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Vol. 44, No. 2 **February, 1961**

TRANSACTIONS AND COMMUNICATIONS

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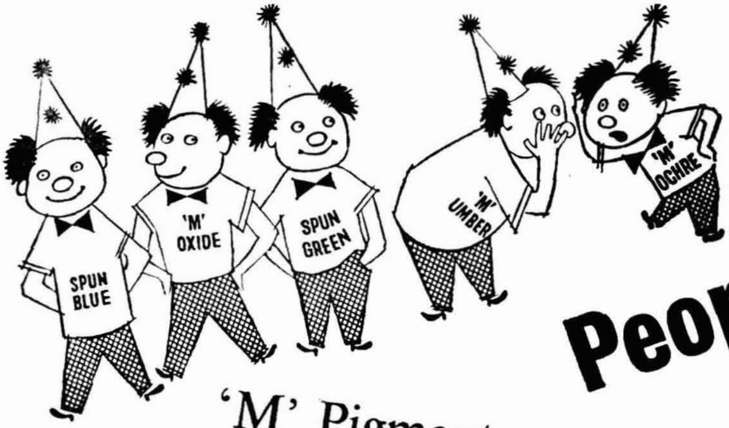

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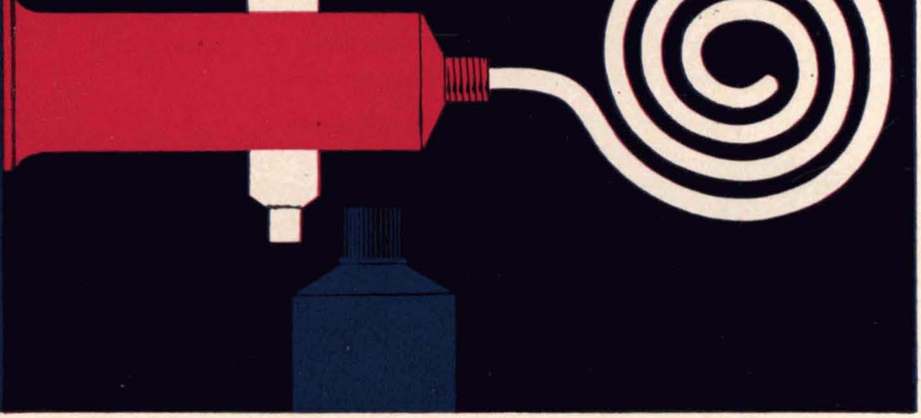

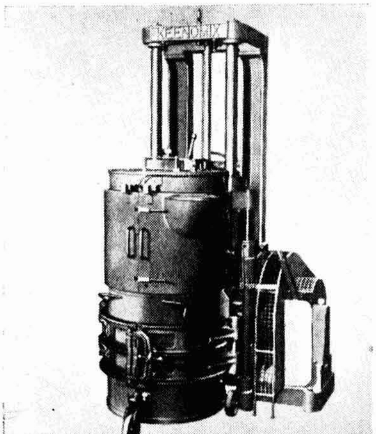
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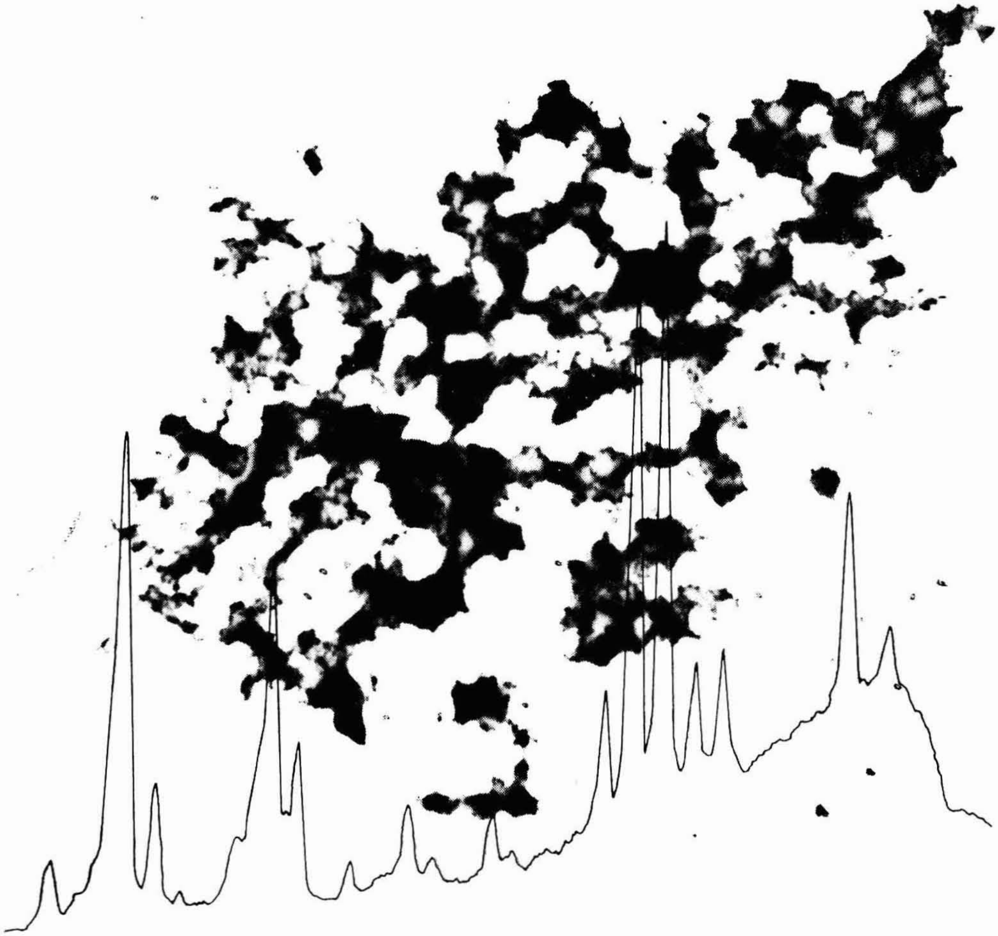

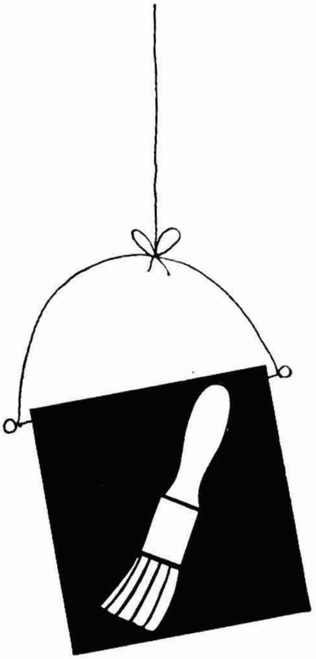

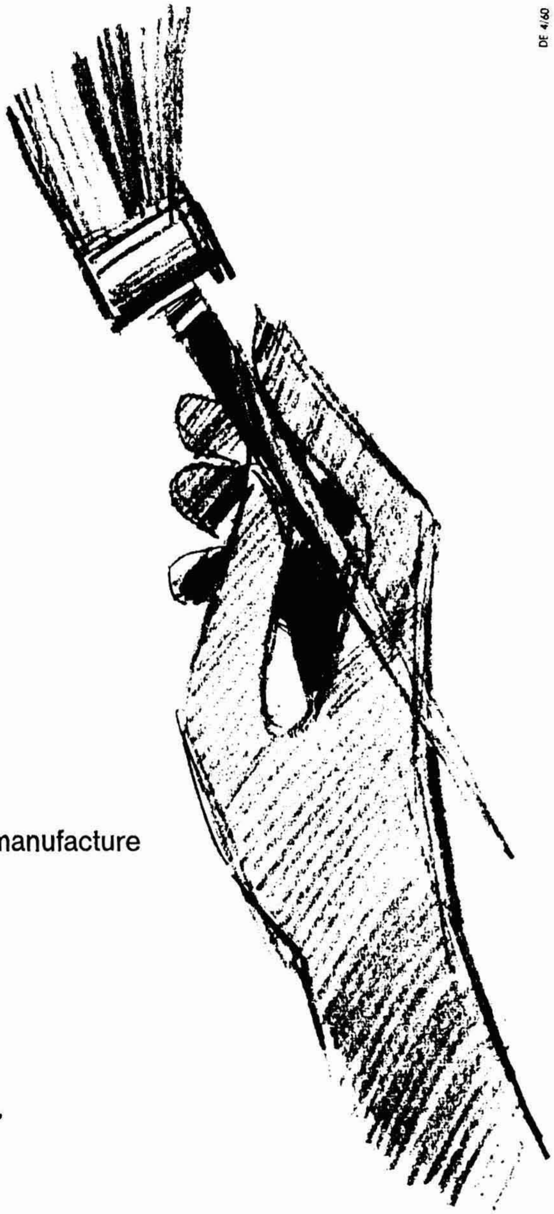

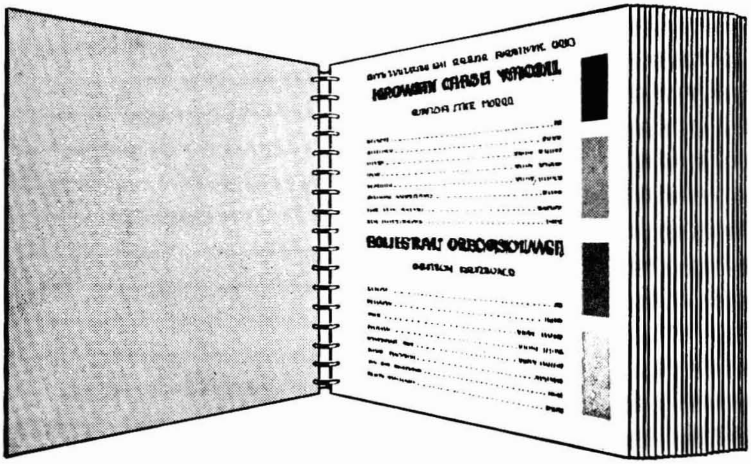

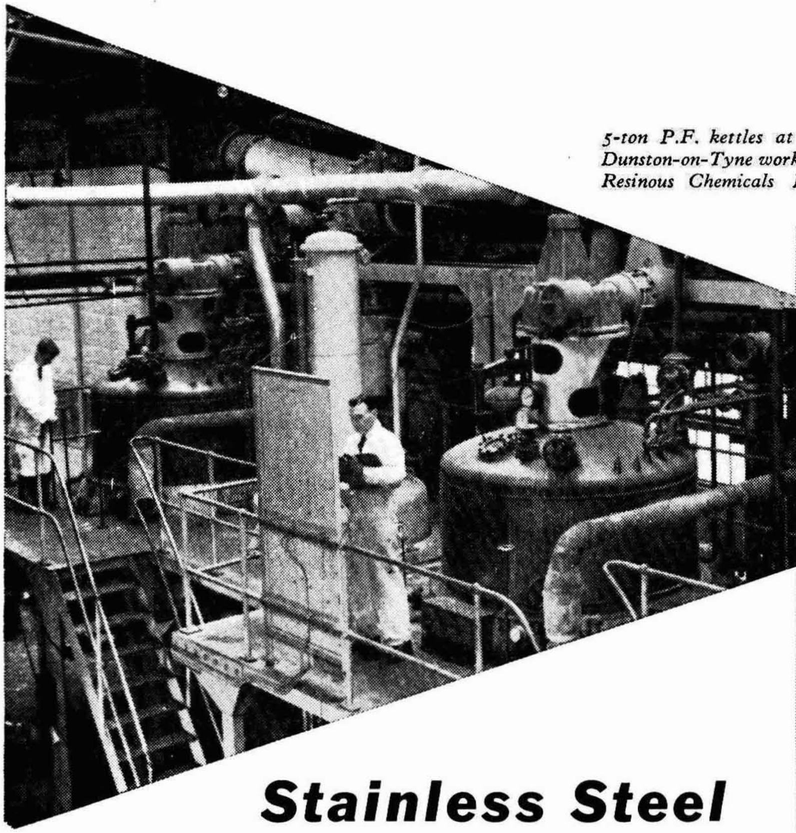

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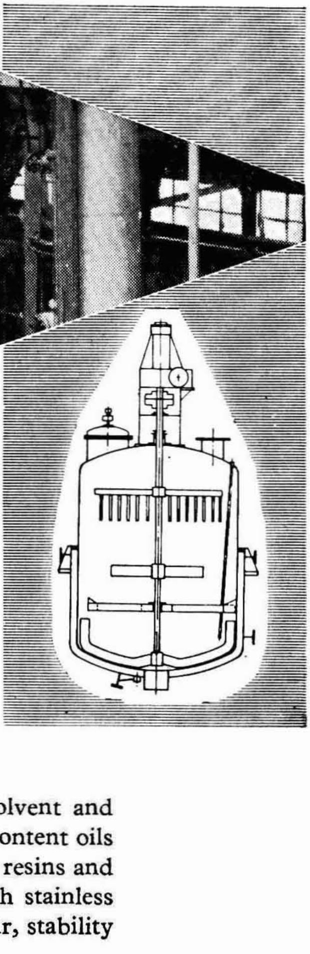

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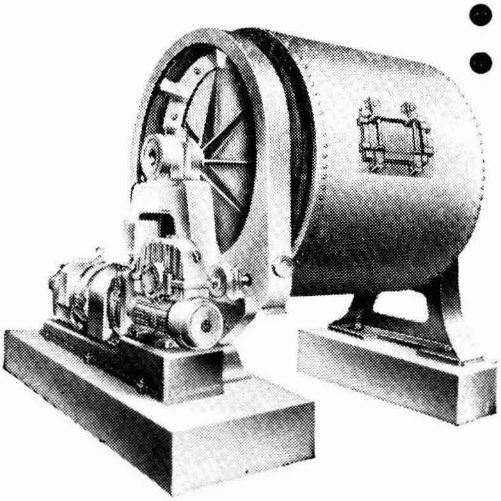

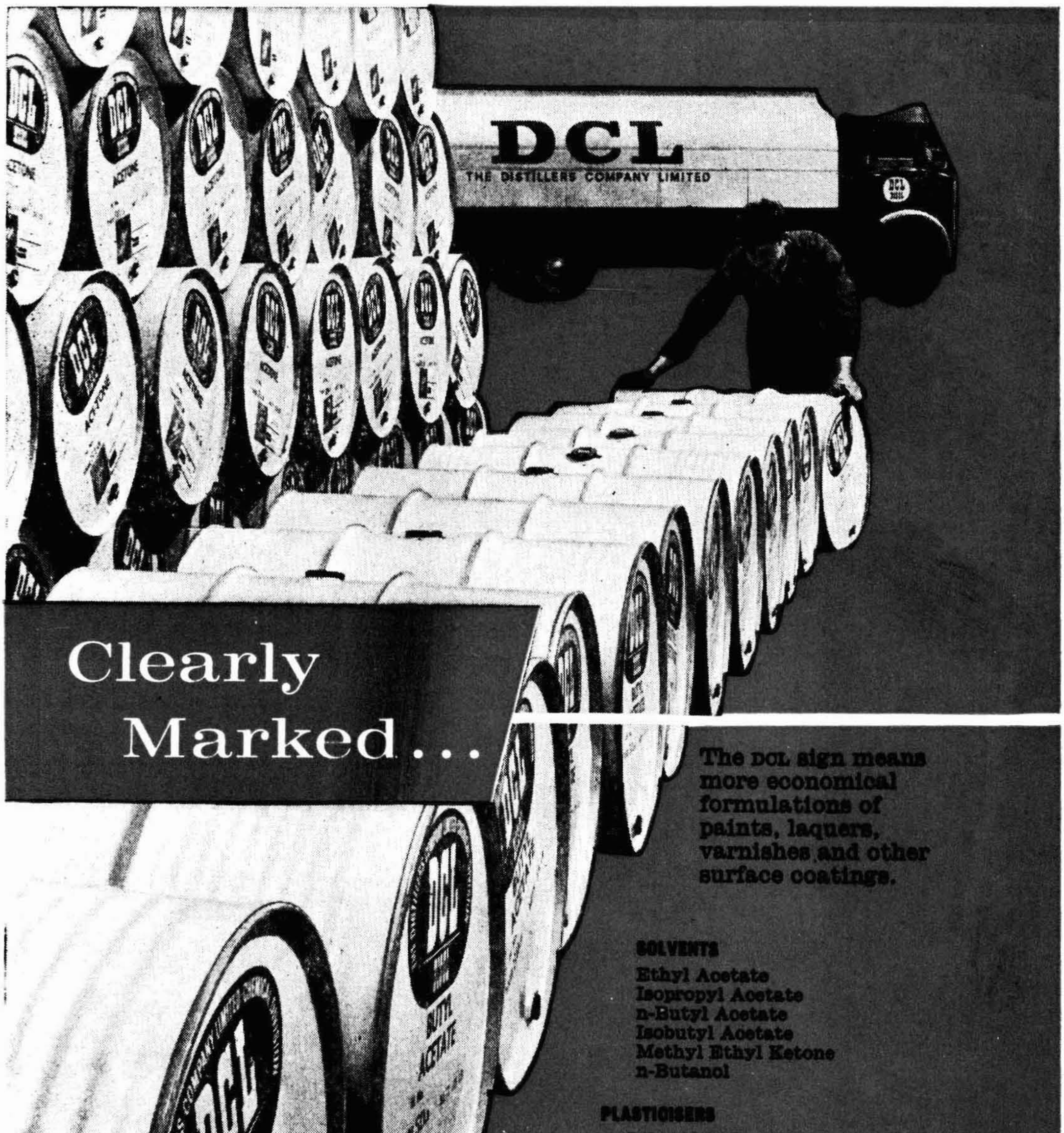
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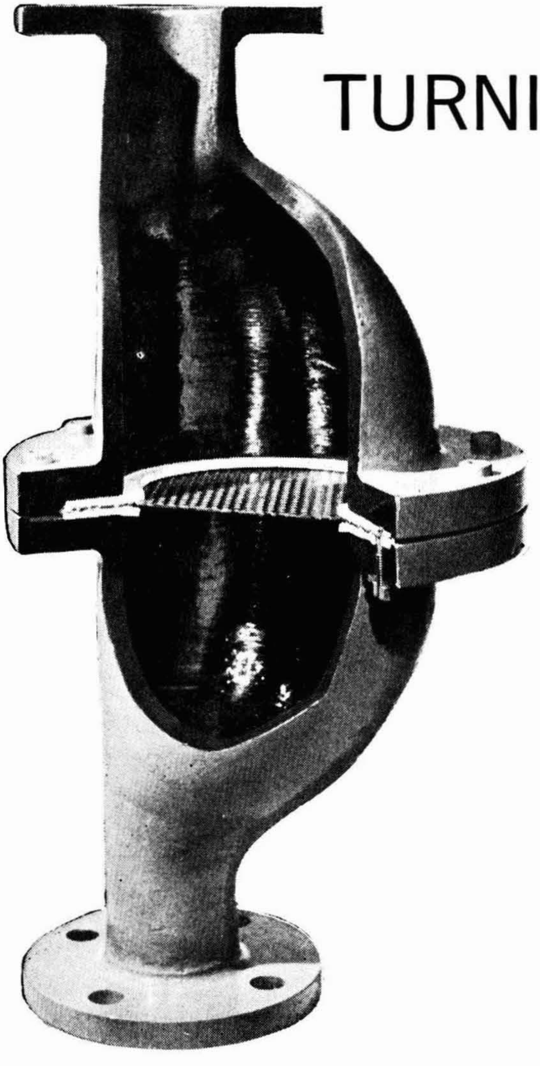

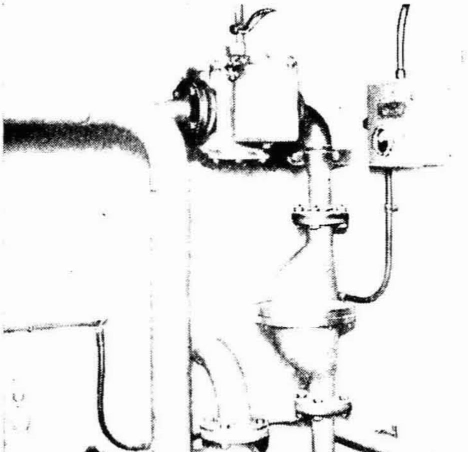

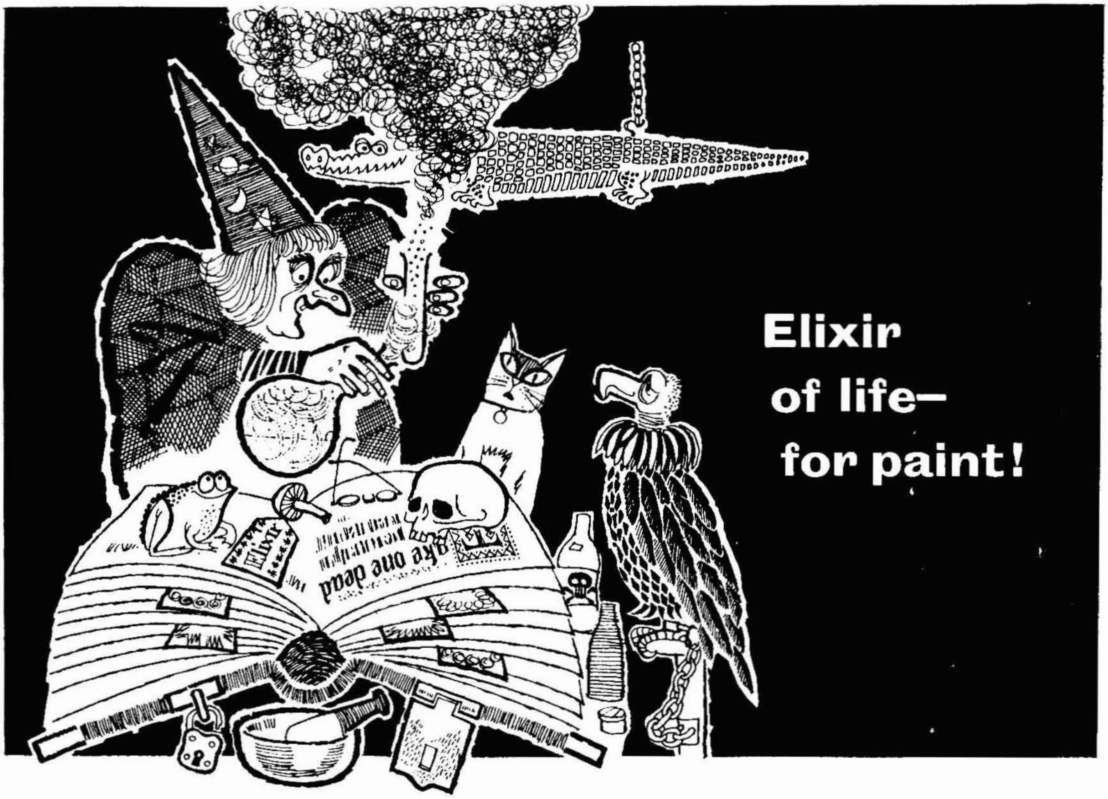

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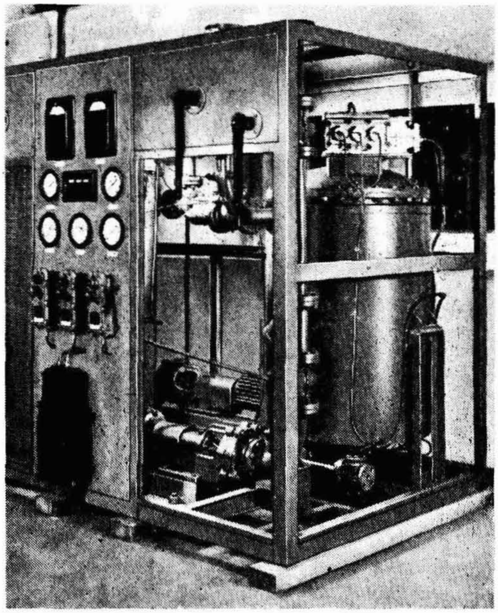

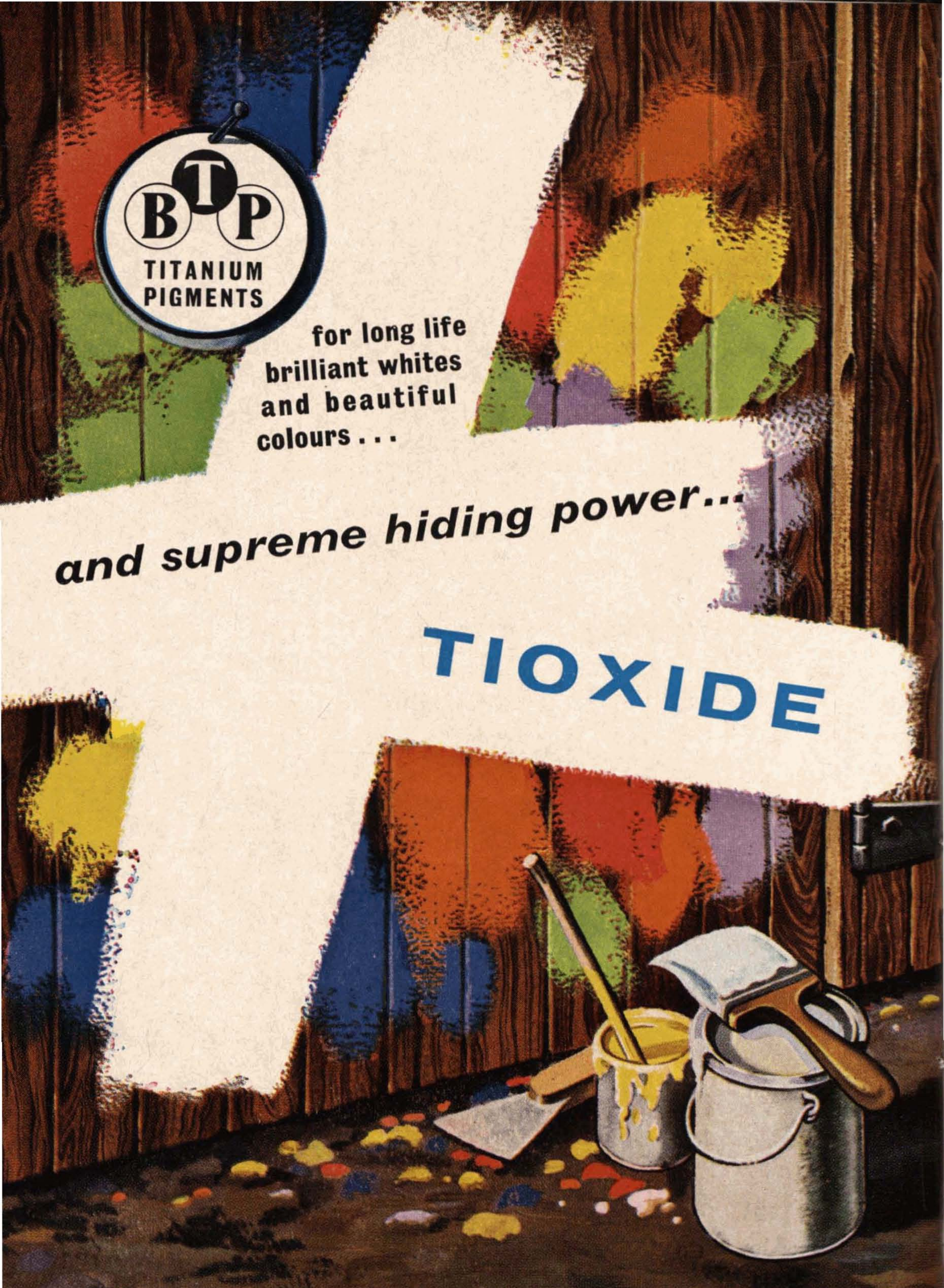
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TRANSACTIONS AND COMMUNICATIONS

Lacquer Coating of Aluminium/Magnesium Alloys*

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Summary

Lacquer films on aluminium/magnesium alloys often fail on deformation and subsequent exposure to warm and humid atmospheres. The failure is usually due to the magnesia-rich oxide film that is always present on normal production material. It is not practicable to modify production techniques to such an extent as to produce aluminium/magnesium sheet without the undesirable oxide film. Lacquer systems have been developed for use on normal production N4 sheet, but their composition is critical and the choice of materials from which they can be compounded is restricted. Moreover, even these special lacquers are not satisfactory for alloys containing more than 2 per cent magnesium. Satisfactory adhesion of commercial lacquers to a wider range of aluminium/magnesium alloys can be achieved by chemical or electrochemical pretreatment prior to lacquering. Degreasing by organic solvents and treatment with alkaline degreasers are insufficient. Chemical acid pretreatment gives satisfactory results, nitric acid being particularly effective. Electrochemical pretreatment is even better. The anodic sulphuric acid bath is easy to operate, requires short immersion time, causes negligible weight losses, produces an anodic film which affords protection during storage, and is applicable to all commercial aluminium/magnesium alloys. Adhesion of ordinary commercial lacquers to suitably pretreated aluminium/magnesium alloys is at least as good as to any other aluminium alloy.

INTRODUCTION

Aluminium has been successfully used for many years for a range of applications in the packaging industry. Toothpaste tubes, preserve closures and bottle caps can be quoted as a few examples. The majority of the applications in this field require that aluminium sheet should be coated with a protective or decorative lacquer in the flat form and then deformed. Commercial lacquers are available which satisfactorily adhere to commercial purity aluminium (SIC) and the $1\frac{1}{4}$ manganese alloy (NS3) and give satisfactory performance in these varied uses. (Throughout the paper the alloys are designated according to B.S. 1470-1477, "Wrought aluminium and aluminium alloys".) Recently a demand has arisen for closures and containers with higher mechanical properties than those afforded by the above materials. Magnesium-containing alloys such as NS4 (2 per cent magnesium) and NS5 ($3\frac{1}{2}$ per cent magnesium) possess the required mechanical properties, but difficulties have been experienced with the adhesion of lacquer coatings to them.

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*Read before the London Section on 18 October, 1960.

Lacquer failures occur when the sheet is deformed during manufacture of the closure or container and when it is subsequently exposed to humid or corrosive atmospheres. Failure of decorative lacquers is unsightly, but failure of protective coatings is more serious and may give rise to corrosive attack on the metal, unsatisfactory shelf-life and spoilage of the pack. Two recently published papers[1, 2] provide clear evidence that the shelf-life of lacquered food containers made of aluminium/magnesium alloys is shorter than that of containers made of magnesium-free alloys. However, not so much difference was found in the shelf-life of unlacquered cans made from either metal. It appeared that the difference lay in the performance of the lacquer coatings. The present paper describes investigations carried out to ascertain the reasons for poor performance of lacquer applied to aluminium/magnesium alloys, and describes methods that will improve adhesion.

Preliminary Considerations

Lacquers applied to aluminium alloys are in fact applied to an oxide film covering these alloys, since aluminium is a very reactive metal which, in contact with air, rapidly becomes covered with a film of oxide. On pure aluminium the oxide film is impermeable to oxygen and the rate of growth is governed by the rate of diffusion of aluminium ions through the oxide film to the oxide-air interface, where the reaction between the diffusing ions and the oxygen of the air takes place[3, 4]. The rate of diffusion of aluminium ions, and consequently the rate of oxidation varies parabolically with time. In practice, the oxidation rate of pure aluminium drops rapidly to such a low value that no further thickening of the oxide film is apparent, as is evident from Fig. 1. The thickness, and to some extent the nature of the oxide film, depends on the temperature of oxidation. The thicknesses of the oxide film formed on super-purity aluminium at room temperature and at 500°C are thus approximately 45Å and 3000Å, respectively[5, 6].

