.655	99
PVA/nBA ..	nBA	"	.378	.375	99
"	"	"	.473	.490	104
"	"	DMF	.206	.200	97
PVA ..	"	MeOH	.095	.092	97
"	"	"	.189	.192	101
"	"	DMF	.103	.106	103
"	"	"	.309	.314	102

Finally the GLC isothermal method described above was briefly compared with the bromine number method referred to earlier for determining vinyl acetate monomer. The results are shown in Table 6. It is concluded that both methods give broadly comparable results.

Table 6
Analysis of polyvinyl acetate by bromination and GLC

Sample	Percentage w/w vinyl acetate found in sample	
	Bromination*	GLC
A	1.5	1.2
B	0.6	0.3
C	0.15	0.25
D	0.35	0.3
E	0.15	0.2
F	0.17, 0.18	0.15

*Results by bromination after removal of monomer by distillation except for F, which was by Dodomka's method (2).

Tests of repeatability for isothermal and temperature programmed analysis

A number of analyses were carried out on samples of polymer emulsions by both isothermal and temperature programmed GLC analysis. The results are given in full in Table 7.

Table 7

Comparison of repeat determinations by isothermal and temperature programmed GLC

Method	Solvent	Vinyl acetate	n-Butyl acrylate	2-Ethylhexyl acrylate
Isothermal ..	MeOH	.126, .125	.108, .111	.286, .278
” ..	DMF	.127, .124	.109, .105	—
Temp. progr. ..	MeOH	.126, .133	.105, .111	.283, .275
” ..	DMF	.127, .127	.109, .102	—
Isothermal ..	MeOH	—	.128, .125, .128	.164, .159, .158
” ..	DMF	—	.127, .126, .126, .124	—
Temp. progr. ..	MeOH	.279, .281, .279	—	.125, .129, .127, .131, .134
Temp. progr. ..	MeOH	.07, .07	—	.05, .05

Taking the values for both solvents together in this table and those quoted in Tables 3 and 4, repeatability calculations have been made for both GLC methods and the three monomers. Over the range of monomer concentrations 0.1 to 0.3 per cent w/w in the polymer emulsion the following standard deviations from the mean values for per cent w/w were obtained :

	<i>Isothermal</i>	<i>Temperature programmed</i>
Vinyl acetate003 % w/w	.0025 % w/w
n-Butyl acrylate ..	.002 % w/w	.004 % w/w
2-Ethylhexyl acrylate ..	.003 % w/w	.004 % w/w

For isothermal analysis therefore the 95 per cent confidence limit is just greater than ± 0.005 per cent compared with about .01 per cent w/w for temperature programmed. The precise accuracy of determinations cannot be predicted solely on the basis of these results, but values to ± 0.01 per cent w/w might be expected for vinyl acetate and n-butyl acrylate and perhaps ± 0.02 per cent w/w for 2-ethylhexyl acrylate monomer.

Conclusion

The temperature programmed gas liquid chromatographic method described above may be used to determine vinyl acetate, n-butyl acrylate and 2-ethylhexyl acrylate (or other residual co-monomers) with a single analysis. The technique of diluting the sample in a suitable solvent combined with the use of a sensitive detector system and the removable injection port liner are features of the

method which are in principle capable of application to GLC analysis of many polymer systems.

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The glycerolysis step in the production of oil-modified alkyd resins

The effects of the acid and iodine values of the mixed triglycerides

By N. A. Ghanem and F. F. Abd El-Mohsen

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Summary

The effects of the initial acid value and iodine value of the mixed triglycerides on the rate and extent of alcoholysis with glycerol were examined using oils of different acid values and degrees of unsaturation. Oils with high initial acid values undergo glycerolysis at much reduced rate, while oils with high initial unsaturation proceed at a high rate and produce a higher equilibrium content of monoglycerides. It was found that glycerol has a higher solubility in mixed triglycerides of high unsaturation and low acid value. It can be concluded that two factors are in favour of the reaction : an alkaline or near neutral medium and a high capacity of the mixed triglycerides to dissolve glycerol at the reaction temperature.

L'étape glycérolitique dans la fabrication des résines alkydes modifiées à l'huile

Les effets des indices d'acide et d'iode des triglycérides mixtes

Résumé

On a examiné, à l'aide des huiles ayant des indices d'acide et des degrés de non saturation différents, les effets de l'indice d'acide initial des triglycérides mixtes et son indice d'iode sur le taux et l'étendue d'alcoololyse effectué par glycérol. Des huiles ayant des indices d'acide initiaux élevés se glycérolisent à des taux beaucoup réduits, tandis que des huiles qui sont au début fortement non saturées, se glycérolisent rapidement en produisant une teneur d'équilibre plus élevée de monoglycérides. On a trouvé que glycérol manifeste une solubilité plus élevée dans des triglycérides mixtes ayant un degré de non saturation élevé et un indice d'acide faible. On peut conclure que ces deux facteurs suivants favorisent la réaction : un milieu alcalin ou à peu près neutre ; une grande capacité de la part des triglycérides mixtes pour dissoudre glycérol à la température de la réaction.

Die Glyzerinalkoholyse-Stufe bei der Herstellung ölmodifizierter Alkydharze

Die Auswirkungen der Säure- und Jodzahlen von gemischten Triglyceriden

Zusammenfassung

Es wurden die Auswirkungen der vor der Reaktion vorhandenen Säure- und Jodzahl von Triglyceridmischungen auf die Reaktionsgeschwindigkeit und das Ausmass der Alkohololyse mit Glycerin untersucht, unter Verwendung von Ölen mit verschiedenen Säurezahlen und Gehalten an Ungesättigtem. Bei Ölen mit hohen Anfangssäurezahlen geht die Glyzerinalkoholyse mit grosser Verzögerung vor sich. Dagegen läuft der Prozess bei Ölen mit anfänglich hohem Gehalt an Ungesättigtem schnell ab, und ein grösseres Gleichgewicht im Gehalt an Monoglyceriden wird erzeugt. Es wurde festgestellt, dass die Löslichkeit von Glycerin in

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gemischten, sehr ungesättigten Triglyzeriden mit niedriger Säurezahl besser ist. Man kann daraus schliessen, dass die Reaktion von zwei Faktoren begünstigt wird: einem alkalischen, oder beinahe neutralen Bindemittel und einer grossen Fähigkeit gemischter Triglyzeride Glycerin bei der Reaktionstemperatur in Lösung zu bringen.

Глицеролизная ступень в производстве видоизмененных маслом алкидовых смол

Влияние коэффициента кислотности и иодного числа смешанных триглицеридов

Резюме

Исследовалось влияние начального коэффициента кислотности и иодного числа смешанных триглицеридов на скорость и степень алкоholesиса с глицеролом, с применением масел с различными коэффициентами кислотности и степенями ненасыщенности. Масла с высокими начальными коэффициентами кислотности испытывают глицеролиз значительно медленнее, между тем как в маслах с высокой начальной ненасыщенностью процесс проходит с большой скоростью и производит большее равновесное количество моноглицеридов. Обнаружено, что глицерол обладает более высокой растворимостью в смешанных триглицеридах высокой ненасыщенности и низкой степени кислотности. Из этого можно заключить, что два фактора способствуют реакции: щелочная или почти нейтральная среда и высокая способность смешанных триглицеридов растворять глицерол при температуре реакции.

Introduction

Alcoholysis is the intermediate step in the manufacture of alkyd resins from polyhydric alcohol, dibasic acid and fatty glycerides. It is important as an improperly formed monoglyceride may cause haze and may even cause the alkyd to gel prematurely in cooking. It is therefore useful to study the nature of this reaction and to examine the various factors that influence it.

In previous publications^{1, 2} the authors have determined the rates and extents of monoglyceride formation using two mixed triglycerides, glycerol as the alcoholysis reagent and three basic oxides as catalysts. A classification of these catalysts in order of their efficiency was also obtained. In the course of these experiments it was observed that the reaction was affected by some of the initial properties of the oils used, namely, the acid and the iodine values. These observations were thought to deserve a more thorough examination, the results of which are given in the present work.

In spite of the industrial importance of these factors, little attention has been given to them. Chinoy and Kamath³ claimed that oils of lesser unsaturation than sesame oil (iodine value about 109 cg I/g) required an alkali catalyst or temperature higher than 250°C to complete the reaction within six hours. In a recent paper, Kochhar, Dey and Bhatnagar⁴ studied the glycerolysis of various oils such as groundnut, hydrogenated groundnut, linseed, coconut and mustard oils. They concluded that oils with a predominance of unsaturated fatty acids react more readily.

Materials and methods

Reactants

The physical and chemical properties of the linseed oil, the cottonseed oil and the glycerine used were given in a previous publication¹.

Soyabean oil

This was an imported product obtained from the Paints and Chemical Industries Co., Cairo.

Maize oil

This oil was obtained from the Egyptian Salt and Soda Co. at Kafr El-Zayat. The physical and chemical properties of these two oils are given in Table 1.

Table 1
Physical and chemical properties of soyabean and maize oils

Oil	Acid value mg. KOH/g	Sap. value mg. KOH/g	Iodine value (Woburn) cg. I/g	Sp. gravity at 25°C	Ref. index at 25°C	Colour (Gardner scale)
Soyabean Oil ..	0.45	194	143	0.9115	1.4751	4-5
Maize Oil ..	0.22	192	114	0.9129	1.4741	6-7

The catalysts

Pure and finely powdered PbO, CaO and LiOH were used. Details of their sources and grades of purity have already been given¹.

Method

The physical and chemical constants were determined using standard methods of analysis. The glycerolysis apparatus and quantitative method of following up glycerolysis have already been described¹.

Samples of linseed oil with different acid values were obtained by partial alkali refining of a linseed oil with an initial high acid value. Measured amounts of aqueous NaOH were added to known weights of the oil with vigorous shaking. The mixture was left to settle, the oil layer separated, washed and centrifuged.

The solubility of glycerol in the oils employed was determined at the four temperatures 190, 220, 250 and 270°C. The apparatus used consisted simply of an ordinary test tube fitted with a loose stopper and a glass rod attached to a mechanical stirrer. The test tube containing a known weight of the oil was immersed in a thermally regulated glycerol bath. Glycerine was added dropwise from a grade A burette with continuous stirring. Saturation was considered to be reached when the last drop became insoluble in the oil.

Results*The effects of the initial acid values of the oil*

Runs were carried out with linseed oil of different initial acid values to find out the effects of the initial acid value of the oil on the rate and extent of the glycerolysis reaction. The results are summarised in Table 2.

Table 2

The effect of initial fatty acid content on the rate of glycerolysis and monoglyceride formation

Run no.	Fatty acid content		Catalyst content		Time to reach max. MG† (min.)	% MG†	Colour (Gardner scale)
	%	Mols. $\times 10^4$	%	Mols. $\times 10^4$			
1	0.15	5.35	0.02 CaO	3.56	14	63.5	5-6
2	0.34	12.1	0.02 CaO	3.56	15	65	6-7
3	0.85	30.4	0.02 CaO	3.56	73	60.95	7-8
4	3.85	137.5	0.02 PbO	0.89	195	52.9	12
5*	3.85	137.5	0.02 PbO	0.89	235	38.5	11-12

*At 220°C. †Monoglyceride. Reaction temp. = 250°C. Oil : Glycerol = 1 : 2.5.

It can be seen that the initial acidity has a remarkable effect on the reaction course. In runs 1 and 2 the medium was slightly basic or near neutral and the reaction proceeded quite rapidly leading to a high monoglyceride content. On the other hand, the medium in runs 3 and 4 was definitely acidic due to excess of fatty acids over the basic catalyst. The reaction was strongly retarded and the final monoglyceride content was depressed. These effects are represented in Fig. 1 where the formation of monoglycerides with respect to time in runs 1, 3 and 4 is followed.

