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OIL AND COLOUR CHEMISTS' ASSOCIATION

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Recent progress in coatings technology

Powder coatings—adhesion and permeability studies

Allyl ethers in solventless and water-based coatings

The chemistry of the vinyl cyclic acetals and their air drying reactions

Polyurethane systems for solventless finishes

the last papers from the Torquay Conference

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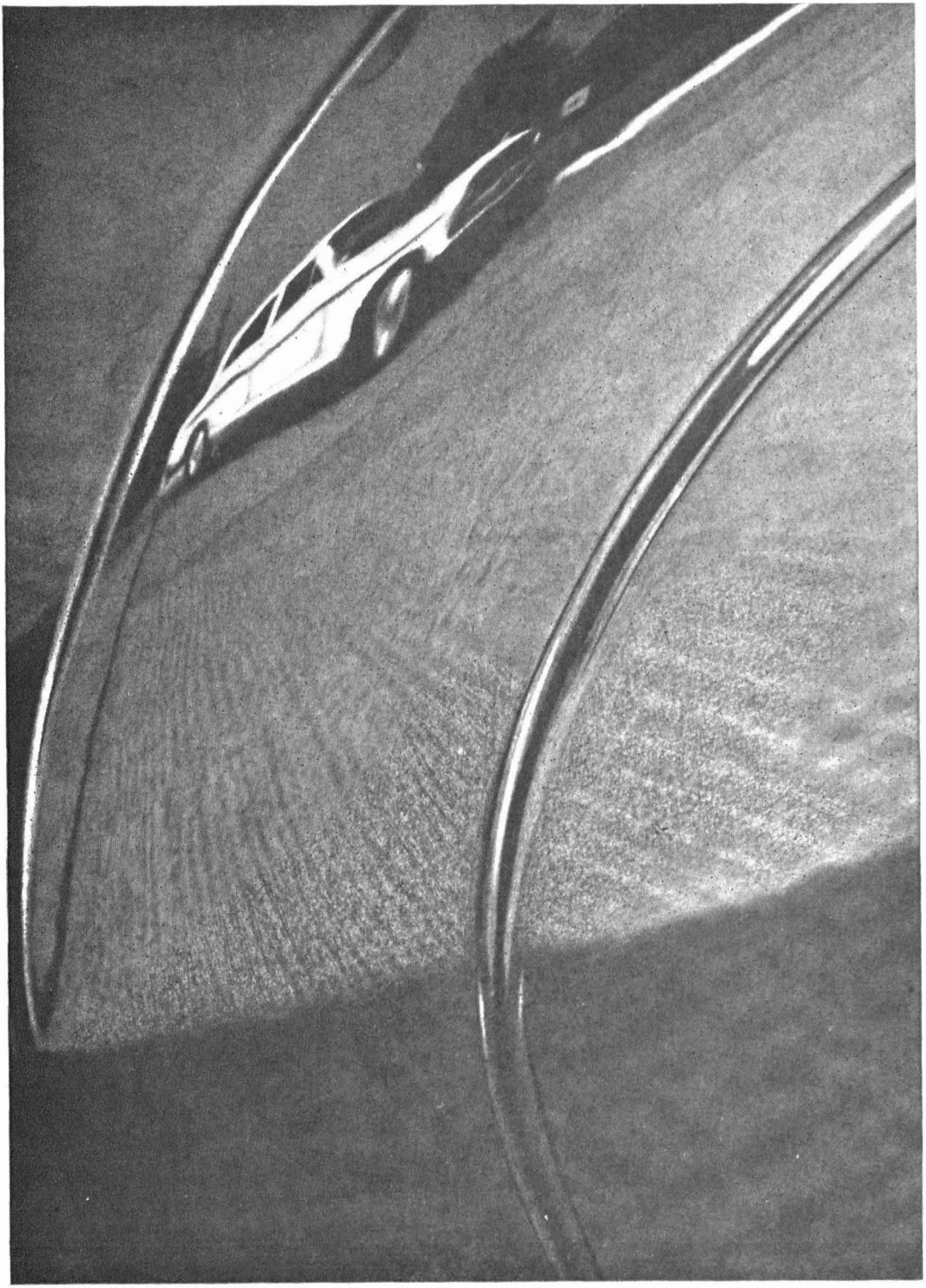

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Powder coatings—adhesion and permeability studies

By L. A. Tysall and J. R. Weber

Shell Chemical Co. Ltd., Egham, Surrey

Summary

The adhesion, water permeability, water absorption and water extractability of several different types of epoxy powder coatings have been measured. Nylon and pvc powder coatings have also been examined. The adhesion of certain epoxy powders to mild steel and copper has given bond strengths of up to 13,000 lb/sq in, of the same order as the tensile strengths of the epoxy powders. The water permeability of the powder coatings has been compared with that of solvent-borne epoxy systems, two drying oil/phenolic systems and a stoving synthetic. The permeability of the latter three was significantly greater than for other systems.

Some data on the water and chemical resistance of the epoxy powder coatings are reported.

Enduits en poudre—etudes sur leur adhésion et perméabilité

Résumé

Les propriétés adhésives, de perméabilité à l'eau, d'absorption et d'extraction de l'eau ont été mesurées pour plusieurs types différents d'enduits en poudre d'époxyde. Les enduits en poudre de nylon et de chlorure de polyninyle ont été examinés également. L'adhésion de certaines poudres d'époxyde sur l'acier doux et le cuivre s'est avérée correspondre à des résistances liantes atteignant 13,000 livres/pouce carré, similaires à leurs résistances à la traction. La perméabilité à l'eau des enduits en poudre a été comparée à celle de composés d'époxydes en suspension dans un solvant, de deux composés phénoliques/huile siccative et d'un composé synthétique d'étuvage. La perméabilité de ces deux derniers composés s'est avérée considérablement supérieure à celle des autres composés.

Cet article comprend également quelques renseignements touchant à la résistance des enduits en poudre d'époxyde à l'eau et aux produits chimiques.

Pulverbeschichtung—Haftungs- und Durchlässigkeitsuntersuchung

Zusammenfassung

Die Haftfähigkeit, Wasserdurchlässigkeit, Wassersaugfähigkeit und Wasserausfällung verschiedener Arten von Epoxyd-Pulverbeschichtungen sind gemessen worden. Auch Nylon und PVC wurden geprüft. Die Haftfähigkeit bestimmter Epoxyd-Pulver auf Flusstahl und Kupfer haben Bindungsstärken bis zu 13,000 lb pro Quadratzoll ergeben, die also in der selben Grössenordnung liegen wie die Zugbeanspruchung. Die Wasserdurchlässigkeit der Pulverbeschichtungen ist mit derjenigen von in Lösungsmitteln getragenen Epoxyd-Systemen verglichen worden sowie mit zwei Trockenöl-Phenolsystemen und einem synthetischen Aufbrennmaterial. Die Durchlässigkeit der beiden letzteren war beträchtlich grösser als bei den anderen Systemen.

Einige Angaben über die Widerstandsfähigkeit der Epoxyd-Pulverbeschichtungen gegen Wasser und chemische Substanzen werden mitgeteilt.

Introduction

Epoxy powder coatings represent a relatively recent addition to the range of organic protective coatings. The present paper reports a study of some of the properties of these coatings which might be expected to influence their performance. In particular their adhesion to mild steel and other metals has been determined, and also their water permeability and water absorption characteristics.

Powders based on five different types of curing agent have been examined, each varying in reactivity towards epoxy resin. The curing agent types are listed below together with the relative reactivities of the particular powders prepared, as measured at 180°C by a simple gel-time test. Full details of the powder formulations are given in Appendix I.

Table 1

Curing agents used and relative reactivities of the powders examined

System	Curing agent type	Relative reactivity of the powder measured at 180°C†
*1B**	Dicyandiamide	125
2	BF_3/Amine complex	165
3	Aromatic amine	230
4	Acid anhydride	625
5	Phenolic resin/acid catalyst	100

*Powders based on various *Epikote* resin blends were made using dicyandiamide—see Appendix I.
†Relative to the least reactive powder (No. 5) = 100.

Adhesion

A number of techniques have been described in the literature for measuring adhesion. The method used for the present studies involved a direct pull-off technique similar to the one developed by the Paint Research Station[1]. Initial trials using the latter technique showed the adhesion of the powder coatings to be beyond the upper limit of this test method.

Test method and preparation of test specimens

The principle involved was to join two mild steel cylinders of cross-sectional area 0.30 sq in with the coating, using it as an adhesive, and then to pull the cylinders apart in a *Hounsfield Tensometer*. It was not possible to use cylinders of larger cross-sectional area because measurement of bond strengths was then outside the capabilities of the *Tensometer*. A photograph of the test piece cylinders is shown in fig 1.

The machined faces of the mild steel cylinders were abraded with 0 grade emery paper, taking precaution not to deform the plane faces. They were

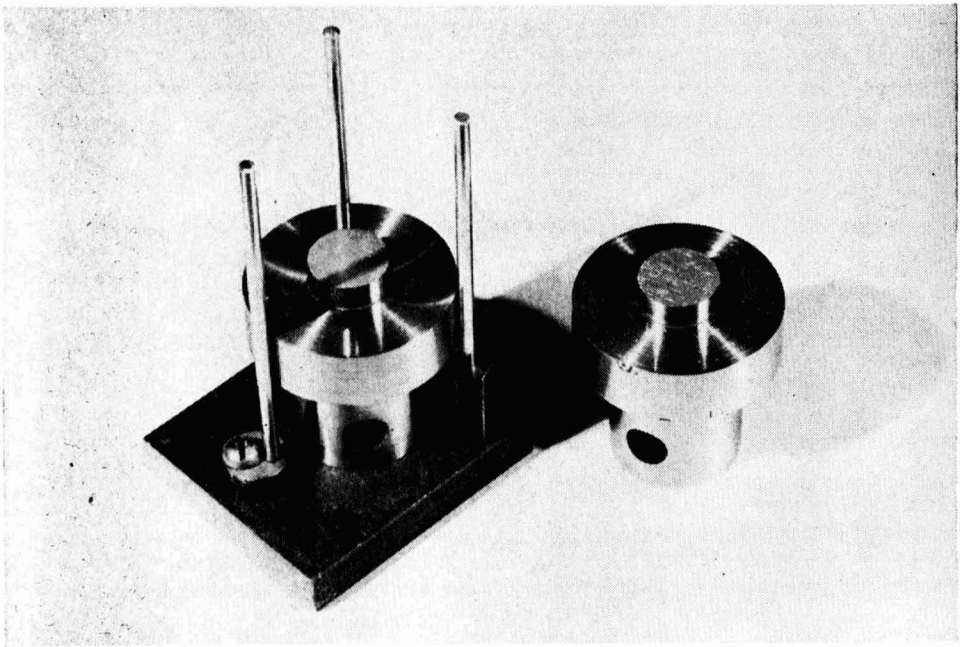

Fig 1. Mild steel cylinders and test rig used for adhesion tests.

thoroughly cleaned with 60/80 petroleum ether and then coated with powder using an electrostatic spray technique. The two cylinders were placed in an air circulating oven at a temperature corresponding to the cure temperature of the particular powder.

After allowing time for flow-out of the powder, the coated faces of the two cylinders were brought into contact by placing the blocks vertically in a jig so that the faces were aligned in a horizontal plane, cure was then allowed to proceed. No pressure other than that due to the upper cylinder was exerted on the joint. An allowance of 15 minutes in addition to the cure time quoted in Table 2 was made in all cases in order that the jig and cylinder might reach the temperature of the oven.

After the requisite cure-time, the jig was removed from the oven and allowed to cool. Excess powder which had been squeezed out from the joint was removed and the specimens were then stored overnight at 23°C and 60 per cent relative humidity before testing. They were pulled apart in the *Hounsfield Tensometer* using a cross-head speed of $\frac{1}{16}$ in per minute. The results obtained are given in Table 2 and represent the mean of four determinations. Film thickness of the powder coatings was in all cases 1-3 mil.

Minor modifications of the above technique of preparing test specimens were necessary in order to assess the bond strength of two thermoplastic powders to mild steel and a solventless liquid epoxy system to mild steel. Results are given in Table 3. They are considered to be directly comparable with the results in Table 2.

Table 2

Bond strength between various epoxy powder coatings and mild steel

System	*Epikote* resin blend	Curing agent	Stoving schedule (min/°C)	Bond strength (lb/sq in)	Type of failure
1A	1004	Dicyandiamide	30/180	12,800	Cohesive
1A	1004		30/200	12,100	Cohesive
1B	1004/1001 (25/75)		30/200	13,800	Cohesive
1C	1007/828 (70/30)		30/200	13,400	Cohesive
2	1004/1001 (25/75)	BF_3/Amine complex	30/150	7,000	Cohesive
	1004/1001 (25/75)		30/180	8,400	Cohesive/ Adhesive (50/50)
3	1004/1001 (25/75)	Aromatic amine	30/150	8,500	Adhesive
	1004/1001 (25/75)		30/180	8,200	Adhesive
4	1001	Acid anhydride	30/150	4,700	Adhesive
5	1007/828 (70/30)	Phenolic resin/ acid catalyst	30/200	11,200	Cohesive

Table 3

Bond strength between mild steel and nylon, pvc and a solventless liquid epoxy system

System	Flow-out temperature	Bond strength (lb/sq in)	Type of failure
Nylon	250°C	7,400	Adhesive
Pvc	250°C	2,100	Adhesive
Epikote 815/polyamide	30 min at 120°C[1]	8,000	Cohesive

[1]Stoving schedule.

Some further adhesion tests were carried out using different metals. The test apparatus and techniques were once again similar ; the metal under test in the form of a disc having the same cross-section as the steel cylinders was sandwiched into the test rig so that one had a mild steel/epoxy powder/metal (*M*)/epoxy powder/mild steel series of joints.

Table 4

Adhesion of epoxy powders to various metals

System	Curing agent	Stoving schedule (min/°C)	Metal	Bond strength (lb/sq in)	Type of failure
1C	Dicyandiamide	30/200	—	13,400	Cohesive (powder)
1C			Copper	13,900	Cohesive (powder)
1C			Zinc	9,900	Cohesive 65% (powder/zinc : 50%/15%) Adhesive 35%
1C			Lead	4,400	Cohesive (lead)
2	BF_3/amine	30/180	—	8,400*	Cohesive/adhesive (50/50)
2	complex		Aluminium	4,400	Adhesive

*Result taken from Table 2.

Discussion

If a paint is able to come into intimate contact with a substrate it has been suggested that values obtained for adhesion are determined by secondary bonding forces and forces associated with charge separation between atoms and molecules of the two media, i.e. Van der Waal's forces.

According to Bikerman[2] however, when a sharp boundary exists between an adherend and an adhesive, mechanical separation does not proceed along this boundary, because of the improbability of rupture following a complex predetermined path. He suggests, and has considered the probability, that if failure starts in " adhesion " it is very unlikely that failure will continue by rupture between subsequent adherend and adhesive atoms. He also states that as a general rule, if the attraction between *A* and *A* is greater than between *B* and *B*, then the attraction between *A* and *B* is weaker than the former but stronger than the latter. If this is indeed the case then the bond strength of a joint, in the absence of weak boundary layers, is mainly determined by the strength of the adhesive if rupture takes place in the adhesive film or the strength of the adherend, if this is weaker than the adhesive.

An examination of the results in Table 2 shows that cohesive failure has taken place for the two least reactive systems (see Table 1) where wetting of the substrate has probably had a good chance to occur before gelation of the film. The high bond strengths for powders *1* and *5* are of the same order as the tensile strengths normally associated with stoved epoxy resin casting systems (10-15,000 lb/sq in). The slight differences between bond strengths for the powders *1* are probably due to a combination of the different wetting abilities of the epoxy resins, which have different melting points (see Appendix 2), and the different inherent tensile strengths of these systems.

The more reactive powders, *3* and *4*, have probably begun to gel before they have had a chance to wet the substrate completely, thereby trapping air or other contaminants.

With the presence of a weak boundary layer, the propagation of rupture between adherend and adhesive (i.e. an adhesion failure) would be much more

likely to occur. It might be expected that when adhesive failure takes place, the spread on results for one particular powder would be large. However, for both systems *3* and *4*, the spread on four repeat determinations was no more than 700 lb/sq in.

The adhesive failure of nylon can be explained by its inability to thoroughly wet the substrate at the flow-out temperature used. However, this is within the recommended range for processing this powder. In the case of pvc the presence of plasticiser probably contributes towards the formation of a weak boundary layer.

The adhesion of powder *1C* to various metals (see Table 4) shows little difference between mild steel and copper. A complex type of failure took place between the powder and zinc involving both cohesive failure in the powder and in the zinc and some degree of adhesive failure. A photograph of the specimen after test is shown in Fig. 2. The result can probably be explained by the similarity in the tensile strengths of the powder and zinc. A value of 7,000-13,000 has been quoted for the latter[3]. The result of 100 per cent cohesive failure in the lead (see Fig. 3) for the lead/powder bond is hardly surprising when it is considered that the tensile strength of lead is 2,600-3,300 lb/sq in.[3]

The adhesive failure of powder *2* to aluminium can be explained by formation of a weak boundary layer by reaction between BF_3 and aluminium.

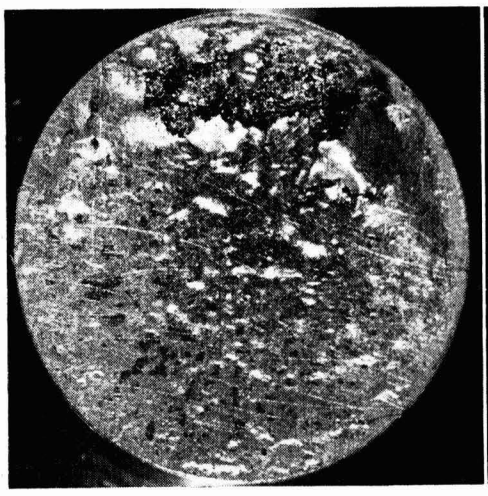

Fig. 2.

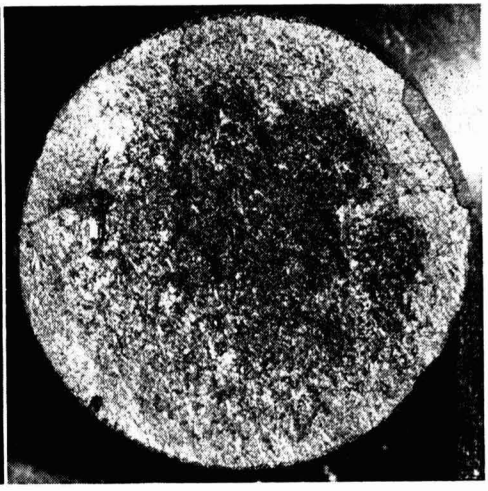

Fig. 3.

Fig. 2. Photograph of test piece showing powder coating/zinc rupture. Note that cohesive failure has taken place in both the powder layer and the zinc layer.

Fig. 3. Photograph of test piece showing 100 per cent cohesive failure in the lead layer

Water permeability

The water permeability of the epoxy powder coatings was determined by a technique which has been described elsewhere[4] ; only a brief account is given here.

Test method and preparation of specimens

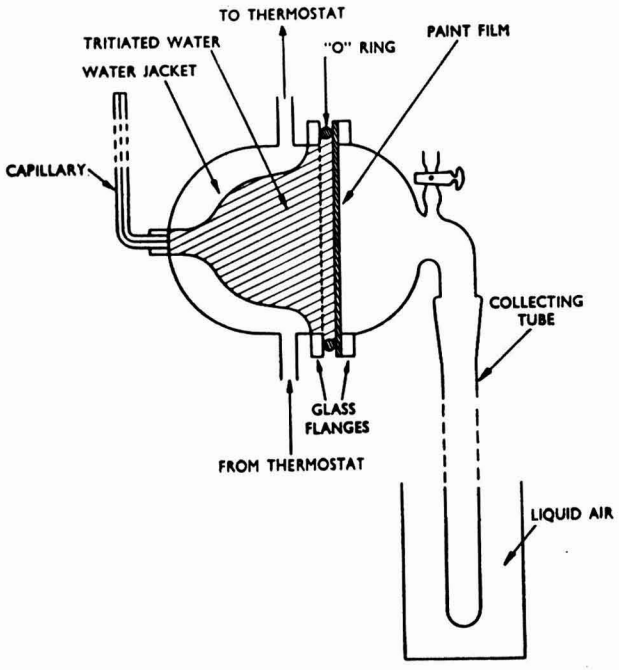

Fig. 4

In the apparatus shown in Fig. 4, tritiated water (water labelled with tritium) permeates a detached film supported vertically between two glass flanges. The tritiated water on one side of the film was kept at constant temperature (20°C) and was in contact with the atmosphere. The other side of the film was also at atmospheric pressure and was connected to a tube cooled with liquid air into which any water transferred across the film collected. The collected samples were assayed by liquid scintillation counting in a very sensitive *Packard Tricarb Liquid Scintillation Spectrometer*. Samples were collected until a steady rate of water transfer was attained. This has been found previously to depend not only on, for example, pressure but also on the type of paint film used, its thickness and the temperature of the experiment. For the data presented below, two to three weeks was found to be sufficient time to establish an equilibrium transfer rate. Film thicknesses varied between 3 and 6 mils ; previous work has shown the permeability constant to be relatively independent of film thickness above 3 mils. Below this thickness minor film imperfections are more likely, with the consequent risk of anomalous results.

Films were prepared on a tin foil substrate which was afterwards dissolved by mercury. Results in Table 5 represent the arithmetic mean of determinations carried out on three specimens.

It was thought that it would be interesting to compare the water permeability of coatings prepared from 100 per cent solids systems with that of coatings prepared from similar solvent-borne systems. Accordingly, systems *1A* and *2*

Results

Table 5

The water permeability of powder coatings

System	Curing agent	Stoving schedule (min/°C)	Water permeability constant (g cm/cm²/hr/mm Hg × 10^{10})
1A	Dicyandiamide	30/180	48
1A		30/200	56
1B		30/200	51
1C		30/200	52
2	BF_3/amine complex	30/150	57
		30/180	53
3	Aromatic amine	30/150	41
		30/180	42
4	Acid anhydride	30/150	58
5	Phenolic resin/acid catalyst	30/200	37
Nylon*			51
Pvc		250†	49

*The measurement was carried out on some supplied rolled nylon film on the manufacturer's recommendation as the production of a film free of faults from the powder proved difficult.

†Flow out temperature.

were dissolved in a glycol ether and films were prepared from these solutions using a multicoat technique to achieve the same film thicknesses as for the above test. Results are given below in Table 6 together with results for two conventional solvent-borne epoxy systems and one liquid solventless epoxy system. Once again, film thicknesses were between 75 and 150 microns.

Table 6

The water permeability of films prepared from liquid epoxy systems

System	Solvent type	Stoving schedule* (min/°C)	Water permeability (g cm/cm²/hr/mm Hg × 10^{10})
1A (dicyandiamide)	glycol ether	30/200	41
2 (BF_3/amine complex)	glycol ether	30/180	49
Epikote 1007/PF	ketone/aromatic hydrocarbon	30/200	28
Epikote 1001/ polyamide	glycol ether/ketone/ alcohol/aromatic hydrocarbon	30/120	60
Epikote 815/polyamide	—	30/120	60

*The technique used with the solvent-borne systems was to spray wet-on-wet until the required film thickness was achieved. An overnight flash-off was allowed. The films were then force dried for one hour at 50°C before stoving for the above schedules.

Finally, the water permeability constants of three non-epoxy systems were determined. The conditions for the tests were the same as for the above tests. Results are presented in Table 7.

Table 7

The water permeability of films prepared from three non epoxy systems

Type of system	Water permeability constant (g cm/cm²/hr/mm Hg × 10^{10})
Stoving synthetic ..	140
Linseed oil/phenolic	135*
Tung oil/phenolic ..	159*

*Values reported at the International Congress on Fouling and Marine Corrosion, Cannes, June 1964.

Discussion

The results obtained for the water permeability of powder coatings (Table 5) were all remarkably similar. It is considered that for the epoxy powder coatings the only differences of significance are shown by systems *3* and *5* and that it can be said that coatings of these two systems have lower water permeability than coatings of the other systems. The results in Table 6 show that systems *1A* and *2* have slightly lower permeabilities when films are prepared from solutions of the powders in a glycol ether. This might, at first, seem surprising but can possibly be explained by the fact that the solvent-borne systems are multi-coat ones and as such could contain fewer film faults. The long flash-off times which were allowed for the thick coatings and the force-dry at 50°C appear to have negated any effects which might have been due to solvent retention. It is interesting that for both the powder and solvent-borne systems, the epoxy/phenolic systems have the lowest water permeability.

It can be seen from a comparison of results in Table 7 with results in the preceding two tables that the water permeabilities of epoxy coatings, nylon and pvc are considerably lower than the water permeabilities of coatings of some of the more conventional paint systems.

Water absorption and water extractability

The water absorption and water extractability were determined for four of the epoxy powder coatings and for nylon and pvc. Tests were carried out on $\frac{1}{4}$ in thick castings having a diameter of 2 in and weighing approximately 10 g. These test specimens were adopted because the small weight changes involved made it difficult to obtain reliable data from thin films. It was found difficult to prepare specimens for powder *5* so that results were not obtained for this system.

Test procedure

Test specimens of each system (in quadruplicate) were boiled in distilled water for 24 hours. The exterior of the specimens was then dried with absorbant tissue and the weight increase was determined. They were then placed in a

vacuum oven (20 mm Hg) at 110°C and weighed periodically until constant weight was attained. For most of the systems, this was reached after 48 hours.

Table 8

Water absorption and water extractability of 10 g castings of powder systems

System	Curing Agent	Cure schedule (min/°C)	Wt increase (%) after 24 hr water boil	Water extractables (%) after 24 hr water boil	Water absorption (%) after 24 hr water boil†
1B	Dicyandiamide	30/200	4.61	Zero	4.61
2	BF_3-amine complex	30/180	3.65	0.18	3.83
3	Aromatic amine	30/180	2.64	0.24	2.88
4	Acid anhydride	30/150	2.98	0.21	3.19
Nylon		250*	1.82	Zero	1.82
Pvc		250*	2.52	1.01	3.53

*Flow out temperature for the preparation of castings.
†Sum of columns 4 and 5.

Discussion

Results for the epoxy powders show that system *1B* (dicyandiamide) has the highest water absorption (although it has zero extractables), and system *3* (aromatic amine) the lowest water absorption. The differences involved, however, are not large. Overall, nylon has the lowest water absorption ; the relatively high percentage of extractables for pvc can probably be accounted for by the presence of plasticiser.

It is interesting to note that the percentage water absorption of these systems after a 24 hour water boil is of the same order as the percentage water absorption found for a variety of air drying paint systems after a mere 24 hour immersion in distilled water at room temperature (*5*). The test method used was different from the one above but the results obtained gave percentage water absorption for an alkyd, an epoxy/polyamide, a vinyl and a urethane of 2.25, 2.10, 1.32 and 2.34 respectively.

Water and chemical resistance of epoxy powders

Fifteen mil coatings on mild steel rods of powders, *1B*, *2* and *3* (containing small amounts of pigment) have been on immersion tests at room temperature in distilled water, 20 per cent wt/wt sulphuric acid, 20 per cent wt/wt sodium hydroxide and xylene for a period of 2½ years without any deterioration taking place. Powders *4* and *5* were not included because they were not developed at the time. Tests have since been carried out on 5 mil coatings of systems *1B*, *2*, *3* and *4* on mild steel panels using reagents which are normally more aggresive towards coatings. Results are given below.

Table 9

Resistance of 5 mil coatings to reagents at room temperature

System	Curing agent	Cure schedule (min/°C)	Time to initial breakdown of coating (months)			
			20% wt/wt ammonia	10% wt/wt acetic acid	20% wt/wt nitric acid	Ethanol
1B	Dicyandiamide	30/180	6	9	6	>12
		30/200	6	9	6	>12
		30/220	6	9	6	>12
2	BF_3-amine complex	30/150	<1	>12	6	9
		30/180	<1	>12	>12	9
3	Aromatic amine	30/150	4	>12	12	>12
		30/180	6	>12	12	>12
4	Acid anhydride	30/150	<1	>12	12	>12

Immersion tests have been carried out on the same systems (5 mil coatings on mild steel panels) at 90°C.

Table 10

Resistance of 5 mil coatings to reagents at 90°C

System	Curing agent	Cure schedule (min/°C)	Time to initial breakdown of coating (hours)		
			Distilled water	5% wt/wt sulphuric acid	10% wt/wt sodium hydroxide
1B	Dicyandiamide	30/180	250	<20	110
		30/200	>250	<20	110
		30/220	>250	<20	110
2	BF_3-amine complex	30/150	<20	250	250
		30/180	<20	>250	>250
3	Aromatic amine	30/150	>250	250	>250
		30/180	>250	250	>250
4	Acid anhydride	30/150	140	>250	<20

Discussion

It does not seem possible to trace any consistent relation between the results of the water and chemical resistance tests and the properties previously measured —namely adhesion, water permeability, water extractables and water absorption. However, it should be borne in mind that as regards water resistance, immersion tests at room temperature have to date shown no differences between the systems studied, and that at 90°C values obtained for the water permeability and adhesion of the coatings would almost certainly be different from values obtained for these properties at room temperature.

There are some speculative connections which can be made, however, between the chemical resistance tests which have yielded differences to date

and the chemical type of curing agent used in each of the epoxy powder systems as the following shows.

System *4*, cured by an acid anhydride will contain many ester linkages in the final film. Correspondingly, this system shows the poorest resistance to hot caustic soda and to acqueous ammonia. On the other hand its resistance to all acids is very good and to hot water fairly good. It is known that its MEK resistance is very good and it can be considered that the particular acid anhydride used is a good cross-linking agent. The properties shown by this system are in good agreement with the properties of the numerous epoxy/anhydride systems used in applications outside the surface coatings field.

System *1* (dicyandiamide) shows approximately the opposite properties having fair to good resistance to hot caustic soda and aqueous ammonia and the worst resistance to acids. Its water resistance is very good. Unfortunately it is not possible to speculate very fruitfully on this system because the mechanism of cure is obscure. However, it is clear that the final film must contain many basic nitrogen atoms (presumably the reason for the limited acid resistance) and, according to Levine[6] it probably contains amide groups also.

System *2* (boron trifluoride-amine complex) shows very good resistance to acids which can be related to the presence of only a few basic groupings. The other results seem puzzling at first sight. Resistance to hot caustic soda is very good but to hot water, aqueous ammonia and ethanol it shows the worst resistance. It is known that the MEK resistance of these coatings stoved at the particular temperatures used is poor and this would suggest a rather limited degree of cross-linking. Again the mechanism of cure is not clearly understood though it is known that a catalytic polymerisation of the epoxy resin is involved and that the final film is linked by ether bridges. According to Landua[7] the main reaction in the solid epoxy resins, which are the ones used in this powder system, will be between epoxy and hydroxy groups.

If, as suggested above, the system is not very well cross-linked, it is possible that some thermoplastic flow takes place at 90°C giving rise to poor adhesion and consequently poor water resistance. Poor ammonia resistance could be explained if the small polar molecules were acting mainly as a solvent but if this were the case, one would expect a somewhat similar behaviour with water and this is not reflected in the results for water absorption and water permeability (see Table 8).

The general properties of system *2*, namely good chemical resistance but limited solvent resistance, are fairly similar to those of the very high molecular weight epoxy resin *Epikote OL-55*, which is normally used for coating purposes without a cross-linking agent.

Finally, system *4* (aromatic amine) shows much the best properties generally. The curing mechanism involves a simple addition of labile hydrogen atoms from the amine to epoxy groups. It is a little surprising that such a system with its many basic nitrogen groupings should show such good acid resistance. It is possible that the acid resistance is helped by effective cross-linking and by steric effects due to the proximity of the basic nitrogen groupings to the aromatic rings.

Conclusions

Studies on the adhesion of various powder coating systems to mild steel and other metals indicate that in the absence of weak boundary layers, bond strengths are determined above all by the tensile strength of the coating or the substrate depending on which is the weaker.

The water permeability constants of a variety of epoxy stoving systems, both powders and solvent-borne, are similar to each other and to nylon and pvc. Of the systems studied the epoxy/phenolic coatings have the lowest permeability. All coatings have significantly lower water permeability constants than coatings of a stoving synthetic and two drying oil/phenolic systems.

The measured properties of adhesion, water permeability, water absorption and water extractability of epoxy powder coatings do not account in any simple way for the water and chemical resistance of those coatings. Some speculative connections can be made, however, between the latter two properties and the chemical type of curing agent used in each of the epoxy powder systems.

Acknowledgments

The authors would like to thank Mr. D. W. Brooker and Mr. A. F. Flores who, along with colleagues at the Thornton Research Centre, carried out the experimental work. They would also like to thank the staff of the Paint Research Station for their help and discussions in connection with the work on adhesion.

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Appendix 1

*Composition of epoxy powder systems**

System	*Epikote* resin blend	Curing agent	Curing agent supplier	Resin : curing agent ratio
1A	1004	Dicyandiamide	Cyanamid GB Ltd.	100/5
1B	1004/1001 (25/75)			100/5
1C	1007/828 (70/30)			100/5
2	1004/1001 (25/75)	*Anchor* 1040	Anchor Chemical Co. Ltd.	100/10
3	1004/1001 (25/75)	*Anchor* 1145	Anchor Chemical Co. Ltd.	100/25
4	1001	TMX—330	R. W. Greef & Co. Ltd.	100/20
5	1007/828 (70/30)	*Pioneer* PC897/ *Anchor* 1162 (40/5)	Fredk. Boehm Ltd./ Anchor Chemical Co. Ltd.	100/40/5

*The powders used for the chemical resistance tests contained a small amount of pigment. For the other tests the powders prepared contained no pigments. All systems, however, contained a small percentage of a polyvinyl butyral resin in order to overcome the tendency of films to exhibit " cissing."

The nylon powder used was unpigmented and based on *Nylon 11*. The pvc powder was based on a medium K value polymer and was plasticized with about 40 parts of mixed phthalates to each 100 parts of pvc ; the powder also contained a small amount of pigment.

Appendix 2

The melting point/viscosity of Epikote *resins*

Epikote resin grade	Melting point (°C) (Durrans mercury method)	Viscosity (poises at 25°C)
1001	64—74	
1004	96—104	
1007	125—132	
815	Liquid	7—11
828	Liquid	100—150

Discussion

DR. K. M. OESTERLE said he had three questions. The first question was about water permeability. In their paper the authors had showed interesting differences between films of epoxy resin powder and solutions of epoxy resins in conventional solvents. They had said that the reason for the slightly lower permeability of films of solutions of the resin in the glycol ethers would be the effect of the multi-layer, but for Systems 3 and 4, *Epikote 1001*, Tables 5 and 6, showed the opposite. Dr. Oesterle said, therefore, that there were other effects in action. On one side when the glycol ether-formed film had no lower permeability, it seemed possible that there would not be less interfaces than with the film formed of powder. The powder particle was able to absorb water during the flight, giving certain interfaces.