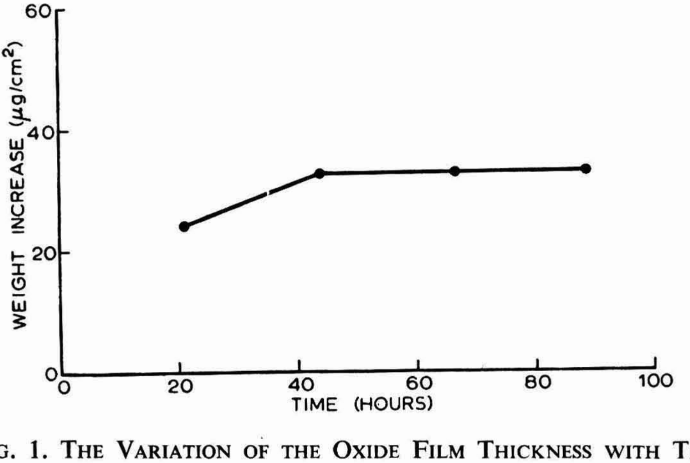

FIG. 1. THE VARIATION OF THE OXIDE FILM THICKNESS WITH TIME

One of the conditions for a parabolic rate of oxidation is that the oxide film must be continuous. This is satisfied by pure aluminium at temperatures between room temperature and at least 550°C. Many aluminium alloys behave in a similar manner, and while the alloying elements affect the rate of oxidation, they do not alter its parabolic nature. This is not true of aluminium/magnesium alloys. At room temperature they become covered with a continuous oxide film which soon reaches its maximum thickness. However, at elevated temperatures the type of oxidation is much more complicated. In dry air or dry oxygen an initially parabolic oxidation soon becomes linear[7], and the growth of the oxide film continues indefinitely. In humid air, parabolic or approximately parabolic oxidation continues for much longer periods and is followed by an increasing rate of oxidation of a rather complex type[8]. The oxidation curves for a commercial aluminium alloy (NS5), containing 3.5 per cent magnesium, at elevated temperatures in dry oxygen and in humid air, are shown in Fig. 2.

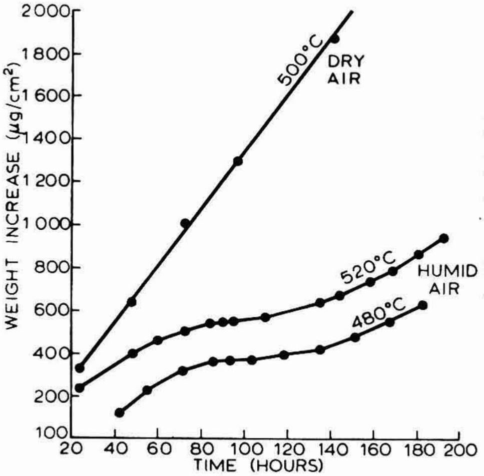

FIG. 2. OXIDATION CURVES FOR A COMMERCIAL ALUMINIUM ALLOY (NS5)

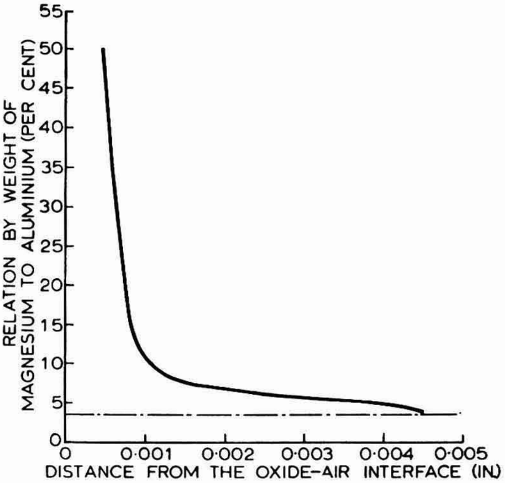

FIG. 3. DISTRIBUTION OF MAGNESIUM IN OXIDE FILM

The explanation of the differences between the type and rate of oxidation of pure aluminium and of aluminium/magnesium alloys lies chiefly in the fact that at elevated temperatures magnesium ions diffuse much faster through the oxide film than do aluminium ions. As a result of a rather complex mode of diffusion, a gradient of magnesium concentration forms across the oxide film, the outer layers containing a higher proportion of magnesium[8] (Fig. 3).

The oxide film on pure aluminium is compact because the volume of aluminium oxide is greater than the volume of aluminium from which it is formed. On the other hand, the volume of magnesium oxide is smaller than the volume of replaced magnesium so that the films formed on magnesium at elevated temperatures are porous[9]. In the oxidation of aluminium/magnesium alloys in dry air or dry oxygen, the parabolic rate continues only as long as the proportion of magnesium oxide to aluminium oxide in the outer layer of the film is sufficiently small for the film to remain compact. However, as oxidation progresses freshly-formed oxide layers become richer and richer in magnesia until a stage is reached when the ratio of magnesia to alumina becomes sufficiently high for the film to become discontinuous. Oxygen can then penetrate the oxide film and the oxidation becomes linear. In humid air the type of oxidation of aluminium/magnesium alloys is even more complex, probably due to the presence in the oxide film of molecules of hydroxides and perhaps hydrides. In this instance also a gradient in magnesium concentration across the oxide film is formed as oxidation at elevated temperatures progresses.

From the point of view of the adhesion of lacquer films, the important fact is that in the case of aluminium/magnesium alloys, which at some stage of fabrication have been annealed, oxide films differing considerably from those present on other aluminium alloys are encountered. Mechanically, the magnesia-rich oxide films are hard and brittle, whilst chemically they are hygroscopic and alkaline. These characteristics are detrimental to lacquer adhesion, particularly if the lacquered materials are subsequently to be deformed and exposed to humid atmospheres.

Preliminary Tests

The aim of the preliminary tests was to confirm that lacquer coatings failed more easily on aluminium/magnesium alloys than on commercial purity aluminium and to check whether this failure was due to the magnesia-rich oxide film as suggested by theory. The tests consisted of coating degreased specimens of 0.010 in. thick sheet with a commercial lacquer system, pressing them into $\frac{7}{8}$ in. deep cans of $\frac{13}{16}$ in. diameter, and exposing them to air saturated with water vapour at 95°F for 120 hours. The adhesion of the lacquer film was checked after pressing and every twenty-four hours during the exposure. An occasional additional test consisted of measuring the strength of "direct adhesion" by a technique described elsewhere[10]. The direct adhesion test shows the minimum force which must be applied normal to the lacquer film in order to detach it from the metal surface.

The experiments confirmed that lacquers which were satisfactory on commercial purity aluminium failed on aluminium/magnesium alloys. This is shown in Table I, which also demonstrates that the failure was much more pronounced in the case of NS6 (5 per cent magnesium) than in the case of NS4 (2 per cent magnesium).

TABLE I

BEHAVIOUR OF PROPRIETARY LACQUERS (A AND B) ON ALUMINIUM/MAGNESIUM ALLOYS IN THE PRESSING AND EXPOSURE TEST

Material	Nominal content of Mg	Number of specimens		Number of failures on pressing		Number of failures on exposure to hot humid atmosphere					
						24 hr.		72 hr.		120 hr.	
		A	B	A	B	A	B	A	B	A	B
SIC	0	10	10	0	0	0	0	0	0	0	0
NS4	2%	10	10	2	5	6	8	10	10	—	—
NS6	5%	10	10	8	10	10	—	—	—	—	—

In order to check whether the failures were due to the oxide film, this was removed mechanically or chemically from a number of NS4 specimens before the application of lacquer. The radical improvement obtained in the case of specimens from which the surface layer was removed mechanically is illustrated in Table II. The lacquer coatings were also satisfactory on specimens stripped in caustic soda, but only when all traces of alkali had been removed from their surface by immersion in weak nitric acid and thorough rinsing in water.

TABLE II

EFFECT OF THE REMOVAL OF THE SURFACE LAYER FROM THE NORMAL PRODUCTION NS4 ON THE PERFORMANCE OF PROPRIETARY LACQUER A IN THE PRESSING AND EXPOSURE TEST

Material	Nominal content of Mg	Treatment prior to lacquering	Number of specimens	Number of failures on pressing	Number of failures on exposure to hot humid atmosphere		
					24 hr.	72 hr.	120 hr.
NS4½H	2	Degreasing only	10	2	6	10	—
NS4½H	2	Mechanical removal of app. 0.001 in. from surface followed by degreasing.	10	0	0	0	0
NS4½H	2	5 min. immersion in 10% NaOH solution followed by water rinse.	10	1	4	4	4
NS4½H	2	5 min. immersion in 10% NaOH solution and rinse in water and dip in 5% HNO_3 rinse in water.	10	0	0	0	0

Whilst the experimental results shown in Tables I and II indicated that the difficulty with the lacquer adhesion was caused by the magnesia-rich oxide film, some doubt was created by the fact that the mechanical and chemical pretreatments not only removed the oxide, but also produced surfaces of a different topography. It could be argued that the roughness of the surface, and not its chemical composition, was of decisive importance. In order to obtain further evidence concerning the importance of the composition of the oxide film, an additional experiment was carried out in which specimens of NS4 0.050 in. thick were interannealed at various temperatures, cold rolled to 0.010 in., degreased, lacquered and examined by the pressing and hot humid atmosphere test.

TABLE III

EFFECT OF ANNEALING TEMPERATURE ON ADHESION OF LACQUER B TO NS4 SHEET 0.010 IN. THICK

Temperature of interannealing (°C)	Time of interanneal	Number of specimens	Number of failures on pressing	Number of failures on exposure to hot humid atmosphere		
				24 hr.	72 hr.	120 hr.
300	60 min. at 0.050 in. and 30 min. at 0.014 in.	10	3	6	10	—
350	60 min. at 0.050 in. and 30 min. at 0.014 in.	10	5	10	—	—
500	45 min. at 0.050 in. and 30 min. at 0.014 in.	10	10	—	—	—

It can be seen from Figs. 2 and 3 that the thickness of the oxide film formed on aluminium/magnesium alloys and the concentration of magnesium in its upper layers depend on the time and temperature of annealing. Hence, by varying the temperature of interannealing, different thicknesses and compositions of the oxide film were produced. Table III shows that the higher the temperature of interannealing the more pronounced was the failure of the lacquers. In a confirmatory test, direct adhesion measurements were carried out on NS4 and SIC specimens interannealed at various temperatures and for various times. The results presented in Table IV show that direct adhesion to commercial purity aluminium was practically unaffected by the changes in annealing conditions, but that direct adhesion to aluminium/magnesium alloy decreased with the increase of time and temperature of annealing.

TABLE IV

EFFECT OF TIME AND TEMPERATURE OF INTERANNEALING ON THE ADHESION OF LACQUER B TO S1C AND NS4 SHEET

Alloy	Thickness before interannealling (in.)	Temperature of anneal (°C)	Time of anneal	Thickness after final rolling (in.)	Breakdown tension (direct adhesion test) (lb./in.^{2})
SIC	0.050	480	20 min.	0.024	2,700
,,	0.050	480	24 hr.	0.024	2,700
,,	0.050	540	24 hr.	0.024	2,600
NS4	0.050	480	20 min.	0.024	1,880
,,	0.050	480	24 hr.	0.024	1,200
,,	0.050	540	24 hr.	0.024	840

The experiments described above provided convincing evidence that the lacquer adhesion was strongly affected by the type of oxide film present on aluminium/magnesium alloys, and that the greater the thickness and the higher the magnesia content, the more likely was the failure of lacquer coatings.

DEVELOPMENT OF METHODS FOR LACQUERING ALUMINIUM/MAGNESIUM ALLOYS

The problem of overcoming the difficulties involved in lacquering aluminium/magnesium alloys was approached in three different ways. First, the possibility was examined of changing production techniques with the aim of producing a sheet with thinner oxide films containing less magnesia. Secondly, methods were investigated of removing chemically or electrochemically the magnesia-rich oxide film, and finally, a selection and development was attempted of lacquer coatings suitable for ordinary production material.

Pressing the lacquered sheet into deep caps and exposing them to air saturated with water vapour at 95°F (as described earlier) was used throughout the investigation as the performance test. In each test at least ten specimens were examined, and the lacquer coating was considered satisfactory only when no failures whatsoever were observed after pressing, followed by 120 hours of exposure to the hot humid atmosphere.

Modification of Production Techniques

A number of experiments were carried out in which techniques for producing NS4 were modified by reducing the time and temperature of anneal. A number of commercial lacquers were applied to the sheets produced in this way, and the lacquer adhesion was examined in the pressing and hot humid atmosphere test; Table V shows the results obtained. The percentage of failures decreased as the temperature and time of annealing were reduced, but even those specimens which were produced at the lowest temperature and shortest time of annealing were not fully satisfactory; further reduction of temperatures would not be practicable. The experiments were not extended to alloys containing more magnesium than NS4, because it was realised that with such alloys there would be even less chance of achieving satisfactory lacquer adhesion.

TABLE V

EFFECT OF MODIFICATION IN ANNEALING PRACTICE ON LACQUER ADHESION TO 0.010 IN. THICKNESS TEMPER ROLLED NS4 SHEET (ALL SPECIMENS WERE DEGREASED IN ACETONE AND CHLOROFORM)

Details of anneal	Number of specimens		Number of failures on pressing		Number of failures on exposure to hot humid atmosphere									
					24 hr.		48 hr.		72 hr.		96 hr.		120 hr.	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B
1st interanneal $4\frac{1}{2}$ hr. at 450°C. 2nd interanneal 6 hr. at 380°C. No final anneal.	10	10	0	4	4	6	5	8	9	10	10	—	—	—
1st interanneal 6 hr. at 380°C. 2nd interanneal 6 hr. at 380°C. No final anneal.	10	10	0	2	3	4	4	6	8	8	10	10	—	—
1st interanneal 3 hr. at 340°C. 2nd interanneal 2 hr. at 340°C. No final anneal.	10	10	0	2	1	4	3	4	4	4	5	6	8	8
1st interanneal 2 hr. at 300°C. 2nd interanneal 2 hr. at 300°C. No final anneal.	10	10	0	0	1	2	2	3	3	3	4	3	7	7

Pretreatment of Sheet

The preliminary tests described earlier showed that satisfactory lacquer adhesion to NS4 sheet could be obtained by chemical pretreatment. However, the 10 per cent caustic soda solution used in these early tests is not suitable for commercial application, because attack on the underlying metal would lead to considerable loss of weight. Further, the immersion time in the preliminary experiment was quite long, and satisfactory results were obtained only if the treatment included immersion in an acid to neutralise any alkalinity remaining on the surface; this made the process complicated and uneconomical.

In order to find a commercially acceptable pretreatment, inhibited alkaline cleaners, acidic solution and electrochemical baths were examined. The effectiveness of a pretreatment process was assessed by coating the pretreated specimens with commercial lacquers known to be satisfactory on SIC$\frac{1}{2}$H and submitting them to the pressing and hot humid atmosphere test. A number of commercial inhibited alkaline cleaners were examined by immersing in them specimens of NS4 sheet for various times and at various temperatures.

Although an improvement in the lacquer coating performance was observed in some instances, the results of these pretreatments were erratic and on the whole unsatisfactory. The reason for this was probably that magnesia was not soluble in alkaline solutions and could be removed by them only through an attack on the underlying metal. However, such an attack is unwelcome for obvious reasons and is in fact largely inhibited in most of the commercial alkaline cleaners. Furthermore, the experiments showed that any trace of alkaline solution remaining on the surface impaired lacquer adhesion. This meant that alkaline pretreatments had to be followed by an acid wash, and even then they gave at best only a slight improvement in lacquer adhesion.

Considerably better results were obtained with acid chemical pretreatments. A number of these were examined, but for the sake of brevity only the most satisfactory of them will be described. Acid solutions differ in their action from those which are alkaline in that they dissolve both alumina and magnesia, and hence attack first the oxide film and only then the underlying metal. By restricting the time of immersion to the minimum required for stripping the undesirable oxide film, the weight losses of the specimens can be minimised.

In commercial practice it is, of course, desirable that the time of immersion should be short, the temperature of the bath low and any rinsing operation as simple as possible. The above requirements were met most satisfactorily by nitric acid solutions, although sulphuric acid was also effective. The rinsing operation after both nitric and sulphuric acid treatment was quite simple and consisted of washing the sheet in cold running water. The minimum times and temperatures of pretreatment which resulted in completely satisfactory lacquer performance on NS4 specimens are shown in Table VI. It should be noted that nitric acid solutions containing a little sodium chloride were particularly effective.

TABLE VI

MINIMUM TEMPERATURE AND TIME OF ACID PRETREATMENT NECESSARY TO ELIMINATE COMPLETELY FAILURES IN PRESSING AND HOT HUMID ATMOSPHERE TESTS OF PROPRIETARY LACQUER COATINGS ON NS4½H SHEET (NOMINAL MAGNESIUM CONTENT 2 PER CENT)

Description of bath	Temperature of bath (°C)	Time of immersion (sec.)
20% H_2SO_4	80	120
10% H_2SO_4 1% wetting agent	80	75
30% HNO_3	50	90
15% HNO_3 3% NaCl	50	30
15% HNO_3 3% NaCl	30	60
15% HNO_3 1% NaCl	50	40

For alloys with a higher content of magnesium, and hence covered with a thicker layer of magnesium-rich oxide film, longer times of immersion in the acid solutions were necessary, as can be seen from Table VII. However, in all cases it was possible to produce lacquered specimens which behaved fully satisfactorily in pressing and hot humid atmosphere tests.

TABLE VII

Minimum Temperature and Time of Acid Pretreatment Necessary to Eliminate Completely Failures in Pressing and Hot Humid Atmosphere Tests of Proprietary Lacquer Coatings on Aluminium Alloys with a High Magnesium Content

Description of bath	Alloy	Nominal magnesium content (%)	Temperature of bath (°C)	Time of immersion (min.)
15% HNO_3 6% NaCl	NS5	3.5	50	1
,, ,, ,,	NS6	5.0	50	2
,, ,, ,,	NE7	7.0	50	2
20% H_2SO_4 1% wetting agent	NS5	3.5	80	2
,, ,, ,, ,,	NS6	5.0	80	3
,, ,, ,, ,,	NE7	7.0	80	3

Electrochemical pretreatment was tried only in sulphuric acid and nitric acid solutions. Of these the first proved to be particularly effective. Under correct conditions of potential, current density and temperature, satisfactory specimens of NS4 sheet were obtained after only 20-30 seconds of pretreatment in 15 per cent sulphuric acid solution. Moderate variations in current density, voltage and temperature had no adverse effect, making control of the operation easy. The conditions under which the electrochemical pretreatment in sulphuric acid was carried out are shown in Table VIII. The same table also gives results obtained by electrochemical pretreatment in nitric acid.

TABLE VIII

Conditions for Satisfactory Electrochemical Pretreatment of NS4 Sheet (Nominal Magnesium Content 2 Per Cent)

Type of bath	Type of current	Potential	Current density (amp./ft.^{2})	Temperature of bath (°C)	Time of treatment (sec.)
15% H_2SO_4	d.c.	13-19	15-25	20-50	20-30
15% HNO_3	a.c.	4.5	10	20-50	60
15% HNO_3 1% NaCl	a.c.	2.7	5	30	30
15% HNO_3 1% NaCl	d.c.	2.7	15	30-50	60
30% HNO_3 1% NaCl	d.c.	4	15	30	30
15% HNO_3 3% NaCl	d.c.	3	15	30	30

Sulphuric acid gave satisfactory results with direct current, but with nitric acid the application of direct current led to severe blackening of the aluminium/magnesium alloys, and although better results were obtained with alternating current, the conditions of voltage and current density were much more critical than with sulphuric acid. High voltage and current density resulted in the formation of a powdery deposit on the surface of the specimen, and low current density and voltage were not efficient enough in removing the magnesia-rich oxide films. Direct current could be used without undue blackening of specimens if a small addition (1-3 per cent) of sodium chloride was made to the nitric acid solution. Such a bath could be worked either with direct current or alternating current. It was quite efficient, but had to be operated under strictly controlled conditions of voltage and current density for the same reasons as in the case of nitric acid solutions containing no sodium chloride.

Acid chemical pretreatments and electrochemical pretreatment in nitric acid solution remove the detrimental oxide films and leave the sheet with a thin oxide film about 0.05 μ thick. The anodic pretreatment in sulphuric acid differs in that it replaces the detrimental film with an anodic film, the thickness of which depends on the time of treatment. The formation of an anodic film 0.25-0.50 μ thick has two advantages. First, it reduces the weight loss of the pretreated material to a negligible value, and secondly, it is beneficial when the material is to be stored for a long time. This last point was demonstrated by storing a number of pretreated specimens for three months before lacquering. A few failures occurred in the pressing and hot humid atmosphere tests among the specimens pretreated chemically in nitric and sulphuric acids and among specimens electrochemically pretreated in nitric acid solution, but no failures were observed among specimens anodically pretreated in sulphuric acid. There appears to be no benefit in applying anodic films thicker than 0.50 μ, and there is evidence to suggest that lacquers applied over excessively thick anodic films tend to fail during deformation.

In order to complete the study of electrochemical pretreatments, these were also applied to alloys with higher magnesium content. The anodic pretreatment in sulphuric acid was found effective in all cases. The same conditions of voltage, current density, temperature and even time which were used for pretreating NS4 proved satisfactory for an alloy containing as much as 7 per cent magnesium. Electrochemical pretreatment in nitric acid was much less satisfactory. An addition of sodium chloride to nitric acid solutions considerably improved their performance, but the minimum time of pretreatment increased with increase of magnesium content.

The conditions under which various aluminium/magnesium alloys can be pretreated satisfactorily in sulphuric and nitric acid electrochemical baths are shown in Table IX.

TABLE IX

Conditions for Satisfactory Electrochemical Pretreatment of Alloys with High Magnesium Content

Alloy	Magnesium content (%)	Type of bath	Type of current	Current density (amp./ft.^{2})	Temperature of bath (°C)	Time of treatment (sec.)
NS5	3.5	15% H_2SO_4	d.c.	15	30	30
NS6	5.0	15% H_2SO_4	d.c.	15	30	30
NE7	7.0	15% H_2SO_4	d.c.	15	30	30
NS5	3.5	15% HNO_3 3% NaCl	a.c.	5	50	60
NS5	3.5	15% HNO_3 5% NaCl	a.c.	5	50	45
NS6	5.0	15% HNO_3 6% NaCl	a.c.	5	50	60
NE7	7.0	15% HNO_3 6% NaCl	a.c.	5	50	60

Development of Lacquers for Aluminium/Magnesium Alloys

Whilst the chemical or electrochemical pretreatment provided a way of overcoming the problem of lacquering aluminium/magnesium alloys, it was still of interest to discover whether lacquers could be selected or developed which would not fail even if applied over unpretreated sheet. The examination of a large number of commercial lacquers, such as vinyls, epoxies, polyesters, polyacrylates and nitrocelluloses, showed that they all failed on unpretreated NS4½H sheet in the pressing and hot humid atmosphere test. However, there were differences in the performance of various types and grades of lacquer, which are demonstrated in Table X.

TABLE X

PERFORMANCE OF VARIOUS LACQUER COATINGS ON NS4½H SUBJECTED TO PRESSING AND HOT HUMID ATMOSPHERE TEST

Type of lacquer	Number of specimens	Number of failures on pressing	Number of failures on exposure				
			24 hr.	48 hr.	72 hr.	96 hr.	120 hr.
Methyl cellulose	10	2	10	—	—	—	—
Proprietary polyester A	10	10	—	—	—	—	—
Proprietary polyester B	10	2	4	4	10	—	—
Adduct cured *Epikote*	10	0	4	10	—	—	—
Amine cured *Epikote*	10	0	10	—	—	—	—
Phenolic cured *Epikote*	10	0	4	6	10	—	—
Vinyl chloride/vinyl acetate copolymer.	10	10	—	—	—	—	—
Vinyl chloride/vinyl acetate/vinyl alcohol copolymer.	10	10	—	—	—	—	—
Vinyl chloride/vinyl acetate/maleic acid (1 %) copolymer.	10	0	0	6	8	8	8
A proprietary vinyl lacquer with a copolymerised acid.	10	0	0	2	2	6	8

The fact that the coating was to be applied over a hard, brittle, hygroscopic and alkaline type of oxide film suggested to the authors that a lacquer was required which was characterised by high extensibility, high film strength, strong adhesion, even to slightly alkaline surfaces, and impermeability to water. Each of the lacquers was in turn examined for these properties using experimental techniques developed for this purpose and described elsewhere[10]. It soon appeared that the best direct adhesion to NS4½H sheet was exhibited by lacquers, the molecules of which contained acidic groups such as are present in vinyls interpolymerised with maleic acid, and in phenolic-cured epoxies (see Table XI).

However, even a very strong adhesion was not sufficient if the extensibility and film strength of the lacquer were not high enough. This was demonstrated in a series of laboratory experiments in which the direct adhesion of the coatings was increased, sometimes at the cost of extensibility and film strength. In all these cases failures occurred in the pressing and hot humid atmosphere test, as is evident from Table XII.

A number of lacquers showing good adhesion to NS4½H were selected and an attempt was made to increase their extensibility by adding plasticisers, or by mixing with them resins of various extensibilities. Many plasticisers were unsatisfactory, apparently because they tended to reduce the strength of

TABLE XI

STRENGTH, EXTENSIBILITY, ELASTICITY AND DIRECT ADHESION OF VARIOUS LACQUERS TO NS4½H SHEET

Type of lacquer	Breakdown tension (direct adhesion test) (lb./in.^{2})	Tensile strength of cross-section (kg./in.^{2})	Extension at breaking load (%)	Elastic component of extension (%)
Vinyl chloride/vinyl acetate copolymer.	1,400	345	0.68	94
Vinyl chloride/vinyl acetate/vinyl alcohol copolymer.	1,050	623	0.86	85
Vinyl chloride, vinyl acetate/maleic acid (1 %) copolymer.	4,000	1,425	0.48	100
A proprietary vinyl with a copolymerised acid.	3,800	2,060	2.17	80
Adduct cured *Epikote*	2,200	Too brittle to be tested		
Amine cured *Epikote*	1,540			
Phenolic cured *Epikote*	4,800			

TABLE XII

CORRELATION OF MECHANICAL PROPERTIES AND PERFORMANCE OF LACQUERS APPLIED ON NS4½H

Type of lacquer	Breakdown tension (direct adhesion test) (lb./in.^{2})	Tensile strength of cross-section (kg./in.^{2})	Extension at breaking load (%)	Elastic component of extension (%)	Percentage of failures on pressing	Percentage of failures on exposure to hot humid atmosphere				
						24 hr.	48 hr.	72 hr.	96 hr.	120 hr.
Proprietary vinyl with a copolymerised acid.	3,800	2,060	2.17	80	0	0	20	20	60	80
Vinyl chloride/vinyl acetate/maleic acid (1 %) copolymer.	4,000	1,425	0.48	100	0	0	60	80	80	80
Phenolic cured *Epikote*	4,820	Very brittle			0	40	60	100	—	—
Vinyl chloride/vinyl acetate/maleic acid (1 %) copolymer plus 1 % adipic acid (added to the lacquer but not properly copolymerised).	5,200	400	2.00	87	100	—	—	—	—	—
Vinyl chloride/vinyl acetate/maleic acid(1 %) copolymer plus 1 % maleic acid (added to the lacquer but not properly copolymerised).	6,000	830	1.40	93	0	0	20	20	60	80

the lacquer and, in some cases, also rendered it more permeable to moisture. However, by carefully blending various resins a combination of direct adhesion, extensibility and film strength was eventually achieved which produced a coating giving no failures on NS4½H in the pressing and hot humid atmosphere test. It was found that only lacquers possessing the following minimum values were satisfactory: direct adhesion 4,000 lb./in.^{2}; extension of free film under breaking load 1.25 per cent; and film strength 1,650 kg./in.^{2} of cross-section; this is illustrated in Table XIII.

TABLE XIII

Correlation of Mechanical Properties and Performance of Lacquers Applied on NS4½H Sheet

Type of lacquer	Modification	Breakdown tension (direct adhesion test) (lb./in.²)	Tensile strength of cross-section (kg./in.²)	Extension at breaking load (%)	Elastic component of extension (%)	Percentage of failures on pressing	Percentage of failures on exposure to hot humid atmosphere				
							24 hr.	48 hr.	72 hr.	96 hr.	120 hr.
Vinyl chloride/vinyl acetate/maleic acid (1%) copolymer.	None	4,000	1,425	0.48	100	0	0	60	80	80	80
,, ,, ,,	Plasticiser A	3,800	1,300	2.00	80	0	0	60	60	80	100
,, ,, ,,	Plasticiser B	3,150	1,200	3.50	70	0	80	100	—	—	—
,, ,, ,,	1% maleic acid (added to the lacquer but not properly copolymerised)	6,000	830	1.40	93	0	0	20	20	60	80
Proprietary vinyl with a copolymerised unspecified acid.	None	3,800	2,060	2.17	80	0	0	20	20	60	80
,, ,, ,,	Plasticiser C	1,950	239	100	72	0	100	—	—	—	—
Vinyl chloride/vinyl acetate/maleic acid (1%) copolymer	Blended with 10% of resin A	4,000	450	0.92	98	0	0	0	20	20	20
Vinyl chloride/vinyl acetate/maleic acid (1%) copolymer	Blended with 20% of resin A	4,000	1,690	1.25	94	0	0	0	0	0	0
,, ,, ,,	Blended with 30% of resin A	3,200	1,700	1.5	93	0	0	0	40	40	40
,, ,, ,,	Blended with 20% of resin B	4,800	1,750	1.3	95	0	0	0	0	0	0

The correlation of the performance on NS4½H with adhesion, strength and extensibility of the lacquer was found to be valid in the case of all clear lacquer systems. However, systems incorporating pigmented lacquers often failed even if the size lacquer possessed the specified minimum mechanical properties. This appeared to be due to the hygroscopic nature of some pigmented films or to their permeability by water vapour. Fortunately, it was found possible to incorporate water-repellent ingredients into the basic formulation of certain lacquers and so improve their performance.

In effect, a number of lacquer systems of various colours were developed which could be satisfactorily used on unpretreated NS4½H in the production of bottle caps and closures. However, in each case the formulation of the lacquer was critical, and the choice of components was restricted to very few commercially available materials. Furthermore, even the few selected lacquers which were good enough for application on unpretreated NS4½H failed on unpretreated alloys with a higher magnesium content (NS5, NS6 and NE7).

DISCUSSION

Among the three methods of improving the performance of lacquers on aluminium/magnesium alloys discussed in this paper, the first, namely, the modification of annealing practices in the production of sheet, proved to be impracticable. Any changes in standard production techniques are as a rule both troublesome and costly; in the present case they also proved to be largely ineffectual.

The approach to the problem through the selection and development of special lacquers was much more promising. Unpretreated NS4½H can be successfully coated with lacquers compounded from readily available materials. However, the number of lacquers suitable for this purpose is very restricted and their compositions as well as the conditions of application are highly critical. Although the lacquers are satisfactory for decorative purposes, it is not yet known whether they would be fully satisfactory for protection. It has been shown that they are restricted to alloys containing not more than 2 per cent magnesium.