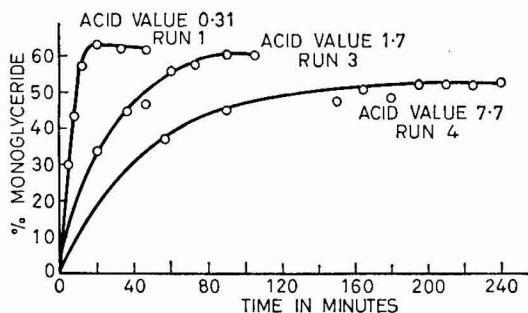


Fig. 1. The effect of initial acid value of the oil on the formation of monoglyceride

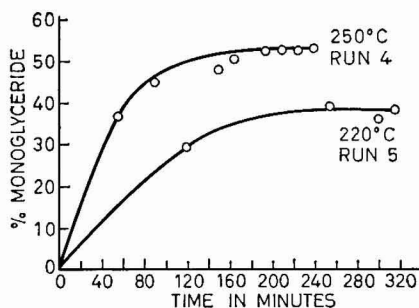


Fig. 2. The glycerolysis of linseed oil of high acid value

Run 5 was performed under the same conditions as run 4 except that the reaction temperature was 220°C instead of 250°C. It can be shown from the results of run 5 that the retardation of the glycerolysis reaction under acidic conditions is more pronounced at lower temperatures. The differences between runs 4 and 5 in rate and amount of monoglyceride formed can be readily seen in Fig. 2.

An alternative method of obtaining rapid glycerolysis without refining the oil would be through neutralisation of the free fatty acid present in the oil with the basic catalyst. Experiments were therefore designed in such a way that the calculated amount of catalyst, exactly sufficient to neutralise the excess fatty acid in the unrefined oil, was added together with the standard amount employed in a corresponding run using refined linseed oil. The results of these experiments are brought together in Table 3.

Table 3

Glycerolysis of unrefined linseed oil with catalyst amounts sufficient to neutralise the excess fatty acid, and the corresponding runs with refined oil

Run no.	Acid value mg.KOH/g	Catalyst		Reaction temp. °C	Time to reach max.MG (min.)	Max. MG %	Colour (Gardner Scale)
		Type	Amount*				
6	0.30	LiOH	0.02%	220	135	57.6	7
7	1.70	LiOH	0.2815 (0.02% + amount to neutralise free FA)	220	29	60	10
8	0.30	LiOH	0.04%	220	46	57.2	7
9	1.70	LiOH	0.3518 (0.04% + amount to neutralise free FA)	220	26	60	9-12
1	0.30	CaO	0.02%	250	14	63.5	5-6
10	1.70	CaO	0.3167 (0.02% + amount to neutralise free FA)	250	9	64.4	8-9

*On weight of oil. Weight of oil=351.6 gm. Oil : Glycerol = 1 : 2.5.

It can be seen that the neutralised runs proceeded at a higher rate than the corresponding runs performed with refined oil and produced somewhat higher yields of monoglycerides. These findings are represented graphically in Figs. 3a, 3b and 3c.

The influence of double bond unsaturation

Runs were performed with oils of different iodine values, but of comparable small acid values in order to examine the influence of the double bond

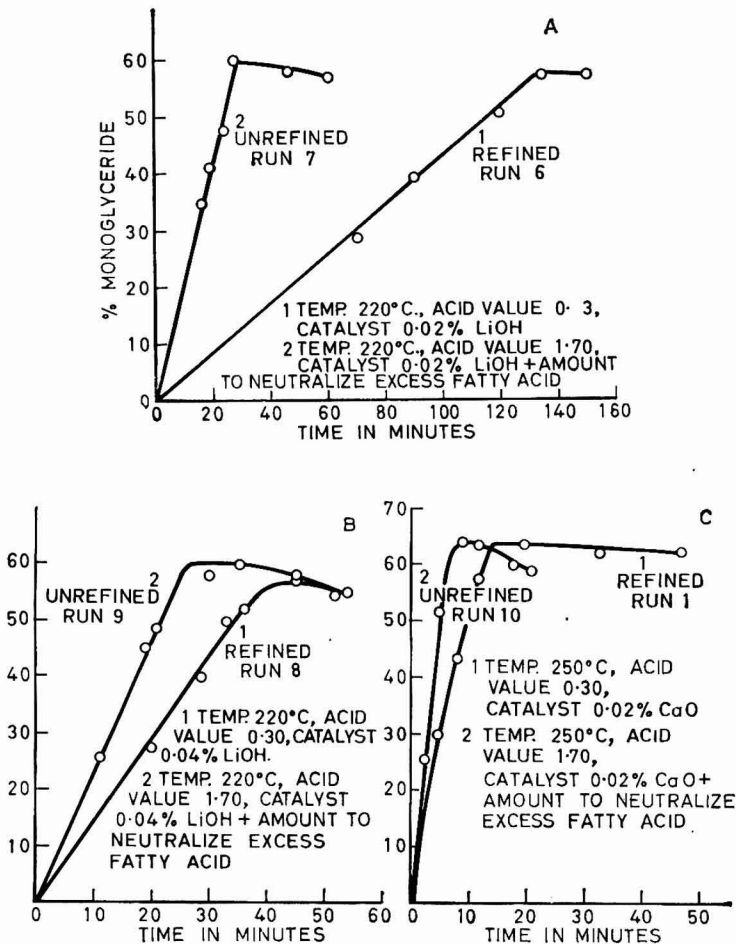


Fig. 3. The glycerolysis of refined and unrefined linseed oil

unsaturation of the fatty acid chains on the rate and extent of the glycerolysis reaction. Cottonseed, maize, soyabean and linseed oils were used with catalyst concentrations of 0.02 per cent at reaction temperatures of 220 and 230°C. The results are summarised in Table 4.

It is readily shown that the reaction time required to reach maximum monoglyceride content is smaller the higher the iodine value of the mixed triglycerides. It can be also indicated that the equilibrium amount of monoglycerides formed is proportional to the degree of unsaturation of the oil. These results are graphically represented in Figs. 4 and 5. In Fig. 4 the relation between the iodine value and the time to reach maximum monoglyceride content is plotted. It indicates that the more unsaturated oils react faster than the less unsaturated ones.

Table 4

The influence of the iodine value of the starting oil on the rate and extent of monoglyceride formation

Run no.	Tri-glycerides	Iodine value (Woburn) cg.I/g	Reaction temp. °C	Catalyst		Time to reach max. MG content (min.)	% Mono-glyceride
				Type	%		
11	Cottonseed	102	230	PbO	0.02	107	55
12	Maize	114	230	PbO	0.02	88	56
13	Soyabean	143	230	PbO	0.02	52	57.5
14	Linseed	174	230	PbO	0.02	46	59.9
15	Cottonseed	102	230	CaO	0.02	45	55.7
16	Maize	114	230	CaO	0.02	37	55
17	Soyabean	143	230	CaO	0.02	33	57.6
18	Linseed	174	230	CaO	0.02	31	61.4
19	Cottonseed	102	220	PbO	0.02	142	52.6
20	Soyabean	143	220	PbO	0.02	81	55.9
21	Linseed	174	220	PbO	0.02	78.5	56.8
22	Cottonseed	102	230	LiOH	0.02	135	52
23	Soyabean	143	230	LiOH	0.02	70	56.2
24	Linseed	174	230	LiOH	0.02	66	59

Oil : Glycerol = 1 : 2.5

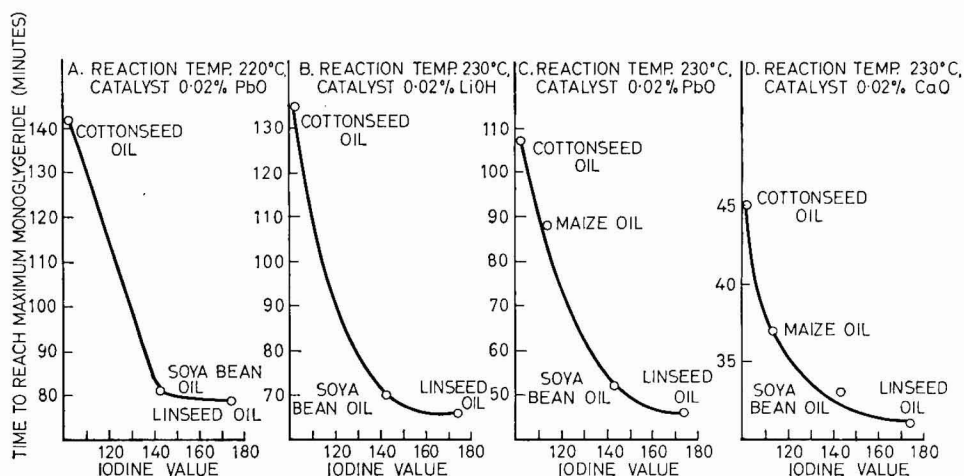


Fig. 4. The effect of the degree of unsaturation on the rate of the glycerolysis reaction

In Fig. 5 the relationship between the iodine value and the equilibrium monoglyceride content is displayed. It is shown that oils with high unsaturation produce a higher monoglyceride content when all other conditions are kept identical.

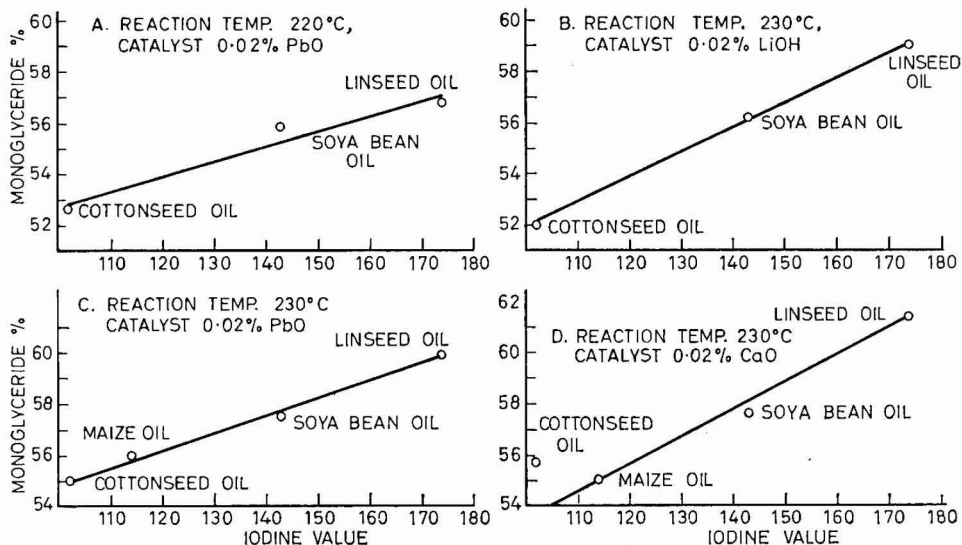
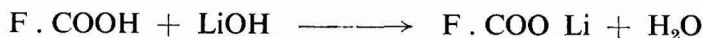


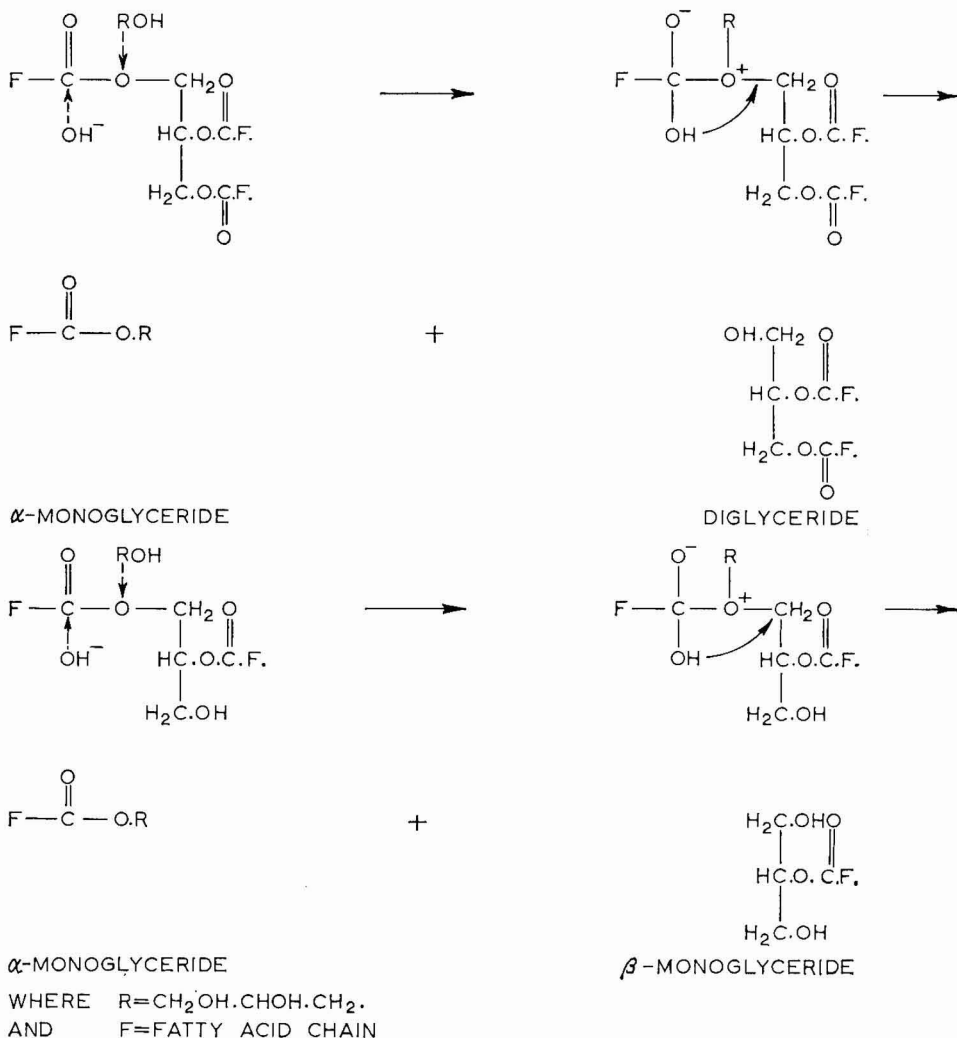
Fig. 5. The effect of the degree of unsaturation on the equilibrium content of monoglycerides produced in the glycerolysis of oils