Similar effects seemed to occur in solvent based films containing hydrophylic and hydrophobic solvents. It was possible that micelles would be formed producing film inhomoginities with partially increased water permeability. Therefore, he would suggest that the wetting effects, both effective and pseudo-wetting, must be considered, especially in pigmented systems. For example, zinc powder in epoxy-amine systems had effective wetting and blistering was possible. If the effective wetting was changed in pseudo-wetting there would immediately be electrochemical action corrosion protection of the zinc powder and the blistering disappeared.

Secondly, a question concerning adhesion. Table 2, System 1A and 3 : why was there less adhesion with higher stoving temperature ? Was there a destructive effect on the resin by the film forming process, or by the higher stoving temperature, or by the change of the surface of the substrate by the ingredients introduced by the powder ?

For his last question, Dr. Oesterle asked if the authors had observed a difference in adhesion between stoving in one step or stoving in two steps and did they have any suggestions as to the cause for possible differences.

MR. L. A. TYSALL said with regard to the first question it was suggested that multicoats would be part of the explanation for the rather better permeability. The difference was not very high and it may very well be that Dr. Oesterle's suggestions were either the real explanation or that both explanations held. There was one point he would mention : in this particular work, for simplicity, pigments had been omitted in order to avoid one complicating factor.

On the second question concerning the change of adhesion with stoving temperature, he said they did not know whether there was a reaction with the substrate. They suspected that in the case of aluminium there might be a reaction, but there was no special reason to think this was so in other cases. It was considered as being a race between flow-out of the resin and the curing reaction. It must be realised that this resin had a fairly high melting point (it had to have this otherwise the powder blocked on storage), so the resin did not, presumably, flow out rapidly. This would correlate with the general point that the faster the resin was curing the less chance it had to flow out. In fact, in the formulation of these systems it was normal procedure to add a small proportion of material such as a polyvinyl butyral resin to assist the flow-out.

Mr. Tysall said that they had not investigated any possible differences between one- and two-stage stoving, but it was a most interesting idea. It would be expected that if a flow-out period was given at a temperature at which the system was relatively not very reactive and then the temperature was raised in order to effect the cure, in principle, better contact should be obtained and therefore better adhesion. However, he was not sure that this idea would be attractive to the people who used powders, in practice, because it would add to the time, but it was certainly a possibility.

They had not said very much about the detailed methods of application, but they had tended to think in terms of electrostatic powder guns which could be used on cold surfaces. It was quite possible to use these guns on hot surfaces and then an immediate flow-out was obtained. The same principle applied in a fluidised bed where it was essential to have a hot surface.

DR. J. R. WEBER added that Dr. Oesterle's views about the lower permeability of multicoat systems as shown in Table 6 were not borne out by the polyamide curing system. There was no corresponding powder to this one, so it was not, in fact, contradictory to what had already been stated.

DR. H. W. TALEN said he also wanted to ask about the adhesion problems, but it was his intention to delve into the fundamentals of adhesion. In the method used by the authors the resin powder was cured between the surface of the steel cylinders. Although his question was partly answered in the paper when they said " no pressure other than that due to the upper cylinder was exerted on the joints," he wanted to know what this pressure was and did the authors make a systematic investigation of the results obtained by varying this pressure? He thought the final result of the adhesion tests must be influenced by the pressure exerted between the two cylinders. If the powder coating was applied either by fluidised bed or by electrostatic spraying there was practically no pressure and, therefore, the film formation was under different circumstances to those between these two cylinders, and he felt that this must influence the adhesion values. So perhaps it might be possible to investigate this influence by counterbalancing the upper cylinder or perhaps by varying systematically the pressure because, according to most theories on adhesion, the adhesion was influenced predominantly by the points where the resin or the glue was sticking to the surface and other places where it was not, and that, of course, must be influenced by the pressure. He asked if the authors would give their comments.

MR. L. A. TYSALL said the simple answer was that they did not know the effect of varying the pressure. The actual pressure was about 1½ lb per square inch,

approximately 0.1 kilograms per square centimetre, but whether this had any influence he did not know. He thought that it would be possible to put a counter weight so that there was zero pressure.

MR. D. M. JAMES said he would like to ask a question concerning the adhesion figures which related to the rheology of the coatings. Was the figure obtained in this type of test affected by the elasticity of the coating? Following on, the figures which were given in the paper would imply that at least the better of the coatings had an extremely high adhesion. Mr. James thought it was true to say that the number of times in which the consumer was concerned with directly pulling a coating off a substrate was small ; the effect of impact chipping, etc., was of more practical interest. He wondered if the authors would comment on the general mechanical properties of these films and how they might affect adhesion in a practical sense.

MR. L. A. TYSALL said that they had not, in this paper, dealt with impact adhesion. It was known that the impact adhesion of a properly formulated epoxy powder coating was very good. If one took into account the fact that one tended to use thick films, the mechanical properties that were obtained in the more conventional coating tests and certainly on impact adhesion were similar to those obtained for corresponding conventional epoxy paints at the same sort of thicknesses. Some of these were quite impressive, e.g. on the Ericson slow indentation test. Whether the mechanical properties were affected by the elasticity he did not know.

He agreed that a direct-pull test was rather a long way from the practical performance of coatings but, as mentioned at the beginning of the paper, they were trying to obtain some simple basic measurements, having performed a great deal of more or less conventional work with these paint systems.

DR. WEBER said that they did know that the slower reacting curing agents gave coatings with the best impact adhesion. In this particular series the acid anhydride cured system did have the lowest impact adhesion. This was thought not to have wetted the surface of the substrate thoroughly and this would account for the poor impact adhesion.

MR. S. V. SATHAYE asked whether any measurements had been taken of the vapour permeability, water permeability and flexibility of these films.

DR. WEBER said that they had not yet measured the water vapour permeability. However, something was known about the flexibility of these coatings. This was very much in line with the impact resistance results obtained. Very good flexibility had been obtained from the systems which were rather slow reacting. Good flexibility was not obtained from the rapidly reacting systems, in particular the acid anhydride system.

MR. P. WALKER said he thought that the figures quoted by the authors for adhesion were among the highest recorded in the literature. The only comparative figure he could recall was one of 10,000 to 12,000 for an ex-primer, determined by that rather artificial method, the ultra-centrifuge. He thought it had been suggested by Witcoff and also by Bullet that, providing the adhesion was high enough, then the corrosion resistance would be excellent, since the system would not be pushed from the substrate.

Unfortunately these initial values for adhesion were not particularly meaningful, since one was really interested in adhesion under the worse conditions, such as water soaked. In addition to the wet adhesion it was possible that it was also important to measure the relative adhesion when the system had dried out. He thought that a system of this sort, i.e. highly cross-linked which was stiff in a physical sense, was extremely unlikely to go back to the substrate once it had dried out. This would suggest that perhaps failure might occur by horizontal or lateral spread of loss of adhesion from points of damage. Had the authors in fact measured wet adhesion


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and would they confirm that the failure of the system might be in adhesion from breaks in the film?

MR. TYSALL said that they had not done these experiments, but this was the next stage of the programme. The only other comment that he would make was that he would not agree with Mr. Walker in saying that these systems were stiff. He did not know whether there was a psychological point here in seeing a pot of dry powder and feeling that it must, therefore, give a rather stiff film. These films had very good flexibility. They compared very well with almost any type of paint unless it was one which gave a very soft film indeed. Whether this meant that they would be able to be pushed off a surface under wet conditions and then return, of course, he did not know, but this they hoped to find out.

DR. E. SUNDERLAND said he would like to follow up Dr. Talen's question. The authors had said that the normal method of pull-off adhesion was unsuccessful and that they were therefore forced to use this new method where you have pressure during the curing of the films. He wanted to know what kind of gap there was between the failure of the adhesive in the normal method and the figures which were obtained in the method finally adopted.

DR. WEBER said using the normal pull-off technique they were getting failure between the powder coating and the adhesive at values of the order of 5,000 lb/sq in.

MR. D. S. NEWTON expressed a certain amount of sympathy with the authors in being unable to relate tensile strength of the films as given. He wondered whether in fact the argument had not been over-simplified and the spread that one obtained in this sort of thing forgotten. Could one obtain any information from the wideness of the adhesive strength that one could get within a system?

The other point which might be of assistance was, it had been shown over the past two or three years that tensile strengths were not normally distributed. They were in fact skew, and if one took a series of tensile strengths and obtained a mean by other methods one very often got far more meaningful results. Mr. Newton thought that this work had been published in the *Institute of Rubber Industries Journal* previously.

DR. WEBER referred to the spread of the results obtained for the adhesion and said they were getting a spread of ± 500 lb/sq in. Four repeat determinations were performed for each of the figures quoted and a mean taken.

DR. J. A. W. VAN LAAR said he had admired the meticulous way in which the authors had determined the water permeability. From page 1013 he saw there was a film on one side of which was a film of water in a liquid state and on the other side there was no vapour pressure at all. This meant that there was an equilibrium with pure water on one side and zero on the other side. He doubted if this was a condition which occurred in practice. He thought that the water permeability of the film would depend upon the equilibrium with the humidity in a certain state. He thought there would be films that had the same water permeability at a humidity of zero as at 100 per cent. He was willing to accept that these were epoxy films, but there were other films where the water permeability was 100 per cent or near to 100 per cent different at 0 per cent because the film was swollen in the first case. This could never be ascertained with the authors' method because they integrated in a manner of speaking all the different states in the film and the different equilibriums with pure water and with humidity at zero. If they performed an experiment in which one side you have, for instance, 90 per cent and on the other side 80 per cent, perhaps they would find that there were very different films that differed little in their properties with the experiments described in the paper. He wanted to stress this point because testing permeability with little difference in relative humidity on both sides of the

film was more in accord with practical circumstances, for in practice there were not always big differences in water vapour pressure.

THE CHAIRMAN said the authors felt that this question would be best answered by Dr. Wilson, who carried out the actual experiments.

DR. R. W. WILSON said they had published some of the work and he could tell the questioner where he would be able to find most of the answers. With regard to water on both sides of the film, they had performed a number of experiments with variations such as salt water on one side, fresh water on the other, water on both sides, active water on one side and not on the other, and it had been found that the water passed through the film at the same speed at a particular temperature.

MR. J. HOWARTH-WILLIAMS asked if it was possible to produce solid epoxy resin polyamide powder coatings.

MR. TYSALL said he imagined this would be extremely difficult because of the high reactivity of the polyamide resin. It would be noticed that all the curing agents that were used were, roughly speaking, inactive at room temperature. It was very difficult, for instance, to use an ordinary aliphatic amine like diethylene triamine because the reaction tended to become rather uncontrollable. They had not had very much time to explain methods of manufacture, but to put the position into perspective the most usual method of making the powders was to melt the appropriate resin blend in a Z-blade mixer at a temperature in the region of 90°C and at this temperature polyamide or aliphatic amine would be violently reactive. Hence the general choice of curing agents.

DR. WEBER thought it would be possible to make what was referred to as a B stage powder, using an epoxy polyamide system. What would be done was to mix a liquid epoxy resin with a liquid polyamide, pour the mix into a tray and let it solidify to the B stage, but he thought this type of powder would have a very short shelf life even if stored at temperatures below 0°C ; it would not be a very practical powder to use.

Allyl ethers in solventless and water-based coatings

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Summary

Allyl ethers form a basis for a range of media which dry by oxidation in air. The mechanism of this autoxidation and the properties of films of the simple allyl ethers have been studied. In comparison with drying oils the polymerisation mechanism involved in drying is more efficient, but this sometimes tends to embrittlement of the simpler products. A particular feature is the greatly reduced tendency to yellow in the absence of light.

The liquid allyl ethers may be used as reactive solvents in conjunction with conventional alkyds, forming solventless systems. Allyl ether groups may also be incorporated into water-soluble alkyds providing a basis for a new range of water thinnable air-drying and stoving media.

Les éthers d'allyle dans les enduits depourvus de solvant et a base d'eau

Résumé

Les éthers d'allyle constituent une base pour une série d'agents chimiques séchant par oxydation à l'air. Des études ont porté sur le mécanisme de cette auto-oxydation et sur les propriétés de pellicules à base d'éthers d'allyle simples. Comparé aux huiles siccatives, le mécanisme de polymérisation en cause lors de la dessication est plus efficace, mais ce degré d'efficacité tend parfois à rendre fragile les produits les plus simples. L'une des caractéristiques saillantes est la tendance à jaunir considérablement réduite en l'absence de la lumière.

Les éthers d'allyle liquides peuvent être utilisés en tant que solvants réactifs en conjonction avec des alkyds de type classique pour former des combinaisons dépourvues de solvants. Des groupes d'éthers d'allyle peuvent également être ajoutés à des alkyds solubles dans l'eau, formant ainsi une base pour une nouvelle série d'agents chimiques pour étuvage et séchage à l'air, se prêtant à la dilution dans l'eau.

Ally äther in Wasserbasierten Schichten und in Uberzügen ohne Lösungsmittel

Zusammenfassung

Allyläther bilden die Grundlage für eine Reihe von Medien, die durch Oxidierung in der Luft trocknen. Der Mechanismus dieser Selbstoxidierung und die Eigenschaften der Uberzüge der einfachen Allyläther sind untersucht worden. Im Vergleich zu trocknenden Olen handelt es sich hier um einen leistungsfähigeren Polymerisationsmechanismus. Doch neigt dieses Verfahren manchmal zur Versprödung der einfacheren Erzeugnisse. Die stark verringerte Tendenz zum Vergilben in Abwesenheit von Licht ist ein spezielles Merkmal.

Die flüssigen Allyläther können als reaktive Lösungsmittel zusammen mit herkömmlichen Alkyden eingesetzt werden und bilden so System ohne Lösungsmittel. Allyläthergruppen können ebenfalls in wasserlösliche Alkyde eingebaut werden und bilden die Grundlage für eine neue Reihe von wasserverdünnbaren, in der Luft und im Ofen trocknenden Medien.

Introduction

Autoxidation is the simplest means of curing a paint film. Although there are several systems which undergo rapid oxidation/polymerisation reactions on exposure to air, only drying oil based media have been used to any extent so far by the paint industry.

The disadvantages of the drying oil system are that the polymerisation is very inefficient because a large amount of oxygen is taken up to produce a comparatively small amount of polymerisation, and there are numerous wasteful side reactions, particularly chain scission. Furthermore, the oxidation does not cease when the film is dry, but continues slowly throughout the life of the film, causing its eventual breakdown.

Among compounds which cure to insoluble films on oxidation in air are allyl ethers ; esters of fumaric acid with ether containing polyols ; and mixed polyol esters of fumaric and tetra-hydrophthalic acids. The molecular requirements appear to be unsaturation and active methylene groups—akin to the non-conjugated drying oils.

There have been various attempts to develop special types of film-forming media incorporating allyl ethers. Allyl ethers of starch[1] and sucrose[2] have been made, but one difficulty was to introduce more than a small number of allyl groups per glucose unit, resulting in products with a high content of free hydroxyl groups. Resins of the alkyd type have been formed from allyl ethers of glycerol[3] or trimethylol propane[4] and phthalic anhydride. Allyl ether groups have been built into the polyester chain of unsaturated polyester systems to overcome inhibition of the vinyl polymerisation by air[5] and low molecular weight polyallyl ethers have been used as monomers[6].

The present paper is concerned particularly with the mechanism of autoxidation of the simpler allyl ethers and their film-forming properties in comparison with drying oil systems and the possibility of developing drying systems free of organic solvents, on the basis of allyl ether compounds. These include solventless systems and stoving and air-drying water-thinnable media. The water-thinnable media are the subject of British Patent Application 4155/63 and some foreign applications.

Film-forming properties

The autoxidation of allyl ethers has been followed by methods used in the study of drying oils. To obtain adequate air-drying properties it was necessary to use compounds containing several allyl groups per molecule ; typical compounds included sorbitol tetra-allyl ether, dipentaerythritol tetra-allyl ether and dipentaerythritol tetramethallyl ether. In comparison to natural drying oils such as linseed oil the autoxidation showed many outstanding differences, namely :

(*i*) The touch dry time was longer, but the allyl ethers eventually dried more sharply to hard, rather brittle, films. The methallyl ethers gave softer films.

(*ii*) Much less oxygen was taken up in the drying process and much less volatile scission products were formed.

(*iii*) The solvent-inextractable content of the films was much higher.

(*iv*) Cobalt catalysed the autoxidation, but lead and manganese were inhibitors.

The film properties of the allyl ethers showed some attractive features, but there were also serious disadvantages which would render them unsuitable as sole media.

The water resistance was good and not accompanied by proneness to crystalline bloom. An important property was the greater resistance to yellowing of the type promoted by atmospheric ammonia. This was good for the allyl ethers, but the methallyl ethers were almost non-yellowing.

Weaknesses were poor pigment-dispersing properties, poor wetting of substrates, leading to crawling or cissing, and, worst, rapid failure on accelerated weathering in the form of embrittlement and detachment from the substrate.

Some features can be improved in conventional ways, for example pre-oxidation by blowing with air improves wetting properties, but it is apparent that the valuable properties of the allyl groups are best utilised in combination with, or built into, more developed media.

Mechanism of autoxidation

To obtain better insight into the mechanism of drying of allyl ether systems, some aspects were examined in more detail.

In common with drying oil systems the first autoxidation step is the formation of a hydroperoxide presumably at the active methylene group.

$$CH_2{=}CH{-}CH_2{-}O{-} + O_2 \longrightarrow CH_2{=}CH{-}\underset{\displaystyle O\,O\,H}{\underset{|}{CH}}{-}O{-}$$

Probably some isomeric hydroperoxide is formed by resonance of the initial allyl radical, namely $CH_2{-}CH{=}CH{-}\underset{\displaystyle O\,O\,H}{\underset{|}{O}}{-}$

(In the linoleic system energy considerations favour almost complete production of the isomeric hydroperoxide because it is conjugated.) The development of peroxide groups in the drying allyl ether film may be followed chemically. The rise and fall typical of the drying oil system is found, the maximum with sorbitol tetra-allyl ether occurring a little before the touch dry point.

The amount of oxygen taken up by sorbitol tetra-allyl ether in the drying process is about 12 per cent, after which no further amount of oxidation is measurable, whereas with linseed oil the amount is still rising after 30 per cent has been taken up. Comparison of the oxygen uptake and the change in weight of the film gives a measure of volatile scission products evolved and these are very much less for the allyl ether. These points are illustrated in Fig. 1.

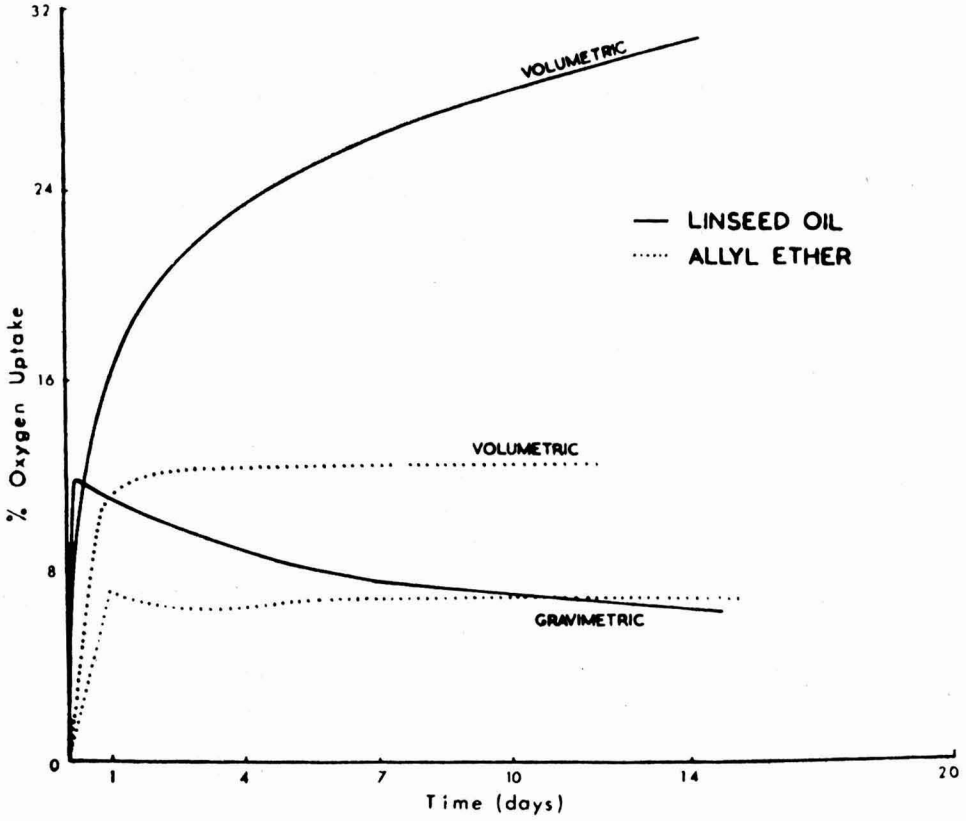
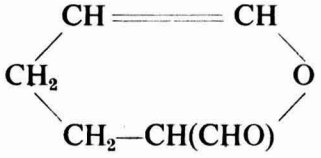


Fig. 1. Oxygen uptake of linseed oil and sorbitol tetra-allyl ether

Examination of the scission products from sorbitol tetra-allyl ether showed that the predominant product was acrolein, as would be expected from scission of the initially formed hydroperoxide. A methallyl ether gave the expected methacrolein. From the allyl ether some other breakdown products were separated by thin layer chromatography. One was probably a cyclic dimer of acrolein having a pyran ring structure



and the other was acidic.

The allyl ethers rapidly form films of high solvent inextractable content, limiting any chemical studies of the dried film.

The film-formation process can, however, be followed by infrared spectroscopy and the changes observed are shown in Fig. 2.

Unfortunately, the spectra, owing to the complexity of the oxidation products, do not give a complete picture of all the reactions occurring. The uptake of oxygen is reflected in a large increase in the carbonyl absorption at

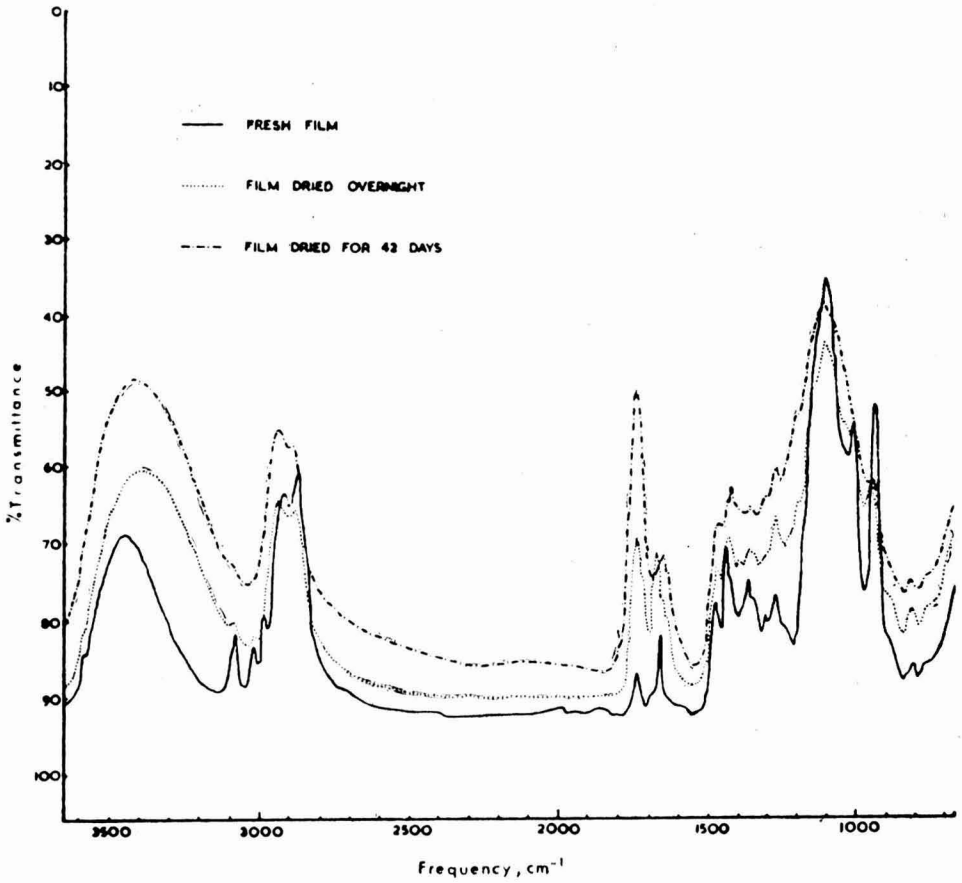
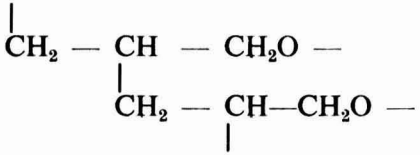


Fig. 2. Infrared spectra of films of sorbitol tetra-allyl ether

1725-1730 cm^{-1} (due to carbonyl or carboxyl groups) and an increase in hydroxyl absorption at $\sim$ 3400 cm^{-1} (due to hydroxyl or hydroperoxide groups). The absorption due to ether groups at 1090 cm^{-1} decreases slightly, but most of the ether groups appear to be retained in the oxidised film. There are complex changes in the carbon-carbon and carbon-hydrogen band absorptions, e.g. at 990, 1650 and 3100 cm^{-1}, but the general pattern shows an appreciable loss of unsaturation.

The autoxidation process undoubtedly includes polymerisation reactions involving the initially formed hydroperoxides, but the exact mechanism, as with the drying oils, is difficult to establish. Radicals formed from breakdown of the hydroperoxide (stimulated by the presence of cobalt drier) could initiate polymerisation of the allyl double bond giving polymers with the grouping



The polymer chains are likely to be very short as termination by the active methylene groups will compete with addition to other double bonds. (It is known that high polymers cannot be produced by radical polymerisation of allyl ethers.) Since the allyl ethers examined contain several allyl groups, even dimerisation of an allyl group can lead to an overall cross-linked polymer structure.

Two other features of the autoxidation are noteworthy ; of the common drier metals only cobalt is a drying accelerator, manganese and lead being inhibitors. This property is related to the oxidation-reduction potentials of the different valency states of the metals and shows that different energies are involved in the formation and decomposition of the allyl ether hydroperoxides, compared to fatty acid hydroperoxides.

The lower degree of yellowing of the oxidised allyl system, and particularly the methallyl system, in the presence of ammonia indicates that the chromophoric groups responsible for yellowing in the autoxidised drying oil system are not formed to the same extent.

Allyl ethers in solventless coatings

Although a simple pigmented linseed oil is a solventless paint, the trend to polymerised media has necessitated the presence of solvent to give suitable application properties at normal temperatures. Attempts are now being made to develop solventless coatings on the basis of modern media. The advantage of a paint in which the whole of the vehicle remains in the final film has obvious attractions. Two air-drying systems in present use are capable of meeting these requirements—the unsaturated polyester coating in which styrene is used to reduce the viscosity of the polyester and is eventually incorporated into the film by copolymerisation ; and the epoxy resin/polyamine coating using a low viscosity resin. Both these are two-pack systems of specialised applications and there is scope for a more conventional product. That is, a one-pack material capable of application to a wide range of surfaces for decorative and industrial purposes.

The requirements can be met by using a non-viscous liquid of low volatility which reacts with the medium as the film cures. The allyl ethers, which cure by an autoxidation process, are likely to interact with conventional air-drying media and have possibilities in this direction. A solventless coating should therefore be obtainable from a suitable allyl ether and drying alkyd. Some of the simple allyl ethers, as already indicated, have some useful film-forming properties, but also disadvantages. In combination with alkyds there would seem to be a good chance of obtaining combinations with a favourable balance of properties. Initial trials showed that whilst there was sometimes a tendency to slight incompatibility of the initial components, as evidenced by haziness of the initial mixture or applied film, the dried films were usually completely clear and bright, indicating a measure of copolymerisation of the components on autoxidation.

In combination with drying alkyds it is also possible to use allyl ethers not having satisfactory drying properties alone. For example, trimethylol propane diallyl ether in combination with a long oil alkyd gives films of

reasonable drying properties. In general film properties, however, such compositions have been found to be inferior to those from drying allyl ethers.

Systems which were examined in detail included combinations of sorbitol tetra-allyl ether and long oil alkyds. Comparison of the properties of some of these combinations with a 75 per cent drying oil alkyd with those of the original ether and alkyd are shown in Table 1. It can be seen that from 1 : 1 combinations, vehicles of about 10 poises could be obtained.

Table 1

Properties of sorbitol tetra-allyl ether/alkyd combinations

Material	Appearance* of liquid	Viscosity poises at 25°C	Touch dry time† (hours)	Hard dry time† (hours)	Percentage Inextractable† in benzene after four days
Sorbitol tetra-allyl ether	Clear, mobile	0.5	9	9.5	100
Alkyd (75 per cent drying oil) ..	Clear, viscous	200	3.5	6	71
2 : 1 alkyd/ether ..	Hazy	35	4	6.5	74
1 : 1 alkyd/ether ..	Rather cloudy	13	5	8	77

*Dried films were clear in all cases.
†With 0.05 per cent Co.

These media were also examined for general film properties both clear and on pigmentation with rutile TiO_2 (pigment : binder 3 : 4). Compared with the straight alkyd in hydrocarbon solvent in both clear and pigmented finishes, the combinations had a rather longer touch dry time, but gave harder films. There was an improvement in water- and alkali-resistance and a marked improvement in resistance to yellowing. The tendency to rivelling in thick films and to crystalline bloom was reduced. The durability on accelerated weathering was, however, greatly reduced, as shown by embrittlement of the clear finishes and loss of gloss of the pigmented, and these systems could be considered only for interior finishes.

Allyl ethers in water-based coatings

Media based on drying oils solubilised in volatile aqueous bases can be cured by oxidation/polymerisation reactions at stoving temperatures around 120°C to give hard, tough films. Such coatings, however, whether of the maleinised oil or alkyd type, suffer from one serious defect—that of poor initial colour due to the yellowing that takes place during the stoving process. This severe yellowing can also occur on air-drying and is the inevitable result of exposing an oxidised drying oil type of system to the vapours of nitrogenous bases present in the aqueous solution. This deterioration in colour imposes

considerable limitations on the usefulness of these materials. Good colour can be obtained in stoving systems by using water soluble non-drying alkyd/melamine resin combinations, but such two component systems often show poor storage stability partly due to the reactive nature of the melamine resin component.

In view of the reduced yellowing tendencies of allyl type compounds compared with drying oils in the presence of ammonia, as already noted, the potentialities of allyl ethers in these systems were examined.

The preparation of water soluble resins containing allyl ethers has been reported[7]. These were polyester type materials containing maleic anhydride, solubilised without the use of volatile base by employing a very large excess of polyol in the reaction mixture and cured at 200°C by the addition of potassium persulphate catalyst. The present work is concerned with base-solubilised systems that cure at much lower temperatures. A number of routes in the development of suitable alkyd type compositions have been explored, and these fall into two groups, namely (*a*) stoving and (*b*) air-drying systems.

Stoving systems

Allyl modified alkyds were examined for their suitability as stoving media based on :

(*A*) Phthalic anhydride and di- or trifunctional* allyl ethers, and

(*B*) Trimellitic anhydride and difunctional* allyl ethers.

Preparation of alkyds of both (A) *and* (B) *types* : The procedure for making allyl ether modified alkyds in the first small scale (100-200 g) experiments followed a normal fusion cooking under an atmosphere of nitrogen at an esterification temperature of 175°C. This led to products of poor colour and very high viscosity. In later experiments it was found that a higher degree of reaction could be achieved without an excess viscosity increase by using the solvent process with xylol as entraining agent. The use of solvent, however, required a short vacuum treatment (1 mm Hg at 90 to 100°C) to remove the xylol prior to dissolving the sample in aqueous base.

Type A *alkyds :* Two formulations containing phthalic anhydride were used to study the behaviour of both linear and branched systems :

Alkyd A_1	Alkyd A_2
1.25 mols α-allyl glycerol	4.0 mols dipentaerythritol triallyl ether
1.0 mols phthalic anhydride	5.0 mols phthalic anhydride

Alkyd A_1 would have approximately 18 per cent by weight of allyl groups ($CH_2=CH.CH_2$-).
Alkyd A_2 would have approximately 23 per cent by weight of allyl groups ($CH_2=CH.CH_2$-).

Provided no polymerisation of the double bonds occurred during processing, and from studies of the heat treatment of allyl ethers this was believed to be essentially true under the conditions of esterification used, alkyd A_1 would give a linear type polyester structure.

*With respect to free hydroxyl groups.

Alkyd A_2, having one three-functional component, would give rise to a normal alkyd branched structure. It was found that both alkyds could be dissolved in aqueous trimethylamine to give a 50 per cent solids solution provided the acid value of A_1 did not fall below 70 and that of A_2 not below 50. The poorer solubility of A_1 was no doubt related to its COOH distribution, which would be limited to a maximum of two per molecule due to the nature of its polyester structure.

Film properties of media : If cobalt driers were used with allyl systems stoved at 120°C for half-hour, a number of film defects were found, such as fine rivelling, discoloration. If, however, driers were omitted and the stoving period extended to 1 hour, alkyd A_1 gave rather tacky films with very poor water resistance, but A_2 produced hard, tack-free films of excellent colour, good water resistance although of rather restricted flexibility. The branched type of structure present with the original alkyd A_2 apparently gave better film properties for a comparable allyl content.

Type B *alkyds* : In this series of alkyds trimellitic anhydride was used to promote the good water solubility characteristics noted with other resins based on this material[8]. Alkyds prepared from trimellitic anhydride would build up a branched polyester structure.

The following general formulation was used :

8 mols difunctional allyl ether
2 mols adipic acid
3 mols trimellitic anhydride
(Excess hydroxyl—23 per cent)

Alkyds B_1, B_2 and B_3 were prepared using the following difunctional ethers :

(1) α-allyl glycerol
(2) Pentaerythritol diallyl ether
(3) Sorbitol tetra-allyl ether

Data on these alkyds is given in Table 2.

Table 2

Data on allyl modified trimellitic alkyds

Alkyd	Allyl ether	Acid value	Hydroxyl value	Degree of reaction* (%)	Calculated allyl content % by wt. (approx.)
B_1	α-allyl glycerol	53	118	86	19
B_2	Pentaerythritol diallyl ether	48	114	7	27
B_3	Sorbitol tetra-allyl ether	44	64	77	38

*With respect to acid groups.

Alkyds B_1, B_2 and B_3 were all soluble at 50 per cent solids in aqueous trimethylamine. The use of trimellitic anhydride enabled lower acid values to be obtained compared with the type *A* alkyds and still retaining good solubility characteristics.

