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Further investigation of short oil lactic pentaerythritol alkyds

Pit corrosion in internally painted cargo and cargo/ballast tanks of ocean-going crude oil tankers

Phthalocyanine pigments and their application

Photochemistry of vinyl chloride/vinyl-iso-butyl ether copolymer: Part II

Selection of research and development projects

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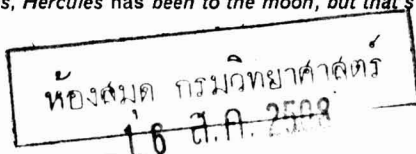
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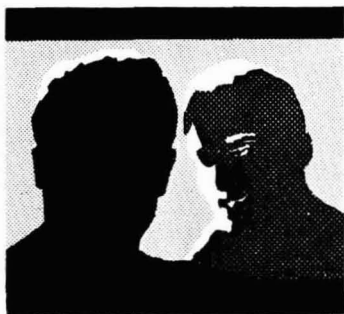
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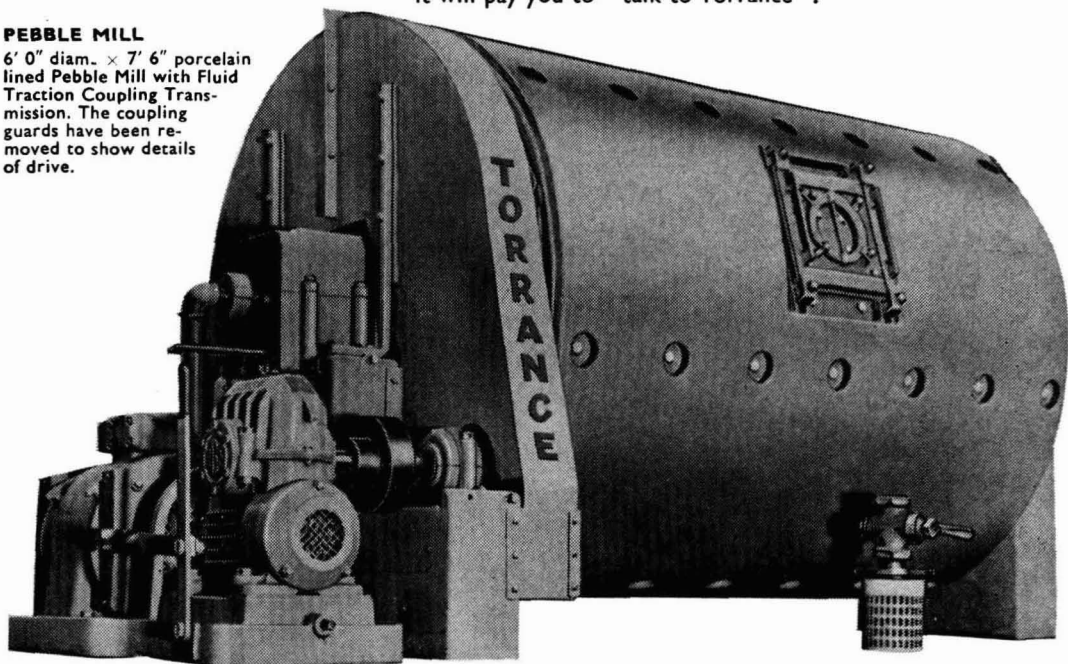