It could be argued that once it has been established what basic properties permit a lacquer to perform satisfactorily over unpretreated aluminium/magnesium alloys, it should be possible to develop modified resins which would be suitable for both protective and decorative purposes and could be applied equally well over aluminium alloys with any magnesium content. This may be true, but it would require a major development in the production of lacquers, and it would be unwise for the manufacturers of coated strip to rely on this possibility. Hence, whilst the selection of lacquers can provide a restricted solution in certain cases when a limited production of lacquered NS4 is necessary, a more general answer to the whole problem of lacquering aluminium/magnesium alloys is still needed.

Such an answer is provided by a suitable pretreatment of the sheet prior to lacquering. Among the pretreatments so far examined, electrochemical treatment in sulphuric acid is clearly the most effective and the most generally applicable. It is easy to operate, requires only short times of immersion, hence permitting high output, and causes only negligible weight losses. Further, it produces an anodic film which affords protection during prolonged periods of storage and provides a good key for lacquer, and is applicable to all commercial aluminium/magnesium alloys. It may be added that large-scale production experience with sulphuric acid anodic pretreatment of aluminium strip is already available, because the process has been introduced by A/S Nordisk Aluminiumindustri, where it is giving very satisfactory results[11] at a comparatively low cost.

Acid chemical pretreatments also give satisfactory results, but they have a number of limitations from which the sulphuric acid anodic treatment is free. The main drawbacks are that they cause a noticeable weight loss and that when applied to high magnesium alloys they require a long immersion time. Also they must usually be preceded by a more thorough degreasing than is needed in the case of sulphuric acid anodic treatment. They do not, however, require any electrical installation. For this reason they may be preferable where only small-scale production of lacquered strip is in question, or where aluminium/magnesium alloys constitute only a small part of the production.

CONCLUSIONS

Failure of lacquer coatings occurs more easily on aluminium/magnesium alloys than on other aluminium alloys. Such failure is unsightly in the case of decorative coatings and shortens the shelf-life of containers lacquered for protection. The main cause of such failure is the presence of a hard, brittle and slightly alkaline oxide film formed on the aluminium/magnesium sheet in the course of usual production processes. An increase in the magnesium content of the alloy makes the lacquer more prone to failure.

Modifications to production techniques are unlikely to produce sheet with more than 0.5 per cent magnesium that is sufficiently free from magnesia-rich oxide film to be satisfactorily coated with ordinary commercial lacquers. Special lacquers can be compounded which do not fail when applied on alloys containing up to 2 per cent magnesium. Such lacquers are, however, not readily available and the choice of materials is restricted. The development of lacquers suitable for aluminium alloys containing more than 2 per cent magnesium presents even greater difficulties.

Poor lacquer adhesion can be overcome by applying an acid, chemical or electrochemical pretreatment. The adhesion of commercial lacquers to aluminium/magnesium alloys so pretreated is at least as good as to any other aluminium alloy. The anodic pretreatment in sulphuric acid is particularly efficient and most generally applicable. It has been successfully used in the laboratory and by at least one manufacturer of lacquered strip. Chemical pretreatment in nitric acid solution may be preferred for a small production line where an electrolytic plant cannot be economically justified.

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DISCUSSION

DR. HÖFLING remarked that in a recent publication of Nordisk Aluminium the effective range for the thickness of the anodic coating was given as 0.2-0.4µ and he asked whether the authors considered this correct.

MR. R. D. GUMINSKI stated that in the case of anodic pre-treatment in nitric acid the thickness was 0.05µ and in sulphuric acid 0.25-0.5µ.

DR. G. E. GARDAM, commenting on the formulation of lacquers for adhesion to magnesium-containing alloys and the limitation of 1 per cent of co-polymerised maleic acid, enquired whether it was not possible to produce resins with a higher co-polymerised acid content and whether these might be expected to solve the problem of adhesion without the necessity for chemical pre-treatment.

MR. GUMINSKI thought that this was possible, but they had only tried direct acid addition to the VMCH type of lacquer. Direct adhesion of the films was considerably improved, but the tensile strength deteriorated rapidly, possibly due to the lack of co-polymerisation of the additional acid, allowing the formation of a discontinuous film.

MR. J. A. L. HAWKEY remarked how pigmentation influenced the adhesion by affecting the water permeability and brittleness characteristics of the film. He suggested that the groups in the medium which might be expected to influence adhesion might also be preferentially adsorbed on to the surface of the pigment and consequently fail to fulfil their prime function.

MR. E. S. J. FRY asked whether failure in adhesion occurred between the lacquer film and the oxide layer, or in the oxide layer itself.

MR. GUMINSKI replied that there was no evidence of part of the oxide layer being removed from the metal. Most failures occurred on exposure to hot humid conditions after deformation, and these conditions could not affect the oxide layer directly.

MR. M. J. BEGGS asked whether the applied lacquers were stoved before deformation tests and suggested that acetic acid addition might also enhance adhesion of lacquers to aluminium.

MR. J. F. BARTON asked whether the lecturers had any experience of the use on aluminium/magnesium alloys of clean metal conditions derived from wash primers, as that would seem to provide the acidic requirement and lacquer in one operation.

MR. GUMINSKI said that such experiments had been carried out, but although many acidic treatments improved adhesion, nitric acid was the most effective.

DR. F. A. CHAMPION commented on the curve for the magnesium content of the oxide film and noted that it showed two slopes. He said that it had been shown by others that the film consisted of magnesia overlying alumina and he enquired whether there was appreciable magnesium in the lower layers, or if the shallow slope of the curve in those areas was due to the difficulty in sampling a film which varied across the metal surface, owing to the successive annealing, fracture of the oxide film on rolling and then further annealing.

MR. GUMINSKI replied that the specimens were annealed after rolling, machined and then annealed or heated at various temperatures in various gases. Two techniques were used for removing the oxide film, one used nitric acid vapour, but with this there was some doubt as to the attack on the magnesium and so a mechanical method was then adopted. In this case there was some limitation as the specimen was never perfectly flat and on taking any specific layer only the corner could be removed. The second and successive layers would be larger, but the last layer would contain little oxide with pieces of metal under the film. In consequence, the exact shape of the curve was not wholly reliable, but the main point was that the top of the oxide film was much richer in magnesium than the lower part.

MR. L. E. COLYER asked if there was a possiblity in the near future that lacquer formulations would be developed suitable for direct application to aluminium/ magnesium alloys which would withstand the stringent conditions of processing in a cannery, *i.e.* steam at 260°F.

MR. GUMINSKI explained that all the lacquers tested had been designed for decorative purposes only and the chemical and steam resistance was not given in the paper. If pre-treatment processes were used, it was known that any lacquer could be applied without failure, and any lacquers which were resistant to steam on normal aluminium would also be resistant on magnesium alloys.

MR. HAWKEY queried the thickness of the lacquer films applied and the variation in thickness found.

MR. F. M. P. MEREDITH said that for external coatings the weight was 0.8-1.2 mg./in^2. and for internal coatings 3-4 mg./in.^{2}, both figures being for clear lacquers.

MR. GUMINSKI added that the film thickness was closely controlled and that these figures were for deformation and hot, humid atmosphere tests. For direct adhesion tests, different film thicknesses were used owing to the fact that reliable results could only be obtained where the film had a limited minimum thickness. Below that thickness the results were erratic. In all cases test results were on strictly controlled film thicknesses.

MR. F. ARMITAGE referred to the results obtained for various types of lacquer and asked whether all coatings other than the co-polymerised vinyl/maleic acid type were unsatisfactory, and if these alternative lacquers were commercial types recommended by lacquer manufacturers.

MR. GUMINSKI said that the best results were obtained with the VMCH type lacquers, but these had to be modified to increase the film strength, although direct adhesion was sufficient. The commercial types tested all failed quite badly, including the *Epikote*, which had very strong direct adhesion but was brittle.

MR. ARMITAGE presumed that all *Epikote* systems could not be condemned because of the failure of one lacquer and asked whether the manufacturers had recommended it as the best.

MR. GUMINSKI agreed with this remark, but said that the point he wished to make was that presumably any type of lacquer which had sufficiently high direct adhesion, sufficient extensibility, and sufficient strength and elasticity of film would prove satisfactory. He had quoted specification figures for these properties and he expected that compliance with these would give good results whatever the type of lacquer used.

MR. M. M. D. POWELL was surprised at the brittleness and lack of adhesion of the *Epikote*/phenolic system and asked for details of the composition and stoving schedule.

MR. MEREDITH replied that there was no information relating to composition, but that the films were cured either at 300°C for a short time, or at 200°C for about 20 minutes. He emphasised that the films were brittle only in so far as they were not suitable for sheet which had to undergo severe deformation.

MR. GUMINSKI added that curing conditions were as recommended by the manufacturer.

MR. K. L. HEDGECOCK commented that such lacquers were used satisfactorily on steel which was subject to post-forming.

MR. GUMINSKI agreed and added that they were also used satisfactorily on aluminium, but not on aluminium/magnesium alloys, where the oxide film condition was much more critical, so that there was a greater demand on the film properties of the lacquer.

MR. HEDGECOCK suggested that it would seem to be a question of adhesion rather than extensibility of film.

MR. GUMINSKI said that the adhesion was probably impaired by the alkaline nature of the oxide film. He felt that if the direct adhesive properties were extremely high, it was probable that extensibility or film strength could be slightly reduced. Equally, if the film had extremely high extensibility, it was probable that a slight reduction in direct adhesive qualities would also give a satisfactory result.

MR. J. W. ARMSTRONG questioned the lecturers about the stoving conditions used for the lacquers, and asked for information regarding the maximum temperature and time which could be used without detriment to the mechanical strength of the alloy.

MR. GUMINSKI replied that there was a limit to the temperature which could be used when the strength of the alloy was in question. The vinyl type lacquer which had been quoted in the paper could be stoved quite adequately at 130°C, and temperatures up to 200°C would not adversely affect the mechanical properties. It was known that at 300°C, 30 seconds treatment would affect the strength of the alloy.

MR. A. W. BRACE added that one of the other points which had to be considered was the temper of the alloy. If soft material was used, the stoving temperature was not quite so critical as if the material was hard. At 200°C he thought that 20 minutes was a reasonable stoving period.

MR. HAWKEY commented that as the oxide film varied in composition throughout the depth so also did the lacquer film, and this might also play some part in adhesion and flexibility.

MR. C. R. PYE (contributed). The lecturers mentioned in Table IV the reduction in direct adhesion of lacquer to aluminium/magnesium alloys with increased time or temperature of annealing, but the figures quoted in the same table for SIC, pure aluminium, showed no such similar marked decrease, although there was a small reduction with an increase in temperature from 480°-540°C. In his experience there was a marked decrease of adhesion where annealing temperatures higher than this, *e.g.* 600°C, were used. There seemed to be a critical point at about 550°C, below which only slight reduction was found, but above which adhesion fell off rapidly. Mr. Pye asked whether it would be considered that the crystalline nature of the oxide film could vary with these different conditions of annealing, producing a permeable, amorphous film capable of absorbing the lacquer, at the lower temperatures and an impermeable, highly compact and crystalline film, incapable of giving an absorptive bond with lacquer, at the higher temperatures. The criterion of adhesion was taken throughout the paper as that under hot, humid conditions. He further inquired whether it would be expected that the results would vary under humid conditions at 0°C, which are often encountered as specification requirements in the packaging industry.

THE AUTHORS had had isolated experiences of this kind which had not been adequately explained. They felt that it had probably been connected with the surface activity of the aluminium, but the factors responsible for this had not been adequately investigated, and an explanation at present was not possible. The authors knew that the annealing temperature affected the crystalline form of the oxide film and it was possible that higher annealing temperatures might produce a more compact, adherent, crystalline oxide film than did the lower temperatures. Regarding tests at 0°C, similar effects, although somewhat modified, would be expected in these conditions.

Methods of Testing Certain Mechanical Properties of Lacquer Films

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Summary

In an investigation carried out by the authors it was necessary to measure the strength, extensibility and elasticity of lacquer coatings as well as their adhesion. Established techniques were not always adequate and had to be modified. The details of testing methods and apparatus successfully used by the authors are described.

INTRODUCTION

The authors were recently confronted with the problem of selecting or developing lacquer coatings suitable for application over aluminium/magnesium sheet. The lacquered sheet was to be used for the production of bottle caps and had to undergo severe deformation. Many lacquers which are satisfactory in production of bottle caps from SIC, commercial purity aluminium, and NS3, aluminium/manganese (1.25 per cent), fail on aluminium/magnesium (2 per cent) alloys such as NS4. Aluminium/magnesium alloys are known to be covered with a thick oxide film composed of alumina and magnesia. The ratio of magnesia to alumina is often considerably higher than the ratio of magnesium to aluminium in the alloy[1]. The film is therefore rather hard, brittle and slightly alkaline. It was considered that these characteristics of the oxide film were responsible for the failure of many lacquers on deformation.

In order to select or develop lacquers suitable for use under these difficult conditions, it was necessary to correlate their performance with physical and chemical characteristics. Among these the strength, extensibility and elasticity of the films, as well as the strength of their adhesion to aluminium/magnesium alloys, were expected to be of considerable importance. Established testing methods for measuring these properties were found difficult to apply and they often required elaborate equipment. This paper describes simplified techniques developed by the authors and successfully used in their investigations of lacquer coatings for application on aluminium/magnesium alloys, the results of which are described elsewhere[2].

MEASUREMENT OF MECHANICAL CHARACTERISTICS OF LACQUER FILMS

The usual methods of measuring the mechanical properties of lacquer film are by the Erichsen test and by winding over mandrels of various diameters[3, 4, 5]. The limitations of these methods are that they determine properties of films adhering to metal surfaces and the values obtained are, in fact, affected by the influence of the base. This difficulty can be eliminated if measurements are carried out on detached films.

Preparation of Detached Films

Several methods of preparing detached films have been described[6]. The authors treated aluminium panels with a thin film of common soap. The soap was moistened slightly in order to make it sufficiently pliable to be dispersed into an even film over the panel. The moisture was then driven off by heating the specimen for half an hour at 100°C. The lacquer to be tested was flowed on to the soap-treated surface. This method of application was found to be satisfactory for coatings of the thickness and uniformity required for measuring the properties of strength, extensibility and elasticity. After stoving at the specified temperature and time for the lacquer under test, the film was removed in the following manner. A small area of the stoved lacquer at the edge of the panel was carefully detached by means of a razor blade and then the specimen was immersed in water for a few minutes to enable the lacquer film to be removed. The underlying soap film dissolved in the water, the lacquer film could then be easily removed.

This method could not be used for some lacquer coatings because their properties were known to be adversely affected by contact with water. In the case of these coatings it was necessary to use an alternative method. This comprised uniformly flowing the lacquer over a panel of tin strip, stoving and placing the panel lacquered side up on a bath of mercury. The tin amalgamated rapidly with the mercury and the detached film of lacquer was thus obtained.

Measurement of Film Strength and Extensibility

The determination of the film strength and extensibility was carried out in a way similar in principle to but simpler than that described by Conolly[7]. The films were cut into strips measuring 10 in. × 1 in. The ends of the strip were attached to two camera spools and wound once round each spool to prevent the film breaking at the spool. The two spools with the film attached were suspended from the upper beam of the framework of the testing apparatus (Fig. 1) so that the film was in the form of a loop. A container to carry lead shot was suspended from a circular rod placed in the loop. Two points were marked on the film, one near the top and the other near the bottom. The exact distance between the two points was determined by means of two travelling microscopes, as illustrated in Fig. 1. The container was loaded with successive 75 g. loads of lead shot, and the increase in distance between the two gauge marks on the lacquer film was determined at half-minute intervals after each addition, until the film broke. The load required to break the strip was therefore obtained, as well as the extension under this load. The thickness of the lacquer film was determined with a micrometer, and from these data the ultimate tensile strength per square inch of the lacquer could be calculated.

Measurement of Elasticity

In order to determine the components of extension, a second film was fixed to the two spools in the manner described and lightly loaded to ensure that the lacquer film was straight. Gauge marks were made with red ink and their positions read by means of the travelling microscopes. The film was then stretched with a load slightly less than that required to break it. After one

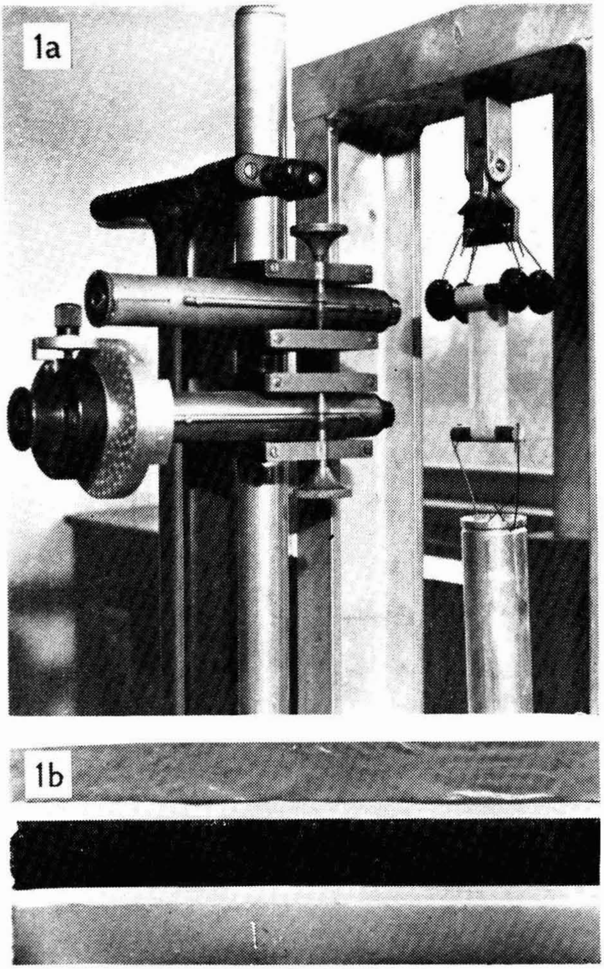

FIG. 1.

(a) The apparatus used for measuring the ductility and total strength of lacquer coatings.

(b) Three specimens of stripped lacquer films.

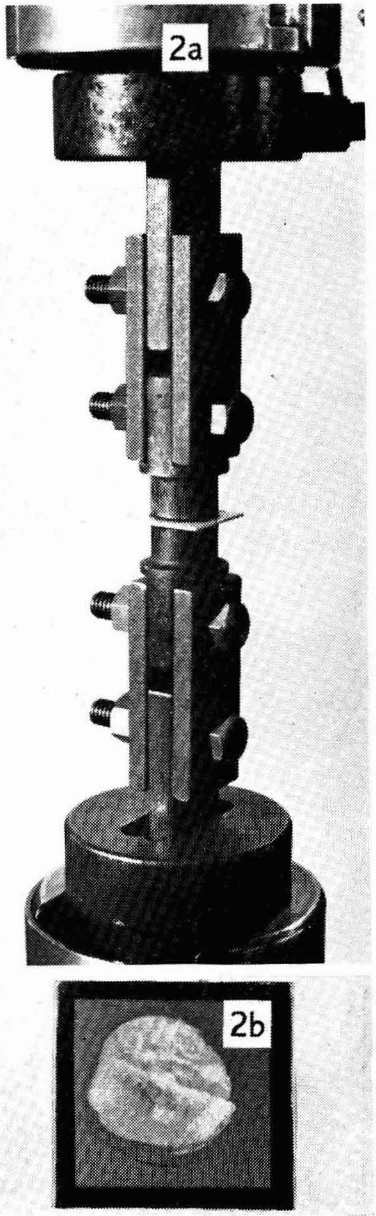

FIG. 2.

(a) The lacquered specimen attached to the platens in position on the Amsler Universal Testing Machine.

(b) The specimen with the lacquer removed.

minute the distance between the two points was again determined. The load was removed and replaced by the original light load and the distance between the two points measured. From these data the plasticity and elasticity were calculated as a percentage of the total extension, using the following formula:

$$\text{Plastic component of the extension} = \frac{(z-x)\,100}{(y-x)}$$

Where x = distance between gauge marks under original light load,
y = distance between gauge marks under heavy load,
z = distance between gauge marks under the final light load.

The percentage elastic component could now be obtained by subtracting the figure for the plastic component from 100.

MEASUREMENT OF ADHESION

A number of tests have been used for measuring adhesion of lacquers to the surfaces on which they are used. Examples of these are bend tests and scratch tests. Another method consists of making a series of parallel cuts through the lacquer film in one direction, and another series at right-angles to the first one. The lacquer film is thus divided into a number of small squares. The number of squares from which the lacquer comes off are counted[8]. Sometimes the conditions of test are made more exacting by pressing *Sellotape* across the squares and then removing it.

The measurement of adhesion is affected not only by the property of adhesion but also by other properties such as hardness, elasticity, flexibility and brittleness. The *Sellotape* test perhaps comes nearest to the true adhesion measurement, but it is complicated by the presence of shear.

The Direct Adhesion Test

The direct adhesion is the force which is applied at right-angles to the film to detach it from the underlying surface. A true assessment of direct adhesion can be obtained using a method, developed by I.C.I. Ltd., in which a lacquer-coated specimen is shot against a target which stops the support but allows the lacquer to fly off through a hole in the target. The minimum speed necessary to remove the lacquer from its support can be measured and from this the force of direct adhesion can be determined[9]. This method is rather complex and requires specialised equipment.

A method in which two freshly lacquered surfaces are placed one on top of another, stoved and then pulled apart has also been tried. It has the weakness that stoving of a lacquer in a sandwich is difficult. The solvent does not evaporate from the sandwich uniformly; consequently, the properties of the lacquer film are not uniform and rather erratic results are obtained.

In the test used by the authors, lacquer was sprayed on both sides of panels of suitable size and thickness. After stoving, each lacquered specimen was joined to steel platens by means of a selected adhesive. The adhesion of the lacquer was measured by determining the force required to separate the platens by pulling off the lacquer as shown in Fig. 2. An important feature of this test was that the applied force was normal to the lacquer surface. The platens used in this test were constructed from mild steel with a flat circular face having an area of one square inch. The outer ends of the platens were shaped to form shackles for mounting in the Amsler Universal Testing machine.

The lacquered panels were 1.5 in. square and 0.048 in. thick. The thickness of the sheet used in these tests was important, because it was found that below this thickness the metal became distorted during testing. This resulted in the lacquer being removed by a force which was not entirely axial but subjected the film to shear, varying with the degree of deformation of the metal that occurred, so that erratic figures were obtained.

Accurate control of the film thickness of the coatings to be tested for direct adhesion was found to be essential and the best method of achieving this was by spraying. Experiments showed that with both very thin and thick films uniform results could not be obtained, but within a certain range the results were quite consistent. In the case of thin films the adhesive used for joining the specimens to the platens appeared to have penetrated the coating at some points so that it was, in fact, in contact with the metal, acting as reinforcement for the film. With thick films it was found that the break occurred partially or wholly in the lacquer itself. From Fig. 3 the large scatter of results obtained with too thin and too thick films and the consistency within a certain range of film thickness for one lacquer may be seen. Similar results were obtained with a number of other lacquers. Even with specimens covered with a suitable thickness of lacquer there was some variation in the results obtained for direct adhesion. In order to improve the reliability of the test the mean of five results was taken as the direct adhesion value of the coating.

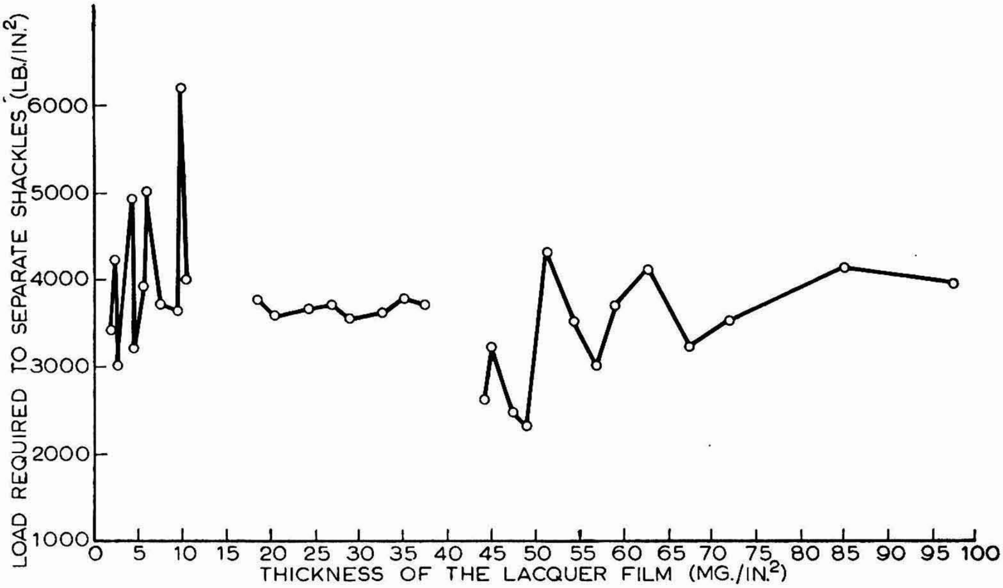

FIG. 3. VALUES OF THE ADHESION OF A COMMERCIAL LACQUER TO NS4 ALLOY OBSERVED IN THE DIRECT ADHESION TEST AT VARIOUS LACQUER FILM THICKNESSES

A basically similar method of determining the strength of direct adhesion has been described by May *et al.*[10], but in it organic coatings were applied to two cylindrical steel platens and joined by an adhesive. This arrangement can give rise to non-uniform stresses at the edges of the test pieces. It also makes the control of the thickness of coating more difficult; in fact, it appears that the problem of coating thickness had not been properly considered. Finally, if it is desirable to test adhesion of lacquers or paint to a number of metals, it is much easier to use the same pair of platens and vary the specimens of sheet than to have a separate pair of cylindrical platens for each alloy to be tested.

The Scratch Resistance Test

A frequently applied practical test of the quality of lacquer coatings is to scratch them with a coin or penknife blade under pressure of the hand. This gives an approximate indication of the adhesion of the lacquer, but it is merely qualitative. A standard quantitative method for measuring scratch resistance is to use an apparatus known as a scratch tester. A modified form of the apparatus in which the needle is replaced by a scraper is shown in Fig. 4. It consists of a horizontal sliding panel to which the lacquered specimen is clamped. The sliding panel is drawn beneath the point of a needle with a hardened steel hemispherical point of 1 mm. diameter; the needle is loaded with weights. The needle and sliding panel are connected to a battery in series with a small lamp. When the film is penetrated the circuit is completed and the lamp glows. If this apparatus is used by loading the needle with the sliding panel stationary, the reading obtained is related to hardness of the lacquer only. If the panel is moved during the test the reading is to some extent influenced by the adhesion of the lacquer. The authors considered that this test does not provide as good a test of adhesion as the coin test.

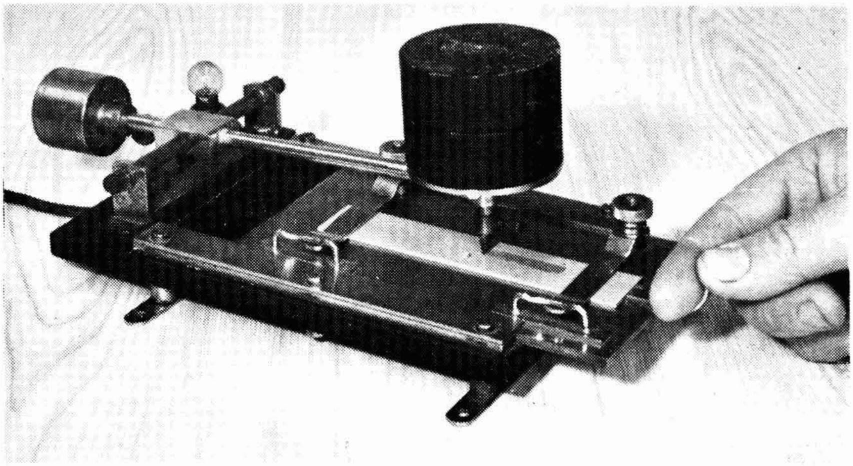

FIG. 4. PHOTOGRAPH OF THE SCRATCH TESTING APPARATUS ILLUSTRATING THE MANNER IN WHICH A LACQUER FILM IS REMOVED BY THE SCRAPER

In order to obtain quantitative values of scratch resistance under conditions closely similar to those of the coin test, the scratch tester was modified in the following manner. A scraper was made of hardened steel and was designed with a blade $\frac{1}{4}$ in. wide with an included angle of 30°. The base of the blade was not, however, brought to a sharp point, but was machined to a narrow flat, measuring 0.010 in., in order to avoid digging into the metal; the dimensions and design are shown in Fig. 5. The scraper was fitted into a sleeve in such a manner that it was allowed to swivel freely on its own axis. If the scraper was held in a rigid position, it was found to be difficult to set the blade exactly at right-angles to the line of motion of the lacquer film. This had the result that one end of the blade dug into the lacquer film and removed a narrow strip of the coating at a much lower load than that required to remove the total area covered by the blade. In addition, similar behaviour occurred if the metal to which the lacquer film was applied was not uniformly flat, or if the lacquer film itself was uneven. When the plough was allowed to swivel freely this difficulty was overcome. Although this worked quite well, the ideal device would be to mount the scraper on some type of universal bearing.

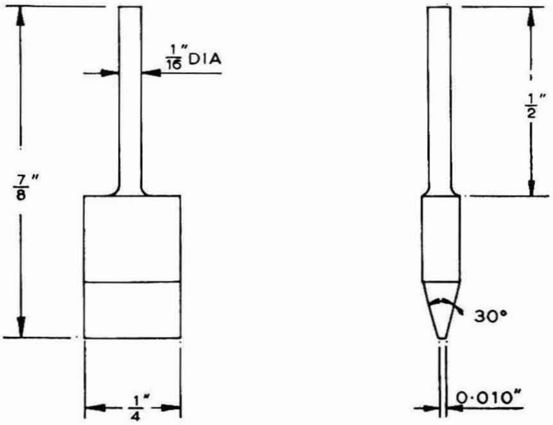

FIG. 5. DIAGRAM OF SCRAPER FOR SCRATCH TEST APPARATUS

An important feature of this test, which was established as a result of a number of experiments, was that in order to obtain reproducible results, the direction the scraper was facing must remain the same; the leading edge must always be the same edge. This was due to the fact that the narrow flat to which the blade was machined was not truly horizontal. Different results were obtained with different scrapers, although the panels were rated in the same order of merit.

Somewhat similar methods of testing scratch resistance have been described before[11, 12], but they required rather elaborate equipment, whereas the technique described in this paper is simple and suitable for taking rapid yet reliable measurements.

REMARKS ON THE USEFULNESS OF THE DEVELOPED TESTING METHODS

The authors have so far used the testing techniques described above in only one investigation. It was confirmed that extensibility, elasticity, strength and adhesion were all of considerable importance from the point of view of the performance of lacquers used in production of aluminium bottle caps. The minimum values of each of the above characteristics necessary for a lacquer to be satisfactory when applied on a selected aluminium/magnesium alloy were determined, and this led to the development of lacquer coatings particularly suited to this application. There is little doubt that extensibility, strength and adhesion are important in many other applications of lacquer coatings. It is hoped that the techniques described might prove useful for other workers studying the properties of lacquers.

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Water-Dilutable Stoving Finishes*

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Summary

A great deal of interest is now being shown in stoving finishes which are partly or completely thinned with water. The use of water as a diluent can give both cost and technical advantages, but a number of new problems are evident in water-based systems and these are considered in some detail. The relative merits of emulsion and solution systems are discussed and the practical formulation and use of water-based coatings is illustrated by reference to new types of water-soluble alkyd-phenolic and alkyd-amino resin combinations. A number of comparisons of water-based and conventional stoving finishes are described and from these it is concluded that these new resins are generally similar in performance.