Film properties of media : Some film properties of alkyds B_1, B_2 and B_3 are shown in Table 3, stoving in all cases being carried out at 120°C/1 hour.

Table 3
Film properties of alkyds B_1, B_2 and B_3

Alkyd	Appearance	MEK inextractable (%)	Flexibility (mandrel bend test)	Cold water immersion 24 hours
B_1	Good gloss and colour	84	9	No clouding, blistering or softening
B	Good gloss and very good colour	93	9	
B_3	Good gloss and colour	93	3	

These results showed that the build-up of cross-linked material in the film was quite considerable as shown by the high methyl ethyl ketone (MEK) inextractable content of the films. Increasing allyl content led to a maximum inextractable figure, but marked deterioration in the flexibility of the film occurred.

Use of β-methallyl ethers

It has been noted that films containing β-methallyl ethers were even more resistant to yellowing in the presence of ammonia than comparable allyl ether based films. Methallyl ether modified alkyds were therefore briefly examined to see whether reasonable stoving systems could be produced.

Pentaerythritol dimethallyl ether and sorbitol tetramethallyl ether were prepared and used in the general formula noted above (type *B* alkyds). Resins readily soluble in aqueous trimethylamine were obtained and those on stoving at 120°C for 1 hour produced films of excellent colour. Cross-linking was not quite so extensive as with the allyl modified systems as shown by MEK inextractable figures. This appeared to lead to a slightly softer film, since although excellent flexibility ratings could be obtained, water resistance was not so good as that found with the allyl modified types.

Storage stability of solutions

Solutions of allyl and methallyl modified alkyds in aqueous trimethylamine have been stored in a laboratory for over six months without any notable change in appearance or obvious increase in viscosity. Although no detailed studies have been carried out under different conditions of storage, this would seem to indicate that no major difficulties should be experienced in practice.

Pigmentation of allyl and methallyl modified alkyds

The pigmentation of these modified alkyds can be readily accomplished by ball milling techniques. A convenient method is to use the whole of the pigment

with half the binder, reduced to a suitable consistency, as the initial grinding charge. After milling, the remainder of the medium can be added with stirring, thinning as necessary. Hegman gauge readings of 9-10 have been obtained in laboratory ball mills by this method without difficulty using rutile titanium dioxide at a pigment/binder ratio of 0.9 : 1.

Properties of pigmented films

Although the anticipated good initial colour was obtained after stoving at 120°C/1 hour with both allyl and methallyl modified paints containing rutile titanium dioxide as the only pigment, marked inconsistencies in the gloss of the films were noted. The gloss was lost in some cases after 30 minutes' stoving and showed signs of deterioration in the worst cases after 15 minutes.

A number of factors were studied in attempts to overcome the erratic gloss of stoved films. These included the effect of different solubilising agents, grade of titanium dioxide pigment, preoxidation of allyl alkyd, use of additives, but no satisfactory remedy was found.

In many cases the poor gloss appeared to be due to the formation of a thin layer of some decomposition product in the surface of the film. One possibility is the conversion of acrolein (a known decomposition product of allyl oxidation) to polyacrolein, which could disturb the uppermost layers of the film.

Air drying systems

A survey of the allyl modified alkyds described above for stoving systems suggested that for air drying applications an alkyd based on sorbitol tetra-allyl ether had the best potentialities particularly from the point of view of speed of dry. Slight modifications were introduced into the original sorbitol tetra-allyl ether alkyd to improve flexibility, the final formulation chosen for more detailed evaluation being as follows :

Alkyd C

5 mols sorbitol tetra-allyl ether
2 mols diethylene glycol
2 mols adipic acid
3 mols trimellitic anhydride
(Excess hydroxyl—8 per cent)

This alkyd was readily prepared by the procedure noted above, an acid value of 50-55 being aimed at in order to give the alkyd the required solubility in aqueous bases.

Drying properties of alkyd C

As with non-aqueous allyl ether systems, the air drying of the water soluble allyl alkyds was adversely affected by the presence of lead and manganese metal. Drying studies were therefore restricted to the use of cobalt as catalyst, this being added in the form of the acetate.

Effect of drier concentration

The effect of cobalt drier concentration on the touch dry time of films of alkyd *C* spread at approximately 25μ thickness from 50 per cent aqueous triethylamine solutions was examined.

Although increasing cobalt content led to an apparent decrease in touch dry times, films tended to be rather soft. Also, the lower the cobalt content, the higher was the proportion of MEK inextractable material. There was some indication of embrittlement occurring with the film containing 0.5 per cent Co. It was decided that 0.1 per cent Co gave the best compromise and this level of Co was used in subsequent work.

Effect of type of solubilising agent

The effect on touch dry time of solubilising the alkyd in a number of different bases was examined. In all cases a 50 per cent solids solution was used with 0.1 per cent cobalt (in the form of acetate) added as catalyst. A solution of the alkyd in solvent (no base added) was also included for comparison. A film thickness of $\simeq 25\mu$ was used throughout. Results are given in Table 4.

Table 4

Effect of type of solubilising agent on drying of alkyd C (0.1 per cent Co added as drier)

System	Solubilising agent	Touch dry time (hours)	Condition after seven days
Alkyd *C*	Ammonia	>8<16	Tack free
Alkyd *C*	Trimethylamine	3	Tack free
Alkyd *C*	Triethylamine	3	Tack free
Alkyd *C*	2-dimethylamine ethanol	5½	Tack free
Alkyd *C*	2-methyl 2-amino 1-propanol	≃72	Slight tack
Alkyd *C*	Triethanolamine	>72	Very tacky
Alkyd *C* in xylol/butanol	—	2½	Tack free

Although the high volatility of ammonia might be expected to give a fast drying speed, this was clearly not the case as presumably the cobalt became inactivated in complex reaction with free ammonia or ammonium salts. The slow drying of the 2-methyl 2-amino 1-propanol solubilised system could possibly be attributed to the presence of the primary amine group which acted as a temporary antioxidant. The extended drying period of the solution containing triethanolamine was presumably caused by the relatively low volatility of this base. Tertiary bases of high volatility gave the shortest touch dry times, these being comparable to that of the alkyd dissolved in an organic solvent mixture.

Properties of pigmented films

Pigmentation of alkyd *C* could be readily carried out by the method described above. Thus, using rutile titanium dioxide at a pigmentation of 0.9 : 1, a paint was prepared with trimethylamine as solubilising base and 0.1 per cent Co

as drier. Films ($\simeq 25\mu$) of this paint had touch dry times of $2\frac{1}{2}$-3 hours (i.e. about the same as the clear medium), gloss of >90 per cent (PRS 45° Glossmeter) and excellent initial colour. A characteristic of the film was the rapid attainment of a tack-free condition, this being quicker than a normal long oil pentaerythritol type alkyd.

Simple immersion tests in cold water, however, showed that both clear and pigmented films of this alkyd blistered severely within a few hours. The films only partially recovered on drying out and also tended to become very brittle.

Further work on the use of allyl ethers in air drying water finishes was therefore concerned with attempts to improve the water susceptibility of the dried film.

Factors affecting water resistance of air-dried allyl alkyds

The susceptibility to blistering and embrittlement of allyl modified air drying alkyds on immersion could arise from the following factors :

(*a*) High residual base content in the film giving rise to a large proportion of water sensitive material, even after several days' air drying,

(*b*) The presence of significant amounts of low molecular weight material in the original alkyd of an extremely water sensitive nature, and

(*c*) The nature of the polymer film, which will be high in ester and ether content, low in long hydrocarbon chain, and containing an appreciable proportion of polar groups formed in the oxidation/polymerisation reaction.

These three possibilities were studied in the following manner :

(*a*) (*i*) Measurement of the rate of loss of base from a trimethylamine solubilised alkyd film at room temperature,

(*ii*) Vacuum treatment and force drying of the allyl alkyd film to help removal of base, and

(*iii*) Elimination of base altogether by using xylol/butanol as solvent mixture,

(*b*) Fractionation of the original allyl alkyd to remove a proportion of the low molecular weight components to see whether this greatly improved the film properties of the remainder,

(*c*) Modifying the structure of the basic allyl alkyd.

Results

Rate of loss of base : Nitrogen determinations carried out on films of alkyd *C* dissolved in aqueous trimethylamine and aged for varying periods in the laboratory were as shown in Table 5.

After reaching the touch dry state it would appear that the rate of release of the trimethylamine was very slow. The results suggested that a relatively large proportion of base would be retained in the film which could give rise to water sensitive material.

Table 5

Nitrogen content of drying film

Sample	Percentage N (on solids)	Percentage original nitrogen lost
Original solution	1.4	—
Film (touch dry 3 hours)	0.98	30
Film (dried 6 hours)	0.98	30
Film (dried 24 hours)	0.92	34.5
Film (dried 48 hours)	0.90	36

Effects of vacuum treatment and force drying for short periods : Films of alkyd *C*+0.1 per cent Co were placed under vacuum for periods up to 2 hours and then allowed to air dry in the normal way.

Similar films were force dried at 60-70°C for periods up to 2 hours and then allowed to age at room temperature.

Immersion tests carried out after a seven-day ageing period showed that both treatments led to a very small improvement in water susceptibility, mainly in a slight reduction in blister size.

Elimination of volatile base : Solutions of alkyd *C* in MEK and xylol/butanol containing 0.1 per cent Co were used to prepare films for immersion tests in the absence of base.

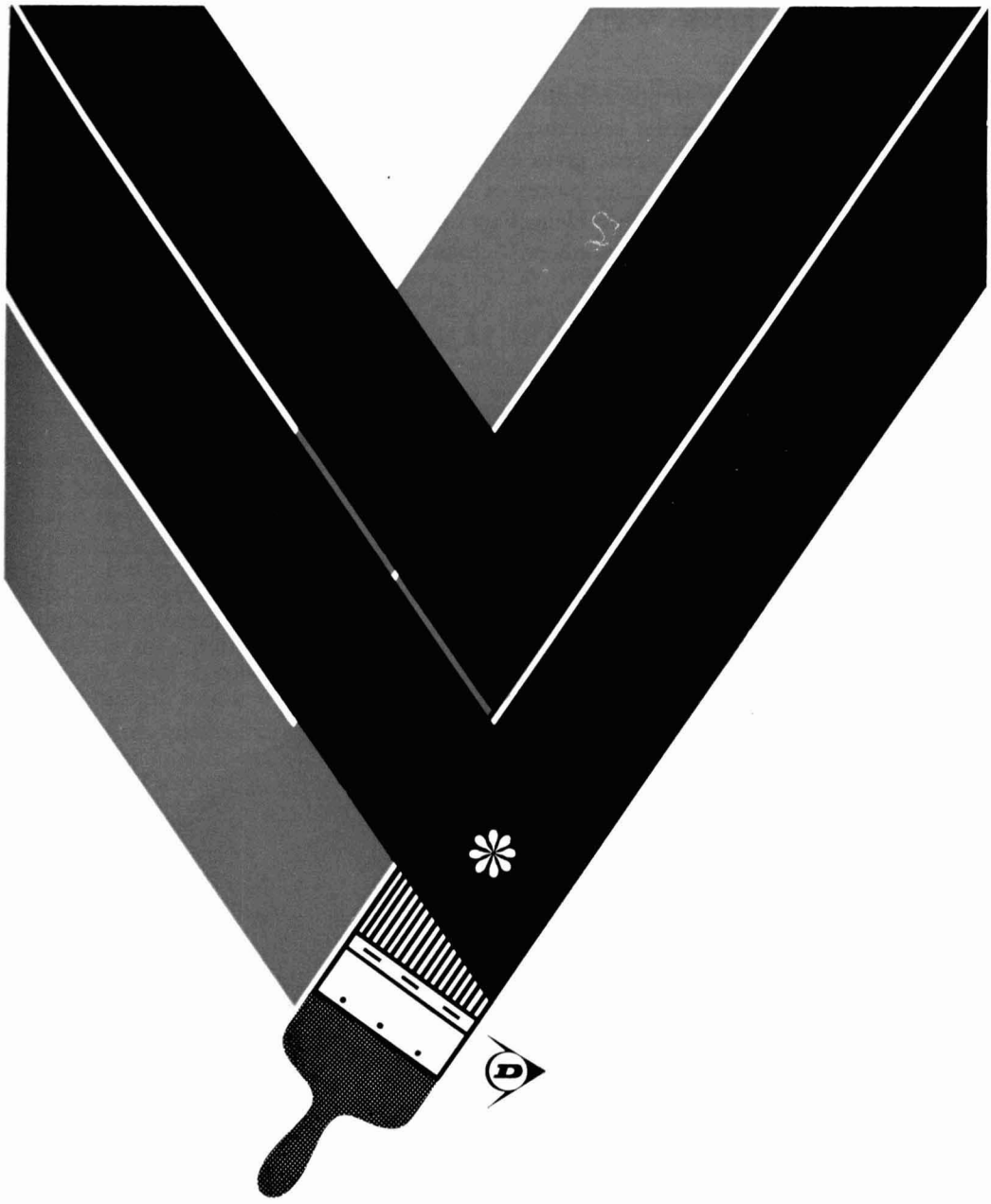
The results showed that even in the absence of solubilising base, considerable blistering was obtained. This indicated that either the type of polymer network structure produced in the allyl alkyd film was intrinsically of a water sensitive type, or the original alkyd contained an exceptionally high proportion of low molecular weight non-convertible components.

Removal of low molecular weight components

Allyl alkyd *C* was subdivided into lower and higher molecular weight components by using a petroleum ether/acetone solvent fractionation technique. The higher molecular weight material was dissolved in aqueous trimethylamine and diluted with water/isopropanol. Films of this solution still showed a marked tendency to blistering on immersion in cold water. This supported the suggestion above that the network structure itself obtained from this allyl alkyd on oxidation at room temperature was particularly sensitive to water.

Variations in alkyd structure

There are many possible ways of altering the structure of the original alkyd ; the nature and amounts of the acid, alcohol or allyl ether components may all be varied. Often improvement in properties such as water-resistance is accompanied by drawbacks such as slower drying. Nevertheless some of the resins produced so far are very promising (as the basis of water-thinnable decorative gloss paints) and this field is under investigation at the present time.



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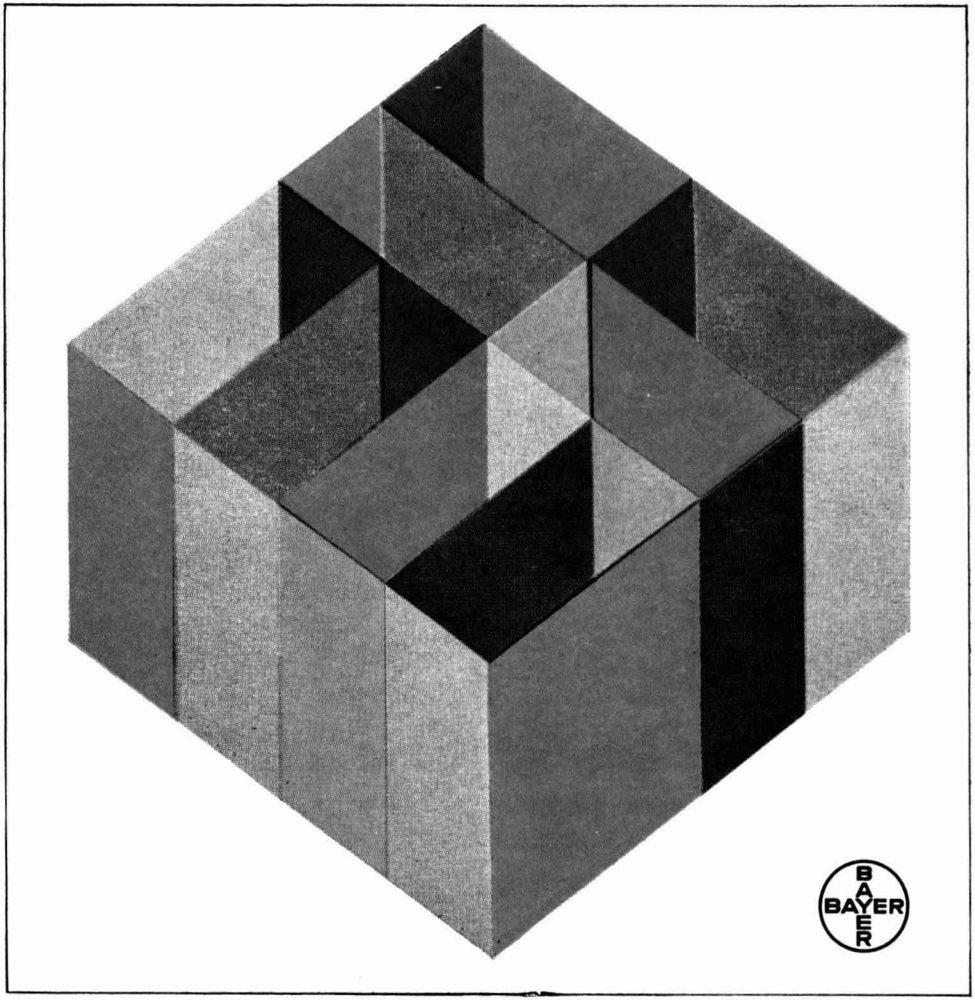

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Discussion

DR. E. SUNDERLAND said he would like to welcome this paper, quite apart from its intrinsic merit, as evidence that the Paint Research Station was being allowed to do the kind of work it should have been doing years ago, i.e. developing new types of binder for the benefit of the industry as a whole. Dr. Sunderland thought the basic allyl derivatives were produced commercially in the mid-'thirties—he had gallon samples of allyl alcohol and allyl chloride before the war—and the potential drying property of the allyl radical was also known at this time. However, during 30 years no individual paint company had developed media with drying properties based on the allyl radical, and it was certainly time something was done about it.

There were two questions he would like to raise on the content of the paper. First, since one of the objectives of the work was to produce alkyd type resins having sufficient residual acidity to give solubility in aqueous bases, why were formulations used having an excess, in most cases a large excess, of hydroxyl ? By choosing such formulations only low degrees of reaction could be used if a high acid value was to be maintained. It seemed to be more than likely that some of the deficiencies of the products were associated with these low degrees of reaction.

Secondly, concerning the inconsistencies in the gloss of the stoving enamels, he asked if any investigation of the topography of the surfaces of these films were made. Direct observation of white enamel surfaces was rather difficult, but he had had success with a very simple replica method which was a modification of a technique due to the late Courtney Bryson. Examination of alkyd-melamine finishes which were giving inconsistent gloss revealed the cause as the formation of very small Bénard cells, which had disintegrated to varying extents and in different ways before they were frozen by film gelation.

MR. R. A. BRETT said it was generally found that water soluble alkyds were easier to prepare and had better solution properties if there was excess hydroxyl present. Making an alkyd the " other way round " with an acid excess usually meant that one had to leave more unreacted acid groups in the alkyd to achieve water solubility. This would certainly be undesirable from the point of view of alkali resistance, but he agreed that too much excess hydroxyl would also be undesirable from the point of view of general water sensitivity. It should be noted that with the air drying alkyd, alkyd *C* in the paper, the hydroxyl excess was reduced 8 per cent.

Mr. Brett said that they had not used the microtopographic technique Dr. Sunderland had suggested. There had been, however, one curious feature about this loss of gloss, and that was that in some cases one could wipe off what seemed like a deposit from the surface of the film, and underneath the gloss was reasonable. It was felt that

possibly the acrolein which was evolved as part of the oxidation breakdown products had polymerised while in the top layers of the film producing a kind of surface bloom.

One obvious way of deciding whether it was acrolein polymerisation would be to analyse the surface of the film to see if the product could be identified, but this problem of loss of gloss had not been investigated too closely, because the authors were more interested in the development of the air drying types described in the paper, which did not normally suffer from poor initial gloss.

DR. A. W. DE R. VAN STEVENINCK said he would like to ask three questions and he apologised for reverting to the gloss problem. He asked if the authors had noticed any crude correlation between the degree of poor gloss and the allyl ether content in the binder.

MR. R. A. BRETT said that they had not noticed any correlation and that in fact the gloss had been very erratic for on one or two occasions quite a good gloss was obtained.

DR. A. W. DE R. VAN STEVENINCK said his second question was what would be the optimum allyl ether content needed of the water soluble stoving medium in order to get good overall properties ? Binders had been mentioned which contained various amounts of allyl ether content, but he wondered whether the authors had looked at what the optimum allyl ether content was.

MR. R. A. BRETT referred to Table 2 in the paper, in which it would be noticed that three different types of alkyds were mentioned, and he suggested that the optimum lay somewhere in the middle of the three at about 27 per cent. It could be seen that the last one, with an alkyd content of 38 per cent, gave very poor flexibility, for the film was clearly far too brittle, and he thought that the lower figure, of 19 per cent, gave a rather poorly cured film, so he suggested that about 27 per cent would be the nearest for optimum properties.

DR. A. W. DE R. VAN STEVENINCK said his third question concerned the mechanism of curing shown on page 1029. Dr. van Steveninck said that when the oxygen-oxygen bond in the hydroperoxide formed by the reaction of the allyl ether with oxygen was broken a radical was left which could either break away from the molecule and form acrolein, as had been shown, or it could eject a hydrogen atom, and thus the original allyl ether would be converted to an ester of acrylic acid. In view of the context of the next lecture by Dr. Hochberg, he asked whether the authors had been able to demonstrate the presence of acrylic esters during the drying process.

MR. R. A. BRETT agreed that it seemed a reasonable idea and they had in fact looked for acrylic groups by an infrared technique, but had not found evidence for any significant amount.

MR. F. ARMITAGE first congratulated the Paint Research Station on entering this field of development work, which might lead to valuable new products in the industry, and certainly from Dr. O'Neill's standpoint he thought one of the most important products that the paint industry could look for, certainly in the decorative field, was a water-based gloss drying paint.

Mr. Armitage said that when Dr. O'Neill had suggested the most serious competitor was maleinised oil, he thought he had overlooked the work that had been done eight or nine years ago on polyethylene glycol modified alkyds. Mr. Armitage said that he had noticed only the previous week British patents from an American company who were continuing this work on the use of polyethylene glycol alkyds, and they had claimed that they had finally achieved a good flow and 95 per cent gloss, which previously had been a difficulty with this particular type of product.

He thought that perhaps Dr. O'Neill might have overlooked the work that had been done on straight chain emulsions. At the last OCCA Exhibition there had been

one or two very good examples and he thought this was a field where interesting work might be carried out to produce the same type of product. In this connection one must have in mind the possibility that a straight chain polymer accepting a modified alkyd was likely to give better outside durability.

Dr. O'Neill had said that one of the weaknesses of the natural drying oil systems was that from the moment they had begun oxidising they were also degrading, and the polymerised oil, as was known, only had a life of two years at the limit.

Perhaps it might have been possible for the speakers to have formed a theory as to what kind of durability they would expect from a polymer which depended on oxygen intake through allyl ether groups, i.e. had they any comments about the theoretical resistance to break down an exterior exposure as compared with a film which took up oxygen through vinyl groups.

Mr. Armitage suggested that perhaps it might have been a good idea to have made up a substance similar in structure to a natural drying oil, except that either groups were involved. Does the percentage and mechanism of oxygen uptake by the allyl ether radical allow one to anticipate the rate and type of ultimate breakdown on exposure as compared with a natural drying oil ?

DR. O'NEILL said that his remark that the only competitor was the maleinised oil system referred to gloss paints based on water soluble resins. There were two routes to make a water-based gloss system, either the solution route or the emulsion route ; the Paint Research Station was working upon both lines. The problem with a water soluble system was that one had to obtain a system that cured thoroughly and also gave adequate mechanical properties and with an emulsion system to obtain adequate gloss. It was still very open as to which of the two routes was the better, or whether it might perhaps be a combination of the two.

Dr. O'Neill said he was worried about answering the question on durability for in the reaction between linseed oil and oxygen there was so much resulting breakdown one would not expect a great durability. Volatile and water soluble compounds were being formed for months after the film had been laid down, yet the durability was better than that of other systems in which the rate of formation of these compounds was negligible.

MR. A. R. H. TAWN said that he believed it was well known that the allyl radical was highly resonance stabilised. Could it be supposed that the hydroperoxy radical derived from it was similarly stabilised, because this would seem to be the case in view of the relative inactivity of some of the " drier metals " such as lead and manganese ?

Following that point, he said that if this were the case it would seem a little difficult to reconcile a relatively highly stabilised radical with the very high conversion to cross-linked polymer which was reported for in the tetra-allyl ether, as 100 per cent inextractable.

Mr. Tawn said he believed it was Zettlemoyer who suggested the use of certain complexing agents such as *o* phenanthroline to enhance the performance of driers such as lead and manganese, and it was alleged that this was due to a change in redox potential, bringing it into line with that of cobalt. Had the authors examined the use of such complexing agents and had they found that these agents upgraded the drying performance of lead and manganese in that manner ?

MR. BRETT said it was rather unfortunate that lead and manganese did not act as driers in these systems, and in fact current work was being performed at the Research Station on the use of the sort of complexing agents that had just been mentioned, i.e. the phenanthroline type. The main aim, however, was really to obtain good drying with an ammonia solubilised allyl alkyd, the use of a tertiary base, such as trimethylamine, being undesirable because of its unpleasant smell.

Unfortunately cobalt was not effective in the presence of ammonia, but it was hoped that cobalt, manganese or some other drier metal in the presence of complexing agents would give a reasonable drying time when ammonia was present.

DR. O'NEILL said that the autoxidation mechanism proceeded in the presence of cobalt and it was not understood why it did not with other metals. The manganese/phenanthroline complex did not work with allyl ether as it did with drying oil system.

DR. B. FRANIC referred to this matter of gloss to suggest something he had experienced in stoving in particular with acrylic alkyd finishes. After or during drying there was loss of gloss. These conditions could be partially corrected by solvents and by including much better resins. It was curious that the same situation had been found in these allyl ether alkyds and it was realised that the cause might not have been poor wetting as was first thought but flocculation of the pigment. He felt that there was something similar in the stoving of these compounds.

MR. BRETT said that they had evidence in some cases that flocculation was occurring and there was sometimes a problem in maintaining good pigment dispersion in these systems. There was something in what the speaker had just said in explaining the poor gloss in some of these systems.

MR. C. R. PYE referred to the solventless alkyd combinations that were mentioned in the paper, and he wanted to ask the authors whether they had obtained any information with regard to the flexibility, the gloss and particularly properties such as the vapour permeability.

He also asked whether any work had been performed in combining the allyl ethers with medium oil alkyds as opposed to the 75 per cent long oil alkyds.

DR. O'NEILL said the gloss gave no trouble, but the flexibility was certainly not as good as was hoped. The main weakness was the loss of flexibility on ageing. No measurements of permeability had yet been made on these systems.

The difficulty of using medium oil length alkyds was that they were of too high viscosity and to make a solventless finish one needed to start with a fairly low viscosity alkyd.

The chemistry of the vinyl cyclic acetals and their air drying reactions

By S. Hochberg

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Summary

The cyclic acetals from acrolein and glycols absorb oxygen, particularly in the presence of cobalt, and go through a series of reactions which results in polymers. Polyfunctional compounds containing acetals result in cross-linked films. The reactions leading to film formation and the nature of the polymer are discussed.

Modifications of drying characteristics are brought about by changes in environment and by changes in the molecule to which the cyclic acetal is attached. The nature of these modifications is discussed.

La chimie des acetals cycliques de vinyle et leurs réactions au séchage à l'air

Résumé

Les acétals cycliques provenant de l'acroléine et des glycols obsorbent de l'oxygène, spécialement lorsqu'ils sont en présence de cobalt ; de plus, ils subissent une série de réactions aboutissant à la formation de polymères. Les composés polyfonctionnels contenant des acétals se transforment en pellicules " hybridées." Cet article commente les réactions aboutissant à la formation des pellicules et décrit la nature des polymères.

Les modifications des propriétés siccatives sont déterminées par des changements intervenant dans le milieu ambiant et dans la molécule à laquelle l'acétal cyclique est combiné. Divers commentaires sont donnés quant à la nature de ces modifications.

Die chemischen Eigenschaften von zyklischen Vinylacetaten und ihre Reaktion beim Trocknen an der Luft

Zusammenfassung

Die zyklischen Acetale des Acroleins und der Glykole nehmen Sauerstoff auf—vor allem bei Anwesenheit von Kobalt—und machen verschiedene Reaktionen durch, bei denen schliesslich Polymere entstehen. Verbindungen, die Acetale enthalten und die mehrfach reagieren, fuehren zu querverbundenen Filmen. Es werden die Reaktionen fuer die Filmbildung beschrieben, sowie die Eigenschaften der entstehenden Polymere.

Die Trocknungscharakteristik werden durch Veraenderung der Umgebung und der Molekuele, mit denen das zyklische Acetal verbunden ist, modifiziert. Diese Veraenderungen werden beschrieben.

The place of the vinyl dioxolanes in the technology of finishes

The vinyl cyclic acetals were developed at the Fabrics and Finishes Department of Du Pont into a series of new paint vehicles which generally required little or no solvent and are therefore appropriate to the theme of this conference. However, the vehicles have not been made available commercially. In their

tests they failed, perhaps temporarily, to provide the cost-property-volume balance required for a successful commercial venture. Nevertheless, the observations and the science developed in the course of the research on the vinyl cyclic acetals, and in particular on the 2-vinyl 1,3-dioxolanes, might well be interesting to many who are working on solventless finishes, drying oils, free-radical reactions, polymerisation and many other allied subjects.

The vinyl cyclic acetals react with oxygen under appropriate conditions to cause a proliferation of chemical bonds and a change from liquid to solid. They have the same function in finishes as the unsaturated fatty acids of drying oils, but with a somewhat different property balance.

The structure of vinyl dioxolanes

The 2-vinyl 1,3 dioxolanes, the acetals of greatest interest, have the structure shown in Fig. 1. The important features of this structure are the vinyl double bond, the two acetal oxygens, and the hydrogen atom attached to the central carbon atom of the 5-membered dioxolane ring.

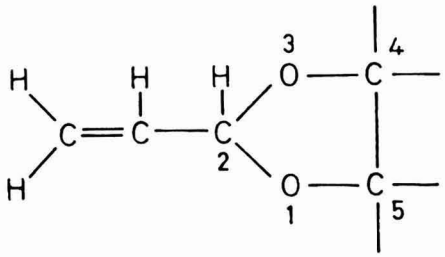


Fig. 1. 2-vinyl 1, 3-dioxolane

The acetal oxygen atoms and the vinyl double bond combine to make the hydrogen atom attached to the central carbon easily removable. There is independent evidence for the weakness of the H-C bond in this position. In the mass spectrograph, atoms of a gas are bombarded with electrons so that electrons, usually one electron, are removed. Often the molecule is disrupted into many fragments by the energy of the bombarding electrons, but generally there will be many molecules which have lost only an electron, retaining the mass of the parent molecule. Under similar conditions acetals, both linear and cyclic, always lose at least one hydrogen atom and a positively charged molecule of unchanged mass is never found. The removal of a hydrogen atom is also exemplified in the reaction of Fig. 2 in which a free radical causes the transfer of a proton from the dioxolane to the unsaturated ester.

Preparation of vinyl cyclic acetals

The 2-alkyl 1,3 dioxolanes are usually prepared by the reaction of an aldehyde with a glycol containing two hydroxyl groups on adjacent carbon atoms. If the hydroxyl groups are on carbons separated from each other by one carbon, then 2-alkyl 1,3 dioxanes result as in Fig. 3. The reaction of aldehydes with glycols requires a strong acid catalyst and is reversible ; aromatic aldehydes react similarly.

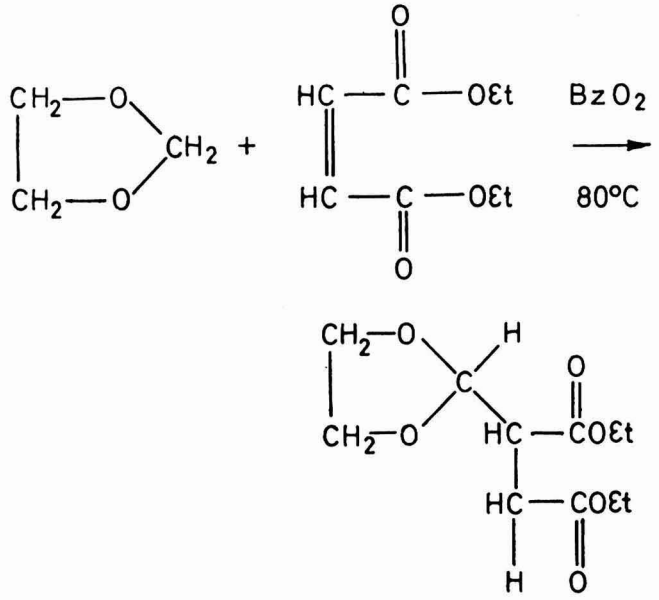


Fig. 2

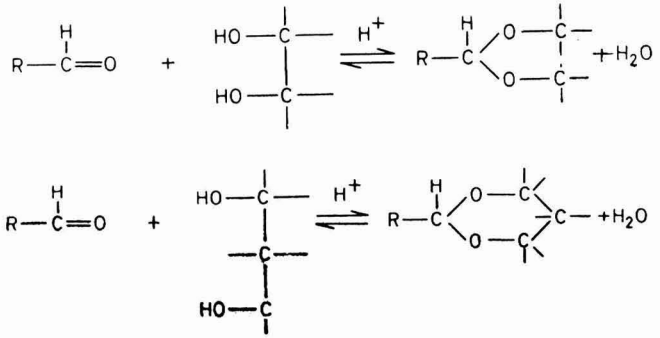


Fig. 3. (Top) 2-alkyl 1,3-dioxolane. (Bottom) 2-alkyl 1,3-dioxane

When the aldehyde used is acrolein, a 2-vinyl 1,3-dioxolane is produced. Water is removed to drive the reaction to high conversion. There are several possible side reactions, for example, the addition of hydroxyl across the vinyl double bond. However, yields of the 2-vinyl 1,3 dioxolane can be 90 per cent or more if temperature and catalyst concentration are properly controlled.

If the molecule to which the acrolein is attached contains functional groups other than the two neighbouring hydroxyl groups these extra groups may be used for the preparation of compounds containing more than one 2-vinyl 1,3 dioxolane group per molecule. In general such compounds, with 2 or more vinyl dioxolane groups, are desired for film formation.

Preparation of vinyl cyclic acetal alcohols

The most useful 2-vinyl 1,3 dioxolane derivative found was that prepared from acrolein and 1,2,6 hexanetriol. After the condensation to yield the cyclic

acetal, the product, primary alcohol containing a cyclic acetal Fig. 4 can be distilled. The alcohol can then be used for the formation of molecules with a plurality of cyclic acetal groups.