Discussion

Vegetable oils for industrial purposes contain almost invariably a small percentage of free fatty acids. The complete removal of such a small proportion can only be achieved by thorough refining which usually involves some losses in the triglyceride content. It was previously shown² that glycerolysis runs performed without any catalyst at all proceeded at a much reduced rate and produced low yields of monoglycerides. Runs with low catalyst concentrations also gave results in the same direction. At the high temperatures used in a glycerolysis reaction the basic catalyst readily interacts with the free fatty acids forming metallic soaps, thus :



When the amount of catalyst is insufficient completely to neutralise the free fatty acid, the ionisation of the metallic soap will be suppressed by common ion effect and its effect as basic catalyst hindered. The results of runs 3, 4 and 5 substantiate this postulate. On the other hand, when the catalyst is present in excess (see runs 7, 9 and 10), complete neutralisation of the free fatty acid takes place and the reaction proceeds normally under the prevalent basic conditions. The following mechanism can be proposed :



The basic metal soaps are strong glycerolysis catalysts provided that their ionisation is not suppressed by acid. It should, however, be borne in mind that an excess of basic catalyst is objectionable since it will react with the dibasic acids in the subsequent step of the alkyd preparation, forming colloidal precipitates which cause production troubles. For the production of high quality alkyds it is advisable to use oils with small acid values and catalysts in minimum amounts. Similar views have been expressed⁵ when using pentaerythritol as alcoholysis reagent and litharge as alcoholysis catalyst.

As shown in the previous section, the rate and extent of monoglyceride formation increase with the iodine value of the starting oil. Glycerol has a limited solubility in oil and the glycerolysis reaction should be favoured by bringing the oil and the glycerol into intimate contact. The use of mutual

solvents was found to increase the yield of monoglycerides^{6, 7}. It is therefore reasonable to believe that oils with better mobility and higher capacity to dissolve glycerol will interact more easily. The oils used in this work were tested, in the range of the reaction temperatures applied, for their capacities to dissolve glycerol. The results given in Fig. 6 show that within the temperature range used (190-270°C) the solubility of glycerol in any particular oil is almost constant.

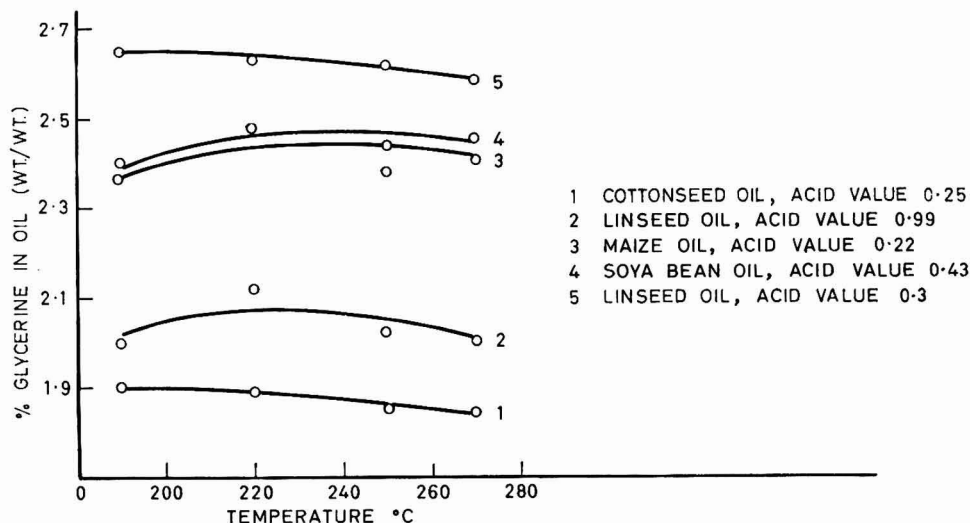


Fig. 6. The solubility of glycerol in different oils at different temperatures

This solubility varies, however, from one oil to the other, being greater the higher the iodine value of the oil. The figure also indicates that an increase in the acidity of an oil (Plot 2) reduces its capacity to dissolve glycerol. According to Kochhar, Dey and Bhatnagar⁴, coconut oil and castor oil give high yields of monoglycerides. These two oils are expected to have higher capacities for dissolving glycerol; the first for being composed of low molecular weight fatty acids and the second for the presence of hydroxyl group in the fatty chain.

Conclusions

By virtue of their greater capacity to dissolve glycerol, oils with high iodine values and low acid values undergo glycerolysis at a higher rate and produce a higher equilibrium content of monoglycerides.

[Received 17 February 1966]

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Correspondence

Testing of Paints for use in Radioactive areas

SIR,—In the paper on this subject by Mr. P. Walker in the February 1966 issue (Vol. 49, No. 2) the author described his method for measuring the decontamination properties of surface coatings.

It may be of interest to your readers to know that a B.S.I. Sub-committee (NCE/5/2) was formed in January 1964 to consider preparing standards for surface materials for radioactive areas. The terms of reference included the preparation of a standard test procedure for measurement of resistance to decontamination. A draft standard, based on experimental work carried out by members of the Sub-committee over the last two years, is now in course of preparation and should be issued for comment to industry in the near future. A summary of the standard and the supporting experimental work is also to be presented at the forthcoming International Symposium on Decontamination of Nuclear Installations at AERE, Harwell, in May.

One of the major differences in our approach and the method described by Mr. Walker is in the formulation of the contaminating solution. Mr. Walker has used a mixed cerium 144 and plutonium 239 solution designed to simulate practical contamination. The inclusion of plutonium may be technically sound but its use creates appreciable administrative problems for laboratories who may be asked to carry out a standard decontamination test and who do not normally handle plutonium. We have also found that cerium 144 is adsorbed from dilute solutions by the walls of normal glass and polythene containers, the activity of such solutions is, therefore, unstable during storage. The contaminating solution in the NCE/5/2 draft standard is based on a mixed caesium 134 and Cobalt 60 isotopic solution which we believe is free from these disadvantages.

Yours faithfully,

K. Smith.

25 March 1966.

*Central Electricity Generating Board,
Walden House,
24 Cathedral Place,
London, E.C.4.*

SIR,—I am of course aware of the work being carried out by B.S.I. Sub-Committee (NCE/5/2) since the Atomic Weapons Research Establishment Materials Section is assisting in the joint experimental work described in Mr. Smith's letter.

The points raised by Mr. Smith about the method of assessing decontamination properties described in my recent paper (February 1966) are relevant, and readers will no doubt recall that a footnote in the original paper indicated that the method described was not of general applicability. The use of plutonium 239

and cerium 144 as contaminants was dictated by the need to test paints against conditions likely to arise within a particular establishment, and I appreciate that the use of plutonium militates against the general acceptance of the test.

The fact that cerium 144 may be adsorbed on to glass and polythene surfaces certainly prevents its use in collaborative tests, or when a continuous lengthy test programme is envisaged. However, when a control paint of known performance is included and the original level of contamination applied is used as the datum line for assessment, this adsorption is not considered to be a serious defect.

Our experience has shown that the degree of variability associated with the application and cure of test coatings by different laboratories is likely to be as great as the precision of the test method.

*Atomic Weapons Research Establishment,
Building SB43,
Aldermaston,
Berkshire.*

Yours faithfully,

P. Walker.

5 April 1966.

Editorial

“ . . . but if the salt have lost his savour . . . ”

It has been said that chemists and physicists are at the peak of their creativity at the age of 24. Upon what evidence this statement was based we have been unable to discover, but we suspect that it may have been heavily weighted by the number of postgraduate theses and associated publications emanating from this age group. If so, statistics have been misused yet again, for there must surely be many who, having published the work leading to their higher degrees and diplomas, remain silent for ever more from choice or necessity.

We are reminded of the many column inches devoted by an eminent contemporary to correspondence on the topic, “ Too old at 40,” and are led to wonder whether age *per se* has anything to do with the alleged misfortunes of the plaintiffs. We are not aware of any scientific evidence attributing the relatively slow progress of later years to an inverse relationship between age and ability. Is it not more probably associated with diminished motivation, aggravated, in many cases, by the stultifying effect of long service with one employer? How many over-forties have made a real effort to maintain anything approaching the rate of progress usual in the professions during the ten years or so following qualification? How many have put comfort and convenience first and, exchanging the study for the television lounge, have failed to come to terms with themselves in a realisation of what this must necessarily imply?

But stagnation is by no means wholly attributable to the individual, who all too frequently finds himself faced with a choice restricted to moving elsewhere or becoming part of the furniture. In the words of a recent BIM lecturer, it is high time that management recognised the total inadequacy of the gold watch philosophy and grasped the elementary principle that there is no substitute for recognition of the job itself. Long service employees form a rather high proportion of those engaged in British industry, and it is to descend to the level of unreasoning emotion either to deride them for lack of initiative or to glorify them (as they are apt to do themselves) for their steadfastness and loyalty. Stark reality dictates that management must *use* them, and use them to the best advantage.

Everything, then, is to be gained by providing a fresh stimulus from time to time. The trinket at 50 can profitably be replaced by an injection of new experience at 40—say a sabbatical year at the University, six months with an overseas company, a change in responsibilities however temporary, or just a few weeks in a language laboratory. These ideas are not original and there is no shortage of others. The man who does these things for himself is admired for his initiative on the one hand and damned as a rolling stone on the other, particularly when his search for new experience leads him round the employment circuit. The best of both worlds is surely not unattainable for employer and employee if both can be persuaded to play their part in the game. The fact must be faced that the job can go sour from both their viewpoints for all sorts of reasons, and if we all blame “ them ” instead of doing something about it—“ . . . *wherewith shall it be salted.*”

Reviews

PARTICLE SIZE—THEORY AND INDUSTRIAL APPLICATIONS

By RICHARD D. CADLE. Reinhold Publishing Corporation, 1965. Pp. 390. Price \$16.50.

With few exceptions, the sizes and size distributions of particles in systems of finely divided materials are of interest only insofar as they relate to other properties of the systems. This book ostensibly covers generally the importance of particle size in terms of applications to industries concerned with fine particle technology. Although only the last chapter (some 60 pages) is directly devoted in this way—and here, even if one includes the pages covering “aerosol” technology, there are only some 20 pages directly applicable to the technologies of paint and allied products—for an understanding of the effect of particle size on such applied or derived situations one has to study the effects of particle size on basic physical properties. So, Chapter 2 (some 100 pages) is also of indirect interest to the industries mentioned.

This book is a valuable contribution to the literature falling under the general heading of particle size and in two particular ways, viz. for Chapter 2 on General Principles and for Chapters 3, 4 and 5 (some 160 pages) broadly on the special field of atmospheric research, on which the author is a leading authority.

The effects of particle size on the following basic properties appear to be adequately covered in a theoretical manner : light scattering, Brownian motion, sedimentation, inertial effects, packing, cohesion, heat conduction, rheology, electric properties, surface properties, and the dynamics of particles under thermal and concentration gradients. Atmospheric research aspects covered, with some welcome descriptions and illustrations of equipment are : inhaled particles, particles deposited on the skin, “smog,” industrial air pollution, and clean rooms. The need for clean rooms is increasing in relation to the production of pure compounds and precision equipment, including solid-state, pharmaceutical and aerospace applications.

R. J. COLE

WEATHERING AND DEGRADATION OF PLASTICS

ED. S. H. PINNER. Columbine Press, Manchester. 1966. Pp. xii, 131. Price 40s.

