JOURNAL of the OIL AND COLOUR CHEMISTS' ASSOCIATION



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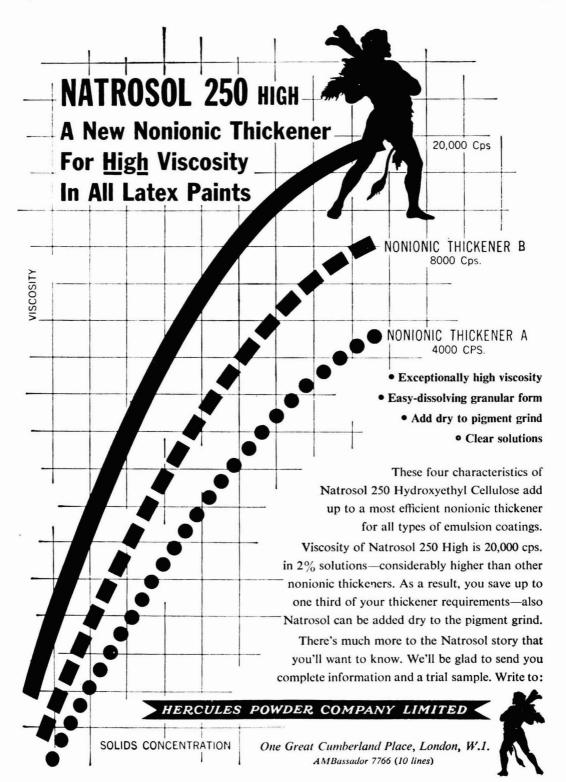
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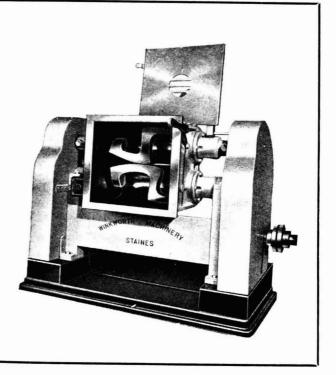


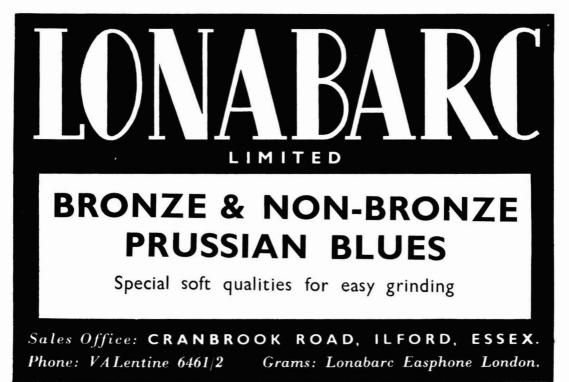
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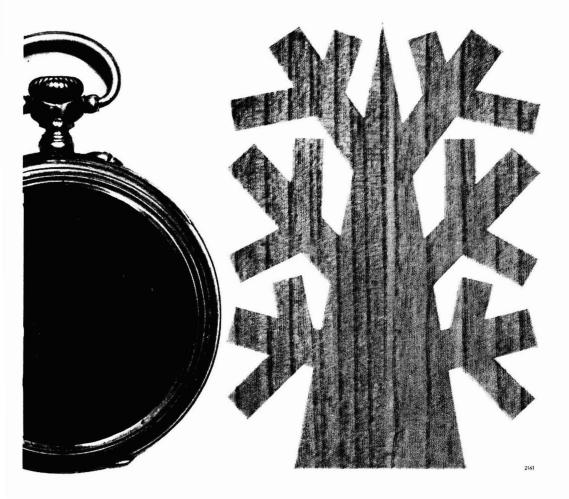
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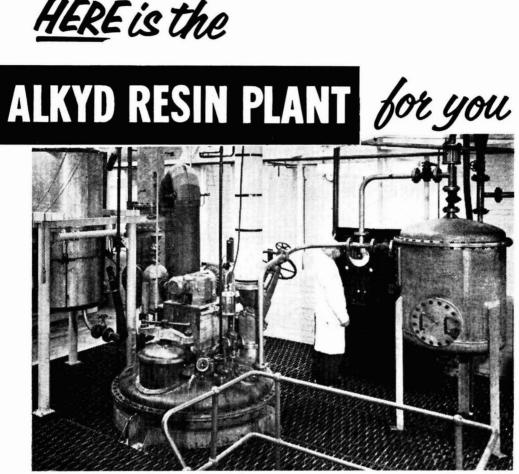
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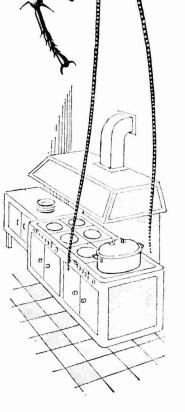
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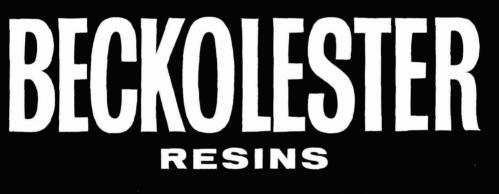
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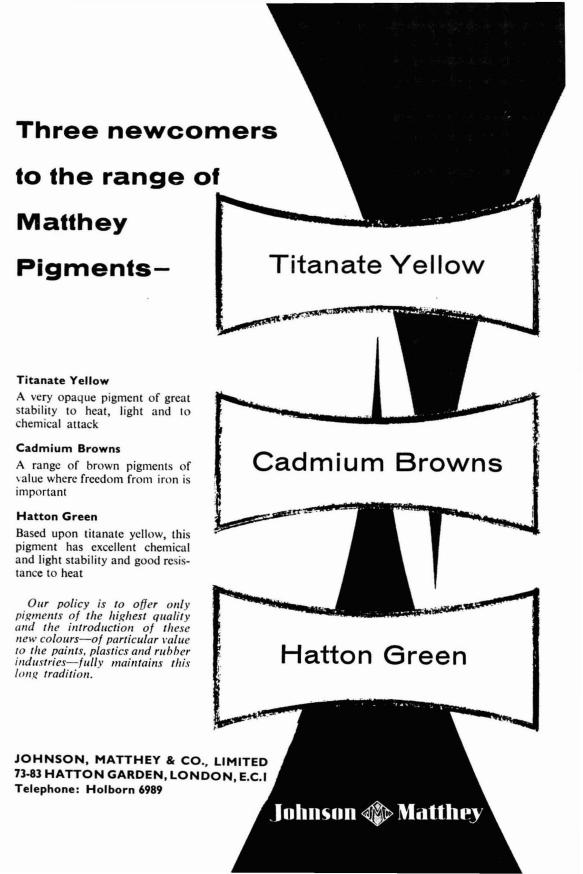


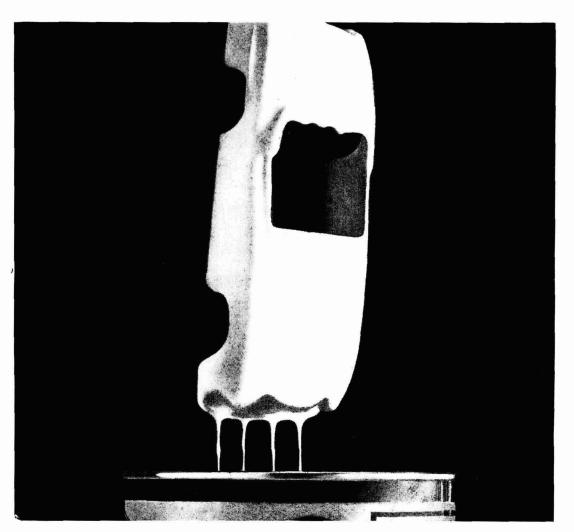
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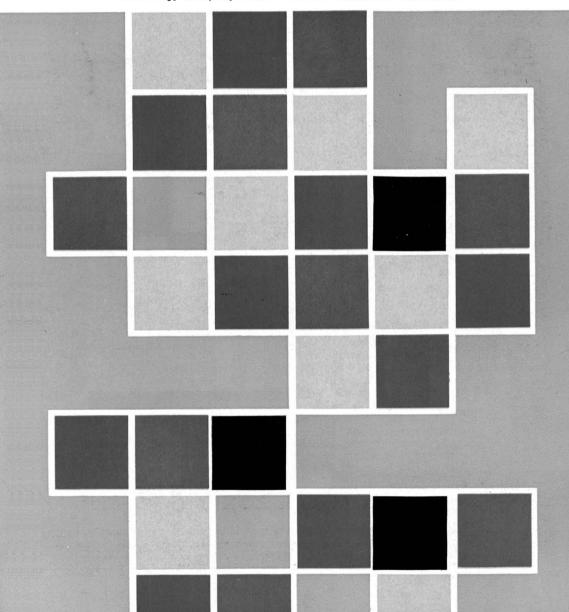
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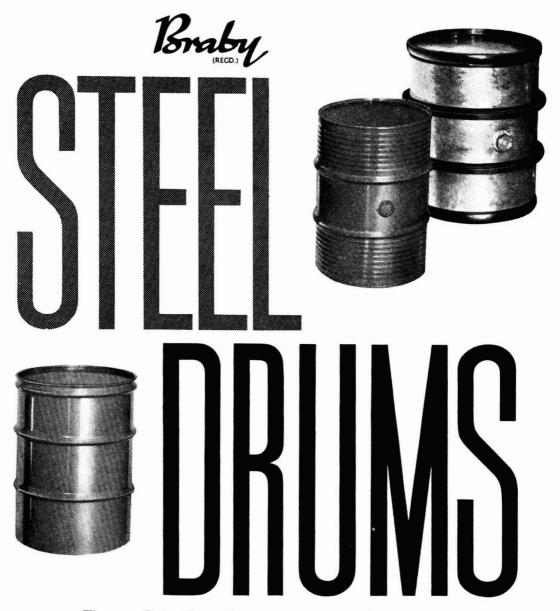
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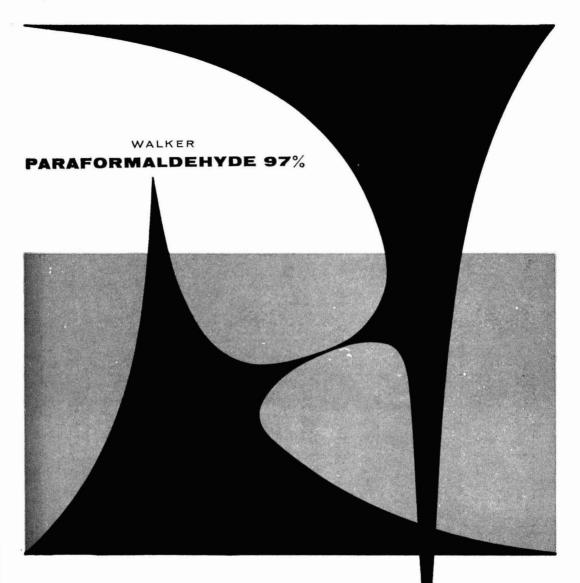
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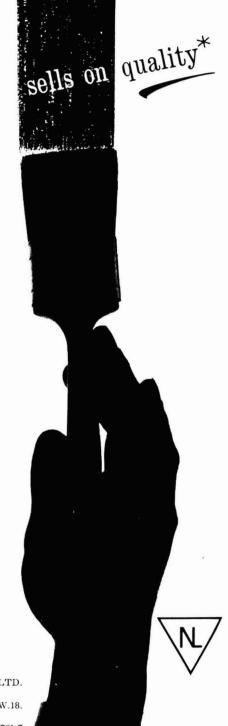




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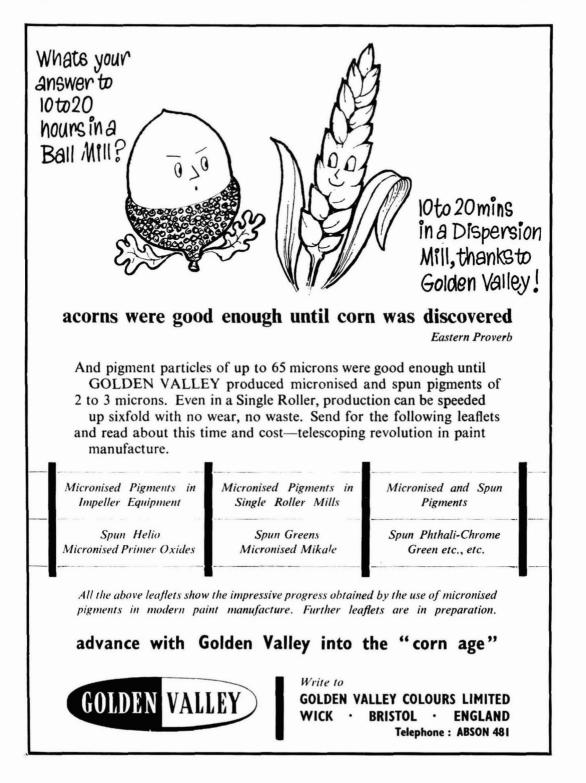
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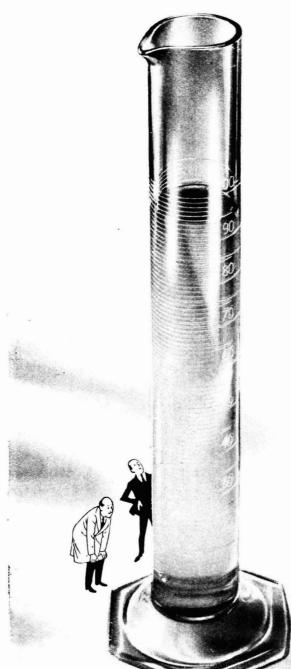


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JOURNAL OF THE OIL & COLOUR CHEMISTS' ASSOCIATION

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No. 8

TRANSACTIONS AND COMMUNICATIONS

The Alcoholysis and Acidolysis of Triglyceride Oils

By R. S. MCKEE and A. W. E. STADDON

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Summary

Changes in conductivity during the reaction between pentaerythritol (PE) and triglyceride oils were studied. The conductivity rose to a maximum as the reaction mixture became homogeneous and then fell gradually as equilibrium was approached. Constant conductivity and maximum methanol tolerance were both reached when the concentration of unreacted PE was a minimum. Curves of the same general shape were obtained over a range of oil lengths and using different grades of PE.

During the acidolysis reaction of isophthalic acid (IPA) and linseed oil, the conductivity reached a maximum when the acid value of the liquid phase was a maximum and the concentration of unreacted IPA a minimum. The measurement of conductivity therefore provides a means of following continuously the progress of both alcoholysis and acidolysis reactions and eliminates the need to take samples.

INTRODUCTION

Three common methods of deciding when sufficient reaction has taken place in the alcoholysis stage of alkyd resin manufacture employ the solubility of phthalic anhydride in the alcoholysate, the clarity of the hot reaction mixture, and the solubility in methanol or ethanol¹. Various forms of alcohol solubility tests have been cited, ranging from solubility in fixed proportions of methanol or ethanol to maximum methanol tolerance or infinite solubility in ethanol. Runk² showed that during glycerolysis infinite methanol tolerance corresponded to maximum monoglyceride content, while Mort³ showed that the relationship between methanol tolerance and monoglyceride content was not linear. $Mraz^4$ and his co-workers studied alcoholysis with PE and concluded that the methanol tolerance test gave "variable results under the most closely controlled conditions". These workers proposed the quantitative precipitation of the unreacted PE as an alternative method for following the course of alcoholysis, and this is possibly the most convenient way of determining directly the change in concentration of one of the reactants in the PE/oil system. Mleziva⁵ et al. examined the change in dielectric constant of centrifuged samples from the reaction between PE and linseed oil. Under their particular conditions they

concluded that the optimum time for the addition of phthalic anhydride coincided with a maximum in the dielectric constant, alkyds made using shorter or longer alcoholysis times both showing insoluble material.

Experience extending over many years in the surface coating laboratory at Stevenston indicates that for laboratory control in the alcoholysis of oils with PE, the methanol tolerance test enables satisfactory alkyd resins to be prepared provided that

- (a) the samples are centrifuged;
- (b) the clear oily layer is titrated with anhydrous methanol to permanent turbidity, the temperature at the end-point being rigidly controlled;
- (c) the end-point of alcoholysis is taken as the time at which the methanol tolerance reaches its maximum rather than a specified value.

Such a procedure is clearly inconvenient for routine plant control, and even in the laboratory it necessitates the carrying out of separate runs solely to determine alcoholysis times. Mort's work' indicated that electrical conductivity measurements might afford a means of detecting the equilibrium stage of the alcoholysis reaction immediately, without the need for taking samples. The main object of this paper is to present the results obtained using this method to follow the alcoholysis reaction between oils and PE. It is shown that the equilibrium stage of the reaction, as determined by the minimum free PE content of the mixture, is accurately indicated both by conductivity measurements and by the attainment of maximum methanol tolerance. It is also shown that conductivity measurements may be used to indicate the equilibrium stage in the acidolysis reaction between oils and isophthalic acid.

ALCOHOLYSIS OF OILS WITH PE

The alcoholysis stage in the preparation of PE alkyds presents certain differences from the reaction of oils with glycerol. These arise entirely from the fact that PE is a solid and glycerol a liquid. In the laboratory using glass vessels, a good indication of the progress of the early stages of the reaction can be obtained by simply observing the reaction visually. Soon after reaching reaction temperature, usually within the range 230°-270°C, the PE begins to form a crust around the walls of the flask, just above oil level; some PE also sublimes into the upper parts of the flask. As the reaction proceeds, the crust of PE slowly dissolves and the sublimed PE is washed back into the oil, possibly by traces of refluxing glycerol. At this point the alcoholysate is still opaque, owing to the presence of suspended PE and the immiscibility of the unreacted oil with the small amount of partial esters present. As more oil reacts the two liquid phases become miscible, the PE dissolves and the reaction mixture becomes clear. This is the "hot clear" end-point and in a typical long oil alkyd formulation it corresponds to the attainment of infinite solubility in absolute ethanol. Maximum methanol tolerance is reached somewhat later, and phthalic anhydride solubility somewhat earlier.

It has been found that clear, homogeneous alkyds are obtained by adding the phthalic anhydride any time after it is soluble, and the formation of insoluble

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material resulting from prolonging alcoholysis beyond the attainment of maximum methanol tolerance has never been observed.

Conductivity Changes During Alcoholysis

The apparatus used for each reaction consisted of a 1 litre round bottomed flask with a B34 centre neck and three B19 side necks, a D-shaped stainless steel stirrer running at 300 r.p.m., a carbon dioxide leak, a thermocouple in a glass sheath fitted through a stillhead which vented to atmosphere, and a conductivity/capacity cell with the electrodes immersed in the reaction mixture. The flask was heated by an *Electrothermal* mantle regulated by an electronic controller.

The electrodes consisted of two 2 cm. $\times 1$ cm. $\times \frac{1}{16}$ in. stainless steel plates separated by a 0.5 cm. gap. A tungsten rod was silver soldered to each plate and the rods fused through a $\frac{1}{2}$ in. diameter glass tube; nickel wire connected the tungsten rods to screened leads. The simple design of the cell facilitated cleaning and ensured a free flow of reactants between the electrodes (Fig. 1). Conductivity and capacity measurements were made using a *Wayne Kerr Universal Bridge, Type B221*. The complete set-up is shown in Fig. 2; the actual cell shown is made of *Fluon*, with the terminals encased for added robustness. It was subsequently found that the *Fluon* swelled slightly under the experimental conditions and the design is being further modified.

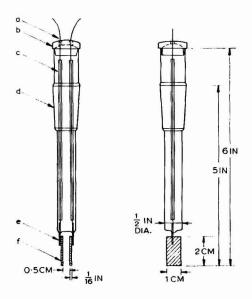


FIG. 1. CONDUCTIVITY CELL

- (a) Nickel leads welded to tungsten rods
- (b) Polythene caps
- (c) Glass insulators
- (d) Glass tube with B19 cone
- (e) Tungsten rods fused into tube
- (f) Stainless steel plates soldered to rods



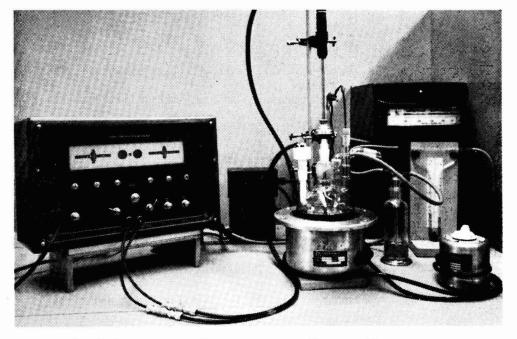


FIG. 2. APPARATUS FOR CONDUCTIVITY AND CAPACITY MEASUREMENTS

In each experiment alkali refined oil, PE and catalyst were weighed into the flask at room temperature and heated with stirring to the reaction temperature. Except where otherwise stated the PE used was a standard mono-grade.

Variation of Conductivity and Capacity during Alcoholysis

An alcoholysis reaction was carried out at 250° C using a 1.3:1 molar ratio of PE: linseed oil, corresponding to a finished alkyd of 65 per cent oil length. Sodium carbonate (0.074 mole per cent on the PE) was used as catalyst. Conductivity and capacity readings were made at intervals during the reaction, and the results are illustrated in Fig. 3.

The results show that the conductivity and capacity measurements tend to vary directly. As the PE begins to react, conductivity and capacity decrease until point A is reached. As the remaining PE becomes more soluble in the products of reaction, the crust dissolves and the conductivity rises to a maximum at B corresponding to the "hot clear" stage. With all the PE in solution the reaction proceeds rapidly and the curves fall to the equilibrium point C. Both conductivity and capacity continue to drop very slowly but constantly after C, possibly due to loss of glycerol or to ether formation.

During the reaction the temperature cycled between 248° and 253°C and this was found to affect the equilibrium stage readings considerably. In later experiments meter readings were taken at the same point in each temperature cycle. Since capacity and conductivity measurements both gave the same end-point for the reaction, and since conductivity meters were more readily available, subsequent work was based on conductivity.