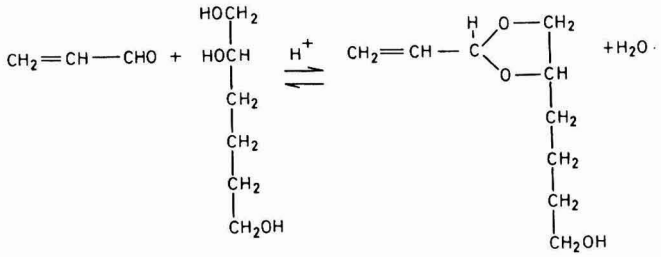


Fig. 4. Preparation of V-54 alcohol

A scheme for naming the reaction products of aldehydes with triols was adopted and is illustrated by the name for the acetal of Fig. 4. *V* stands for vinyl, *5* stands for the number of elements in the ring and *4* stands for the length of the carbon chain attached to the ring.

As a further illustration, the reaction of glycerin with acrolein yields a mixture of *V-51* and *V-60* alcohols as in Fig. 5.

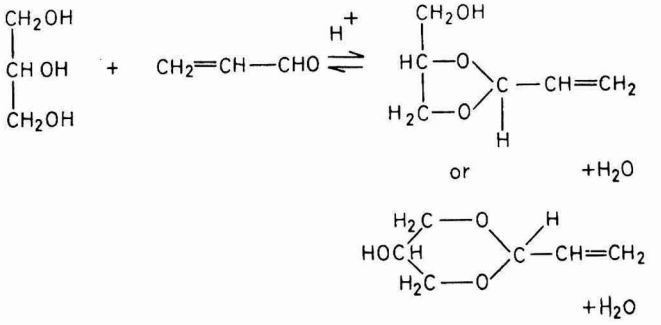


Fig. 5. Reaction of glycerine with acrolein to form (top) V-51 alcohol and (bottom) V-60 alcohol

Preparation of simple esters from vinyl cyclic acetal alcohols

While the acetal ring is reactive under acidic conditions it is quite stable under alkaline conditions. The same is true of the vinyl double bond. If the *V-54* alcohol is to be used to make an ester the ester must be made under alkaline conditions. The alcohol interchange process, whereby *V-54* alcohol is reacted with a methyl ester to yield methanol and a *V-54* ester, has been used for the preparation of a large variety of esters. Alkaline catalysts, like litharge or sodium methoxide, are effective in producing acceptable rates of reaction.

The preparation scheme is applicable to a wide range of esters made in turn from a wide range of aldehydes, polyols and methyl esters as indicated in Table 1.

Table 1

Examples of raw materials for vinyl cyclic acetal esters

Aldehydes	Triols	Esters
Acrolein	Glycerin	Dimethyl phthalates
Methacrolein	1, 2, 4-butanetriol	Dimethyl succinate
Crotonaldehyde	1, 2, 6-hexanetriol	Dimethyl adipate
Cinnamaldehyde	Trimethylolethane Trimethylolpropane	Dimethyl sebacate Dimethyl fumarate Dimethyl itaconate
		Methyl benzoate
		Methyl pelargonate
		Tetramethyl pyromellitate

Preparation of compounds with many vinyl dioxolane groups

The preparation of polymers containing many vinyl dioxolane groups per molecule can be accomplished by alcohol interchange with a polymeric methyl or ethyl acrylate, as in the case of the simpler esters, or by vinyl polymerisation of a vinyl dioxolane methacrylate or itaconate through the methacrylate or itaconate groups.

The free radical polymerisation of a *V-54* acrylate or methacrylate results in cross-linking because of the tendency, though weak, of the vinyl dioxolane to take part in the vinyl polymerisation. The slight tendency to cross-link may be overcome by chain transfer agents like carbon tetrachloride.

Other similar air-drying compounds

During the course of development of the vinyl cyclic acetals a large number of compounds were examined which had structures similar in some ways to those of the vinyl cyclic acetals. Their properties are instructive in connection with the vinyl cyclic acetals. Table 2 gives some of these properties. Note that the presence in the molecule of a free-radical self-propagating vinyl group like methacrylate or itaconate results in unstable systems. Note, also the presence of the allyl ether groups and tertiary hydrogen. Note that the structures 7, 8 and 9 allow rapid air dry and yet are quite stable. The choice between structures like 7, 8 and 9 was made partly on economic grounds and partly on the basis of small differences in properties.

The effect of ring size in the cyclic acetals was studied by oxygen absorption for a set of 2-vinyl 1,3 cyclic acetals containing respectively 5, 6, 7 and 8 membered rings. The rates are given in Table 3, from which it can be seen that the rate is greatest for the five-membered ring.

Table 2
Air drying compounds

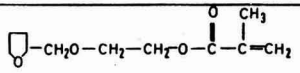
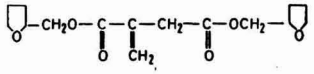
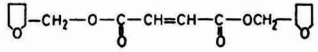
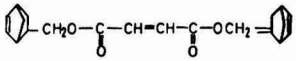
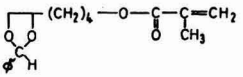
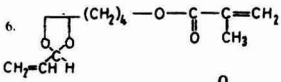
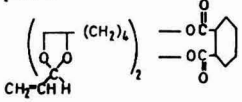
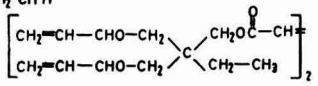
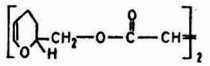
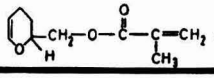
Compound	Mols O_2 absorbed per mol compound per hr.	Mol Wt.	Stability Gel	Dry Time Days
1. 	0.15	214	2 hrs.	1
2. 	—	299	7 days	2
3. 	0.05	285	> 6 mos.	2
4. 	0.016	328	6 mos.	4
5. 	—	290	7 days	2 (tacky)
6. 	.11	198	2 days	1
7. 	—	475	> 1 yr.	0.4
8. 	—	460	> 1 yr.	0.4
9. 	—	208	> 1 yr.	0.2
10. 	—	182	1 day	1 day

Table 3
Oxygen absorbed per minute per mol of 2-vinyl 1,3 cyclic acetals as a function of ring size

No. of atoms in ring	cc oxygen/min
5	0.20
6	0.065
7	0.05
8	0.02

The effect of the substituent on the central carbon atom is shown in Table 4. It is observed that the phenyl group is the most active in absorbing oxygen, however, it cannot participate later in film formation. As between the vinyl and the isopropenyl group, the greater availability of acrolein as compared with methacrolein and the greater reactivity of the acrolein derivative favoured the adoption of the vinyl substituent.

Table 4

Oxygen absorbed per minute per mol of 2-substituted dioxolane as a function of substituent

Substituent	cc oxygen/min.
Phenyl	0.34
Vinyl	0.20
Propenyl ..	0.16
Isopropenyl	0.14

The diesters of 2-vinyl 1,3 dioxolane alcohols

Many esters of 2-vinyl 1,3 acetal alcohols with di-basic acids were prepared and their properties studied. Anyone who has experience with drying oils will recognise the difficulties in determining the drying rate, the hardness, tensile strength and elongation of a vehicle which dries by oxidation. Nevertheless,

Table 5

Properties of diesters of vinyl cyclic acetal esters and their oxidised films

	Liquid		Film properties (aged 1 month)			
Ester	Viscosity Poise	Dry to touch time (hrs.)	Tensile strength (psi)	Elongation (%)	Modulus (psi)	Hardness (knoop)
V-54 o-phthalate ..	3.7	6	1,000	47	13,000	2.0
V-54 i-phthalate ..	4.0	6	2,400	31	53,000	3.0
V-54 t-phthalate ..	4.7	6	4,100	6	137,000	3.8
V-54 itaconate ..	1.3	4	1,900	1	235,000	15.2
V-54 maleate ..	2.0	5	2,800	9	88,000	8
V-54 fumarate ..	2.5	3	1,900	9	61,000	5
V-51+*V-60* sebacate	1.7	26	600	22	53,000	1.1
V-61 sebacate ..	Solid	48	1,300	20	37,000	—
54 sebacate ..	3.2	16	soft, weak film			
i-p-*54* sebacate ..	0.85	10	90	10	1,000	1.0
V-54 pyromellitate	23.0	Badly wrinkled, hard. brittle film				
V-54 C-36 dicarboxylate ..	1.0	Tacky, very soft film				
Linseed oil ..	0.5	Tacky, very soft film				
Alkyd 45% solids	1.4	3-4	400	140	3,000	3

standard conditions were adopted, i.e., a cobalt level of 0.05 per cent, 77°F, 50 per cent Relative Humidity, and a film thickness of 2.5 mils, with the risk that the best drying conditions will have been missed.

The properties of a series of cyclic acetal esters are given in Table 5 ; obviously a wide range of film properties can be obtained. The combination of short drying time and acceptable film properties favoured the adoption of a few of these esters, primarily *V-54* itaconate and *V-54* *o*-phthalate for concentrated study. These two esters have certain drying properties to be described later which complement each other and make the combination of greater value than either ester alone. Their viscosities are such that they require little or no solvent for brush or spray application.

Chemistry of oxidation of the 2-substituted 1,3 cyclic acetals

The absorption of oxygen by 2-alkyl 1,3 cyclic acetals takes place in the absence of cobalt but cobalt accelerates the absorption and goes through valence changes in the process. Depending on the choice of substituted acetal and the conditions of the reaction the products formed will contain hydro-peroxides, peroxides, and esters in varying amounts ; aryl dioxolanes react similarly.

Saturated compounds like 2-phenyl 1,3 dioxolane yield in the presence of cobalt a hydroxy ester as is shown in Fig. 6. Unsaturated substituents on the 2-position like vinyl and isopropenyl yielded predominantly polymers, probably because of the intermediate formation of an acrylate. However, a yield of 10 per cent of hydroxypropyl methacrylate was in fact recovered. A propenyl substituted dioxolane yields a crotonate which is less prone to polymerisation than the acrylates or methacrylates.

In the absence of cobalt, vinyl dioxolanes absorb oxygen to form hydro-peroxides and peroxides. Under acidic conditions spirocyclic peroxides are formed, probably by addition of the hydroperoxide across the double bond. The reactions are shown in Fig. 7.

The reaction of a 2-vinyl 1,3 dioxolane to form polymers on oxidation in the presence of cobalt is detailed in Fig. 8. The initial reaction is only hypothetical but the other reactions have been studied in some detail.

Polymers formed from the oxidation of a 2-vinyl 1,3 dioxolane are of short kinetic chain length, only 5-10 units long and are not homopolymers of hydroxy acrylates. The short kinetic chain length is probably due in part to chain transfer by abstraction of a susceptible tertiary hydrogen atom. Because of the short kinetic chain length, the formation of a polymer of high molecular weight or of a crosslinked network requires the presence of more than one vinyl dioxolane group to a molecule. Gelation will occur at lower and lower conversions as the number of vinyl dioxolane groups per molecule increases. Hence, one expects a decreased dry time with increasing functionality. Mixtures of compounds containing respectively one and two vinyl dioxolane groups should be capable of yielding permanently soluble highly branched polymers or highly cross-linked polymers depending on ratios and conditions of oxidation.

The reaction of radicals to abstract hydrogen from other portions of the dioxolane molecule than the 2-position, the addition of oxygen to the growing radicals, recombination of radicals terminated in carbon, oxygen or peroxide

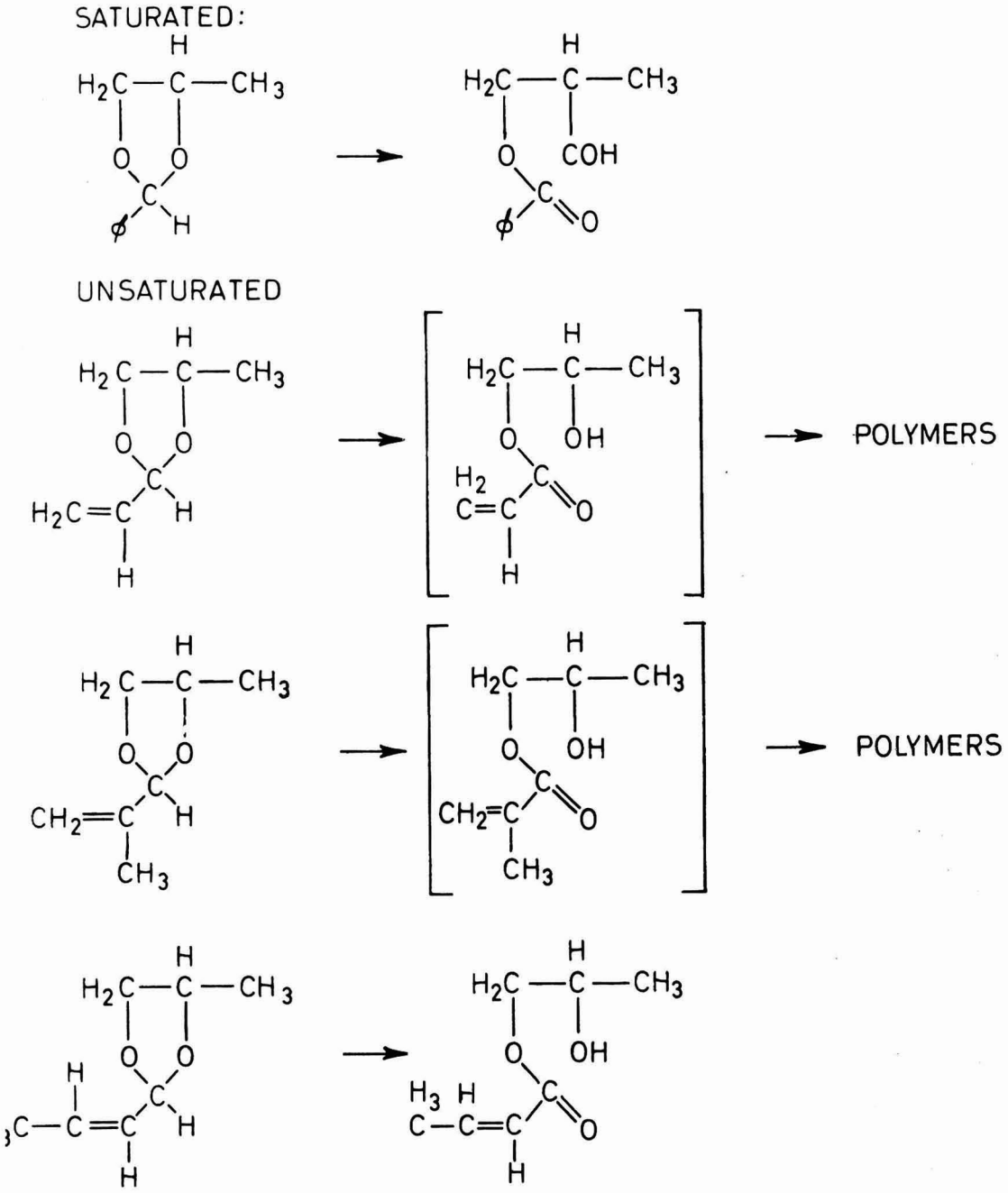


Fig. 6. Oxidation of dioxolanes in air in the presence of cobalt

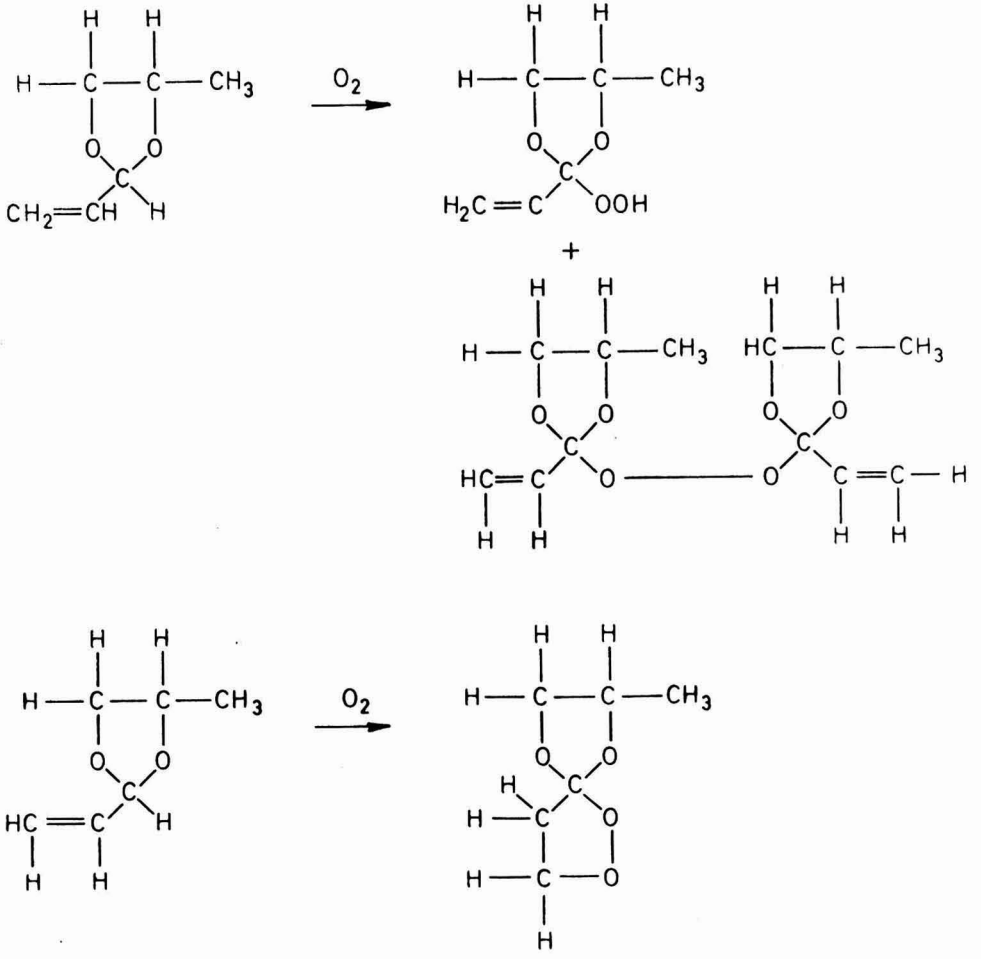


Fig. 7. Oxidation of vinyl dioxolanes in the absence of cobalt

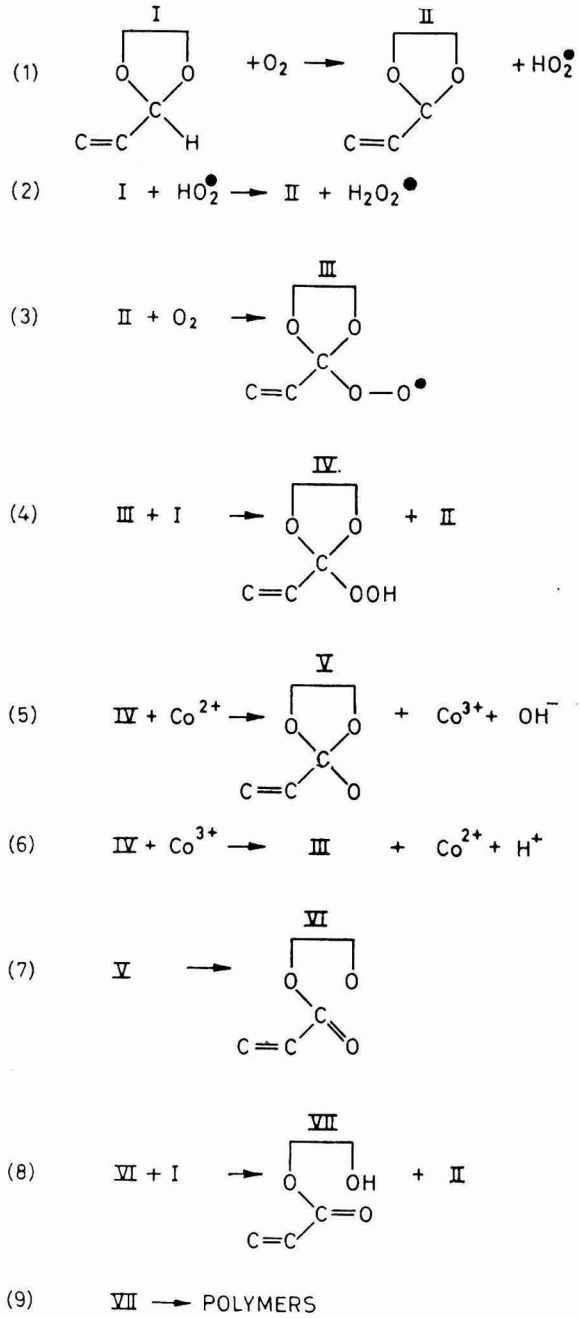


Fig. 8. The oxidation of a 2-vinyl 1,3 dioxolane by air in the presence of cobalt to form polymers

with each other combine to provide an overall structure containing not only the hydroxy acrylate polymer but also acetal, vinyl, peroxy and hydroperoxy groups. All of these groups have been detected.

The carryover of the dioxolane oxidation chemistry to the diesters was checked for the *V-54* sebacate and *V-54* *o*-phthalate.

Infrared curves of very thin (0.1 mil) films in Fig. 9 show the appearance of hydroxyl (2.8μ) and the appearance of acrylate bands (6.1 and 12.1μ) after

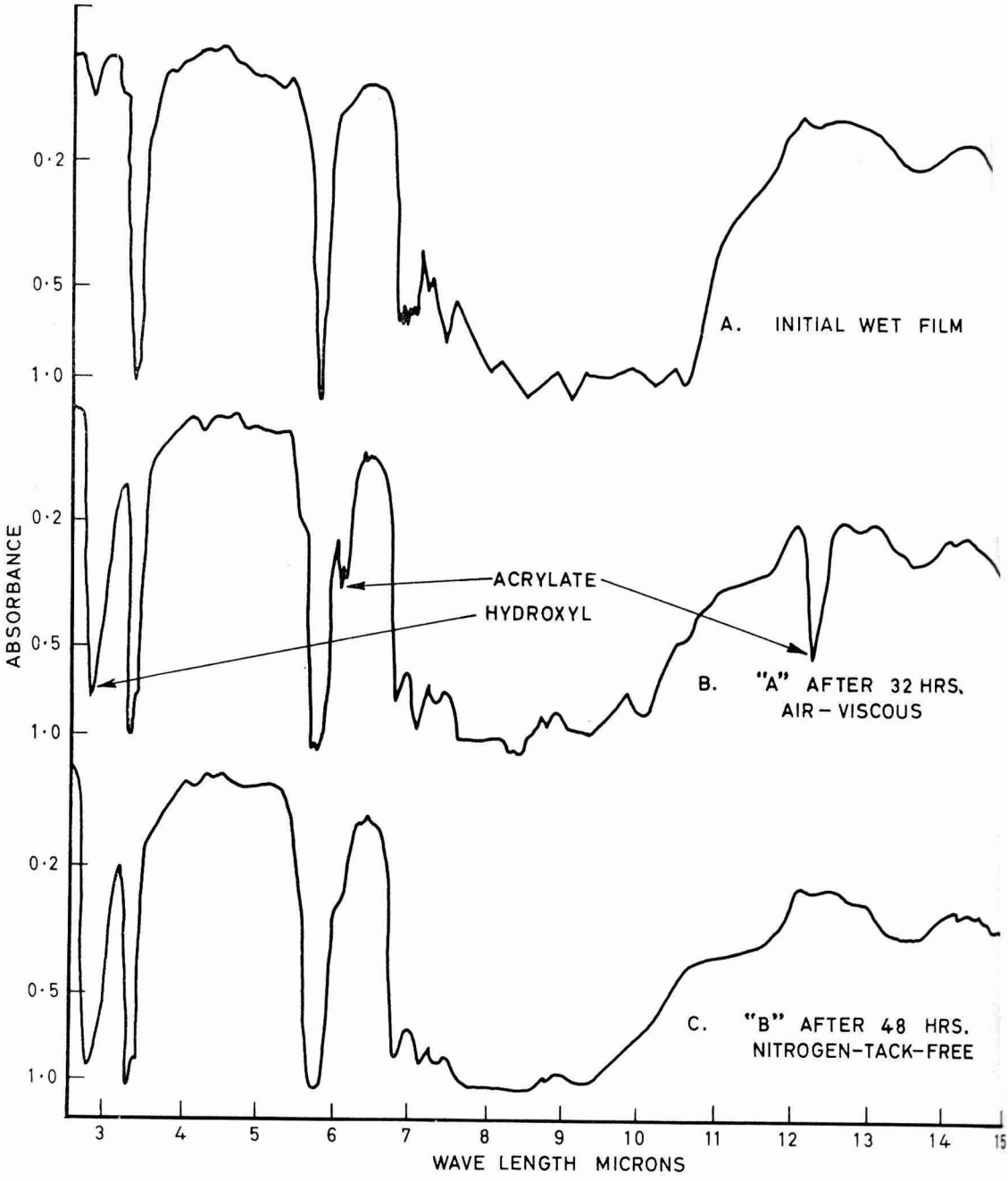


Fig. 9. Oxidation of V-54 sebacate—infrared spectrum

exposure to oxygen. Exposure to nitrogen then caused the acrylate bands to disappear and the film to harden. The change that occurs when the very thin film is put into nitrogen is explained on the inhibiting effect of oxygen on the polymerisation of acrylates. This is an illustration of the fact that while oxygen is necessary for some of the chemistry of the film formation it also is an inhibitor in high concentration. High concentration of oxygen is favoured by thin films and low temperatures.

V-54 o-phthalate film was broken down by hydrolysis, etc. From the data obtained it was concluded that the acrylate chain length is only about 5 acrylate units long. There is about one peroxide link for each 5 acrylate units and about one double bond left for each 5 acrylate units.

Factors governing the drying potential of a vinyl acetal vehicle

Table 6 lists the factors important in making fast drying vinyl-dioxolane esters. Table 7 shows that the rate of attainment of a gelled structure increases with increasing number of vinyl cyclic acetal groups/per molecule. Compounds containing only one vinyl cyclic acetal group without other polymerising functional groups do not form cross-linked products at all. Since the polymerisation proceeds only to a short chain length the resulting material is generally a viscous liquid. Increasing the number of vinyl cyclic acetal groups per molecule results in more rapid dry, but there is usually a slow period during which the radical concentration is increasing from zero and during which oxygen must penetrate or diffuse into the liquid film. Increased viscosity which is a conse-

Table 6

Factors affecting crosslinking potential of cyclic acetal esters

(*i*) Number of cyclic acetal groups per molecule.
(*ii*) Nature of the acetal ring—ring size.
(*iii*) Nature of the alkyl substituent. Vinyl best, isopropenyl next.
(*iv*) Presence of other groups in the molecule capable of polymerisation.

Table 7

V-54 *esters—attainment of dry as a function of* V-54 *groups per molecule of ester*

Ester	Dry time
Benzoate	—
Acetate	—
Succinate	8 hours
o-phthalate	6 hours
Pyromellitate ..	5 hours

quence of larger molecules reduces the diffusion rate. Increasing the number of vinyl dioxolane groups per molecule above 2 or 3 therefore does not shorten cross-linking time to a practically important amount. The effect of ring size is exemplified in Table 8. The effect of unsaturation is exemplified in Table 9. The hardness of the film that results is also increased by the presence of a polymerisable double bond.

Table 8

Drying time of vinyl 1,3 acetals

	Dioxolane	Dioxane
Sebacate ..	16	26
o-Phthalate ..	6	10

Table 9

Dry time of V-54 *esters*

Succinate	8
Maleate	6
Fumarate	3
Itaconate ..	4

The vinyl dioxolane esters can be conveniently divided into three classes—monoacetal, bisacetal and polyacetal as shown in Table 10. The three types differ in their viscosities, rates of dry, and ultimate mechanical properties. Within types considerable variation can be made by choice of the acid component; long hydrocarbon chains and low reactive unsaturation favouring softer, more flexible films. While monoacetal esters will not cross-link exclusively through the vinyl dioxolane group, an unsaturated polymerisable acid group will help.

Table 10

Types of vinyl cyclic acetal esters

Type	Examples	Typical GH viscosity	Dry	Resemble
Monoacetal ..	*V-54* linoleate, stearate	A (.50 poise)	24 hours, soft, flexible, tacky	Drying oils
Bisacetal ..	*V-54* itaconate, *o*-phthalate	E-P (1-4 poise)	4-8 hours, hard	Oil viscosity alkyd dry
Polyacetal ..	*V-54* acrylate/ methyl methacrylate copolymer	V-Z at 60% (8-23 poise)	2-4 hours, hard	Short oil alkyds

Most of the development work centred on two esters, the itaconate and the *o*-phthalate of *V-54* alcohol. They were selected because (*a*) itaconate forms a hard relatively brittle film while the *o*-phthalate forms a soft, flexible one and mixtures can be made of intermediate hardness and flexibility, (*b*) the drying properties are such that each makes the other more useful, and (*c*) they are adaptable to a considerable number of applications.

The ideal properties of dioxolane for finishes

The properties of the *V-54* itaconate and the *V-54* *o*-phthalate can be related to their chemistry and some important ideal properties for finishes. Some of these are given in Table 11. The degree to which the esters meet these ideals will be discussed.

Table 11

Important ideal properties

1. Stability in the absence of air.
2. Rapid conversion.
3. Low volatility.
4. Small dimensional change on conversion.
5. Low viscosity.
6. Relative insensitivity of rate of dry to environmental conditions of temperature, humidity, pigments, substrates, film thickness.
7. Durability.

The *o*-phthalate is stable in the absence of air for periods of years. It is stable to temperatures of 200°C for hours. The itaconate has a lesser degree of stability probably because of spontaneous polymerisation through the itaconate double bond. However, stabilisation of the itaconate for long periods is achieved by the addition of small quantities of well-known inhibitors, e.g. hydroquinone ; stability of the order of years is then achieved even with the itaconate.

Some properties of the two diesters are given in Tables 12-17. Viscosity slightly higher than that of drying oils but considerably lower than that of alkyd resins, rapid conversion, and low shrinkage on drying are evident. It is seen from the data that the films harden with age and exposure, that heating accelerates hardening, that the films lose thickness on exposure at the same rate as a 50 per cent linseed oil-chinawood oil alkyd resin.

Table 12

Properties of V-54 *esters at 25°C*

	V-54 *o*-phthalate	*V-54* itaconate
Viscosity	3.7 poise	1.0 poise
Density	1.145 g./cc	1.119 g./cc
Refractive index	1.508	1.478
Weight increase on drying ..	10%	11%
Shrinkage in volume on drying	about 5%	about 5%

Table 13

Properties of films of V-54 o-*phthalate and* V-54 *itaconate—2 mil-measured after 1 month dry*

	Dry time (hours)	Tensile strength (psi)	Elongation %	Tensile modulus (psi)	Knoop hardness
V-54 o-phthalate	6	1,000	47	13,000	2
V-54 itaconate ..	4	1,900 (brittle)	1	235,000	15

Table 14

V-54-*op-film properties as a function of time films dried 1 month in laboratory then exposed*

Time	TS (psi)	E (%)	M (psi)	H (knoop)
(Indoors at RT)				
1 month	900	47	13,000	2
2 months	1,300	58	23,000	3
3 months	900	49	16,000	2
4 months	1,500	58	42,000	5
7 months	1,300	64	32,000	3
(Indoors at 150°C) ..				
0 hour	900	47	13,000	2
4 hours	1,400	35	46,000	3
8 hours	3,200	23	138,000	3
16 hours	5,100	8	201,000	15
40 hours	7,100	4	244,000	20
(Weatherometer)				
0 hour	900	47	13,000	2
100 hours	5,500	3	258,000	14
(Outdoors Delaware) (Silvered glass substrate)				
0 month	2,100	53	41,000	3
1 month	5,300	7	145,000	14
2 months	5,000	6	165,000	—
3 months	4,500	3	610,000	—
6 months	4,300	9	786,000	—

Table 15

Hardness increase on Florida exposure—vehicle contains TiO_2 *pigment Pigment/vehicle=1/2 (wt.)*

Vehicle	Initial (knoop)	After 6 weeks 45°S, Florida	Increase
Poly (BMA)	3	4	+1
Drying oil alkyd ..	2	7	+5
Nitrocellulose ..	10	14	+4
V-54-OP	3	10	+7
V-54-I	13	18	+5
V54-OP/I (50/50) ..	9	17	+8

Table 16
Erosion rate—clears-45°S Florida

Vehicle	Total decrease in film thickness (mils) Original film thickness 1.3 ± .2 mils			
	4 weeks	10 weeks	18 weeks	23 weeks
Drying oil alkyd	.094	.130	.178	.188
Polybutyl methacrylate	.010	.015	.016	.017
V-54-OP	.073	.155	.225	.252
V-54-I	.032	.137	—	—
V-54-OP/I (50/50) ..	.062	.127	.186	.213

Table 17
Erosion rates—vehicles pigmented with TiO_2
Pigment/vehicle=50/100—45°S Florida

Vehicle	Total decrease in film thickness (mils)			
	4 weeks	10 weeks	18 weeks	23 weeks
Linseed-chinawood oil-alkyd	.051	.115	.142	.149
Nitrocellulose	.045	.092	.122	.129
Polybutyl methacrylate	.013	.020	.023	.024
V-54-OP	.040	.080	.120	.124
V-54-I	.046	.081	.112	—
V-54-OP/I	.035	.068	.094	.100

Table 18 shows a list of the environmental factors affecting rate of dry. Many of the items in Table 18 are familiar to those dealing with drying oils. Cobalt is at least ten times as effective as lead. There is no need for cobalt or

Table 18
Environmental conditions affecting rate of dry of vinyl acetal esters

1. Catalysts—driers, peroxides
2. Temperature
3. Film thickness
4. Pigments
5. Inhibitors—certain woods, phenolic materials, nitrocellulose, copper
6. Humidity

other catalyst when the temperature is raised to 100°C, where the hydroperoxides decompose spontaneously. Peroxides like benzoyl peroxide may be added to increase the reaction rate.

The drying rate of *V-54* esters is strongly dependent on temperature as shown in Table 19. The dependence of the rate on temperature is complicated by the requirement that oxygen be absorbed in order for drying to take place. In the case of the itaconate a considerable amount of chain extension through the itaconate group may take place without the absorption of oxygen.

Table 19

Drying time of V-54 *itaconate as a function of temperature*

Temperature	Drying time
26°C	120 min
37°C	54 min
90°C	10 min

Whether or not the film has absorbed oxygen prior to heating strongly affects the drying rate on heating. For example, a film containing *V-54-o*-phthalate and *V-54* itaconate will dry in six hours at room temperature but will remain fluid at 0°C for 48 hours. If exposed 24 hours at 0°C it will then take only one hour to harden at room temperature. Apparently during the low temperature exposure a considerable amount of absorption of oxygen and probably a fair amount of reaction occurs without hardening.