INTRODUCTION

The success of emulsion paints has led resin and paint chemists to seek other paint applications where water might profitably be employed as a solvent or diluent. Apart from economic considerations there are two main advantages of water as a diluent—lack of toxicity and smell, and lack of fire risk. The two fields of paint usage that are obviously suitable for study are glossy air-drying decorative finishes and general purpose stoving finishes. The latter field is now receiving considerable attention and many experimental systems and a few production systems are now available.

There are copious references to water-based stoving finishes, particularly in the United States press, where the interest in water-based stoving finishes has been encouraged by the possibility of eliminating fire risk in large factories. The suggested systems divide fairly clearly into emulsion and solution types, and the sections that follow give many of these, together with literature references.

EMULSION SYSTEMS

The best-known examples are styrene-butadiene emulsions[1, 2, 3]. These deposit a coherent film at low temperature, but for adequate resistance and adhesion properties they require curing. Since they contain residual unsaturation, curing proceeds by oxidation which can be accelerated by metallic driers or by metallic substrates such as mild steel. These emulsions have been commercially used for stoving primers for two or three years. Other emulsions that are available, either experimentally or in quantity, are based on thermosetting acrylic resins[4]. Polyvinyl acetate emulsions[5] have also been offered. In general, all emulsion types used for air-drying paints could be adapted for stoving work, but it would appear highly desirable that the resins should be thermoreactive and this usually involves the production of special polymers.

SOLUTION SYSTEMS

Drying oils and alkyds

These are commonly solubilised in water by producing a high acid value resin and then neutralising or partially neutralising this with ammonia or

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*Read before the London Section on 10 November, 1960.

organic nitrogenous bases. High acid value with sufficient remaining functionality to allow polymer formation can be achieved by maleic anhydride adduct formation (maleinised oils) or by use of a trifunctional acid such as trimellitic acid. These resins lose water-solubility by loss of alkali and can cure by oxidation or esterification.

Amino resins

The use of low molecular weight alcohols for etherification or the use of the amino resin in the unetherified methylol stage gives rise to water-solubility with both urea and melamine resins. These lose water-solubility and cure by the condensation of methylol groups to yield methylene bridges or by other well-known mechanisms.

Phenolic resins

Simple methylol derivatives of phenols are water-soluble. These cure and lose water-solubility in the same manner as the amino resins.

Acrylic resins

Water-soluble acrylic polymers are now available. These are probably acid-containing polymers solubilised with alkali as in the case of alkyds. They can become insolubilised by loss of alkali only, but to effect a cure a cross-linking mechanism such as reaction with a water-soluble amino resin must be available.

Many other water-soluble resins are known, but few have the requirements of ready insolubilisation and curing during the stoving operation. Few also have the stability requirement of paint media since a viscosity increase or a loss of water-solubility is common in many systems. Furthermore, the need for high solids content solutions rules out many possible products, such as thickeners used for emulsion paints and the like (polyacrylamide is typical of this class). It is of course possible to combine soluble resins and this article deals primarily with patented[6, 7, 8] amino resin-alkyd and phenolic resin-alkyd compositions.

In addition to the emulsion and solution types, combinations of soluble and emulsion resins have been suggested, for example, alkyd emulsions combined with water-soluble melamine resin[9] and water-soluble resin combined with styrene-butadiene latex[10]. There are also systems where water is used to dilute solvent solutions of epoxy esters or epoxy and polyamide resin, and to produce oil in water emulsions[11, 12] and these can be regarded as a half-way house.

Many of the problems associated with water-thinned finishes are common to both emulsion and solution resins and typical of these are the need for oil-free surfaces and the allowance that must be made for the slower evaporation rate of water during the flash off period and in the stove. The major characteristic problems of the two approaches are given below.

(i) With all emulsion systems the pigment invariably has to change phase during the drying process where it passes from the water to the resin phase. This makes it difficult or impossible to produce high gloss finishes at high pigment volume concentration. Furthermore, to produce gloss and good film performance in emulsion systems it is essential that all colloids and wetting agents used in the emulsion preparation and in the pigment dispersion stage are compatible with the resin phase after stoving and are then water-insoluble. This limitation is a very real one and so emulsion systems are generally rated to be more suitable for primers and semi-gloss finishes than for gloss finishes.

(ii) The presence of emulsifying agents in emulsions usually leads to trouble with foaming.

(iii) The characteristic film formation in emulsions on non-absorbent surfaces is by coagulation on the surface so that, in stoving, water in lower layers has difficulty in escaping. Thin film application and high pigmentation can be a partial solution.

(iv) If a high degree of solubility is induced in the system, high solids content and good build, but difficulty in eliminating water-soluble components during stoving are found, while if water solubility is reduced to obtain good water resistance in the final film then low solids, low build solutions or low molecular weight resins that require more heat conversion to provide satisfactory films result.

These basic problems largely determine the choice of system. It is believed that the soluble system is the more useful at the present stage of development. The use of an alcoholic solvent in conjunction with water can largely overcome any problems of low build.

WATER AS A DILUENT

Water differs appreciably in many characteristics from organic solvents. A comparison between water, xylene and *n*-butanol is given below.

Property	Xylene	*n*-Butanol	Water
Specific gravity	0.868*	0.810	1.000
Specific heat .. .. .. (cal./g.)	0.398*	0.716	1.000
Latent heat of evaporation at boiling point .. .. (cal./g.)	125†	141	539.55
Approximate total heat input to convert from liquid at 20°C to vapour at 100°C			
Calories per gram	157	198	620
Calories per ml.	136	160	620
Evaporation rate (Ether=1)	13.5	33	80‡

*Average of *o*, *m*, and *p*-xylene †Probable figure. ‡Approximate.

It is obvious from these figures that the evaporation of water requires considerably more heat input than that of organic solvents. This can be achieved by use of longer flash-off times or by a more gradual heat up rate of the paint film in the oven. It should be realised that water vapour is always present in the air and is in equilibrium with water in the paint film. At high relative humidities therefore, the water evaporation rate is greatly retarded. This can be overcome by a slight increase of temperature during the flash-off stage. Another problem is that the boiling point of water is below the normal stoving temperature employed and therefore, unless it is substantially removed before the film reaches 100°C, film bubbling can take place. With water-soluble systems these disadvantages of water as a solvent can to some extent be mitigated by the addition of alcoholic solvents. The use of these in reasonable proportions does not invalidate the main advantages of water, namely, economy, lack of toxicity and fire hazard.

RESIN TYPES

In the studies that follow, two basic types of resin have been used. The first is an alkyd resin-amino resin combination *Resydrol M471*, referred to throughout for brevity as *M471*, and the second is an alkyd resin-phenolic resin combination *Resydrol P411*, referred to as *P411*. Both are supplied as 67 per cent solids content solutions in alcoholic solvent/water mixtures. Water-solubility of these resins is largely effected by the presence of salt groups derived from acid groups in the polymers and ammonia or organic amines. They are slightly alkaline in aqueous solution and must be maintained within the pH range of approximately 7.0 to 8.5, if necessary by the addition of ammonia (*P411*) or tertiary amines, such as triethanolamine (*M471*). When these resins are stoved they cure to a thermoset condition and simultaneously lose water-solubility. The loss of water solubility occurs by thermal breakdown of the alkali salt either to acid and volatile alkali or by amide formulation, *e.g.*

$$R.COOH + NH_3 \rightarrow R.CO.ONH_4 \rightarrow R.CONH_2 + H_2O$$

Complete curing is essential to obtain maximum water resistance so these resins usually require a little longer stoving time than their organic solvent-thinned counterparts. Typical schedules are:

Melamine-alkyd type:	30 minutes at 135°C.
Phenolic-alkyd type:	40 minutes at 160°C.

PAINT FORMULATION

Pigmentation

With soluble resins as distinct from emulsion types, pigmentation can be achieved by direct dispersion into the medium. Most pigments, particularly those which are neutral and substantially insoluble in water are satisfactory. Strongly basic pigments and those containing appreciable quantities of water-soluble salts are generally unsatisfactory in that they affect the stability of the paint on storage, or decrease the water resistance of the stoved film. Pigment water-solubles can be the cause of corrosion in conventional finishes, but there are indications that their effect is even more marked in aqueous systems. The effect of using low and high water-soluble red iron oxides in a primer submitted to corrosive conditions is illustrated in Fig. 1. Pigments which are strongly hydrophilic, such as china clay, may delay the evaporation of the water from the paint film and therefore should be used with care. In limited quantities they may often be useful in controlling the flow of the paint after application. It will be noted that many anticorrosive pigments are not satisfactory for use with these resins because of their excessive basicity. However,

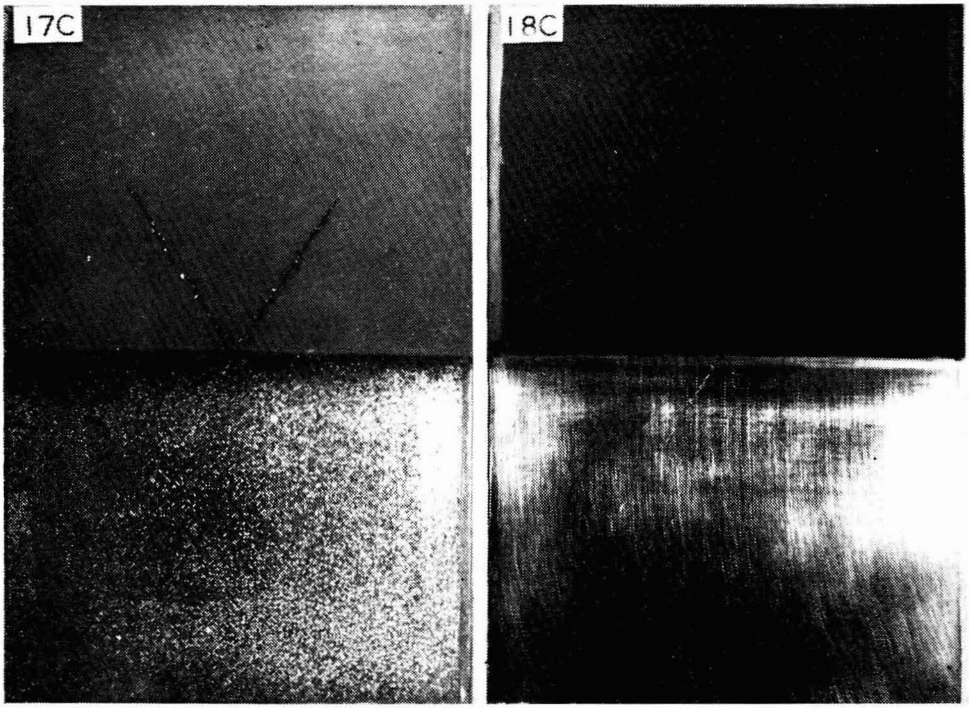


FIG. 1. EFFECT OF PIGMENTS WITH HIGH WATER-SOLUBLES, IN *Resydrol P*411
18C: Good red oxide, 400 hr. humidity.
17C: Poor red oxide (3% solubles), 250 hr. humidity.

the resins themselves have as will be shown later, anticorrosive properties apart from a purely barrier effect, and consequently anticorrosive pigments are not normally necessary. A partial list of satisfactory and unsatisfactory pigments is given in Table I.

TABLE I

PIGMENTS

Suitable		Unsuitable
Titanium dioxide	Strontium chromate*	Zinc oxide
Antimony oxide	Hansa yellow†	White lead
Lithopone	Chrome green	Basic lead sulphate
Zinc sulphide	Phthalocyanine blue	Calcium silicate
Calcium carbonate	Prussian blue	Calcium plumbate
Barium sulphate	Ultramarine blue*	Zinc chromate
Mica	Helio red†	Red lead
Talc	Lithol red†	
China clay	Iron oxide	
Lead silicochromate	Carbon black	
Lead chromate		

*Individual grades should be checked for stability.
†Bleeding may occur with some grades.

Pigment milling methods include the use of all the conventional machinery such as roller mills, ball mills and dispersion mills. Ball mills have been found particularly satisfactory and suitable milling techniques have been evolved. In this work both the vehicle solids of the grinding vehicle and the nature of the reducing solvent have been varied. The optimum mill paste was established for each composition by means of a Daniel flow point[13]. This test which is essentially an oil-absorption taken to the point of flow in the mix, can be used with various end points, but in this case the "snap back" point where the mixed vehicle—pigment thread when broken has enough flow to snap back due to surface tension was used. Ideal milling conditions should correspond with minimum quantity of vehicle and maximum of pigment in order to obtain maximum efficiency and the Daniel flow point figure can be used directly to calculate ball mill charges in the laboratory. On a works scale vehicle demand may be a little less.

Using *P411* the pigmentation was 33 per cent by weight red iron oxide and 67 per cent by weight blanc fixe. The resin was diluted with ethanol/water, ethylene glycol monoethyl ether (ethyl glycol)/water, and isopropanol/water mixtures with the alcohol contents varying from 10—60 per cent of the thinner.

With *M471* the pigmentation was 75 per cent by weight titanium dioxide and 25 per cent by weight blanc fixe. The resin was again diluted with ethanol, ethyl glycol and isopropanol mixtures with water.

The results of all these tests can be presented in different ways. In Fig. 2 the relationship of vehicle demand by the flow point method to vehicle solids using *P411* is shown. In Fig. 3 the same relationship is shown for *M471*. In Figs. 4 and 5 on the other hand, the effect of alcohol percentage of the thinning solvent at constant vehicle solids is shown in relation to Daniel flow point.

Examination of the curves gives rise to the following conclusions.

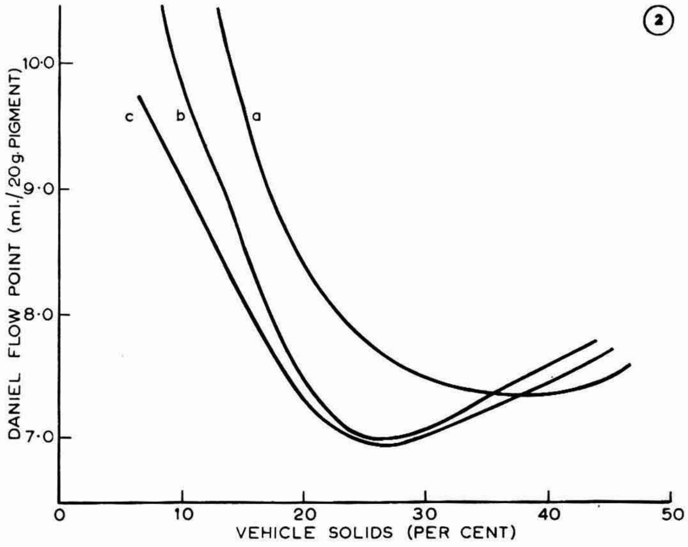
(i) With *M471* the optimum vehicle solids for mixtures of ethanol, ethyl glycol and isopropanol with water at a 15 : 85 alcohol: water ratio is 15—18 per cent.

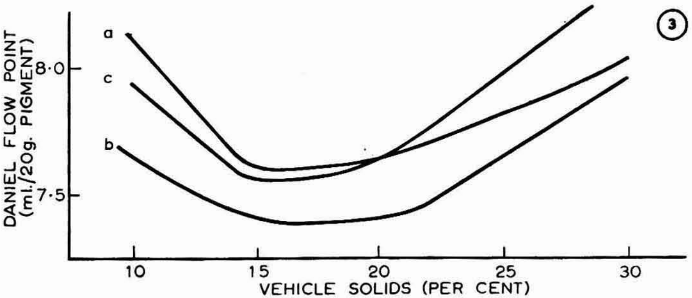
(ii) With *P411* the optimum vehicle solids is 25 per cent with 15 : 85 ethyl glycol/water and isopropanol/water mixtures, but 40 per cent with a 15 : 85 ethanol/water mixture.

(iii) With *M471* the Daniel flow point figure drops with increasing ethanol content in the ethanol/water thinner to an optimum figure at 40-50 per cent ethanol. The shape of the curve is not steep however, and lower ethanol contents could obviously be used without serious loss of efficiency.

(iv) With *P411* the relationship of flow point to alcohol content in the thinner is such that with ethanol a marked optimum occurs at 40 per cent content. With isopropanol there is little or no change in results above 38 per cent content, while with ethyl glycol, changes in the range of 15-60 per cent content are insignificant.

All of these effects may be summarised by saying that for each alcohol/water/resin system there is an optimum vehicle solids. There may also be an optimum alcohol content in the thinning solvent but this is less significant and so could be governed by other factors. These other factors might be the final percentage of alcoholic solvent required in the paint to achieve the desired solids content, flash-off time and sag resistance. The use of some alcohol in the ball mill paste is desirable also because it minimises foaming which can be a problem in the grinding of aqueous systems.



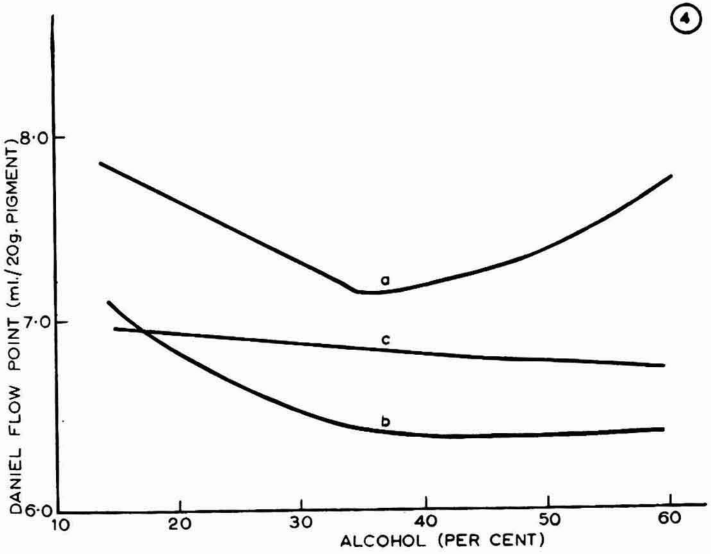


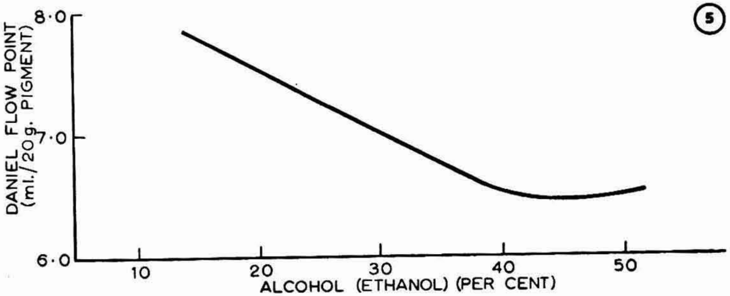
EFFECT OF VEHICLE SOLIDS CONTENT ON DANIEL FLOW POINT

FIG. 2. *Resydrol P411* (33% red iron oxide, 67% blanc fixe).

FIG. 3. *Resydrol M471* (75% titanium dioxide, 25% blanc fixe).

The curves indicate 15 : 85 mixtures (by weight) of
(*a*) Ethanol : Water. (*b*) Isopropanol : Water.
(*c*) Ethyl Alcohol : Water.





EFFECT OF ALCOHOL CONTENT ON DANIEL FLOW POINT

FIG. 4. *Resydrol P411* (33% red iron oxide, 67% blanc fixe)
(*a*) Ethanol. (*b*) Isopropanol. (*c*) Ethyl glycol.

FIG. 5. *Resydrol M471* (75% titanium dioxide, 25% blanc fixe).

It is normal practice to use pigments in dry form, but where they can be obtained in water paste condition economically, mixing only is required. The tinting of paints with aqueous colour dispersions, such as those available for emulsion paint use, has been studied. While most types are unsatisfactory due to excessive quantities of surfactants being present, some grades low in water-solubles can be used. Some of these pigment pastes require milling, however, to disperse them effectively and in general tinting is more readily achieved by using pastes of dry pigment in the base resins.

The effect of level of pigmentation on anticorrosive properties is dealt with in the performance section. Apart from anticorrosive properties, however, it is often advantageous to use higher pigmentations than necessary for colour and opacity. The extra pigment can, of course, be extender. With higher pigmentation there is less tendency for surface defects such as pinholing to develop since the formation of these is often encouraged by the mobility of the paint film during the initial heating in the oven. Choice of extender is significant in determining the pigment volume concentration for a particular degree of gloss. This in turn affects the vehicle solids of the paint and hence the cost, which is directly related to water content. Some appreciation of this may be gained from comparison carried out on thirteen typical extenders.

No.	Grade	Average particle size (microns)
1	Barytes, micron grade	2
2	Barytes: talc, 6 : 1	2 : 0.9
3	Barytes: diatomaceous silica, 6 : 1	2 : *ca* 2
4	Micronised dolomite	2.6
5	„ „	3.7
6	Micronised calcium carbonate	2.5
7	Natural whiting	5
8	„ „ stearate coated	1.5
9	„ „ hydrophilic	5
10	„ „ „	5
11	„ „ hydrophobic	5
12	Precipitated calcium carbonate	<1
13	„ stearate coated carbonate	<1

Of these extenders, Nos. 3, 4, 5, 9 and 10 gave severe settlement and were not examined further although they obviously could be used by employing suspending agents. The remaining types when used at a pigment : binder ratio of 2 : 1 by weight with 37.5 per cent *r*-titania, 62.5 per cent extender gave gloss figures as follows:

No.	Grade	Gloss (45°) (%)
1	Barytes	64
2	Barytes—talc	52
6	Micronised whiting	20
7	Whiting	40
8	Whiting—stearate coated	16
11	Whiting—hydrophobic	43
12	Precipitated calcium carbonate	5
13	„ stearate coated carbonate	25

From these grades four representative types were studied in more detail. Paints were made at 1 : 1, 2 : 1 and 4 : 1 pigment : binder ratios and were then blended to achieve gloss figures of 25 per cent (semi-gloss) and 10 per cent (eggshell). Precautions were taken to ensure equal pigment dispersion as far as possible; the results are given below.

Pigment	25% gloss		10% gloss	
	Pigment/Binder Wt	P.V.C. (%)	Pigment/Binder Wt	P.V.C. (%)
Barytes	3.2	43	4+	48+
Micronised whiting	1.0	28	1.5	37
Natural whiting	2.0	44	3.6	58
Calcium carbonate pptd.	1.6	38	2.0	44

The vehicle solids of three of these paints at semi-gloss pigmentation were, 35 per cent for barytes, 40 per cent for natural whiting, and 29 per cent for precipitated calcium carbonate.

These results demonstrate the big variations in formulation possible with minor changes in pigment grade. While this applies to all stoving finishes, choice of extender grades is probably more significant in water-soluble systems.

Some practical pigmentations are shown in the later section which gives typical formulae.

Reducing Solvent

It has already been indicated that advantages can be obtained by the use of alcoholic solvents in the thinning of water-soluble systems. These advantages are mainly increased vehicle solids and faster film set, which allows reduced flash-off time and less draining during dipping or flowcoating. Other benefits are reduced foaming tendencies and higher pigmentation in ball mill charges. In Fig. 6 the effect of various blends of alcoholic solvent and water is shown in terms of viscosity versus solids content. It is evident from this graph that the solids content at very low viscosities varies little with type of diluent. At viscosities in the normal usage range of about 40 seconds B.S. Flow Cup Type B, however, the range of solids obtainable varies between 20 and over 40. This range of obtainable solids is one big attraction of the water-soluble system in which alcoholic solvents can be incorporated. The more volatile alcohols, such as ethanol and isopropanol, give greatest benefit in reducing flash-off time and allowing greater wet film thickness without sagging. Higher boiling alcohols, in particular diacetone alcohol, are useful in preventing bubbling in thick films and on fat edges. Surprisingly, alcohols of only limited water-solubility such as *n*-butanol can be used without affecting the water tolerance.

Additives

Few additives have any real value in modifying the properties of water-based coatings of the type considered. The resins are slightly oxidisable and therefore metallic driers can be used with some slight advantage in curing speed.

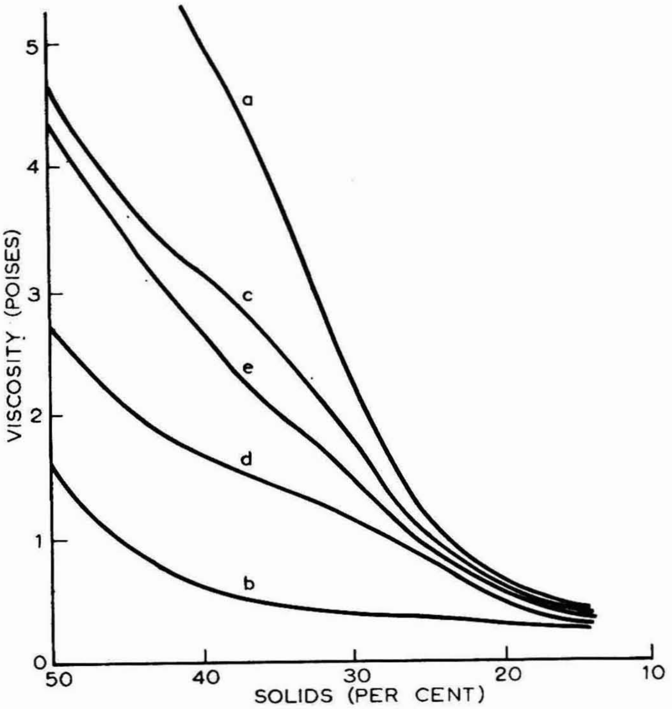


FIG. 6. VISCOSITY—SOLIDS RELATIONSHIP WITH VARIOUS DILUENTS

Curve	Mixture	Ratio by Weight
a.	Water	—
b.	Ethanol	—
c.	Ethanol : Water	1 : 9
d.	Ethanol : Water	2.5 : 7.5
e.	*Sec*-butanol : Water	1 : 9

Of the driers examined, manganese acetate has been found to be the most useful, used at a ratio of just below 0.1 per cent metal on solid resin. Another additive that has been used is the ammonium salt of a weak organic acid which decomposes at stoving temperatures to liberate the free acid. A slight improvement in curing rate results from the presence of this acid, but again the effect is not of significance except in cases where borderline improvement is required.

The question of compatibility of water-based resins does not so far seem to have any real significance because of the limited number of types available. For example, the inclusion of emulsions of resins, such as butadiene-styrene copolymers, is likely to add the problems associated with emulsions without any comparable benefit. The addition of water-soluble colloids is largely impossible because of compatibility limitations.

Typical Formulations

The combination of the previous sections on pigmentation, reducing solvent and additives, gives a number of typical formulations. These are listed below, together with comments on their typical usage and recommended stoving schedule.

	Black semi-gloss dipping finish	Green gloss spraying enamel	Red oxide spraying primer	Metal furniture semi-gloss spraying finish
Carbon black	2.2	—	—	—
Barytes, 2 micron	24.4	—	—	—
r-Titania	—	5.5	—	—
Phthalocyanine green	—	0.6	—	—
Red iron oxide	—	—	15.3	—
Blanc fixe	—	22.0	30.5	33.8
Lamp black	—	—	—	2.0
Yellow iron oxide..	—	—	—	10.0
M471	39.0	34.0	—	30.4
P411	—	—	30.4	—
Ethanol	—	3.5	3.2	3.2
Diacetone alcohol	3.9	—	—	—
S.B.P. 5	1.0	—	—	—
Water	29.5	34.4	20.6	20.6
	100.0	100.0	100.0	100.0
Specific Gravity	1.29	1.31	1.55	1.54
Viscosity, B.S. Cup Type B sec. at 20°C	130	120	160	170
Dilution for application, (% by volume of water)	60	20	20	20
Stoving schedule	30 min. at 140°C	30 min. at 140°C	40 min. at 160°C	40 min. at 160°C

APPLICATION

These water-based systems can be applied by all normal methods of application. The only limitations so far known are that in hot spray coatings care should be taken to ensure that the paint does not remain at an elevated temperature for too long a period, since changes in water-solubility will take place at temperatures above about 50°C. It is also thought that application by electrostatic spraying, using some of the systems which are currently available, does present problems. Nevertheless, there are reports of satisfactory electrostatic spraying by other systems. Points of significance with various possible methods of application are listed below.

Spraying

Water-soluble systems appear to spray quite satisfactorily at viscosities considerably above those which would be necessary in equivalent solvent thinned systems. This is probably explained by the negligible evaporation rate of water in the atomised stage which allows good flow out and film integration under conditions where solvent-based finishes might show severe orange peeling. It is less obvious to see why water-based systems should, in general, atomise very readily at these higher viscosities, but successful spraying at normal pressures with viscosities in the 60-90 second B.S. Flow Cup Type B range has been carried out on many occasions. It is probably desirable to give less attention to viscosity when deciding the correct dilution for water-soluble systems, because the paint will often perform satisfactorily at much higher viscosities than normal, and also because the effect of the diluting water will be to change viscosity only slowly.

A satisfactory technique is to take the paint at about 120 seconds viscosity in its compounded state and then to dilute with a 20 per cent addition of water, after which portions of the paint are diluted with successive 10 per cent additions. Each of the diluted paints is then sprayed on to a panel which is successively masked so that three film thicknesses are obtained. The degree of flow out and the degree of sag resistance obtained in terms of maximum film thickness applied without sagging is then a good guide to the best reduction to use. Some idea of the results obtained in such a test is given in Table II. A further point of significance in these finishes is that since water additions have relatively little effect on viscosity, it is possible to control the dry film thickness of paint applied by water additions. In a solvent system, if an addition were made of say 20 per cent of solvent, then the viscosity reduction would be so great that spraying would be impracticable. With the water-based system, a reduction of only 5 seconds in viscosity for a similar addition might well be found and this would allow similar wet film thickness, but reduced dry film thickness.

Effective use has been made of the good stability of dilute aqueous solutions of these resins in a continental factory where water washed spray booths are employed. For a period of over two years an aluminium paste pigmented finish has been used for spraying bicycle frames and accessories. The overspray is, collected in the normal way on a water curtain, but this water curtain is passed through a recirculating system of about 20 gallons capacity. After some three days of operation, the water has picked up sufficient paint to justify its usage. It is then used as diluent in further paint and this contributes noticeably to the economy of the coating system. A diagram of the assembly used is given in Fig. 7.

Use of a clean air supply in spraying is essential as one or two cases have been found where surface defects in the film in the form of pinholes and ciss marks have been found to be due to globules of oil from the compressed air. Such an oil spray is not of significance in normal solvent-based coatings but must be removed in aqueous systems. Surface defects can also be caused by the presence in the atmosphere, or on articles being coated, of overspray from solvent-based systems. It is therefore essential that good segregation of solvent and aqueous spraying is achieved. Overspray can if necessary be rendered harmless by stoving the objects concerned before coating with the aqueous enamel.

TABLE II

Effect of Diluent on Film thickness and Properties

Vehicle Solids	Water		Water: Ethanol 8 : 1		Water: Ethanol 4 : 1		Water: Ethanol 2 : 1		Water: Ethanol 1:1	
	Flow†	Thickness‡	Flow	Thickness	Flow	Thickness	Flow	Thickness	Flow	Thickness
43							P	1.6	P	1.6
40							P	1.5	G	—
37					P	1.2	F	1.5	G	1.0
34	P	1.2	P	1.1	P	1.2	G	1.3		
32	P	1.0	P	—	F	1.0	G	1.2		
30	F	—	F	1.0	G	1.0	G	0.8		
28	G	0.7	G	0.8	G	0.9				
26	G	0.7	G	0.5	G	0.9				
25	G	0.6								
Maximum dry film thickness applied without sagging*.	1.6		1.6		1.7		2.6		1.6	

†P=Poor. F=Fair. G=Good.