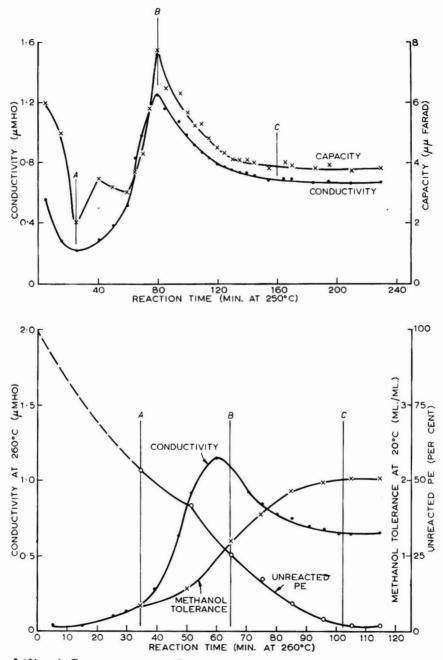
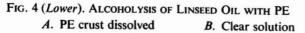


FIG. 3 (Upper). CONDUCTIVITY AND CAPACITY PLOTTED AGAINST REACTION TIME DURING ALCOHOLYSIS



C. Equilibrium

Conductivity Compared with Methanol Tolerance and Percentage Unreacted PE

The variation of conductivity with percentage unreacted PE and with the methanol tolerance of the liquid phase of the cooled reaction mixture was studied by repeating the previous experiment at 260°C. Conductivity readings were taken and samples withdrawn at intervals after the PE crust had dissolved. The samples for methanol tolerance determination were cooled and centrifuged, and 2 ml. aliquots were titrated with anhydrous methanol at 20°C to the point where a dense cloud was produced. In order to determine the unreacted PE, weighed samples were digested with about five times their weight of benzene on the water bath and filtered through a tared sintered crucible. The filter cake was then washed and dried and the crucible re-weighed. Analysis showed that the PE recovered in this way was only slightly contaminated with ester impurities (saponification value: 5-6 mg. KOH/g.). The results obtained are illustrated in Fig. 4.

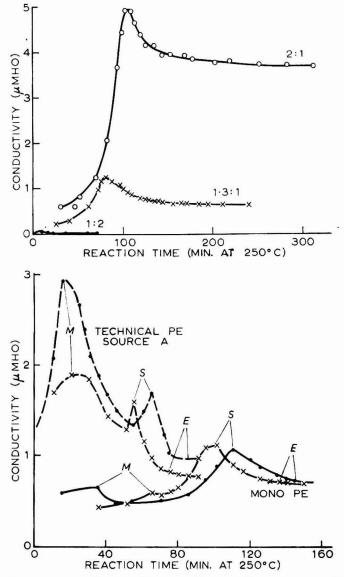
The results confirmed that both the equilibrium conductivity and the maximum methanol tolerance coincided with the minimum concentration of unreacted PE (point C). The "hot clear" stage B, at which the concentration of dissolved PE is a maximum, is marked by a sharp maximum in the conductivity curve also. The gradient of the methanol tolerance curve begins to increase just before this point and is at a maximum at B. The step in the unreacted PE curve on the other hand, suggests that the liquid phase is approaching equilibrium at B, only to have this equilibrium shifted as soon as the residual undissolved PE goes into solution.

From a practical point of view, the conductivity/time curve is particularly useful, since the occurrence of the maximum gives forewarning of the approach of equilibrium. On the other hand, not all the tests for completion of alcoholysis indicate the attainment of equilibrium and it has been stated⁶ that formulations are sometimes designed to have low quantities of monoglycerides. The use of conductivity to follow such reactions would present no difficulty. As already shown, the "hot clear" end-point coincides with the maximum in the conductivity/time curve, and it is probably not good practice to stop alcoholysis before this point.

Alcoholysis Using Different Proportions of PE and Oil

The effect on the conductivity of varying the ratio of PE : oil was studied by carrying out reactions at molar ratios of 2 : 1 and 1 : 2, PE : linseed oil. The higher ratio is the maximum theoretical ratio for monoester formation, while the lower ratio might be considered a practical minimum, since it corresponds to an oil length of 82 per cent. Again sodium carbonate was used as catalyst at a concentration of 0.074 mole per cent on the PE; the reaction temperature was 250°C. The conductivity measurements are illustrated in Fig. 5. The previous results with a 1.3:1 molar ratio of PE : oil are included for comparison.

Each reaction gave a curve of the same general shape, but as the oil length increased the conductivity decreased and the fall in conductivity from maximum to equilibrium amplitude became smaller. At the two highest PE : oil ratios, a meter range of 0-10 μ mho was required, whereas at 1 : 2 the range had to be reduced to 0-0.1 μ mho. The appearance of the 1 : 2 curve might suggest that



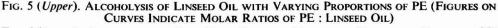


FIG. 6 (*Lower*). Alcoholysis of Soya Bean Oil with Mono- and Technical Grades of PE the method is inaccurate for very long oil length resins but, in practice, the scale would be increased to give a sharp peak and end-point.

Alcoholysis Reactions with Different Grades of PE

The results of runs carried out using technical grades of PE from two different sources (A and B) and one mono-grade at a 1.3:1 molar ratio of PE: soya bean oil are illustrated in Figs. 6 and 6A. The temperature (250°C) and catalyst (0.074 mole per cent sodium carbonate on the PE) were as before. The technical

PE from Source A was of poor quality with an ash content of 0.21 per cent and a melting point below the reaction temperature, whereas the mono-PE (ash 0.02 per cent) melted at around the reaction temperature. The technical PE from Source B also had a low melting point but a relatively low ash content (0.03 per cent).

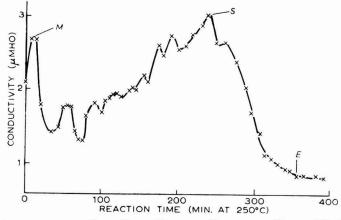


Fig. 6A. ALCOHOLYSIS OF SOYA BEAN OIL WITH TECHNICAL GRADE PE, SOURCE B

In these experiments it was found that the conductivity curves given by the technical PE from Source A showed an additional maximum (M) before the clear solution stage (S). A closer examination of the earlier part of the reaction with the mono-PE revealed a corresponding but far less pronounced maximum. This difference in amplitude between the maxima (M) is believed to be associated with the difference in melting point between these two grades of PE. The technical PE from Source A also gave sharper solution peaks (S) than the mono-PE and reached equilibrium (E) more quickly. The more rapid alcoholysis with this particular technical grade is entirely due to its high ash content and the finished resins made from this PE were consequently much darker than those from the mono-grade and very cloudy.

Conductivity curves for alcoholysis with the mono-PE and Source A technical PE are shown in duplicate. The reproducibility of these results was considered to be reasonable, provided that the end-point of the reaction is deduced from the general shape of the curve rather than from a particular conductivity reading.

The considerable variation in amplitude of the peaks (M) for Source A technical PE could possibly be reduced by using a continuous recording conductivity bridge. The technical PE from Source B, on the other hand, seemed to dissolve somewhat irregularly and the initial peak was followed by a series of smaller peaks before equilibrium was finally attained. The reproducibility of the conductivity curves given by this PE was not good and the principal maximum, corresponding to the "hot clear" stage, was frequently ill-defined. Reaction was much slower than with the mono-PE and for this reason one of the more satisfactory curves given by Source B technical PE is shown separately in Fig. 6A on a reduced time scale.

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CONTINUOUS RECORDING OF CONDUCTIVITY

In considering the use of the cell with a continuous recording conductivity bridge for the type of work described, it has been found necessary to increase the size of the plates in order to cope with the low conductivities found in PE alcoholysis reactions at very long oil lengths. A continuous automatic method of controlling alcoholysis developed by Gol'dberg¹¹ et al. also makes use of conductivity measurements.

THE ACIDOLYSIS OF OILS WITH ISOPHTHALIC ACID

The first extensive evaluation⁷ of isophthalic acid in oil modified alkyds was confined to resins made by the alcoholysis process. Some years later Carmody⁸ reported that solubility and sublimation problems of the alcoholysis process could be overcome by reacting the isophthalic acid directly with the oil (acidolysis). This reaction appears to proceed readily at temperatures above 280°C and because no catalyst is required, finished resins are free from the colour and cloud effects associated with the use of catalysts in alcoholysis. Subsequently, various time and temperature schedules for the acidolysis stage have appeared but, as far as is known, Carlston's is the first published work¹⁰ in which the extent of oil modification during acidolysis was followed by means of a simple test, namely, the acid value of the oil after dilution with solvent and removal or unreacted isophthalic acid by filtration. Such a test is unlikely to commend itself to a resin manufacturer for routine control. The second part of this paper presents results which show that conductivity measurements can also be used to indicate the point where the acid value of the oil phase is a maximum and the concentration of free isophthalic acid (IPA) is a minimum.

Prior to the work described here, Burkel's recommendation⁹ for acidolysis, namely, half an hour at 270°C, had been followed. At the end of this time the reaction mixture was still cloudy and a heavy deposit of IPA had formed round the flask wall above and below the liquid level. On adding the PE at this point, a very dark cloudy resin with substantial amounts of undissolved IPA was obtained. In a second preparation the oil was heated to 270°C with a quarter of the IPA, the rest being added in portions over an hour. After a further half an hour at 270°C, it was found that the oil layer became clear. Although there was still an appreciable crust of IPA still present, a clear, homogeneous resin was obtained by adding the PE at this point.

In the work which follows the oil was usually heated to the reaction temperature and the IPA then added. Alkyds have also been made successfully by heating IPA and oil together from the cold, and either of these procedures seems to be satisfactory provided that acidolysis is carried out at 280°-300°C.

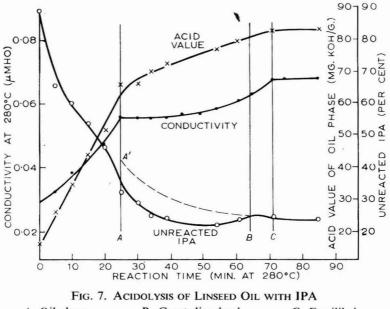
Conductivity Changes during Acidolysis

In order to find if a relationship existed between the conductivity, percentage unreacted IPA and acid value of the liquid phase in an acidolysis reaction, equimolar proportions of IPA and linseed oil were heated together at 280°C. Conductivity readings were taken and samples withdrawn periodically for acid value and unreacted IPA estimations. The apparatus used was the same as that employed for the alcoholysis reactions.

The unreacted IPA was determined gravimetrically by a similar method to that used for PE in the alcoholysis experiments. The acid value of the filtered

precipitate corresponded to isophthalic acid. The samples for acid value determination were centrifuged, and a known weight of the oil was diluted with 50/50, benzene/methylated spirits before titrating against N/10 sodium hydroxide solution.

The results, illustrated in Fig. 7, show that the acid value and conductivity increased and the percentage unreacted IPA decreased rapidly to point A, where the oil became clear. The conductivity then remained constant for a time, while the acid value and unreacted IPA curves indicated an appreciable retardation of the reaction. Between A and B the crust of IPA gradually dissolved and at first, presumably, the increase in conductivity due to the IPA dissolving was just balanced by the diminution in conductivity resulting from further reaction. At this stage the acid value curve gives a better idea of the progress of reaction than the unreacted IPA crust. The correction to be applied to obtain the true values for the unreacted IPA over the period A to B would gradually decrease from a maximum at A to zero at B, where the last piece of undissolved crust fell into the flask. No attempt was made to determine this correction, but the dotted curve A'B (Fig. 7) shows where the true unreacted IPA curve might reasonably be expected to fall.



A. Oil clear B. Crust dissolved C. Equilibrium

Equilibrium was reached at C, where the acid value of the oil phase and the percentage unreacted IPA both became constant. This stage was also indicated by a second levelling off in the conductivity, and it was concluded that

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conductivity measurements could be used to detect the equilibrium stage in acidolysis reactions.

Acidolysis Reactions with Various Ratios of IPA : Oil

Acidolysis reactions were run at 280° C using 1:1, 2:1, and 3:1 molar ratios of IPA : linseed oil (Fig. 8), corresponding to oil lengths of about 80, 70 and 60 per cent, respectively. As in previous experiments conductivity readings were taken at definite points in the temperature cycle.

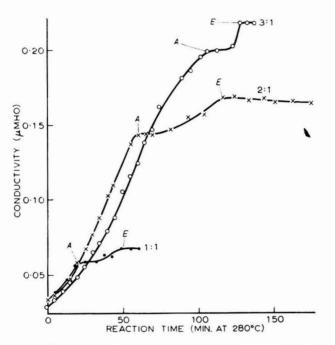


FIG. 8. ACIDOLYSIS OF LINSEED OIL WITH VARYING PROPERTIES OF IPA. (FIGURES ON CURVES INDICATE MOLAR RATIOS OF IPA: LINSEED OIL.)

The three curves were all of the same general shape, the amplitudes increasing as the ratio of IPA : oil increased. It is of interest to note that only at 80 per cent oil length did the IPA crust finally dissolve completely. Equilibrium occurs at point E in each case, the earlier levelling of the conductivity curves at A corresponding to the "clear oil" stage already described.

Effect of Temperature on Reaction Rate

Typical conductivity curves referring to acidolysis reactions between alkali refined linseed or soya bean oils and IPA at various temperatures are given in Fig. 9. They confirm that reaction is unduly prolonged below 280°C. The duplicate curves for a reaction with soya bean oil at 300°C do not show the initial levelling off observed with linseed oil at 280°C, presumably due to the increased solubility of IPA at the higher temperature.

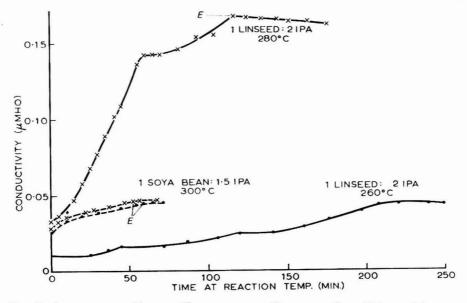


FIG. 9. ACIDOLYSIS AT VARIOUS TEMPERATURES. (RATIOS OF OIL : IPA ARE MOLAR)

CONCLUSION

The work described shows that the shape of the conductivity/time curves can be used to determine suitable end-points for the alcoholysis of triglyceride oils with pentaerythritol and the acidolysis of oils with isophthalic acid.

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Sealers for Insulating Paint Films with a High Content of Lead

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Summary

An investigation was carried out to find a suitable material to form a seal between paint films containing large amounts of lead and subsequent paint films. Formulations based on chlorinated rubber, wood oil, p.v.a. dissolved in ethanol, a tetrapolymer and acrylic ester polymer latexes gave excellent performance. The latter two are preferred because they are easy to apply, dry quickly and have the usual advantages connected with water-thinnable formulations.

INTRODUCTION

The causes of sulphide staining and a simple remedy for sulphide stains were discussed in a previous paper¹, in which it was pointed out that the cure proposed could be effective only if the lead content of the paint film did not exceed 0.5 per cent. The lead content of some paint films is considerably higher than this owing to the use of pigments containing lead, and the only remedy in these cases is to redecorate with a paint in which there is no lead. However, this is not always effective and staining has been observed on the originally lead-free paint film; this has been traced to the diffusion of slightly water-soluble lead compounds from the underlying paint film. This is likely to happen if frequent condensation of water vapour occurs on the painted area. Therefore, to ensure that sulphide staining does not recur, it is necessary to insulate the paint film containing lead from the lead-free finishing coat by applying a suitable sealer. Nothing is known about the permeability of the various sealers towards lead compounds under the conditions described, and it became desirable to investigate this point and to try to develop a suitable sealer.

EXPERIMENTAL DETAILS

The compositions of the twenty-two sealers used in the experiments are detailed in Appendix I. They may be divided into four groups according to the type of base material, *viz.* (*a*) chlorinated rubber (No. 1), (*b*) safflower alkyd (Nos. 2-4), (*c*) wood oil (Nos. 5-12), and (*d*) latexes (Nos. 13-22). Sealers in groups (*a*) and (*c*) were chosen because they form films that are impermeable to water. Sealers of group (*b*) are slightly permeable to water, and those in group (*d*) were included because they are easiest to apply. Five brands of lead-free alkyd paints and five brands of latex paints were used as finishing coats.

Preparation of Specimens

Plaster pieces (3 in. square) were first given a coat of pink primer containing 25 per cent white lead, over which one or two coats of sealer were applied. The specimens were then painted with two coats of a white, lead-free flat alkyd enamel or two coats of a latex paint. (Twenty-four hours was allowed between

the application of the different coats.) A piece of filter paper was then laid on top of the test piece and covered with glass. The filter paper was kept wet by moistening it in the morning and in the evening. At specified times the specimens were exposed to an atmosphere of hydrogen sulphide and any lead that had leached to the surface showed up as a black stain on the paint film (Fig. 1).

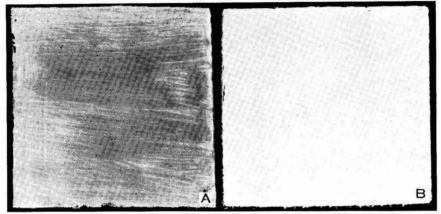


FIG. 1. PLASTER PANELS FINISHED WITH LATEX PAINT OVER PRIMING COAT CONTAINING LEAD A. No sealer, one month after painting. B. With Sealer No. 17

Preparation of Hydrogen Sulphide Atmosphere

A well-defined atmosphere of hydrogen sulphide was obtained by placing a solution containing 12 g. sodium sulphide $(Na_2S.9H_2O)$ and 6 g. boric acid in 1 l. water² at the bottom of a glass tank (20 in. \times 12 in. \times 10 in.). This gave an atmosphere that blackened lead acetate paper immediately.

RESULTS AND DISCUSSION

A sealer will be effective if its permeability to water is low or if the film is impermeable to the dissolved lead compound. The effectiveness of the sealers investigated here seems to be directly related to their impermeability to water, *e.g.* the sealers based on latexes made from the tetrapolymer, which are very effective, also seem to have a low water permeability. The impermeability of dissolved compounds through films may also play a major role, but at the present time it is impossible to say whether this is the case as nothing has been published on the subject.

The results of the tests which are recorded in Table I were assessed as a subjective rating scale in which 0 represents no discolouration, 1 represents a trace of discolouration, and 5 represents strong discolouration. An excellent performance was obtained with sealer No. 1 (chlorinated rubber), but the aromatic solvent used, together with its high viscosity, makes it disagreeable to apply. The sealers based on safflower alkyd (Nos. 2-4) did not perform very well and should not be used. It is of interest to note that the addition of lead naphthenate as driers to sealer No. 3 did not impair its performance compared with that of other sealers in the group. The sealers based on wood oil varnish

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were very good. They were easier to apply than sealer No. 1 and would be a practical proposition for painting large areas.

Sealer	Binder	No	Time exposed to atmosphere of hydrogen sulphide						
No.	Binder	No. of coats	1 day	3 days	7 days	14 days	I month	2 months	4 month
No sealer		-	1	5	>5	>>5	>>>5	-	—
1	Chlorinated rubber	12	0 0	0 0	1 0	10	1	1 0	1 0
2	Safflower alkyd	1 2	0 0	2 1	2 1	3 2	2	3 2	4 3
3		1 2	0 0	2 1	2 1	3 2	2 1	3 2	3 3
4		12	0 0	1	ł	22	2 1	3 2	4 2
5	Wood oil varnish	12	0	0	1 0	1 0	1 0	1 0	1 0
6		1 2	0	0 0	0	1 0	0	1 0	1 0
7		12	0	0 0	0 0	1 0	1	1 0	1 0
8		12	0 0	0	0	1 0	1	1 0	1 0
9	,,	12	0 0	0 0	0	0 0	1	1 0	1 0
10	"	12	0 0	0	0	1 0	1	2 0	3 0
11	"	12	0 0	0 0	0 0	0 0	0	0 0	00
12		12	0 0	0 0	0 0	1 0	1	1 0	1 0
13	P.v.a.	12	0 0	1	22	33	4 4	}5 ≶5	>5 >5
14		12	0 0	1	22	3 2	22	3 3	4 4
15	,,	2	0	0	0	0	0	0	0
16	Tetrapolymer based on styrene	12	0 0	0 0	0	0 0	0	0 0	0 0
17	"	12	0 0	0 0	0 0	00	0	0 0	0 0
18	,,	2	0	0	0	0	0	0	0
19	Acrylic polymer	2	0	0	0	0	0	0	0
20	**	2	0	0	0	0	0	0	0
21	Polymer powder based on styrene	12	0 0	1	1	ł	1	1 1	2 1
22		1 2	0	ł		1	1	1	1

TABLE I

PERFORMANCE OF SEALERS

0 No discolouration 1 Trace 5 Very strong discolouration The finishing coat in sealers 16 to 22 was a latex paint

The sealers based on p.v.a. showed interesting behaviour. Sealer No. 13, which is widely used in paint formulations, gave a very poor performance for this purpose. Sealer No. 15, a p.v.a. emulsion dissolved in ethanol, performed excellently. The chemical composition in the two cases is the same, but the performance was very different. The conclusion may be reached that the structure of the film in these two cases must be very different. *Emultex 1500*, on which sealer No. 13 is based, has a particle size of 2 to 4μ . Mowilith, the basis of sealer No. 15, could be regarded as a form in which the smallest possible particle size of the p.v.a. aggregate is achieved. It could be surmised, therefore, that the effectiveness of a film as a barrier to lead compounds depends more on the particle size of the emulsion than on its chemical composition.

No incompatibility was noticed except with sealers 15, 16 and 18. Crazing occurred in the latex and the alkyd paints over sealers Nos. 15 and 16. Sealer No. 18 was satisfactory under latex paints but unsatisfactory with alkyd paints, which were difficult to apply. However, if mica was added to sealer No. 16, the tendency to crazing disappeared with latex paints and was considerably improved with oil paints. Sealers based on tetrapolymers and those based on acrylic ester polymer gave excellent performance; they are easily applied, and have all the advantages of a water-thinnable formulation. Sealers Nos. 17, 19 and 20 are compatible with latex paints and alkyd enamels, and are therefore recommended to separate paint films containing large quantities of lead from subsequent coats of paint. Sealers formulated with a polymer powder based on styrene gave a reasonable performance, but not quite as good as was expected.

ACKNOWLEDGEMENT

The co-operation of Lewis Berger and Sons (N.S.W.) Pty. Ltd. and of Smith and Walton (Australia) Pty. Ltd. in preparing the sealers in groups (a), (b) and (c) is gratefully acknowledged.