During their gradual oxidation the *V-54* diesters convert rather suddenly from a wet state to a dry state without going through a tacky state. However, certain esters like the *o*-phthalate tend to dry first at the surface and the surface then tends to wrinkle, while the rest remains fluid. Other esters, like *V-54* itaconate, tend to dry below the surface and for a time have a hard deep layer and a fluid top layer. Mixtures of the two types of ester dry nicely into films up to 20 mils thick. Drying is most rapid when neither top dry nor bottom dry is predominant. Table 20 shows how the balance of top against bottom dry is adjusted to provide the most rapid rate of dry throughout the film without wrinkling.

Table 20

Favour top dry	Favour bottom dry
High cobalt level	Low cobalt level
High temperature	Low temperature
Addition of drying oils—tung oil	vinyl monomers which are air inhibited
V-54 o-phthalate	*V-54* itaconate

A variety of pigments (see Table 21) can be used without inhibitory effect. Other pigments inhibit strongly. The carbon blacks often inhibit drying. Some have blamed inhibition on phenolic materials, others believe drier is absorbed. Usually inhibition by pigment can be balanced out with acceleration by peroxides.

Table 21
Pigments

Non-inhibiting	Inhibiting
Titanium dioxide	Toluidine red
Zinc oxide	Carbon black
Lithopone	Iron blue
Zinc	BON maroon
Zinc yellow	Indanthrone blue
Cadmium reds	Maroon Gold
Litharge	
Red lead	
Iron oxide	
Talc	
Phthalocyanine blue	
Phthalocyanine green	
Chrome green	
Silica	
Silicate extenders	
Barytes	
Calcium carbonate	
Aluminium flake	
Lampblack	
Molybdate orange	
Thioindigo red	
Anthranthrone orange	
Quinacridone red	
Sun yellow (nickel titanate)	

The inhibition by wood is described in Table 22. Walnut, redwood and cedar contain extractable materials which inhibit drying. Mahogany and oak inhibit drying but added cobalt and peroxide compensate. Yellow pine has extractable resins which result in tackiness.

Table 22
Drying of vinyl dioxolane diesters over wood

No inhibition	Weak inhibition	Strong inhibition
maple	mahogany	walnut
birch	oak	cedar
white pine		redwood

Mahogany and oak require large amounts of peroxide and cobalt for dry.

High humidity prevents the dry of *V-54* esters as is shown in Table 23. Films exposed for long periods at high humidity will still dry when the humidity is

decreased, indicating that side reactions which might prevent drying do not occur during the humid period. A tendency to yellow is seen when drying occurs at high humidity. This yellowing, whose mechanism has not been established, is not as marked as in the case of drying oil alkyd resins.

Table 23

V-54-OP dry time against humidity

RH	Dust free (hours)	Dry to touch (hours	Zapon tack-free (hours
0%	2.0	2.5	4.5
50%	3.8	5.0	8.0
90%	3.8	4.5	8.0
100%	48	48	48

Formulation of practical finishes

A few problems encountered in formulation are described for purposes of illustrating the chemical properties of the vinyl dioxolanes.

The incorporation of pigments into *V-54* *o*-phthalate or itaconate in deflocculated condition generally requires the presence of a wetting agent. While the more ordinary wetting agents work, the partial oxidation of *V-54* ester merely brought about by contact with air will often suffice to produce an effective dispersant for pigments.

The *V-54* itaconate and phthalate are strong solvents and compatible therefore with a wide variety of polymers. On oxidation they generally remain compatible, probably because of a certain amount of grafting that must occur during the many free radical reactions. Table 24 lists compatible and incompatible resins. The compatible resins in some cases prevent the drying of the

Table 24

Mixtures of resins with V-54 *itaconate and* V-54 *phthalate*

Compatible	Incompatible
Drying oils	Polystyrene
Alkyd resins	Silicones
Phenolic resins	Oils of low unsaturation
Melamine resins	
Epons	
Epon-esters	
Cellulose acetate butyrate	
Cellulose nitrate	
Polyurethanes	
Polyvinyl acetate	
Polyvinyl chloride	
Polymethyl methacrylate	
Polybutyl methacrylate	

V-54 esters. Polyurethanes containing residual isocyanate groups apparently interfere with cobalt drier. Epoxy resins and epoxy esters of non-drying oils prevent dry while the epoxy drying oil esters do not prevent dry. Nitrocellulose is an effective inhibitor. Not much is known of the reasons for inhibition.

Mixtures of *V-54* esters with drying oils or drying oil alkyds yield products having properties intermediate between the properties of the pure components.

The addition of vinyl monomers to *V-54* esters results in their taking part in film formation. While such monomers alone or in a mixture with a polyester often do not harden in thin films exposed to air because of inhibition by oxygen, they do co-react with vinyl dioxolanes when exposed to air in the presence of cobalt. The usual addition of wax to a styrene-polyester finish, which results in low gloss but allows it to polymerise on the surface, is unnecessary for polymerisation when a vinyl dioxolane ester is used with the styrene and polyester.

Use in aqueous systems

The vinyl cyclic acetals esters are decomposed by water at the ester linkage and at the acetal linkage. Alkaline solutions hydrolyse the ester and acid solutions hydrolyse both the ester and the acetal. Therefore, use of the vinyl cyclic acetals in aqueous systems, for example as converting coalescing agents, requires careful attention to pH. Because of the irritating effect of trace quantities of acrolein produced in acid hydrolysis it is best to hold aqueous suspensions at an alkaline pH close to neutral.

Conclusions

As is usual with research, work on the vinyl dioxolanes opened up more questions than it answered. It uncovered a complex maze of reactions, many of which must be left to others to solve.

Acknowledgment

The work reported here was the effect of a common effort by numerous chemists of the Fabrics and Finishes Department of DuPont. Most prominent among these was Carol K. Ikeda who provided the basic patentable ideas and helped organise some of the data. The following also made valuable contributions :

R. A. Braun
A. E. Brachman
C. E. DeBoer
W. M. Duffy
J. C. Fang
E. E. Fischer
P. Heiberger
R. M. Kirkpatrick
J. G. McNally
C. J. A. Peters
N. Pappas
P. F. Sanders
J. J. Sanderson
B. E. Sorenson

Reaction rates of the elementary reactions were measured by E. J. Burrell of DuPont's Radiation Physics Laboratory.

References

Some of the more complex experiments and the detailed conclusions from them are better obtained in a study of the original papers :

Autoxidation of 2-Alkenyl Dioxolanes and 2-Alkenyl-1,3-Dioxanes by C. K. Ikeda, R. A. Braun and B. E. Sorenson—*J. Org. Chem. 29* 286-290 (1964).

Pulse Radiolysis of Vinyl Dioxolane. Determination of the Mechanism of Oxidation and Measurement of Absolute Rate Constants—E. J. Burrell. To be published.

Discussion

DR. A. W. DE R. VAN STEVENINCK said that the presence of oxygen would certainly lead to the formation of hydroperoxides which understandably would break down before the acrylic esters, but it was a well-known fact that acrylic esters did not polymerise in the presence of oxygen. When, for instance, making acrylic esters, the best way to prevent polymerisation of the acrylic esters was to bubble through plenty of oxygen. He wondered how film formation took place in the presence of oxygen, after the first formation of the acrylic esters.

DR. S. HOCHBERG said that as each molecule of oxygen was absorbed some acrylic acid or rather esters of acrylic acid were formed. He said the oxygen level was important in determining whether oxygen acted as an inhibitor or not. A low level of oxygen would hasten polymerisation instead of inhibiting and under the film surface where there was oxygen being absorbed to form hydroperoxides the actual oxygen level was low. Under those conditions the polymerisation could continue and still be fairly rapid, although he admitted that every time an acrylate chain absorbed an oxygen molecule the subsequent reaction rate would slow down. Nevertheless, because the oxygen concentration was low under the film there might still be polymerisation. However, at the top surface of the film there would often be a very long delay in the dry and if one cast an extremely thin film of *V-54* itaconate it would not dry.

DR. VAN STEVENINCK thanked Dr. Hochberg and asked if he could put a second question. In Table 2 there were two compounds (Nos. 9 and 10) having a dihydropyrane structure, and he asked what Dr. Hochberg would give as the mechanism of the drying of these compounds, because they were definitely different from the vinyl dioxolanes.

DR. HOCHBERG admitted that this had puzzled him and that he would hesitate to write any mechanism for it, but he would be reasonably sure that hydroperoxide was involved. He thought that it was formed at that tertiary hydrogen next to the ether oxygen atom, but hesitated to say what the subsequent steps would be.

He said that if one took a similar dihydropyran group and put two methyl groups in that critical position where the tertiary hydrogen was and if one used compounds derived from it, one did not obtain the same degree of air-drying potential. Certainly if there was any air-drying potential it was very much reduced by the replacement of that hydrogen by carbon.

DR. E. SUNDERLAND said that if for the moment the aim of producing a low viscosity material was left aside it would seem that one of the very obvious polyols to investigate would be polyvinyl alcohol or partially hydrolysed polyvinyl acetates. He asked if any work had been performed on additional products of this kind.

DR. HOCHBERG said that vinyl cyclic acetals could be made from polyvinyl alcohol in the same way as one would make vinyl butyral and if this was done air-drying potential was obtained. They had not investigated how important these products would be because the basic raw materials were expensive.

DR. L. VALENTINE said he had two questions. Frequently one obtained novel effects if one had mixtures of pvc with unsaturated compounds, for example, ethylene glycol dimethacrylate, which could be used as an additive with pvc to get special effects. There was also the work that had been performed more recently with other forms of polymerisable plasticisers where special adhesion promoting effects could be obtained with pvc compounds. The question was therefore—was there any evidence that, in mixtures with pvc, any of the compounds investigated in this work had any special beneficial effects ?

DR. HOCHBERG thought that one of the benefits to be obtained was in many cases improved adhesion. He did not think that there were any other particular benefits to be realised except that mentioned : that was that one could obtain a plastisol which converted to a very high viscosity, very much like ethylene glycol dimethacrylate or polyethylene glycol dimethacrylate.

DR. L. VALENTINE said the second question referred to the fact that when preparing the monomers there were undesirable side reactions in the presence of acid, and the vinyl hydroxyl reaction took place ; in other words that the vinyl group could react in the presence of strong acids with hydroxyl groups. This, of course, was undesirable when one was attempting to isolate the monomer. This reaction had been investigated in the past and there had been attempts to use this as a basis for actually making a polymeric system. There had been a lot of work done many years ago on diallylidene pentaerythritol and its reaction with pentaerythritol and more recent work still in which this had been taken up again. Dr. Valentine asked if Dr. Hochberg would comment on the potentialities of this reaction.

DR. HOCHBERG said the same reactions with diallylydene pentaerythritol in which it bridges across, for example, phenols and other hydroxyl compounds such as alcohols also occurred in the case of the vinyl dioxolanes and probably acrolein itself. It was known that these reactions occur and the resulting products could be useful materials, but materials of this type were not covered in this report.

DR. K. M. OESTERLE said that, as Dr. Hochberg had said that his products were in liquid form, could he ask if he had also proved products in half-way polymerisation in order to get solid products that were capable of entering into a reaction with a second agent such as pvc.

DR. HOCHBERG asked if Dr. Oesterle had meant a situation where for instance *V-54* orthophthalate was oxidised for a while and then the oxygen was removed from the neighbourhood and the resulting material used, or did he mean to take a polymer and place pendant vinyloxylane groups on it ?

DR. OESTERLE said that it seemed that the second way was the reaction he was thinking of. For example, epoxy resins could be combined with amides in half-way polymerisation, in the sense that a second polymerisation could be performed in a second stage of the coating production line.

DR. HOCHBERG said that his example contained elements of both types of reactions mentioned. He would say that certainly polymers had been made where there were a number of vinyl cyclic acetal groups on a long polymer chain. Those were useful materials ; they might even show lacquer-type dry to a soft material, and then subsequently a much harder dry.

The other type of material, where it was partially oxidised, had also been investigated. The products were equivalent in some respects to the result of air-blowing a linseed oil, polymerising it part of the way with air, and then using that as a partially polymerised product. The result was very much like the air oxidised blown linseed oils.

One of the results was that there was a change in the pigment dispersing qualities, which was found not only when air was blown through hot material but even when

the compounds were just handled in the open air. If everything was handled under nitrogen these vinyl cyclic acetals were very poor wetting agents, and therefore good pigment dispersions could not be obtained and a low gloss reached.

Dr. Hochberg said during the course of oxidation one obtained good pigment wetting agents, and it might be remembered that if one added a good wetting agent to a system which was dispersed the result was often flocculation, and by commencing with a good pigment dispersion and a non-air oxidised material one could finish with poor dispersion.

If, on the other hand, these materials were handled in open air and absorbed a lot of oxygen, they would make good wetting agents. When pigment dispersions were made from these materials they do not spoil when they dried ; this results in high gloss products.

He thought that the same comment might be applied in the case of the allyl ethers discussed before for they probably had identical problems.

MR. R. W. HALL asked if Dr. Hochberg could comment on the technological performance of these materials in practical paints. In the paper the exterior durability was discussed in terms of mechanical properties, also thickness on erosion, etc. Could he comment on the performance in respect of gloss retention, blistering and chalking, etc. ?

DR. HOCHBERG said that these materials, in general, would perform well in tests for blistering, and certainly before exposure in tests of flexibility, hardness, adhesion, etc. On exposure all these materials did harden up, and in some cases they might become too brittle, in the sense that if they were exposed, for example, as a paint for bridges, after a couple of years there might be some cracking. On the other hand they could be formulated so that they would do well for two years, and the same was true over substrates like wood where blistering was at a relatively low level. He thought all these paints came close to being commercially acceptable products, and many of them came to be acceptable commercial products in respect of quality.

He thought gloss retention was somewhat better than that of an automotive air-drying alkyd, but not as good as that of a non-dry melamine type alkyd.

MR. C. R. PYE said that he noticed in Table 14 that there was a rather odd situation that occurred in the films exposed indoors at room temperature. All the various mechanical properties mentioned seemed to rise and then fall and rise and fall, whereas in the remainder of the exposure types quoted there was either a steady increase or a steady decrease ; was there any definite explanation for that ?

DR. HOCHBERG did not think there was a good explanation for this situation. This had been the subject of some concern. The same situation was often encountered in the case of drying oils, where the material seemed to harden first, then soften, and then harden again. He did not think that the chemistry of the reactions and the theory of the mechanical properties was very closely tied together. He thought it was not possible to decide from the chemical formula whether something would have a low or high modulus. The same, of course, was true probably to an even greater degree for elongation and for tensile strength.

MR. C. R. PYE said another point was that in the rather comprehensive list of properties of the films which was given there was no great reference to gloss nor, again, to film permeability. In certain cases film permeability was a fairly important property and he wondered if there was any information available on these two particular properties. Mr. Pye said that in this case he was not referring to gloss retention on exposure, but the initial gloss produced by the film.

DR. HOCHBERG said that the gloss level that could be produced in, for example, a titanium dioxide pigmented film was of the same level that could be obtained in an unbuffed automotive finish, i.e. very high.

On the question of permeability he thought there were measurements, but he did not remember the numbers. There was something, however, which would be pertinent to Mr. Pye's question, and that was that quite good primers for steel could be made from these materials, so the permeability level, although probably higher than that of an air-dried material, was low enough to give a good non-blistering primer.

MR. C. R. PYE asked if he could put one more question. In the list of resins with which these compounds were compatible both non-reactive and reactive resins were mentioned, and he wondered whether any co-polymerisation took place with the reactive resins or whether just pure mixtures were formed.

DR. HOCHBERG thought that there was co-polymerisation taking place with all the resins both reactive and non-reactive because whenever there was an active free radical formed in the presence of another material hydrogen could be extracted and more free radicals would be formed which would combine with each other. It was only by assuming this reaction that one could explain why these resins remained compatible even after polymerisation was proceeding. With mixtures of polymers the usual situation was for them to be incompatible, whereas actually when an initially compatible system was used the end product was a system which was compatible, even though one of the materials had been polymerised very markedly. This suggested that there was co-polymerisation taking place during the course of the reaction.

DR. W. FUNKE asked if it was possible to perform two-step polymerisation with these vinyl dioxylane compounds. For example, first to polymerise only the double bond of the vinyl group and then open the rings, or first polymerise the rings and then in the second step to polymerise pendant vinyl groups?

DR. HOCHBERG asked if Dr. Funke meant was one able to polymerise a vinyl dioxlane by free radical mechanism through the vinyl group?

DR. W. FUNKE said that Dr. Hochberg had interpreted his question correctly, and continued that it would probably be necessary to use two different catalysts, one which would polymerise only the vinyl group and the second which would only polymerise the cyclic ether group.

DR. HOCHBERG thought that the situation that occurred was that when a free radical was added to just attach the vinyl groups that soon a reaction that occurred was the extraction of hydrogen from the central position, and the final product was very much as the allyl ethers. This was very nearly the same type of polymerisation that Dr. Hochberg had described. In the literature Dr. Hochberg said there was a patent in which the co-polymerisation of an acrylic monomer with a vinyl dioxane by free radical mechanism was described.

Whereas ordinarily one might use a ½ per cent of peroxide to obtain a good polymer, in this particular case several per cent peroxide had been used. What he thought they were doing was oxidising the vinyl dioxane compound to the acrylate and the acrylate was polymerising.

DR. L. A. O'NEILL said that in most of the work described cobalt had been used as a drier system. He asked if Dr. Hochberg would comment on the possible activity of some of the other drier metals, or did the compounds behave as allyl ethers where only cobalt worked as a drying catalyst?

DR. HOCHBERG said that cobalt was the most active of all catalysts tried. However, it had been found that addition of other catalysts helped. He thought that lead was certainly effective as a catalyst, and of course no catalyst at all was needed if the temperature was about 80 or 90°C. He believed that the addition of zirconium was also effective.

With regard to comparison with allyl ethers, there had not been a broad enough study to indicate that these driers were acting differently in the allyl ethers. However,

lead was reported not a catalyst at all for the allyl ether polymerisation so this case was apparently different.

MR. I. S. MOLL said it was encouraging to find in a paper concerning the study of a new class of film-forming polymer information on the effect of pigments. From the list given in Table 21 of inhibitors of drying it would seem that several different types of factor could be responsible. Toluidine Red could contain significant quantities of *beta*-naphthol which might act as anti-oxidant, particularly in full depths of shade. Iron blue, on the other hand, normally contained an appreciable mineral acidity, and this might also be the explanation for BON maroon and maroon gold. It was surprising, however, to find Indanthrone Blue on the list of inhibiting pigments, although it could under some conditions be oxidised at the imino grouping without being destroyed. No doubt similar consideration of the table dealing with inhibition of the diesters on different types of wood could provide other probable factors causing inhibition.

Polyurethane systems for solventless finishes

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Summary

Combinations of castor oil and poly-alcohols can be used for cold-curing, solventless polyurethane coatings if used in the presence of molecular sieves. The available technically produced polyisocyanates are examined for their suitability as a co-reactant. A homologous mixture of diphenylmethane di-isocyanate is found suitable.

The properties of castor oil polyurethanes were compared with those modified by a bi-functional polyester alcohol. The film properties are compared in their dependence on the NCO/OH ratio. In addition, there is a description of a modification of castor oil—polyurethane with a tri-functional polyether-alcohol, producing hard coating materials. Catalysts such as tin and amine compounds are important for the mechanical treatment of polyurethane lacquers.

Systèmes Polyuréthanes pour enduits de finissage dépourvus de solvant

Résumé

Des composés d'huile de ricin et de polyalcools peuvent être utilisés pour des enduits polyuréthanes dépourvus de solvant et durcissant à froid, s'ils sont appliqués en présence de filtres moléculaires. Les polyisocyanates, produits artificiellement en connus à l'heure actuelle, sont examinés du point de vue de leur appropriation en tant que co-réactifs. Un mélange homologue de biisocyanate de biphénylméthane s'avère approprié.

Les propriétés des polyuréthanes d'huile de ricin ont été comparées à celles modifiées par un alcool polyester bi-fonctionnel. Les propriétés de la pellicule sont comparées dans le cadre de leur dépendance du rapport NCO/OH. Cet exposé décrit en outre une modification de polyuréthane d'huile de ricin avec un alcool polyéther tri-fonctionnel, modification permettant d'obtenir des substances pour enduits durs. Les catalyseurs tels que l'étain et les composés de l'amine sont importants pour le traitement des vernis polyuréthanes.

Polyurethansysteme fuer Anstriche ohne Loesungsmittel

Zusammenfassung

Kombinationen von Rizinusoel und Polyalkoholen koennen fuer Polyurethananstriche ohne Loesungsmittel zur Kaltverarbeitung benutzt werden, wenn sie in Anwesenheit von Molekularsieben aufgetragen werden. Die verfuegbaren, grosstechnisch hergestellten Polyisocyanate werden auf ihre Eignung als Koreaktans untersucht. Eine homologe Mischung von Diphenylmethan-Diisocyanat wird fuer geeignet befunden.

Die Eigenschaften der Rizinusoel-Polyurethane wurden mit den Eigenschaften solcher Polyurethane verglichen, die durch einen Polyesteralkohol mit Doppelfunktion modifiziert waren. Die Eigenschaften des Films werden in ihrer Abhaengigkeit vom NCO/OH Verhaeltnis verglichen. Darueberhinaus liegt eine Beschreibung von einem mit einem dreiwertigen Polyaetheralkohol modifizierten Rizinusoel-Polyurethan vor, das Hartbeschichtungswerkstoffe erzeugt. Katalysatoren wie Zinn und Aminverbindungen sind von Bedeutung fuer die mechanische Behandlung von Polyurethanlacken.

Introduction

Two-component systems based on polyisocyanates and polyols are widely used today with their main application in the field of plastics. The plastics chemist takes it for granted that polyurethanes, being the product of an isocyanate—alcohol reaction, can be processed and manufactured in a solventless system, the most important products being soft foams and elastomers. Solvents are only used in exceptional cases, e.g. in adhesives or textile coatings. Liquid isocyanate compounds are starting materials for foams, and are also used for the sprayable elastomers. In the production of polyurethane elastomers higher temperatures are used in order to liquefy the isocyanates and polyols, thereby achieving a sufficiently low working consistency to enable a solvent-free system to be used.

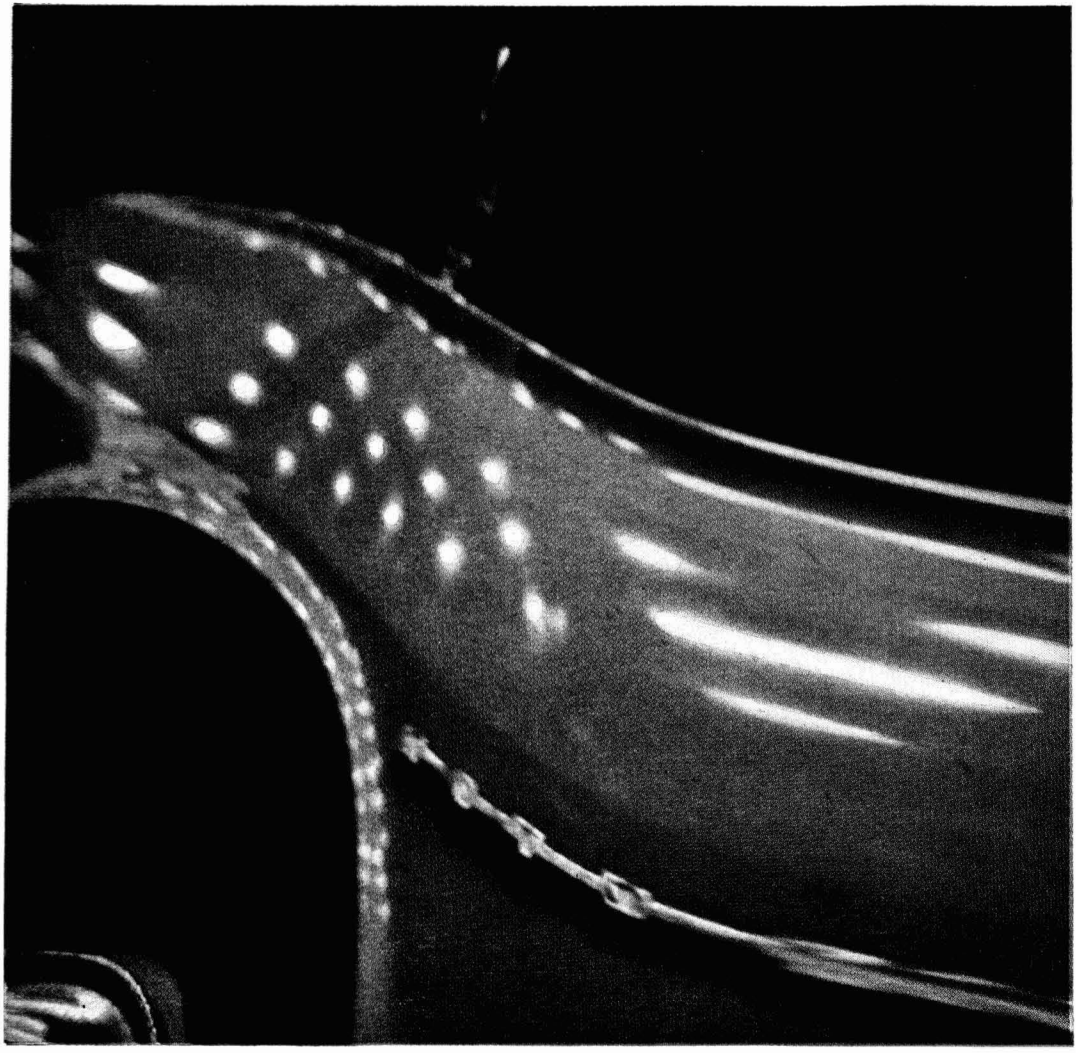
In lacquer chemistry, solvents are used, but the interest in 100 per cent solventless systems has increased in the last few years, mainly because of rationalisation. In the case of polyurethanes the extensive knowledge gained in the plastics industry would be utilised but only to a limited extent, as the conditions for a paint system are quite different to those of a plastic material. It is not sufficient merely to know the mechanical properties of the binder for the coating has to take into account the properties of the substrate, the weather and the properties of the fillers and pigments. For a coatings system the " environment " in its widest sense thus plays a deciding part. This is especially true for polyurethane systems. A side reaction of the isocyanates with water has a decisive influence on the film formation. Small amounts of water are present in the atmosphere, on the substrate, in the polyol as well as in the pigments and fillers.

$$2\ R{-}NCO + H_2O \longrightarrow R{-}NH{-}CO{-}NH{-}R + CO_2$$

In the above reaction polyureas are formed from the isocyanates, whereby carbon dioxide is evolved. This is the basic reaction for the production of polyurethane foams. The carbon dioxide causes the foam formation, which is essential in the production of foam, but most undesirable in lacquers. In the usual solvent containing polyurethane systems the gas formation only rarely causes difficulties. The water in the lacquer mixture can leave the coating together with the solvents. The carbon dioxide caused by atmospheric moisture does not cause difficulties with careful working. The reaction of the free isocyanate groups with atmospheric moisture can be utilised for film formation. In these moisture-hardened polyurethane lacquers the carbon dioxide can easily diffuse through the coating, provided a sufficient proportion of solvent is used. The solids content of a classical polyurethane lacquer rarely exceeds 50 per cent. Clear lacquers normally have a solids content of 35 to 48 per cent. If one leaves out the solvent in a polyurethane lacquer, strong blistering can be expected, as in practice no absolutely moisture-free pigments and fillers are known, even without taking into account the ever-present atmospheric moisture. The carbon dioxide evolved during film formation has no opportunity to escape from the film in the absence of solvents, and causes the undesirable foam effect.

The action of water absorbing aids in polyurethane systems

In the last few years different ways of including water-retention aids in the lacquer mixture have been tried. An obvious way would be to use isocyanates



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to dry the fillers and pigments, but for various reasons this procedure has not proved practical. The use of calcium oxide and other known water absorbers have also been suggested and a certain amount has been achieved, but the efficiency of the common water-retention aids is not sufficient. Lately chemically reactive substances have been used for the water absorption in moisture-hardened polyurethane systems; these form alcohols and esters with water. These additives were useful in solvent-containing polyurethane systems, but in solvent-free systems the proportion of low molecular compounds had a disturbing effect.

In the last few years a number of zeolite-type aluminium silicates have been synthesised showing a specific absorbtion action not only with regard to water, but with low molecular organic compounds as well. It has, for instance, been possible to separate mixtures whose boiling point does not permit fractionating. This method has been applied to petrochemistry to separate straight chain from branched alkanes. A further surprising experience with the specific absorption properties of synthetic zeolites led to the term " molecular sieves " for these substances. A field of application which directly concerns lacquer chemistry is the absorption of amines by zeolite. Combined with epoxy resins, no reaction takes place initially, so that the molecular sieve amines are suitable for single unit epoxy systems. Only by the addition of moisture, e.g. from the atmosphere which occurs during application, will the amine react with the epoxy resin. The energy of absorption of water towards zeolite is greater than that of amines. An unlimited pot life of the single unit systems can of course not be expected, as this is a case of equilibrium reactions.

In the special case of Zeolith 4 A, the water which is in equilibrium with the zeolite has been determined with silica gel.

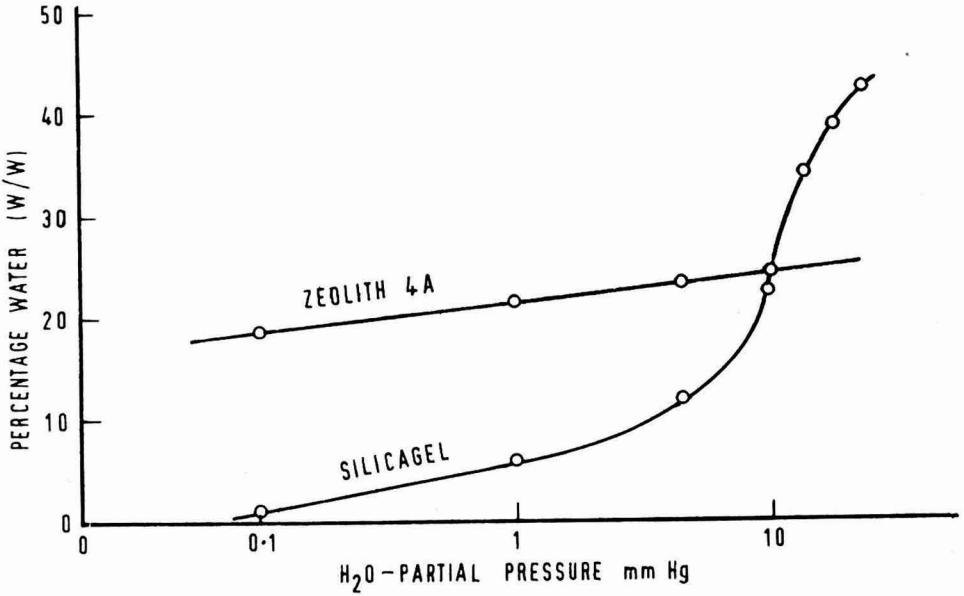


Fig. 1. Isotherms at 25°C

It can be determined from this curve, that with a water content of 20 per cent the partial pressure of the water vapour at equilibrium is 0.1 mm Hg. This corresponds to the partial water vapour pressure of ice at −40°C. At very low water vapour pressures on the other hand, a strong absorbing action remains which lies outside the range of the silica gel used for comparison.

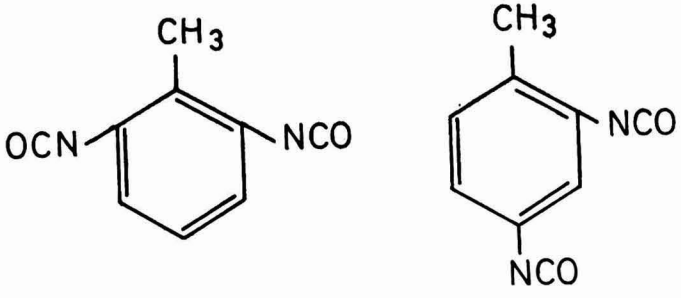
The reason for this remarkable power of absorption of the synthetic zeolites can be found in their crystalline structure. It consists of a crystal structure where the layers are connected by atom bonding in contrast to the layer-structured silicates, thus forming a space net penetrated by channels. The types mentioned have channels of 4 angstrom units diameter, large enough to contain water molecules. At high temperatures the crystal water is expelled, without altering the structure of the crystal lattice. In this form the zeolite is used as a water absorber, whereby the drying intensity can be compared to that of P_2O_5.

In the field of polyurethane lacquers the zeolites should have helped to solve an old problem in polyurethane chemistry, which was the stabilisation of pigmented, moisture-drying single pot systems. The addition of finely powdered zeolite causes a close-drying of the lacquer system and thereby gives a longer pot life (up to six months) in the case of the pigmented single pot lacquer. After six months thickening may occur, caused by the small amounts of water in equilibrium with the zeolite. As already mentioned, chemically reactive drying agents are of help here.

In addition, zeolites were used to prevent blistering in solventless lacquer systems. This could lead to interesting technical applications, which are discussed later.

Raw materials for solventless polyurethane lacquers

Amongst the technically produced isocyanates which can be used for 100 per cent lacquer systems consider the liquid compound tolylene di-isocyanate (TDI).



Properties of the 80/20 TDI—Isomer mixture

Melting point	12°C
Boiling point	106°C/5 mm Hg
Viscosity	3 cps
Colour	Colourless

The low viscosity and light colour has made it attractive for use in solventless lacquer systems. TDI is used at times for solventless floor coatings in the United States, in this case the two-part spray application with catalysts is used, which causes a quick hardening of the polyurethane coating. The inclusion of catalysts causes a rapid decrease in the TDI concentration. Even so, the use of TDI remains a dangerous undertaking as the vapours of TDI cause a strong irritation of the respiratory organs. Regulations do not permit the concentration on the site to exceed 0.02 ppm.

The use of prepolymers, successfully used as an alternative in solvent-containing lacquers, is not possible. The viscosity of TDI free prepolymers is unfortunately so high that they can hardly be used in solventless systems.

The aliphatic hexamethylene di-isocyanate is also produced technically.