‡Thickness of dry coating in inches × 10^{-3} applied by one pass of the spray gun.

*Maximum thickness was applied in two or three wet on wet coats.

Formulation used: 1 Red oxide: 2 Blanc Fixe: 1 *P411* (solids).

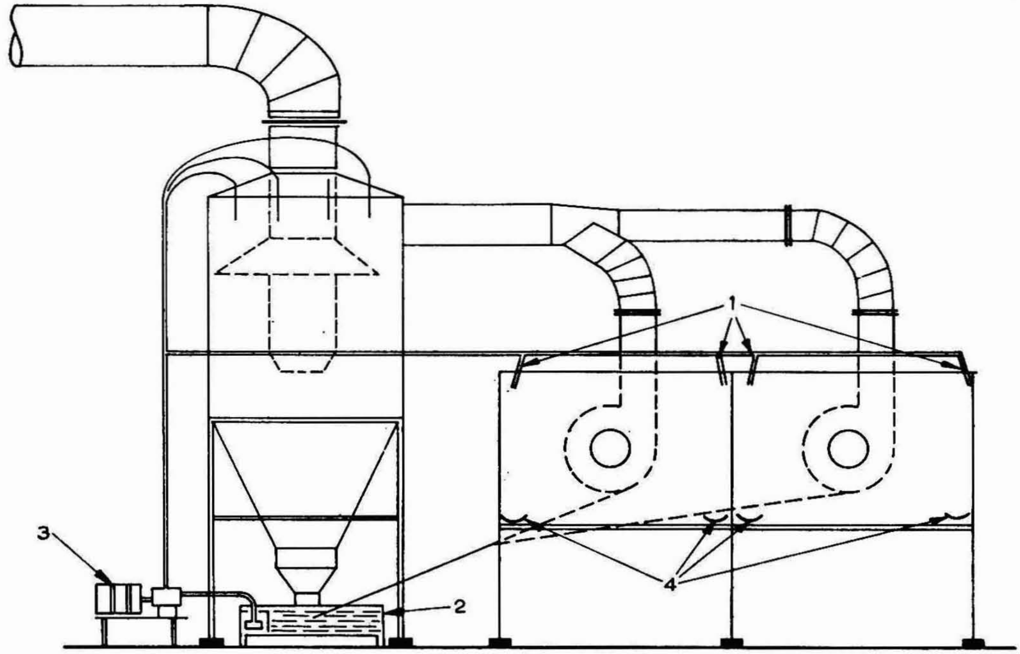


FIG. 7. WATER-WASHED SPRAY BOOTH WITH RECIRCULATION

1. Recirculated water sprays.
2. Water tank—100 litre capacity.
3. Circulating Pump.
4. Water drainage channels.

Dipping

Water is a particularly good solvent in dipping work since its low evaporation rate and the lack of toxicity and fire risk are all of great interest where large areas of paint are exposed. Dip tanks have been in operation for over two years without any attention other than small water additions to correct viscosity, and, of course, further paint additions. In formulations containing alcoholic solvent it does not appear necessary to add this as an extra diluent, since the formulation change occasioned by small losses in alcoholic solvent does not significantly change the properties of the coating. A general problem in dipping water-based systems is the formation of foam on the surface. This has been so severe in some emulsion-based paints that it has prevented their use in many dipping applications. Because of the absence of added surfactants, the water-soluble resins have less tendency to foam. However, some trouble may still be experienced as the resins themselves behave as surface active agents. Some general methods can be applied to decrease this; for example, it is found that an increase in pigmentation decreases foaming, as also does a decrease in viscosity and an increase in alcoholic solvent content. Where alterations of this type cannot be made, various antifoaming additives can be used.

Many proprietary additives used in air-drying emulsion paints and paper manufacture have been examined. In general, they are critical in use because excessive quantities promote pinholing. They are best used in specific formulations on a trial and error basis. A more general remedy is to add a small percentage of volatile hydrocarbon solvent, which presumably forms a very thin layer on the top of the paint although no layer is visible. A suitable quantity is 1 per cent of S.B.P.5 (aliphatic hydrocarbon, boiling range 90°-105°C). Higher boiling aliphatic solvents are more critical in their usage in that the point of defoaming is closer to the point at which film defects occur on the coated objects. In the case of the more volatile hydrocarbons, such as the example mentioned, the quantity suggested can be doubled without the danger of film defects. It is probable that in all cases where antifoaming additives are used, their efficiency decreases over a period of time and that regular small additions are more effective than the incorporation of large percentages initially.

With the low volatility of water and the excellent flow it gives in the pigmented finish, the problem with dipping paints is more likely to be excessive drainage, for example, from sharp edges, than inadequate drainage. The best answer to edge control is undoubtedly the use of a suitable pigmentation and findings have been incorporated in the earlier section on formulation.

Flowcoating

Some of the most outstanding advantages of aqueous paints occur in the flowcoating process. This is generally of little consequence at the present time in the United Kingdom although much greater use is made of flowcoating in Europe. Part of the reason for this relative neglect is that viscosity control presents a continuous problem. With water as the diluent it appears as if flowcoating is a process which could well be revived, since practical use has shown not only that it largely overcomes the viscosity maintenance problem, but also that very little trouble is experienced in drying the paint in jets, a problem which has also been associated with this process. So successful has flowcoating been that a number of very large installations are using aqueous paints for flowcoating for all sizes of plants ranging from small car pressings to agricultural tractors. Even after an overnight closedown the flowcoating can be resumed without jet cleaning and the only correction needed is a small addition of water which can be fed into the system by means of a simple automatic viscosity control.

Roller Coating

The use of water borne resins in roller coating of tinplate is rather limited by the inevitable film of oil that is applied to tinplate and which is not normally removed before coating. This prevents the formation of a completely satisfactory film from aqueous paint but when removed, excellent results can be obtained. On surfaces which are normally free from oil, such as hardboard, practical use is being made of roller coating and here again, water as a diluent has the requirements of low volatility at room temperature.

SURFACES

Probably the biggest limitation of aqueous stoving enamels is their need to be applied over clean surfaces. Large quantities of industrial stoving enamel are applied to surfaces which are not degreased at all, or degreased inefficiently and, in general, water-based coatings are unsatisfactory for application to these surfaces. In some cases satisfactory results can be obtained by using high pigmentation, and, of course, water-based systems can be applied perfectly satisfactorily to a solvent-based primer, or size that has been fully cured. Both solvent and aqueous detergent degreasing of metals can be used with equal efficiency, but it is possible that the advent of water-thinned stoving enamels will increase the relative use of aqueous degreasing, since this is normally cheaper, apart from the cost of drying the surface after degreasing. With an aqueous enamel this drying stage can be eliminated, and it is perfectly feasible to go from a final water wash to the paint spraying or dipping operation with only a few minutes draining time.

Phosphating or chromating processes as applied to mild steel, light alloys and other metals commonly finished, are all perfectly satisfactory and are recommended whenever possible. As with solvent-based enamels, improved adhesion and corrosion resistance are obtained by these treatments. There appear to be no limitations to the use of these paints on a variety of substrates, and in fact on some surfaces, in particular, electro deposited zinc on mild steel, it has been found that both the adhesion and performance of the aqueous enamel are noticeably superior to that of a solvent-based control.

STOVING SCHEDULES

After application it is very desirable for an extended flash-off time to be allowed before stoving, because first, resins of the type considered reduce considerably in viscosity on heating and this can give rise to excessive sagging or drainage from sharp edges. Secondly, and more importantly, water boils at a temperature below the final stoving temperature and a large volume of water left in the film during the stoving run up will often give rise to bubbling. The situation is probably made worse by the low evaporation rate of water and by the decrease in the evaporation rate at high relative humidity. It is therefore considered that at normal ambient temperatures, a 20 minute flash-off period is desirable. The time can be shortened considerably to a matter of a few minutes by flash-off at somewhat elevated temperatures and, in practice, with conveyor ovens, if a suitable low temperature zone is available before the main heating zone, the flash-off time can be reduced to a few minutes. Curing of the melamine resin *M471* takes from 40 minutes at 130°C to 15 minutes at 150°C. Above 150°C some discolouration takes place. The phenolic type requires schedules of from 40 minutes at 160°C to 10 minutes at 180°C. Curing rate by Persoz hardness is shown graphically in Fig. 8.

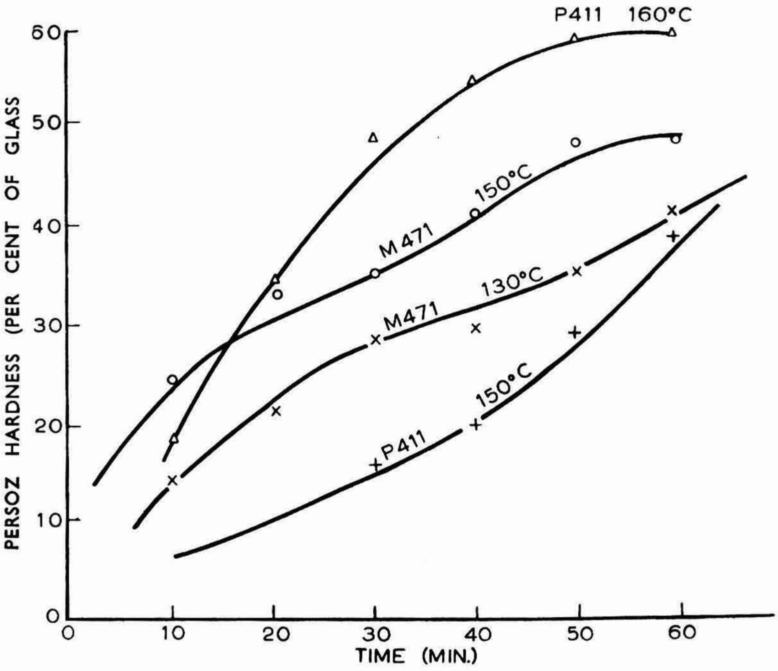


FIG. 8. CURE RATE BY PERSOZ HARDNESS

PERFORMANCE

Several series of tests have been carried out comparing the melamine resin *M471* with three alkyd-amino resin combinations. All the paints were made with a pigment : binder ratio of 0.75 : 1 using fine particle size *r*-titania. References to the systems have been made as follows:

A. *M471,* 36 per cent vehicle solids.
B. Dehydrated castor alkyd and urea resin at solid ratio of 7 : 1, 42 per cent vehicle solids.
C. Dehydrated castor alkyd and urea resin at solid ratio of 1.5 : 1, 43 per cent vehicle solids.
D. Castor alkyd and urea resin at a solid ratio of 1 : 1, 38 per cent vehicle solids.
E. Hydrogenated castor alkyd and melamine resin at a solid ratio of 4 : 1, 41 per cent vehicle solids.

These finishes were all applied at a film thickness of between 1-1.2 $\times 10^{-3}$ inches dried coating, and the results of tests are summarized in Table III. From these initial tests it is apparent that the water-based system *M471* is comparable in overall properties with the solvent-based systems. Points of difference are a somewhat lower Persoz hardness than the oxidising systems and slightly lower

TABLE III

M471 vs. CONVENTIONAL FINISHES—GENERAL COMPARISON

System reference	Substrate	A *M471*	B D.C.O. alkyd/UF	C D.C.O. alkyd/UF	D Castor alkyd/UF	E Hydrog. castor/MF
Stoving schedule, 30 minutes at .. .. (°C)		140	120	120	120	120
Persoz hardness .. .. (% of glass)	Mild steel	29	49	60	42	34
Scratch hardness .. .. (g.)	Tinplate	1300	900	1000	1000	1100
Bend test .. .. (in.)	,,	Passes ⅛	Passes ⅛	Passes ⅛	Passes ⅛	Passes ⅛
Adhesion (cross hatch method)	Mild steel	Good	Good	Good	Good	Fair
Reverse Impact* (mm.)	,,	1.8-2.1	3.2-3.5	2.4-2.6	2.4-3.0	2.2-2.4
Gloss (45° reflectance):						
Normal	Aluminium	97	89	68	77	75
Overstoved 3 hr. at 150°C		82	19	10	17	41
Difference		15	70	58	60	34
Colour (% reflectance of blue light):						
Normal	Aluminium	88	88	89	91	91
Overstoved 3 hr. at 150°C		68	56	72	84	90
Difference		20	32	17	7	1

*Falling weight method on reverse of panel. Measurements are greatest indentation not causing paint failure and smallest indentation causing failure.

impact resistance than the solvent-based systems. Gloss retention is particularly good, while colour retention is comparable with the lower alkyd content dehydrated castor alkyd system. The relatively poor initial gloss and gloss retention of certain of the solvent-based systems could probably be improved significantly by more careful attention to the pigmentation methods, but as the paints were made by identical ball milling methods, it does give some indication of the good pigment wetting properties of the water-based system.

In the next series of tests, the resistance behaviour was examined both in spot tests, in which the reagent was allowed to remain on the stoved panel for a period of up to 16 hours, and in immersion tests in distilled water and dilute solutions of detergent, sodium carbonate and citric acid. The immersion tests in detergent, sodium carbonate and citric acid were generally too severe to show any significant differences between the panels. It is sufficient to note that the dehydrated castor system with high urea content, and the castor alkyd with high urea content were the only two finishes to show any significant resistance to the alkaline solutions. This, of course, is in line with common experience. The results of the spot tests and of the hot distilled water immersion testing are given in Table IV. In this table a rating system has been used on the basis of no damage=0, complete removal=5 and based on the summation of these figures the water-based system is seen to compare well with the solvent-based finishes.

The next series of tests were concerned with accelerated weathering behaviour. The paints were exposed as single coat finishes on mild steel and results are given in Table V. Certainly external weathering carried out on a number of occasions does not support the suggestion that this type of resin has any significantly improved exposure properties. None of the finishes showed any signs of chalking after 600 hours' exposure and, although all were scored before exposure, little corrosion took place either from the score mark or on other parts of the panel. Minimum creep of corrosion was about 3 mm. from the score mark and maximum no more than 5 mm. The assessed order in terms of this creep and isolated corrosion spots in the film was in order from best to worst: E, D, B, A, C.

Further testing was concerned with resistance to humidity (DEF.1053, Method 25) and salt spray (Method 24). Results of these tests on various substrates are given in Table VI. These results are typical of many which have been obtained on comparable water-based systems. The invariable pattern is that:

(*a*) on mild steel the water- and solvent-based resin will often perform similarly in terms of onset and degree of blistering but usually shows significantly improved corrosion resistance when the film is stripped. Even under severe examples of blistering it is common to find no signs of corrosion.

(*b*) on phosphated steel the differences between the water-based and solvent-based systems are comparatively small since corrosion is reduced in all cases and the advantage in anti-corrosive behaviour of the water-based resin for equivalent degrees of blistering virtually disappears.

TABLE IV

CHEMICAL RESISTANCE

Spot Tests.

System reference	A *M471*	B D.C.O. alkyd/UF	C D.C.O. alkyd/UF	D Castor alkyd/UF	E Hydrog. castor/MF
Aqueous NaOH (30%)	Lifted 2 hr. (5)	Lifted 8 hr. (4)	Blistered overnight (2)	Lost gloss only (1)	Blistered over night (2)
Battery acid (33%) H_2SO_4	Blistered overnight (2)	No damage (0)	Discoloration (1)	Blistered 3 hours (4)	Discoloration only (1)
Glacial acetic acid	No damage (0)	Lifted 40 min. (5)	No damage (0)	Blistered 2 hr. (4)	No damage (0)
Linseed fatty acids	No damage (0)	No damage (0)	No damage (0)	Lifted overnight (3)	No damage (0)
Phenol	All lifted in 15 minutes				
Light mineral oil	All undamaged				
Total score	7	9	3	12	3
Immersion Test: (Distilled water 80°C for 8 hr.)					
Blistering	2	2	3	2	2
Lifting	3	0	2	3	2
Loss of gloss	2	1	1	1	0
Total	7	3	6	6	4

Stoving schedules as Table III. Spot tests on mild steel. Immersion test on aluminium.

TABLE V

ACCELERATED WEATHERING

		Initial	100 hr.	200 hr.	300 hr.	400 hr.	500 hr.	600 hr.
		Gloss: 45° Percentage reflection						
A	*M471*	95	84	82	68	66	42	59
B	D.C.O. alkyd/UF	77	27	23	11	11	9	6
C	D.C.O. alkyd/UF	64	22	15	6	3	4	2
D	Castor alkyd/UF	74	16	8	12	4	3	1
E	Hydrogenated castor alkyd/MF	79	69	67	56	47	49	33
		Colour: Percentage reflectance of blue light, Mg0 standard						
A	*M471*	88	84	80	78	75	73	71
B	D.C.O. alkyd/UF	84	82	78	76	68	69	68
C	D.C.O. alkyd/UF	91	84	76	77	68	67	64
D	Castor alkyd/UF	89	86	82	78	71	68	68
E	Hydrogenated castor alkyd/MF	89	85	80	79	73	73	71

TABLE VI

SALT SPRAY AND HUMIDITY RESISTANCE

System reference	A *M471*		B D.C.O. alkyd/UF		C D.C.O. alkyd/UF		D Castor alkyd/UF		E Hydrog. castor/MF	
Humidity	1st blisters (hr.)	After 240 hr.	1st blisters (hr.)	After 240 hr.	1st blisters (hr.)	After 240 hr.	1st blisters (hr.)	After 240 hr.	1st blisters (hr.)	After 240 hr.
Mild steel	24	Little corrosion (Best)	140	Severe corrosion (Worst)	40	Severe corrosion (4th)	24	Some corrosion (3rd)	100	Some corrosion (2nd)
Phosphated steel	140	No corrosion (2nd)	180	Slight corrosion (3rd)	140	Slight corrosion (Worst)	140	Slight corrosion (Worst)	140	No corrosion (Best)
Zintec	24	No corrosion; poor colour (Best)	24	Zinc erosion (2nd)	24	Zinc erosion (2nd)	24	Some corrosion (Worst)	24	Some corrosion (Worst)
Salt Spray	1st blisters (hr.)	After 400 hr.	1st blisters (hr.)	After 400 hr.	1st blisters (hr.)	After 400 hr.	1st blisters (hr.)	After 400 hr.	1st blisters (hr.)	After 400 hr.
Mild steel	200	Severe corrrosion; edge creep (Worst)	200	Some corrosion creep (Best)	200	Some corrosion creep (2nd)	200	Some corrosion creep (4th)	200	Some corrosion creep (3rd)
Phosphated steel	No blisters	Slight corrosion (2nd)	No blisters	No corrosion (Best)	400	Slight corrosion (3rd)	200	Slight corrosion (4th)	200	Film lifting; severe corrosion (Worst)
Zintec	Edge blisters 400	No corrosion (Best)	400	Zinc erosion (2nd)	200	Zinc erosion (3rd)	200	Zinc erosion and corrosion (Worst)	200	Film lifted (4th)

(*c*) on zinc coated steel (*Zintec*) the aqueous system invariably performs well, giving little or no corrosion, although blistering may occur. With the solvent-based systems, erosion of the zinc seems to take place at a fast rate, and when this is virtually complete, corrosion of the underlying steel occurs. (See Fig. 9).

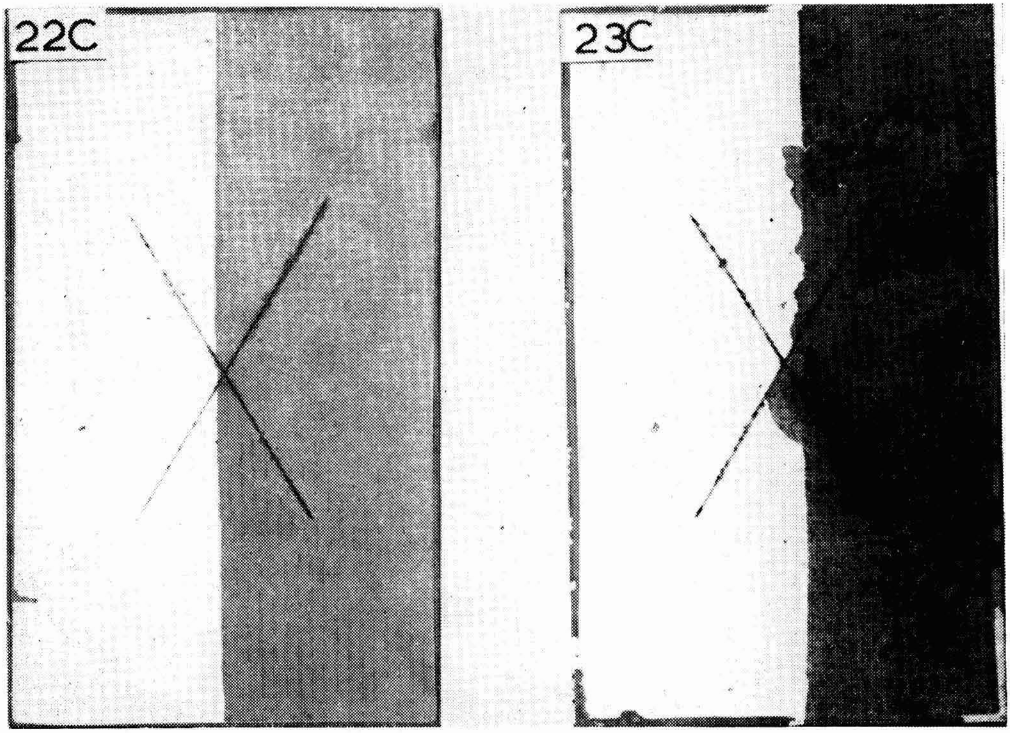


FIG. 9. COMPARISON OF FINISH A (*Resydrol M*471) AND FINISH E (hydrogenated castor alkyd/MF) HUMIDITY TESTING ON *Zintec*
22C: Finish A. 23C: Finish E.

In testing for salt spray resistance the pattern is generally similar, but all the water-based systems tested, including emulsions, give relatively poorer results than in humidity testing.

The comparisons given are simple ones made at low pigmentation and the properties of water-based systems can be very considerably improved by using optimum pigment loading (see Fig. 10). It should also be noted that the phenolic resin *P411* gives superior corrosion and salt spray resistance to that of the melamine type *M471*.

The effect of pigment concentration and type can be determined from the results of a series in which a number of extender pigments were examined in conjunction with red iron oxide in paints based on the phenolic resin P411. The extenders were natural barytes (5 micron size), fine particle size blanc fixe, natural whiting (5 micron size), and precipitated calcium carbonate. Thus in each case there was a natural and a precipitated extender. The pigments

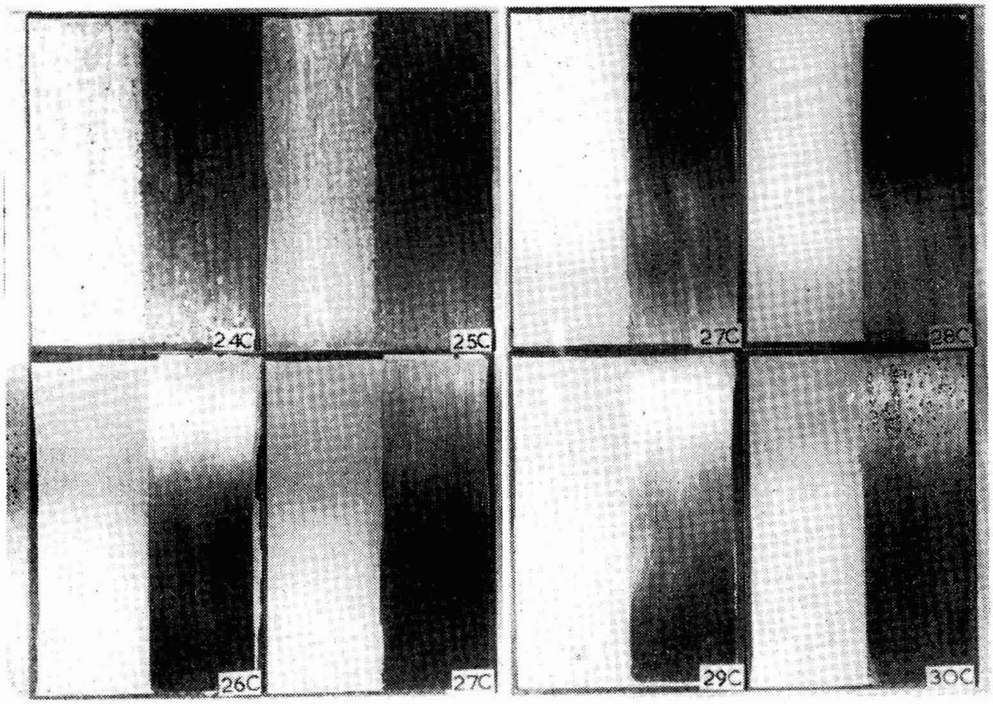


FIG. 10. EFFECT OF PIGMENT LEVEL ON SALT SPRAY RESISTANCE WITH *Resydrol M*471

Photograph	Pigment : binder ratio	Pigment volume concentration (%)
25C	5 : 1	58
24C	4 : 1	52
30C	3.5 : 1	49
29C	3 : 1	45
28C	2.5 : 1	41
27C	2 : 1	36
26C	1 : 1	22

were dispersed by ball milling at high pigment volume concentration (P.V.C.) and then were successively let down with medium to give pigment vehicle concentrations of 20, 25, 28, 32 and 35 per cent. The paints, after dilution, were applied to cold rolled mild steel by dipping and were stoved at 170°C for 30 minutes. The primers were tested without a finishing coat in order to accelerate breakdown and testing was by distilled water immersion at 30°C over a period of 60 days; the results are summarised below.

Barytes

This gave the best results of the four extenders. Isolated blisters were seen on two of the panels after 46 days' immersion. These probably random results occurred at 25 and 32 per cent P.V.C. The only other change noticed was that after 21 days' immersion the highest P.V.C. content paint at 35 per cent showed some loss of water repellancy in terms of the extent to which water wetted the panel on removal from immersion.

Blanc Fixe

Here the first random signs of blistering were with a 20 per cent P.V.C. after 39 days. All panels showed slight blistering at 46 days. Loss of water repellancy after 14 days was noted with the 32 and 35 per cent P.V.C. paints.

Whiting

All panels showed slight blistering at 18 days. This was mostly confined to edge effects. Water repellancy was lost quite quickly and only the two lowest P.V.C's. retained this after 4 days' immersion.

Precipitated calcium carbonate

The highest P.V.C. panel blistered at 11 days; the remainder blistered at 18 days. Water repellancy was lost quite quickly and only the three lowest P.V.C. paints had any water repellancy after 4 days' immersion.

After the 60 day immersion most of the panels were still in good condition and blistering, where it occurred, was of quite a minor order so the testing was increased in severity by increasing the temperature to 80°C. After 5 days at 80°C all the panels had blistered to varying extents and the tests were therefore discontinued. Blistering was more severe in all cases on the whiting and calcium carbonate panels than on the barytes and blanc fixe.

In corrosion effects it was noticeable that after the initial low temperature immersion none of the panels showed any significant rust creep from the score mark, and after the complete immersion period corrosion was only slight on all panels. In fact the calcium carbonate type extenders gave less corrosion than barium sulphate. From these results it is concluded that barium sulphate is a satisfactory extender and is generally preferable to calcium carbonate. The slightly superior corrosion resistance imparted by the calcium carbonate, despite the greater tendency of films based on it to blister, is possibly a function of the more alkaline nature of this pigment.

In this particular series it is evident, mainly from the onset of blistering and the changes in water repellancy that the fall off in properties starts at a P.V.C. of about 35 per cent. Other related series confirm this and, despite use of a wide variety of extenders and prime pigments, pigment volume concentration should not, with the phenolic type, be above 35 per cent if good corrosion resistance and film properties are to be maintained. As with many stoving resins, there is a lower limit below which there will be an increased tendency to blistering under humid conditions, but this lower limit of P.V.C. is not very definite. The region between 20 and 30 per cent P.V.C. is one which would be chosen for optimum all round properties, and the precise figure used will depend more on the degree of gloss and the nature of the enamel being produced than on the corrosion resistance required.

One of the less expected properties of the water-based resins is that they give good results in conjunction with aluminium pigments, not only aluminium after 21 days' immersion the highest P.V.C. content paint at 35 per cent showed some loss of water repellancy in terms of the extent to which water wetted the panel on removal from immersion.

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One of the less expected properties of the water-based resins is that they give good results in conjunction with aluminium pigments, not only aluminium powders, but also normal solvent wet pastes can be used with the resins under consideration. Although in most applications it is recommended that the system be treated as a two pack type, good retention of leafing properties has been shown over considerable periods and no pressure development has been observed in paints on this basis. Optimum results appear to be obtained in terms of humidity and salt spray resistance with the phenolic resin *P411* and aluminium pigment to give a 3 : 7 ratio of aluminium paste to solid resin. Single coat systems on steel of such a paint will show little or no breakdown after 400 hours in a standard humidity chest or 140 hours in a salt spray cabinet.

Some of the more important uses of these resins so far developed are concerned with a water-based primer being used under conventional solvent-based finishes, and it is therefore interesting to have some idea of the performance of such two-coat combinations. Tests were carried out in which four typical finishes were compared as single coat finishes on steel and over a *P411* red oxide primer. The finishes were a dehydrated castor alkyd-epoxy resin-melamine system (the so-called three component finish), a dehydrated castor-urea resin system and finishing paints based on the *M471* and *P411* types. In Table VII the onset of blistering and the final conditions of the panels are summarised. It will be seen that on average the presence of the primer at least doubled the time to the onset of blistering in both the humidity test and salt spray conditions. The series also provides a further comparison of water-based finishing paints against two conventional systems. One could conclude from these figures that the water-thinned finishes are rather better than the D.C.O. or urea system for humidity resistance, but somewhat inferior for salt spray resistance. The three component system, as might be expected, gives maximum results in all cases.

It is sensible at this point to sum up the main advantages of water-based systems of the type described, together with some of the disadvantages and as yet unsolved problems.

ADVANTAGES

Fire Risk

One of the immediate potential interests in water-based coatings is lack of fire risk and some criticism has been made of these systems in that an alcoholic solvent should sometimes be included to bring out their maximum advantage. Although under closed flash point determination conditions this may lead to a flash point similar to that of a conventional paint, in fact there is no fire risk attached to the use of water-based paints containing some percentage of alcoholic solvent. Tests have been carried out on a large scale and provided that the water content of the diluent is over 75 per cent, it is quite impossible to ignite the paint containing even the more volatile alcoholic solvents. With the percentage of alcoholic solvent normally likely to be experienced, not only is it quite impossible for the paint to support combustion, but it is not even possible to obtain any ignition at considerably elevated temperatures.