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APPENDIX I

COMPOSITION OF SEALERS

	Constituent	Content
1.	Chlorinated rubber r-Titanium dioxide Magnesium silicate Xylol	21.5 17.4 12.2 48.9
	P.V.C.	37.7

2. Safflower alkyd (oil length 65 per cent) at 39 per cent non-volatile matter in mineral spirits, containing 0.08 per cent cobalt as naphthenate on non-volatile matter. 1961 SEALERS FOR INSULATING PAINT FILMS WITH A HIGH LEAD CONTENT 513

- 3. As No. 2, but with the addition of 0.5 per cent lead as naphthenate, on non-volatile matter.
- 4. As No. 2, but with the addition of 0.25 per cent zirconium naphthenate.
- 5. Resin modified wood oil varnish (70 per cent wood oil, 30 per cent resin), 28 per cent non-volatile matter containing 0.02 per cent cobalt as naphthenate, 0.02 per cent manganese as naphthenate, and 0.25 per cent lead as naphthenate.
- 6. Resin modified wood oil varnish as No. 5, 28 per cent non-volatile matter containing 0.03 per cent cobalt as naphthenate and 0.03 per cent manganese as naphthenate.
- 7. Resin modified wood oil varnish with 36 per cent non-volatile matter.

Constituent	Content	
	%	
Pigments used		
Titanium dioxide	32.0	
Calcium sulphate	53.0	
Siliceous material	15.0	
Driers		
Calcium, as resinate	0.95	
Cobalt, as naphthenate	0.01	
Manganese, as naphthenate	0.005	
Constituent	Content	
	%	
Wood oil coumarone varnish	70	
Coumarone indene resin	31.0	
China wood oil	31.0	
Xylol	19.0	
Mineral turpentine	19.0	
Wood oil coumarone varnish	27.5	
<i>r</i> -Titanium dioxide	32.4	
Diatomaceous earth	5.8	
Magnesium silicate	17.6	
Mineral turpentine	15.5	
Cobalt naphthenate 6% solution	0.2	
Calcium naphthenate 3% solution	2.0	
Butyraldoxime	0.2	
P.V.C.	46.0	

8. Pigmented resin modified wood oil varnish, P.V.C. 35 per cent.

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	Constituent	Content				
		°/0				
11.	Wood oil phenolic varnish Pure phenolic resin, Bakelite BR254	14.6				
	China wood oil	48.0 12.0				
	Xylol Mineral turpentine	12.0				
	Dipentene	9.4				
12.	Wood oil phenolic varnish	25.8				
	r-Titanium dioxide	30.7				
	Diatomaceous earth Magnesium silicate	5.6 16.8				
	Mineral turpentine	17.6				
	Cobalt naphthenate 6% solution	0.3				
	Cobalt naphthenate 6% solution Calcium naphthenate 3% solution	3.0				
	Butyraldoxime	0.28				
	P.V.C.	47.0				
13.	P.v.a. latex Emultex 1500 plasticised with 7 pe	er cent dibutyl phthalate.				
14.	As No. 13, containing mica to a P.V.C. of 22 pe	er cent.				
15.	Mowilith p.v.a. resin dissolved in ethanol.					
16.	<i>Lytron 680</i> , tetrapolymer of styrene, 2-ethyl methacrylate and acrylonitrile.	hexyl acrylate, methyl-				
17.	Lytron 680 containing mica to 22 per cent P.V.C	2.				
18.	Equal parts of 2.5 per cent methyl cellulose sol	ution and Lytron 680.				
19.	Acrylic emulsion AC33.					
20.	Equal parts of 2.5 per cent methyl cellulose solu	ation and AC33.				
21.	Gunn powder plasticised with 45 per cent. dibut	yl phthalate.				
22.	As No. 20, but containing mica to 22 per cent P	P.V.C.				

Pigments in Corrosion Protection*

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Summary

Corrosion protection is not wholly attributable to the physical properties of a paint film. In addition to physical protection (resistance inhibition) paint films can protect by the process of chemical inhibition, which can be either anodic or cathodic. Useful information regarding corrosion can be obtained from a study of electrode potentials. A method of measurement is described which provides data capable of quantitative interpretation, measuring individually the potential changes of cathodic and anodic areas of a partially painted test specimen. The results are presented in the form of potential distribution curves around the painted/unpainted boundary of the specimen. The shape of the curve provides an indication of whether chemical inhibition contributes to the protection of a substrate by a paint film. Results are given for lead, iron oxide, chromate and metal pigmented films. Autoradiographic studies indicate that one form of protection afforded by red lead is by deposition of lead. A study of electro-osmotic transfer of water through paint films is given, and an attempt is made to relate this transfer to the degree of protection afforded by the film.

INTRODUCTION

The protection of metals by paints has assumed considerable importance with the increasing use of steel for structural and other industrial purposes. In recent years non-ferrous metals have also provided substrates for painting. either in massive form or as protective cladding materials on steel. The mechanism by which a paint may protect a substrate to which it is applied is likely to depend, at least in part, on the physical and mechanical properties of the paint film, e.g. moisture resistance, which in turn are influenced by the nature of the medium and the pigmentation in terms of particle type, size and distribution. Many workers¹⁻⁴ have studied the protection by paints in terms of physical properties, but relatively less importance has been attached to the study of the electrochemical aspects of protective mechanisms. Corrosion protection by paint systems in practice cannot be wholly attributed to the physical properties of the films, and the emphasis in the work described in this paper has been placed upon studies of the chemical composition of the paint films and their chemical and physico-chemical behaviour in corrosive conditions.

It is well known that corrosion in an aqueous environment is an electrochemical phenomenon. A detailed consideration of the electrochemical theory would be out of place here, and a brief account only is given. The corroding metal surface may be considered to be made up of short-circuited galvanic cells, local anodic and cathodic elements being interspersed over the surface. In the immediate vicinity of any one local element in an aqueous environment there is either an oxidation or a reduction reaction taking place; oxidation reactions occur at the anodes and reduction reactions at the cathodes. A local element cannot be an anode and a cathode at the same time. Corrosion may be defined as the loss of metal ions from the parent metal lattice and their

^{*}Read before the London Section on 23 February, 1961.

transfer to a foreign environment, and therefore it occurs only at the anode, where the metal is oxidised to positive metal ions, with the production of electrons.

At the local cathodes the reduction reactions differ in character depending upon the conditions. Possible reactions are reduction of the cations, reduction of positive hydrogen ions to hydrogen gas, or reduction of oxygen to form hydroxyl ions, electrons being consumed during these processes. The resulting electron deficiency at the cathode is then remedied by the transfer of electrons from the anode to the cathode through the metallic conduction path. This corresponds to an electric current flowing in the metal from the cathode to the anode.

In the case of corrosion of iron, the overall reaction may be simply expressed as

$$4Fe+3O_2+2H_2O\rightarrow 2Fe_2O_3H_2O$$

This equation can be broken down into its component anodic and cathodic reactions, the one producing the other consuming electrons. The anodic reaction may be written as

 $4Fe \rightarrow 4Fe^{++} + 8e$

and the cathodic reaction as

 $2O_2 + 4H_2O + 8e \rightarrow 8OH^-$

The net result is the formation of ferrous hydroxide $4Fe+2O_{2}+4H_{2}O\rightarrow 4Fe(OH)_{2}$

In the presence of oxygen, the ferrous hydroxide is converted into rust according to the equation

 $4Fe(OH)_2 + O_2 \rightarrow 2Fe_2O_3 H_2O + 2H_2O$

The corrosion may be controlled *via* either the anodic reaction or the cathodic reaction, or by preventing or impeding the movement of the ions in the electrolyte or the flow of electrons in the metallic circuit; the last cannot occur in practice because the local anodes and cathodes are in metallic contact on the metal surface. It is, however, well within the bounds of possibility for a paint film to provide protection by one or all of the other ways mentioned above, complete corrosion inhibition probably depending on more than one factor.

All paints provide a means of inhibition, known as "resistance inhibition" by isolating the metal from the corrosive environment. Indeed, paint systems for metals are generally designed to provide a physical barrier against the ingress of water and oxygen. However, it has been shown^{5, 6, 7} that all paint films are to some extent permeable to water and oxygen. A paint meeting the requirement of complete impermeability does not exist and, therefore, the metal cannot be completely shielded from the influence of corrosion. The inhibition of corrosion brought about by interference with the electrode reactions is loosely called "chemical inhibition", also provide "chemical inhibition". It is pertinent to mention, however, that despite intensive research, chemical inhibition is still not properly understood, although it is certain that in most cases the nature of the

pigment is a dominant factor in providing this inhibition. It is likely that most inhibitors function as chemically or physico-chemically adsorbed films, which either alter the electrochemical properties of the metal substrate or act as barriers to corroding materials.

It has been recognised that pigments can inhibit or stimulate rusting, or be inert in this respect⁸. Inhibitive pigments, by their presence and nature, interfere chemically or physico-chemically with reactions occurring at the anodes or the cathodes, or both. In this respect individual pigments are usually quite specific in their action. Accordingly, they are classified as either "anodic", "cathodic", or "mixed" inhibitors. Pigments that do not provide inhibition by interference with anodic or cathodic reactions are classified as "inert". Such inert pigments may, however, provide protection by imparting improved film-forming properties, greater impermeability, *etc.*; their protective action is generally attributed to the "resistance inhibition" mentioned previously, owing to their contribution to the physical characteristics of the paint.

ELECTRODE POTENTIAL MEASUREMENTS

Since corrosion is an electrochemical phenomenon, it is reasonable to expect that a study of potentials on the surface of a corroding metal would yield valuable and interesting information concerning the corrosion process. Useful information has already been obtained from the study of changes in the potentials of metal surfaces corroding in an aqueous environment⁹⁻¹⁶. The presence of single coats of oil paints on the metal surface does not substantially interfere with the process of potential measurement because both water and dissolved oxygen permeate the paint film sufficiently rapidly. A study of the changes in the potentials when corroding metal surfaces are coated with different paint films is, therefore, likely to provide information on the mechanism of protection provided by the paint films.

A method of measurement of electrode potentials of painted metal specimens was first suggested by Burns and Haring¹⁷ and has subsequently been used with some modifications by several investigators 18-22. The aim of this work was to relate potential/time curves to the corrosion behaviour of painted metal surfaces immersed in a corroding environment. A cathodic potential (or a trend of potential in this direction) is generally associated with passivity, but a shift of potential in an anodic direction generally denotes corrosion. Whilst this approach is useful in understanding the corroding system, the measurement of such compromise potentials has drawbacks. The potential/time curves of specimens exposed to corrosive environments are generally subjected to random fluctuations. The results obtained are only qualitative, since the interpretation of the curves must in all cases depend not upon the actual values, but upon the direction of the drift of such potentials with time. Furthermore, depending on the anodic and cathodic polarisation characteristics of the metal, a measured potential may be associated with either a very low or a very high anodic current density. The measurement of such potentials also does not provide any conclusive information on the nature of any corrosion inhibition, i.e. whether anodic or cathodic.

A new method has been devised to provide data capable of quantitative interpretation, measuring individually the potential changes of anodic and cathodic areas of a partially painted test specimen. Since painted areas are generally found to be cathodic with respect to unpainted steel areas^{23, 24}, a single specimen half-coated with a paint (primer) may be regarded as forming a "contact couple" when immersed in a corroding environment. A schematic representation of such a contact couple is shown in Fig. 1. The current lines are seen to be more concentrated at the painted/unpainted boundary, with the different equipotential lines at right angles to current lines.

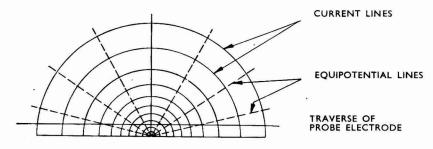


FIG. 1. SCHEMATIC REPRESENTATION OF A "CONTACT COUPLE"

Experimental

The method consists essentially of scanning the surface of a specimen, halfcoated with a paint and immersed in a suitable electrolyte, and noting the potentials recorded at regular distances (1 cm., 2 cm., 3 cm., *etc.*) from the boundary between the painted (cathodic) and the unpainted (anodic) areas. The scanning is effected by means of a probe calomel electrode with a potassium chloride/agar bridge with a fine capillary tip (0.60 mm. diameter). The reference (calomel) electrode is placed at a fixed distance from the probe electrode and does not traverse the surface of the specimen. The tip of the probe electrode is kept at a distance of approximately 1 mm. from the surface of the specimen. The potential values are recorded on a valve potentiometer. The theoretical potential distribution curves near the boundary between the anode and cathode of a "contact couple" are shown in Fig. 2.

A potential change is observed in all cases in passing from the anodic (unpainted) to the cathodic (painted) area. With an electrolyte of almost infinite resistance, both the anodes and the cathodes essentially retain their original unpolarised potentials e_a and e_c , the resistance of the electrolyte keeping the two electrodes disconnected. In the opposite case in which the electrolyte has a very high conductivity, the potential curve is a straight line parallel to the abscissa, the ohmic resistance having no appreciable influence. In the intermediate case where the resistance of the electrolyte has an appreciable influence, an "S" curve is normally to be expected²⁵.

As mentioned earlier, a paint film may provide protection by two types of inhibition, *viz.* resistance inhibition and chemical inhibition. Both types of inhibition can be detected by deviations from the theoretical "S" shaped curve. Variations in the dimensions of the "S" shaped curve may be correlated with

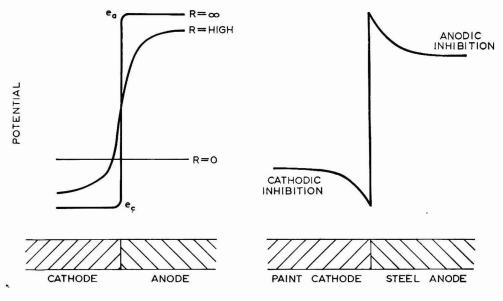
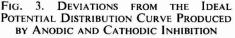


FIG. 2. THEORETICAL POTENTIAL DISTRIBU-TION CURVES FOR THE AREA NEAR THE PAINTED / UNPAINTED BOUNDARY OF A CONTACT COUPLE



the different degrees of resistance inhibition, a curve that is small and compressed indicating better resistance inhibition than one that is large and elongated. Changes in the shape of the "S" curve (showing a decrease in the potential values over either the anodic or the cathodic areas, or both) may be assumed to signify chemical inhibition. Such changes over the anodic area will indicate anodic inhibition, whilst changes on the cathodic areas will indicate cathodic inhibition. A schematic representation of such deviations from the ideal curve appears in Fig. 3.

Preparation of Test Specimens

Mild steel panels were abraded with fine emery paper and then degreased and cleaned using successively carbon tetrachloride, alcohol and finally acetone. Half of each panel was subsequently coated with the paint to be studied, using a doctor blade adjusted, where appropriate, to give coatings in a series of different thicknesses. The coated panels were allowed to dry and harden for twenty-one days prior to making measurements. All the above operations were carried out under controlled conditions of temperature and humidity (25°C/65 per cent R.H.). Before measurement the unpainted areas of the panel were once again cleaned and degreased, care being taken not to damage the painted area. The dimensions of each panel were 7.5×2.4 cm; the thickness of each paint film was measured to an accuracy of $+5\mu$ using an electromagnetic thickness meter.

After a number of experiments with various electrolytes, triacetin (glyceryl triacetate) containing approximately three per cent water was chosen. This had

an electrical conductivity of 1.1180×10^{-8} mho/cm. at 25°C. The choice of triacetin was made on account of its low electrical conductivity, stability, and non-reactivity with the paint film for the duration of the experiment. Because of the low electrical conductivity of the solution used in the experiment, precautions were taken to shield the entire solution system, including the leads, from pick-up of induced e.m.f. Various pieces of the apparatus were also well earthed.

Method of Measurement

The test panel was placed flat, painted side up, in the solution of triacetin and scanned with a probe electrode from end to end, potential values being recorded at regular distances from the boundary. Readings were taken for each distance, the values of potential taken for the construction of the curve being those obtained when the corrosion cell had reached a steady state and when these potentials had remained constant for half an hour. A quick scanning was also carried out along two different paths over the panel to check the uniformity of the potential values. The potentials actually recorded were the potentials in the electrolyte very near the surface of the specimen; reversal of the sign of these potentials gave the potentials on the panel at the various points. The potentials were measured to an accuracy of ± 4 mV.

A variety of pigments, including some commonly classed as corrosion inhibitors, was examined using this technique. For the purposes of convenience the pigments were classified into three categories, *viz*. lead pigments, iron oxide pigments and chromate pigments. In all cases, except where otherwise stated, primers were made from these pigments using pale boiled linseed oil, at a pigment binder ratio of 50 : 50 by volume. They were applied to steel strips in order to provide specimens for the electrical measurements exactly as described previously. The primers were applied in a range of thicknesses from 25μ to 150μ .

LEAD PIGMENTS

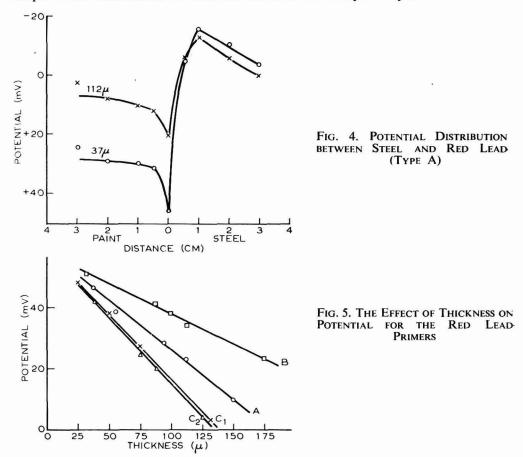
Red lead is possibly the most widely known of all anti-corrosive pigments, and the corrosion inhibiting properties of the different types of red lead pigments were studied. The composition of these pigments is given in Table I.

Гуре	Lead peroxide content (%)	Litharge content (%)
A	28.2	9.3
B C ₁ C ₂	21.7	19.1
C_1	33.0	2.4
C_2	34.7	< 0.1

TABLE I

The potential distribution curves for red lead (Type A) primer at thicknesses 112μ and 37μ are shown in Fig. 4. Both curves show departure from the theoretical "S" shape shown in Fig. 2. The curve for 112μ film thickness is

more compressed than that for the 37μ thickness, indicating that the thicker film afforded the better protection. The same type of curve, showng a deviation from the theoretical "S" curves was obtained for the other red lead primers, indicating that red lead, in addition to providing protection by resistance inhibition, interfered with the anodic and cathodic electrode reactions. This suggests the provision of both anodic and cathodic chemical inhibition by this pigment. The anodic inhibition provided by red lead has been attributed to the adsorption on the anodic sites of hydrolytic decomposition products of lead soaps²⁶. The mechanism of cathodic inhibition is not yet fully understood.



It can be seen from Fig. 4 that, whilst the cathodic inhibition took place from the paint/metal boundary, the anodic inhibition came into effect from a distance of 1 cm. from the boundary. In order to examine this unusual behaviour, experiments were undertaken to ascertain if the particular geometry of the specimen was a contributory factor. Large specimens $(15.3 \times 5 \text{ cm.})$ were used to investigate the possible "edge" distortion caused by the small width of the original specimen. Potential plots were obtained using these specimens. It was found that, despite the changes in the dimensions of the specimens and the precautions taken to obviate the edge effect, this peculiarity of anodic inhibition

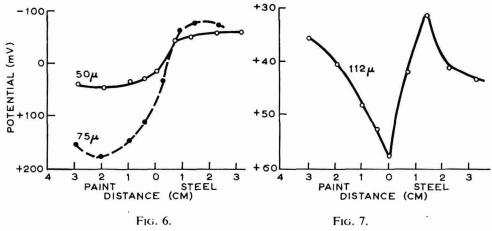
persisted. It is thought that this aspect of anodic inhibition may be attributed either to some intrinsic property of red lead or to the manner by which anodic inhibition occurs.

All other things being equal, the protection provided by a paint film appears to be a function of film thickness, which was also studied. Curves were obtained showing the variation with the film thickness of the potential difference between points at 1 cm. on either side of the paint/steel boundary. These are shown in Fig. 5 and are all approximately straight lines, the potential falling off with the increase in thickness of each coating. This substantiates the well known fact that the greater the film thickness, the greater is the protection provided by a paint. A measure of relative degrees of protection provided by these primers was also obtained from these curves. It was shown, therefore, that the ascending order of merit for the types of red was B, A, C, and C₂ (Table I); this order of merit shows some correlation with the peroxide content of the pigments used. The curves for Type C_1 and Type C_2 , were found to be very near each other. These two pigments contained widely differing percentages of reactive lead monoxide, but their peroxide contents were very similar, from which it might be deduced that the protection provided by red lead is more intimately connected with the peroxide content than with the reactive litharge content.

The other lead pigments examined for their corrosion inhibiting properties were calcium plumbate, basic lead chromate, basic lead silico-chromate, lead cyanamide, white lead, basic lead silicate, lead peroxide and basic lead sulphate. The potential distribution curves for all the primers, with the exception of calcium plumbate, conformed to the theoretical "S" curve shown in Fig. 2, suggesting, therefore, that all these primers provided protection by resistance inhibition only and did not interfere with the electrochemical reactions at either the anode or the cathode.

Although basic lead chromate has sometimes been considered to possess chemical inhibitive properties, no such properties were revealed in the potential distribution curve (Fig. 6). This may be attributed to the sparing watersolubility of the pigment, the less soluble chromates generally proving to be less reliable chemical inhibitors. From the behaviour of the basic lead chromate it was expected that basic lead silico-chromate would also prove non-inhibitive, and this was confirmed. Basic lead silico-chromate was, however, superior in performance to basic lead chromate in that at a 50μ thickness it provided much better protection than did basic lead chromate at 75μ thickness (Fig. 6). This may be attributed to some feature of pigment distribution with the paint film based on basic lead silico-chromate; indeed, it is likely that dispersion and packing characteristics play a not inconsiderable part in the degree of protection afforded.

The potential results from calcium plumbate were rather less reproducible than from other pigments, but the potential distribution curve (Fig. 7) always shows a deviation from the "S" form such as to suggest that this pigment, in addition to providing protection by resistance inhibition, also gave some chemical inhibition. It appeared that this pigment could interfere with the anodic and cathodic electrode reactions, but in thin films the level of anodic inhibition was found to be less than for similar films of red lead. It seemed, therefore, that



POTENTIAL DISTRIBUTION BETWEEN STEEL AND BASIC LEAD SILICO-CHROMATE AND (dotted) BASIC LEAD CHROMATE (FIG. 6) AND CALCIUM PLUMBATE.