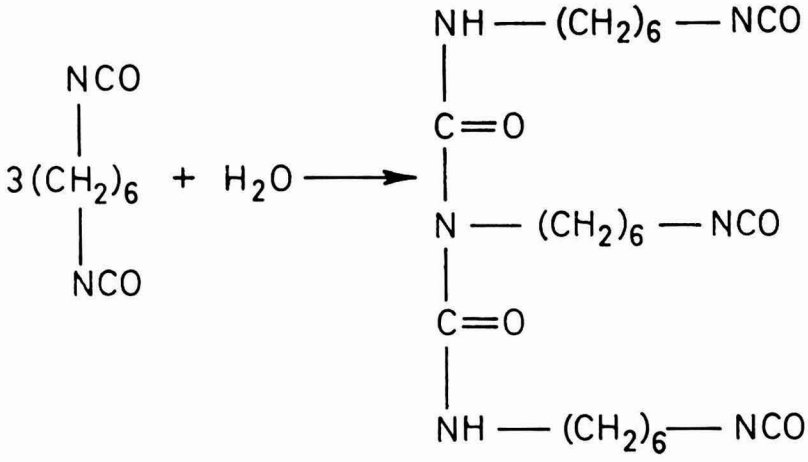
$$OCN - CH_2 - (CH_2)_4 - CH_2 - NCO$$

Properties of hexamethylene di-isocyanate

Melting point	−67°C
Boiling point	112°C/5 mm Hg
Viscosity	1.5 cps/50°C
Colour	Colourless

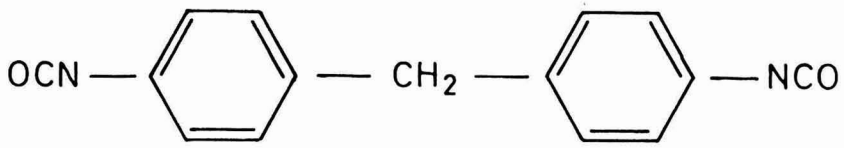
It can be used as an intermediate for light-stable and weather-proof polyurethane lacquers. The monomers themselves cannot be used in lacquers. Conditions similar to those given for TDI again apply, but it is possible to produce a monomer-free modification with a higher molecular weight which in a 100 per cent form is still sufficiently liquid.

In converting 3 moles hexamethylene di-isocyanate with 1 mole water, a compound containing isocyanate groups is obtained, giving extremely good light stability and weather resistance.



This compound has been tested in solventless systems. The results are discussed later.

In the field of elastomers diphenylmethane—4, 4′—di-isocyanate is being used.

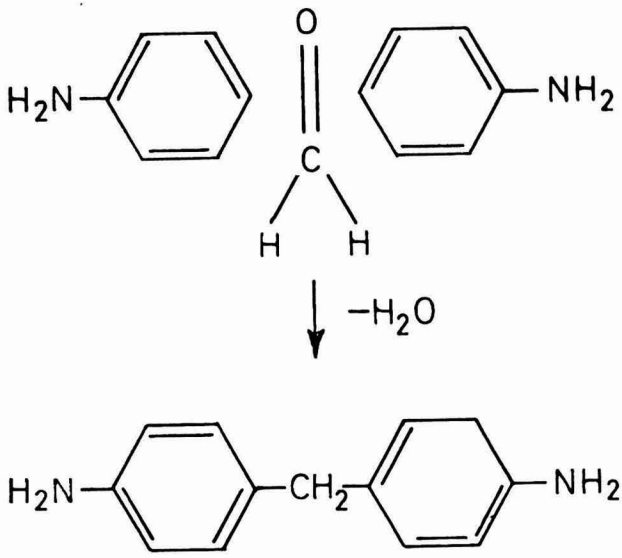


Properties of diphenylmethane di-isocyanate

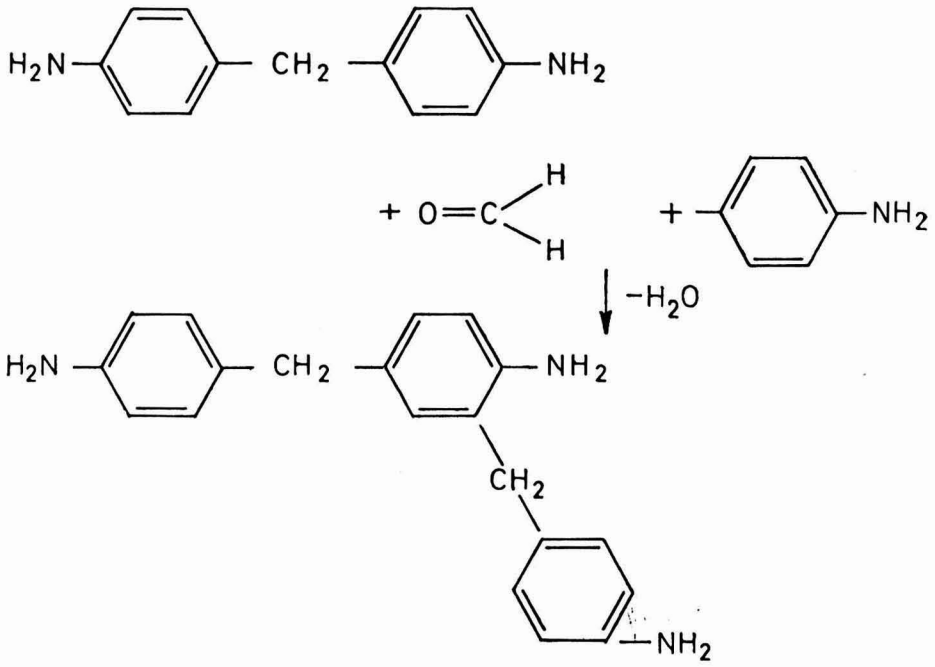
Melting point	38°C
Boiling point	190°C/5 mm Hg
Colour	White to yellow flakes

Because of its high melting point, this product is not used for solventless coatings. For solvent-containing polyurethane lacquers this compound is also not particularly interesting, as the solubility of the di-isocyanates is not sufficient in the usual solvents.

The technical intermediate, however, still containing homologues of diphenylmethane di-isocyanate, has been applied in practice. This mixture of homologues has a low melting point and a low viscosity at room temperature. As a commercial product, however, it has a dark colour and is rarely clear. The starting compound for its production is the condensation product of aniline with formaldehyde :

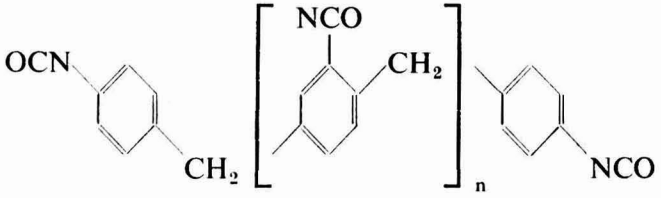


The condensation reaction can proceed in the following manner.



The polymer mixture is reacted with phosgene and then saponified to form the polyisocyanate. As a main product it contains the bifunctional diphenylmethane di-isocyanate. By-products are the polyfunctional isocyanates.

The following general formula may be given :



Properties of polymethylene polyphenylisocyanate

Melting point	5°C
Boiling point	190°C/5 mm Hg
Viscosity	150—200 cps
Colour	dark
NCO-content	30—32 per cent

This is a liquid with a low vapour pressure which is safe from a health point of view.

Difficulties with regard to the physiological actions of the homologue mixtures may arise if small amounts of aniline are still present. In this case phenylisocyanate may be formed after the phosgenation and saponification, which may give rise to severe irritation of the mucous membrane. All homologous mixtures used for coating must be free from phenylisocyanate.

It is obvious that the health considerations only apply when coating by hand. When spraying the polyisocyanates one has to consider the formation of aerosols. In this case eyes and respiratory organs have to be protected (filter-mask and goggles). No skin irritations have been ascribed to the isocyanates mentioned.

Apart from the commercial homologous mixtures, promising liquid derivatives of the diphenylmethane di-isocyanates are known. One has, however, to allow for a distinct yellowing, even with these purified products: a liquid, modified diphenylmethane di-isocyanate, was included in the trials.

Properties of the modified diphenylmethane di-isocyanate

Melting point	5°C
Viscosity	25 cps/25°C
Colour	Light yellow
NCO-content	31 per cent

Liquid polyols would be considered first as co-reactants for the liquid isocyanates mentioned. One could, of course, also imagine the use of liquid amines or amides as co-reactants. Experience, however, shows that the reaction of an amine and isocyanates is so vigorous, that the pot life would be too short.

If the polyalcohols are considered, a great number of technically produced polyesters and polyethers, containing hydroxyl groups, could be useful, quite apart from natural products, such as castor oil. But only a limited choice is available for solventless coatings. An adequate compatibility with isocyanates is required—the polyols should at least be compatible after a short initial reaction. In addition, the reactivity of the hydroxyl groups must be right for the type of polyol used. Polyalcohols with primary hydroxyl groups react faster than those with secondary hydroxyl groups. In practice, the pot life and the drying time of polyurethane lacquers depends on this reactivity. A certain water-repellent action of the polyalcohols is also an advantage, in that the absorption of moisture does not exhaust prematurely the capacity of the molecular sieve.

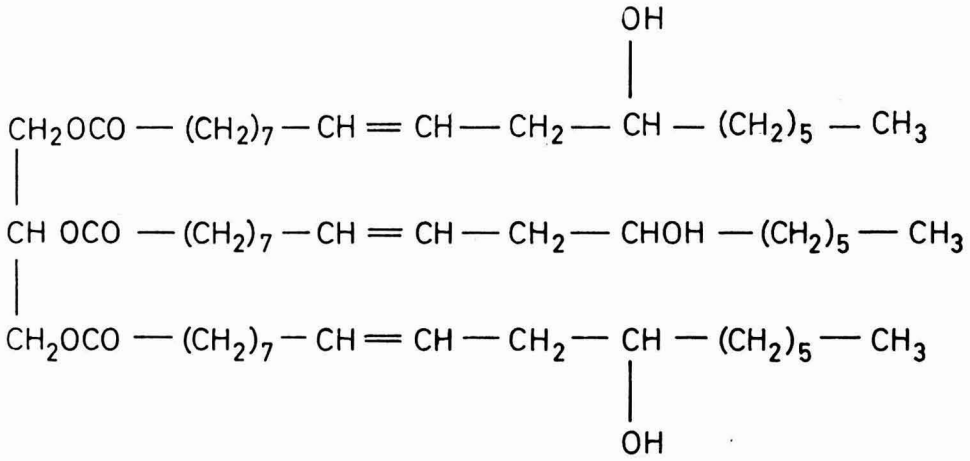
In practice, however, it is necessary to compromise, as an adequate hydroxyl content is required in order to achieve hard coatings. On the other hand, it is known that an increase in the hydroxyl-content makes the polyalcohols more hydrophilic.

Polyalcohols pose no health risk; the fact that the technically interesting polyols are odourless is also important for their application. The same applies incidentally to the polyisocyanate homologue mixture previously mentioned. The polyol components can take up the necessary amounts of fillers, pigments and additives. An adequate proportion of the molecular filter is added to the polyol components with the fillers.

Zeolite can be used in powder form or in a paste made with the binder. A 50 per cent paste with castor oil has proved successful. Mixing with castor oil retains the activity of the molecular sieve during storage by reducing its sensitivity to atmospheric moisture. The activity is rapidly achieved by mixing the zeolite paste with moist pigment and polyol. An excess of zeolite has so far

not shown any detrimental effect on the film properties. It should be mentioned here, that zeolite, being a mineral substance, cannot, of course, be used in clear solventless lacquers based on polyurethane.

Of the available polyols, castor oil is used as an hydroxyl-group containing natural product for solventless polyurethane lacquers.



Castor oil may be regarded as a mixture of about 70 per cent pure triricinoleate given in the above formula, with 30 per cent of di- and monoricinoleate. With respect to isocyanate chemistry castor oil may be regarded as 70 per cent trifunctional and 30 per cent bifunctional.

Properties of castor oil

Melting point	—10 to—18°C
Viscosity	950—1100 cps
Colour	Pale yellow
OH-content	4.8 per cent

The long fatty acid chains in the triglyceride molecule give the castor oil-based polyurethanes good water resistance. One disadvantage these polyurethanes have is the susceptibility of the ester bonds to saponification. The hydroxyl-number is relatively low, resulting in flexible coatings, therefore it is not usual to use castor oil alone but blended with other hydroxyl-containing compounds, in particular polyesters and polyethers.

The saturated polyesters used to modify the castor oil polyurethanes have a disadvantage in their high viscosity, as well as in their ester groups which are also sensitive to saponification. On the other hand, the great selection of available types enables special effects to be achieved. A bifunctional, saturated polyester has been examined.

Properties

Melting point	6°C
Viscosity	380 cps/75°C
Colour	Colourless
OH-content	8.5 per cent
Functional groups	2

A great selection of polyethers is also available, characterised by a low viscosity. The water resistance of polyurethanes incorporating them may, however, show certain weaknesses. In as far as the hydroxyl-group containing polyethers are derived from polyalcohols and propylene dioxide, secondary hydroxyl-groups are obtained which determine the rate of reaction, and thereby the pot-life of the solventless coatings. Branched and straight chained polyether types are known. The hydroxyl-group containing polyether type used was branched.

Properties

Viscosity	.. 600 cps/25°C
Colour	.. Colourless
OH-content	.. 11.5 per cent
Functional groups ..	.. 3

Experimental results

Production and testing of castor oil polyurethanes

Films of commercially available polyisocyanates and castor oil were made, incorporating 2.5 per cent Zeolite 4A as a drying agent. The results of the tests made on the film are shown in Table 1.

Table 1

Mechanical properties of different castor oil polyurethanes

Castor oil combined with	Pot life (Mins)	Tensile Strength DIN 53 504 kg/cm²	Elongation at break %	Shore hardness A	Propagation tear resistance kg/cm²
TDI—2.4	200	12.5	68	62	3.8
TDI—2.6	200	12.1	54	63	4.7
TDI—80/20	200	13.3	65	63	3.9
Aliphatic diurea isocyanate	*	16.3	32	79	4.4
MDI—Homologue	25	11.8	70	60	2.8
MDI—modified	25	42.6	130	70	10.0

*0.2 per cent Zn-octoate was used as a catalyst

The pot life shows that the reactivity of the diphenylmethane di-isocyanate products (MDI) is greater than that of the tolylene di-isocyanate products. This is due to the position of the isocyanate groups in the molecule. Aromatic isocyanates substituted in the *p-* position react faster than the *o-* or *m-* substituted aliphatic ones. Aliphatic isocyanates react even slower, so that catalysts have to be used. Metallic catalysts such as zinc-octoate or the even more effective dibutyl-zinc-dilaurate are suitable.

The properties of polyurethanes made with TDI and isomers show no great differences. The trifunctional diurea-isocyanate shows the lowest elongation at break, while the bifunctional diphenylmethane di-isocyanate has very good properties. The commercially applicable isocyanate-homologue mixture has a moderate propagation tear resistance. The lacquer chemist, however, cannot be quite satisfied with these values.

It has therefore been chosen to improve the properties of the castor oil-based polyurethanes by blending with polyesters or polyethers. Two cases will be discussed :

(*a*) Polyurethane systems with castor oil and polyesters, corresponding to the above-mentioned specifications ;

(*b*) Polyurethane systems with castor oil and polyethers, corresponding to the mentioned specifications.

Example 1

Mixtures of castor oil with 15 per cent polyester were prepared, pigmented with 50 per cent titanium dioxide. The polyester used was bifunctional with an hydroxyl content of 8.5 per cent. Five per cent zeolite, calculated on the total mixture, was also added. Testing of the film gave the following results :

Tensile strength (DIN 53 504)	67 kg/cm²
Elongation at break	82%
Shore hardness A	80°
Propagation tear resistance	17 kg/cm²
Abrasion resistance (Taber Abraser CS 10 at 1,000 revolutions)	22 mg

It is striking that all these values are superior to those shown in Table 1. Particularly noticeable is the abrasion resistance as measured with the Taber Abraser, giving 22 mg at 1,000 revolutions. The remarkable improvements of the properties of the solventless systems can be ascribed to the linear structure of the polyester alcohols, giving the coating a better " nerve."

The values given are related to a stoichiometric crosslinking, i.e. the amount of polyisocyanate used is equivalent to the hydroxyl-content. Crosslinking above and below the normal level can be used for special effects. Solvent containing polyurethane lacquers have been thoroughly investigated, and the dependence of the film properties on the NCO/OH ratio closely examined. Experience generally shows that excess isocyanate-groups render the coatings harder and increases their chemical resistance ; similar results were obtained with solventless polyurethane lacquers.

Fig. 2 shows how the film test values depend on the NCO/OH ratio. The tensile strength and hardness increase markedly with the excess isocyanate, while the abrasion resistance is only slightly reduced. These results led to the use of excess isocyanate in many applications, corresponding to a NCO/OH

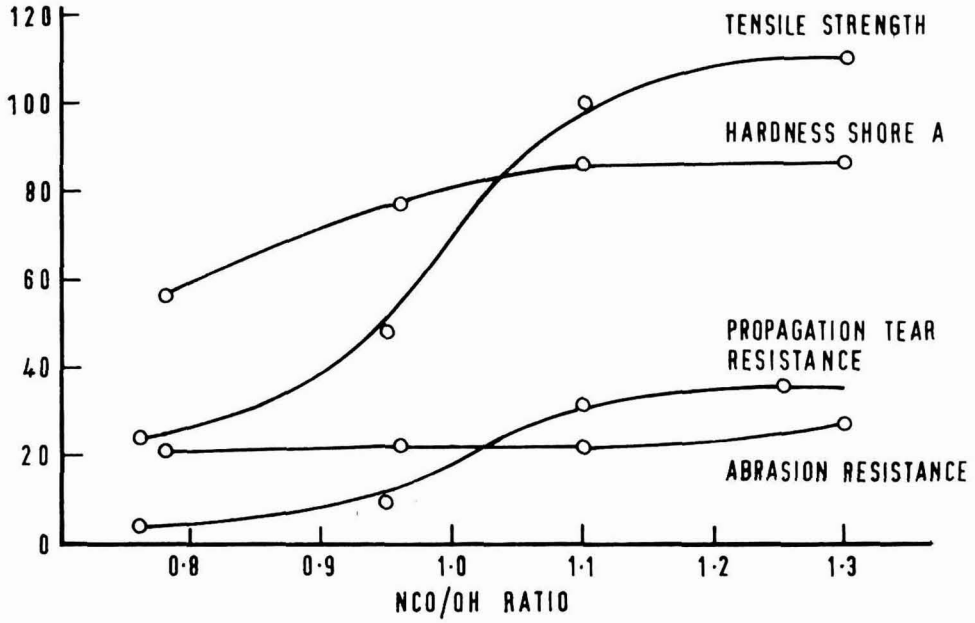


Fig. 2. Mechanical properties of solvent-free polyurethanes

ratio of about : 1.3. In cases where more flexible films are desired, such as in the coating of flexible foams, a NCO/OH ratio of 0.9 would be better. The chemical resistance of this combination is shown in Fig. 3.

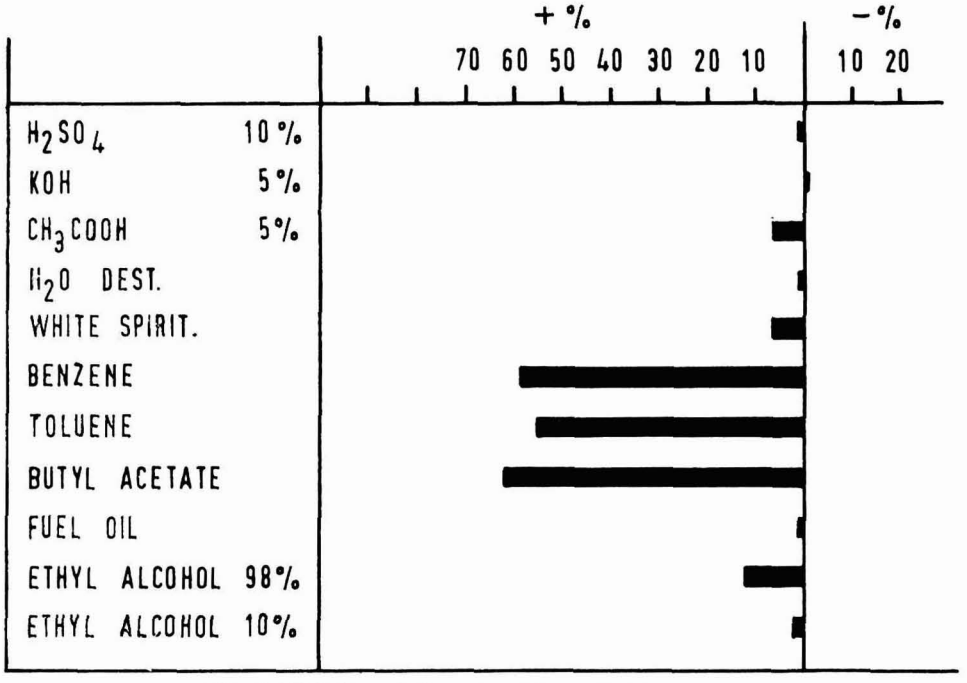


Fig. 3. Weight variation after 12 months' immersion

Fig. 3 shows the change in weight of free films kept in different media for one year. One has to take into account that this method of testing leaves out the influence of the substrate. The weight changes do, however, show what has already been proved in practice :

Acid resistance	good
Alkali resistance	moderate
Water resistance	good
Oil and petrol resistance ..	good
Ester and aromatics resistance ..	poor

Figs. 4 and 5 show an application of the above combination. It concerns a protective coating of a concrete floor on the technical floor of a high building. A seamless, flexible coating was applied in the form of a basin, protecting the rest of the building against water penetration. Similar work has been done in atomic reactor installations, where the problem of jointless sealing of the floor also exists. Demands for radiation protection and decontamination are both met.

Fig. 4

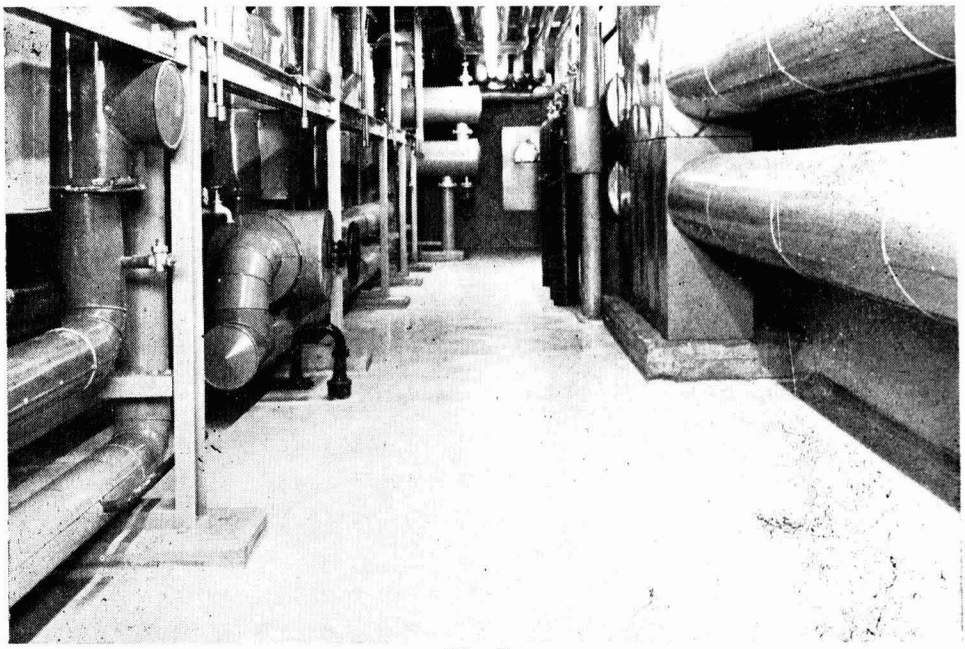


Fig. 5

Example 2

Mixtures of castor oil and 50 per cent polyether were prepared. The ether used was trifunctional with an hydroxyl-content of 11.5 per cent. The compatibility of castor oil and polyether is unlimited so that any proportion may be used. The tests were made on unfilled cast films ; 2.0 per cent zeolite was included.

Results

Tensile strength DIN 53 455	424 kg/cm²
Impact resistance DIN 53 453 ..	13.8 kg/cm²
Flexural strength DIN 53 452	700 kg/cm²
Compressive strength DIN 53 454 ..	543 kg/cm²
E—modulus	18,600
Heat resistance DIN 53 458 (Martens)	36°C

The above results show the influence of the high hydroxyl-content and branching of the polyether on this combination. In contrast to the previously discussed castor oil polyester system these are hard, solventless substances which retain some resilience, as shown by the value for flexural strength. The high crosslinking results in improved chemical resistance, as for instance complete resistance to 30 per cent KOH can be obtained. Water resistance is still good ; it will, however, be reduced with an increasing proportion of polyether. As already mentioned, this is due to the hydrophilic nature of polyether. Resistance to benzene hydrocarbons and esters is not achieved by this system.

The low viscosity of the polyether alcohols enable more filler to be included. Fig. 6 shows measurement of compressive strength and flexural tensile strength found in a polyurethane-combination filled with 300 per cent quartz-powder.

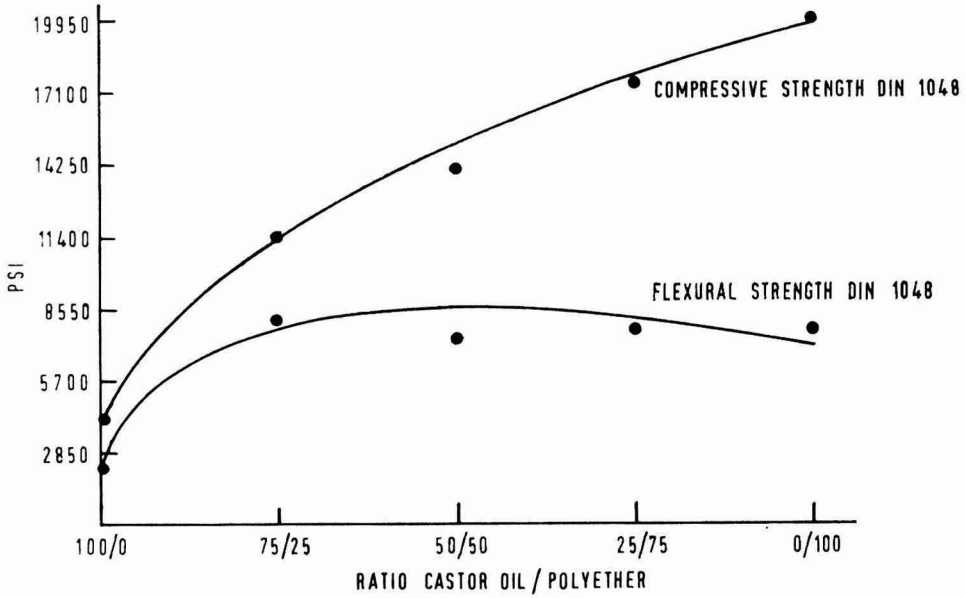


Fig. 6. Mechanical properties of polyurethanes

As expected, the compressive strength increases with an increasing proportion of polyether, while the flexural strength reaches a maximum at equal parts of castor oil and polyether. A 1 : 1 castor oil : polyether blend crosslinked with the diphenylmethane di-isocyanate homologue mixture has proved successful in practice.

The best results are obtained with a NCO/OH ratio of 1.1. This may be seen in Fig. 7 which shows the influence of the NCO/OH ratio on the compressive strength and flexural strength.

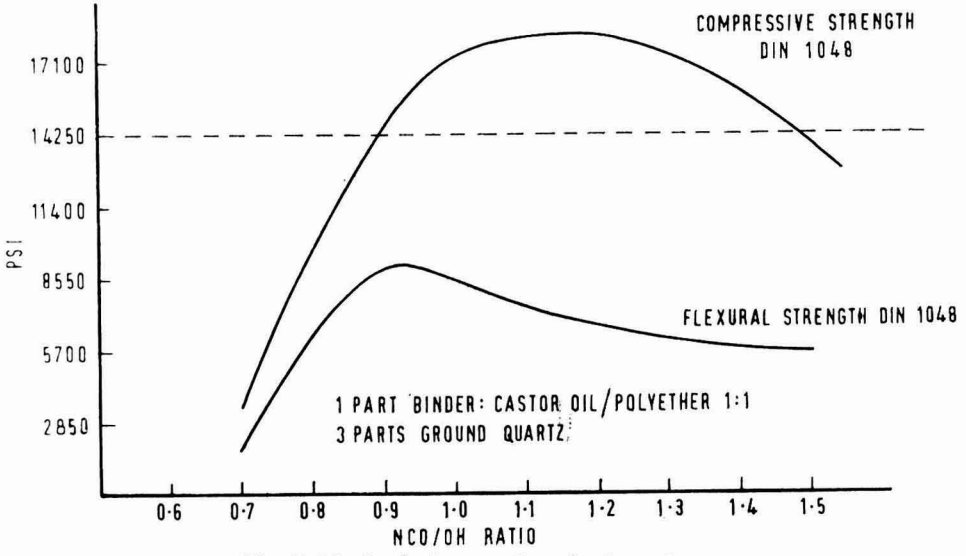


Fig. 7. Mechanical properties of polyurethanes

The graph shows that compressive strength values may exceed 1,000 kg/cm² in the NCO-OH range of 0.9 to 1.5. This is important for practical applications, as one cannot be certain that the mixer uses the exact proportions.

An increase of the filler content is of course possible. The ground quartz proportion has been raised to 14 parts to 1 part polyurethane, using dry sand. The result of the strength tests are shown in Fig. 8. Maximum compressive strength is reached with a binder-filler ratio of 1 : 8.

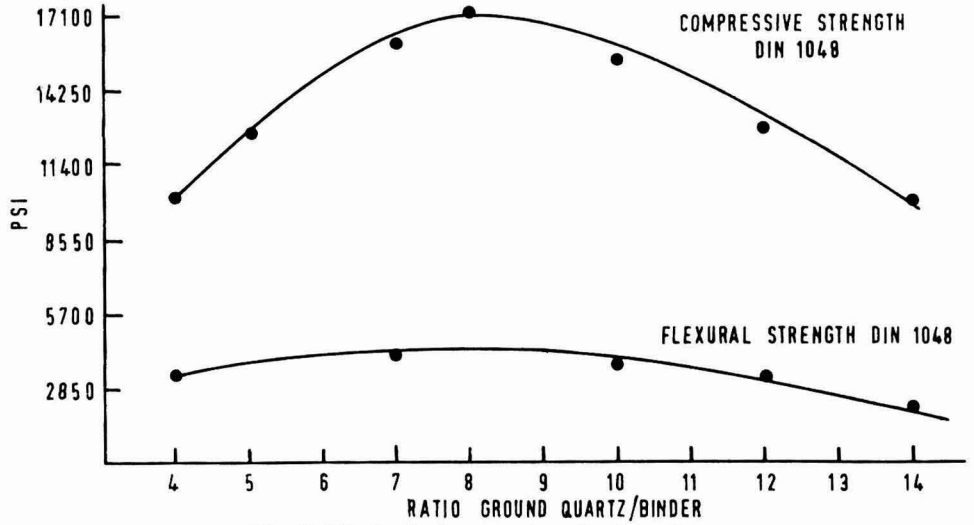


Fig. 8. Mechanical properties of polyurethanes

The conditions shown here are examples from practical applications.

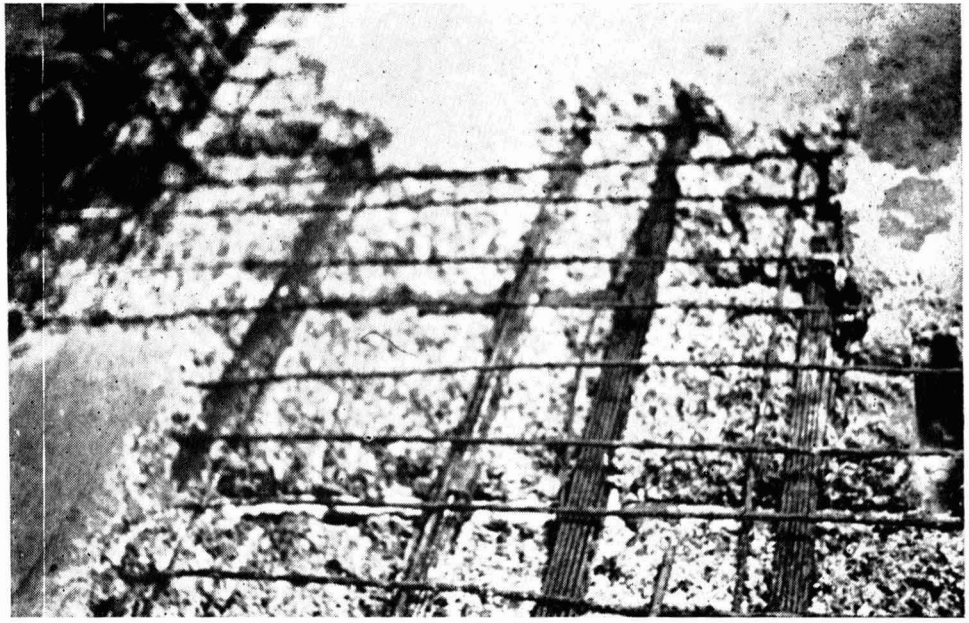


Fig. 9

Fig. 10

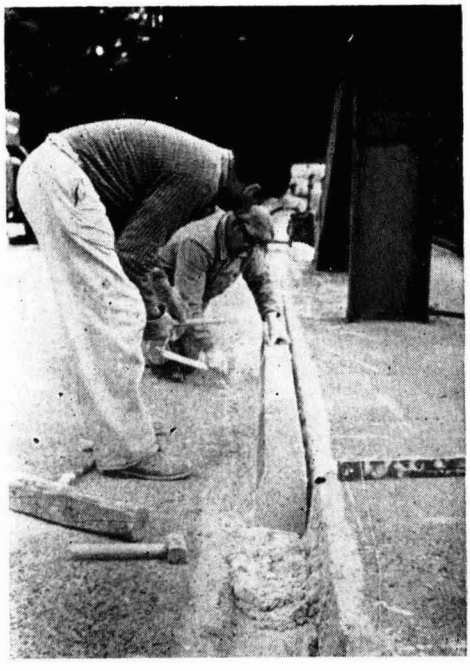


Fig. 11

Fig. 12

It concerns the coating of the roadway of a concrete bridge showing signs of corrosion.

Fig. 9 shows the underside of the bridge. The iron structure is exposed and is attacked by water seeping through. The border stones are taken out (Fig. 10) and reset in a highly filled polyurethane mortar. The roadway gets an epoxy resin based primer and a double application of a solventless polyurethane coating.

Problems of application

The application of the described polyurethane systems is usually done by hand. The pot life of the preparations is between 30 and 60 minutes, depending on their size and temperature. The speed of cure is such that the coated surface may be used after overnight cure, but complete hardening takes about one week. The rate of hardening is sufficiently rapid even at low temperatures, such as +5°C.

There has been no lack of attempts to apply the solventless polyurethane lacquers by machine, but a number of problems arise.

(*a*) Single-unit sprayguns or the airless method cannot be used as the pot life of the preparation is too short. (*b*) Pouring machines cannot be used for the same reason. (*c*) Double-unit sprayguns with external mixing, as used with

unsaturated polyester resins are not suitable for the poly-addition reactions because the mixtures obtained are not sufficiently homogeneous. (*d*) Double-unit sprayguns with internal mixing can be used. The construction of the apparatus must be arranged in such a way that the pumped liquid components meet in the mixing chamber of the spraygun. The construction of the mixing chamber is decisive in determining the suitability of the apparatus, as the mixture must become homogeneous in a very short time. If this is achieved, as in some known cases where this system has been applied, the pot life will no longer restrict the method of application of the polyurethane coatings.