This book is based on the papers read at a symposium held at Borough Polytechnic, London. It is claimed to be a comprehensive assessment of existing knowledge on the weathering and degradation of plastics and to constitute a progress report on the subject. Not all the chapters, contributed as they are by a number of authors drawn from both academic and industrial circles, can be said to justify this claim completely although those chapters towards the end of the book which deal specifically with one type of material i.e. the thermal degradation of polyvinyl chloride by W. I. Bengough ; degradation and weathering of polystyrene and styrenated polyester resins by C. B. Bucknall ; and the degradation of polyolefines by J. M. Heaps and A. Austin are certainly clear and concise summaries of present knowledge.

In the first chapter Dr. Grassie gives an account of the general fundamental chemical principles involved in the oxidative, radiative and thermal degradation of polymers.

In the following chapter Dr. D. R. J. Hill deals with experimental techniques for studying degradation phenomena and includes pyrolysis studies, differential thermal analysis and nuclear magnetic resonance amongst others. A chapter by C. A. Brighton on the correlation of accelerated and natural weathering tests quite rightly stresses the dangers and difficulties involved in this operation. Whilst there is a chapter dealing with heat stabilisers, antioxidants, antiozonants, and ultra violet absorbers as small scale additives to plastics to inhibit the action of the various degrading influences perhaps more detail might have been given of the various systems in current use.

The increasing use of plastics in building makes this book a very timely publication and the increasing use of high polymers as the initial raw materials for surface coatings in the form of organosols, plastisols, emulsion coatings etc. for both decoration and protection against corrosion makes the information contained within these pages of great value to the worker in the surface coating fields where the plastics and oil and colour technologies are now tending to become so closely integrated.

It is unfortunate that there has been such a delay in the publication of this book since the papers were originally prepared for the symposium because this means that the most recent references, apart from some to the chapter on polyolefines, are to papers published in 1963, and this again tends to counter the claim made that the treatment gives an up to date and comprehensive account of the subject. A tribute should be paid to the Editor, Dr. Pinner, for the way in which duplication of content in the chapters has been kept to a minimum. The book is well set out and printed and remarkably free from typographical errors.

C. R. PYE.

Information Received

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

BRITISH RESIN PRODUCTS LTD. has specially developed a new low cost, oil soluble, non-reactive type of phenolic resin. The Company states that it is suitable for the production of varnishes for marine and chemical resisting finishes.

WELTERS ENGINEERING LTD. has recently added paint electrodeposition equipment to its range of products. Both laboratory and production scale equipment is available, in addition to suitable power supply units. Prices are claimed to be very competitive and plant can be produced to meet customers' individual needs.

BADISCHE ANILIN-UND SODA FABRIK AG has announced the introduction of Nigrosine base LTK, specially developed for ball pen inks. It is claimed to have a very low content of insoluble material, a low pH, good solubility in ball pen inks containing benzyl alcohol, glycols and glycol ethers, and high infrared absorption.

A new medium oil length alkyd based upon linseed oil has recently been introduced by STYRENE CO-POLYMERS LTD. under the trade name of Scopolux 221SP. The product is supplied in a fast evaporating aliphatic hydrocarbon and is recommended for quick air drying and force cured or low temperature stoving applications.

KUNSTHARSFABRIEK SYNTHESE NV has published a brochure setting out comprehensive details of synthetic resins suited to the manufacture of a wide range of

printing inks. Copies are available from the distributors of their products in the United Kingdom, BERK LIMITED.

VINYL PRODUCTS has recently published a new booklet entitled *Emulsion Paint Problems—Causes and Cures*, which has been prepared as a trouble-shooting aid for the paint industry. Problems arising during manufacture, storage and application, and of the dried film are listed, together with their possible causes and the remedial and preventive action to be taken.

At a recent première, IMPERIAL CHEMICAL INDUSTRIES LTD. showed a new film entitled "Paint Without Tears." This deals with the use of tri-chlorethylene as a solvent for paint and describes "Tri-Paint" dipping and spraying methods. The film illustrates the rapid drying, non-inflammability and trouble-free application claimed for these paints.

WILLIAM HOUNSLOW LTD., manufacturers of dyestuffs, fine colours and chemicals, have announced that plans have been carried out for closer co-operation with Nederlandsche Kleurstof Industrie, of Amersfoort, Holland, who manufacture food colours, dyestuffs and inks.

The JEFFERSON CHEMICAL COMPANY INC., of Houston, Texas, has announced that it is forming a company, Jefferson Chemicals Ltd., for the manufacture of morpholine and piperazine and related products in the United Kingdom. They claim that they will be the only manufacturers of these chemicals in current operation in the United Kingdom. Morpholine is used as a corrosion inhibitor, as an emulsifier, and as an intermediate in the manufacture of surface active agents and plasticisers.

MOLYN & Co., NV, Rotterdam—the Dutch member of the Transocean Marine Paint Association—announce that they have completed a licensing agreement for Western Europe with the Ball Chemical Company, of Glenshaw, Pennsylvania, USA, for the manufacture of a range of the latter's tube coating materials.

Extensive information illustrated by photographs, electron micrographs, tables and graphs is included in a new three-colour technical bulletin on the uses of precipitated calcium carbonate in paint, published by chemical manufacturers JOHN & E. STURGE LTD.

SCOTT BADER & Co. LTD., who are manufacturers of polymer emulsions and solutions, polyester resins, plasticisers and pvc pastes, are co-operating with John & E. Sturge Ltd. in establishing a manufacturing company in France.

Manchester

Mechanism of Film Formation

The second meeting of the session for the junior members of the Section was held at the Manchester Textile Institute on 1 April when Mr. W. G. Topham gave a lecture entitled "Mechanism of Film Formation."

Mr. H. F. Clay, from the Chair, welcomed the audience of approximately 60 members and visitors and commented on the encouragement it gave to the Section Committee to continue to provide these lectures which it was hoped would supplement the normal courses of study available in the area.

Mr. Topham explained that the object when applying a protective or decorative coating to a surface was to obtain a high molecular weight preferably cross-linked film, tensile strength and performance being proportional to molecular weight for a given system.

Films could be produced in several different ways, namely :—by the deposition of a polymer solution, by deposition of an aqueous dispersion and in the third case by eliminating the volatile components entirely in which case hot melt or solventless systems were involved. This classification could be used irrespective of whether or not a curing mechanism was involved.

Where deposition from a solvent was concerned the properties of the deposited film were essentially that of polymer employed and inherently high viscosities limited the application of this type of system. Correct solvent choice could influence the viscosity and the use of new polymerisation catalyst systems could bring about improvements.

Aqueous dispersions involving a curing mechanism were not normally encountered at the present time, synthetic resin latices having largely taken the place of alkyd and drying oil emulsions. The lecturer explained how in the case of a lattice coalescence of the dispersed resin was essential and in practice this meant that most latices were designed to have a glass transition temperature within the range of 15-25 C.

Two component systems could cure either at ambient or elevated temperatures. Room temperature curing systems employed in the simplest cases need atmospheric oxygen or moisture as the second component and in the case of drying oil containing systems the advantages of high functionality were explained. The simple chemistry of other common two component systems, namely Alkyd/Amino resin, Epoxide/Poly-amine or Poly-amide, Isocyanate/Hydroxylated resin was explained and the curing mechanisms explained diagrammatically in a series of interesting and informative slides.

Mr. Topham finally compared the thermoplastic and thermosetting acrylic resins explaining how a variety of functional groups could be built into the resin during polymerisation. It was then possible to utilise many of the cross-linking mechanisms which had been dealt with earlier.

Dealing with questions that were raised Mr. Topham commented on the possibility of replacement of drying oils by synthetic polymers and use of catalysts including stereo-specific catalysts. He also dealt with questions relating to the curing mechanisms of epoxy resins with a variety of catalysts and the differences between the chemical constitution of thermo-plastic and thermo-setting acrylics and their physical properties.

In proposing a vote of thanks, Mr. Hume thanked the lecturer for the amount of effort which he must have put into the classification and simplification of such a complex subject and he now realised the scientific and versatile nature of polymer chemistry involved in the surface coating industry. He also congratulated the lecturer on the presentation of his slides which had enabled such complicated polymers to be simply understood and the audience demonstrated their thanks in the usual manner.

W. F. MCD.

Midlands

Newton Friend Lecture

Robert Boyle and his experiments touching colour

Each year the Midlands Section includes in its programme a lecture to which members' ladies are invited and these lectures are named in tribute to Dr. J. A. Newton Friend. The Newton Friend Lecture for 1966 was given on 25 March at Birmingham Chamber of Commerce when Dr. Newton Friend and his wife were present. Since this lecture the sad news of the death of Dr. Newton Friend has been received. The lecture was given by Mr. G. A. Campbell, a Past President of the Association, and the subject was "Robert Boyle and his Experiments Touching Colour."

Mr. Campbell said that he had always been fascinated by the history of Robert Boyle and almost as fascinating was the life of Robert Boyle's father, the Earl of Cork. Richard Boyle was born in 1566 and went to Ireland at the age of 22. He married in 1595 but his wife died shortly afterwards, leaving him a small fortune. He returned to London after the rebellion in Munster and married Katherine Fenton in 1603. He was favourably received at court and in due course became a Knight, a Privy Counsellor and finally Earl of Cork. His aspiration to become Lord Deputy of Ireland was never fulfilled and he died in 1643 whilst defending his estates in Ireland against the rebels.

Robert Boyle was the 14th child and 7th son of the Earl of Cork. He was born in 1627 at Lismore Castle in Southern Ireland and was sent to a foster home, as was the custom with members of large families. He returned to Lismore when he was seven for tuition from a private tutor and went to Eton when he was nine. In 1639 he and his sister, Frances, went on a grand tour of Europe. On the way home they learned of the civil war in Ireland and the death of their father. Robert Boyle never married and suffered from poor health for most of his life. In 1647 he began writing and publishing papers on a variety of subjects ranging from love poems to ethics.

Robert Boyle was chiefly known for two things ; Boyle's Law and "The Sceptical Chymist." His enunciation of Boyle's Law was hesitant. He did not appreciate the effect of temperature and he missed the discovery of oxygen, which was to come a century later. He was however the first to demonstrate the materialistic nature of air and his outstanding contribution to science was his continual preaching that the mechanistic corpuscular theory was the rational way of thinking. The corpuscular theory was the forerunner of present atomic theory. In 1661 he published "The Sceptical Chymist" which was a treatise on the usefulness of experimental philosophy.

In 1664 he published "Experiments and Considerations Touching Colour." It was a "history" of 50 experiments and did not propose any theory. Boyle missed the relationship between colour and light and concentrated on surfaces. The significance of the work lay in its being the first treatise in English to discuss colour. It appeared in two English and six Latin editions and was reprinted in 1964.

Hooke, who had been an assistant to Boyle, published his "Micrografia" in 1665 giving the first rational theory of combustion.

After several moves Boyle went to Pall Mall in 1669 and lived with his sister Catherine, Lady Ranelagh. A further fruitful period of writing and publication of scientific papers ensued. Boyle and Lady Ranelagh both died in 1691 and were buried in St. Martin in the Fields.

Dr. Newton Friend proposed a vote of thanks to the speaker for a most interesting lecture and congratulated him on his pleasant manner of delivery.

L. R. S.

Newcastle

To automate? . . . to speculate?

The final lecture of the 1965-66 session was held on 3 March with Mr. E. L. Farrow in the chair. Mr. H. R. Touchin presented the paper.

Mr. Touchin commenced his talk with a survey of the aims and efforts of automation in the paint industry.

The continuation of batch processing in the preparation of paint was queried. In relation to the plastics industry the paint industry was behind in productivity, and its price index had risen within recent years where that of the plastics industry had fallen.

Mr. Touchin suggested that computer control could revolutionise production and gave examples of controlling systems. Four main stages of production were itemised :

1. Raw material storage ; Weighing and measuring.
2. Premix ; Grind ; Let-down.
3. Tint ; Thin ; Adjust.
4. Fill ; Label ; Store ; Dispatch.

It was suggested that the industry might divide into two groups—automated mass production on the one hand and specialist batch production on the other.

In the case of automated systems a mathematical model could be used for design purposes by means of simulation techniques. The cost of £50,000 to £100,000 for a computer could bring about savings of 50 to 500 per cent.

Questions were asked by Mr. Marsden, Dr. Banfield, Mr. Anderson, Mr. Pegman, Dr. Neville, Mr. Towers and Mr. Saul.

K. V. H.

Association Dinner Dance 1966



Photo by

Lawson & Co.