(Figures on curves indicate film thickness)

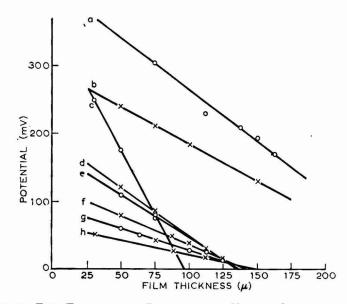
the major protective (chemical) property lay in the effect on the cathodic reaction. This pigment, like red lead, may be classified as chemically inhibitive. The aqueous extracts of calcium plumbate paint films contain quantities of calcium compounds and these are probably closely involved in the inhibition process. Read ^{27, 28} has attributed anodic inhibition to the action of calcium compounds in precipitating iron salts. Alternatively, he suggests that the calcium compounds may be adsorbed on the anodes, thus inhibiting the anodic reaction. The cathodic inhibition is attributed by the same author to the formation of an adherent inhibitive calcium carbonate layer on the cathode by the reaction at the cathode of calcium hydroxide and carbon dioxide. He has, however, pointed out that no such layer of calcium carbonate has been observed underneath a calcium plumbate paint film.

The anodic inhibition of red lead has been attributed by Mayne²⁹ to watersoluble lead compounds (formed by interaction of the pigment and the oil) acting as adsorption inhibitors, *i.e.* blanketing the anode. In contrast, the aqueous extract of a calcium plumbate paint film contains no lead, although, as mentioned previously, the extract does contain calcium compounds. The efficiency of the inhibitive compounds has been shown by Mayne³⁰ to decrease from lead, through calcium, to sodium. Although as already indicated, calcium compounds from calcium plumbate provide some anodic inhibition, it is less than that provided by the lead compounds from red lead.

Of the several lead-containing pigments examined by the potentiometric method, only red lead and calcium plumbate have been shown to provide protection by chemical inhibition. In both these pigments lead is present in the tetravalent state, the tetravalent lead being absent in all the other lead pigments examined except lead peroxide. The provision of chemical inhibition appears at first sight, therefore, to be linked with the presence of tetravalent lead; indeed, Knudsen³¹ has postulated a mechanism involving the quantity of

tetravalent lead, in order to explain the specific rust inhibiting action of plumbates in linseed oil. He has suggested that the carbon-carbon link of a glycol compound, formed during the autoxidation of a drying oil, is broken by tetravalent lead, to yield compounds of the same type as those isolated by Mayne and Van Rooyen, which were found to be inhibitive. He further suggests that, for this mechanism to operate, the pigment should be at least slightly soluble in the vehicle. However, the present observations on lead peroxide indicate protection by resistance inhibition only, despite the presence of tetravalent lead. It may be, therefore, that factors such as the solubility of the pigment in the vehicle, *etc.*, are of great importance and that lead peroxide is insufficiently soluble for the chemical features outlined by Knudsen in this paragraph to come into play.

For all the primers tested, increasing the thickness decreased the potential values (Fig. 8), indicating again the dependence of protection on film thickness. The same experimental curves indicated the relative degrees of protection afforded by the primers, the ascending order of merit being white lead, basic lead chromate, basic lead sulphate, basic lead silicate, lead peroxide, basic lead silico-chromate, lead cyanamide and calcium plumbate. The basic lead sulphate primer proved particularly interesting in its very rapid decrease in potential with increasing thickness. The slope of the thickness/potential curve for this pigment was quite different from those of the curves for the other pigments. This gave the rather unusual indication for a paint film that no further improvement in protection would occur after a thickness of 100μ ,





(a) White lead

(b) Basic lead chromate

- (e) Lead peroxide
- (f) Basic lead silico-chromate
- (c) Basic lead sulphate (
- (d) Basic lead silicate (h) Ca
- (g) Lead cyanamide
 - (h) Calcium plumbate

whereas most of the others went on improving up to $130-150\mu$. Judged in this way, basic lead sulphate is a much better pigment than is suggested by the order of merit stated above, which was based on the experimental data taken at more normal film thicknesses in the 25 to 50μ range.

IRON OXIDE PIGMENTS

The corrosion inhibiting properties of five iron oxide pigments, viz. Spanish oxide, Indian red, purple oxide, black oxide and Burntisland red were investigated. The potential distribution curves for all the iron oxide-containing primers conform to the theoretical "S" shape curve. The distribution curve for films of Indian red at two thicknesses is shown in Fig. 9. The curve for 125μ film thickness is somewhat more compact than that for the 100μ film thickness, indicating that the greater thickness provided better protection. Since the potential distribution curves were all "S" shaped, this is taken to indicate a lack of chemically inhibitive properties.

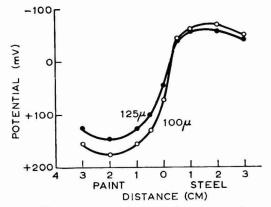
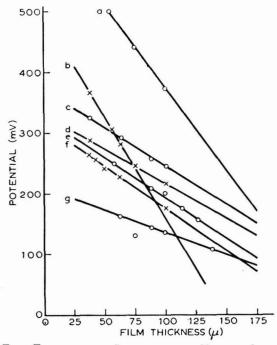


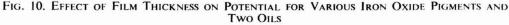
FIG. 9. POTENTIAL DISTRIBUTION BETWEEN STEEL AND INDIAN RED OXIDE (Figures on curves indicate film thickness)

Iron oxide pigments are, of course, widely used as primer pigments for iron and steel, but none of those examined showed any chemical inhibition. It must be remembered that there are many varieties with variable properties even within a given class and that some ferric oxide pigments have been stated to possess inhibitive properties. It is probable, however, that the general value of iron oxide pigments lies mainly in their structural effects on paint films, *i.e.* in assisting the formation of a good physical barrier; indeed, there is little doubt as to the good protection that can be afforded by an adequate thickness of an iron oxide pigments examined were unable to stifle corrosion once it had started and that consequently their value in practical use was likely to be much less than that of truly inhibitive pigments.

Inhibitive properties have been claimed for Burntisland red and similar pigments from bauxite residues, and it has been suggested that such pigments are sufficiently alkaline to act as anodic inhibitors, but insufficiently so to saponify the media. Burntisland red in the present experiments gave indications of neither anodic or cathodic inhibition and was similar to the other iron oxide pigments in the general character of its corrosion protection.

The effect of thickness on potential is shown in Fig. 10. Once again it can be seen that increasing the thickness of each primer decreased the potential values. The same curves gave an indication of the relative degrees of protection provided by the primers, the ascending order of merit being Spanish oxide, Indian red, black oxide, purple oxide and Burntisland red. Although, as stated above, Burntisland red was found not to possess any chemically inhibitive protection, it afforded superior protection by virtue of a high degree of resistance inhibition. This may be attributed to the chemical nature of the pigment, which, by interaction with the medium, results in superior filmforming properties.





- (a) Pale boiled linseed oil
- (b) Linseed stand oil
- (c) Spanish oxide
- (d) Indian red
- (e) Black oxide
- (f) Purple oxide
- (g) Burntisland red

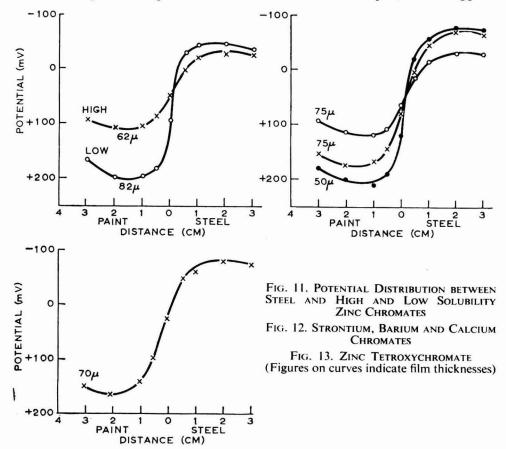
The important role of pigments in improving the structural barrier of oil films may also be assessed from Fig. 10. Unpigmented pale boiled linseed oil and linseed stand oil were examined by the potentiometric technique, and as expected the oil films, of themselves, showed no provision of chemical inhibition. The straight line plots in Fig. 10, however, indicate that linseed

stand oil provides a greater measure of resistance inhibition than pale boiled linseed oil. It is also evident that the incorporation of each of the iron oxide pigments has improved the structural barrier by increasing the resistance inhibition.

CHROMATE PIGMENTS

The pigments examined were the chromates of barium, strontium, calcium, zinc (low and high solubility) and zinc tetroxychromate. The results for basic lead chromate and basic lead silico-chromate have already been quoted. The potential distribution curves for low solubility zinc chromate primer of 82μ film thickness and high solubility zinc chromate primer of 62μ film thickness are given in Fig. 11. The two primers conform to the theoretical "S" curve, and may therefore be regarded as providing protection by resistance inhibition only. However, the curve for the high solubility pigment is more compact than that of the low solubility type, despite the lower film thickness of the former. Zinc chromate of high solubility provides, therefore, better resistance inhibition than zinc chromate of low solubility.

The potential distribution curves for strontium, barium and calcium chromates are given in Fig. 12. All these curves were "S" shaped, which suggests



that these primers also afforded protection by resistance inhibition only. Both calcium and strontium chromates had film thicknesses of 75μ . However, the curve for calcium is smaller than that for strontium, indicating that calcium chromate provides better resistance inhibition that strontium chromate. The potential distribution curve for zinc tetroxychromate is shown in Fig. 13, which is also "S" shaped, indicating that zinc tetroxychromate affords protection by resistance inhibition only.

All the chromate primers afforded protection to steel by resistance inhibition only. For ferrous metals, therefore, it seems likely that chromate pigments of the type examined may be classified as "inert", in the sense that they do not interfere with the electrochemical reactions at either the anode or the cathode. A measure of the relative degree of protection provided by these primers can be deduced from Fig. 14, the primer giving lowest potential value for a given thickness offering the best protection. It can be seen that the ascending order of merit is low solubility zinc, barium and strontium chromates, zinc tetroxychromate, lead, calcium and high solubility zinc chromates and basic lead silico-chromate. These experiments were conducted with paints prepared from pale boiled linseed oil and conclusions and the relative efficiencies derived from the results are strictly applicable to these paints only. It is quite probable that a different order of relative efficiencies would be found with paints prepared from other organic media and synthetic resins which could be expected to change the barrier efficiency of the systems.

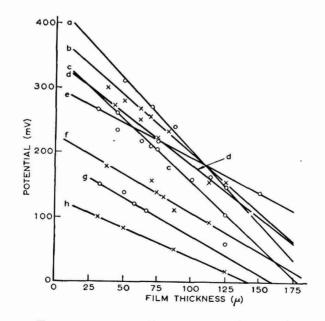


FIG. 14. EFFECT OF FILM THICKNESS ON POTENTIAL FOR VARIOUS CHROMATE PIGMENTS

- (a) Zinc (low solubility)
- (b) Barium
- (c) Zinc tetroxychromate
- (d) Strontium
- (e) Lead
- (f) Calcium
- (g) Zinc (high solubility)
- (h) Lead silico-chromate

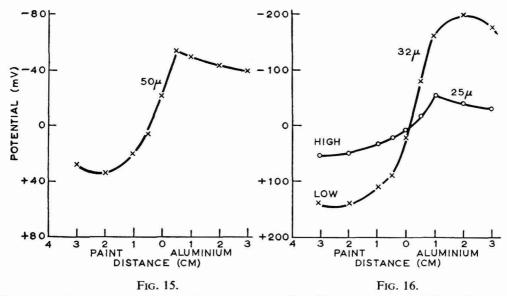
The outstanding corrosion inhibiting properties of chromate ions are well recognised, although the precise mode of inhibition and the nature of the protective film are still controversial. The failure of the chromate pigments to provide any chemical inhibition may be associated with such factors as the solubility of the pigment, the possible presence of corrosion stimulating ions, such as chlorides or sulphates, in the pigment, complex ion formation, *etc.* For chemical inhibition to be operative, it is essential for the pigment to provide an adequate supply of chromate ions at the metal/paint interface. The solubility of chromate pigments is, therefore, most important for corrosion resistance, although other factors may operate in their use in paints. The importance of the solubility factor is borne out by Fig. 12, which shows the protective value of stontium, barium and calcium chromate primers. Of the three, calcium chromate provided the best protection, followed by strontium chromate and finally by barium chromate. The solubility figures for these three pigments as given by Sherman³² are given below.

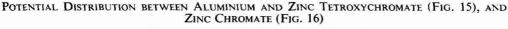
Pigment	Solubility of Chromate in Water at equilibrium (g./l.)
Calcium chromate	17
Strontium chromate	1.1
Barium chromate	0.001

It is clear, therefore, that solubility considerations play an important, though not necessarily a dominant role in the corrosion protection provided by chromate primers. It is suggested that chromate ions oxidise the corrosion products to insoluble ferric compounds which are precipitated within the paint film, and contribute to resistance inhibition by impeding the movement of the ions.

The poor anti-corrosive properties of some of the chromate pigments, as revealed by the potential doin, was confirmed to some extent by the exposure trials made several years ago at Hurst Castle, a highly corrosive marine environment, and at Teddington. Zinc chromate, barium chromate and zinc tetroxychromate primers based on stand oil gave poor protection, filiform corrosion and pitting being severe in some instances. There was no apparent correlation between chromate pigment concentration and performance. Primers based upon calcium chromate, the most soluble of the pigments examined, provided good protection against filiform corrosion and pitting and allowed only mild rust spotting. The importance of the electro-osmotic factor in relation to corrosion inhibition by chromate pigments is briefly considered later.

Since the chromate-containing primers were originally developed for nonferrous substrates, the behaviour of the three zinc chromate pigments, viz. low solubility zinc chromate, high solubility zinc chromate and zinc tetroxychromate, on aluminium substrates was also studied. The potential distribution curve for zinc tetroxychromate of 50μ thickness applied on aluminium is shown in Fig. 15. The plot shows a deviation from the theoretical "S" curve on the anodic area (bare metal) which suggests that zinc tetroxychromate on aluminium surfaces provides some chemical inhibition. As previously mentioned this pigment failed to provide any chemical inhibition on mild steel specimens.





(Figures on curve indicate film thickness)

The potential distribution curves for low and high solubility zinc chromates applied at thicknesses of 32μ and 25μ , respectively, are given in Fig. 16. From these curves it may be deduced that low solubility zinc chromate does not provide chemical inhibition and that high solubility zinc chromate provides anodic inhibition. It is also shown that the high solubility pigment provides much better overall protection than that of low solubility, despite the slightly greater thickness of the latter.

METALLIC PIGMENTS

The two most important cathode reactions in corrosion systems are oxygen reduction to hydroxyl ion, and hydrogen ion reduction to hydrogen. The metal does not participate in either of these reactions. It is therefore possible to prevent corrosion of a metal by making it the cathode and paint the anode of a corrosion system. The paint then affords sacrificial protection. In order to provide this sacrificial protection, a metal pigment must be able to give off electrons to the metal substrate and must be in electrical contact with it. In effect, the metal pigment must be less noble, *i.e.* it must have an electrical potential more negative than that of the metal substrate it is supposed to protect; a sufficient number of the pigment particles must be in electrical contact with the substrate and with each other in order to ensure a continuous passage of electrons to the substrate. The standard e.m.f. series provides an indication whether a metal is capable of protecting another metal in this manner. From the series it is clear that the only metals of any practical significance capable of protecting iron sacrificially are magnesium, aluminium and zinc. The first two metals, in the form of pigments, however, become quickly coated with an oxide film of very high resistance, so that the required current for sacrificial protection is not obtained. Zinc in pigment form is likely to be the only metal capable of providing initial and continuing protection to iron by a sacrificial mechanism. Mayne³³ has measured, by means of a calomel reference electrode, the electrode potential of steel panels coated with various paints pigmented with metallic pigments, and he has shown that neither magnesium powder nor aluminium powder in paints gave the necessary metallic contact with the steel substrate. Zinc dust particles, however, made excellent contact, offering no resistance to the flow of electrons.

The corrosion inhibiting properties of zinc rich primers were examined using the potentiometric technique. The zinc rich primer was made with polystyrene at a pigment concentration of 93 per cent by weight on the dried paint film. Some difficulty was experienced in preparing suitable films, and the reproducibility of the results was not good. However, the potential distribution curve revealed that in all cases the painted area of the steel specimen was the anode, and the bare metal area the cathode of the "contact-couple". The distribution curve for the zinc primer of 58μ film thickness is shown in Fig. 17. The potentials (-E) used in the construction of this curve were those at the end of the six-hour period, since the corrosion took an inordinately long time to come to equilibrium. This confirms that the zinc pigment should provide sacrificial protection to the iron, at least in the early stages of the corrosion process. The sacrificial protection may be expected to last as long as the zinc particles are in metallic contact with each other and with the metal substrate.

Finely divided metallic lead, a pigment of growing importance in protection against corrosion, was also studied by the methods described. The potential

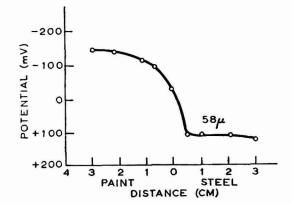
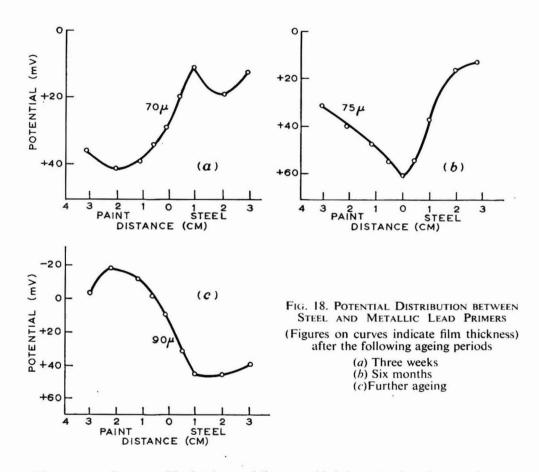


FIG. 17. POTENTIAL DISTRIBUTION BETWEEN STEEL AND A ZINC RICH PRIMER (Figure on curve indicates film thickness)

distribution curve for a metallic lead primer (Fig. 18) showed that, initially, metallic lead, in addition to providing a high level of barrier protection, also provided anodic inhibition. With painted specimens kept a number of months, the same primer showed an indication of cathodic inhibition and subsequently an interesting change in polarity occurred, which suggested that metallic lead was, at this stage, providing sacrificial protection.



The reason for metallic lead providing sacrificial protection is not clear at first, since lead is more noble than iron in the standard potential series. The standard electrode potentials are the calculated or measured potentials of the half-cell when the metal is in contact with a solution of its ions at unit activity. The electrolyte solutions to which the above electrode potentials correspond are very concentrated and are seldom, if ever, met in actual practical corrosion problems. The substitution of more dilute solutions changes the potentials, the change being more marked with some metals than with others because of differing valency. For a monovalent ion a ten-fold dilution results in a shift of potential in the less noble direction by 59 mV, and for a divalent ion by 29 mV. In normal corrosion processes the concentration of the ions involved is much less than 1 gram ion per 1000 g. of water, with the result that the potential relationship of specific pairs of metals may be reversed.

AUTORADIOGRAPHIC STUDIES

As indicated above, potentiometric studies revealed that red lead in linseed oil provided chemical inhibition. This has been attributed to a number of factors, such as the oxidising nature of the pigment, coupled with basicity, good barrier protection by soap formation, and the action of inhibitive ions which are the hydrolytic decomposition products of various soaps. It has also been suggested that red lead primers could provide protection by local deposition of lead. A search of the literature failed to reveal any direct experimental evidence, these inferences about lead deposition being largely derived from experiments using either aqueous extracts, or aqueous suspensions, of red lead.

In view of the possibility of deposition of only minute quantities of lead, and the complexity involved in the analytical techniques for detecting small amounts of lead in the presence of large quantities of iron, a radiochemical technique was adopted to investigate any possible deposition of lead. This technique has the advantage of providing information about the amount and the distribution of such deposition. Using Pb-210, a red lead pigment with a peroxide content of 33.2 per cent was prepared following the normal method and, using this pigment and linseed oil, a primer was made containing 43 per cent pigment by volume.

Three mild steel and two aluminium panels were prepared for this investigation by painting areas 5 cm.² in the centre of the panels with the test paint. The remaining areas of the panels and the edges were painted with a similar, inactive preparation, and the back was protected with a tung oil/phenolic varnish. After ageing for fourteen days, a diagonal scratch was made across the active area. The panels were exposed to accelerated weathering for twenty-three hours a day, five days a week for a total of twenty-five days. After the completion of the accelerated weathering test, the paint films were thoroughly stripped from the panels and autoradiographs of the panels were prepared. The autoradiographs of steel and aluminium panels showed that the deposition of lead on steel was unevenly scattered, except at the regions surrounding the scratch mark. Even in this area, however, there was only a slight deposition of lead, and by comparison, it was evident that the deposition of lead on aluminium panels was even smaller. The surface concentration of lead, as measured by scanning with a colimated Geiger Counter having a small defined acceptance angle, was found to be approximately 15 μ g./cm.² for mild steel and approximately 1.5 μ g./cm.² for aluminium. There was evidence also of a fairly large concentration of lead in the actual scratch on both the steel and aluminium panels.

The deposition of lead is more likely to be anodic than cathodic as indicated by the relatively heavy deposit of lead at the scratch, and the fairly random and sparse distribution of deposited lead. The scratched area is relatively anodic to the unscratched (stress-free) area³⁴, and the painted area is cathodic to the unpainted, *i.e.* scratched area. Both these considerations would imply that, if the deposition of lead is an anodic process, the scratched area should have a

larger deposition of lead with comparatively lead-free areas around the scratch, *i.e.* at the cathodes. An examination of the autoradiographs showed this to be the case. It is probable that during the making of the scratch some red lead was forced into the panel and mechanically trapped. However, the almost total absence of deposited lead on the areas surrounding the scratch mark (the predominantly cathodic areas) suggests very strongly that the deposition of lead was anodic.