Catalysts

Catalysts are important for the double unit sprayguns. A whole row of catalysts with progressive activity are known in polyurethane chemistry. They include metallic compounds such as zinc-octoate and in particular tin compounds, such as dibutyl-tin-dilaurate. A second group includes tertiary amines. Piperazine derivatives are amongst the most active catalysts.

Fig. 13 shows the influence of two catalysts on the reaction between Tolylene di-isocyanate—adduct and polyester. 2.5 g catalyst was added to 100 g isocyanate. Measurements were made by infrared spectroscopy in a dry atmosphere.

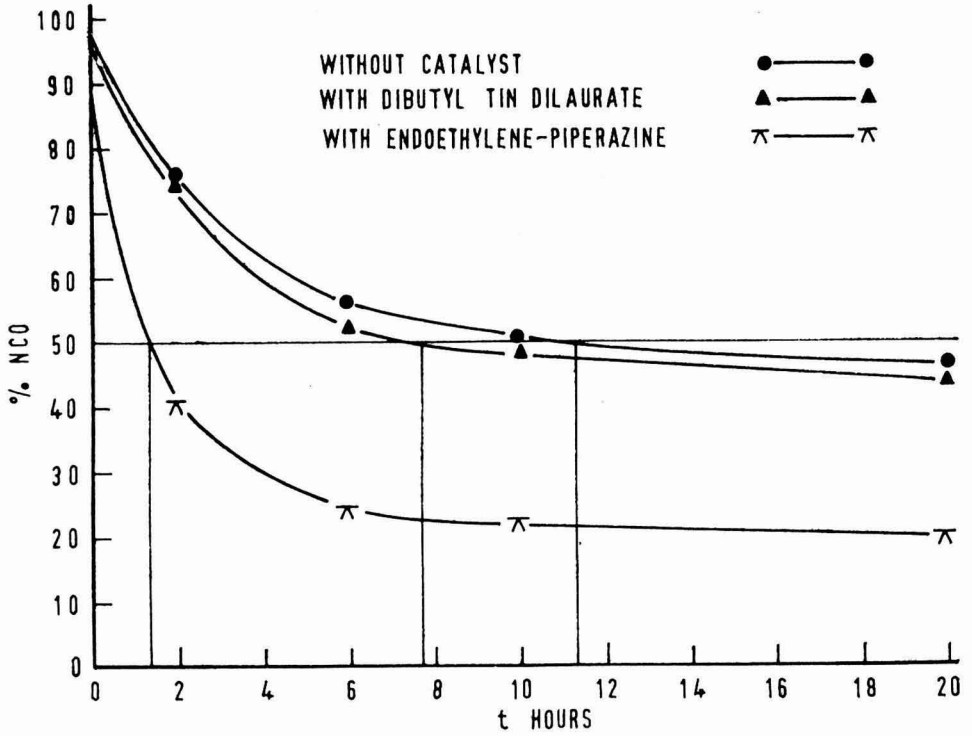


Fig. 13. Influence of catalysts

Half-life periods

Without catalysts ..	.. 11 hours
Dibutyl-Zn-dilaurate	.. 7.5 hours
Endo-ethylenepiperazine	.. 1.5 hours

Practical experience has shown that solventless coatings with catalysts can be sprayed, having a drying time of less than 30 minutes.

The difficulties arising from this method of application cannot be denied. As already mentioned, the worker must be protected by a breathing mask and protective goggles from the spray. Between work-periods the sprayhead must be cleaned, as the polyurethane mass may harden in the mixing jets. Thus the work is generally done by hand.

Fields of application

Solventless polyurethane finishes are used for the surface protection of metals, concrete, foams and other materials. If used in the open one has to expect yellowing as well as chalking after a few months. Solventless polyurethane filler coats are used for sealing in building and industrial applications. Hydrogenated castor oil has proved an excellent thickening agent for this purpose. The advantage of the hydrogenated castor oil lies in its film forming properties as well as in its physical action. Because of its remaining hydroxyl-group it is incorporated in the binder structure.

Further applications, as the elastic sealing of seams, are based on the characteristic properties of the polyurethanes, which may be made hard or flexible.

Discussion

MR. L. ORSINI said his question referred to the water absorbent materials which were required to prevent foaming in solventless polyurethane systems. Dr. Gruber had said that molecular sieves alone were sufficient to prevent the foaming, but molecular sieves were very expensive. In uses such as the gasket in masonry in which cheap materials were required, and in which a little foaming did no harm, he wondered whether some desiccated plasters were efficient enough to prevent foaming to some extent, and he asked if Dr. Gruber had experimented with some plasters.

DR. H. GRUBER said that normally zeolite was used in these systems, but only about 5 per cent was added. He agreed that the molecular sieves were not cheap and he knew that in the American literature there was some work on the water absorbing products. He said that they had found that gypsam—a special type of gypsum—had an effect. A large number of drying materials were also tried, but by no means were there the same results that were obtained with the molecular sieve.

DR. K. CULEMEYER said that as Dr. Gruber had mentioned the formation of certain polyurethane systems by adding isocyanates to the hydroxyl groups of castor oil, he wondered whether the work had been confined to castor oil exclusively, or whether it had been extended to other oils containing active groups that react with isocyanates. It was known that Oiticia oils contained a reactive keto group and it would be interesting to know something of the comparison of the properties of these oils, with special regard to the fact that castor oil was a non-drying oil, whereas the Oiticia oils were good drying oils.

DR. GRUBER said that castor oil had a hydroxyl content of about 4.8, and as far as he knew castor oil was the only one with such a large hydroxyl content. There were some other natural oils like izano oil, with hydroxyl groups. Izano oil had a hydroxyl content of about 1½ per cent, and the branching in these oils would not be enough to make a coating. All the cheaper oils such as Oiticia oil had keto groups, but these keto groups did not react with isocyanates. However, in special cases tung oil was used for solvent free coating systems. Normally the solvent free systems dried with a high gloss, and this high gloss was not preferred in most cases as matt surfaces were required. The tung oil was used in concentrations of 3 per cent.

During the curing the tung oil seemed to swim up to the surface, nearly as much as the paraffin used in air-drying unsaturated polyesters, therefore on the surface there was an air-drying effect a little like orange peel and it gave a very pleasant frosted effect.

DR. H. A. HAMPTON said he would like to make a comment and then ask a question. As one who had done quite a lot over the past years to popularise the use of MDI, he was most grateful to Dr. Gruber for his paper and for stressing the value of this non-toxic isocyanate in yet another application. The non-hazardous nature of this type of isocyanate was obvious from the photographs shown illustrating the working conditions when it was being used.

His question concerned the use of zeolites. These absorbed the water, or at least they would control the water effect for a long time, but he thought it was also mentioned that they would absorb other small molecules. He asked if there was any evidence that zeolites would control or absorb small quantities of TDI in a finish, and so perhaps eliminate the hazardous nature of that particular vapour.

DR. GRUBER said the special zeolite used was one with a channel diameter of 4 Angstroms. The diameter of this channel was large enough to trap water molecules, but it was too narrow to contain other molecules. The TDI mentioned was too large to be contained in these channels. There were other zeolites, such as zeolite 12-A, that had a channel with greater diameter, and he tried to trap the TDI in this zeolite, but with no success.

MR. E. A. DULIGAL said that he had one or two practical questions to put to Dr. Gruber. First of all he noticed in the paper that in the work on the bridge the primer used was an epoxy primer. From this was it correct to assume that the adhesion of the solventless polyurethane was not as good as the epoxies, or was there some other reason for the use of an epoxy primer?

DR. H. GRUBER said that he had referred to the epoxy primer because this was what was actually used. He would not recommend an epoxy primer ; but a polyurethane primer. In the last few months some work had been done with primers. Very good results were obtained using MDI together with a mixture of branched and linear polyether to make a pre-polymer, and to have a moisture-curing one-component system. He believed this one should be very good as a primer, not only for solvent free coatings, but also for other types.

MR. E. A. DULIGAL said his next question concerned Fig. 6. He could not understand the line given for the flexural strength. On the points shown, it would appear that the shape of that curve should be similar to the curve given for flexural strength in Fig. 7. In other words, that the highest flexural strength was at a ratio of 75/25.

DR. H. GRUBER said that in Fig. 7 there was shown the relation between the mechanical properties and the cross-linking, and in Fig. 6 there was shown stoichiometrically cross-linking, but the ratio of the castor oil to polyether had been altered.

MR. E. A. DULIGAL said he understood that and apologised for not making his question very clear. What he said was that in the graph for flexural strength in Fig. 6 the curve drawn did not follow the points shown. If a line was drawn through the points then he suggested that the shape of the curve would be the same shape as the flexural strength curve obtained in Fig. 7. Hence the flexural strength would be at 75/25 and not at 50/50 as stated.

DR. H. GRUBER agreed and said that in this case he did not know if the point given as 50/50 in this graph was correct, but many other results had been obtained confirming that the best flexural strength was in this region.

MR. E. A. DULIGAL, for his final question, asked if Dr. Gruber could give an approximate comparison of the cost between a solventless polyurethane and a solventless epoxy amine.

DR. H. GRUBER said it was not easy for him as he was a chemist.

MR. P. WALKER said it was well known that the mechanical properties of typical polyurethane coatings were adversely affected by atmospheric moisture when they were applied at high relative humidities. He asked if similar effect could be expected with the solventless coatings, and if it was so, what limits would Dr. Gruber place on humidity at the time of application?

DR. H. GRUBER said that the solventless coatings were only influenced by atmospheric humidity while it was curing. That means that it was sensitive to higher humidity in the first three or four hours. Then high humidity might cause blistering. But he had found that the influence of the humidity could be kept under control by using castor oil, for castor oil was somewhat hydrophobic; also it could be controlled by the molecular sieve. Another way was to have a large content of fillers, for one could dilute the system with the filler, for humidity only had a slight effect on a highly filled polyurethane system.

MR. E. L. FRENCH asked whether when a fast curing polyurethane primer was used there was likely to be a bond failure between the primer and top coat and was it reasonable to expect that a less reactive epoxy primer would provide better intercoat adhesion.

DR. H. GRUBER said that he had hoped to have some reactions between the primer and top coat, especially in the case of an epoxy primer. There was a very fast reaction between the isocyanates of the top coat and the residual amino groups of the primer, but in practice it was shown that this did not give good adhesion, therefore it was necessary to try many primers. Chlorinated rubber was used as well as several other one-component systems but, as mentioned before, the best results obtained with one-component moisture-curing system. It was very remarkable, for normally the adhesion by overcoating with a moisture-curing TDI pre-polymer was not very good, but it was very surprising to find that the MDI had a better effect in adhesion by overcoating.

DR. H. W. KEENAN said he would like to ask Dr. Gruber a few questions. He mentioned resilience and he was wondering how he could convince his customers that he has effected it. Dr. Keenan expressed surprise that he had used such thin films when one considered that in order to get adequate compressive strengths a film build of greater than of the order of about 3 millimetres was required. If the coating was going to experience a great deal of traffic, how would this thickness stand up to the wear?

Dr. Keenan said another question of practical importance concerned the coefficient of linear expansion of the cured floor. The order of this coefficient in the polyester field was approximately 100×10^{-6}, but there would be certain influencing factors such as temperature, and he would like to ask Dr. Gruber what happened in his

case when contraction or expansion was restricted. Did he rely to any extent on plastic deformation to correct whatever distinction may arise? His final question was, can you repair this floor? Dr. Keenan felt that was one of the first things one ought to know.

DR. H. GRUBER said in answer to Dr. Keenan's question on compressive strengths that the test used was DIN 1048; this method used $4 \times 4 \times 16$ cm blocks. He agreed nobody knew if the compressive strength in the 3-millimetre coat was in practice the same as measured in the test, but it had been proved by the bridge that compressive strength would be good enough. If it was realised that a normal concrete floor had a compressive strength of about 250 kg per sq cm and that those found with the polyurethane had compressive strengths about four times higher, then one could see that the properties were better. Another point was that a normal concrete floor had a flexural strength of about 60 or 80 kg per sq cm and those found with the polyurethanes were about 650 kg per sq cm. This was very remarkable and that was why polyurethanes were used for the coating of concrete floors.

On the question about the expansion by higher temperatures, Dr. Gruber said the polyurethanes could be made flexible or hard, and if the case arose that you had to contend with a higher expansion a flexible one could be used, in the other case a harder one.

Concerning repair, it had been found that in some cases, especially with polyether polyurethanes, there was good adhesion of a new coat, but in other cases, especially where a flexible coating where an over cross-linking was used, there were worse results in overcoating. A general answer could not be given to this question for the overcoating might give both good or bad results.

Correspondence

Notes on the use of optical brightening agents in emulsion paints containing Tioxide titanium oxide pigments

The effectiveness of optical brightening agents in white emulsion paints containing Tioxide rutile or anatase titanium oxide pigments and extenders has been assessed visually and instrumentally. An expensive OBA soluble in aromatic solvents increased the blueness and brightness of paint films containing it whereas a water soluble OBA designed for use with textiles or paper was without significant effect. The former material requires to be added to the paint dissolved in an aromatic solvent and, most essentially, in the presence of dibutyl phthalate or some similar water immiscible plasticiser since the absence of the plasticiser renders the OBA ineffective. It is believed that the plasticiser, migrating to the surface of the paint film, carries the OBA with it where, unshielded, it can make a maximum contribution to brightness by fluorescence.

Tioxide pigments, especially the rutile grades, in common with other titanium dioxide pigments, act as UV absorbers and reduce the fluorescence due to the OBA. Nevertheless, an OBA concentration of 0.05 per cent used with a Tioxide rutile pigment produces a significant improvement in brightness. Tioxide A-LF, an anatase pigment, absorbs less radiation than rutile in the violet and near UV, allows of more fluorescence and paints containing this pigment need less OBA for improved brightness.

Previous experience with optical brightening agents has suggested that fluorescence of materials containing them diminishes on exposure to light. Films of emulsion paints containing the more powerful OBA have, however, been exposed behind glass for three months and to date no decrease in fluorescence has occured. The possibility was also considered that the effectiveness of the OBA may be reduced on storage of the paint in the can but panels prepared from stored paints show the same level of fluorescence as those prepared from freshly made paints.

The extra cost of including the aromatic soluble OBA in emulsion paints at 0.05 per cent by weight depends upon the formulation of the paint but will probably be about 1s. to 1s. 6d. per gallon of paint.

British Titan Products Co. Ltd.,
Central Laboratories,
Stockton-on-Tees.

J. R. Kane

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).*

Celacol plant extensions

To meet the growing demand for Celacol, BRITISH CELANESE is to increase existing plant capacity at Spondon by 25 per cent. The new extensions are expected to come on stream by the autumn of 1966.

Review

Coulometric Analysis

By K. Abresch and I. Claassen, translated from the German by L. L. Leveson. London : Chapman & Hall Ltd. 1965. Pp. 275. Price £1 16s.

The German edition was published in 1961 and this, as we are reminded on the dust cover of the present volume, was well reviewed. Little if anything of the lucidity of the original has been lost in translation but unfortunately little has been gained either. One cannot but feel that the lapse of four years between the two editions has had a noticeable dating effect in view of the rapid development of the subject, and it seems a pity that the translator did not at least insert some of the many references which have become available since 1959. However, the text is both clear and concise and, with the foregoing reservation, should appeal to student and research worker alike.

The book is written in two parts ; Part I on principles, apparatus and instrumentation, and Part II on applications, are in good balance, whilst the references adequately cover the literature up to 1959. Both text and illustrations are commendably clear.

A feature of Part I is the stress laid on instrumentation. In these days of instrumental analysis it is imperative that laboratory workers be aware of what electronics has to offer, and we find here numerous electronic circuits presented which, if not always uniform in their symbolism, are, for the most part, distinguished by giving the values of the components used. All too frequently in publications of this kind one is faced with a galaxy of unlabelled valves, resistors and capacitors and left to find out for oneself just which types to employ. Whilst the chapters dealing with these matters cannot be said to be an adequate substitute for a primer on electronic circuitry they do nevertheless provide a wealth of information on the subject and there must be many ingenious laboratory workers who will be stimulated into trying their hands at building some of the instruments described, several of which, with but little modification, can be seen to have applications outside the field of coulometry. However, only one circuit employing transistors is described and the sparse references to solid state devices will do little to encourage the adoption of the more recent techniques.

The applications section includes two comprehensive sets of tables listing determinations at constant voltage and constant current respectively. They include references to the original work, notes on the electrode systems used, and on the range and accuracy of the determinations. Both inorganic and organic applications are described though the chemist in the surface coatings industry would be better served were the latter group amplified by the inclusion of some of the methods reported more recently.

The book is commendably free from misprints, only one (page 22, line 19) being noted on a first reading. It is adequately indexed, well produced and represents very good value indeed at £1 16s. It may justifiably be regarded as the standard work on coulometric analysis until another appears which spans the literature of the last five years and at the same time provides such a firm grounding in first principles.

D. GRIME.

London

The decoration of plastics

The first meeting of the 1965-66 session was held on 16 September at a new venue, the Physics Lecture Theatre, at Imperial College, South Kensington. In accordance with tradition this was the Chairman's evening and the new Chairman, Mr. C. R. Pye, spoke on " The Decoration of Plastics."

Mr. Pye dealt particularly with the processes used in printing thermoplastic containers and films mainly based on polyethylene. Various methods of printing, *e.g.*, flexographic, silkscreen and offset letterpress, were used, depending on the type of product, and the main problem in all cases was that of adhesion to the polymer surface. A variety of methods of pretreatment of the surface was used to improve adhesion. Liquid phase methods included solvent treatment or chemical treatment with oxidising agents, and such methods involved washing and drying the surface before printing. UV or gamma radiation treatments had been suggested, but had not come into general use.

One method which had been used commercially was electrical treatment with a corona discharge at 10-30 kV ; quite short times of treatment were sufficient and relatively high speeds could be used in treatment of continuous film. The most widely used method was heat treatment with an oxidising gas flame, which was in contact with the plastic for periods of the order of 1-2 seconds.

Certain problems arose in selection of the printing process and materials which were related to the end use of the package. Thus certain plastics were permeable to solvents, other ink components and atmospheric oxygen which could result in deterioration of the product. Consequently many attempts had been made to produce a satisfactory barrier lacquer. Another related problem was that in some cases the contents of the package could permeate back through the walls of the container, and thus remove the lacquer films.

In the lively discussion which followed the paper, questions were asked by Mr. E. L. French, Mr. T. R. Bullett, Mr. A. R. H. Tawn, Mr. J. S. Marsh, Mr. P. G. Richardson, Mr. P. J. Quorn, Mr. G. C. Hurst, Mr. V. F. Jenkins, Mr. J. F. Barton and Mr. R. N. Wheeler, the subjects raised covering the effect of electrical pretreatments on adhesion, the permanence of the effects of pretreatment processes, metallising processes and protective lacquers.

Mr. H. C. Worsdall in proposing a vote of thanks to the lecturer, said that Mr. Pye had presented an excellent lecture on a quite unusual subject, and the extent of the discussion had indicated the large amount of interest which had been aroused. The vote of thanks was carried with acclamation.

V. T. C.

Midlands

To automate . . . to speculate?

The Section met at the Birmingham Chamber of Commerce on 17 September to hear Mr. H. R. Touchin deliver a paper entitled " To Automate . . . To Speculate ? "

Mr. Touchin began his talk with some comparisons between the paint and plastics industries. The plastics industry was a mass-producing industry with long runs of a few products whereas the paint industry was bedevilled by batch processing and the average annual output per man was only 1,900 gallons. Increased productivity would

require imaginative thinking and the reception of ideas from other industries. The feasibility of automation should be considered.

Whilst automation was usually considered in terms of computer-controlled processes, considerable mechanisation was possible without a computer. Anything that could be measured could be controlled but in the paint industry many properties could not be adequately measured.

Paint manufacture could be divided into four main stages: loading, processing, tinting and filling. Automated processes of weighing and measuring were already well established in other industries. The processing stage involved premixing, grinding and letting down. Plant of the " ribbon-flow " type was available for continuous premixing and sand mills and continuous mills provided a basis for continuous grinding. However, methods of on-line testing for fineness of grind needed developing. The closer control of processing by automatic controllers would reduce the amount of testing needed.

On-line blending was well known in other industries and could be used for letting-down paints. Methods of on-line blending were needed and here the development of universal stainers would be advantageous. A computer would build up its memory to give reproducibility. On-line testing for colour was already in use in an American textile process.

Automation of filling and labelling was standard in other industries and computers could control stock-levels.

Some effects of automation would be the development of universal stainers, of pigments with very strong colour and of media with wide ranges of application. There would be reductions in labour, supervision, testing and time ; the process would be better controlled and the products would show less variation. Products most suited to automated manufacture were decorative and major industrial paints. Smaller companies would be at a great disadvantage but they could still make special products which would not fit conveniently into an automated scheme. Whilst automation would tend to encourage mergers of companies to form units large enough to justify automated processes, it would also stabilise the industry by reducing the incentive to diversify.

After a lively discussion period Mr. E. D. O'Connor proposed a vote of thanks to the speaker for a well-planned and provocative paper.

L. R. S.

Scottish

Student Group

Film show

The first meeting of the new session was held on 11 September at More's Hotel. Three films were shown :

1. " Armchair Visit "
2. " Radioactivity "
3. " Man Against Insect "

The first film gave the members an insight into the ICI paint factory at Slough, the second concerned the discovery of radioactive metals and particles, and the last illustrated man's continual fight against insects and the disease caused by them.

R. F. H.

Section Annual Reports

(The following report is based on those approved by Section Annual General Meetings, and it has been edited in order to preserve a unity of style.)

Australian Federal Committee

It is felt that members of the Association will be interested in extracts of the Annual Report of the AFC, presented to the Seventh Convention, at Terrigal, N.S.W. on 17-20 *June* 1965.

It is not possible to reproduce the report in full. Certain items contained therein are still under consideration by the Council.

ANNUAL REPORT FOR THE YEAR ENDING, JUNE 1965

The Committee

At the Annual Meeting, held at Warburton in July 1964, the delegates comprised Messrs. J. Foxton and D. Martin (NSW), G. Smith and J. Fannin (Queensland), H. D. Bruce and A. E. Allen (SA), J. F. Walker and F. Funnel (Victoria) and D. Cole and G. Parsons (WA). Mr. J. R. Rischbieth was re-elected as Chairman for 1964-65. Messrs. D. Cairns and B. Wilcher continued their appointments as Honorary Treasurer and Honorary Secretary respectively.

During the year, due to changes on Section Committees, Messrs. M. Leahy (NSW), L. Curtis (Queensland), M. Pack (Victoria) and E. Fletcher (WA) replaced Messrs. Foxton, Fannin, Walker and Cole respectively. Due to pressure of other business Mr. D. Cairns resigned as Honorary Treasurer and Mr. W. Nunn assumed office.

Messrs. M. Browne, K. F. LeLievre, K. R. Russell and C. G. Bray acted as Proxy Representatives on the Committee for the New South Wales, Queensland, South Australia and Western Australian Sections, respectively.

Meetings

Apart from the Annual Meeting, the Committee held two meetings by Proxy, one of these involving an adjournment. The excellent representation afforded by the Proxies is much appreciated by the Sections concerned.

Financial

The Consolidated Income and Expenditure account for the year ending 31 December 1964 and the Consolidated Balance Sheet as at 31 December 1964 are set out at the end of these extracts from the Report.

Result for year

The overall deficit for the financial year ended 31 December 1964 was £A98 compared with £A367 in the previous year.

The deficit incurred by *Proceedings and News* was £A70.

The surplus on 1964 Raw Materials Index operations was £A55. The cash at bank for the Raw Materials Index Sub-Committee is £A960. but this consists principally of deposits received against entries and advertising in the Second Edition of the Raw Materials Index.

The AFC is very dependent, under the existing method of operation, on Grants from Council to perform its various functions. The Income derived from Convention Surpluses can, to date, be regarded as very satisfactory from the financial point of view. However, it must be appreciated that this constitutes a major source of income. As it cannot be regarded as an assured source of income each year, and as the AFC continues to record deficits each year, consideration should, at this stage, be given to alternative means of operating on a sound financial basis.

Report of the publications sub-committee

The membership of the Publications Sub-Committee for 1964-65 was as follows :

Chairman	Mr. J. R. Rischbieth
Honorary Editor	Mr. D. A. Kalwig
Honorary Secretary/Treasurer	Mr. M. Pack
NSW Member	Mr. L. Jones (1964)
	Mr. A. Adomenas (1965)

Queensland Member	Mr. B. N. Auld (1964) ; Mr. H. B. Payne (1965)
South Australian Member	Mr. K. L. Jones
Victorian Member	Mr. D. W. Berryman (1964) Mr. G. Hartshorn (1965)
Western Australian Member	Mr. P. E. Wilson

The sub-committee is pleased to be able to report that the production and finances of *Proceedings and News* are now on a much sounder basis than applied at the time of its last report in July 1964. The various facets of the publication for the year under review and the possibilities existent for the future are referred to below :

A change to letterpress printing and the use of higher quality paper effected in March, 1965 has resulted in cleaner and stronger text together with more positive colour in the advertisements.

The average size of *Proceedings and News* over the 12 months covered by this review was a little under 28 pages per issue, and 146 pages of text matter was published in total. Thirteen full length technical papers were included together with over 180 general items. The Balance Sheet of the Publications Sub-Committee shows a moderate loss to the end of 1964 ; support by Sections minimised this to a considerable degree. Due appreciation also must be given to the voluntary reduction in professional fees by our Assistant Editor/Advertising Manager during this difficult period. The operational margin with the new printing process has enabled the Committee substantially to recover previous losses. The further growth of *Proceedings and News* rests on members' active participation, balanced finances and the continued support of professional assistance.

The Executive desires to record its appreciation of the support of the other members of the Sub-Committee lacking which, it would not have been possible to produce this Federal Committee publication. The Sub-Committee feels that *Proceedings and News* is taking its place. in the technical world as an essential requirement of the Industries.

Report on the Raw Materials Index Sub-Committee

The membership of the Sub-committee for 1964/65 was as follows :

Chairman	Mr. H. D. Bruce
Hon. Secretary/Treasurer	Mr. I. D. Pike
Hon. Publications Officer	Mr. K. L. Jones
SA Section Representative	Mr. R. L. Struthers
Victorian Section Representative	Mr. C. P. Hartshorn
NSW Section Representative	Mr. D. M. Martin
WA Section Representative	Mr. E. Fletcher
Queensland Section Representative	Mr. B. Auld

The Sub-committee takes pride and pleasure in announcing that the printing, binding and packing of the Second Edition RMI's has been completed on schedule and that the new books are now ready for distribution to OCCA Members throughout Australia.

Financially, the RMI will be a success as the revenue from entry fees and advertisements will be approximately £A200 higher than all costs incurred. Sales of the Index to non-members will naturally increase the excess of income over expenditure.

The RMI Executive wish to take this opportunity to thank the Insterstate Members of the RMI Sub-Committee for their great assistance during the gathering together of data for the Index, which contains something like 3,500 product entries obtained from no less than 127 suppliers of Raw Materials for paint.

Sixth Australian Convention.

The Sixth Australian Convention which was organised by the Victorian Section on behalf of the Federal Committee and held in July 1964, at The Mayer Chalet, Warburton, Victoria, was very successful, technically, financially and socially. Papers of a high standard were presented and approximately 160 persons attended. The guest speaker at the Official Dinner was Mr. E. P. Sanford, Managing Director, BALM Paints Ltd. and many prominent men from the paint and allied industries attended this function.

In conclusion the Committee places on record its appreciation of the vast amount of voluntary work performed by its Office Bearers, Section Proxies and all the Members of its Sub-Committee.

CONSOLIDATED INCOME AND EXPENDITURE ACCOUNT FOR THE YEAR ENDED 31 DECEMBER 1964

	£A s. d.	£A s. d.
Production expenses for publications	4,525 17 6	
Less: Sales of publications and advertising revenue	4,396 19 9	
Loss on publications	128 17 9	
Subsidies received from OCCA Australian Sections	222 9 9	
		93 12 0
Interest received on bank accounts		11 3 2
Surplus on Sixth Australian Convention		251 2 6
		355 17 8
Less: General administration expenses of committees	126 17 4	
Sponsored lectures, SA and WA	33 15 0	
Accommodation and travelling for Australian Federal Committee meeting	293 11 6	
		454 3 10
Net deficit for 1964		£A98 6 2

	£A s. d.	£A s. d.
Note: The above deficit comprises :		
Surplus on Sixth Australian convention		251 2 6
Surplus on *Raw Materials Index*, First edition		55 9 4
		306 11 10
Less: Deficit on *Proceedings and News*	69 10 7	
General committee deficit	335 7 5	
		404 18 0
		£A98 6 2

CONSOLIDATED BALANCE SHEET, 31 DECEMBER 1964

ACCUMULATED FUNDS

	£A s. d.	£A s. d.
Funds at 31 December 1963	962 4 6	
Add : Adjustment of 1963 advances to a sub-committee treated as expenses	40 15 0	
	1,002 19 6	
Add: Surplus on Sixth Convention, 1964	251 2 6	
Surplus on *Raw Materials Index*, First edition	55 9 4	
		1,309 11 4
Less: Deficit on *Proceedings and News*, 1964	69 10 7	
General committee deficit	335 7 5	
		404 18 0
		904 13 4
Add: Capital grant from the Council		187 10 0
ACCUMULATED FUNDS, 31 December 1964		£A1,092 3 4

	£A s. d.	£A s. d.
Represented by:		
Cash at banks	1,841 13 1	
Subsidy receivable from OCCA, NSW Section	79 17 9	
Debtors from advertising	997 19 6	
Preliminary expenditure and advances		
Raw Materials Index, Second edition (1965)	77 13 0	
Seventh Australian Convention (1965)	101 12 0	
		3,098 15 4
Less: Creditors for printing	886 13 0	
Deposits received against entries and advertising—*Raw Materials Index*, Second edition	932 9 0	
Loan from Council	187 10 0	
		2,006 12 0
		£A1,092 3 4

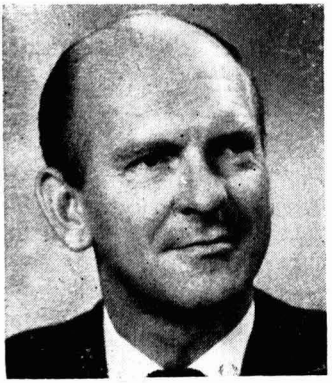
Note: There is a contingent liability not exceeding £A313 for a printing creditor's account in dispute, against which provision has not been made in the balance sheet. The committee has taken independent advice and is of the opinion that sufficient and sound grounds exist for the non-payment of this amount.

Report of the Auditors

The accounts have been prepared from the books and records of the Oil and Colour Chemists' Association, Australian Federal Committee and its sub-committees which, in our opinion, have been properly kept. We obtained all the information and explanations we required.

In our opinion, the accounts give a true and fair view of the state of affairs and results of the Committee and its sub-committees.

COOPER BROS. Melbourne
Chartered Accountants. 30 June 1965.



Association Honorary Editor

A. R. H. TAWN, F.R.I.C.

Following the resignation of Mr. D. S. Newton as Honorary Editor, after three years of distinguished service, Council has entrusted responsibility for the Association's publications to Mr. A. R. H. Tawn, F.R.I.C., who has for some years held office as Honorary Programmes Officer of London Section and has represented that Section on Council.

Born at Hornsea, Yorkshire, in 1923, Mr. Tawn was educated at Kingston High School, Hull Technical College and The Polytechnic where he qualified as an A.R.I.C. He was elected to the Fellowship of the Royal Institute of Chemistry in 1957. During the past 20 years he has studied numerous subjects ranging from polymer science and theoretical rheology to statistics, experimental design and computer programming. He counts himself fortunate in having been selected to attend a recent residential course on Management Studies at St. Catherine's College, Oxford.

After some years with British Oil & Cake Mills Limited, he entered H.M. Forces and, at the end of hostilities, was appointed Head of the Chemistry Department at No. 6 (later No. 1) Army College where he was called upon to run short courses in various branches of the subject with a small staff, and *sic* sometimes had difficulty in keeping more than one lesson ahead of his students. He joined the Coates group of Companies in 1947 where his specialisation in polymer chemistry led to his present appointment as Research and Development Manager of Cray Valley Products Ltd., the synthetic resin division of the group. In this capacity he travels widely in Europe and the United States.

Mr. Tawn's personal scientific interests are in the physical chemistry of polymers and in the application of mathematical techniques to research and management.

His interest in education, aroused during the immediate post-war years, has led Mr. Tawn to found and teach several regular and short courses at the London College of Printing, the North West Kent College of Technology and the Borough Polytechnic, and he has recently been appointed a visiting post-graduate lecturer at the University of Aston in Birmingham. He is, of course,

well known as a lecturer and contributor of papers to both OCCA and FATIPEC.

He is married, with two daughters, and, when time permits, enjoys sailing, bridge, cabinet-making, and trying to play golf. As he has just bought a new house at Petts Wood in Kent, D-I-Y and furniture making will be in close competition with his other interests, but we are reassured by his statement that his best paperwork has always been done between the hours of 10 p.m. and 2 a.m. when neither he nor the neighbours feel like creating a disturbance by more violent activities.

OCCA 18

(EIGHTEENTH TECHNICAL EXHIBITION)

Largest ever OCCA Exhibition

The Exhibition Committee is pleased to report that OCCA 18 (the Eighteenth Technical Exhibition), to be held on 14, 15, 16, 17 and 18 March 1966, will cover a larger floor area (25,000 sq. ft.) than any previous Exhibition. A full list of the companies to whom space has been allocated is given below.

The Exhibition will take place once again in the Great Hall of Alexandra Palace, London, N.22.

In order to assist those planning to visit the Exhibition a map showing the various ways in which Alexandra Palace can be reached from Central London will be reproduced in each copy of the *Official Guide*, which will be sent without charge to all members of the Association early in the New Year. Copies of the *Official Guide* will also be sent individually to chemists and technologists on the Continent of Europe, to technical colleges and, through the courtesy of trade associations, to companies in the paint, printing ink and pigment industries in the United Kingdom.

The map is also being reproduced separately in a folder which gives directions in four languages (French, German, Italian and English) and copies of these will be sent with the *Official Guide* despatched to the Continent. Copies are also available to intending visitors and they will be despatched without charge upon application to the General Secretary of the Association. The four-language cards will also be sent to many paint and printing ink manufacturing companies on the Continent of Europe.

A free bus shuttle service will be operated by the Association from Wood Green Underground Station (Piccadilly Line) and there are ample free car parking facilities at Alexandra Palace.

Amongst the facilities available at Alexandra Palace are two restaurants, together with four buffets and several bars. The London Telecommunications Region of the GPO will be installing a complete telecommunications centre with Inland and Overseas Telegraph, Telephone and Telex services.