From left to right the above photograph shows Dr. W. J. Nijveld (President of FATIPEC), Miss P. Grosvenor who accompanied the President, Dr. S. H. Bell (President), Mrs. Masek and Mr. E. L. Masek (President of the Institute of Metal Finishing)

The Biennial Dinner and Dance of the Association was held on Friday 15 April 1966, when 300 members and guests gathered at the Savoy Hotel, London, for the evening function. Before dinner the President (Dr. S. H. Bell) received members, guests and their ladies.

The guests of the Association were : Mr. S. G. Barnett, Immediate Past President of the Paintmakers Association, and Mrs. Barnett, Mr. E. A. Bevan, President of the Research Association of British Paint, Colour and Varnish Manufacturers, and Mrs. Bevan, Mr. R. T.

Bowes, President of the Society of British Printing Ink Manufacturers, and Mrs. Bowes, Mr. E. L. Masek, President of the Institute of Metal Finishing, and Mrs. Masek, Dr. W. J. Nijveld, President of FATIPEC, and Mr. L. Morton Wood, President of the Society of Dyers and Colourists, and Mrs. Wood.

It was also pleasant to see a number of Past Presidents in attendance : Dr. H. W. Keenan (1944-47) and Mrs. Keenan, Mr. H. Gosling (1953-55) and Mrs. Gosling, Mr. C. W. A. Mundy (1955-57) and Mrs. Mundy, Mr. N. A.

Bennett (1957-59), Mr. P. J. Gay (1959-61) and Mrs. Gay, and Dr. J. E. Arnold (1963-65) and Mrs. Arnold. The Chairman of the West Riding Section, Mr. N. Cochrane, and Mrs. Cochrane were also present.

After the dinner and the "Loyal Toast," the "Toast to the Association" was proposed by Mr. E. L. Masek. In his speech, Mr. Masek said he was interested to note the increase in the Association's membership and felt that, far from being in competition, electroplating and organic finishing of metal were complementary. He thought that some of the money raised by levies to the Engineering Industries Training Board might well be distributed to those research organisations that would benefit the finishing industries. He said the Association, along with others, bore a responsibility to guide the manufacturers in the fields of product finishing in order to stimulate overseas trade.

Dr. Bell, in reply, said that the Institute of Metal Finishing and the Oil and Colour Chemists' Association had a great deal in common for they were both of an age—the IMF having recently celebrated its Ruby Anniversary whilst OCCA was approaching its Jubilee.

The President thanked the General Secretary and his staff for the excellent arrangements made in connection with the dinner-dance and paid tribute to the work of the Hon. Officers, Council Members and Section Committee Members who serve the Association in many parts of the world.

Dr. Bell welcomed all the guests, both official and personal, not forgetting the ladies. He mentioned the strong ties that OCCA has with kindred societies abroad and gave examples of the varied interests of the Association overseas. He read a telegram expressing good wishes for a successful evening from the President of the Federation of Scandinavian Paint and Varnish Technicians, Mr. H. Meyer.

He welcomed Dr. W. J. Nijveld and told of his many meetings with him and the esteem with which Dr. Nijveld was held in both his own country and the industry. Along with many of those present, Dr. Bell was looking forward to attending the VIIIth FATIPEC Congress in The Hague in June.

He then asked those present to rise and join in the toast to "The Guests and Ladies."

Dr. Nijveld said, in response to the toast, that he found it a little difficult to reply for the ladies as he was not a member of the fair sex and did not feel authorised to speak on their behalf! He expressed his thanks on behalf of the guests not only for the hospitality extended to them on this occasion, but pointed out that this was constantly evident in the initials formed from the name of the Association, since OCCA also stood for "Others Can Come Always."

After the speeches, dancing continued until 1 a.m. with a break at 11.30 p.m. for refreshments, after which a cabaret entitled "Champagne" entertained the company.

The Foundation Lecture

(Instituted in 1963 in memory of the late H. A. Carwood Esq.)

As already announced, the 1966 Foundation Lecture will be given on 30 June following the Annual General Meeting of the Association at Painter Stainers Hall.

The lecturer on this occasion will be Dr. N. F. Astbury, Director of Research

of the British Ceramic Research Association and Chairman of the Committee of Directors of Research Associations, who has provided the following synopsis of the lecture, which will be entitled "Craft Against Craft Makes No Living":

“The title of this lecture is due to George Herbert, who is credited with making this provocative generalisation over three centuries ago. The author has chosen to take this as a starting point for the thesis that the statement is both true and false: true because in the modern world there are large areas, notably in scientific and technological development, in which competition is expensive and possibly useless, and in which co-operation is likely to be a better investment. He suggests then that the premise is false, because without individual development and application, co-operation may after all prove sterile. He surveys the co-operative scene, as he knows it, in Britain, on the continent and in America, and tries to mark the

successes, the strength and the weakness of co-operative applied research. He attempts to deal with the question of the universality of co-operation and whether some industries have no need of it. He asks whether direct involvement in training and education—which by definition is almost a co-operative enterprise—is a responsibility of co-operative research bodies, and he concludes with some unanswerable questions on the economics of the whole enterprise.”

There will be a dinner following the lecture, and tickets for this function, which is restricted to members of the Association, can be obtained from the General Secretary at the address shown on the front cover.

OCCA Biennial Conference, 1967



The Bay at Scarborough with the Castle in the background

The Association's next Conference will be held from 20-24 June 1967 at Scarborough. Most of the delegates will be accommodated in the Grand Hotel, where the Technical Sessions and the

Official Functions will be held. The remainder of the delegates will stay at the St. Nicholas Hotel, situated just across St. Nicholas Cliff from the Grand Hotel. The theme of the Conference will

be "Interfacial Behaviour" and it is hoped that each of the Technical Sessions will be devoted to a particular aspect of the theme.

It is also proposed to continue with the Workshop Sessions, at which topics not directly connected with the main theme of the Conference but of interest

to delegates will be discussed. A full social programme is also being planned, details of which will be announced later.

Full details of the Conference will be circulated to members early in 1967, but others wishing to receive this information should write to the General Secretary at the address shown on the front cover.

OCCA 19

OCCA Nineteenth Technical Exhibition, 13-17 March 1967. Alexandra Palace

As already reported in the May issue of the *Journal*, the Eighteenth Technical Exhibition (OCCA 18) was a great success and the Exhibition Committee has pleasure in announcing that arrangements are now in hand for OCCA 19, which will be held in 1967. The venue will once again be Alexandra Palace, which has proved so satisfactory for the last two years. The dates and hours of opening will be :

Monday		
13 March	..	3.00 p.m.-6.30 p.m.
Tuesday		
14 March	..	10.00 a.m.-6.00 p.m.
Wednesday		
15 March	..	10.00 a.m.-6.00 p.m.
Thursday		
16 March	..	10.00 a.m.-6.00 p.m.
Friday	17 March	10.00 a.m.-4.00 p.m.

Admission will be free of charge.

This year OCCA 18 was visited by an increased number of people, the total being 11,500, including many visitors from 26 overseas countries.

In addition to sufficient display space, Alexandra Palace provides ample car parking facilities and is easily accessible by Underground. A free coach service will again be provided by the Association, between the Exhibition and Wood Green Underground Station. At Alexandra Palace there are two restaurants, in addition to two buffets and several bars.

The "Official Guide"

The *Official Guide*, which is distributed free of charge, will be available early in 1967 prior to the Exhibition and at the Exhibition itself. Each member of the Association, wherever resident, will receive a copy as soon as they are available for it is appreciated that this arrangement helps members to plan their itineraries. A map is included with the *Guide* showing main line and Underground services, together with suggested routes for those travelling by car.

Copies of the *Guide* are also sent to individual scientists and technologists on the Continent of Europe with interests in the paint and printing ink industries. They are also distributed, through the courtesy of the trade associations, to manufacturing companies in the United Kingdom. In addition, an invitation card giving the dates and general information in several languages will be widely distributed well in advance of the Exhibition to manufacturing companies on the Continent. Any non-member, company or organisation who wishes to receive a copy of the *Official Guide* should write to the General Secretary before the end of the year.

Technical Education

A feature of the Exhibitions, which will be repeated at the Nineteenth Technical Exhibition, has been the stand devoted to Technical Education, on which information on technical courses

and careers will be available. The Committee has decided not only to invite parties of Sixth Form science students but also first year technical college students to visit the Exhibition, when they will be given short introductory lectures by members of the Association.

Exhibition Luncheon

An Exhibition Luncheon will be held at the Savoy Hotel, London, W.C.2, on Monday 13 March, prior to the Opening Ceremony. A form of application for Luncheon Tickets will be enclosed with each copy of the *Official Guide*.

Application forms

The Exhibition Committee wishes to make known as widely as possible the rules governing participation in the Exhibition, which exhibitors agree to accept when sending in their application forms. The rules state that companies exhibiting shall present technical advances in the paint, printing ink and allied industries relating to :

- (a) New products ;
- (b) New knowledge relating to existing products and their use ; or

- (c) In suitable cases, existing knowledge which is not generally available in the consuming industries.

The Committee stipulates that exhibitors should present a technical theme, that is, to display in a technical manner the technical developments in raw materials, plant or apparatus illustrated by experimental evidence. Furthermore, it is a feature of the Exhibition that technically or scientifically trained people should be available on the stands throughout the official hours of opening.

Copies of the Invitation to Exhibit and application forms have already been dispatched to companies both in the United Kingdom and on the Continent of Europe ; applications for stand space must be returned to the General Secretary by **Friday 2 September 1966**.

Companies who have not previously exhibited and would like to have their names submitted to the Committee for consideration should write to the General Secretary, R. H. Hamblin, M.A., F.C.I.S., F.C.C.S., Oil and Colour Chemists' Association, Wax Chandlers' Hall, Gresham Street, London, E.C.2.

London Section

Twenty-eighth Annual General Meeting, 1966

The 28th Annual General Meeting of the London Section was held on 21 April 1966 at the Criterion in Piccadilly, with Mr. C. R. Pye in the chair and 42 members present.

Mr. R. N. Wheeler proposed the adoption of the Committee's report, which was taken as read, and in seconding, Dr. S. R. W. Martin commented that the Section had had a good session of technical meetings, including the European Liaison lecture, and the Ladies' Night had been very enjoyable. The question of student group activities presented a problem, and it was difficult to know what was the best course to follow. He also referred to the activities of the Branches, which were on the whole very encouraging.

Mr. C. A. Carey, speaking on behalf of the Chairman of Southern Branch, Mr. J. C. Kingcome, who was unable to be present, referred to the difficulties which were being experienced with attendance at meetings, which had caused the question of the future of the Branch to be discussed at the AGM ; he himself still felt optimistic about the outcome. Mr. W. J. Arnott said that membership of the Thames Valley Branch had increased slightly in this period of consolidation. Meetings would again be held at the White Hart at Beaconsfield in the coming season. At the AGM, Mr. A. G. Holt had been elected Chairman.

Discussion of the Annual Report was concerned with student activities, and Mr. N. R. Fisk referred to the strenuous

work which had been undertaken a few years ago to encourage such activities. Mr. D. E. Eddowes spoke of the activities this year, and agreed with Mr. Fisk that the junior members themselves should be encouraged to take part in the organisation of the lectures. The President, Dr. S. H. Bell, spoke of the challenge presented by the problem of student activities; the students of today were the members of the future. The whole pattern of education and training was changing, and the Association should where necessary adapt itself to and take their due part in these new trends. Mr. J. A. L. Hawkey supported these views, but mentioned the particular problems in the London area, with its distances of travel, and the fact that there was no single centre for educational activities which could act as a focus for OCCA junior activities. The Chairman, Mr. Pye, said that the Committee were not too pessimistic, and would continue to search for ways of engendering enthusiasm amongst junior members. The Committee's report was adopted unanimously.

Mr. J. E. Pooley, proposing the adoption of the financial report, referred to the steady reduction over the last few years of the cost of London Section activities, and thanked Mr. W. H. Campbell for continuing to act as Honorary Auditor. The report was adopted unanimously.