The fairly random and isolated distribution of deposited lead also suggests that the deposition was an anodic process. The anodic areas, which are generally pores or breaks in the oxide film are, in the early stages of corrosion, few compared to the much larger oxide covered cathodic areas. As corrosion proceeds this area relationship changes, with the anodic areas gradually increasing. The lack of even moderate corrosion on the steel specimens indicates that the process of corrosion was stifled in its early stages. A cathodic deposition of lead would have shown much greater deposition. The isolated and sparse distribution of lead suggests that lead has been deposited at anodic areas. The lead was deposited much less on aluminium than on steel which was to be expected as aluminium is known, in the conditions of these tests, to corrode less than steel. Essentially the mode of deposition of lead on aluminium is the same as that on steel.

Since aluminium is known to behave as the anode of the aluminium-lead galvanic couple, it has been suggested that the deposited lead, or its oxide, can stimulate the corrosion of aluminium. If, however, the deposited lead, in whatever form, is converted into an insoluble compound, such as basic lead carbonate, this risk is considerably reduced, because basic lead carbonate is not an efficient electronic conductor and would therefore provide a poor cathodic surface. Under certain conditions of exposure, where there is likelihood of the deposited lead being converted into basic compounds, red lead-based primers may be expected to provide adequate protection to aluminium without incurring the risk of accelerated corrosion. This work would indicate, therefore, that one form of protection afforded by red lead is by deposition of lead, although this mechanism in no way detracts from the possibility of other means of protection.

ELECTRO-OSMOSIS

Extensive investigation of water absorption by paint films has been carried out in the past, because maximum resistance to attack and penetration by water is a desirable property of paints. These investigations have been carried out largely on non-corrodible substrates, such as tin-foil, so that the effects of water on the properties of the film alone were observed.

A paint film, when immersed in water, absorbs water at a rate, and to a degree, determined by the difference in osmotic pressure of the aqueous environment and that of the solution formed within the paint film. The transfer of water is dependent on the solute concentration gradient. However, this simple transfer of water through the paint film will be modified when an electric field or gradient is applied across it. The effect in some cases is to increase the transfer of water which is due to osmotic effect only. The transfer of water through a membrane under the influence of an electric field is called electro-

osmosis. Electro-osmosis may be expected to play a significant role in the behaviour and life of a paint coating process, because there is a potential gradient set up between the anodic and cathodic areas of a corroding structure. This potential gradient may assist the transfer of water through the paint film. For electro-osmosis to take place two basic assumptions are necessary, (a) that a network of fixed charges exists, and (b) that a capillary structure of the membrane exists.

The direction of movement of water under a potential gradient depends upon the sign of the electric charge in the membrane. The origin of the charge has been attributed to dissociable groups (probably stray end groups) which form an integral part of the molecules of these membranes. In some instances membranes, devoid of electrochemically dissociable groups, have been activated by the adsorption of dissociable substances of high molecular weight. In the case of electronegative membranes these dissociable groups will be acidic, such as carboxyl groups. The oil bound paint films generally have negative charges which are believed to arise from the carboxyl groups present in the film. Upon immersion in water these groups ionise and the system consists of fixed anions associated with mobile cations. As any current which flows across the membrane is transported by the counter ions of the fixed charge groups, these cations may be displaced if a ready supply is maintained at one side. The paint film is, therefore, cation permeable.

The existence of a charge on paint films is readily proved. When two solutions of potassium chloride, of 0.1N and 0.01N concentrations are separated by a membrane, equally permeable to both ions, no junction potential will develop. However, if the membrane is selectively permeable to one ion only, a diffusion potential will arise, the theoretical value for such a potential being 52 mV. It has been shown by Mayne³⁵ that membranes of linseed oil, polystyrene and coumarone resin gave potentials of 43-53 mV, the dilute solution being always positive to that which is concentrated. This clearly indicates that the charge in these membranes is negative.

It is not clear whether paint films should be regarded as being full of capillaries or be treated as continuous membranes. Electron microscope examinations have so far failed to reveal any definite evidence for the existence of pores or capillaries in a paint film^{36–38}. Woleck and Hains³⁹, by measuring the adsorption of krypton on dried unsupported films of linseed oil, found that these films had a low roughness factor of 1.14, smooth metals having a value of 1.3. From this roughness factor, which is the ratio of the apparent to true area, they concluded that films are free of pores, although at pigment loadings approaching the critical pigment volume concentration, pores developed. It is, however, conceivable that, whilst paint films are pore-free when dry, they develop pores in the wet condition. These pores may be interstices between micelles and present a mosaic of wide and narrow channels.

A study of the role of electro-osmosis was made by Kittleberger and Elm⁴⁰, who used four different types of paint. Their method involved immersing painted steel panels in sodium chloride solutions and comparing the rate and amount of water absorbed by isolated panels with that of identical panels in electrical contact with an area of bare metal. The former yielded the data necessary for

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calculating the water adsorbed under osmotic influence, and the latter furnished data for estimating the water absorbed under a combination of osmotic and electro-osmotic influences. By difference it was possible to obtain a measure of the electro-osmotic factor alone. This method has the two disadvantages that (a) the painted panels were not subjected to the same potential gradient in each case, and the effects measured can be attributed to the differences in the potential gradient, and (b) the osmotic and electro-osmotic factors were not obtained from the same experiment. It is likely that the flow of an electric current through a paint film so changes the properties of the film that the quantity of water then absorbed is different from that absorbed in the absence of a potential gradient. An experimental set-up was devised to obviate both these drawbacks. Experiments were carried out on red lead and red iron oxide primers in pale boiled linseed oil. Preliminary results indicated that whilst red lead absorbed less water, it allowed a larger transfer of liquid through it as a result of electroosmosis. Red iron oxide, on the other hand, retained a much greater quantity of liquid and the amount of water transferred electro-osmotically was much less. It seems that the good protection provided by red iron oxide primers in practice may be attributed to the poor electro-osmotic transfer.

On the same basis it would appear that, since red lead allows a much greater transfer of water, its natural performance should be less protective than red iron oxide. However, red lead primers are shown by potentiometric studies to provide protection by both resistance and chemical inhibition. The chemical inhibition has been attributed to the hydrolytic decomposition products of lead soaps, such as lead azelate, lead suberate, *etc.*, being preferentially absorbed at anodic sites. Since the electro-osmotic transfer of water is towards the cathode, this would very probably result in increasing the concentration of these inhibitive agents in the vicinity of the anodic areas.

The greater electro-osmotic transfer of water through red lead films can be attributed either to large pores or to the difference in magnitude of the charges on the red lead and red iron oxide films. The sign and magnitude of the charge on the pigment will considerably influence the charge of the paint film as a whole. Paint films consist of positively charged pigment particles embedded in a negatively charged medium. It was shown by Wirth⁴¹ with dye absorption tests. that positively and negatively charged areas existed in the films, the positive charges being generally located where the film had been cut with a razor blade. With an inert pigment, such as iron oxide, where the possibility of soap formation is excluded, the positively charged pigment particles would be expected to assert themselves once the insulating envelope of oil has been impaired. The total negative charge, on which the transfer of water by electroosmosis depends, would be accordingly diminished, resulting in low transfer rates of water through iron oxide paint films. In the case of red lead the pigment particles react with the oil medium to form soaps. The pigment particles are, therefore, surrounded by an envelope of soaps which are, however, negatively charged. The influence of the positively charged pigment in the negatively charged medium, is, therefore, likely to be lessened, and the paint film as a whole will retain its negative charge for a much longer time. Consequently, a greater degree of electro-osmotic transfer of water may be expected with red lead films than with red iron oxide films.

The failure of chromate pigments to provide chemical inhibition on steel surfaces as already described, may also be partly explained on electro-osmotic considerations. The prevalent view of chromate inhibition is that inhibition in chromate solution takes place by the dual mechanisms of cathodic depolarisation and anodic polarisation. Since an oil film is negatively charged, it can be expected to hinder the movement of the chromate ions towards the cathodes where they would be expected to undergo reduction. Since the reduction of chromate ions is an essential step in the inhibition of corrosion, any difficulty in this direction is likely to result in impairment of inhibition. If, however, the paint medium is positively charged, this can be expected to facilitate the migration of chromate ions to the cathode and satisfy the condition of cathodic reduction. It is interesting to note that some of the more successful results obtained with chromate primers on steel indicate the use of a more complex and highly developed media as the vehicle.

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DISCUSSION

MR. P. TARGETT asked whether calcium plumbate would be expected to provide better protection than iron oxide at a scratched area on a mild steel panel immersed in sea water.

DR. BHARUCHA considered this very possible.

MR. TARGETT said that when comparing the two pigments dispersed in linseed oil. the corrosion on the scratch with calcium plumbate was much more severe and resulted in penetration in a matter of months, whereas with iron oxide the corrosion spread but did not deepen.

DR. BHARUCHA felt that one probable explanation was that the calcium plumbate provided protection by both anodic and cathodic inhibition, the cathodic inhibition being more marked. It was also known that the cathodic inhibition was highly sensitive and under certain conditions, calcium plumbate films would provide protection by weak anodic inhibition, leading to marked pitting.

MR. P. WHITELEY commented that Dr. Bharucha had shown that chromate pigments acted solely by resistance inhibition, and yet had also stated that the more soluble pigments produced the greatest inhibition. He asked whether this indicated that chemical inhibition was also involved.

DR. BHARUCHA said that the chromate ions might oxidise the ferrous ions to insoluble ferric compounds within the paint film and thus introduce an additional resistance in the circuit and thereby reduce the corrosion currents.

MR. A. T. S. RUDRAM added that there seemed to be some difficulty when arguing chemical inhibition. As an electrochemist Dr. Bharucha considered chemical inhibition only as it affected the anodic and cathodic reactions and was inclined to ignore the chemical effects which might take place within the film or at the interface. He thought that the properties of the chromate ions were sometimes not sufficiently stressed.

MR. H. F. CLAY was concerned with the validity of the use of triacetin as the "corroding environment", because he considered that it had a conclusive bearing on the true significance of the results obtained. He said that measurements of potentials in triacetin no doubt gave some indication of the electrical resistance of the paint film, although he doubted whether the method could measure inhibition produced by pigments and thought that Dr. Bharucha's results were misleading. He supported this statement by the following experimental evidence.

(a) Half-painted steel specimens immersed horizontally in the mixture of triacetin and water showed no rust on the bare metal or under the paint film, even after three months' immersion. He contended that it was difficult to see how any measurements on such a panel could be used to assess corrosion.

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(b) A bare steel specimen placed horizontally in triacetin acquired a potential of about +150 mV. on the hydrogen scale, and this showed little overall change during one month. On the other hand the potential of a panel, partially immersed vertically, began to fall after a few days, and after about fourteen days became negative, with the appearance of rust. He suggested that the reason why the horizontal panel did not corrode in triacetin was the lack of oxygen to depolarise the cathodes and to permit the cathodic reaction.

(c) The so-called "soluble pigments", e.g. zinc chromate, were much less soluble in triacetin than in water, which was a good reason in itself for not using triacetin as the electrolyte. The addition of chromate to triacetin produced exactly the opposite effect to that produced when chromate was added to water. If pure triacetin was mixed with 3 per cent of potassium chromate solution, instead of 3 per cent of water, and allowed to stand forty-eight hours, some reduction of the chromate appeared to take place, the solution became water-white, and the pH was lower by about one unit than that of the solution with water. Specimens placed vertically in the triacetin/chromate solution assumed a negative potential within twenty-four hours and showed rusting by forty-eight hours, whereas specimens placed in an aqueous solution of potassium chromate acquired a positive potential and did not rust.

(d) Hancock and Mayne had stated that a number of anodic inhibitors functioned by limiting the anodic area, so that a high current density was produced at the remaining active anodes which were thereby sealed. If this hypothesis were correct, these inhibitors could not function in triacetin solution, having a conductivity of 10^{-9} mho.

DR. BHARUCHA replied that the experiments carried out with partially immersed specimens were complicated by water-line corrosion and that was the reason for working with specimens immersed flat. He did not know what significance should be attached to partially immersed vertical panels. As far as the choice of electrolyte was concerned, he thought that the important point was not the identity of the electrolyte, but the interpretation of the results obtained. He also said that with regard to the lack of detection of corrosion, the process occurred very slowly and rust was observed on his specimens when left over a period of about three days.

MR. K. REISER asked what the dielectric constant was of the electrolyte, because he thought that many of these mechanisms were dependent on ionisation and the degree of dissociation, both of which were dependent on the dielectric constant. He suggested that some progress might be obtained by measuring the degree of dissociation obtained with certain soluble or critical pigments.

DR. BHARUCHA stated that he had not measured the dielectric constant, but he thought that this might provide some useful information.

MR. H. A. NEWNHAM suggested that the work might be extended by the addition of sulphuric acid or sodium chloride to the triacetin/water electrolyte, and he asked whether Dr. Bharucha thought that this would alter the type of curve obtained.

DR. BHARUCHA said that the addition of chloride ions would destroy inhibition and he doubted whether an increase in the aggressiveness of the medium was justifiable.

MR. NEWNHAM added that the progressive relative performance of a pigment might be changed by the addition of an electrolyte to the triacetin/water mixture.

DR. BHARUCHA stated that he had not tried any electrolyte other than triacetin but agreed that such a programme might be a possible extension to the work.

DR. F. WORMWELL said that the electrolyte used was so unusual that the onus was on the author to show that the behaviour was similar to that in more usual electrolytes and that had not been achieved. He thought that the absence of corrosion of the bare metal was disturbing and that the treatment of the electrochemistry seemed

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to have been over-simplified. The potentials measured were compromise potentials and referred to points in the solution not to the metal itself. He also inquired as to the influence of time on the measurements, because he considered that the time factor was all-important in deciding whether the paint was going to protect or not. Conclusions had been drawn about the resistance inhibition, but he asked whether the author had carried out any measurements of the electrical resistance of the paints to support these conclusions.

DR. BHARUCHA replied that no electrical resistance measurements had been made, and with regard to the time factor, the potentials were obtained when the corrosion reached a steady state. The potential did not alter appreciably with longer periods of time seemingly indicating that a state of equilibrium was almost reached. The potentials measured were in fact compromise potentials in solution. Reversal of the sign of the potential, however, gave the potential on the metal. As far as comparison with other electrolytes was concerned, the results obtained by the potentiometric technique were very full and were borne out by exposure trials so that they seemed to be reasonably comparative.

DR. O. LIEBERMANN discussed the influence of impurities in the pigments, especially soluble chlorides in chromate pigments, and referred to the work carried out by Pourbaix in Brussels. Working with very pure pigments he had shown that the anodic passivation of iron and steel was destroyed by the addition of sodium chloride solutions and that the concentrations of those solutions was an important factor. He thought that 0.01 mole of sodium chloride was the critical concentration to cause this destruction. The lecturer had not observed anodic, but only resistance inhibition with chromate pigments. He asked whether this was due to the use of relatively impure pigments and if any attempt had been made to control the impurities and suggested that with purer pigments the observations might have been totally different.

DR. BHARUCHA replied that he had pointed out that the failure of the chromate pigments to bring about chemical inhibition might have been due to the presence of chloride or sulphate ions. He had used commercial pigments and there was no control over the impurities.

DR. T. WHITE congratulated the lecturer on a technique of considerable value but regretted the absence of any reference in the lead pigment group to lead tannates. He said that certain of the lead tannates, like red lead, showed chemical inhibition, and in relation to the effect of thickness of film, a lead tannate film containing 20 per cent lead gave protection comparable with a red lead film containing 90 per cent lead. It would seem, therefore, that in the red lead film the amount of lead present was something like four to five times that necessary for protection. He suggested that when atomic lead was combined with fairly large labile hydroxy groups, it was possible to get better protection than by other techniques.

DR. BHARUCHA agreed that inhibitive properties of the anodic type were shown by lead tannate.

DR. BHARUCHA (in a written contribution) amplified his reply to the points raised by Mr. Clay (page 538) about the validity of the use of triacetin as the electrolyte. He said that the triacetin solution had a very low conductivity, and it was, therefore, not surprising to find that the corrosion process was considerably reduced and the appearance of visible rust very much delayed. On specimens coated with unpigmented pale boiled linseed oil and left in triacetin solution for three days, it was possible to detect a slight but very definite trace of corrosion at the metal/film boundary. The schematic representation of the contact couple formed by a half-painted specimen (Fig. 1) showed that the current density was highest at the painted/bare metal boundary and corrosion was likely to be confined to just this area. With regard to the tests carried out by Mr. Clay, the most important point was that the present technique was designed to test the mode of inhibition within a paint film. The results of tests carried out on bare panels immersed in the electrolyte plus an inhibitor could not be used to invalidate the results obtained with actual paint films. Moreover it had been emphasised in the literature that the single potential of metal specimens was not a dependable guide to the corrosion rate. As pointed out in the paper the single potential may move in an anodic or cathodic direction or may even remain nearly the same though the corrosion rate may be altered by several orders of magnitude as a result of some treatment. In fact it was dissatisfaction with just this method which had led to the present technique.

It was true that pigments, such as zinc chromate, were much less soluble in triacetin than in water, although it was not clear why this was a good reason in itself for not using triacetin as the electrolyte. It was a fallacy to assume that, at the paint/metal interface, the nature and composition of the solution was the same as that in the bulk of the electrolyte. During the oxidative drying of the paint film several acids and acidic materials were formed. The pH of the aqueous extract of an oil film had been found to be highly acidic, at least in the early stages of its life. The important consideration was, therefore, not the solubility of the pigment in water, but in the highly complex acid solution inside the paint film. The objections to the use of triacetin would be more convincing if it were shown that the corrosive environment under an oil film were relatively simple and well defined. It was fair to suggest that triacetin solution was probably a good deal less complicated and artificial an electrolyte than would appear at first sight.

Hancock and Mayne explained the action of non-oxidising inhibitors in terms of the action of oxygen and the remarks of these authors should be considered in this context. In oxidising inhibitors, such as chromates, the role of oxygen was likely to be subsidiary and a number of other important factors arose in chromate inhibition, such as tafel slope, exchange current, *etc.*

Reviews

LABORATORY MANAGEMENT AND TECHNIQUES

By J. A. EDWARDS. London: Butterworths Publications Ltd., 1960. Pp. 224. Price 35s.

In this volume of some two hundred pages the author has succeeded in giving an outline of most aspects of the work of laboratory administration. He ranges from planning, building and equipping a new laboratory and its ancillaries, to the safe working of the personnel occupying the buildings and the provision for their material and personal needs. Side by side with the broad outline are many helpful "tips" gathered during the author's long experience.

The inclusion of eighteen pages dealing with various aspects of safety is indicative of a welcome change in the outlook of laboratory supervisors over the past twenty-five years. Perhaps in the paint trade, one is unusually aware of the hazards involved; nevertheless, the commercial availability of many novel raw materials and intermediates emphasises that safety precautions are a matter that needs constant review.

Because of his background and experience, Mr. Edwards inevitably thinks mainly in terms of university laboratory practice and draws most of his examples from this field. It follows, as the author indeed admits, that the details will need modification and interpretation in order to be applicable to any industrial laboratory. This in no sense detracts from the value of the book. It would indeed have proved an impossible task to take note of all the possible alternative requirements, even if many times the present number of pages had been allowed for the exercise. The precise requirements of each industry and even each company within one industry will vary, and the ultimate plans and procedures will also bear inevitably the stamp of the personal preferences, and sometimes, unfortunately, the personal prejudices, of both the departmental manager and the laboratory supervisor.

Two examples from our own industry will serve to emphasise this point. One company doing research on resinous polymers will need substantial facilities for synthetic organic chemistry, involving laboratories fully equipped with fume extraction and all the usual services. By contrast, another firm may devote most of its attention to formulation of surface coatings where a much less elaborately furnished laboratory will allow very satisfactory work to be done. Again, we must inevitably keep many storage samples, hence the stores must be organised for this service as well as for dispensing apparatus and chemicals.

What Mr. Edwards has done, and what makes his book a valuable addition to the literature of laboratory management, is to list the headings that must be considered at all stages of laboratory operation. With this book before him there is no excuse for the planner or administrator to overlook any significant requirement for smooth and efficient operation of his laboratory.

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F. G. NOBLE

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SYSTEMATIC QUALITATIVE ANALYSIS: AN INTRODUCTION

By G. A. MORRISON, London: Butterworths Publications Ltd. 1961. Pp. ix + 198. Price 25s.

At one time the boundary between qualitative and quantitative analysis scarcely existed. The same basic methods were used in each, and a method became quantitative when an isolated compound was weighed. The development of spectroscopy in all its forms, and, to a lesser extent, of paper chromatography, has removed the need for chemical identification methods for most substances.

The author describes in his preface how the book arose from a set of notes for first year university students, and was subsequently expanded to help older students. In a book of this size it is impossible to deal adequately with both the common and the rarer metals. The most important chemical principles may be observed very fully in the analysis of mixtures of the common metals, leaving the rarer metals to be studied as single substances. By omitting the expanded scheme, the first chapter, *Theoretical Introduction*, could have been usefully enlarged. Some treatment of coprecipitation would have been of value here.

A chapter on Apparatus and Techniques is followed by a description of preliminary tests and of methods for obtaining a solution of the mixture. This follows mainly the usual procedure. The tables quoting the solubilities are too incomplete to give full value. Since most of the acids quoted give largely soluble salts, a tabulation under acids, quoting insoluble salts, would have been more useful. There are also many misleading entries in the tables, *e.g.* aluminium fluoride, given as soluble in water, is nearly always supplied as the insoluble anhydrous salt. In the section dealing with insoluble materials, the suggestion that stannic oxide should be fused with potassium cyanide cannot be recommended.

The chapter describing the theory of group separations is very well set out, and the tables showing how much of the various metals might be left in solution are very useful. The methods for carrying out the separations within the groups are set out in a convenient semi-tabular form, and a progressive system used for labelling the precipitates and solutions obtained is very helpful. Several new methods of separation have been introduced. A good system is given for the identification of anions, by their reactions with a series of reagents such as barium chloride and silver nitrate.

The book is well set out and the style is pleasant, in spite of the demands of brevity, although some people may not approve of the use of "supernatant" and "ferric" as nouns. By using the methods set out in this book for mixtures containing properly selected compounds, students should obtain, as quoted in the introduction—" . . . a working knowledge of chemical principles, and of the main properties of elements and compounds." R. E. COULSON

PROCESSING OF THERMOPLASTIC MATERIALS

Edited by E. C. BERNHARDT, New York: Reinhold Publishing Corporation, 1959. Pp. xv+690. Price 146s.