The total number of stands allocated for the Exhibition will be 106 and, of the companies showing, ten have never shown at previous OCCA Technical Exhibitions, while 22 others did not show at the 1965 Exhibition. Amongst the overseas countries from which exhibits will be shown are Belgium, Finland, France, Germany, Holland, Italy, Sweden, Switzerland and the United States of America.

As in previous years the Exhibition Luncheon will be held at the Savoy Hotel, London, W.C.2. on the opening day, 14 March. Principal officers of other scientific bodies, industrial research associations and organisations representing both suppliers and consumers will be invited to attend.

Following the successful innovation at the 1965 Exhibition, the Committee has decided that the Exhibition will again be open on five days and it is felt that this arrangement will benefit companies, particularly those in the provinces and overseas wishing to arrange a rota for their technical staff to visit the Exhibition. The hours of opening will be as follows :

Monday 14 March ..	15.00 to 18.30
Tuesday 15 March ..	10.00 to 18.00
Wednesday 16 March	10.00 to 18.00
Thursday 17 March	10.00 to 18.00
Friday 18 March ..	10.00 to 16.00

Following the practice at recent Exhibitions, a stand will be devoted to Technical Education and parties of sixth form science students will be invited

to attend in the mornings, when they will be given short introductory talks before touring the Exhibition. The Technical Education Stand will show the courses available in the technology of the paint, printing ink and allied industries, and the technical careers open to new entrants.

Representatives from 27 overseas countries attended the 1965 Exhibition, and in order to assist the increasing numbers of both overseas visitors and exhibiting companies, interpreters will again be in attendance. There will be no charge for admission to the Exhibition, or for copies of the *Official Guide* at the Exhibition or from the Association's Offices prior to the Exhibition. Over 11,000 people visited the 1965 Exhibition.

Any company or individual who wishes to receive a copy of the *Official Guide*, when available in the New Year, 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.

ALPHABETICAL LIST OF EXHIBITORS

Albright & Wilson (Mfg.) Ltd.
Allied Chemical Corporation
Allied Colloids Ltd.
Amoco International, S/A, Geneva
Anchor Chemical Co. Ltd.
*Armour Hess Chemicals Ltd.

Baird & Tatlock (London) Ltd.
Bakelite Ltd.
*Beck Koller & Co. (England) Ltd.
Beckman Instruments Ltd.
Berk, F. W., & Co. Ltd.
†N.V. Billiton Chemie
BIP Ltd.
Blagden, Victor, & Co. Ltd.
Boehm, Fredk., Ltd.
Boulton, William, Ltd.
British Celanese Ltd.
British Oxygen Co. Ltd.
British Resin Products Ltd.
British Titan Products Co. Ltd.
Bush, Beach & Segner Bayley Ltd.
Byk Gulden Lomberg GmbH

*Campbell, Rex, & Co. Ltd.
Carless, Capel & Leonard Ltd.
Chemische Werke Huels A.G.
Churchill Instrument Co. Ltd.
Ciba (A.R.L.) Ltd.
Ciba Clayton Ltd.
*Cornbrook Resin Co. Ltd.
Cornelius Chemical Co. Ltd.
*Coulter Electronics Ltd.
*Crosfield, Joseph, & Sons Ltd.
Croxton & Garry Ltd.

D. H. Industries Ltd.
*Dow Chemical International Inc.
†Draiswerke GmbH

Dunlop Chemical Products Division
*Durham Raw Materials Ltd.

Elecometer Instrument Ltd.
*Elga Products Ltd.
English Clays, Lovering, Pochin & Co. Ltd.

Farbenfabriken Bayer A.G
Ferranti Ltd.

*Gardner Laboratories Inc.
Geigy (UK) Ltd.
Grampian Press Ltd.

Hercules Powder Co. Ltd.
†Hilger & Watts Ltd.
Hoechst Chemicals Ltd.

Imperial Chemical Industries Ltd.
Imperial Smelting Corporation Ltd.
*Industrial Solvents Division of the Distillers Co. Ltd.

Johns-Manville Co. Ltd.
*Joyce, Loebl & Co. Ltd.

Kingsley & Keith (Chemicals) Ltd.
Kronos Titanium Pigments Ltd.
Kunstharsfabriek Synthese NV

*Lancashire Tar Distillers Ltd.
Laporte Industries Ltd.
Lennig Chemicals Ltd.
Little, J. H., & Co. Ltd.
Livingston Electronics Ltd.

*Marchant Bros. Ltd.
Maschinenfabrik Heidenau Veb.
Meyer's, Rudolf, Inc.
Mitchell, L. A., (Metal Propellers) Ltd.
†Molteni Off. Mecc. of Milan

Novadel Ltd.

Paint, Oil & Colour Journal
Paint Research Station
Pfizer Ltd.
Plastanol Ltd.
Premier Colloid Mills Ltd.
*Price's (Bromborough) Ltd.
†Pure Chemicals Ltd.
†The Pyrene Co. Ltd.

Reeves & Sons Ltd.
Research Equipment (London) Ltd.
*Resinous Chemicals Ltd.
†Rhone-Poulenc, Societe des Usines Chimiques

†Sangamo Controls Ltd.
Sawell Publications Ltd.
Scado-Archer-Daniels NV
*S.C.C. Colours Ltd.
*Scott Bader & Co. Ltd.
*Shawinigan Ltd.
Sheen Instruments (Sales) Ltd.
Shell Chemical Co. Ltd.
Silverson Machines Ltd.
Spelthorne Metals Ltd.
Steele & Cowlishaw Ltd.
*Sturge, John & E., Ltd.
Styrene Co-Polymers Ltd.
Surface Coating Synthetics Ltd.
*Svenska Oljeslageri Aktiebolaget

Titanium Intermediates Ltd.
Torrance & Sons Ltd.
*Torsion Balance Co. (Great Britain) Ltd.

*Universal Oil Co. Ltd. & Associates

Vinyl Products Ltd.
†Vuorikemia OY

Winkworth Machinery Ltd.

Technical Education Stand
OCCA Information Bureau
National Provincial Bank
British Red Cross Society
GPO Telex and Postal Units

*Denotes exhibitors who did not show at the 1965 Exhibition.

†Denotes exhibitors who have not shown at previous Exhibitions.

Manchester Section

Conversazione on modern instrumentation in the surface coatings industry

A conversazione for Junior Members and others interested was held jointly with the North East Liverpool Technical College, at the College, on the afternoon of 10 September.

The conversazione, which was attended by more than 70 visitors, included a demonstration of laboratory equipment and data and the Section gratefully acknowledges the help given by the Companies concerned namely :

Optical Instruments :

Donald Macpherson and Company Limited ; Goodlass Wall and Company Limited ; Hilger and Watts Limited ; Livingstone Electronics Limited ; Optica (United Kingdom) Limited ; Perkin Elmer Limited ; Stanhope-Seta Limited ; The Tintometer Limited.

General Instruments :

Baird and Tatlock (London) Limited ; Chandos Products (Scientific) Limited ; F. Copley and Company ; Elcometer Instruments Limited ; Funditor Limited ; Grant Instruments Limited ; Research Equipment (London) Limited ; Sheen Instruments Limited.

During the afternoon a most interesting lecture and demonstration was given by the Section's Honorary Research Liaison Officer, Dr. F. M. Smith, and his colleague on " Colour Consciousness " in which Dr. Smith dealt with the effect of various additive and subtractive mixtures of colours. Colour sensation and the way the eye worked was also described and the lectures ended with a demonstration of the Land Effect.

In proposing a vote of thanks the Chairman, Mr. H. F. Clay, thanked the College and the Principal, Mr. G. V. Hargreaves and Mr. K. Tickle for the facilities and efforts and also Dr. F. M. Smith and the other Section Committee Members who had arranged such a successful venture for younger members in the Liverpool area and thought that the Committee would be encouraged to continue to provide items for the younger members.

W. F. MCD.

Visit to ICI Ltd., Mond Division, Petrochemical and Polymer Laboratories, Runcorn Heath, Cheshire

On 17 September, the Chairman, Mr. H. F. Clay, and 45 members of the Section visited the Technical Service Laboratory and Petrochemical and Polymer Laboratories of ICI Ltd. (Mond Division).

The Mond Division, which is an amalgamation of the General Chemical Division and the Alkali Division, is concerned, at Runcorn, very largely with chlorinated materials (e.g. chlorine, vinyl chloride monomer, chlorinated ethylene). Hence the morning visit was concerned with the Technical Service Laboratory dealing with chlorinated solvents and the processes associated with metal pretreatment including degreasing with non-flammable solvents and trichlorethylene thinned paints.

After lunch, kindly provided by the Company, the parties visited various laboratories of interest in the Research Buildings and saw demonstrations, including mass spectrophotometers, an infrared process analyser and nuclear magnetic resonance equipment which is used to identify experimental materials. The use of chlorinated rubber in paints, printing ink and paper coatings was also demonstrated as was the use of chlorinated, fluorinated hydrocarbons as propellents and a brominated chlorinated, fluorinated hydrocarbon as a fire extinguishing agent.

In proposing a note of thanks to the Company and Mr. Roberts, the Director of Group B of the Mond Division, Mr. H. F. Clay said that he was sure that all the members had thoroughly enjoyed the visit and he was confirmed in the opinion he had held since his youth that all chemists could benefit from making the pilgrimage to the Widnes and Runcorn works.

After the visit members gathered at the Fiddlers Ferry Hotel for a social evening and despite the enforced wait and stormy weather in a setting reminiscent of the best suspense films an enjoyable evening completed the day. W. F. MCD.

Midlands Section

Annual Ladies' evening

The Midlands Section Annual Ladies' Evening will be held this year on Thursday 6 January 1966, at the George Hotel, Solihull, commencing with a reception at 7 p.m., followed by dinner at 7.30 p.m. prompt. Dancing will commence as soon as possible and will continue until 1 a.m. Tickets are two guineas each and those members requiring tickets are advised to apply as soon as possible to the Honorary Secretary of the Midlands Section, Mr. D. J. Silsby, 356 Baldwins Lane, Hall Green, Birmingham, 28, enclosing their remittance with the application.

City and Guilds of London Institute examination results

Congratulations are extended to the following members of the Association upon their success in the recent City and Guilds of London examinations. The class of membership and the Section to which the member is attached are shown in italics.

Intermediate Examination in Paint Technology

B. F. Gilliam (*Associate—London, Thames Valley Branch*), D. F. Langfield (*Associate—London*), A. P. Kershaw (*Junior—Manchester*), B. Townson (*Junior—Manchester*), R. Macdonald (*Junior—Newcastle*), D. Morris (*Ordinary—West Riding*).

Advanced Examination in Paint Technology

D. S. Aldis (*Associate—London*), J. Bell (*Junior—London*), D. W. Hemsley (*Ordinary—London, Thames Valley Branch*), D. C. Timpson (*Junior—London*), G. Asten (*Ordinary—Manchester*), J. Inch (*Junior—Manchester*), M. E. Williams (*Ordinary—Manchester*), R. Greenland (*Junior—Midlands*), D. Logan (*Junior—Newcastle*), R. W. Pye (*Junior—Newcastle*).

Paint Technology—Full Technological Certificate in Works Organisation

M. M. Eames (*Ordinary—London*).

Paint Technology—Full Technological Certificate in Application of Surface Coatings

P. A. Morriss (*Junior—Manchester*).

Paint Technology—Full Technological Certificate in Polymer Chemistry in Surface Coatings Technology

J. W. Kennedy (*Junior—London*), A. C. Saxby (*Ordinary—London*), D. G. Songhurst (*Junior—London, Thames Valley Branch*), P. G. Staples (*Ordinary—London*), A. R. Crump (*Junior—Midlands*).

Printing Ink Technicians' Certificate: Part I

B. S. R. Guy (*Junior—London*), M. J. P. Heath (*Junior—London*).

Printing Ink Technicians' Certificate: Part II

J. W. Bird (*Junior—London*), Mr. J. P. Heath (*Junior—London*).

Amendments

The following amendments to the list of Section Committees published in the August *Journal* have been notified :

Bristol Section—Insert *Immediate Past Chairman*, L. J. Brooke, 39 Abbots Way, Westbury on Trym, Bristol.

Bristol Section, Irish Branch—Ex Officio Member—Delete L. J. Brooke and insert R. J. Woodbridge, Chairman of Bristol Section.

South Australian Section—Insert *Honorary Publications Officer*, K. A. Metcalfe, B.MET.E., 1 Corona Avenue, Fulham, South Australia. *Committee*—Delete J. W. A. Matthews, K. A. Metcalfe. Insert R. G. Moon, 71 Finniss Street, Marion, South Australia ; R. A. Priest, B.SC., 77 East Avenue, Clarence Park, South Australia.

News of members

Retirements

We have been informed that the following members have retired from business. Dr. H. A. Hampton (President 1961-63) retired from his post as Technical Manager in the Polymer division of ICI Ltd. on 31 October, and Dr. V. G. Jolly, a Past Chairman of Manchester Section, has retired from the Walpamur Company, in which he was Research Director.

Mr. S. W. Kettle, an Ordinary Member attached to London Section, retired from the Burrell Group after 47 years with that company. Mr. L. Bowden, one of the Founder Members of the Manchester Section, and Northern Sales Director of SCC Colours Ltd., has retired after 50 years' service with Cornbrook Chemicals Ltd.

Mr. R. J. Ledwith, an Ordinary Member attached to the London Section, has been appointed Technical Manager (Special Projects) of Pinchin Johnson and Associates.

Obituary

Maurice E. Dougherty

We learned with regret of the death of Maurice E. Dougherty. He was one of our oldest members and rendered valuable service to the Association during the critical years between the wars, particularly in the realm of finance. From 1924 to 1938 he was continuously engaged as auditor, treasurer or on the Finance Committee, and in recognition of his sound and conscientious work was made Vice-President, 1934/6. Apart from these activities he was always ready with help and advice which, based on a long and varied experience, was of especial value to the Association at a period of rapid growth in particularly difficult times. He deserves to be remembered among those whose disinterested services laid the foundations of the Association's present high status among technical societies.

T. HEDLEY BARRY.

Particle Size Analysis Conference 1966

The Society for Analytical Chemistry is organising a Particle Size Analysis Conference to be held at Loughborough College of Technology from 14-16 September 1966.

The papers and discussions will describe original work covered by the review of Particle Size Analysis published in the *Analyst*, 1963, 88, 156-187.

Intending authors are asked to submit titles and summaries of their papers to the Editor of the *Analyst* by 8 November 1965. Any further details can be obtained from Mr. D. C. Soul, Society for Analytical Chemistry, 14 Belgrave Square, London, S.W.1.

Third International Corrosion Congress

It has been suggested by the British Joint Corrosion Group, of which OCCA is a participating member, that if sufficient members of this Group are interested in travelling in a party to the Third International Corrosion Congress in Moscow, to be held in May 1966, it may be possible to arrange a block travel booking with a reduction in cost for individual members.

In order that this possibility can be explored, members who propose to attend the Congress are asked to inform the Honorary Secretary of the British Joint Corrosion Group, Dr. J. G. Hines, c/o 14 Belgrave Square, London, S.W.1., and state whether they would be interested in a block booking if it could be arranged.

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

BASSETT, PETER, B.SC., Dulux Ltd., PO Box 704, Alrode, Transvaal, South Africa. (*South African*)

DAVIDSON, IAN RICHARD, 4 Bassenhally Road, Whittlesey, Nr. Peterborough. (*Midlands*)

FIRMINGER, ERROL, Chegwyn Street, Botany, PO Box 56, New South Wales, Australia. (*New South Wales*)

GUTTERIDGE, WILLIAM JOHN, 51 Peel Street, Belmore, New South Wales, Australia. (*New South Wales*)

JENSON, BERNARD GILMOUR, 24 Brookland Crescent, Durban North, Natal, South Africa. (*South African*)

KARIUS, HELMUT, Hoechst SA, PO Box 65, Mobeni, Natal, South Africa. (*South African*)

LILLEY, KENNETH ALBERT, 46 Boyer Road, Beacon Hill, New South Wales, Australia. (*New South Wales*)

MCKELVIE, ARCHIBALD NEIL, B.SC., 75 Bearwood Road, Wokingham. (*London—Thames Valley Branch*)

NOLAN, JOHN DEVEREUX, Permutit Company Ltd., Permutit House, Gunnersbury Avenue, Chiswick, London, W.4. (*London*)

VAN MARCKE, ERIC, 6 Highbury Gardens, Cavendish Road, Bellevue, Johannesburg, South Africa. (*South African*)

WALDNER, GASTON, 40 Clarendon Rise, London, S.E.13. (*London*)

YOUNG, PETER, Flat 8, The Manor House, Bewdley, Worcestershire. (*Midlands*)

Associate Members

BERRELL, PAUL JOSEPH, c/o PO Box 280, Durban, South Africa. (*South African*)

CHOOI, THOR HOR, 71 Meru Road, Klang, Selangor, Malaysia. (*Overseas*)

DEUTER, ROBERT HOLMAN, Meggitt Ltd., PO Box 64, Port Adelaide, South Australia. (*South Australian*)

KING, ROY, Pomeroy, South Furzeham Road, Brixham, South Devon. (*Bristol*)

NEIL, JOHN ROBERT, c/o Hardie Trading Ltd., 109 South Road, Hilton, South Australia. (*South Australian*)

RUDD, CHARLES MINCHIN, c/o Box 280, Durban, Natal, South Africa. (*South African*)

SMITH, STANLEY THOMAS, 77 Queen Victoria Street, Bexley, New South Wales, Australia. (*New South Wales*)
TOWNSEND, JOHN REX MAURICE, Maytree Cottage, Sandford Orcas, Sherborne, Dorset. (*Bristol*)
WAITE, RENNIE ADAIR, 308 Hillsborough Road, Mount Roskill, Auckland, New Zealand. (*Auckland*)

Junior Members

BARNES, FREDERICK GRAHAM, 47 Judd Street, Mortdale, New South Wales, Australia. (*New South Wales*)
BUINING, PIETER JAN JACOB, 40a Day Road, Cheltenham, Sydney, New South Wales, Australia. (*New South Wales*)
LAMBLE, DEREK LAURENCE, 7 Ennisdale Drive, Durban North, Natal, South Africa. (*South African*)
OLIVER, GEOFFREY FRANK, 10 Walpole Street, Preston, Lancs. (*Manchester*)
THOMAS, KEITH GREENWOOD, 15 Carnarvon Place, Durban North, Durban, South Africa. (*South African*)

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 after publication.

Monday 1 November

Hull Section. "The Protection of Structures," by F. G. Dunkley. To be held at the Royal Station Hotel, Hull, at 7 p.m.

Thursday 4 November

Bristol Section. "Design of a Modern Paint Factory," an open discussion. Joint Meeting with Birmingham PVL Club, to be held at the Imperial Hotel, Birmingham.

Newcastle Section. "Pretreatment Primers for Structural Steel," by D. A. Bayliss and D. C. Wall, to be held at the Royal Turk's Head Hotel, Grey Street, Newcastle upon Tyne, at 6.30 p.m.

Monday 8 November

West Australian Section. "Film Night."

Tuesday 9 November

West Riding Section. "Trichlorethylene Paints," by I. M. Cairncross, to be held at the Great Northern Hotel, Leeds, at 7.30 p.m.

Thursday 11 November

London Section. "Airless Spray Painting," by F. G. Dunkley, to be held at the Small Physics Lecture Theatre, Imperial College of Science and Technology, South Kensington, London, S.W.7, at 7 p.m.

Midlands Section—Trent Valley Branch. "Atoms and Ions," by T. Fullwood, of the Liverpool College of Technology, to be held at the British Railways School of Transport Lecture Theatre at 7.30 p.m.

Scottish Section. "Painting An Imp," by J. Lauder, to be held at More's Hotel, India Street, Glasgow, at 6.30 p.m.

Friday 12 November

Manchester Section. "The Printing and Decorating of Tinplate," by A. D. Lott, to be held at the Constitutional Club, Tithebarn Street, Liverpool, at 6.30 p.m.

Saturday 13 November

Scottish Section—Junior Group. Tutorials: (1) "Formulation of Paints," by A. McGuire, (2) "Organic Pigments (2)," by K. G. Hargreaves, (3) "Wood Finishes," by A. McLean, at More's Hotel, India Street, Glasgow, at 10.30 a.m.

Tuesday 16 November

London Section—Thames Valley Branch. "Costing and Accounting in the Paint Industry," by F. J. K. Hillebrandt, to be held at the Royal White Hart Hotel, Beaconsfield, Buckinghamshire, at 7 p.m.

Thursday 18 November

New South Wales Section. Lecture given by A. G. Aliotti and Z. T. Nowark, on "Some Physico-Chemical Aspects of Carbon Black."

South Australian Section. "Colorimetry and Colour Match Production," by A. Barlee.

Friday 19 November

London Section. Ladies' Night at the Criterion-in-Piccadilly, London, W.1.

Midlands Section. "Paint Additives," by Dr. G. A. Wolstenholme, at the Birmingham Chamber of Commerce, 75 Harborne Road, Birmingham, 15, at 6.30 p.m.

Wednesday 24 November

Scottish Section—Eastern Branch. "Colour," by C. T. Donaldson, to be held at the North British Hotel, Princes Street, Edinburgh, at 7.30 p.m.

London Section—Southern Branch. "Elastomeric Sealants," by K. Beaumont, to be held at the Polygon Hotel, Southampton, at 7.30 p.m.

Friday 26 November

Bristol Section. "Colour Experiments and the Land Process," by D. F. Gibbs, at the H. H. Wills Physics Laboratory at 7.15 p.m.

Bristol Section—Irish Branch. "Printability of Paper and Board," by Miss E. J. Pritchard, to be held at the Dolphin Hotel, Essex Street, Dublin, at 8 p.m.

West Riding Section. Annual Dinner and Dance at the Granby Hotel, Harrogate.

South Australian Section. Annual Dinner to be held at the Buckingham Arms Hotel, Gilberton.

Thursday 2 December

Newcastle Section. "Car Finishes: Present Position and Future Trends," by G. Hind, to be held at the Royal Turk's Head Hotel, Grey Street, Newcastle upon Tyne, at 6.30 p.m.

Monday 6 December

Hull Section. "The Glyceride Composition of Cottonseed Oils," by Dr. M. L. Meara, of NS Department of Agriculture. Joint meeting with SCI Oils and Fats Group, to be held at the Royal Station Hotel, Hull, at 7 p.m.

West Australian Section. Annual Golf Day, then dinner at night.

Tuesday 7 December

West Riding Section. "Advertising—Salesmanship Magnified," by J. C. Wells, to be held at the Great Northern Hotel, Leeds, at 7.30 p.m.

Wednesday 8 December

London Section. "The Use of Computers in Process Control," by T. B. M. Rybak, in the Small Physics Lecture Theatre, Imperial College of Science and Technology, South Kensington, London, S.W.7, at 7 p.m.

Thursday 9 December

Bristol Section—Irish Branch. Annual Dinner and Dance at South County Hotel.

London Section—Thames Valley Branch. "Aerosols," by W. H. Brown, at the Royal White Hart Hotel, Beaconsfield, Bucks, at 7 p.m.

London Section—Southern Branch. "Decorating Plastics," by S. E. Francis, at the Chemistry Department Lecture Theatre, Southampton University (joint meeting with Southern Section of the Plastics Institute), at 7.30 p.m.

Scottish Section. "The Place of Computers in the Paint Industry," by T. Henegan, at More's Hotel, India Street, Glasgow, at 6.30 p.m.

Friday 10 December

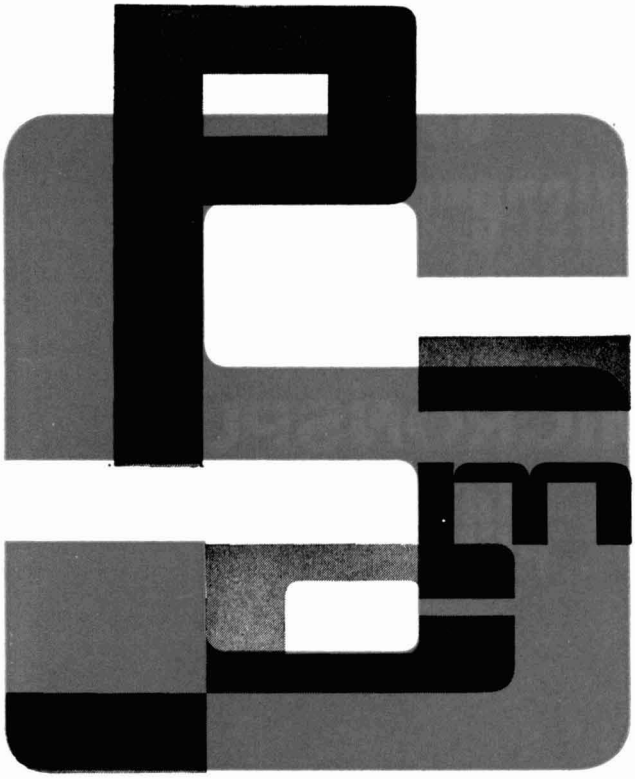
Manchester Section. "Powder Technology," by J. C. Williams, to be held at the Manchester Literary and Philosophical Society at 6.30 p.m.

Saturday 11 December

Scottish Section—Student Group. Film Show.

Wednesday 15 December

Scottish Section—Eastern Branch. "Advantages of Epoxy Marine Paints," by A. McIntosh, to be held in the North British Hotel, Princes Street, Edinburgh, at 7.30 p.m.



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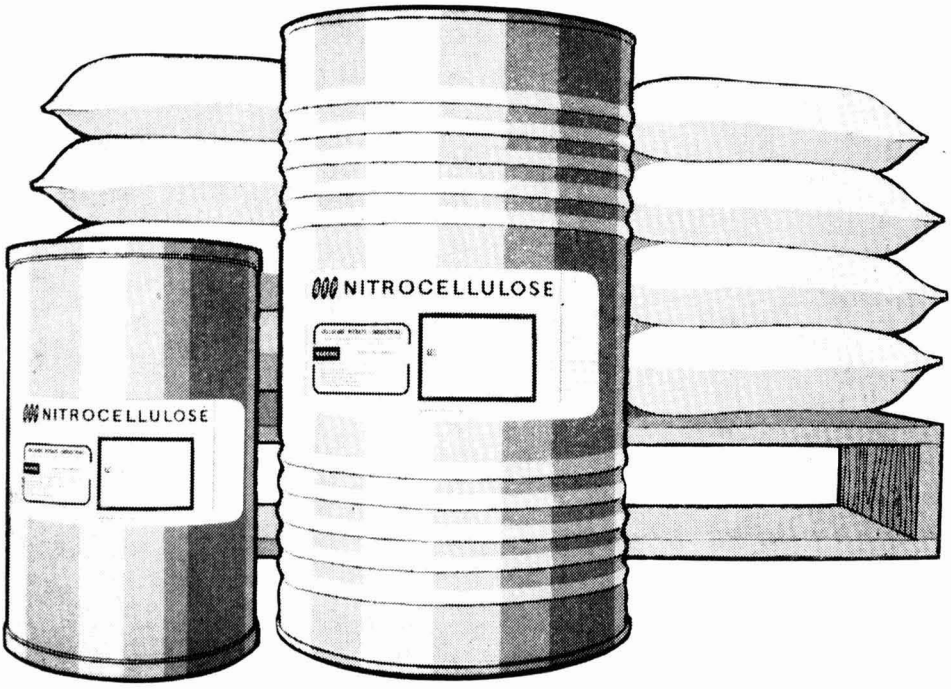

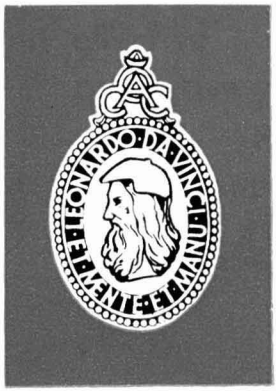

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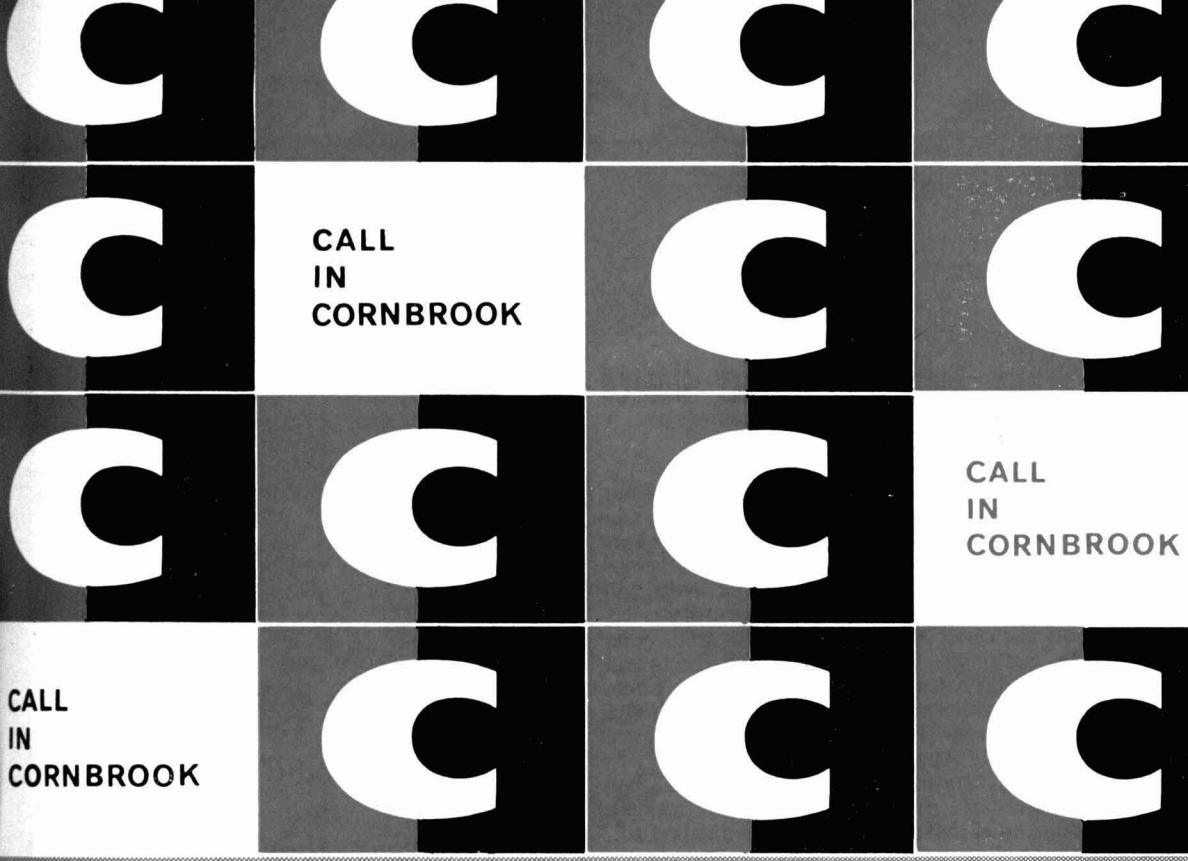
A full list of Exhibitors is given on page 1102 of this issue



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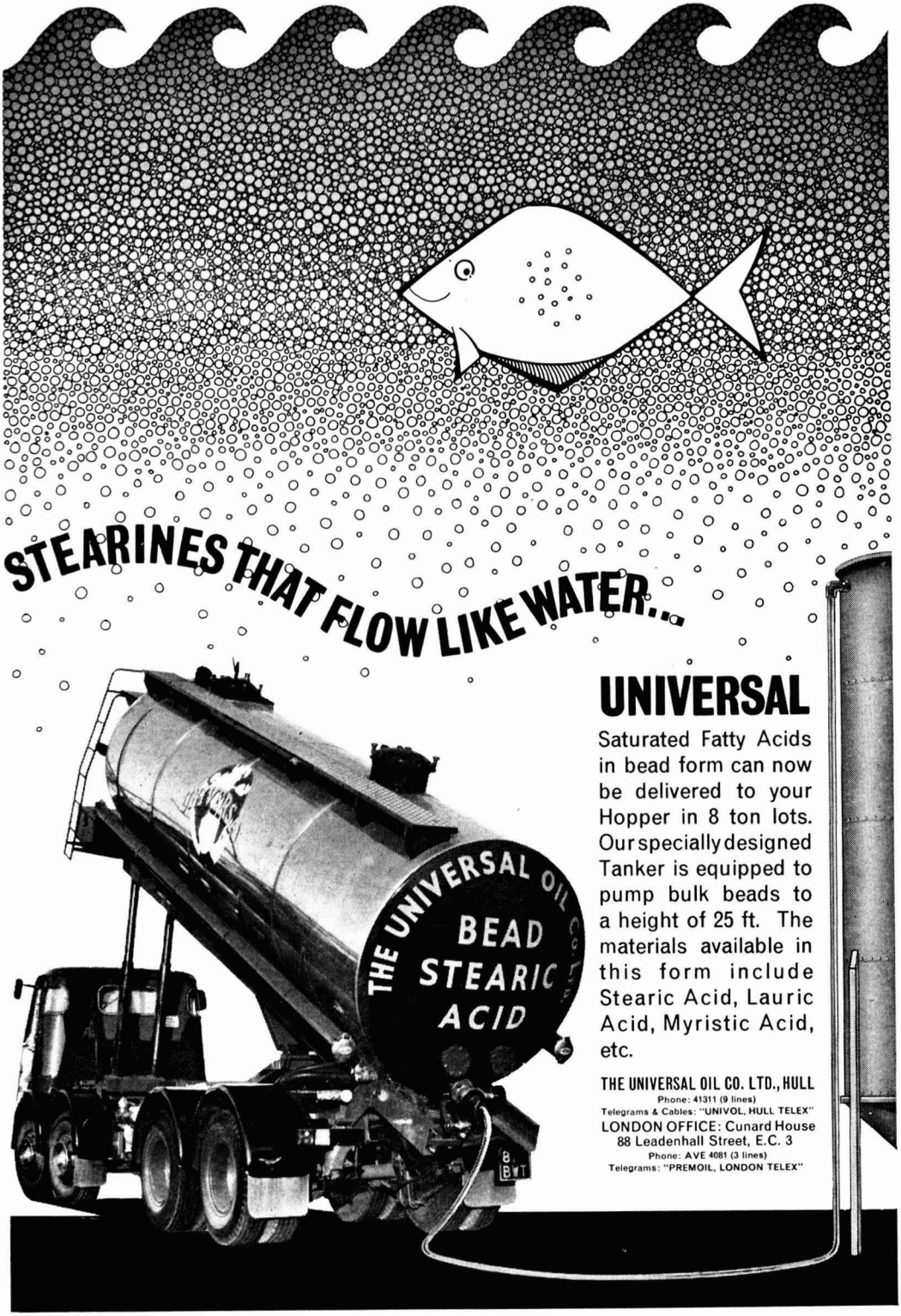

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