The following Officers of the Section were elected:

Hon. Secretary	Mr. R. N. Wheeler
Hon. Treasurer	Mr. J. E. Pooley
Hon. Publications Officer	.. Dr. V. T. Crowl
Hon. Programmes Officer	Mr. D. E. Eddowes
Hon. Auditor	.. Mr. W. H. Campbell

In proposing the re-election of Mr. C. R. Pye as Chairman, Mr. J. A. L. Hawkey referred to Mr. Pye's service to the Committee, and his wide sympathy with all the interests of the members. Mr. A. R. H. Tawn, seconding the proposal, said that very little needed to be added. Mr. Pye was not a flamboyant

Chairman; he was, however, very efficient and one knew that he was there. Mr. Pye was re-elected unanimously with acclamation. Mr. Pye expressed his thanks to the meeting for the renewal of confidence in him, and thanked Mr. M. R. Mills for having taken the chair at the last two meetings. He hoped, however, to be able to carry out his duties without hindrance during the coming session.

The following new members of the Committee were elected: Mr. V. F. Jenkins, Mr. W. O. Nutt and Mr. D. G. Soar.

The meeting was followed by the dinner, after which Mr. C. L. Boltz, scientific editor of the *Financial Times*, gave a talk on "The Presentation of Scientific Information to the Public Through the Medium of Radio and Print." Mr. Boltz, in a very amusing speech, said that he was concerned more perhaps with technology than pure science, and described how information was obtained; it was necessary to be extremely careful in accepting information, and yet one needed to retain enthusiasm in presenting the facts. One particular feature of the newspaper world was speed; it was essential to be able to obtain and verify the facts immediately, frequently in the latter part of the afternoon for publication in the next morning's edition. It was really remarkable that so much information passed through the various stages of sub-editing, composition and correction by non-technical staff so accurately.

With radio, the time factor was not so pressing, but when one was on the air every word counted, and there was a consequent need for excessive caution and verification of facts. Writing for radio was quite different from writing for the press; the speaker needed to sound as though he were talking naturally, and not reading from a script. Following the talk, Mr. Boltz answered a number of questions on subjects such as the value of press releases and public relations activities, "scoops," and the type of scientific information presented to the public.

V. T. C.

Manchester Section

Annual General Meeting

The 42nd Annual General Meeting of the Section was held at the Waldorf Hotel, Manchester on 22 April 1966 with Mr. H. F. Clay in the Chair.

After approval of the Minutes of the last Annual General Meeting the Committee's Annual Report and Financial Report were presented, discussed and adopted.

The Officers of the Section were then nominated and elected as follows :

Chairman :

Mr. I. S. Moll

Vice-Chairman :

Mr. W. F. McDonnell

Hon. Secretary :

Mr. H. G. Clayton

Hon. Treasurer :

Mr. S. Duckworth

Hon. Publications Secretary :

Dr. D. A. Plant

Hon. Research Liaison Officer :

Dr. F. M. Smith

Hon. Programmes Officer :

Mr. C. Williams

Hon. Social Secretary :

Mr. M. J. Heavers

Mr. L. Boden and Mr. F. A. Walker were also re-elected as Hon. Auditors.

A ballot was held to fill the two vacancies on the Committee from the four nominations received. As a result of the ballot Mr. N. Ashworth and Dr. C. Barker were elected to join the previously elected Committee members, namely : Mr. T. Graham, Mr. J. J. Kavanagh, Mr. W. G. Topham and Mr. G. T. Williams, and the ex-officio members, Mr. H. F. Clay (immediate Past Chairman), Mr. T. E. Johnson, Mr. J. Smethurst, and Dr. H. A. Hampton.

Under any other business, various topics were discussed including the thanks that were due to the Hon. Research and Liaison Officer, Dr. F. M. Smith for the success of the Symposium on Emulsion Paints held earlier in the week.

In proposing a vote of thanks to the Committee Mr. H. R. Touchin referred to the continuing growth of the Section and its activities which he felt certain were due to the energy and effort expended by the Committee under the direction of its successful and able Chairman. He particularly wanted to thank the retiring Chairman, Mr. H. F. Clay who had looked after the activities of the Section so ably in the last two years and brought what he referred to as a "homely, modest touch" to the proceedings of the Section. He also referred to the good work done by the retiring members of the Committee, Mr. A. G. Wolstenholme and Dr. D. A. Plant who had now been elected Hon. Publications Secretary.

Mr. H. F. Clay, the retiring Chairman, in reply, said how much both he and his wife had enjoyed his period of office and how he felt he could not have been better supported by his Committee members. The Chairman then concluded the meeting by cordially inviting the past Chairman and Officers of the Section to a Dinner which would follow the Committee's summer Committee meeting.

After the meeting the traditional Hot-Pot Supper was held followed by entertainment by a professional comedian, Len Annett and a professional pianist which was supplemented by members' stories and Mr. E. Mountain who gallantly volunteered to sing several classical ballads.

W. F. MCD.

A Symposium on Emulsion Paints

The Section held a highly successful Symposium on Emulsion Paints on 18 and 19 April in the Reynold Building of the Manchester College of Science and Technology which was attended by some



The Lecturers and Chairmen are shown assembled on the platform



Mr. H. F. Clay, the Chairman of Manchester Section, is pictured addressing the third session

360 people representing all aspects of the Surface Coatings Industry from this country and overseas.

The papers presented are noted below and the discussion on these papers was only limited by the time available :

“The next ten years : an analysis of current trends and future outlook for

emulsion paints.” P. O. Miles and G. R. Harrison, Vinyl Products Ltd.

“Regulation of Particle Size in the Semi-Batch Preparation of Vinyl Acetate/Vinyl Ester of ‘Versatic’ 911 Copolymer Latices.” Dr. G. C. Vegter and E. P. Grommers, Shell International Chemical Co. Ltd.

"The influence of comonomers, plasticisers and coalescing solvents on the minimum film forming temperature and film hardness of polymer dispersions." I. Llewellyn, British Resin Products Ltd.

"Surface treatment and optical properties of titanium dioxide pigments." J. Taylor, Laporte Titanium Ltd.

"Coloured pigments in emulsion paints." P. Birrell, Geigy (U.K.) Ltd.

"Extenders in emulsion paints." L. Tasker, S. Hodgson, British Resin Products Ltd.

"Water Soluble Colloids in Emulsion Paints." A. Reveley, British Celanese Ltd.

"The role of surfactants in emulsion polymerisation and emulsion paints." Dr. C. Bondy, Revertex Ltd.

"Types of Emulsion Paint." Dr. G. L. Foster, Dr. W. L. W. Ludekens, ICI Ltd., Paints Division.

"Manufacturing process and plant." S. Duckworth, Walpamur Ltd.

"Paint storage stability in relation to pigment surface characteristics." J. Taylor, Laporte Titanium Ltd.

"Emulsion paint properties and structure." E. F. Redknapp, The Paint Research Station.

"The influence of polymer make up and composition on paint performance." A. C. Fletcher, D. A. Brightman, J. K. Rankin, E. Swales, Vinyl Products Ltd.

It is hoped that many of these papers will be considered suitable for publication in the Journal in due course.

The three sessions were Chaired by Mr. T. E. Johnson, Dr. S. H. Bell and Mr. H. F. Clay. The Chairman of the Section, Mr. H. F. Clay, presided over a Dinner on the evening of 18 April at which approximately 230 participants attended when he formally thanked the Chairmen and Lecturers for their part in the proceedings and particularly thanked Dr. F. M. Smith the Section Honorary Research Liaison Officer who had carried out all the considerable work involved in organising and running the Symposium, together with Mrs. Gledhill, his Secretary. He also thanked Mr. T. E. Johnson who had originally produced the tentative programme on which the Symposium had been planned and who had co-operated with Dr. Smith in producing such an informative programme.

Mr. Clay also thanked Dr. Bell for Chairing the second session and hoped that he would be prepared to tell the Council that they were justified in agreeing to the Manchester Section running the Symposium. He was sure that all those attending would agree that the College was an excellent venue for this type of venture, providing the most up-to-date lecture facilities and residential accommodation on the same site.

The Chairman concluded by saying he was most gratified to see the support given to the venture from both the UK and the Continent and he hoped that the Section would continue to organise similar Symposia in the future.

W. F. MCD.

Midlands Section

Annual General Meeting

The 18th Annual General Meeting of Midlands Section was held on 22 April at the Grosvenor House Hotel, Hagley Road, Edgbaston, Birmingham, with Mr. R. D. Calvert presiding. At the commencement of the meeting members stood in tribute to Dr. Newton Friend.

After adoption of the Annual Report of the Committee and the Statement of Accounts, Officers and Committee for the session 1966-67 were elected. The newly elected officers are :—

Chairman :

Mr. C. H. Morris

Immediate Past Chairman :

Mr. R. D. Calvert

Hon. Secretary and Representative on Council :

Mr. D. J. Silsby

Hon. Treasurer :

Mr. H. J. Griffiths

Hon. Publications Secretary :

Mr. L. R. Seaborne

Committee :

Mr. F. W. Cole, Mr. P. C. Daley, Mr. A. S. Gay, Mr. J. R. Green, Mr. D. Hooper and Mr. D. Penrice

Hon. Auditors :

Mr. N. A. Bennett and Mr. F. Cooper

Mr. W. Edwards proposed a vote of thanks to the retiring Chairman, Mr. R. D. Calvert, to Mr. D. J. Morris who had been Hon. Treasurer for six years and to the retiring Committee members, Mr. R. E. Howse and Mr. L. V. Jennings.

After the AGM members sat down to a supper with a choice of main course from tripe and onions, sausage and mash and fish and chips. Members then gathered round the piano for a sing-song which included an unusually energetic rendering of "Swing Low Sweet Chariot."

L. R. S.

Newcastle Section

Annual General Meeting

The AGM was held on Thursday 7 April. Forty-five members and four visitors attended.

The officers elected were :

Chairman : Mr. E. L. Farrow

Vice-Chairman : Mr. D. M. James

Secretary : Mr. B. Ridley

Treasurer : Mr. A. W. Blenkinsop

Co-ordinating Officer for Technical Education : Mr. P. C. Edbrooke

Publications Officer : Mr. D. M. James

Research Liaison Officer : Dr. T. A. Banfield

Secretary of Junior Activities Sub-Committee : Mr. K. F. Baxter

Representative on Council : Mr. H. D. Jefferies

The Committee was unchanged with the important exception of the Secretary. The Chairman presented a gift to Mr. J. A. Willey, expressing the Section's appreciation of his excellent work for the past six years.

There were three vacancies on the Committee since Mr. Palmer and Mr. Proudley retired and Mr. Ridley became Secretary. After a ballot the following were elected :

Mr. C. N. Finlay,

Mr. G. L. Lewis,

Mr. J. A. Willey,

the existing elected members being :

Mr. J. G. Bell,

Mr. K. V. Hodgson,

Mr. P. B. Marsden.

The Junior Activities Sub-Committee was constituted as before, namely Mr. Farrow, Mr. Baxter and Mr. Edbrooke from the Committee, plus Mr. H. Fuller, Mr. D. W. Hudson and Mr. W. Phillips as elected members.

The Auditors were Mr. F. G. Palmer and Mr. T. W. Robinson.

The reports of the Committee, Treasurer, Research Liaison Officer and Junior Activities Sub-Committee were presented and adopted. The programme for 1966-67 was presented and two additional items were mentioned: the Technical Education Symposium on 25 May 1966; and Ladies' Night, which will be some time in February 1967.

The evening ended with a talk by Mr. A. J. E. Spray, of Northern Goldsmiths Co. Ltd., on "Precious Gem Stones, Synthetics and Pearls," followed by refreshments.

D. M. J.

Scottish Section

Annual General Meeting and Smoking Concert

The Annual General Meeting of the Scottish Section was held in More's Hotel, Glasgow, on Friday, 1 April, with Dr. D. Atherton in the chair. The following Office Bearers and Committee were appointed.

Chairman :

Mr. I. S. Hutchison

Vice-Chairman :

Mr. J. Miller

Hon. Secretary :

Mr. E. M. Burns

Hon. Treasurer :

Mr. T. B. Hannah

Representative on Council :

Mr. A. S. Fraser

Hon. Publications and Education Officer :

Mr. A. McLean

Hon. Programme and Research Liaison Officer :

Mr. A. McGuire

Hon. Junior Section Liaison Officer :

Mr. P. Birrell

Committee :

Messrs. G. Anderson, D. Rowley, W. Peden, A. Smith, T. Pisacane, Dr. J. D. Easton

At the close of the meeting, an augmented company adjourned to the

Eglinton Arms Hotel, Eaglesham, to celebrate the Annual Smoking Concert. After an enjoyable meal, entertainment, provided by the same group as last year, continued until a late hour. During the course of the evening, the new chairman, Mr. I. S. Hutchison, made a presentation to the retiring Chairman, Dr. D. Atherton, this taking the novel form of an electric carving knife.