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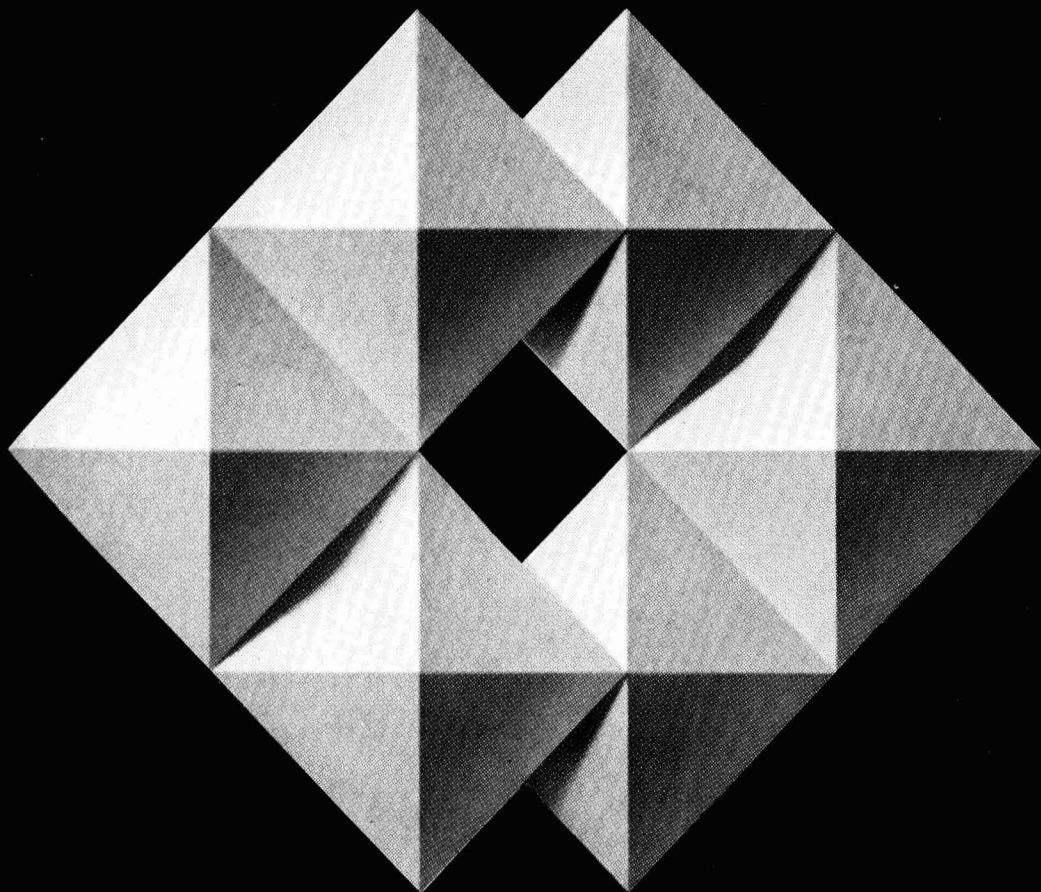
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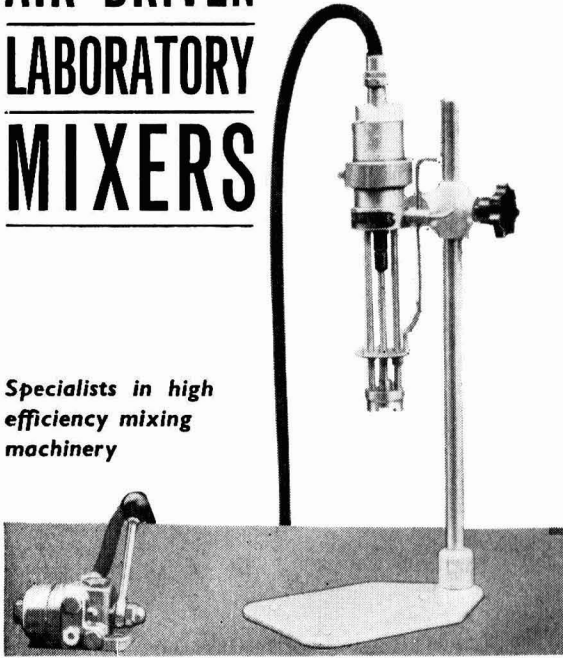
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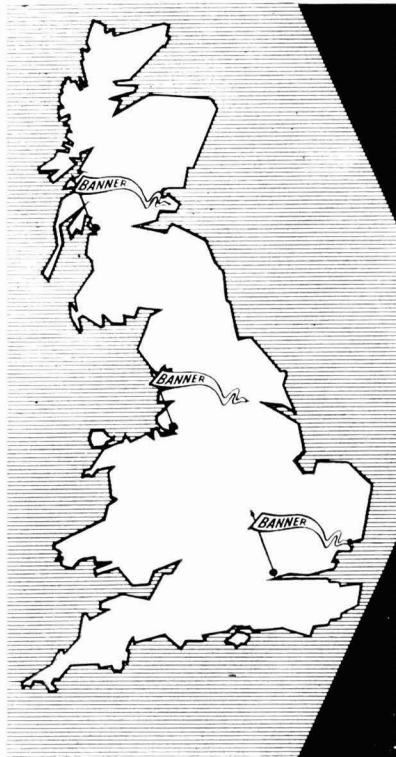
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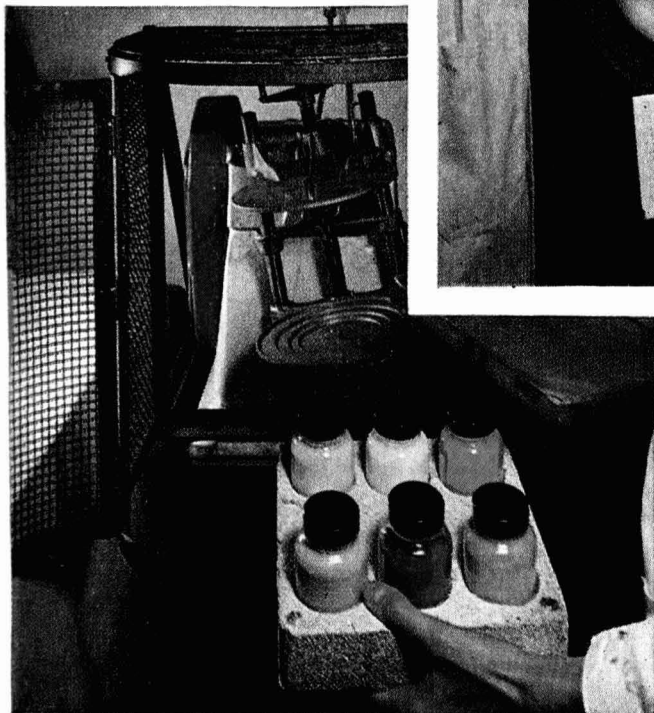