Toxicity

It is apparent that the toxicity of water thinned paints is less than that of paints which are currently being used. While this is of no great consequence in

TABLE VII

PERFORMANCE OF VARIOUS FINISHES AS SINGLE COATS AND OVER *P411* PRIMER ON MILD STEEL

	Epoxy 3 component		*M471*		*P411*		D.C.O. alkyd/UF finish	
	One coat	Over primer	One coat	Over primer	One coat	Over primer	One coat	Over primer
Humidity 1st blistering (hours)	350	1250	168	425	168	750	48	170
Final condition	1500 hr.		1500 hr.		1500 hr.		420 hr.	
	Slight corrosion under blisters (1)	Less blistering and corrosion (1)	Slight corrosion under blisters (2)	Slight blistering no corrosion (1)	Slight blistering no corrosion (2)	Slight corrosion (3)	Severe corrosion under blisters (worst)	Slight corrosion under blisters (worst)
Salt Spray: 1st blistering (hours)	350	1250	150	350	240	350	200	350
Final condition	1500 hr.		420 hr.	700 hr.	700 hr.		700 hr.	
	Slight corrosion under blisters (1)	Slight corrosion under blisters (1)	Severe corrosion under blisters (3)	Slight corrosion under blisters (2)	Severe corrosion under blisters (3)	Slight corrosion under blisters (2)	Film lifting; slight corrosion (4)	Film lifting; some corrosion (4)

Primer Formulation:

Red iron oxide	15.25
Blanc Fixe	30.50
P411	30.40
Ethanol	3.18
Water	20.67

normal good industrial practice, it is probable that increasing attention will be paid to this aspect with regard to atmospheric pollution.

Surface preparation

While the need for clean surfaces is to some extent a disadvantage of water-based systems, it probably only acts to encourage the proper cleaning of surfaces which is desirable in any paint system. The water-based paint does show considerable advantages in automatic and semi-automatic plants, where aqueous degreasing or pretreatment is used, in that immediate application of the paint over damp surfaces is feasible.

Cost

The immediate interest of water in stoving finishes might be thought to be the use of water to replace expensive solvent and thereby to give the cost advantages in the selling price of the paint. In fact, in a normal stoving enamel the cost of the solvent is seldom more than three or four shillings in a gallon, and the formulation changes needed to obtain water-solubility may remove much of this price advantage. If alcoholic solvents, particularly the higher boiling ones, are necessary to modify the coating properties, then the difference may disappear completely. Nevertheless in many cases the water-based system shows an economy when comparison is made on the basis of the cost per unit volume of applied paint. The cost advantage may come from elimination of the solvents used by the paint consumer; it may come from collection of overspray in a water washed spray booth, as has been discussed earlier, or it may come from savings on cleaning solvent or in the drying of objects prior to painting, or from the elimination of expensive storage facilities. It is important to realise that because of the high specific gravity of water, both the specific gravity of the paint per gallon and the volume solids related to weight solids are in favour of the water-based system.

Volatility

In paint application methods where the paint in use is exposed continuously to the atmosphere, the low volatility of water at ambient temperatures can be a favourably deciding factor both economically and for the convenience of handling.

DISADVANTAGES

Water-based stoving finishes as a class are comparatively new and as such, from the many different types of resins suggested, many faults might be expected. Neglecting emulsion-based finishes, which have a number of specific problems which have been mentioned earlier, it is believed that the water-soluble types have only three basic problems which are not capable of easy solution.

(i) Water-based solutions need higher heat input for evaporation, and since understoving of water-soluble resins results in a very severe loss of film properties, the combined effect is that stoving schedules are longer than with conventional solvent-based systems.

(ii) The cleaning of surfaces with a high degree of efficiency will always be necessary in the case of gloss finishes and is almost as essential in the more highly pigmented paints.

(iii) The only mechanism of obtaining water-solubility and finally water-insolubility that has achieved any real success depends on the use of an acid-containing polymer and a nitrogenous base. Inevitably with the elimination of some of the base during stoving, acid groups on the polymer are available for alkaline attack and there are no immediate prospects of improving substantially the alkali resistance of water-soluble coatings.

In lightly pigmented gloss finishes there is often a tendency for pinholes and ciss marks to appear during the stoving operation. Fry[14] has ascribed this to " critical surface tension ". In fact the resin solutions have a much lower surface tension than is needed to wet metallic surfaces and good wetting of clean metal surfaces can invariably be achieved. Ciss marks may appear in the stoving operation and this is probably due to the formation during the curing stage of micelles of water-insoluble resin. Correct formulation of the resin can overcome this particular problem which may be accentuated by excessive mobility of the film due to slow evaporation of water and the greater temperature dependence of water-soluble coatings compared with solvent-based coatings. It has been found that very small quantities of thixotropic pigments, such as bentonite or finely divided clays or calcium carbonate, will prevent this occurrence, but care must be taken to maintain a satisfactory gloss.

CONCLUSIONS

Water-thinnable resins for stoving finishes are now commercially feasible and are being used industrially in large scale applications. In general they compare well with conventional systems in performance, and no sacrifice in properties is entailed in changing to these new systems. In using any water-based paint, due consideration should be given to the particular properties of water, particularly in ensuring that reasonable flash-off conditions and good water vapour removal conditions are available in the oven. While all types of stoving finish in general use can probably now be made on these water-dilutable resins, it is sensible to concentrate attention on those applications which show the greatest advantage. This means cases where adequate degreasing can be achieved and where the longer stoving times and high stoving temperatures of these systems can be obtained. It is expected that once these resins have established themselves, development will occur in a number of directions for specialised uses. It is impossible for the small number of resins now available to compete with the extremely wide range of solvent-based stoving finishes and there will always be plenty of applications in which specific resistance properties will require solvent-thinned resins. Nevertheless, it is believed that within the next few years a serious swing to water-based stoving finishes will be achieved.

ACKNOWLEDGEMENT

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Discussion

Mr. R. N. Wheeler asked if the purity of the water used was important, especially in the case of primers, and whether water-soluble salts could in some cases cause corrosion of metal substrates.

Mr. A. G. North said that it was thought originally that very hard water would be disadvantageous, because dilution of the resin with water gave a slightly cloudy solution. Tests had shown, however, that neither the condition nor performance of the film showed any disadvantage, so that any water could be used directly from the tap.

Dr. O. Liebermann, in discussing the lower performance of two-coat systems in detergent and salt spray resistance tests, suggested that in the case of one-coat systems the water-soluble salts were leached out, whereas in the case of two coats they might be trapped by the second coat and thus cause the observed blistering failures.

Mr. North thought that this was possible, but unlikely, as generally the water-solubles from the resin seemed to inhibit corrosion. An air-dried solution on steel inhibited corrosion and it seemed that the resin had some quite definite anti-corrosive action.

Dr. M. L. Ellinger, inquiring about the relative durability characteristics of the phenolic- and melamine-based resins, said that in her experience the phenolic type proved superior in water and solvent resistance and had much better adhesion. She added that phenolic-based primers, provided that they were correctly stoved, seemed to be superior to conventional solvent-based primers in water immersion tests and resistance to aromatic and aliphatic hydrocarbons.

Mr. North replied that there was not very much difference in the durability of the two systems, but perhaps the melamine-based system was slightly superior, although it would be dependent on the degree of pigmentation. The melamine system was probably more water sensitive and the phenolic system more sensitive to ultra-violet light.

Dr. Ellinger inquired as to the necessity for the use of pretreated aluminium powder with the resins and commented that bentonite addition did not seem to be effective in preventing cissing at higher pigmentation.

Mr. North replied that it was not necessary to pretreat aluminium powder, nor was it necessary to use powder. The resins were sufficiently tolerant of hydrocarbons to permit the use of conventional aluminium paste. The effective use of bentonite depended upon adequate dispersion in water, which was not an easy matter, it being necessary to mix and grind it and then add it to the paint.

Mr. E. Hammond asked why calcium carbonate should inhibit corrosion less than more inert extenders and what type of calcium carbonate was used in the experiments.

Mr. North stated that it did not give inferior corrosion resistance as such, but tended to embrittle the film in water immersion tests and give a rather more porous film. Some eight different types of calcium carbonate were examined and they were found to vary greatly in overall effects on gloss and general film appearance. There was very little pattern in the results of this investigation, which would be published in due course, but it appeared that the particle size was more important than the origin.

Mr. E. S. J. Fry queried the effect of the high polarity of water on the possibilities of the application of the paints by electrostatic spraying and suggested that on theoretical grounds this would appear to be a real difficulty.

Mr. North said that he had no personal experience of this application, but he had seen a drawing of a Swedish method, said to have been used satisfactorily, which appeared to differ from the type used in this country in that the paint was first atomised by a conventional spray technique and then charged electrostatically. He thought that electrostatic application was not impossible, but that the existing systems were not completely satisfactory.

Mr. G. E. C. Mercer remarked on the use of alcohols to produce adequate solubility characteristics and asked the lecturer to comment on the effect of the relative evaporation rates of alcohols and water on stability.

Mr. North replied that alcohol does not evaporate from aqueous solutions as quickly as might be imagined from a consideration of direct evaporation rates and he had knowledge of a dip tank which had been used satisfactorily with one of these systems containing alcohol for something over two years. It was interesting to note that it was possible to use alcohols satisfactorily in these systems which were not soluble at the ratios at which they were used.

Dr. Liebermann asked what the possibilities were of the production in the future of a resin suitable for finishing coats which would have improved alkali and detergent resistance.

Mr. North, in reply stated that a gradual improvement could be expected as technique developed and that adequate detergent resistance could probably be obtained with the present state of knowledge. The present method of producing water-solubility by solubilising with acidic groups definitely limited the possibilities of producing resistance to strong alkalies.

A Speaker queried the problem of can corrosion.

Mr. North replied that the resins were alkaline in reaction with a pH of about 7.8 and that under those conditions cans do not corrode.

Mr. J. A. Handscomb asked for information on the combination of butadiene/styrene latices with water-soluble resins in primer compositions.

Mr. North replied that he had not carried out any work on this subject, but that recommendations in the United States suggested a combination of 15-25 per cent of soluble resin with the latex. He thought that it might be advantageous to reverse the ratio, but he had doubts as to the true resin compatibility.

Mr. Fry requested confirmation that no anti-corrosive pigment was incorporated in any of the primers used in the salt spray tests.

Mr. North agreed that this was correct.

Mr. A. Gellman inquired about the maintenance of dip tanks and whether it was satisfactory to add tap water only.

Mr. North felt that it was desirable for the paint manufacturer to make the necessary alcohol additions so that the user would only need to add water.

MR. A. G. ROBINSON asked how the water-thinnable resin-based finishes compared with conventional solvent-based finishes in the matter of adhesion to non-ferrous metals, suggesting that as these metals are often hydrophilic they should be superior. He commented that the stoving times seemed to be higher than those normally used with conventional systems.

MR. NORTH agreed that the stoving times were generally longer or temperatures higher. He said that the adhesion to brass was very good and that to aluminium quite adequate and that generally they perform at least as well as conventional systems.

DR. H. G. RAINS commented on the price consciousness of industrial paint users and asked whether the price of the water-thinnable coatings would reduce and become cheaper than conventional solvent-thinned systems.

MR. NORTH replied that the important factor was the cost of the painted object and that calculations had shown that there was a cross-over point where the two types of coating could give similar applied film costs. He did not think that in the foreseeable future these resins would reduce in price sufficiently to show an economic advantage in all circumstances.

MR. WHEELER suggested that the relative humidity of the atmosphere would significantly affect the rate of evaporation of the water from the film and asked whether the flash-off period would have to be varied with varying atmospheric humidity, or if it would be necessary to control the humidity during this period.

MR. NORTH agreed that a situation could be conceived where the relative humidity was such that no evaporation of water would occur from the film. In most cases of conveyorised application it was not necessary to rely on room temperature flash-off as there was a pre-heating period before the painted objects entered the stove, and this should be sufficient to remove all the water before stoving. It was important to try to do this particularly in the case of gloss finishes.

MR. W. J. SMITH inquired about the possibilities of using wet-on-wet finishing techniques, with the succeeding coat either water- or solvent-based.

MR. NORTH replied that with wet-on-wet finishing using aqueous materials there was a danger of sagging and tearing trouble owing to the slower evaporation of the water and the viscosity reduction in the stove. Correct formulation would tend to remove this danger. Non-aqueous finish over aqueous primer could not be used in this technique, but if the aqueous primer was first stoved there would be no objection to the use of a solvent-thinned finishing coat.

MR. R. S. COLBORNE requested general recommendations for the application of the two types of resin and whether they were ever recommended to be used mixed.

MR. NORTH replied that the melamine-based resin would be used for pale coloured, colour retentive and fairly low temperature stoving coatings, whilst the phenolic type would be used where maximum chemical resistance was required.

Coconut Oil-Isophthalic Alkyds for Stoving Enamels

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Summary

The formulating and processing of short coconut oil-isophthalic acid alkyds as a function of polyol type and excess are discussed. Their behaviour in clear and in pigmented baking finishes is compared with similar oil length phthalic alkyds and with epoxy resins.

INTRODUCTION

Alkyd architects of the last decade cannot complain about the scarcity of exciting new building materials for their complex molecules. Isophthalic acid certainly is among the more significant of these, but it presents more problems than could be anticipated after an optimistic perusal of the manufacturers' comprehensive bulletins which, in general, are of a remarkably high technical standard. The authors' aim was to become familiar with isophthalic acid as a tool for alkyd-type industrial media. What are the new fields it opens up for the explorer? Where have the warning signs to be planted? In what respect does it behave differently from phthalic anhydride? Can it upgrade an alkyd as a vehicle for an industrial enamel? What are its limitations?

The oil-modified alkyd is the Proteus among resins; no other paint vehicle offers a similar range of variability. The explorer can set out on hundreds of different paths and many of them will be rewarding[1, 2]. A short coconut oil type has been chosen for the following reasons:

(*a*) Because of its end use in baking enamels; this represents a good compromise between film hardness and flexibility;
(*b*) The oil component will not affect colour retention properties adversely;
(*c*) The polyester part is predominant;
(*d*) Types of suitable polyols can be selected from a fairly wide, but "pleasantly restricted" range.

The oil length has been set at 41 per cent, because this does not confine the polyols to bi-functional ones and because it is often used in commercial alkyds. (Preliminary tests indicated that 36 per cent oil length isophthalic alkyds would be too short, and 45 per cent too long for the authors' purposes.)

EXPERIMENTAL

Formulation and Processing of Resins

The equipment used was a stainless steel, 4 gallon capacity reactor with agitator, equipped for vacuum distillation and fitted with a sampling device which made it possible to take test specimens without interrupting the vacuum. The "solvent-process", *i.e.* the removal of the water liberated in the reaction between polyol and acid by means of an inert immiscible refluxing solvent, such as xylene, is a convenient method for the preparation of alkyds in the laboratory. It has been found, however, that the true advantage of isophthalic acid lies in its amenability to the fusion-type cook for two reasons. First, where solvent processing, IPA, being insoluble in xylene, is carried with the refluxing liquids into the aqueous phase which is continuously removed during the reaction, causing substantial losses (2-5 per cent based on original amount of IPA). Secondly, IPA does not sublime at alkyd processing temperatures in "fusion" cooks. The azeotropic method has, therefore, been avoided except for preliminary studies because of its general convenience.

The following fusion process, employing (i) Alcoholysis, (ii) Resinification and (iii) Thinning, stages was used.

(i) Coconut oil monoglyceride was prepared by holding the oil at 4 : 1 oil polyol ratio with 0.05 per cent (based on oil) quicklime present at 237°C for 40-60 minutes to completion.

The alcoholysis reaction was followed by the cold methanol test[3]. Slow inert gas sparge was applied throughout.

(ii) The remainder of the polyol and the isophthalic acid was added to the coconut oil monoglyceride, and the temperature was raised to 250°C. After holding the reactants at 250°C for 1½ hours, vacuum was applied gradually to 50 mm. and the batch kept under vacuum until the acid value dropped below 10.

(iii) After the release of vacuum and cooling to 180°C, the resin was discharged into a thinning vessel containing xylene, in order to reduce non-volatiles to 60 per cent. The hot resin solution was filtered through a press using 0.2 per cent filter aid, *Celite.*

Polyols

The following range of polyols was selected: glycerol, trimethylolethane, trimethylolpropane, pentaerythritol-ethylene glycol, and pentaerythritol alone, using benzoic acid as a mono basic acid, as well as IPA to reduce the functionality.

Table I contains the formulae for the various alkyd cooks. The viscosity figures were compared at 60 per cent non-volatiles in xylene, acid values being 9-11 on resin solids. Trimethylolpropane can be formulated at the lowest polyol excess; next is glycerol, and then trimethylolethane (see Fig. 1). Pentaerythritol can be used at 1 : 1 mole equivalent ratio with ethylene glycol (Batch No. 16) or by itself when part of the isophthalic acid is replaced by benzoic acid (No. 18). Batch 19 is a comparative glycerol-phthalic alkyd. The epoxy resin, No. 20, is a 41 per cent oil length *Epikote* 1004 ester in xylene.

TABLE I

Batch No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Coconut oil p/w	74	75	75	76	76.5	77.5	85	86	87	88	90	84	85	86	89
Isophthalic acid p/w	83	83	83	83	83	83	83	83	83	83	83	83	83	83	83
Glycerol† p/w	40.4	42	42.6	44	45	46.5	—	—	—	—	—	—	—	—	—
Trimethylol ethane‡ p/w	—	—	—	—	—	—	57.4	58.4	59.4	61.5	63.5	—	—	—	—
Trimethylol propane§ p/w	—	—	—	—	—	—	—	—	—	—	—	55.8	57.4	58.5	63
Polyol excess (%)	30	35	37.5	42	45	50	40	42.5	45	50	55	24	27.5	30	40
Viscosity* (poise)	Gel	120	50	17	11	5	Gel	50	25	18	14	Gel	42	22	9
Batch No.	16	17	18	19											
Coconut oil p/w	155	480	254	70.5											
Isophthalic acid p/w	166	415	166	—											
Ethylene glycol¶ p/w	43.4	—	—	—											
Pentaerythritol p/w	49	264	132	—											
Glycerol p/w	—	—	—	38.5											
Benzoic acid p/w	—	122	122	—											
Phthalic anhydride p/w	—	—	—	74											
Polyol excess (%)	40	26	26	25											
Viscosity (poise)	21	Gel	2	9											

*Reduced to 60% N.V. in xylene at 25°C. †Mole Equivalent found : 31 ‡MEF. : 41 §Mole Equivalent found : 45 ¶MEF. : 31.

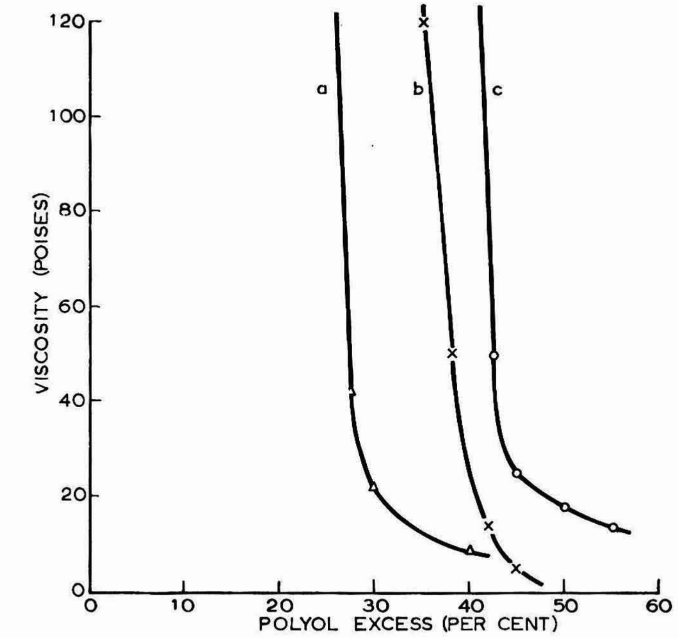

FIG. 1. THE VARIATION OF VISCOSITY AT 25 °C WITH PERCENTAGE EXCESS OF POLYOL.
(a) Trimethylol propane. (b) Glycerol. (c) Trimethylol ethane.

Testing of Clear Films

Films for examination were prepared on glass panels by means of a doctor-blade from blends of the 60 per cent N.V. alkyds with 25 per cent butylated melamine-formaldehyde resin (60 per cent N.V.). The films were stoved for 30 minutes at 270°F.

Alkali Resistance Test: Panels were immersed in 5 per cent caustic soda solution at room temperature; batches 3, 8, 13, 16, 19, and 20 were used for comparison.

In the following they are marked as G (for No. 3, glycerol), TME (8, trimethylolethane), TMP (13, trimethylolpropane), PE-EG (16 pentaerythritol-ethylene glycol), PA (19, phthalic anhydride) and E (20, for epoxy). After 24 hours immersion, E was in the best condition, followed by TMP, TME, PA, PE-EG, G. The adhesion of E was best, followed by TMP, PA, PE-EG, G, TME in that order.

Mar Resistance was compared by marking the films with a steel needle and by fingernail. E was again outstanding, followed by TME, G, TMP, PE-EG, PA in that order.

Compatibility with MF resin: Films were checked for transparency. TME was compatible with up to 30 per cent MF and with 60 per cent UF resin, TMP only up to 15 per cent MF, and 35 per cent UF. E, PA has the best compatibility with butylated amino resins.

Testing of Pigmented Films

The enamels were prepared in ball mills at a pigment: binder ratio of 1 : 1. Cross-linking resin: butylated melamine-formaldehyde at a ratio of 1 : 3 (solid resin). The same batches as above were compared. Tinplate and steel panels were sprayed with samples having a viscosity of 18-21 seconds in No. 4 Ford Cup at 80°F. The panels were stoved at 270°F for 30 minutes.

Alkali Resistance: After 72 hours immersion in 5 per cent caustic soda solution, the E-based enamel was in the best condition, followed very closely by the TMP enamel; G suffered the worst breakdown. It is interesting to note that the TMP-based enamel showed rapid initial deterioration (after 4 hours immersion E was best followed by PA, TME, G, TMP, PE-EG), but its endurance over the longer period was excellent.

Resistance to ultra-violet Light: After 72 hours' exposure, the TMP based enamel had the least discolouration, followed by TME, E. G, PA, and PE-EG was the darkest.

Gloss: E and PA had full gloss, G and PE-EG less, while TME and TMP only about 60 per cent.

Pencil Hardness:

E	2H
PA	HB
TME, TMP	B
G, PE-EG	2B

Overbaking: 2 hours at 270°F caused some yellowing with E, but left the others in a quite satisfactory condition.

Flexibility:

E	No breakdown on $\frac{1}{8}$ in. mandrel,
TME	Very slight cracks $\frac{1}{8}$ in. mandrel,
PA	Only slightly inferior to TME,
TMP	Breakdown on $\frac{1}{8}$ in. mandrel, satisfactory on $\frac{1}{4}$ in. mandrel,
PE-EG, G	Breakdown on $\frac{1}{4}$ in. mandrel.

Mar Resistance: E was best, followed by TME, TMP, G, PE-EG; PA was worst.

Adhesion to Bare Steel: E was best, followed by PA, TME, TMP, PE-EG and G.

CONCLUSIONS

The overall picture does not show any superiority of the isophthalic over the phthalic-type coconut oil alkyds. A serious drawback is their limited compatibility with amino resins. Resistance to marring, an important requirement for industrial enamels, seems to be slightly superior to that of phthalic alkyds. Not even the use of trimethylolpropane or ethane as the esterifying polyol can upgrade the isophthalic alkyds to an appreciably higher level than conventional phthalic alkyds.

ACKNOWLEDGEMENT

The authors are grateful to the Management of Taubmans Group Factories for encouraging the above work and for granting permission to publish the results.

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[*Received* 7 *November*, 1960

Reviews

COST ENGINEERING IN THE PROCESS INDUSTRIES

Edited by C. H. CHILTON. New York, Toronto and London: McGraw-Hill Book Company Incorporated, 1960. Pp. xiii+475. Price 85s. 6d.

This volume consists of reprints of 148 articles published in *Chemical Engineering* between 1947 and 1959. This does not, as might at first sight be thought, make for out-of-dateness, since there has not been any change in the principles of either accountancy or design during this period. Costs have changed, but this becomes true of the most up-to-date figures so soon as a book is published; and the volume itself includes an article on the correction of cost data for current use. In any case, one does not go to a book to get costs, which are, since this is an American production, quoted in American currency. And many happy hours can be spent arguing what rate of exchange to apply.

The articles are grouped into seven sections: Principles of Cost Estimation, Process Equipment Costs, Non-equipment Capital Costs, Plant Costs, Manufacturing Costs, Profitability and Economic Analysis, and Other Areas of Cost Engineering. Within these sections practically every aspect of process costing is discussed, from *Cost Relationships in Preliminary Cost Estimation* to *How to Plan Power Distribution*, and from *Cost and Performance of Centrifugals* to *New Look at Economics of Pricing*. Many of the articles contain carefully worked-out detailed tabular and graphical data. With so many dozen authors a certain amount of overlapping is to be expected, but the amount is surprisingly small; similarly, differences in style and treatment are much less obtrusive than would be expected, largely because nearly all the articles are written with that peculiar mixture of colloquialism and pomposity which seems to come so readily to the pen of the technical writer in the United States. As a result the book is by no means easy to read and gives a definite, but untrue, impression of superficiality and prosiness.

To avoid any misunderstanding, let it be said that this is a compilation of considerable value. It combines sound principle and careful detail with a presentation which, however uneasy the style, is suited to the practising technologist. No doubt better books in this field are possible, but they do not in fact exist. Mr. Chilton deserves full credit for a valuable piece of pioneering.

Do we hear at this stage the paint technologist muttering with sour humility, *All very well for the chemical manufacturer, but not for the likes of me?* If so, we wasted our time in the paint industry. Assuming the worst, we must ask why the paint industry, always obsessed with costs, is so unconcerned with costings. It is surely time for the paint technologist to base his plant design and operation on published data, common sense and simple arithmetic instead of relying on a forty-year-old guess by the managing director's uncle.

M. H. M. ARNOLD.

RUNNERLESS MOULDING

By Ernest P. Moslo. New York: Reinhold Publishing Corporation; London: Chapman & Hall Ltd. Pp. 162+xi. Price 40s.

This volume is the latest addition to the Reinhold Plastics Application Series and is in fact the seventeenth title to be published. With one exception, the previous volumes could be said to deal with plastic materials; this book is one of the first on production processes. It is addressed essentially to plastics engineers and production personnel, and does not hold much to interest the chemist. The book deals fully with all aspects of runnerless moulding, theory, design and application. It is very much up to date, recent developments, such as sequential impact moulding, being fully discussed. The confident handling of the text by the author gives the impression that all of the material in the book, designs, methods, *etc.*, is a product of work which he has carried out himself.

The book is well provided with photographs and designs of nozzles and moulds. The profusion of these, together with clear and concise explanations, make an excellent jumping off ground for an engineer wishing to convert existing plant or design new moulds.

The author is most enthusiastic on the benefits to be accrued from runnerless moulding. To those who are not already aware of these benefits, which include elimination of sprue scrap, greater speed of production, cut down on rejects with subsequent reduction of labour costs, this book will go far towards educating them. In common with its predecessors the volume is a handy pocket size, well printed and bound. A very sketchy index is included, but probably a fuller index is not necessary as the various sections of the book follow each other naturally.

G. Anderson.

PROPERTIES AND STRUCTURE OF POLYMERS

By A. V. Tobolsky. New York: John Wiley & Sons Incorporated, 1960. Pp. ix+331. Price 116s.

Under the rather general title of this book, the subject could be considered from several aspects. It is important therefore that the particular field covered should be realised. The relationship between the properties of polymers and their particular chemical structure, for example, the effect of various chemical groupings, is not considered in any detail. Instead, the effect of the general molecular architecture, that is the size and shape of the polymers on their mechanical properties, is explored. Rather than a general text book, this work provides a series of accounts of specialised topics, concentrating on the field of viscoelasticity, in which the author is one of the outstanding research workers. Much of the matter has been described before only in original papers; there is a good balance between over-simplification and mathematical complexity, and adequate references are given.

There are six chapters, dealing with such matters as the viscosity, elasticity, crystallisation, viscoelasticity, transition points and stress relaxation of polymers, and polymerisation equilibrium. Particular emphasis is given to the value of stress relaxation studies for understanding the behaviour of polymers,

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There are six chapters, dealing with such matters as the viscosity, elasticity, crystallisation, viscoelasticity, transition points and stress relaxation of polymers, and polymerisation equilibrium. Particular emphasis is given to the value of stress relaxation studies for understanding the behaviour of polymers, and examples are given relating to scission and cross-linking in various types of natural and synthetic rubbers. The chapters are followed by ten appendices comprising some of the more advanced mathematical treatments, tabular data and reports of isolated investigations.

This is an outstanding work on polymer physics, but obviously its main value in the coatings field will be to specialised workers.

L. A. O'NEILL.

SMALL PARTICLE STATISTICS

By G. HERDAN. London: Butterworths Scientific Publications Ltd., 1960. Second Enlarged Edition. Pp. 418. Price 80s.

It is always a pleasure to read a new edition of an outstandingly good book and the appearance of the second edition of Dr. Herdan's well-known work will give pleasure to all who are working on or are interested in the application of statistical methods to problems associated with fine particles.

The work is well planned and Dr. Herdan develops his theme in a characteristically lucid and logical manner. It is a "down to earth" treatment of practical problems and the necessary mathematics is clearly presented.

After considering some fundamental aspects of statistics, Part 1 includes methods of sampling, the determination of particle size and methods of graphical representation. The author suggests tests for the reliability of the methods employed and deals very thoroughly with the distribution function and analysis of variance. The relationship between particle size and other characteristics of materials, *e.g.* particle shape, surface area and porosity, is considered in Part 2. The practical methods employed for the attainment of specified degrees of fineness are critically examined in Part 3 and this part also includes an interesting chapter on the distribution of particle sizes in polymers. Coarse disperse systems form the topic of Part 4 and the vexed question of the inequalities of averages is clearly answered. The chapter on the statistical design of experiments is a masterly analysis of the pitfalls and errors inherent in many classical methods.

The experimental side of particle size determination is dealt with very fully in Part 5 by M. L. Smith, W. H. Hardwick and P. Connor. They deal successively with optical (microscope) and sedimentation methods, centrifugal separation and radiometric techniques. Dispersions in gases are treated either by deposition or direct sizing and the various techniques are fully described. Finally, the authors review the methods available for the determination of surface area.

This book can be recommended both to those who are interested in statistical applications *per se* and to workers in the fine particle field who are interested in solving their problems by the most effective statistical methods. The production is excellent and at eighty shillings the book is good value.

W. M. MORGANS.

HOMOLYTIC AROMATIC SUBSTITUTION

By G. H. WILLIAMS. Oxford: Pergamon Press Ltd., 1960. Pp. 133. Price 45s.

Dr. Williams introduces this exciting subject with an introduction to the characteristics of and differences between heterolytic (ionic) and homolytic (free radical) substitution in aromatic nucleii. Various mathematical treatments of these reactions by the isolated molecule and the transition state, and the effects of the reactivity and polarity of the attacking species are critically reviewed. A detailed discussion then follows of the mechanisms and preparation aspects of homolytic substitution by the following reagents: diazo, nitroso and azo compounds, diacyl peroxides, lead tetrabenzoate, phenyl iodosobenzene and silver halide dibenzoates, and by photolytically generated aryl radicals. The quantitative aspects of the subject are discussed in great detail, particularly isomer distribution, relative rates, side chain attack and partial rate factors for phenylation. The final chapters discuss intramolecular arylation (Pschorr reaction) and alkylation, and more briefly, hydroxylation, benzoyloxylation, acetoxylation, halogenation, amination and amidation, and mercuration. The text is provided with many references and author and subject indices. The book is slim and attractive and of good quality materials.