Mr. W. W. Horsburgh

It is with mixed feelings of regret and pleasure that the Scottish Section records the departure across the border of Mr. W. W. Horsburgh, who has been appointed General Manager to the Swift Chemical Co. Ltd. of Liverpool. Mr. Horsburgh has been an active member of the Association for many years. He served first as a committee member and, subsequently, from 1962 to 1966, as Hon. Secretary, in which latter capacity his quiet efficiency and pawky humour were amongst the more notable of his qualities. His assistance in organising the Annual Dinner Dance was an activity which was always deeply appreciated by the Scottish Section.

At a farewell dinner party, held recently at Rowardennan Hotel, and attended by members of Committee and business associates, Mr. Horsburgh was presented with a cut crystal table set. The Scottish Section wishes him every joy and success in his new post.

A. MCL.

News of Members

Dr. L. Barakan an Ordinary Member attached to the London Section has been appointed Manager—Surface Coating Resins (Overseas Division), a new post created within the Export Department of Distillers Chemicals and Plastics Limited Overseas Division.

Mr. L. Firing, an Ordinary Member attached to the Overseas Section and a

Director of Kronos Titanium Pigments Ltd., is returning to Europe from Canada on business. During this time he expects to spend several weeks in both the United Kingdom and Norway.

M. W. MacNay, Associate Member attached to the London Section, retired from the Board of SCC Colours at the end of March.

Mr. I. T. Smith, an Ordinary Member attached to the London Section and contributor in the past three years to the Association's Section in the Annual Report on Applied Chemistry prepared for the S.C.I., is leaving the country to take up a post in the Research and Product Development Laboratory of the Toni Company, Chicago, Illinois.

Dr. D. A. Plant, an Ordinary Member attached to the Manchester Section and Honorary Publications Officer of that Section, is now in charge of the Pigments Section of the Application Research and Technical Service Department of Imperial Chemical Industries. Mr. H. G. Cook, an Ordinary Member attached to the Manchester Section, has been appointed as Assistant Section Leader.

Obituaries

Mr. R. Kershaw

All OCCA members will be distressed to hear of the sudden death of Richmond Kershaw, B.Sc., of the Dyestuffs Division of ICI Limited.

Richmond graduated B.Sc. (Hons. Chem.) from Manchester University in 1949, after serving in the Royal Navy from 1943-1946. He joined W. & J. Leigh Ltd., Bolton, as a chemist in 1949 and moved to Gittings & Hills Ltd., Birmingham, in 1952 as Assistant Chief Chemist. In 1953 he joined the technical staff of ICI Ltd. in the Resins Service Department at Blackley.

His work in this Department involved frequent customer contact and required a sound background knowledge of paint technology, for which his earlier associations stood him in good stead. It was in this aspect of his work that he excelled but as his experience grew he was able to assume increasing responsibility for other features of development. By 1963 his technical service team covered a very wide range of products and included such diverse materials as resins for paints and printing inks, surface active agents, bactericides and other chemicals.

In all the fields covered by him, Richmond's outstanding characteristic lay in the personal relationship he was able to bring to his contacts within and outside ICI. This was of considerable assistance

in creating the high standard of technical service he was always able to maintain. New products and new technologies were regarded by him as a constant challenge not only to his own appreciation of the possibilities but also to his ability to impart his understanding to his colleagues throughout industry.

His warm personality brought him many friends and he will be greatly missed by them. He leaves a wife and two small children and we extend our sympathy to them in their great loss.

A. LOWE.

J. A. Newton Friend

We are sorry to record the death of Dr. J. A. Newton Friend who was President of the Association from 1922 to 1924, an Hon. Member, and also Vice-President from 1925-26 and 1962-64. A full obituary will appear in a later issue of the Journal.



J. A. Newton Friend

Register of Members

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

Ordinary Members

- ALCOCK, ROY, 29 Lynton Street, Derby. (*Midlands—Trent Valley Branch*)
- ANGELL, GEORGE CHRISTOPHER, 29 Rosalind Street, Crows Nest, Sydney, New South Wales, Australia. (*New South Wales*)
- BOOTH, ALFRED DONALD, "Dahland," White Post Lane, Cobham, Kent. (*London*)
- BOWKER, ALBERT EDWARD, Wardley Chemicals Ltd., Greenhey Place, Skelmersdale, Nr. Ormskirk, Lancs. (*Manchester*)
- BROADHURST, CHARLES HAROLD, 63 Sevington Road, Hendon, London, N.W.4. (*London*)
- BROWN, PETER HOWARD ALBERT, 35 Myers Avenue, Glen Waverly, Victoria, Australia. (*Victorian*)
- BUTT, A. HAMEED, M.SC., Ismailsons Paints Ltd., F/59 S.I.T.E., Karachi 13, Pakistan. (*Overseas*)
- BYERS, ALAN, B.SC., Balm Paints (N.Z.) Ltd., PO Box 366, Lower Hutt, Wellington, New Zealand. (*Wellington*)
- CHAPLIN, PHILLIP ARNOLD, B.SC., A.S.T.C., 1 Clarke Street, Chatswood, New South Wales, Australia. (*New South Wales*)
- CHASEMORE, ANTONY ROBIN, B.SC., "Birchwood," The Green, Worplesdon, Surrey. (*London*)
- CHILDS, BRIAN DAVID, 130 Mapleton Road, Hall Green, Birmingham 28. (*Midlands*)
- CUNNINGHAM, DAVID ANDREW, B.SC., 8 Evelyn Street, South Coogee, New South Wales, Australia. (*New South Wales*)
- FITTON, JAMES MICHAEL, 193 Wardle Road, Rochdale. (*Manchester*)
- GILMORE, HARRY, B.SC., A.S.T.C., 149 River Road, Northwood, New South Wales, Australia. (*New South Wales*)
- GOLDSBROUGH, KEITH, B.A., A.R.I.C., 9 Wellburn Road, Fairfield, Stockton-on-Tees, Co. Durham. (*Newcastle*)
- GOOSSENS, HENRI, Statielei 135, Mortsel, Belgium. (*Overseas*)
- GREENALL, BRIAN JOHN, B.E.(CHEM.), W. Graham Hitchins Ltd., PO Box 13, Renwick, New Zealand. (*Wellington*)
- HALL, CHRISTOPHER WISHART, C. Wishart Hall & Co. Ltd., Elder Park Works, 42/48 Uist Street, Glasgow, S.W.1. (*Scottish*)
- HAMANN, JOHN BERNARD, 7 Craiglunds Avenue, Gordon, New South Wales, Australia. (*New South Wales*)
- HARTE, ANTHONY AMBROSE, 66 Winston Drive, Somerset, New Jersey 08873, U.S.A. (*Overseas*)
- HILDITCH, ERNEST MICHAEL HUNTER, M.A., E. M. Hilditch & Co., 356 St. Kilda Road, Melbourne, S.C.2, Victoria, Australia. (*Victorian*)
- HOLMES, CHARLES PETER, 20 Hall Crescent, Epuni, Lower Hutt, Wellington, New Zealand. (*Wellington*)
- JACKSON, HUGH RICHARD, B.SC., L.R.I.C., Midland Silicones Ltd., Reading Bridge House, Reading, Berks. (*London—Thames Valley*)

- KNIGHT, JOHN WILLIAM JEREMY, M.SC., ICI (NZ) Ltd., Box 1592, Wellington, New Zealand. (*Wellington*)
- MANSUKHANI, ISHWAR R., B.SC., Usher Walker Ltd., 16 Marsh Gate Lane, London, E.15. (*London*)
- MAYNE, ALAN JOHN, M.SC., 17 Field Street, Silverstream, Wellington, New Zealand. (*Wellington*)
- MOORE, VINCENT A., "Woodpeckers," The Chase, Wooburn Common, Nr. High Wycombe, Bucks. (*London—Thames Valley*)
- MORRISH, WILLIAM NOEL, M.SC., Bonnington House, Montenotte, Cork, Eire. (*Irish*)
- NERI, MAURICE ALBERT, 102 Chemin de la Montagne, 1224 Chene-Bougeries, Geneva, Switzerland. (*Overseas*)
- O'NEILL, BARRY WILLIAM, A.R.A.C.I., C.S.R. Chemicals Pty. Ltd., Northern Road, West Heidelberg, Victoria, Australia. (*Victorian*)
- READER, CHARLES E. L., B.SC., Burgemeester Caan van Necklaan 285, Leidschendam, The Netherlands. (*Overseas*)
- RHEINECK, ALFRED E., B.SC., CHE., M.SC., PH.D., College of Chemistry and Physics, North Dakota State University, Fargo, North Dakota, U.S.A. (*Overseas*)
- SAUNDERS, JOHN ALAN, B.SC., A.R.I.C., 1 Sandhills Road, Reigate, Surrey. (*London*)
- STOOTMAN, HENRICUS EUGENIUS, 151 Meadowsroad, Mt. Pritchard, New South Wales, Australia. (*New South Wales*)
- TRAVES, JULIAN, 236 Wolverhampton Road, Warley, Oldbury, Worcestershire. (*Midlands*)
- TREADWAY, GERALD DAVID, G.R.I.C., W. P. Fuller Co., 450 East Grand Avenue, South San Francisco, California, U.S.A. (*Overseas*)
- WELBY, ALFRED LESLIE, 19 St. Anns Road North, Heald Green, Cheadle, Cheshire. (*Manchester*)
- WHITE, CYRIL VICTOR, Cromford Colour Co. Ltd., Cromford, Matlock, Derbyshire. (*Midlands—Trent Valley*)
- WHITE, KEITH VALENTINE, A.R.A.C.I., Flat 10, 11/13 Freemont Street, Parnell, Auckland, New Zealand. (*Auckland*)
- WOOD, J. H. J., 52 Tybenham Road, Merton, London, S.W.19. (*London*)
- WRAY, ROBERT JOHN, W. R. Grace (Aust.) Pty. Ltd., 1126 Sydney Road, Fawkner, Victoria, Australia. (*Victorian*)

Associate Members

- BINGHAM, MICHAEL BERNARD, "Three Ways," 57 Maple Road, Sutton Coldfield, Warwickshire. (*Midlands*)
- BRADBROOKE, ROY LANCE DANE, 6 Crocket Close, Northampton. (*Midlands*)
- COX, JEFFREY ROBERT, F. T. Wimble & Co. (NZ) Ltd., PO Box 5024, Nae Nae, New Zealand. (*Wellington*)
- GHOSH, AMAL KUMAR, 5/1 Jagat Roy Choudhury Road, Calcutta 8, India. (*Overseas*)
- HARRIS, JOHN MICHAEL, ICI Ltd., 4 Blythswood Square, Glasgow, C.2. (*Scottish*)
- HATHERALL, FREDERICK CLIFFORD, Shell Chemical Co. Ltd., Downstream Building, Shell Centre, Waterloo, London, S.E.1. (*London*)
- HAYES, ANTHONY JOHN, Albright & Wilson (Aust.) Ltd., 486 Pacific Highway, St. Leonards, New South Wales, Australia. (*New South Wales*)
- HUTCHINS, GRAHAM, 75 Avondale Road, Wigston Fields, Leicester. (*Midlands*)

- SEWELL, JOHN DAVID, 594 St. Kilda Road, Melbourne, Victoria, Australia.
(Victorian)
- WATTS, RONALD STANLEY BRETT, Kreglinger (Australia) Pty. Ltd., 524 Collins Street,
Melbourne, Victoria, Australia. (Victorian)
- WILSON, DOUGLAS JOHN, 19 Lower Tory Street, Wellington, New Zealand. PO Box
3747. (Wellington)
- WINTERBOTTOM, JAMES DAVID, ICI Ltd., 4 Blythswood Square, Glasgow, C.2.
(Scottish)

Junior Members

- BIRD, CRAWFORD, 35 Ferry Road Drive, Edinburgh, 4. (Scottish—Eastern)
- DUNLOP, JOHN TODD, 2 Gilmerton Street, Sandyhills, Glasgow, E.2. (Scottish)
- ELLIOT, THOMAS GEORGE, c/o Wilczek, 52 Elm Row, Edinburgh, 7.
(Scottish—Eastern)
- FAIRBAIRN, JOHN ARTHUR, 4 Carrisbrook Avenue, Bexley North, New South Wales,
Australia. (New South Wales)
- FIRTH, IAIN, 19 Bogany Terrace, Castlemilk, Glasgow, S.5. (Scottish)
- GOTHAM, KEVIN STANLEY, 8 Rose Avenue, Concord, New South Wales, Australia.
(New South Wales)
- HANKEY, EDWARD, 41 The High Road, South Shields, Co. Durham. (Newcastle)
- MACMARTIN, DUNCAN PETER, 18 Matthews Crescent, Blacktown, New South Wales,
Australia. (New South Wales)

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.