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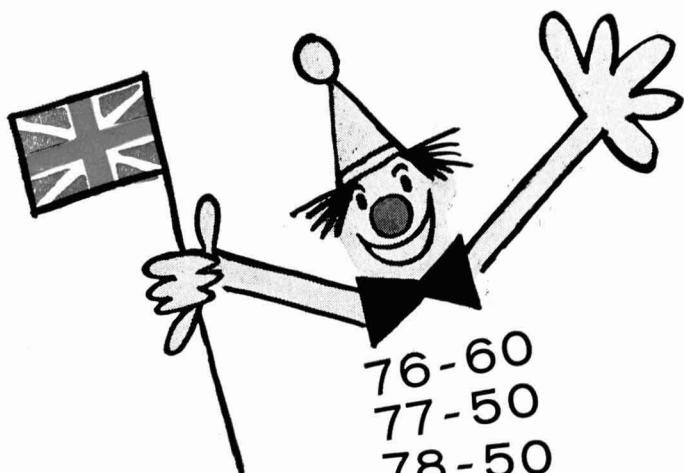


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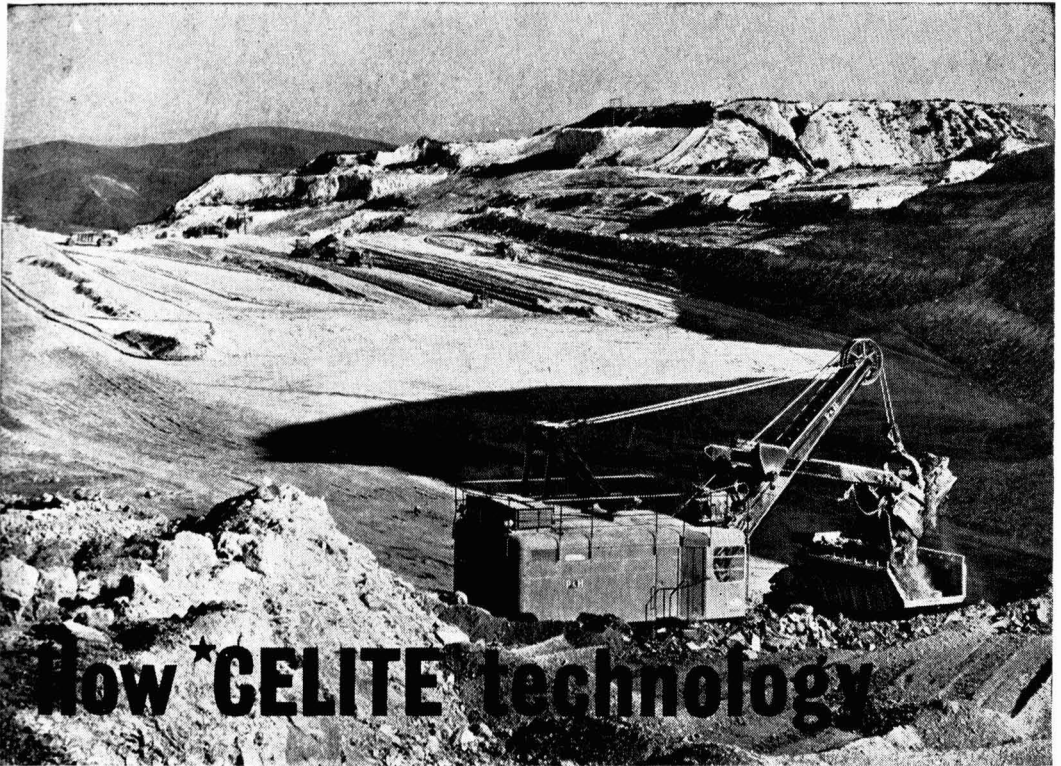
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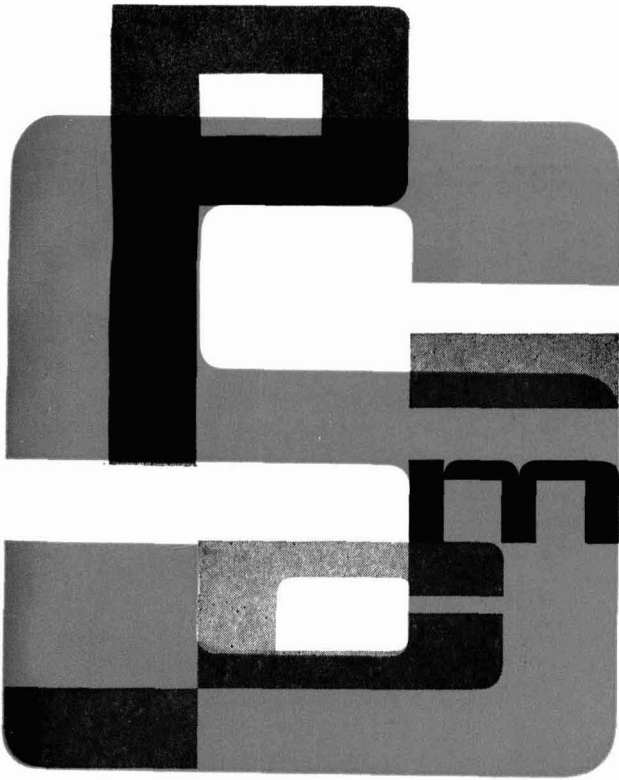