This volume is the second of a series of plastics engineering volumes sponsored by the Society of Plastics Engineers Inc. It is a collection of articles by twenty authors, who have contributed eleven chapters on a comprehensive range of subjects, covering all aspects of the processing of thermoplastic materials. The book is divided into three sections: Section 1 deals with Fundamentals, Section 2 with Applications and Section 3 with Processing Properties.

The first section deals with basic material properties and flow behaviour of thermoplastics. Heat transfer and thermodynamics are treated in a chapter which does not claim to be a unified treatment of these sciences, but which nevertheless manages to give excellent explanations and examples thereof. The final chapter in this section is that on the increasingly important aspect of mixing and dispersing. A fine line of definition is drawn between mixing and dispersing in that the former is defined as the interspersing in space of two or more components, one with the other, and the latter is defined as the process in which some intrinsic change takes place in the physical characteristics of one or more of the components. These definitions, which are perfectly correct, particularly when dealing with plastics, might give rise to some discussion amongst chemists who also handle other materials. The chapter deals fully with the theory behind mixing and also, to a lesser degree, that of dispersion. It is complete and detailed, maybe too much so, as one would suspect this chapter might be too complicated for the majority of processing engineers and technicians. A following chapter on Mixing and Dispersing Processes will be found much more useful and practical.

Section 2 on Applications occupies the greater part of the book. Subjects dealt with in a competent manner are extrusion, injection moulding, calendering, mixing and dispersion processes, sheet forming, forming of hollow articles, sealing and welding of thermoplastics, which gives an idea of the range covered. Each chapter is complete and as up-to-date as can be expected, considering the justifiable delay from conception to publication. Nevertheless a remarkable wealth of information has been accumulated which will greatly assist those engaged in plastics technology, and the editor is to be congratulated on its compilation. The book will serve a useful purpose in focusing attention on the possibilities available when such physical data are correlated to performance. This section covers the design of the major categories of thermoplastic processing equipment, and usefully shows how equations may be arrived at which will indicate and describe the behaviour of various plastic materials in any particular piece of equipment. As this is the ultimate aim of the engineer dealing with plastic processing, this section will be found to be particularly helpful to him in calculating and predicting the performance of his plant from the information available.

The final section, that on Processing Properties, is a useful, one might say necessary, compilation of available information on the properties of acrylic, cellulosic, nylon, polyethylene, styrene and vinyl resins. A wealth of information is given on a remarkable cross-section of resins under each of the above types. This information, which has been supplied by the respective resin manufacturers, has been transposed into a standard set of units and information plotted on standard graphs. The advantage of this is obvious and very welcome. Necessary processing data are provided, *e.g.*, density, melt index or flow index, and various graphs involving apparent shear rate, apparent viscosity, density, shear stress,

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etc. The processing engineer will find this a convenient reference book on its own.

Generally speaking, this volume presents a selected collection of up-to-date data and work done on the applications of basic engineering theory as applied to commercial polymer processing equipment, and to the study of the performance of thermoplastic processing equipment, using available data on the viscose and thermal properties of the resins. It is an ideal combination of text book and reference book. It is primarily written for the engineer, but would be nevertheless a valuable addition to the library of anyone connected with the technical aspects of the plastics industry.

G. ANDERSON.

MICHAEL FARADAY: A LIST OF HIS LECTURES AND PUBLISHED WRITINGS

By A. E. JEFFREYS. London: Chapman and Hall Ltd., 1960. Published on behalf of the Royal Institution of Great Britain. Pp. xxviii+86. Price 42s.

"Catalogue", when it appears in a review of a scientific book, is usually an unfavourable comment. This is a catalogue, pretends to be no more, and it is fascinating. It engenders many reactions. One relates to the great amount of Faraday's work, as there can be amazement at the number of paintings by some old masters: "how did he do it all in one lifetime?" Another relates to its great diversity. Much of it was original work, but he manifestly enjoyed probing the implications of other people's experiments, and he was often called to give technical evidence before official commissions, and to pronounce on matters of industrial and even legislative significance: hence an epitomising index reference: "Ventilation: of lamp burners of lighthouse lamps, of mines, of House of Lords."

In order adequately to indicate the range, would be to give the book's index in full; it cannot be summarised unless by saying that it substantially covers the science and a good deal of the technology and even metaphysics of his time. How can one select a dozen or so representative entries from hundreds as widely different as "Aetna wines", "artificial ruby", "balloons", "boracic acid", "copper bi-sulphuret", "diamond", "fumigation"; to "plumbago and pencils", "silicified plants and fossils", "spiritualism", "tannin", *etc.*; to "Whig and Tory patronage of science and literature", and on to "zinc, muriate of", even without including any of those studies on which his fame mainly rests?

After a foreword by Sir Lawrence Bragg, and an author's introduction explaining the scope and giving the historical background, the presentation is chronological, from 1816, four years after Faraday went to the Royal Institution as Humphry Davy's assistant, to 1866, the year before his death. There are 482 entries covering books (there are only three: "Electrical Manipulations", 1827, and two collections of articles in book form, "Experimental Researches in Electricity" 1839, and "Experimental Researches in Chemistry and Physics", 1860), articles and periodicals, lectures and papers read before societies, extracts from parliamentary papers, and a selection of

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sermons (he was a member of the Sandemanian Christian sect). Some additional notes cover reprints and other publications which appeared later, and there is a list of the main biographies. Each entry gives title, and book or journal references.

"Lectures" are noted separately from papers given before societies, for to Faraday a "lecture" was an especial kind of exposition, transcending a mere verbal report, which in kind can still be enjoyed in the traditional Royal Institution discourses. He gave courses of lectures at many other places; for twenty years he was a lecturer at the Royal Military Academy, Woolwich, and it is interesting to learn that in 1835 he had material for fourteen lectures on electricity to medical students at Guy's hospital. Unfortunately, these were never published and figure only in a note in the author's introduction.

To dwell finally on his lectures is, however, a temptation irresistible to a reviewer who has just read Faraday's "Advice to a Lecturer", recently reprinted by the Royal Institution, and who, as a member of our mature but less ancient Association, is not uninterested in the art. It too should be read by all who aspire to effective transmission of scientific findings and ideas.

S. H. BELL.

Correspondence

THE BEHAVIOUR OF TITANIUM DIOXIDE PIGMENTS IN HIGH SPEED IMPELLER DISPERSION MILLS

Mr. D. G. Dowling's article entitled "The Behaviour of Titanium Dioxide Pigments in High Speed Impeller Dispersion Mills" in the March, 1961, issue of the *Journal* contained many points of interest, yet I cannot help but feel that Mr. Dowling's use of fractional factorial designs is quite unsound.

First, Mr. Dowling's use of the $\frac{1}{8}$ fractional factorial, of course, requires analysis of the variables in groups of eight aliases. To choose on *a priori* grounds one alias as "important", to the exclusion of seven others, assumes remarkable prescience. In a little known process where significant interactions are probable, such a practice strikes me as being somewhat lacking in caution. The normal procedure would be to test several additional blocks of the complete 2^7 design so that significant aliases could be separated to a more meaningful degree.

Secondly, Mr. Dowling's method of estimating error seems open to unlimited bias. If high order interactions are to be combined to form an estimate of error, surely the choice of which interactions be included should be made prior to gathering data. In choosing "small" sums of squares for his estimate, where, and on what grounds, does Mr. Dowling draw the line?

> R. E. CUTFORTH, 29 May, 1961.

Pittsburgh Plate Glass Company, P.O. Box 127, Springdale, P.A., U.S.A.

I realise that there is some justification for the comments Mr. Cutforth has made, although I feel that it is only fairly applicable if my paper is treated as an exercise in statistics rather than a practical study of paint milling, and would, therefore, wish to put the matter into its correct perspective.

High speed impeller dispersion of pigments is a relatively new technique. If my publication was to be of practical value to the paint industry, it was essential that the results, whilst reliable, should be made quickly available. After due consideration of the factors involved, based on a literature survey on agitation mixing, general experience of pigment dispersion, and the three preliminary experiments described, it was decided that a comprehensive evaluation was prohibited, and that some pruning was essential.

Seven factors were, therefore, chosen for investigation and, with the assistance of a respected text on the subject, the $\frac{1}{8}$ fractional factorial experiment was designed. Each of the seven main factors could be identified free from other interactions, the twenty-one first order interactions identified in seven groups each of three aliases, and an independent estimate of error made, on the reasonable assumption that their aliases, *viz.* second and higher order interactions, were relatively non-significant in their effect. Naturally, there was some risk entailed in this procedure—this risk is implicit to a degree in all fractional experiments—but as this experiment was only intended to be a step to further evaluation, I considered the small risk justified by the economy of working and the possibility that the initial choice of factor levels was inappropriate, and new working levels might be required in subsequent work.

In assessing the results, the small sums of squares were only combined with the preselected error sum of squares to form a combined estimate of error after an initial assessment had been made (I realise that this is not clear from the text, but as the paper primarily concerns the milling of pigments, I endeavoured to include only a minimum of the statistical method and calculation) and due caution was observed when it appeared likely that a confusing alias could influence the variability (e.g. p. 199, para. 2).

When the results of the $\frac{1}{8}$ fraction had been assessed, there was evidence that the initial choice of certain factor levels was inappropriate. I therefore designed a further $\frac{1}{2}$ fractional experiment with different factor levels as an alternative to testing additional blocks of the complete 2^7 design, the procedure you describe as normal, merely for the theoretical satisfaction of eliminating confusing aliases. I was thus able to remove the one source of confusion of which there was some evidence, and also progress towards the ultimate goal in one operation.

I feel, therefore, that it is hardly fair comment to say I applied prescience or showed lack of caution, although I admit that I applied a certain amount of experience in planning the experimental work, something frequently done by practical workers. I suggest that I may have erred in using the phrase "a priori" in the text, and in deliberately omitting detail when describing the statistical method and calculation. Nevertheless, the interest shown in the work has led me to believe that its publication was useful and timely. The conclusions have stood the practical test in that good quality decorative paints may be consistently and rapidly made by their implementation, taking due account of the problems involved in scaling-up to plant size equipment, and I therefore feel that the work attained its objective.

British Titan Products Company Ltd., Billingham, Co. Durham. D. G. DOWLING, 29 June, 1961.

THIRD AUSTRALIAN CONVENTION

Leura, New South Wales, 15-18 June, 1961

The Third Australian Convention, organised by the New South Wales Section, took place at the Ritz Hotel, Leura, from 15-18 June, and was attended by 154 delegates. The Convention was divided into sessions on Surface Chemistry, Analytical Techniques and Polymer Technology, with Dr. J. O'Connor, Dr. A. Bryson and Mr. M. Glaser, respectively, in the Chair. The final session took the form of a Quiz Session, under the Chairmanship of Mr. E. V. Collins. An indication of the scope of the papers presented at the sessions is given below. Several photographs taken during the Convention will appear in the September issue of the *Journal*.

SURFACE CHEMISTRY

Recent Advances in Surface Chemistry, by Professor A. E. Alexander.

Surface phenomena were so ubiquitous in the surface coatings industry that it was only possible to outline certain aspects. Elaboration was given to certain problems encountered in the lecturer's laboratories. These problems ranged from the comparatively simple, such as the evaporation of molecules from surface films, through the more complex ones of reactions in monolayers and diffusion of gases through monolayers, to the extremely complex system of emulsion polymerisation.

Some Aspects of the Physical Chemistry of Titanium Pigment Surfaces, by J. Hodgson.

The durability of products pigmented with titanium dioxide was a complex subject which was intimately related to the surface reactions of those pigments. The surface activity of solids in many cases could be explained by their electronic band structures, which explained the electrical properties of the crystals, titanium dioxide being regarded as a semi-conductor. Semi-conductivity in oxides was linked with catalytic activity; titanium dioxide possessed the ability to catalyse certain oxidising reactions. A theoretical treatment of chemisorption on semi-conductor surfaces, as an electronic boundary layer problem, had been developed. The changes in conductivity of a pigment following gas adsorption could not be measured because the pigmentary properties would be destroyed in the process. A suitable experimental method had been developed for determining the oxygen adsorption by titanium dioxide pigment irradiated with ultra-violet light, and some results were given.

The practical aspects of the problem of surface activity were discussed in relation to the durability of finishes containing titanium dioxide pigments. A method of assessing durability was given and discussed in relation to results obtained at Burnie, Tasmania. The effect of coating titanium pigments with various materials was discussed in general terms and various factors were considered.

In zinc oxide pigments, fluorescence in ultra-violet light had been correlated with their chalking characteristics. A parallel comparison in the case of anatase and rutile was not valid since rutile did not fluoresce.

The Role of Surfactants in the Paint Industry, by J. Facer.

The theoretical aspects of pigment dispersion had been given considerable attention in the literature. Surface active agents and the part they play in pigment dispersion had all received attention, but mainly from a theoretical aspect. The selection of surface active agents for specific applications was extremely difficult, and their use in the surface coatings industry appeared to be decreasing, despite the increasing number available. Surfactants had been found more effective when applied to the pigment during manufacture than as an addition to the paint or printing ink. The *Shirley-Ferranti Viscometer* had been used to examine the flow properties of pigments and to demonstrate the effectivity of surfactants. The development of highly dispersed pastes by grinding in the presence of powerful surfactants was described. The difficulties in the use of these pastes in emulsion systems were attributed to a large extent to absorption of surfactant by the pigment.

The familiar problems of flocculation and flotation of phthalocyanine blues in nonaqueous media were seldom solved by the addition of surfactants to the system, but the approach had been towards the development of modified pigments. Attention was given to the use of surface active agents to improve stability and apparent solubility of solvent-soluble dyestuffs.

The possible future use of mixed surfactants or of cationic pigment pastes to print directly on paper, giving water-fast prints without the use of binder was postulated.

ANALYTICAL TECHNIQUES

Colour Control by means of a Tri-stimulus Colorimeter, by W. P. Georgans.

The paper began with an outline of the C.I.E. system of colour specification and of some of the concepts arising from it. An attempt was made to show that the colour analogue of three-dimensional spatial separation could be used as a measure of colour difference.

This was followed by a very brief outline of some of the instruments (both spectrophotometers and colorimeters) which were currently available for the specification of colour. Some idea of the relative sensitivity of the colorimeters was given. The paper concluded with a discussion of some of the problems that would be encountered in attempting to apply any tri-stimulus colorimeter to the routine control of paint colour.

Paper Chromatography Techniques—with Particular Reference to Food Dyes, by Dr. A. J. Ryan.

The general principles of chromatography were outlined with emphasis on partition chromatography and its extension to strips of filter paper as the inert support. The choice of suitable solvent systems and types of paper was discussed. Techniques and apparatus for both qualitative and quantitative analysis were described. The application of paper chromatography to dyes used as food colours, particularly the watersoluble dyes, was discussed.

Quality Control in the Paint Industry, by J. Hall.

Quality Control in the paint industry involved collaboration in various aspects of formulation prior to production. The works chemist needed to be highly practical and experienced in formulation, in order to be qualified for control and salvage operations. Co-operation with standardising bodies was essential. A uniform system of inspection and release was proposed, in order to rationalise the diverse departmental systems now operating.

Restrictions in respect of the economic contents of batchwise testing specifications were suggested, and an orderly classification of test methods was proffered as a basis for simple, brief, explicit and comprehensive presentation of testing specification.

POLYMER TECHNOLOGY

Recent Developments in Isophthalic Alkyds, by P. W. Stevenson.

Isophthalic acid was discussed, with particular reference to those characteristics in which it differed from the other phthalic isomers. Its advantages were being exploited by the synthetic resin and paint industry in the United States and elsewhere. Utilisation of the material in the manufacture of alkyds, unsaturated polyester and other high polymers was also discussed.

Speculations on and Practical Applications of Polyurethane Coatings, by F. Mort.

The electrophilic character of the isocyanate group was explained, and the effect of associated structures on its reactivity with alcohols, water, amines, ureas and urethanes, was discussed. The mechanism of reaction of isocyanates with alcohols in the presence of tertiary amines, with carboxylic acids and with water was outlined.

The formation of dimers and trimers and their reactions was discussed and an indication was given of various catalysts for the urethane reaction and of their relative activity. Some reasons were presented for the outstanding properties of the polyure-thanes and some of their limitations were explained.

Vinyl and Acrylic Modified Alkyds, by Dr. D. H. Solomon.

The properties of vinyl and acrylic modified alkyds, prepared by combining preformed addition polymers with alkyd resins, or alkyd resin components, *e.g.* monoglycerides, by means of esterification reactions, were discussed. The advantages of this technique included its application to alkyds based on non-drying oils, and the control of the molecular weight of the addition polymer. The degree of reaction between the alkyd and vinyl-acrylic components might also be varied within specified limits. The modified alkyds had shown promise in automotive enamel and undercoat formulations, particularly when used in conjunction with melamine-formaldehyde resins.

New South Wales Section

THE DISPERSION OF Tioxide PIGMENTS IN MODERN DAY MACHINERY

On 13 April, ninety-six members gathered at the MLC Building, North Sydney, to hear Mr. I. C. R. Bews, the Honorary Editor, lecture on "The Dispersion of *Tioxide* Pigments in Modern Day Machinery." Typical mill-base compositions were illustrated by slides on three component graphs, and the balancing of pigment, solvent and resin to achieve optimum milling was shown by a shaded area. Among the milling equipment discussed in detail was the ball mill, the kinetic mill, the sand grinder, the high-speed impeller mill, the three-roll mill, the attrition mill, and the uniroll mill. A twenty-minute film illustrating the loading and running of these machines was also shown.

At the conclusion of the paper, slides illustrating emulsion paints on rough and smooth concrete were shown, the panels having been given a twelve months' exposure period at Carlton, County Durham. The paint systems examined and discussed by Mr. Bews were acrylic emulsion, copolymer and homopolymer p.v.a. emulsion. It was mentioned that in heavily extended paints the grade of extender had a significant effect on rate of chalking, resistance to checking and cracking and tint retention. Of the extenders examined, the best chalk resistance was shown by barytes, followed by whiting, talc and china clay, in that order.

At the conclusion of the lecture a vote of thanks to Mr. Bews was proposed by Mr. K. Ellis, the Honorary Secretary of the Section, who also expressed satisfaction regarding the record attendance.

L. R. R.

INFORMATION RETRIEVAL SYSTEMS

On 11 May the Section had the opportunity of inspecting an I.B.M. system on information retrieval and sorting and printing equipment, through the courtesy of The Mutual Life and Citizens Assurance Co. Limited. This was followed by a lecture by Mr. I. J. McAulay of I.B.M. Australia Pty. Limited, who discussed the various types of information retrieval systems, with particular reference to chemical compounds.

1961

Fifty-three members attended and there was a spirited discussion covering such questions as stock control, sales forecasting and the suitability of different types of systems covering chemical operations, including simulated operation research programmes. Mr. T. Backous, in proposing the vote of thanks to the speaker, complimented him on his lucid presentation of a complex subject, so that the fundamentals became obvious even to those who were not familiar with this type of equipment.

J. H. F.

South African Section

ORGANIC PIGMENTS-MODERN TRENDS

At a meeting of the Natal Branch on 9 March at the Marine Hotel, Durban, Mr. J. Smethurst of the Geigy Company Ltd., Manchester, England, lectured on "Organic Pigments-Modern Trends". Mr. Smethurst commenced by saying that the United Kingdom Members of the Association asked him to convey their warm greetings to the South African Section. He said that he had worked as a team with Dr. D. M. Stead, Dr. W. Carr and Dr. F. M. Smith and he would like to thank them for their contribution to the paper that he was about to read. The speaker then gave a comprehensive survey of two separate fields of pigments being manufactured. The new types of pigments entering the market, the attempts to improve the physical properties of pigments and the recent developments in pigment pastes. He emphasised that the manufacture of specialised pigment pastes was an important section of pigment producing industry, and that its importance might well increase. On a long term basis, pastes might be only an interim measure and later pigment powders might be produced in physical forms that have all the advantages of the pigment pastes, without the disadvantages. Mr. Smethurst said that the pigment industry was not standing still but was working steadily to produce the pigments that the industry required, in the best physical form for their use.

An interesting discussion followed, in which Mr. Ward, Mr. Lavender, Mr. Hill, Mr. Draper and Mr. Hart took part. The main discussion centred around the dispersion of pigments in resins, the effect of universal colourants on oil phase films, the type of pigments recommended for p.v.a. emulsion paints, white organic pigments, dyeing viscose and the printing of *Terylene*. Mr. W. Jackson proposed a vote of thanks to the speaker.

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August

NOTES AND NEWS TORQUAY CONFERENCE DIARY



All photographs shown in the Diary, other than that on page 555, by Marsden & Batley, Torquay] The President, Mr. P. J. Gay officially opening the Technical Sessions. On the right is Dr. J. B. Harrison (Honorary Research and Development Officer, and Chairman of the First Session), and on the left is Mr. G. Phillips, the first lecturer.

took place this year in Torquay, Devon, energetic to venture à pied. During the from 30 May to 3 June. The Conference, Conference week the sunshine was prac-entitled "Physics in Surface Coatings", tically continuous. Torquay as "Queen of was centred on the Palace Hotel, where the the English Riviera", could hardly have Technical Sessions and all the major social been more regal. functions were held. The attendance at the Conference was over 420 and as it was not possible to accommodate everyone in the evening of Tuesday, 30 May, and the first Palace Hotel, rooms were allocated in four Technical Session took place the following other delightfully situated hotels: the morning under the Chairmanship of Dr. Babbacombe Cliff, with its distinctive J. B. Harrison, the Honorary Research flavour of architecture, the Osborne, and Development Officer. Having assured overlooking one of the most beautiful the assembled company that he would not seascapes for miles around, the Queens, a get involved, as at Edinburgh in 1959, with mere twenty yards from the picturesque the complexities of classical music, he harbour, and the Victoria, set high in the asked the President, Mr. P. J. Gay, to centre of the town looking seawards. An declare open the Conference. The pattern efficient arrangement of coaches ensured of the Technical Sessions each day was that easy access to the Palace Hotel for the the lecturers elaborated briefly on the Technical Sessions and the social functions, substance of their papers and then the although the weather and the distances Chairman called for questions. At the end

The Association's biennial Conference involved were such as to tempt the more

The Conference assembled on the

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The considerable interest aroused by the lecturers and their subjects is reflected on the faces of those attending the Technical Sessions.

of the Session time was allowed for Dancing continued until midnight, with a questions to any of the morning's authors. brief interval when members were shown a The first speaker was Mr. G. Phillips on brilliant exhibition of ballroom dancing. "The Physical Behaviour of Paint Films", followed by Mr. C. C. Mill on "The Behaviour of Printing Ink on Rollers" and by Mr. S. E. Orchard, who delivered Station. The speakers on this occasion the final lecture of the morning on "The Physics of Brushmarks", with his coauthors, Mr. N. D. P. Smith and Dr. A. J. Rhind Tutt, in attendance. Immediately after the morning Session there followed an Informal Reception of conference delegates and their wives by the President Paints" and Mr. H. Williams on "Some and Mrs. Gay.