This is a most scholarly and comprehensive account of a subject whose kinetics are still incompletely understood. Dr. Williams is to be congratulated on the clarity and detail of his exposition, which, together with the thorough coverage of the literature (up to December, 1958), will earn for this volume a respected place in many libraries. It is, however, primarily for the advanced worker, particularly in aromatic chemistry. It will undoubtedly help the less specialised in understanding a number of processes, but of necessity the number has been limited in this book by the extent to which the subject of homolytic reactions has grown in recent years. For these workers there is, therefore, a need for companion volumes discussing other important homolytic processes, such as aliphatic substitution, oxidation and degradation, which are of obvious importance in the plastics age.

W. HOPKIN.

SOVIET TECHNOLOGY DIGEST

No. 1. December, 1960. Oxford: Pergamon Press Ltd. Pp. 149. Price £10 per annum.

The problem of summarising monthly the latest technological information from the Soviet Union is indeed formidable. In this case it has been attempted by concentrating on three branches: Design and Production, Metallurgy, Welding and Foundry Production, and Instruments and Automation. In each section are translated abstracts from selected papers published during 1959 and 1960, the section being completed by a list of articles in various publications. The remainder of the *Digest*, under the classification "General", contains a report on the annual general meeting of the Technical Services Section of the U.S.S.R. Academy of Sciences, and other items of more general interest. It concludes with tables of contents of a wide variety of Soviet periodicals, mainly concerned with physics and engineering, but including the *Russian Journal of Applied Chemistry* and the *Russian Colloid Journal.* The former mentions a paper on "The Structural Transformation and Properties of the Oxide Film on the Surface of Aluminium" and the latter contains a paper on "The Mechanism of the Stability of Free Films on Solutions of Surface Active Substances".

One assumes and hopes that future issues of the *Digest* will contain translated abstracts of chemical rather than engineering papers. The *Journal* should prove of value to those without translating facilities who wish to survey the Russian scientific literature. Pergamon Press offer translations of any paper mentioned in the *Digest.*

I. C. R. Bews.

PERFUMES, COSMETICS AND SOAPS

By W. A. Poucher. London: Chapman & Hall Ltd., 1959. Volume 1, 6th Edition. Pp. 436, illustrated. Price 75s.

Volume 1 of the three books which form the complete set of Poucher's work is in the form of a dictionary of raw materials. Most of the compounds listed are related to perfumery, but some soap and cosmetic raw materials are also included.

First printed in the 1920's, these three volumes of Poucher were of immense value in breaking down the wall of secrecy which had long surrounded the fragrance industry. Particularly true was this of Volume 1, in which was listed all the important perfume ingredients together with brief details of their manufacture and suggestions for use. Moreover, Poucher achieved the extremely difficult task of presenting this dictionary in an interesting and readable manner, largely because of the author's immense enthusiasm for his subject.

Eighteen years have passed since the last edition of this book and in this period many new aromatics have been discovered, whilst important changes have taken place in the essential oil-producing areas. Unfortunately, the new edition does less than justice to these factors and, in most respects, could be classified as a reprint rather than a revision.

For those making their first acquaintance with the work in its new edition, it can be stated that the dictionary is as valuable as when it was first published and there is no other comparable work in existence. However, a great opportunity has been missed in not bringing the subject matter up-to-date and this omission greatly detracts from the value of the book as a new edition. Sporadic efforts have been made to rewrite some of the sections, but those which remain untouched appear, by comparison, to be really dated. For example, the excellent revision of the sections on lavender oil and related compounds only serves to expose the antiquity of some other sections, *e.g.*, on bergamot oil, where reference is made to pre-war wages of 15s. a week being paid to hired labour.

It could be said that these are trivial details, but the dated photographs of workers and references, which are often thirty years old, convey an overall impression that the book is not up to date.

This work should be on the bookshelf of anyone engaged in the essential oil industry, but it would seem to make little difference which edition was chosen.

T. J. Elliot.

SILICONES

Edited by S. FORDHAM. London: George Newnes Ltd., 1961. Pp. 252. Price 36s.

This is the first British textbook dealing with the basic chemistry, manufacture and applications of silicones, although three American books, published in 1951, 1954 and 1959, have previously covered a similar field. Appearing as it does a few months after Eaborn's *Organosilicon Compounds*, the present work may be considered in part as an extension to Eaborn's volume which, as the author explains, deals with silicones only in outline "mainly because it is impossible to know the full facts about the manufacture and composition of commercial silicone products. It is difficult, moreover, for such a person to assess the accuracy of the very many and wide claims that have been made in connection with properties and potential uses of the silicones" (p. 454). Fordham's book is a co-operative effort of twelve industrial silicone specialists, each dealing with his own subject with Dr. Fordham as editor.

The first hundred pages, which are devoted mainly to those aspects of organosilicon chemistry relevant to the manufacture of silicones, and to the structure and physical properties of polysiloxanes, form a useful introduction to the subject. Nearly four hundred references are included in this section.

There follows a list of the world producers of silicones, an assessment of the total world sales in 1957-58 and a breakdown into major uses and world consumption of the main groups of products. It seems a pity that this survey in such a rapidly expanding field is two years out-of-date at the time of publication. The twenty eight page section on the manufacture of silicones makes no new disclosures about the methods or equipment actually in commercial use, but contains simple flow diagrams of the direct process, distillation and hydrolysis procedures applied to methyl chlorosilanes, and a brief description of the conventional methods for making phenyl chlorosilanes. The manufacture of silicone resins, gums and rubbers is briefly described.

The final one hundred or so pages, which are concerned with the applications of silicones, describe the typical properties and uses of the main groups of silicone products. This section contains references to patents and manufacturers' data sheets and gives physical data relating to typical proprietary products available in this country. This should increase its usefulness to British readers in industry, and the book is to be recommended to those who, either as students or as industrial chemists, feel the need for an authoritative, but easily readable survey of this rapidly growing technology.

R. A. GREGORY.

EDITORIAL

From Corrosion to Conflict

At the Corrosion Exhibition we were pleased to see a number of old friends, some in unexpected guise. Apart from the necessary coating of steelwork, which we feel will always be with us, it is interesting to note developments in the approach to corrosion problems. It almost appears that at last, wittingly or otherwise, those concerned are tending not to combat corrosion, but to avoid it. In other words it is being realised that it is more effective, by choice of suitable materials, by attention to design, and by the many other means, to create conditions in which corrosion cannot take place, rather than to expect miracles from an anti-corrosive paint.

One development which caught our eye was the vinyl coated steel of Dorman Long Ltd. We gathered that the coating is applied in paste form by hot rolls to unprimed steel, a process distinct from the more familiar laminating of vinyl sheet to steel. The samples were quite impressive, and resistance to creep corrosion at edges was claimed. We understand that the p.v.c. composition is prepared by a paint manufacturer, who in fact has worked with Dorman Long in the development. Is this another example of the ways in which some paint companies are meeting the difficulty of competing with the mammoths? We like to think it is.

Quite apart from the fascination to a not entirely disinterested bystander, the present decade in the paint industry will surely form a subject for study by economists. As we see the situation there is a battle of the giants, with numerous smaller members of the community on the threshold of the arena, some deciding that in unity is strength and that united they may join the battle, some diversifying as rapidly as possible, while others stand bemused, wondering what is happening and what the fuss is all about. Yet others, smaller still, gather on the fringe, some with appetites whetted by successes, some content with what small pickings they can make, while some are withdrawing from the melée with all convenient speed. Superimposed on all this is the sound of other larger domestic and international industrial battles, which is slowly causing a growing consciousness that there is an immediate need for concerted action, whatever may be the state of internal strife.

This has taken us a long way from corrosion, but then, plastics don't corrode.

COMMENT

We have recently seen a new development in the technique of attracting graduates to the chemical industry and incidentally to IMPERIAL CHEMICAL INDUSTRIES LTD. I.C.I. have produced a film, "New Minds for New Worlds", which is intended to interest undergraduates and sixth form pupils in the wider aspects of an industrial career. In the film, Chris Chataway takes part in unscripted discussions with undergraduates, academic scientists and industrialists attempting to "illuminate the thoughts and feelings of the people most concerned in the academic world and in industry". Some audiences may feel that this bias of the film is very much towards the older universities and their products, but this may not be a valid ground for criticism. Nowhere more than at Oxbridge is the view more firmly held that "only the Arts can provide a sound civilised foundation for a full life". If I.C.I. in their new effort, contribute to the breaking down of this belief, they will indeed have achieved a useful purpose. There is no doubt that the film will attain at least one of its objects—to stimulate discussion.

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)*

THOMAS INDUSTRIAL AUTOMATION LIMITED have now produced a compact conductivity-operated liquid level controller known as the *Resistron.* The instrument is intended for use with any conducting liquid provided that the specific resistance does not exceed 50,000 ohm/cm^3. It is said to be ideal for the control of various types of acid and of the level in feed tanks, *etc.* It can also be used for boiler level control, and will give audible and visual alarm, as well as taking corrective action when the water in an untended boiler falls to a dangerous level.

A new Stabilised Power Supply Unit has been announced by W. G. PYE & CO. LTD. for general experimental work. Particular attention has been paid to the operation of loads which are highly capacitative. The positive line 0-500V at currents up to 250 mA is the primary facility. This range of voltage covers almost all valve circuits and the current is ample even for power amplifiers.

BRANDRAM-HENDERSON of Montreal, a subsidiary of I.C.I. LTD.'s associate company in Canada, CANADIAN INDUSTRIES LTD., have announced that they will build a 400,000 dollar plant in Jamaica for the manufacture of paint for the West Indian market. Construction of the plant will begin shortly and when completed it will produce paints which have been imported from Canada for the last forty years.

A new *Teflon PEP*-fluorocarbon which can be anchored with common adhesives to a variety of engineering materials has been developed by DUPONT. It is said to offer a wide range of new industrial applications as an anti-stick or protective surface. When epoxy resins are used as bonding agents, end-use applications of the new film include liners for chemical and fuel tanks and cylinders used at low temperatures, ice-release coatings on aluminium trays, and release surfacing on heated or chilled processing rollers. With rubber adhesives the new type can be cemented as a liner for rubber and fabric hose and tubing, and over rubber and asbestos for chemically resistant diaphragms and seals.

A new *Hilflon* P.T.F.E. tape has been introduced by WILLIAM ROSE LIMITED as a pipe sealant and for insulation purposes. It moulds itself readily to threaded materials, and does not harden after prolonged use. It is chemically inert and can tolerate temperatures between —450°F to +500°F.

The Kesting process, licensed by ELEKTROCHEMISCHE WERKE MUNCHEN, is employed at the Luton plant of LAPORTE CHEMICALS LTD., for the production of sodium chlorite. This is the first United Kingdom plant to produce sodium chlorite, which has been previously imported from Europe. It is used for the bleaching of cotton, linen and synthetic fibres, *etc.*, and also for the purification of water supplies and effluents.

MS 2219 is a product of MIDLAND SILICONES LTD. used as a coating for paper, and is said to overcome problems of stickiness encountered in industry. Such paper does not adhere to sticky products, even at high temperature and in high humidity. It does not affect the material with which it is in contact even after long periods, nor is itself affected. It is said to be easy to apply, thin, light and flexible; it will not flake or crack.

A booklet entitled *Origin Rules, Certification and Segregation of Stock* has been recently published by the ASSOCIATION OF BRITISH CHEMICAL MANUFACTURERS. It aims primarily to explain the type, intention and scope of the European Free Trade Association's "origin" rules, both on the bases of "value" and "process" for chemicals and allied products falling in Chapters 27-39 of the Brussels Tariff Nomenclature. Whilst for export of chemicals it may often be necessary to show whether or not the purchased chemical starting material has been made in the area, there are relatively few instances where such information is required about the starting materials in the case of exports which are not themselves classified as chemicals. For example, knowledge of the "origin" of dyestuffs is not required when considering the "origin" of dyed textile piece goods. The ASSOCIATION OF BRITISH CHEMICAL MANUFACTURERS is willing to deal with inquiries on the extent to which knowledge of the "origin" of chemicals is essential in deciding the "origin" of the products they export. Copies of the booklet, on a cash with order basis, price 3s. 6d. post free, are available from the A.B.C.M., Cecil Chambers, 86 Strand, London, W.C.2.

TRANSLATION AND TECHNICAL SERVICES have sent to us a preprint of a monthly abstract journal dealing with organo-metallic compounds, which they intend to publish. The abstracts are divided into sections according to use rather than chemical type, and are apparently comprehensive and up-to-date.

Bristol Section

PREPARATION OF METALS FOR PAINTING

The third meeting of the session was held at the Royal Hotel, College Green, Bristol, on 25 November, 1960, when Mr. S. J. Glossop, of the Bristol Aeroplane Co. Ltd., delivered a paper on the "Preparation of Metals for Painting".

The lecturer opened by discussing the reasons for painting and the normal types of surface preparation used to ensure the adequate performance in service of a surface coating. These included processes for derusting and degreasing, and the advantages and disadvantages of each process were detailed. Mr. Glossop then proceeded to describe the various types of chemical treatments which were used on metals in order to provide a key for paints, and to give a more corrosion resistant surface. These included the various types of phosphate treatments for steel, the chromate or chromate/phosphate treatments for aluminium, and the fluoride anodising treatment used to passivate magnesium.

The discussion, which was opened by Mr. P. L. Gollop, was lively, and a number of questions dealing with such subjects as the preparation prior to painting of *Zintec* sheet and copper piping were dealt with. A vote of thanks was proposed by Mr. A. Turnbull and heartily endorsed.

D. S. N.

London Section

NEWER METHODS OF TESTING PAINT FILMS

The fourth meeting of the twenty-third session was held at Manson House on 6 December, 1960, with Mr. J. A. L. Hawkey in the chair. The Chairman referred to the formation of the Southern Branch of the London Section, which had received the approval of Council at the last meeting on 18 November, and welcomed Mr. F. W. Davies, who had been largely responsible for this venture. He then introduced Mr. G. Phillips and Mr. P. Walker, of the Atomic Weapons Research Establishment, Aldermaston, who presented a paper entitled "Newer Methods of Testing Paint Films".

Mr. Phillips commenced by saying that, although the methods of test were not really new, their application was such that more absolute information on the properties of the films tested was obtained. Four tests had received specific study, namely, adhesion, tensile strength, water permeability and adsorption. Mr. Walker continued by discussing the adhesion test using the Hounsfield Tensometer adapted to take $\frac{5}{16}$ in. bolts with the heads turned down to $\frac{1}{2}$ in. diameter. The films to be tested were applied to the heads of the bolts, which were then stuck together with a fast-setting adhesive. In order to ensure a low deviation in the results obtained, it was important to pay attention to the size of the specimen, hence the limitation of the size of the bolts used as substrates, the surface finish of the bolt head, which should be in the range 8-12 micro inches, the cleanliness of the surface and the type of adhesive used. The most suitable adhesive had been found to be *Eastman 910*, a catalysed cyanoacrylate adhesive. The rate of loading of the machine was also important in keeping the deviation low, a rate of two inches per minute being found to give the best results. He described how this method had been used to study the effects of drying on adhesion and suggested that many adhesion tests were normally carried out before the optimum adhesive properties had been attained by the film. Mr. Walker cited as examples the length of time taken for epoxy ester and long oil alkyd applied to aluminium, the former attaining optimum adhesive strength only after 400 hours, and the latter 21-28 days; the Ultimate Strength of both was of the order of 350 kg./cm.^{2}

Other problems investigated by this method were the effect of pigment volume concentration on adhesion, the effect of multi-coats in which wet-on-wet application had been shown to reduce the ultimate adhesive strength of a single coat application and the effect of hydroxyl concentration in epoxies on adhesion. The latter investigation had indicated that, in the case of steel and brass substrates, increasing hydroxyl concentration gave an increase in adhesion, but on aluminium the adhesive strength was independent of the hydroxyl content. The work on tensile strength using dumbell-shaped specimens cut from unsupported films produced by spinning on an amalgamated tin plate was then described. A dropping beam tensometer was used for this test and amongst the effects studied had been that of pigmentation, catalyst and humidity during drying. It was stated that in these experiments the rate of change of tensile strength was more significant than the absolute value. It was possible by such experiments to determine optimum cure conditions.

Mr. Phillips then proceeded to a discussion of the use of permeability and water adsorption tests, using controlled humidity atmospheres rather than total immersion methods. The permeability tests were carried out using the Payne Cup, but with unsupported films produced as for the tensile strength tests, and it was demonstrated that paint films do not obey Fick's Law. The use of such tests for determining critical pigment volume concentration was illustrated. Water adsorption tests were carried out by producing films on tinplate and subjecting them to exposure to controlled humidity atmospheres. From the results obtained adsorption isotherms could be drawn which gave a good guide to the performance which could be expected from the film studied.

The lecture was amply illustrated with experimental results obtained by the use of these test methods and showed, especially in the case of the permeability and adsorption experiments, how valuable information could be obtained with the use of inexpensive apparatus. Following the lecture a discussion took place, in which Mr. A. G. North, Mr. A. W. Landmann, Mr. J. A. L. Hawkey, Mr. T. R. Bullett, Mr. C. E. Hoey and Mr. W. H. Moss participated. The meeting was concluded by the proposal of a vote of thanks to the lecturers by Mr. I. C. R. Bews, who commented on the emphasis placed by the lecturers on the use of inexpensive equipment and said that this was a laudable approach, for so many investigations were carried out on equipment beyond the reach of all but the largest companies. He expressed himself as a firm believer in the tremendous scope for physical measurement and investigations into paint problems and was convinced that work such as this would be of enormous benefit to the industry.

C. R. P.

SOUTHERN BRANCH OF THE LONDON SECTION

Acrylic Emulsions

The inaugural technical meeting of the Southern Branch was held at the Polygon Hotel, Southampton, on 12 December, 1960. An excellent paper on "Acrylic Emulsions" was given by Mr. W. Peace, of I.C.I. Ltd. (Dyestuffs Division), in the course of which a series of exposure panels were on view. A very lively discussion followed in which Mr. Targett, Mr. C. A. Carey, Mr. R. D. D. Orwin, Mr. A. F. Routley, Mr. J. C. Kingcome and Mr. J. A. L. Hawkey participated. A total of nineteen members attended and the meeting was pleased to welcome among the guests Mr. J. A. L. Hawkey, Chairman of the London Section, and Mr. R. H. Hamblin, General Secretary of the Association.

F. W. D.

Manchester Section

ACRYLIC EMULSION PAINTS

The second lecture of the current session was held in the Constitutional Club, Liverpool, on 11 November, when a well-attended meeting heard a paper delivered by Mr. R. Kershaw and Mr. W. Peace on "Acrylic Emulsion Paints".

The lecturer traced the progress made in the chemistry of acrylic polymers since their original preparation in 1880 up to the present time, when they were already coming into commercial use in solution form. Their technical advantages were enumerated, including resistance to discoloration on exposure to ultra-violet light and heat, and, when suitably cross-linked, their high order of chemical resistance. Emulsions of these polymers were of interest since they were capable of giving relatively low viscosity at high polymer concentration and molecular weight.

Describing the basic mechanism of emulsion polymerisation, and the control of particle size, the lecturer compared the fineness of a typical methacrylate polymer dispersion with those of vinyl acetate copolymer and homopolymer. Electron micrographs showed the much lower particle size of the methacrylate type, about 0.1 μ, and illustrated its better dilution stability.

The drawbacks of relatively low pigment binding power and inadequate adhesion under humid conditions, shown by p.v.a. homopolymer emulsion paints, were substantially overcome by use of an acrylic emulsion. Tests with an apparatus for wet scrub resistance gave rapid stripping of p.v.a. homopolymer paints. Even with copolymer based paints, increasing pigment volume concentration (P.V.C.) caused rapid loss of wet rub fastness, whereas two acrylic emulsions showed negligible drop until a very high P.V.C. was reached. The effect of substrate relative to wet scrub resistance was considerable.

The lecturer continued by describing comparative tests for low temperature film integration and the use of a solubility test for the selection of an integrating agent. Turning to the durability aspect, several series of wooden panels were shown comparing exposures of emulsion paints based on different polymers. These showed the advantage which could be obtained in lower dirt retention with acrylics and the indication that the latter as a group show more chalking than vinyl acetate copolymers.

Difficulties of emulsion instability when using oleophilic organic pigments had led to inclusion of non-ionic agents in such paints. The acrylic emulsions described were stable with such pigments, even at a high level of coloration, in absence of additional non-ionic agent.

Mention was made of the pH changes which can occur by the hydrolysis of p.v.a., and also the need to incorporate bactericides in acrylic-based paints which were close to neutrality. Certain properties of acrylic-based paints remained to be improved, such as the lower ease of flow and consequent tendency to brush-marking.

After the lecture an interesting discussion took place and the vote of thanks proposed to the lecturers was endorsed by the body of the meeting.

I. S. M.

New South Wales Section

RESIN DEVELOPMENTS FOR SURFACE COATINGS

The November meeting of the Section was held in the M.L.C. building on 10 November, when Mr. G. L. Hardy, of Monsanto Chemicals (Aust.) Ltd., lectured on "Resin Developments for Surface Coatings". The lecture was designed to show the interesting and important possibilities for future surface-coating materials arising from current research into new polymer systems. A detailed discussion of emulsion polymer technology was followed by indications of work into improved solvent-polymer systems. The lecturer finally drew a broader picture of polymer research as a whole, indicating how much common ground between the many technologies depended on such fundamental work.

It was emphasised that the polymer chemist now had no shortage of reactions and functional groups; his main aim was to obtain the most efficient and economical arrangement of the starting materials. Fortunately, modern analytical tools could speedily clarify problems of structure; without them the current rate of research would be impossible.

Work with emulsion polymers was divided into the two groups of techniques of production and the polymer systems now under development. Constantly recurring were the manufacturing problems of speed of reaction and procurement of higher solids and the parallel desire for smaller particle size. No obvious advances had been made with production techniques, although these had been refined to allow production of particle sizes down to about 0.05 μ. The difficulties arising from rheological behaviour in this size range might deter further size reduction despite the benefits of improved pigment binding, film properties, water resistance, *etc*. The elimination of conventional protective colloid had also helped, but a mandatary protective charge layer refuted the possibility of a truly "surfactant free" product.

Polymer systems were now using costly comonomers (vinyl and acrylic esters) more effectively by controlling structure (block and graft) and tailoring to desired end-uses, *e.g.* alkali solubility and powerful adhesion result from use of carboxylic groupings, without impairing chain flexibility; this being useful for sealing chalky surfaces. Both emulsion and solution polymers were employing new functional groups to obtain thermosetting or air-drying characteristics. The ethylenic unsaturation of butadiene had already been used for water-based primers, and newer condensation reactions from methylol, hydroxyl, amino and like groups were finding application. In some cases (alkyd resins), new polymeric intermediates with controlled hydroxyl content were of great interest. All the above techniques led to improved rate of cure, hardness, solvent resistance, generally valuable in industrial finishes. Water as a binder vehicle was being used wherever possible.

Recent developments in general polymer research were shown and general ideas for new products for conventional plastics, as well as surface coatings. The material interests in both fields were discussed and the lecturer suggested changes in the pattern of the paint industry by growth into new fields, *e.g.* solvent-free finishes, inorganic-type polymers, and a general diffusion of interests into areas on the fringe of the conventional paint industry.

Scottish Section

SHIPS' PAINTS

The second meeting of the current session was held on 10 November, 1960, at More's Hotel, Glasgow. The Chairman, Mr. E. A. Bullions, cordially welcomed the fifty-two members and friends who had come to hear Mr. J. C. Kingcome deliver a paper with the all-embracing title of "Ships' Paints".

The lecturer commenced by stating that, although his paper dealt with paints in general usage on H.M. ships, particular reference would be made to those used on the underwater parts. After alluding to some of the differences between ships of H.M. Navy and the Merchant Fleet, the lecturer continued by discussing the importance of surface preparation. He said that for new construction the old technique of pickling in cold hydrochloric acid, followed by weathering and finally wire-brushing, had been superseded by grit-blasting methods. This had opened up the possibility of using modern coatings, such as epoxides and polyurethanes, on H.M. ships. The problems consequent to the introduction of grit-blasting were considered: the type of abrasive to use, its size and shape, and the physical characteristics of the surface produced. Correct preparation and painting was important, not only for protection, but also to ensure a smooth finish and so reduce to a minimum frictional losses on the underwater parts of a ship. Underwater paints have to protect the steel surface against corrosion and prevent the attachment of fouling organisms. The development of *Admar* and *A.C. 655*, the anti-corrosive paints used by the Admiralty, was described. Present policy was to use *A.C. 655* on freshly grit-blasted steel and *Admar* as a maintenance coating. The grit-blasted surface was primed with pretreatment primer before painting.

Mr. Kingcome continued by saying that many ships of the Royal Navy were now cathodically protected, and modern underwater paints must withstand the alkaline conditions produced. Non-saponifiable coatings, such as those based on vinyls, epoxides, *neoprene*, *etc.*, appeared to be quite successful. Modifications of epoxies, such as coal tar epoxies, were under consideration for wider marine use, and a description was given of some of the difficulties encountered in using these paints. The problems involved in protecting the waterline area were considered. Normal outerbottom paints were not sufficiently tough and durable, but recently the use of solvent-free epoxy coatings had shown promise. *Neoprenes* had been tried, but had been disappointingly inconsistent.

The seriousness of fouling on a ship's hull in retarding speed and increasing fuel consumption was also discussed. Many remedial measures had been tried over the years, but success had only been assured by anti-fouling paints which provided a poison in solution at the hull surface. Paint containing copper and mercury poisons were the most effective, and to prevent fouling the minimum leaching rate of each in sea water was for copper 10 μg./cm.^{2}/day, and for mercury 2 μg./cm.^{2}/day. The two types of anti-fouling paint, soluble matrix and contact leaching, were described: the standard Admiralty paints were of the former type and contained only copper poisons. Black anti-fouling paints, containing both copper and mercury, were used on submarines and on the boot-topping area of surface ships. Cupric hydroxide had been considered as an anti-fouling toxin because it appeared to prevent fouling while leaching at only 2 to 3 μg./cm.^{2}/day. Results, however, showed cupric hydroxide to be unreliable and its copper utilisation less economical than the more conventional cuprous oxide paints. Another problem peculiar to warships was the effect of fouling on underwater sonar equipment. Again anti-fouling paints appeared to offer the best solution, but the coating must be thin to avoid interference with sound transmission. The lecturer then gave a brief description of the leaching rate test for anti-fouling paints, emphasising its limitations and suggesting ways of accelerating the test.

Exterior paints were next discussed. The alkyd resin type exterior paints introduced during the last war had been found to suffer from some colour instability and loss of adhesion under water-soaked conditions. Colour instability had been overcome in Admiralty exterior paints by specifying that in preparing the alkyd resin mediums an oil with a high linoleic acid content should be used; at present only tobacco seed and soya bean oil were permitted. Loss of adhesion when the paint film was water-soaked had been evaluated by the Admiralty water jet test, a description of which was given. Finally, a brief reference was made to other types of paint of particular interest to the Royal Navy; these included interior fire retardant paints, coatings for aviation fuel tanks and non-skid coatings for the flight decks of aircraft carriers.

At the close of the lecture full advantage was taken of the question period and many points and queries were raised by Mr. G. Anderson, Mr. I. Burns, Mr. G. H. Hutchinson, Mr. A. McGuire, Mr. A. McLean, Mr. J. F. McVey, Mr. W. Peden, Mr. R. A. Sim, Mr. D. M. Stewart and Mr. Soar. At the request of the Chairman, Mr. J. F. McVey, in his own inimitable manner, thanked the lecturer for a most informative and interesting paper.

H. G.

SCOTTISH SECTION STUDENT GROUP

POLYURETHANES

The second meeting of the current session was held on 19 November, 1960, at More's Hotel, Glasgow, with Mr. J. Miller, Student Group Liaison Officer, presiding. Thirty students, senior members and friends were present to hear Mr. J. A. Oates deliver a paper entitled "Polyurethanes".

Before his lecture, Mr. Oates distributed to members printed matter, setting out in detail chemical equations relevant to the study of polyurethanes. This procedure was much appreciated by all present and the notes were constantly referred to during the lecture. The lecturer commenced by referring in detail to the outstanding properties of the polyurethane film. He particularly stressed the extreme resistance to abrasion shown by such films, reputed to have the highest known abrasion resistance of any surface coating. Mention was also made of their excellent non-embrittlement characteristics and resistance to breakdown of film when immersed in water for long periods. The lecturer continued by referring to the many and varied uses of polyurethanes in industry. This part of the lecture was fortified by the showing of a most interesting film depicting stands coated with polyurethane finishes at the last Brussels Exhibition. It also appeared that these versatile films could be applied to many surfaces, including furniture, gymnasium floors, Wellington boots and furnaces, where resistance to abrasion and high temperatures are desirable properties. The necessity of a thorough pre-treatment was stressed; this was usually in the form of a wash primer. In fact, this process was so vital it could be said that the success or failure of subsequent work depended largely on an effective pre-treatment. Regarding the pigmentation of polyurethane systems, the lecturer stated that only organic pigments could be used with complete satisfaction and the usage of inorganic pigments should be avoided where possible. Rutile titanium dioxide was undoubtedly the best of the white pigments. The tendency to yellowing of polyurethane systems was admitted, but it was claimed that by careful formulation this defect could be eliminated.

It was evident by the number of points and queries raised by the members that the lecture had aroused considerable interest. These questions were promptly and suitably disposed of by the lecturer. At the request of the Chairman, Mr. A. Pisacane, the Student Group Vice-Chairman, proposed the vote of thanks. He complimented the lecturer on an excellent and worthwhile contribution to the sum total of information already available on polyurethanes, an appreciation endorsed by all present.

I. G.

Association Conference, 1961

PHYSICS IN SURFACE COATINGS

The Palace Hotel, Torquay, will be the centre of this year's Conference relating to "Physics in Surface Coatings". The Conference assembles in the evening of Tuesday, 30 May, and disperses on the morning of Saturday, 3 June. The technical sessions will take place in the mornings from 9.30 to 12.30 on Wednesday, Thursday and Friday, and it is hoped that synopses of the papers will be given in the March issue of the *Journal.*

Tours to local beauty spots have been planned for the afternoons; facilities for tennis, golf and table tennis are also available and tournaments will be organised. For evening entertainment there will be a civic reception by the Mayor and Mayoress of Torquay on Wednesday, a theatre party on Thursday and an Association Dinner and Dance on Friday, also at the Palace Hotel. The Annual General Meeting of the Association will be held on Friday afternoon at the Palace Hotel.

The Conference registration fees have been fixed by the Council at £4 for members, £5 for non-members and £3 for wives. Leaflets containing details of the lectures and the social programme, together with the necessary registration forms, were despatched in January to all members and must be returned to the General Secretary not later than **1 April, 1961.** Registration forms include reservations for accommodation, garage facilities, tournaments, railway facilities, coach tours, cruises, works visits and the theatre outing. Non-members wishing to register for the Conference may obtain further information and registration forms from the General Secretary at the address shown on the front cover.

13th Technical Exhibition, March 1961

Copies of the *Official Guide* to the Exhibition, which will take place in the Royal Horticultural Society's Old and New Halls on 6, 7, 8 and 9 March, 1961, have now been despatched to all Members of the Association at home and overseas. They have also been sent as far as possible to all paint and printing ink manufacturing firms in the United Kingdom and Western Europe as well as to chemists and technologists individually on the Continent of Europe. Non-Members wishing to obtain copies of the *Official Guide* may do so from the Association's offices prior to the Exhibition, and they will, of course, be available from the Information Bureaux at the Exhibition.

An increased number of overseas companies are exhibiting this year, from the European Free Trade Association, the European Common Market and the Commonwealth. In recent years the number of overseas visitors to the Exhibition has been increasing and interpreters will be in attendance to assist both visitors and exhibitors.