Thursday 30 June

Annual General Meeting and Foundation Lecture, to be held at Painter-Stainers Hall, (Court Room), Little Trinity Lane, London, E.C.4.

Thursday 14 July/Sunday 17 July

Eighth Australian OCCA Convention, to be held at Victor Harbour, South Australia.

Oil and Colour Chemists' Association

President: S. H. BELL, PH.D., D.I.C., A.R.C.S., F.R.I.C.

The Oil and Colour Chemists' Association was formed in 1918, to cover paint, printing inks, pigments, varnishes, drying and essential oils, resins, lacquers, soaps, linoleum and treated fabrics, and the plant, apparatus and raw materials useful in their manufacture. In 1923 it absorbed the Paint and Varnish Society. The stated purpose of the Association is to promote by discussion and scientific investigation the technology of the industries concerned with the above-mentioned products, and to afford members opportunity for the interchange of ideas. This is achieved by the regular holding of ordinary meetings at which papers are presented, and the organisation of annual technical exhibitions, biennial conferences, educational activities and practical co-operative experimental work. Details of these activities are given in the *Journal of the Oil and Colour Chemists' Association*, which is published monthly, and whose pages are open to receive communications and other pronouncements on scientific and technical matters affecting the members of the Association and the industries concerned. The Association's meetings also afford opportunities for members to meet informally and socially.

There are Sections of OCCA in Auckland, Bristol, Hull, Ireland, London (with Southern and Thames Valley Branches), Manchester, the Midlands (with a Trent Valley Branch), Newcastle upon Tyne, New South Wales, Queensland, Scotland (with an Eastern Branch), South Africa (with Branches in the Cape, Transvaal and Natal), South Australia, Victoria, Wellington, West Australia and the West Riding, and these are responsible for the conduct of their own local affairs. There is also a General Overseas Section. There is also a close alliance between the Association, the Federation of Societies for Paint Technology in the United States, and the Fédération d'Associations des Techniciens de l'Industrie des Peintures, Vernis, Emaux et Encres d'Imprimerie de l'Europe Continentale (FATIPEC). The Association also maintains cordial relations with the Scandinavian Federation of Paint and Varnish Technicians (SLF).

Ordinary Membership is granted to scientifically trained persons, and Associate Membership to others interested in the industries covered. Junior Membership, which is intended primarily for students, is open without restriction to persons under the age of 21 and to those up to 25 who are following a course of technical study. The annual subscription in each case is three guineas, except for Junior Members whose subscription is 10s. 6d. An entrance fee of 10s. is payable by all members. Applications for membership are invited from suitably qualified persons who are engaged or otherwise interested in the industries noted above. Applications, which should be supported by two members of the Association (one of whom must be an Ordinary Member) should be forwarded to the General Secretary at the address given below. Application forms and full details of membership may be obtained from the offices of the Association.

PUBLICATIONS

Journal of the Oil and Colour Chemists' Association, Published monthly. Subscription rate to non-members in UK and abroad, £7 10s. p.a. post free; payable in advance.

An Introduction to Paint Technology (Second Edition). Pp. 187, illustrated, with index, 15s. (including postage).

Paint Technology Manuals

Part 1 : " Non-convertible Coatings," Pp. 326, 35s.

Part 2 : " Solvents, Oils, Resins and Driers," Pp. 239, 35s.

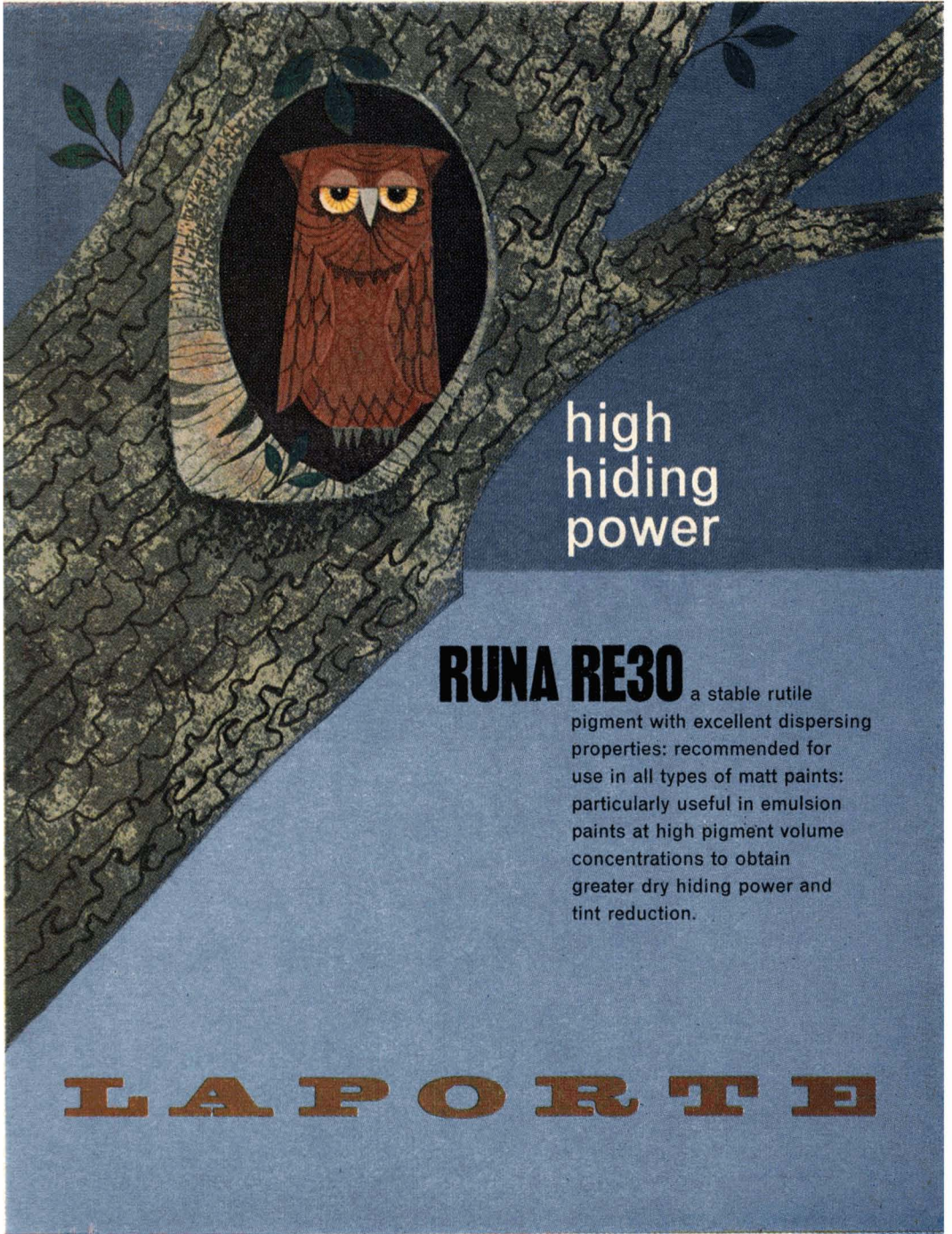
Part 3 : " Convertible Coatings," Pp. 318, 35s.

Part 4 : " The Application of Surface Coatings," Pp. 345, 35s.

Part 5 : " The Testing of Paints," Pp. 196, 35s.

Part 6 : " Pigments, Dyestuffs and Lakes," Pp. 340, 35s.

General Secretary : R. H. Hamblin, M.A., F.C.I.S., F.C.C.S., Wax Chandler's Hall, Gresham Street, London, E.C.2.



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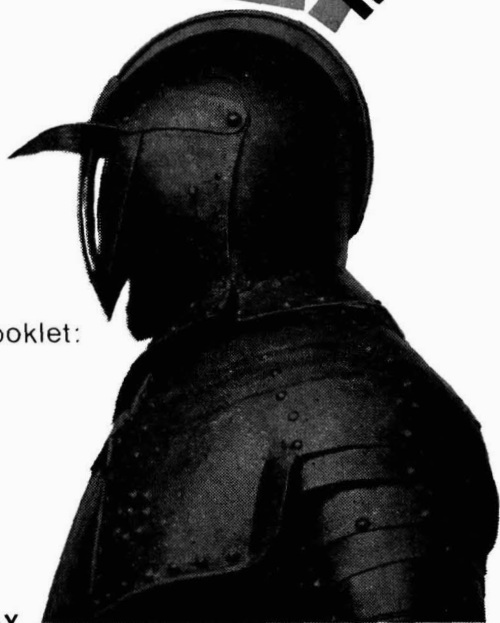
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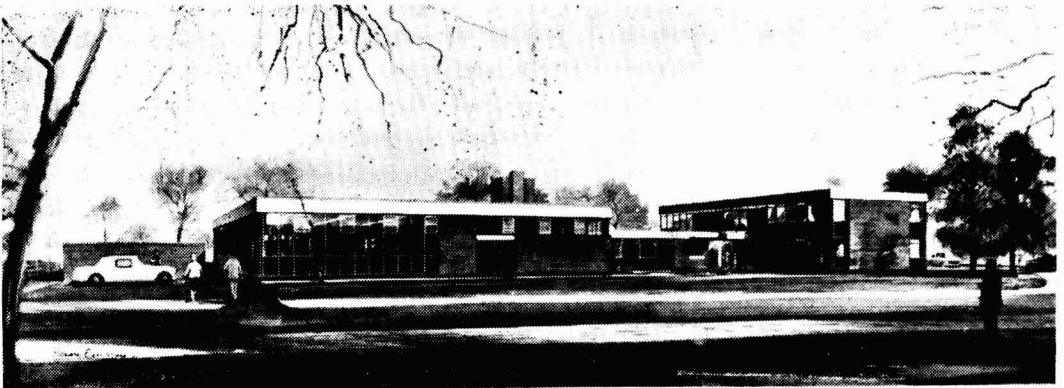
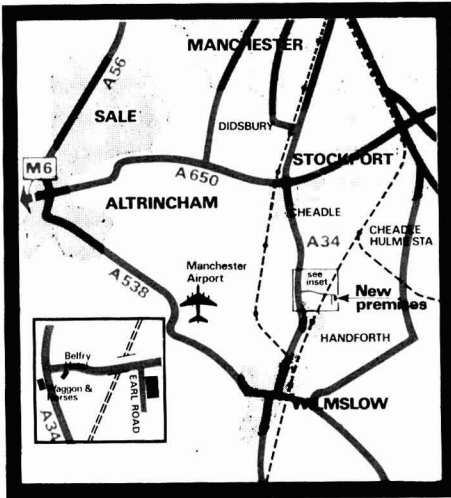
On 1st June, our administrative offices and laboratories are being transferred from Sale, Cheshire, to newly-built premises at Cheadle, Cheshire. The new building will provide twice as much floor space, and every modern concept has been incorporated into its design to ensure maximum efficiency and comfort. The new site, which includes one acre of land for future expansion, is only 9 miles from the centre of Manchester, and is within 10 minutes' drive of Manchester Airport, and Wilmslow Station on the new electrified main Manchester/London railway line.

(The factory address at Carrington, near Manchester, remains unchanged)

The complete address from 1st June, 1966, will be:—

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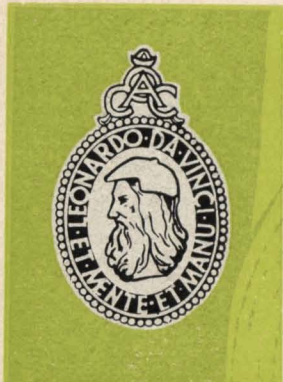
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Thank you for your letter of yesterday's date and in answer to your first query I would recommend the purchase of "Introduction to Paint Technology." I consider that it is an excellent book for introducing a person into the industry and at 15s. I feel that it is outstanding value. It can be obtained from the Oil & Colour Chemists' Association, Wax Chandlers' Hall, Gresham Street, London E.C.2.

Now with regard to your second question . . .

CLASSIFIED ADVERTISEMENTS

Classified Advertisements are charged at the rate of 9s. per line. Advertisements for Situations Wanted are charged at 2s. 6d. per line. A box number is charged at 1s. 0d. They should be sent to the General Secretary, Oil & Colour Chemists' Association, Wax Chandlers' Hall, Gresham Street, London, E.C.2. Telephone: Monarch 1439

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