In the afternoon coach tours had been arranged to Steps' Bridge via the Lustleigh and Teign Valleys. A limited number of members were able to visit the Marine Station of I.C.I. Ltd. at Brixham, where they were shown work on the marine exposure of paints and research work on presented by Rockeys Ltd., was "Fashion the effects of effluents and pollution. The Civic Reception and Dance were held in appropriate for that week of sunshine. the evening, when those attending the Conference were received by the Worshipful afternoon to Dartmeet, where a delicious the Mayor and Mayoress of Torquay. Devonshire cream tea was served, while a

The Chairman for the Technical Session on Thursday morning, 1 June, was Dr. L. Valentine, Director of the Paint Research were Mr. F. G. Dunkley, accompanied by Dr. D. P. Earp, who spoke on "The Correlation of Service Behaviour with Observed Physical Characteristics of Airdrying Paints for Structures", Dr. R. N. C. Strain on "The Solar Reflectivity of Aspects of the Assessment of Emulsion Polymer Films". While those attending the Technical Sessions were dealing with aspects of coatings, their ladies were also viewing their preferred form of "coatings" at a mannequin parade in the Lounge of the Palace Hotel. The theme of the show, on a Summer's Day", certainly most

A coach tour was also arranged for the

Station at Brixham. An alternative visit in the Chair. The Session opened with was undertaken to the works of English Mr. G. W. Mack, whose paper was Clays, Lovering, Pochin & Co. Ltd. at entitled "Painting Porous Building Materi-Lee Moor. For those who had temporarily als". Dr. V. R. Gray followed with a paper tired of a landlubber's existence, the coastal entitled "The Wetting, Adhesion and and river trip up the Dart was a welcome Penetration of Surface Coatings on Wood". relief. It was unfortunate that the weather Finally, Mr. A. T. S. Rudram, assisted was rather dull and, although the sea was by Mr. T. R. Bullett, summarised their by no means rough, at least two of the paper on "The Coating and the Substrate". passengers of Kiloran II were seen to The discussion following each paper on all slip quietly below! However, undoubtedly three days was always vigorous, and at times the most enjoyable feature of the trip almost explosive! Each day too there were was the sight of the Honorary Treasurer more questions than could be accommofeeding an enormous flock of seagulls, dated in the discussion periods. In summing which thereafter remained hopefully sus- up the Sessions, Dr. J. B. Harrison felt that pended above the boat, despite assurances if the vigour of the discussions was anything from Mr. Sowerbutts that all food had in to go by, the conference might be judged fact gone. In the evening many members successful. He also felt that, as the and their wives visited the Pavilion Theatre, phenomenon of "blistering" had featured situated beside the Inner Harbour, where prominently throughout most of the dis-Frankie Howerd starred in what might cussion periods, this might provide a basis be termed a typical and enjoyable seaside for a future conference. In conclusion, the variety show.

Director of the Printing, Packaging and the Technical Sessions for their sustained

second visit was paid to the ICI Marine Allied Trades Research Association, was President thanked the lecturers for pro-For the final Technical Session on viding the Conference with a set of excellent Friday, 2 June, Dr. V. G. W. Harrison, and provocative papers and those attending



The "Swiss Mountain Scene" above was actually photographed at the Lee Moor Works of English Clays, Lovering, Pochin & Co. Ltd., which were visited by a party of Conference delegates on Thursday, 31 May.

August



(Above) At the Informal Reception on Wednesday, 31 May are seen (from left to right) Dr. V. G. W. Harrison (Chairman of Friday's Technical Sessions), Dr. V. R. Gray (Lecturer), Mrs. Harrison and Mr. C. C. Mill (Lecturer).

(Below) Pictured at the Civic Reception on Wednesday evening 31 May are (from left to right) The Deputy Mayoress, Dr. E. A. Becker (President, F.A.T.I.P.E.C.), The Deputy Mayor, Mr. P. J. Gay (President), The Mayor of Torquay, and Mrs. Gay.



Some of the Honorary Officers and Guests are shown here at the Association's Dinner and Dance on Friday evening, 2 June. (*Above, from left to right*) Dr. J. E. Arnold (*Hon. Secretary*) Dr. H. W. Keenan (*Past President*), Mrs. Keenan, Mr. E. Lund (*President, S.L.F.*), Mrs. Lund, and Dr. E. A. Becker (*President, F.A.T.I.P.E.C.*).

(Below, from left to right) Mr. N. A. Bennett (Past President), Mr. I. C. R. Bews (Hon. Editor), Mr. T. R. Bullett (Lecturer), Mrs. Strain, Dr. R. N. C. Strain (Lecturer), Mrs. Bews, Mr. F. Sowerbutts (Hon. Treasurer), Mrs. Hamblin, and Mr. R. H. Hamblin (General Secretary).

Technical Sessions, which considerably eased the work of the reporters.

Early in the afternoon the Association's Annual General Meeting was held, during which Dr. H. A. Hampton was unanimously elected to be the next President of the Association. At the same meeting Honorary Membership of the Association was conferred on Mr. George Copping for his considerable services OCCA over to many years. (A full report of the meeting appeared in the July issue of the Journal.) After the AGM a final coach tour had been arranged to Haldon Moor, Teignmouth and Dawlish, tea being taken at the Highwayman's Haunt. The sporting fraternity took advantage of the fine afternoon to complete the tournaments that had been taking place on the tennis courts and the local golf courses. In the evening came the climax of the 1961 Torquay Conference, the Association's Dinner and Dance. As is traditional on these occasions, the guests, who included the Mayor and Mayoress of Torquay, were applauded by the company to their places on the top table. Touches of distinction were added to the already splendid gathering by members of the Manchester Section, who sported the red rose of Lancaster in their buttonholes, and by the Scottish Section Table, which was graced by the presence of a kilted Highlander mascot. The dinner was excellent and the "Saumon d'Ecosse Fumé, Petite Marmite, Suprème de Turbotin Grand Duc, Caneton d'Aylesbury Rôti à l'Anglaise, Pêche Melba, Delices des Dames" were as delicious as they sound.

After the Loyal toast by the President, Mr. P. J. Gay, the toast to the Borough of Torquay was proposed by the President Federation sincere wishes to the Associa-Designate, Dr. H. A. Hampton, who tion for continued success and progress commented that it was the first time that for the benefit not only of itself, but also the Association had returned to a previous of the paint industry in general. In reply, Conference venue within four years, which the President asked Mr. Lund to convey was in itself a high tribute to the borough. To to his members the greetings of members of

interest for the three days. A full report many people, he said, "Devonshire" meant of the discussions will be appearing, Torquay, and the Association was partogether with the relevant papers, in later ticularly grateful to the Shire for providing issues of the *Journal*, starting in September, its oldest living President, Dr. J. A. Newton The Honorary Editor would like to thank Friend, whose eightieth birthday had Mr. N. R. Fisk, Mr. M. R. Mills and Mr. recently been celebrated (see page 561). A. R. H. Tawn for their kind assistance Dr. Hampton ended by thanking the in distributing the discussion slips at the Mayor for the provision of so many amenities and asked that the toast should be linked with the name of the Mayor. Councillor T. B. Revill. The Major thanked Dr. Hampton for his kind remarks and said that he was pleased to receive the Association again at Torquay and hoped that the Borough would not have to wait too long before they returned.

> Mr. E. Lund, President of the Federation of Scandinavian Paint and Varnish Technicians (SLF), proposed the toast of the



Dr. L. Valentine (Chairman of Thusrdays' Technical Session) seen here with Mrs. Valentine, at the Association Dinner and Dance on Friday, 2 June.

Association. He said that the Federation was intentionally modelled on OCCA, which was regarded in Scandinavia with high esteem and respect. The high level of the Association's activities had been emphatically displayed at the Conference. Mr. Lund extended on behalf of his

the Association, who were very pleased to observe the growing strength and importance of the Scandinavian Federation. The Association was the oldest of the national and international technical associations connected with the oil and colour industries and as such it had always played a leading part in furthering international co-operation at the working level. In concluding, Mr. Gay briefly reviewed his two years of office; he mentioned the decision to seek incorporation, the formation of new Sections in Oueensland and Auckland and of a Federal Committee to co-ordinate the activities of members in Australia. The Annual Technical Exhibition had now become internationally famous and was now a direct responsibility of Council. The first of the Paint Technology Manuals had also recently been published. All this was, he said, indicative of the solid strength of the Association.

The toast of "The Guests and Ladies" was wittily proposed by Mr. H. Gosling, Past President, who welcomed them all on behalf of the Association, extending a special wel- journed to the ballroom where the President Vernis, Emaux et Peintures. d'Imprimerie de l'Europe Continentale (FATIPEC), Dr. E. A. Becker, replied for the Ladies and Guests, thanking his hosts for their kind hospitality. The order pervading all meetings of the Association was, he felt, a notable reflection on the efficient organisation behind them.

Dr. Hampton, who had been unani-mously elected President at the AGM earlier that day, was invested with due ceremony by Mr. P. J. Gay, amid acclamation. Dr. Hampton said that he regarded this occasion as the culmination of his career and that he would strive to maintain the dignity and position of the Association to the best of his ability. His first pleasant duty was to present Mr. Gay with his Past President's Medallion. The company ad-



Dr. H. A. Hampton receiving the Presidential Insignia from Mr. P. J. Gay after the Annual Dinner of the Association on the evening of Friday, 2 June, at the Palace Hotel.

come to Mr. George Copping, the new and his Lady led the dancing, which Honorary Member, and Mrs. Copping. continued until 1 a.m. During the interval The President of the Fédération d'Asso-Mrs. Hampton presented prizes to the ciations de Technicians des Industries des winners of the various tournaments shown Encres below.

GOLF

Churston Competition

First			Mr. A. N. Pirie
Second		••	Mr. J. Hepworth
	Torg	uay C	Competition
First			Mr. S. Sharp
Second			Mr. M. E. Meredith
		TE	NNIS
Women			Mrs. J. A. Oates
Men		• • •	Mr. R. R. Blakey
	Л	TABLE	Tennis
Women			Dr. M. Ellinger
Men			Mr. K. Partington
			RFK

FOURTEENTH TECHNICAL EXHIBITION, 1962

Journal, the Fourteenth Technical Exhibi- are passed on as quickly as possible to the tion, organised by the Association, will technical personnel within the paint, take place on 26, 27, 28 February, and printing ink, linoleum and allied industries. 1 March 1962, at the Royal Horticultural The technical advances may relate to new Society's Old and New Halls, London, products, new knowledge of existing pro-S.W.1. Forms for application for stand ducts and their uses or, in suitable cases, space were dispatched to companies at the existing knowledge which has not been end of June, and a large number of com- available to the consuming industries. pleted forms have already been returned. Those companies intending to exhibit must send in their completed forms of applica- the 1962 Exhibition will include a contion not later than Monday, 4 September, 1961.

the Criterion Restaurant, Piccadilly, patterned linoleum. Arrangements have London, W.1, on Monday, 26 February. also been made for floral decorations, The forms of application for tickets for the which were such a successful feature of Luncheon will be included in each copy recent Exhibitions. of the Official Guide which will be sent to all members of the Association early in 1962. The Official Guide will also be sent, as far as possible, to all consuming firms in Britain and individually to chemists and technologists in the paint and allied industries in Western Europe. They can also be would like to have their names submitted obtained by visitors to the Exhibition to the Committee for consideration should without charge and admission to the write to R. H. Hamblin, General Secretary, Exhibition will be free.

unique in that it is entirely a technical one, London, E.C.2 (MONarch 1439).

As announced in the July issue of the aimed at ensuring that technical advances

The standard shell colour scheme for temporary blue and black wallpaper on the facias with white and red name There will be an Exhibition Luncheon at plaques, gull-grey walls and a distinctive patterned linoleum. Arrangements have

The Exhibition is not confined solely to British firms, and continental companies wishing to be considered for stand space and any companies in the United Kingdom who have not previously exhibited and who Oil and Colour Chemists' Association, It is believed that the Exhibition is Wax Chandlers' Hall, Gresham Street,

Bristol Section

IRISH BRANCH

As announced in the July issue of the Journal, the Council, at its meeting on 15 June, gave consent for the formation of an Irish Branch of the Bristol Section. This followed a resolution from an informal meeting held in Dublin on 10 April, which was attended by Mr. W. J. McWaters (Hon.

Treasurer of the Section), who explained the aims and activities of the Association. A provisional Committee has now been formed to arrange three meetings in Dublin during the forthcoming session. Anyone wishing to obtain further information about the Branch should write to Mr. R. C. Somerville, c/o Lewis Berger (Ireland) Ltd., 134 James's Street, Dublin, Ireland.

Hull Section

MEN'S NIGHT

On 17 May the Section held its second "Men's Night" at the Ferry Inn, Brough, near Hull, when twenty-four members and

iends began a convivial evening with a hot meal served at 8 p.m. The evening passed very quickly with dominoes and two amusing games of darts organised by Mr. Parkinson. Comedy was provided throughout the evening by Mr. Sharp, ably supported by Mr. Armstrong, who also led the sing-song round the piano.

The vocal achievements of these two members and their masterly rendering of a descriptive poem entitled "Cats" had to be heard to be believed. Music was again provided by Mr. P. Briggs.

Mr. N. B. Helmsing, the Honorary Social Secretary, must again be praised for arranging a very pleasant evening's entertainment, and it is hoped more will take the opportunity of meeting their fellow members in such a happy atmosphere on a similar occasion in the future. W. A. R.

Manchester Section

ANNUAL CRICKET MATCH

The fourth annual cricket match between the Manchester and West Riding Sections, played at the ICI Recreation Club, Huddersfield, on 9 June, resulted in a resounding win for Manchester.

Manchester batted first, and after losing the first wicket early, proceeded to amass a total of 139 for 2 wickets in 18 overs, due

to some very fine batting by Mr. J. S. Peet (63 not out) and Mr. R. Sandiford, who was dismissed one short of his half-century. Mr. R. F. Evans (17 not out) helped to accelerate the Manchester scoring, and also assisted in dismissing the Yorkshire side, who were all out for 25. The games are now even at two wins each.

I. S. M.

Midlands Section

CELEBRATION DINNER

A celebration dinner to Dr. J. A. Newton Friend, Senior Past President and an Honorary Member of the Association, Dr. Newton Friend for the twenty-six arranged by the local Sections of the Chamister Department at the Tachnical Royal Institute of Chemistry and the Association, was held at the Chamber of College. Commerce, Birmingham, on 26 May. After the loyal toast by Mr. N. H. Sey- Designate of O.C.C.A., proposed the toast mour, the Chairman of the Midlands of The University, dealing with the impor-Section, a toast to the City of Birmingham tant part it played in the training of science was proposed by Mr. G. Dring, Vice- graduates, and especially chemists, which President of the Royal Institute of the nation required. Professor K. Mather, Chemistry, who extolled the virtues of the Vice-Principal of the University, after City and expressed appreciation at the expressing the University's appreciation

Lady Mayoress of Birmingham, Alderman and Mrs. E. E. Mole. In reply Alderman Mole voiced the thanks of the City to Dr. Newton Friend for the twenty-six Chemistry Department at the Technical

Dr. H. A. Hampton, then Presidentattendance of the new Lord Mayor and of Dr. Newton Friend, dealt with the



[Photograph by kind permission of

'The Birmingham Post & Mail."]

Dr. J. A. Newton Friend shaking hands with Mr. C. E. Hollis after the presentation of an inscribed grandmother clock at the dinner held in Birmingham on 26 May to celebrate Dr. Newton Friend's eightieth birthday. Also in the photograph is Mrs. G. King,

accommodation by the drive to turn out Friend a grandmother clock inscribed: greater numbers of scientists. The toast to King Edwards School was proposed by the Chairman, Mr. G. King, but the Chief Master, the Rev. R. G. Lunt, was unfortunately unable to be present to respond. Mr. S. A. Ray, the toastmaster, read the Chief Master's apology and conveyed the numerous messages of good will to Dr. Newton Friend. Mr. C. E. Hollis, a former student and member of Dr. Newton Friend's teaching staff, gave a brief history of Dr. Newton Friend's dis- College. At Dr. Friend's request the balance tinguished career, not only as a scientist of the subscriptions for the presentation and technologist, but also as a teacher and are to be forwarded to the R.I.C. Benean eminent archeologist and historian. volent Fund and the Paint Trade Benevolent Before asking the audience to drink the Fund. health of Dr. and Mrs. Newton Friend,

problems raised in buildings, costs and Mr. Hollis presented to Dr. Newton

Presented to Dr. J. A. Newton Friend in his eightieth year by members of the Royal Institute of Chemistry, the Oil and Colour Chemists' Association and the Chemical Industry in the Midlands.

Dr. Friend thanked all those who had organised the function, and in his customary interesting and witty style recalled briefly the various phases of his long life, the City, the School, the University and the

R. D. C.



Members of the Midlands Section who flew to British Resin Products' plant at Barry, manufacturing Epok water-soluble resins.

WORKS VISIT TO BARRY

On 12 May, thirty-six members of the Section flew in a chartered plane from Birmingham to Cardiff, to visit the laboratories and works of British Resin Products Ltd. at Barry. On such a notable occasion it is worth recording that on a beautiful morning, the flight over the Wye Valley and the Forest of Dean was very enjoyable indeed, and that within an hour of leaving Birmingham, the party were being welcomed at the works by Mr. J. D. Winston, the General Sales Manager.

The laboratories, which included those of British Resin Products Ltd., British Geon Ltd., and Distrene Ltd., covered research, development and technical service over a wide range of polymers, including surface coating resins, laminating adhesives and foundry resins, polystyrene, p.v.c., polyethylene, polyesters and nitrile rubbers. It was difficult to imagine a better place for illustrating the scope and applications of polymers.

siderable programme of work was evident blown film and bottle blowing. on water-based coatings, for both primer

systems and top coats. As a typical example of work carried out, twenty new resins a week were checked, not only by examination of the properties of free films, but also by adhesion tests in relation to pigment volume concentration, establishing correct stoving conditions, and by exposure tests. This type of work was backed both by the research laboratories, where the rheological properties of such systems were being investigated, and by the technical service laboratories, where the practical aspects were examined. The processes involved in the manufacture of polyester glass fibre laminates, cloth, paper and asbestos laminates, the bonding of chipboard and carborundum for grinding wheels and sand for foundry casting were all explained. The technical service laboratories for the plastics industry were most impressive. For p.v.c. alone it was possible to carry out the majority of industrial operations, such as calendering, extruding, injection moulding, blow moulding and spreading. Added to these are the facilities in the polystyrene and polyethylene labora-In the surface coating section, a con- tories for sheet extrusion, extruded and

Following lunch, Mr. L. G. Prescott,

of the works, showing in particular the and sheet, but interesting work is in progress manufacture of p.v.c. and Hycar nitrile on latexes for exterior emulsion paints and rubbers. On paper the manufacture of for the production of gloves with good p.v.c. is a series of simple chemical resistance to oils and to oxidation. reactions: in the works it is a study in chemical engineering and process control. The present plant operates on the addition of hydrogen chloride to acetylene to form vinyl chloride, whereas the new plant being erected will employ ethylene, with chlorine addition to ethylene dichloride, followed by the removal of hydrogen chloride to form vinyl chloride. The polymerisation to p.v.c. follows in stainlesssteel-lined vessels using a peroxide catalyst with high speed agitation. Hycar nitrile rubbers, based mainly on butadiene and

the Works Manager, arranged for a tour acrylonitrile, are produced as crumb

On completion of the tour, tea was provided at Friars Point, the gardens of which border the sea. Mr. N. H. Seymour thanked Mr. Winston and Mr. Prescott and their colleagues for giving the Section such a splendid day, and asked that their appreciation should also be passed to the Company for their generosity in providing the air and bus transport and for the hospitality during the visit. A flight through the evening sunshine completed a memorable works visit.

R. D. C.

New South Wales Section



Some of the Past Chairmen of the New South Wales Section at the Annual Dinner at "Jonroe" on 4 May. They are (from left to right, standing) Dr. E. Haimann, Mr. R. Kimberly, Mr. L. Cash, Mr. E. V. Collins (present Chairman), Mr. G. J. Crooks, Mr. A. Rileigh and Mr. K. Boland; (sitting) Mr. K. S. Jones, Mr. E. T. Backous, Mr. S. Leech and Mr. H. H. Wyatt.

ANNUAL DINNER

The Annual Dinner of the Section took place on 4 May at "Jonroe". After the the Past Chairmen appears with this dinner Past Chairmen of the Section were report. presented with Past Chairman's badges.

each Past Chairman presenting a badge to his successor. A photograph of some of

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Section Programmes for 1961-62 Session

BRISTOL SECTION

Unless otherwise stated all meetings are held in the Royal Hotel, College Green, Bristol 1, at 7.15 p.m.

1961

Friday, 29 September

New Chairman's Address by A. Aitkenhead.

Tuesday, 3 October

"Management Succession as a Field for Operational Research", by Lord Halsbury. Joint Meeting arranged by the Bristol and Bath Productivity Association. To be held in the Engineering Lecture Theatre of Bristol University.

Friday, 27 October

"Patents and the Paint Chemist", by F. Armitage, A.R.I.C. (Berger, Jenson & Nicholson Limited).

Friday, 24 November

"Wood Preservation", by R. Cockcroft, A.I.W.SC. (Forest Products Research Laboratory).

Monday, 4 December

Annual Dance at the Arnos Court County Club, Bristol.

Thursday, 7 December

Joint Meeting with Birmingham Paint, Varnish and Lacquer Club in Birmingham at the Imperial Hotel, at June 6.30 p.m. "Paint Progress-A Myth?"debate.

Friday, 15 December

Reserved for Paper by I. C. R. Bews, B.SC., A.R.I.C.

1962

Friday, 26 January

"Surface Finishes in Modern Architecture", by R. Moxley, A.R.I.B.A.