Sir Cyril Hinshelwood, O.M., D.SC., F.R.S., President of the Royal Society, 1955-60, will be principal guest at the Exhibition Luncheon, which will be held at the Criterion Restaurant, Piccadilly, prior to the opening ceremony. The Exhibition will be officially opened by Sir Cyril Hinshelwood at 3 p.m. on 6 March and will remain open that day until 7 p.m. On the succeeding days, 7, 8 and 9 March, the Exhibition will be open between 10 a.m. and 7 p.m. Further information can be obtained from the General Secretary at the address shown on the front cover.

Since the *Official Guide* was printed the following further information regarding stands at the Exhibition has been received:

Stand 13. **BX Plastics Ltd.** will be presenting some entirely new grades of dense nitrocellulose.

The company states that this versatile material, together with the well-established BX nitrocotton, will now complete a comprehensive range of all types of industrial nitrocellulose.

Other items which will be included on the stand will be technical and pharmaceutical camphor, B.S.S. dipentene, dense and linters nitrocellulose, terpene resins and *Heveaplus MG. 50.*

Stand 96. **Metal Propellers Ltd.** Further details of the construction of the 1½ ton varnish kettle are now available. The method of heating employs an electric/oil system. Heat transfer to the pot is effected through an external spiral coil jacket formed from half-round section tube. It is stated that this type of jacket offers a high positive flow for the heating media, and therefore temperature distribution is even and consistent. The stiffening effect of the coils permit economies in thickness of the inner vessel shell, which is especially attractive where expensive materials, such as stainless steel, are being used.

Bristol Section

(*Left to Right*) Mr. W. J. McWaters (*Hon. Treasurer, Bristol*), Mrs. McWaters, Mr. H. Smith (*Chairman, Manchester Section*), Mrs. Lock, Mr. L. J. Brooke (*Hon. Secretary, Bristol*), Mr. A. B. Lock (*Chairman, Bristol Section*), Mrs. Brooke, Mrs. Seymour, Mr. N. H. Seymour (*Chairman, Midlands Section*) and Mr. R. H. Hamblin (*General Secretary*).

ANNUAL DINNER

The Section's Annual Dance was held on 5 December, 1960, at the Ashton Court Country Club. The principal guests were Mr. N. H. Seymour, Chairman Midland Section, and Mrs. Seymour, Mr. H. Smith, Chairman Manchester Section, and Mr. R. H. Hamblin, General Secretary. The Chairman, Mr. A. B. Lock, in a short speech welcoming the guests, said the Section expressed regret that the President and Mrs. Gay were unable to be present.

As is customary on these informal dances, a happy atmosphere prevailed throughout the evening and it was rewarding to the Dance Sub-Committee, Mr. N. T. Butler, Mr. R. A. Davis, Mr. W. J. McWaters and Mr. R. J. Woodbridge, that the attendance was higher than in previous years. The Section's thanks are due to the Dance Sub-Committee for arranging a most enjoyable evening.

L. J. B.

London Section

MEETING OF JUNIOR MEMBERS

A meeting was held at Wax Chandlers' Hall on 5 January, when Junior Members of the Section were invited to meet the Honorary Officers and members of the Committee to discuss informally the possibility of the inauguration of junior activities on the lines of those being successfully carried out by other Sections. Mr. J. A. L. Hawkey, the Chairman, introduced the subject and invited suggestions as to the form such activities might take. The Junior Members present gave free rein to their ideas, suggesting works visits and technical lectures as the main programme. Possible venues for works visits were suggested and it was also suggested that the technical lectures should be on general aspects of the industries rather than of a very specialised nature.

It was agreed that any lectures arranged should be carefully selected so as to maintain a high technical standard and stimulate the educational progress of the junior members. A Steering Committee was formed to discuss the project in more detail and formulate concrete plans for an early commencement of such activities. Mr. J. D. Lewis agreed to act as Chairman/Convenor of this Committee and, as a member of the Section Committee, carry out the liaison between it and the Junior Members. The remaining members of the Steering Committee are Mr. C. J. Condon, Mr. G. H. Gully, Mr. M. Heath, Mr. G. F. Julier, Mr. P. J. Quorn, Mr. K. J. Shaw and Mr. T. P. Whitty. The enthusiasm which was shown at this meeting leads the Section Committee to hope that this will become another highly successful activity of the Section.

C. R. P.

West Riding Section

Some of the guests at the West Riding Section's Dinner-Dance (*from left to right*): Mrs. Butler, Mr. C. Butler (*Chairman*), The Mayoress and Mayor of Harrogate, Mrs. Gay, The President, Mr. W. Bowes and Mrs. Bowes.

DINNER AND DANCE

Greatly encouraged by the success of last year's function, the Section held its second Dinner and Dance, again at the Granby Hotel, Harrogate, on 25 November, 1960. The guests, who numbered over 130, were welcomed by the Chairman of the Section, Mr. C. Butler, and Mrs. Butler and the President of the Association, Mr. P. J. Gay, and Mrs. Gay. After a most enjoyable meal, the toast to the Section was proposed by Bill Bowes, the famous Yorkshire and England cricketer. In his speech he recounted the history of the Association and of the West Riding Section. Although the Section might not be very old, he felt that it was certainly keeping up with the tradition of the Association. Turning to a lighter theme, the speaker wondered if it might not be possible for paint manufacturers to produce an impact resistant glossy paint for cricket balls or even day-glow paints for evening matches. Mr. Bowes concluded his most entertaining and interesting speech by reminding members that just in the same way that team spirit plays an essential part in cricket, so also in business and in the Association. Mr C. Butler then thanked Mr. Bowes for his proposal of the toast and mentioning *en passant* that he thought the degree of shine to a cricket ball was arrived at by a sinister agreement between manufacturers and batsmen.

The Chairman then welcomed the guests and felt that the Section was honoured by the presence of the Mayor and Mayoress of Harrogate, Councillor and Mrs. L. Roberts. Bill Bowes had, he said, made his own introduction, but he was very pleased to welcome Mrs. Bowes, who was able to be with him. From our other Sections he was pleased to see the Chairman of the London Section, Mr. J. A. L. Hawkey, and Mrs. Hawkey, the Chairman of the Hull Section, Mr. J. S. Geary, and Mrs. Geary, the Chairman of the Manchester Section, Mr. H. Smith, and Mrs. Smith, the Chairman of the Newcastle Section, Mr. A. D. Hibberd, and Mrs. Hibberd, and the General Secretary of the Association, Mr. R. H. Hamblin.

Mr. Butler said that he was going to take the opportunity of thanking his Committee for the support they had given him in all the activities of the Section. Finally, he said that it was his great pleasure to propose the toast to the ladies and hoped that they would accept the evening as a night of atonement for the other evenings in the year. The response to the toast was given on behalf of the ladies and guests by the Mayor, who thanked the Section for its kindness.

A most enjoyable evening of dancing followed and all too soon it was 1 o'clock and "Auld Lang Syne". Special mention must be made of Mr. R. Smith, who acted as toastmaster, and of Mr. C. Allsop, who again, as Social Secretary, bore the weight of the organisation and contributed so much to the success of the evening.

L. J. W.

Register of Members

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

Ordinary Members

ADAMS, RONALD BRUCE, Penta Chemical Industries (Pty.) Ltd., 102-106 Ordnance Road, P.O. Box 1468, Durban, South Africa. (*South African*)

AMSDEN, RODNEY DOBSON, 163 Abbott Street, Sandringham, S.8, Victoria, Australia. (*Victorian*)

BAILEY, PETER, 177 Cressex Road, High Wycombe, Bucks. (*London*)

CHERRY, WILLIAM ALEXANDER, Smith & Walton (S.A.) (Pty.) Ltd., P.O. Box 46, Jacobs, Natal, South Africa. (*South African*)

COLEMAN, ANTHONY CHRISTOPHER, Roccaporrena House, South Douglas Road, Cork, Ireland. *(Overseas)*

DE GERSIGNY, LOUIS PHILLIPE BROUSSE, c/o Herbert Evans & Co. Ltd., P.O. Box 1386, 208 Gale Street, Durban, South Africa. *(South African)*

DOIG, ALEXANDER JOHN, R. Collie & Co., 130A Murray Street, Perth, Western Australia. *(South Australian)*

FELTHAM, FRANCIS WILLIAM, 16 Anderson Street, Surrey Hills, E.10, Victoria, Australia. *(Victorian)*

FRENCH, RONALD FRANK GEORGE, P.O. Box 9720, Johannesburg, South Africa. *(South African)*

GATE, PETER ATHOLL JACKSON, Penta Chemical Industries (Pty.) Ltd., 102-106 Ordnance Road, P.O. Box 1468, Durban, South Africa. *(South African)*

GIBB, PETER JOHN MACKENZIE, c/o G. J. Wevell (Pty.) Ltd., P.O. Box 1867, Cape Town, South Africa. *(South African)*

SHEEN, RONALD JAMES, c/o Universal Milling Co (Pty.) Ltd., Industrial Area, Welshpool, Western Australia. *(South Australian)*

SODERLUND, BO ERNST ARTUR, Finska Farg & Fernissfabriks AB, Korso, Finland. *(Overseas)*

TELFORD, ROBERT CECIL, Royal Street, Kenwick, Western Australia. *(South Australian)*

TRUKSA, LESLAW KAZIMIERZ, 18 Kings Avenue, Woodford Green, Essex. *(London)*

Associate Members

BROWN, ALAN ROBERT, "Westwards", 38 Mill Lane, Shoreham-by-Sea, Sussex. *(London)*

CHRISTIE, WILLIAM NAISMITH, Rodda (Pty.) Ltd., 65 Beach Street, Port Melbourne, Victoria, Australia. *(Victorian)*

DU CROS, HENRY EDWARD, 17 Florence Street, Nunawading, Victoria, Australia. *(Victorian)*

FREEMAN, BRIAN EDGAR, P.O. Box 1519, Cape Town, South Africa. *(South African)*

HODGES, WILLIAM HENRY, 581 Lt. Collins Street, Melbourne, Victoria, Australia. *(Victorian)*

MCEWAN, NEIL ROWAN, Rodda (Pty.) Ltd., 65 Beach Street, Port Melbourne, Victoria, Australia. *(Victorian)*

MCGOWAN, MANUS EDWARD, Universal Milling Co. (Pty.) Ltd., Industrial Area, Welshpool, Western Australia. *(South Australian)*

RUST, ROBIN GARTON, 42 Dalny Road, Murrumbeena, S.E.9, Victoria, Australia. *(Victorian)*

SMITH, CHARLES FRAMPTON, Edgar, 79 Crombie Road, Sidcup, Kent. *(London)*

TULLY, BRIAN BARRINGTON, Sawell Publications Ltd., 4 Ludgate Circus, London, E.C.4. *(London)*

WHITE, PETER MARSH, c/o Enwite Pty. Ltd., 84-96 Cromwell Street, Collingwood, Victoria, Australia. *(Victorian)*

Junior Members

BARLEE, ALAN ROGER, I.C.I.A.N.Z. (Dyestuffs Div.) Central Research Laboratories, Newson Street, Ascot Vale, Victoria, Australia. *(Victorian)*

BLACK, RICHARD JOHN, 83 Dunstan Parade, Garden City, Victoria, Australia. *(Victorian)*

DEACON, DAVID HUMPHREY, Flat No. 2, Amersham Road, Chalfont St. Giles, Bucks. *(London)*

DREW, ROBERT TRAILL, The Walpamur Co. (Aust.) Ltd., 106-120 Bay Street, Port Melbourne, S.C.7, Victoria, Australia. *(Victorian)*

GOLDSTRAW, PETER JOHN, 7 Aintree Road, Glen Iris, S.E.6, Victoria, Australia. (*Victorian*)

MACKENZIE, RICHARD TERRENCE, 61 Kenmare Street, Boxhill North, E.12, Victoria, Australia. (*Victorian*)

RUSSELL, DAVID FERGUSON, 340 Glasgow Road, Blantyre, Glasgow, Scotland. (*Scottish*)

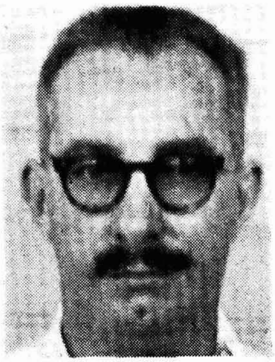
SALVARIS, ANDREW, 361 Glen Eira Road, Caulfield, Victoria, Australia. (*Victorian*)

SEEBERG, KURT CHRISTIAN, 155 Douglas Parade, Williamstown, Victoria, Australia. (*Victorian*)

SHARPE, WILLIAM NAPIER, The Walpamur Co. (Aust.) Ltd., 106-120 Bay Street, Port Melbourne, S.C.7, Victoria, Australia. (*Victorian*)

SHAW, KEITH JAMES, 71 Eland Road, Battersea, London, S.W.11. (*London*)

NEWS OF MEMBERS



MR. D. HASTILOW

Mr. D. Hastilow, an Ordinary member attached to the South African Section, left South Africa in December to take up an appointment in New South Wales, Australia. Except for some years as Chief Chemist of a sugar refinery, he has been exclusively connected with the paint industry, where he has particular knowledge of resin chemistry and production and latterly the application of modern synthetic emulsions. Mr. Hastilow was Hon. Secretary/Treasurer of the South African Section during 1957-58.

CHANGE OF ADDRESS

Members who change their address are asked to notify the Association's offices by separate communication and not by writing their new address on their yearly subscription form, since this may lead to delay in amending the record.

Obituary

CASIMIR HENRY WOINARSKI

It is with great regret that we learn of the sudden passing of Mr. Casimir Henry Woinarski on 20 November, 1960. Mr. Woinarski was a founder Member of O.C.C.A. in Australia and a Past Chairman of the Victorian Section, in whose affairs he always showed keen interest and enthusiasm. He was particularly concerned in developing technical knowledge within the Industry. On 7 November he delivered the 1960 Honour Lecture before the Victorian Section on "Thoughts on the Education and Administration of Technical Staff". He leaves behind him a widow and three children.

B.S. 391 : TUNG OIL

British Standard 391 : 1949, Tung Oil, is now under revision; the main change under consideration being a replacement of the present gel time test. Will members who require further information, or have views on the matter to be passed on to the Association's representative on the appropriate committee, kindly write to the General Secretary at the address shown on the front cover.

BRITISH STANDARDS

The British Standards Institution have announced that the following British Standards have just been issued:

B.S.1284: 1960	Bleached lac	(Price 7s. 6d.)
B.S.3279: 1960	Seedlac	(Price 5s.)
B.S.3280: 1960	Hand-made Shellac	(Price 10s.)

These publications have been prepared under the supervision of the Pigments, Paints and Varnishes Industry Standards Committee, on which the Association is represented by Mr. A. J. Gibson.

B.S.1284, Bleached lac, is a revised version of the 1946 edition and B.S.954, Lac, has been replaced by the two specifications for Seedlac and hand-made Shellac, B.S.3279 and B.S.3280. A further standard for machine-made lac, covering material not previously standardised, will soon be published.

Also issued recently is B.S.3263, Part 2: 1960, Road marking materials, Part 2—Hot-applied thermoplastic materials (inset type), costing 5s. This has been prepared under the supervision of the Road Engineering Industry Standards Committee. Mr. T. R. Bullett is the Association's representative on the Road Marking Compounds Committee, which is a technical sub-committee of the R.E.I.S.C.

Copies of these standards may be obtained from the British Standards Institution, Sales Branch, 2 Park Street, London, W.1.

Forthcoming Events

(Note: Details are given of meetings arranged in the U.K. up to the 15th of the month following publication, and in the Commonwealth up to the 15th of the second month after publication.)

Thursday, 2 February

Newcastle Section: "The Manufacture of Titanium Dioxide Pigmented Paints using Different Mills, with Particular Reference to a High Speed Impeller Mill," by D. G. Dowling, at the Royal Turks Head Hotel, Newcastle upon Tyne, at 6.30 p.m.

Monday, 6 February

Hull Section: "Some Resin Problems of an Electrical Component Manufacturer", by Dr. W. Marshall (Technical Manager, Morganite Resistors Limited), at the Royal Station Hotel, Hull, at 7.15 p.m.

Thursday, 9 February

Scottish Section: "Surface Coatings in Atomic Energy Installations" by H. Wells, at More's Hotel, India Street, Glasgow, C.2, at 7.30 p.m.

Friday, 10 February

Manchester Section: "Plastisols", by A. E. Meazey, B.Sc., at Blackfriars House, Bleachers' Association Ltd., Manchester, 3, at 6.30 p.m.

Saturday, 11 February

Scottish Section Student Group: "Microbiology in Paints", by D. J. Cowley, B.Sc., at More's Hotel, 18 India Street, Glasgow, C.2, at 10.00 a.m.

Tuesday, 14 February

West Riding Section: "Problems Encountered with Air-Drying Soya Bean Oil Alkyds", by P. C. Cox, A.R.I.C., and G. T. Williams, at the Metropole Hotel, Leeds, at 7.30 p.m.

Thursday, 23 February

London Section: "Pigments in Corrosion Prevention", by N. R. R. Bharucha, Ph.D. (The Research Association of British Paint, Colour and Varnish Manufacturers), at Manson House, 26 Portland Place, London, W.1, at 7 p.m.

Scottish Section: "Water Thinnable Stoving Finishes", by A. G. North, B.Sc., at the North British Hotel, Edinburgh.

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Scottish Section: "Water Thinnable Stoving Finishes", by A. G. North, B.Sc., at the North British Hotel, Edinburgh.

Friday, 24 February

Bristol Section: "Zinc Dust in Protective Coatings: Part III", by A. Pass, F.R.I.C., and M. J. F. Meason, B.Sc., (Amalgamated Oxides Ltd.) at the Royal Hotel, College Green, Bristol, 1, at 7.15 p.m.

Friday, 24 February

Midlands Section: "Wall Paper Manufacture". Ladies' Invitation Lecture, at Permoglaze Ltd., James Road, Tyseley, Birmingham, 11, at 6.30 p.m.

Thursday, 2 March

Newcastle Section: "Polyesters in Wood Finishes", by Dr. Deninger, at the Royal Turks Head Hotel, Newcastle upon Tyne, at 6.30 p.m.

Monday, 6 March, to Thursday, 9 March

Thirteenth Technical Exhibition at the Royal Horticultural Society's New and Old Halls, Greycoat and Elverton Streets, London, S.W.1.

Friday, 10 March

Manchester Section: Joint Meeting with the Royal Statistical Society, at the Constitutional Club, Tithebarn Street, Liverpool, at 6.30 p.m.

Monday, 13 March

Hull Section: Discussion Evening. Joint Meeting with Hull and District Chapter of Architects, at the Royal Station Hotel, Hull, at 7.15 p.m.

Tuesday, 14 March

West Riding Section: "Adhesives" by D. Spetch, B.Sc., at The Metropole Hotel, Leeds, at 7.30 p.m.


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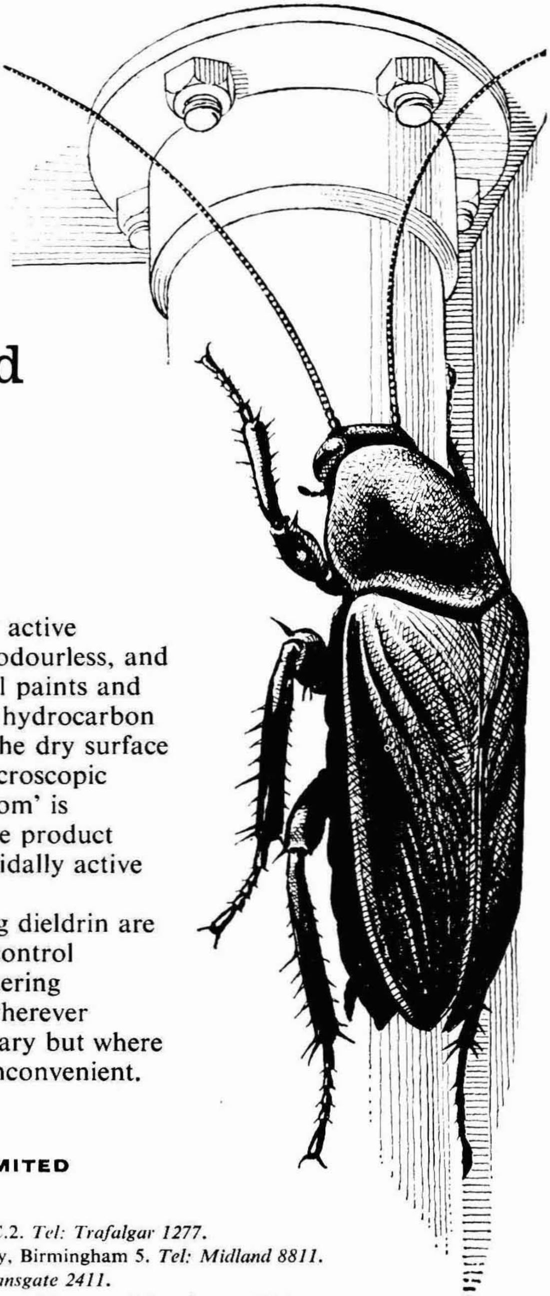

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MANCHESTER	144-146 Deansgate, Manchester 3. *Tel: Deansgate 2411.*
GLASGOW	Royal London House, 48-54 West Nile Street, Glasgow, C.1. *Tel: City 3391.*
BELFAST	16-20 Rosemary Street, Belfast, Northern Ireland. *Tel: Belfast 26094.*
DUBLIN	33-34 Westmoreland Street, Dublin, Republic of Ireland. *Tel: Dublin 72114.*

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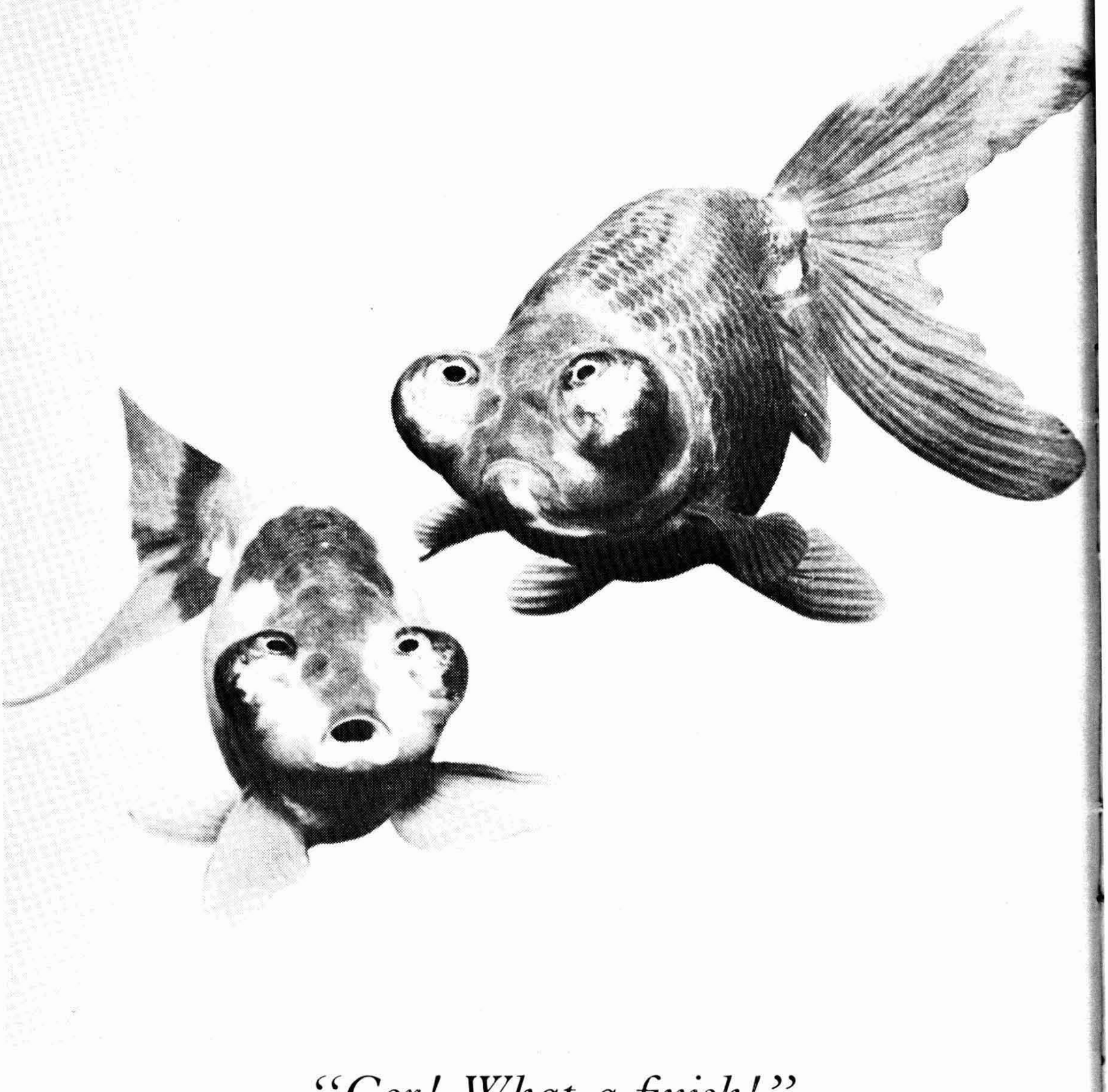

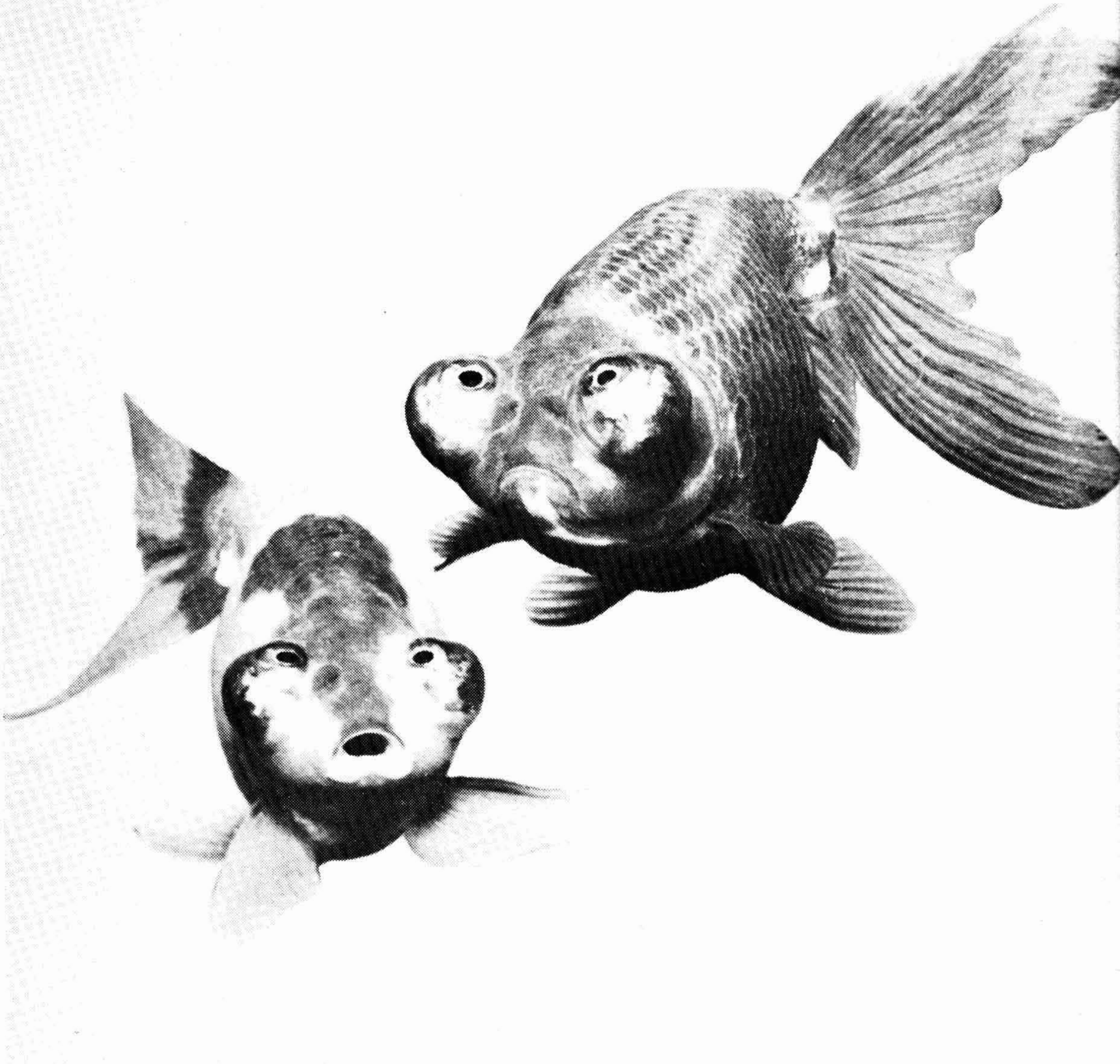

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SITUATIONS VACANT

PAINT TECHNOLOGIST

IF you have a good University Degree in chemistry with at least seven years' industrial experience in paint and varnish technology, and your age is still under 35, IMPERIAL CHEMICAL INDUSTRIES LIMITED, NOBEL DIVISION, has a vacancy that will interest you. In the Division's Research and Development Department on the Ayrshire Coast of the Firth of Clyde, stimulating work on surface-coating agents engages vigorous effort.

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"DIGESTS" WANTED

WANTED, the following 1959 *Official Digests*, May No. 412, August (Part 1) No. 415, September No. 416. Offers, together with price required, to:

The Librarian,
Cellon Ltd.,
Richmond Road,
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Surrey.

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CHEMIST required at the Falkirk Rolling Mills of The British Aluminium Company Ltd., to collaborate in developing the lacquering of strip and other commercial finishes. Graduate preferred or alternatively experience in field and at least H.N.C. qualification. Apply to Director of Research, Chalfont Park, Gerrards Cross, Bucks.

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PAINT TECHNOLOGIST

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His task will be control of production and the preparing and developing of new products. The company is one of the leading in its field in Sweden.

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CLASSIFIED ADVERTISEMENTS

Classified Advertisements are charged at the rate of 7s. 6d. per line. Advertisements for Situations Wanted are charged at 2s. 6d. per line. They should be sent to the General Secretary, Oil & Colour Chemists' Association, Wax Chandlers' Hall, Gresham Street, London, E.C.2. Telephone: Monarch 1439

SITUATIONS VACANT

ASSISTANT TECHNICAL OFFICERS

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has vacancies in its Research Department on Merseyside for Assistant Technical Officers to help in the development of new uses for the Division's products. The particular fields of current concern are paints and adhesives, but the pattern is continually changing with the varied demands of industry and the development of new raw materials. The work is interesting and has an especial appeal to men of a practical and ingenious turn of mind. Applicants should have at least a Higher National Certificate in chemistry or physics, together with experience in some branch of industrial chemistry, preferably the paint trade; they must have drive, initiative and an ability to tackle problems in new fields. Conditions of employment include excellent salaries and a Pension Fund, and there is also a Profit-Sharing Scheme. For married men some assistance can be given in house purchase and in the refund of removal expenses.

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PAINT TECHNOLOGIST required by Company situated in North East England. This expanding firm requires a qualified man having a sound knowledge of Paint Formulation and an ability to direct laboratory research. Accommodation found for suitable applicant. Please reply to Box No. 131/61.

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