Friday, 23 February

"Mould, Fungicides and Paint", by C. N. Finlay and P. M. Proudley (Nuodex Limited).

Friday, 30 March

"Solvents in the Surface Coating Industry", by L. M. Barakan, PH.D. (The Distillers Company Ltd., Chemical Division).

Friday, 27 April

Annual General Meeting.

Friday, 25 May

Annual Skittles Match with the Birmingham Paint, Varnish and Lacquer Club at Ye Olde Hobnails, Little Washbourne.

Afternoon Works Visit. Details to be announced.

LONDON SECTION

Unless otherwise stated, meetings will be held at 7.0 p.m. in the Lecture Theatre of the Royal Society of Tropical Medicine and Hygiene, Manson House, 26 Portland Place, London, W.1.

1961

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Wednesday, 27 September

Chairman's Evening. A. T. S. Rudram (The Paint Research Station).

Tuesday, 10 October

Details to be announced. Lecture by Dr. H. W. Talen (Director, Paint Research Institute, T.N.O., Delft).

Wednesday, 18 October

"Solvents in the Surface Coating industry", by L. M. Barakan, PH.D. (The Distillers Co. Ltd.).

Thursday, 9 November

"Applications of Microwave Spectroscopy", by R. S. Tebble, B.SC., PH.D., F.INST.P. (Department of Physics, The University, Sheffield).

Friday, 17 November

Ladies Night, at the Criterion Restaurant, London, W.1.

Thursday, 7 December

"Aircraft Paints", by A. Macmaster, M.SC., A.R.I.C. (Ministry of Aviation).

1962

Wednesday, 17 January

"New Aspects of Corrosion", by J. B. Harrison, B.SC., PH.D., F.R.I.C. (Goodlass Wall & Co. Ltd.).

Wednesday, 21 February

"The Adhesion of Paint Films", by T. R. Bullett, B.SC., A.INST.P. (The Paint Research Station).

Thursday, 15 March

"The Thermal Decomposition of Esters and Polyesters", by P. D. Ritchie, B.SC., PH.D., F.P.I., M.I.CHEM.E., F.R.I.C., F.R.S.E. (Young Professor of Chemical Technology, Royal College of Science and Technology, Glasgow).

Wednesday, 25 April

Annual General Meeting, at the Criterion Restaurant, London, W.1.

MANCHESTER SECTION

All meetings will take place at the Literary and Philosophical Society, 36 George Street, Manchester, at 6.30 p.m. unless otherwise stated.

1961

Friday, 15 September

Works Visit to Granada Television Studios, Manchester, at 3.0 p.m.

Friday, 13 October

"Modern Chemistry of Organic Pigments", by Dr. H. Gartner.

Friday, 27 October

Annual Dinner and Dance, Alexandra Suite, Midland Hotel, Manchester, at 7.15 p.m.

Friday, 10 November

"Television—A Persuasive Medium", by J. P. Phoenix, M.I.P.R., at the Liverpool Constitutional Club, Tithebarn Street, Liverpool, at 6.30 p.m.

Tuesday, 21 November

"Some Developments in Applied Oleo-Chemistry", by M. Josephs, B.SC., PH.D., A.R.I.C. Joint Meeting with the Society of the Chemical Industry (Oils and Fats Group).

Friday, 8 December

"Architectural Approach to Colour in Building", by A. E. Hurst, F.I.B.D.

1962

Friday, 12 January

"Thermo-Setting Acrylics", by K. E. Piggott, B.SC., A.INST.P.

Friday, 9 February

"Adhesion of Paint Films", by T. R. Bullett, B.SC., A.INST.P.

Friday, 9 March

"New Aspects of Atmospheric Corrosion of Steel, and their Implications", by J. B. Harrison, B.SC., PH.D., F.R.I.C., at the Constitutional Club, Tithebarn Street, Liverpool.

Friday, 13 April

Annual General Meeting.

August

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MIDLANDS SECTION

All meetings will be held at Regent House, St. Philips Place, Colmore Row, Birmingham, unless otherwise stated.

1961

Friday, 22 September

"The Performance of Metallic and Organic Finishes", by R. J. Brown, A.M.I.MECH.E., F.I.M.

Friday, 20 October

"Printing Processes for Paper", by K. D. C. Bruce, and "Paper Preparation Friday, 16 March and Treatment", by K. Wilkinson, B.SC. Lecture at Mander Bros., St. John's Street, Wolverhampton.

Friday, 17 November

"Recent Developments in Polymeric Materials", by J. E. Stuckey, B.SC., A.R.I.C.

Friday, 1 December

Ladies' Evening at the George Hotel, Solihull.

1962

Friday, 19 January

"Toxicity." Lecturer not yet known.

Friday, 16 February

"Marine Paints and Painting", by T. A. Banfield, PH.D., D.I.C., A.R.C.S., F.R.I.C.

"Looking at Colour", by P. Heynes, F.R.S.A.

Friday, 6 April

Annual General Meeting at the George Hotel, Solihull.

May

Works visit to Courtaulds Ltd., Greenfield Works, Holywell, Flintshire, Date to be announced.

NEWCASTLE SECTION

All meetings are held in the Royal Turks Head Hotel, Newcastle upon Tyne, and commence at 6.30 p.m. Meetings are normally held on the first Thursday of each month, but there is one exception this year, *i.e.* the March lecture, which has been postponed a week because of the O.C.C.A. Exhibition.

1961

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Thursday, 5 October

"Consideration of the Different Types of Film Formation", by Dr. H. W. Talen.

Thursday, 2 November

A paper on metal finishing by R. M. C. Logan (title to be decided).

Wednesday, 7 December

A paper on driers by C. T. Morley-Smith Thursday, 5 April (title to be decided).

1962

Thursday, 4 January

"Have Cationic Surfactants any Use in the Manufacture of Paints?", by M. K. Schwitzer.

Thursday, 1 February

"Adhesion of Paint Films", by T. R. Bullett, B.SC., A.INST.P.

Thursday, 8 March

"Experimental Design and Statistics", by Dr. A. J. Elleman.

Annual General Meeting.

SCOTTISH SECTION

Unless otherwise stated all meetings will take place in the Grand Hotel, Charing Cross, Glasgow, at 7.30 p.m.

1961

Thursday, 12 October

"The Microbiology of Paints", by D. J. Cowley and Miss Brown.

Thursday, 9 November

"Solvent Selection for Modern Finishes", by J. E. Loible.

Thursday, 14 December

"Wines, Tasting and Testing", by H. F. Barnes.

1962

Thursday, 18 January

"Paint Testing", by H. Dunkley.

Thursday, 8 February

"Works Management and Industrial Administration", by J. Londen.

Thursday, 22 February

"Some Applications of Rheology", by G. L. Fulton, B.sc., in the North British Hotel, Edinburgh.

Thursday, 8 March

"Carpet Manufacture, Ancient and Modern", by D. Macphee

Friday, 20 April

Annual General Meeting at 5.30 p.m. in the St. Enoch Hotel, Glasgow, followed by the Annual Smoker in the Stuart Hotel, East Kilbride.

SCOTTISH SECTION—STUDENT GROUP

All lectures and film shows commence at 10 a.m., and unless otherwise stated will be at More's Hotel, 18 India Street, Glasgow, C.2.

1961

Saturday, 2 September

Film show.

Thursday, 14 September

Works visit to Canal Distillery of D.C.L. at Port Dundas. 7 p.m.

Saturday, 14 October

"Carpet Manufacture", by D. Macphee, illustrated with coloured slides.

Saturday, 18 November

"Some Recent Developments in the Technology of Drying Oils", by G. H. Hutchinson, A.R.I.C.

Saturday, 16 December

Film show.

1962

Saturday, 20 January

"Silicones in Surface Coatings", by D. R. Goddard, M.Sc., A.INST.P.

Saturday, 10 February

"Recent Developments in Epoxy Resin Coatings", by A. L. S. Brockman.

Saturday, 10 March

"Pigments and Extenders", by A. McGuire.

Saturday, 14 April

Brains Trust

WEST RIDING SECTION

All meetings will be held at the Hotel Metropole, Leeds, commencing at 7.30 p.m.

1961

Tuesday, 12 September

"Metal Preparation and Painting", by D. H. du Reiu (West Riding Section).

Tuesday, 10 October

"Public Service Vehicle Finishing", by Tuesday, 13 February A. Gellman (London Transport Executive).

Tuesday, 14 November

"Advertising to and by Paint Firms", by N. R. Fisk.

Friday, 24 November

Annual Dinner and Dance at Granby Hotel, Harrogate.

1962

Tuesday, 9 January

"The Preservation of Timber", by Dr. Cook.

"Colour and Light", by a member of the Staff of Imperial Chemical Industries Ltd.

Tuesday, 13 March

"Accelerated Weathering and the Paint Formulator", by E. Oakley (British Titan Products Ltd.).

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

BAYLISS, DEREK ARTHUR, 18 Stuart Road, East Barnet, Herts. (London) BERENYI, LESLIE, 12 Andrew Street, Clovelly, New South Wales, Australia. (New South Wales) BORSODY, LORANT, Taubmans Industries Ltd., Mary Street, St. Peters, New South (New South Wales) Wales, Australia. FARRELL, NEVILLE BRUCE, 9 Herbert Road, Edgecliff, New South Wales, Australia. (New South Wales) GREGSON, PETER, The Walpamur Co. Ltd., Darwen, Lancs. (Manchester) HESMONDHALGH, WILLIAM, 97 Exeter Street, Blackburn, Lancs. (Manchester) HILLMAN, DONALD EDWARD, 38 Oregon Square, Orpington, Kent. (London) HORSWELL, KEITH FREDERICK, 340 Lane Cove Road, North Ryde, Sydney, New South (New South Wales) Wales, Australia. KERSHAW, RICHMOND, 2 Wavell Drive, Bury, Lancs. (Manchester) MCCLEMENTS, RICHARD GEORGE CHAPLIN, 109 Gallipoli Street, Bankstown, Sydney, New South Wales, Australia. (New South Wales) MORGANS, WILFRED MORLEY, 115 Norton Way South, Letchworth, Herts. (London) OLSEN, JOHN CHRISTIAN, 150 Beach Street, Coogee, New South Wales, Australia. (New South Wales) REES, KEVIN JOSEPH, 100 Shannon Street, Box Hill, Victoria, Australia. (Victorian) Associate Members GAWRONSKI, EUGENE, 103 Avenue Road, Mosman, Sydney, New South Wales, (New South Wales) Australia. IRWIN, CLEMENT GEORGE, 29 Ernest Street, Brisbane, Queensland, Australia. (Queensland) JAFFRAY, WILLIAM ANDREW, Boundary Road, Mt. Eliza, Victoria, Australia. (Victorian) SZEPANSKY, GABOR, 31 Hunter Street, Bankstown, New South Wales, Australia. (New South Wales)

August

Junior Members

GANNON, FRANK, 275 Westbourne Avenue, Walkergate, Newcastle upon Tyne.

(Newcastle) JAGO, DONALD GEORGE, North Australian Rubber Mills, Bishop Street, Kelvin Grove, Queensland, Australia. (Queensland) OLIVER, GEORGE PARK, Jesmond House, Clayton Road, Newcastle upon Tyne, 2.

(Newcastle)

News of Members

Mr. K. D. Rutter, an Ordinary Member attached to the London Section, has been appointed Marketing Manager, Chemicals Division of Union Carbide Ltd.

attached to the Midlands Section, has and Nicholson Ltd., has been appointed been awarded the Diploma in Chemical Technology. Mr. Pace joined Mander Brothers Ltd. in 1954 and commenced the a member of the board of the former first Sandwich Course in Paint Technology at the Birmingham College of Advanced Technology in 1957. It is believed that few people in the paint industry have obtained this qualification.

Mr. H. J. Northeast, Honorary Secretary of the Midlands Section, has been elected Chairman of the Midland Market Research Group for 1961-62.

Mr. W. J. Vines, an Ordinary Member attached to the London Section, and Mr. G. Pace, an Ordinary Member joint managing director of Berger, Jenson managing director of the International Wool Secretariat. He will, however, remain company.

> Mr. T. G. Moreton, a member of the South African Section Committee, has been elected to Fellowship of the Royal Institute of Chemistry.

Visit to Stanlow

in Australia, Mr. D. S. Newton, who acted duct, or catalytically converted to acetone, as Honorary Editor, visited Shell Chemical hydrogen being produced as a by-product. Company Ltd.'s plant at Stanlow, and his Condensation of the acetone by alkaline report appears below.

Shell Chemical Co. Ltd.'s plant at Stanlow, one of three operated by the Company, is concerned with the production of solvents, detergents, and Epikote resins. Large scale production began in 1942, with the manufacture of *Teepol*, whilst the main chemical plants were erected from 1947 onwards. Based entirely on the by-products of oil refining, the Shell chemical plants utilise three main feed stocks. The solvent plants utilise propane-propylene, and butane-butylene feeds, whilst the yield the required cut of olefines which are Teepol plant uses a slack wax.

Using the propane-propylene feed, propyl hydrogen sulphate is produced by counter-current sulphation, and after hydrolysis, stripping and distillation, yields an isopropyl alcohol/water azeotrope. This is one for the manufacture of diphenylol

During the absence of Mr. I. C. R. Bews either further refined to the anhydrous procatalysis yields diacetone alcohol which is dehydrated to yield mesityl oxide and passed, together with the hydrogen from the acetone cracking furnace, over a heated nickel catalyst to yield methyl isobutyl ketone and methyl isobutyl carbinol. The butane-butylene stock, after the removal of the isobutylene by polymerisation to the dimer undergoes a similar series of processes yielding secondary butyl alcohol and methyl ethyl ketone. The imported slack wax is cracked to treated with sulphuric acid to yield the sulphates and then neutralised to give the sodium alkyl sulphates. Alkyl benzene sulphonates are also produced.

The Epikote plant comprises two units,

propane, and the other for *Epikote* resin which is fed into a furnace with sulphur manufacture. Instrumental control is much and hydrogen sulphide. The product is in evidence with grouped multi-channel cooled, dried and re-oxidised to sulphur recorders occupying a prominent position. trioxide and absorbed to give sulphuric

Recovery of sulphur and sulphuric acid from the various plants is carried out by oxidising hydrogen sulphide to sulphur dioxide, followed by the reaction between these two gases yielding elemental sulphur and steam. The spent acid from the units is decomposed to give sulphur dioxide,

acid and oleum.

The writer's impressions of the plant were its perfect balance, lack of waste products, very high level of tidiness and safety and the relatively low ages of the controlling staff-a youthful industry with staff to match. D. S. N.

PROGRAMME LIAISON COMMITTEE

A liaison committee, comprising two representatives each from the Institution of the Rubber Industry (IRI), the Plastics Institute (PI), the Plastics and Polymer Group of the Society of Chemical Industry (SCI), and O.C.C.A., has been formed in order to obviate the inconvenience caused by the clashing of dates of symposia, conferences, exhibitions, etc., of the different bodies. Forthcoming major meetings or conferences on polymers or related topics planned by the above societies and others are given below; they will be in London, unless otherwise stated.

1961

- 3-8 September: "Elastomers from Petroleum"-Symposium, Chicago. (American Chemical Society)
- 5-8 September: "Engineering Inspection and Non-destructive Testing"-Conference, Oxford. (The Institution of Engineering Inspection)
- 20-22 September: "Science and Craft in both Textile and Non-textile Coloration" -Symposium, Bristol. (Society of Dyers and Colourists)
- 28 September-8 October: International Congress of Industrial Chemistry, Bordeaux. (Société de Chemie Industrielle)
- with Plastics"—Conference. (PI)

29 November-1 December: Meeting of Reinforced Plastics Discussion Group, Brighton. (British Plastics Federation)

1962

- 30 January-2 February: Annual Technical Conference, Pittsburgh. (Society of Plastics Engineers, U.S.A.)
- 26 February-1 March: Fourteenth Technical Exhibition. (OCCA)
- 13-15 March: "Testing for Performance" -Conference. (PI)
- April: Annual Lecture. (PI)
- 1 May: Centenary of Plastics, 1862-1962. (PI)
- 15-18 May: Conference, Torquay. (British **Plastics Federation**)
- 21-26 May: Fourth Rubber Technology Conference. (IRI)
- September: Non-technical Conference, Birmingham. (IRI)
- September: Conference under provisional title "Polymer Techniques". (SCI)

1963

- March: Fifteenth Technical Exhibition. (OCCA)
- March: "Polymeric Progress"-Conference. (PI)
- 31 October and 1 November: "Engineering 25-29 June: Biennial Conference, Scarborough. (OCCA)

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.)

Monday, 7 August

Victorian Section. "Scientific Library Methods", by P. Russell, Librarian in Charge, C.S.I.R.O. Library, Canberra.

Thursday, 10 August

New South Wales Section. "Unsaturated Polyesters", by J. Samios, at the Theatrette, M.C.L. Building, Miller Street, North Sydney, at 6.15 p.m.

Wednesday, 23 August

Western Australian Branch. Visit to Television Studio, A.B.W.2.

Monday, 4 September

Victorian Section. "Surfactants" Special Monday, 2 October Junior/Senior Lecture by O. W. Petzold, Frankston Manufacturing, P/L.

Tuesday, 5 September

New South Wales Section. Annual Golf Thursday, 12 October Day, at Pennant Hills Golf Club.

Tuesday, 12 September

West Riding Section. "Metal Preparation and Painting", by D. H. du Reiu of the West Riding Section, at the Hotel Metropole, Leeds, at 7.30 p.m.

Thursday, 14 September

New South Wales Section. "Radiation Chemistry", by Dr. O'Connor, at the Theatrette, M.L.C. Building, Miller Street, North Sydney, at 6.15 p.m.

Friday, 15 September

Manchester Section. Works Visit to Granada Television Studios, Manchester, at 3.0 p.m.

Wednesday, 27 September

Western Australian Branch. "The Manufacture of Fibrous Plaster", by Mr. Hutchinson of Perth Modelling Works, at the Builders Exchange, Havelock Street, West Perth.

Victorian Section. "The Paint Approvals Scheme", by J. Rischbeith, B.SC., Secretary of Commonwealth Paint Committee.

New South Wales Section. Factory Inspection: Shell Chemicals Epoxy Resin Plant and Laboratory.

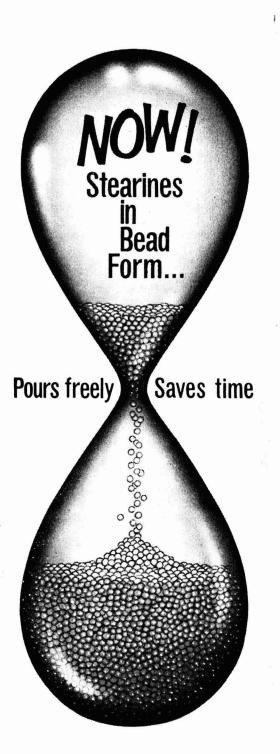
Friday, 13 October

Victorian Section. Ladies' Night at Ciro's, Collins Place, Melbourne.

ASSOCIATION BIENNIAL CONFERENCE, 1961 "Physics in Surface Coatings"

The full text of the papers presented at the first Technical Session, together with the full discussion following each paper will be appearing in the September issue of the Journal. Further papers will appear in succeeding issues.

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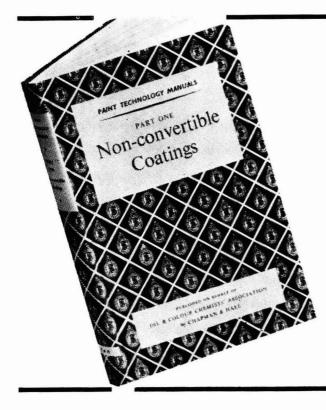


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August

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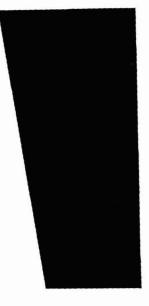
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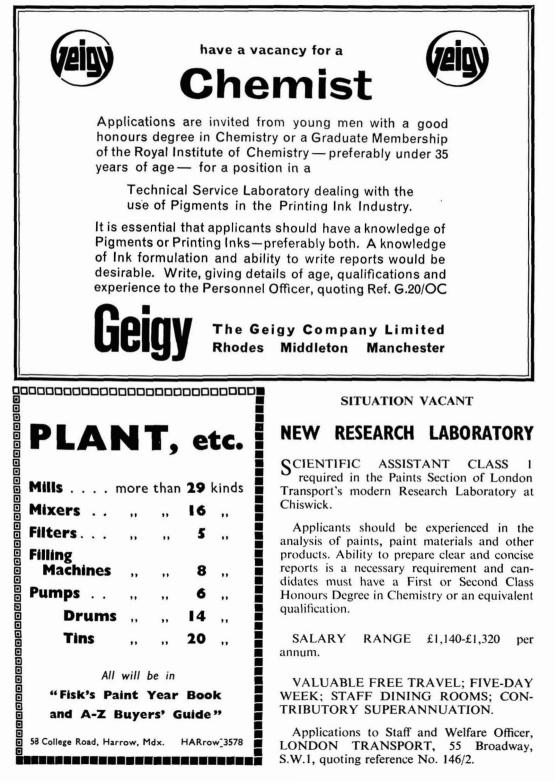


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in Fisk's Paint Year Book and Buyers' Guide, 58 College Road, Harrow, Middlesex. HARrow 3578.

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City and County of Bristol Education Committee

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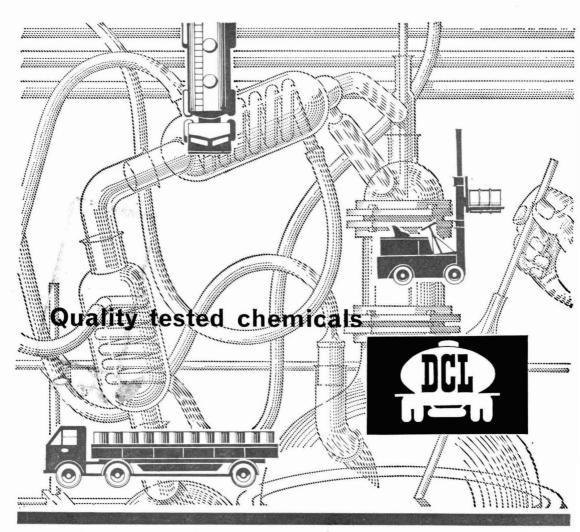
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