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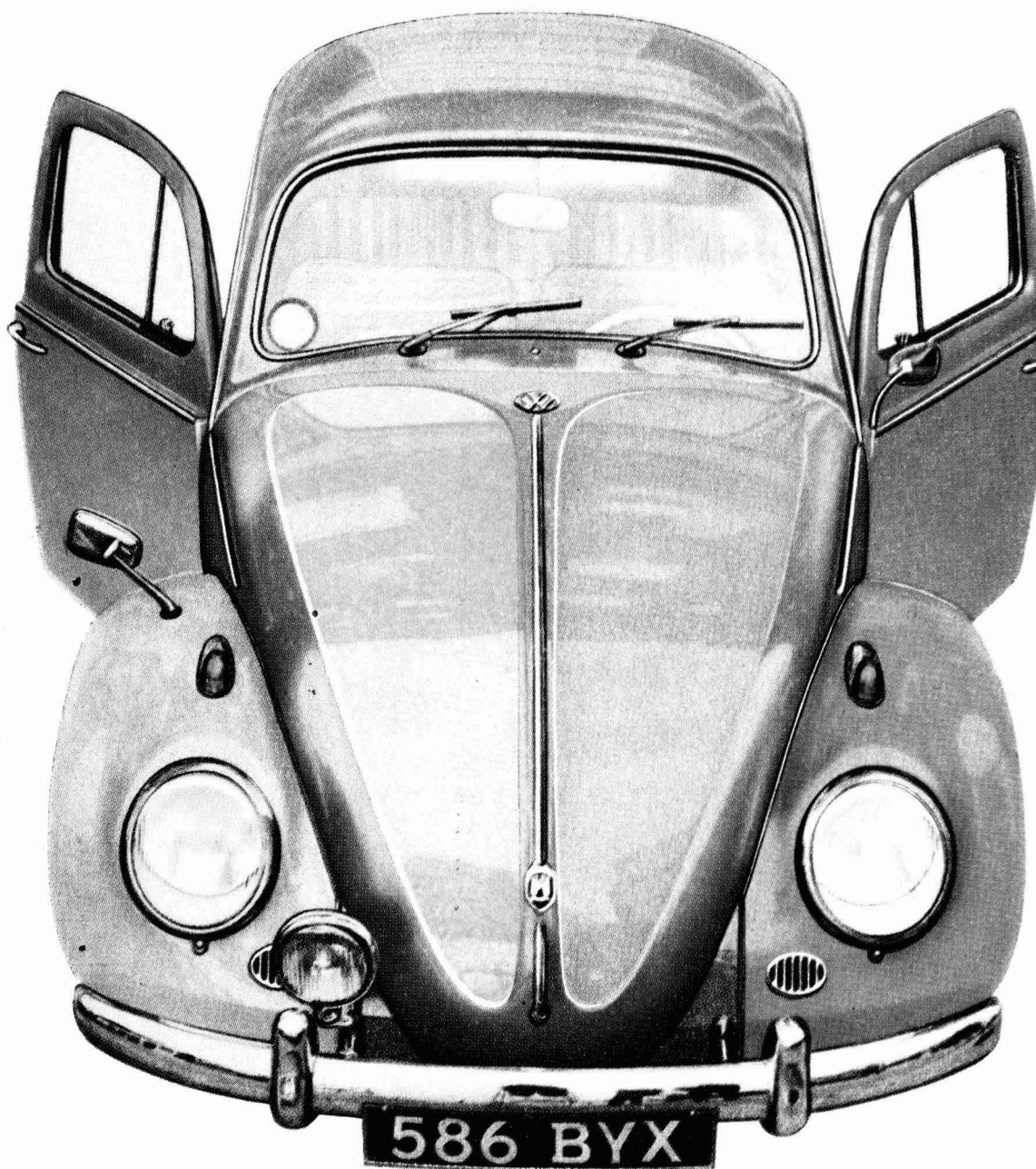


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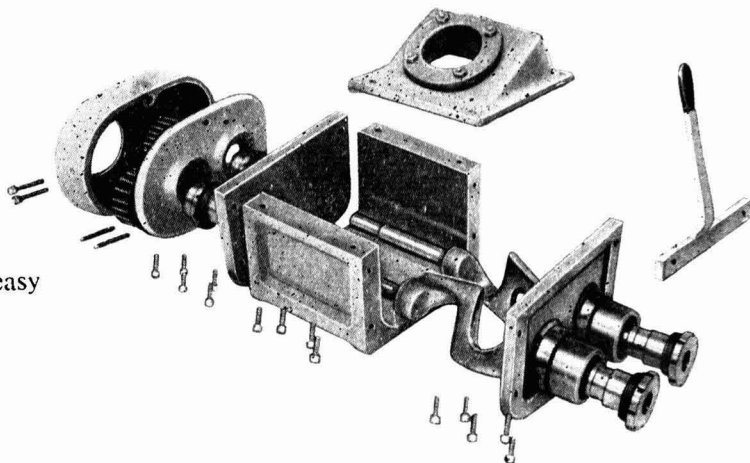
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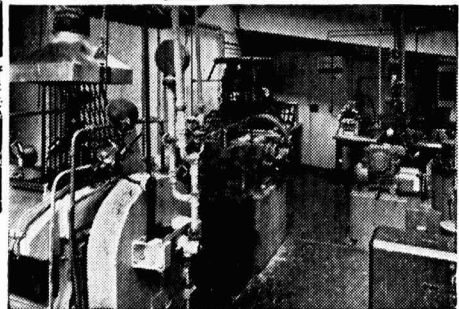
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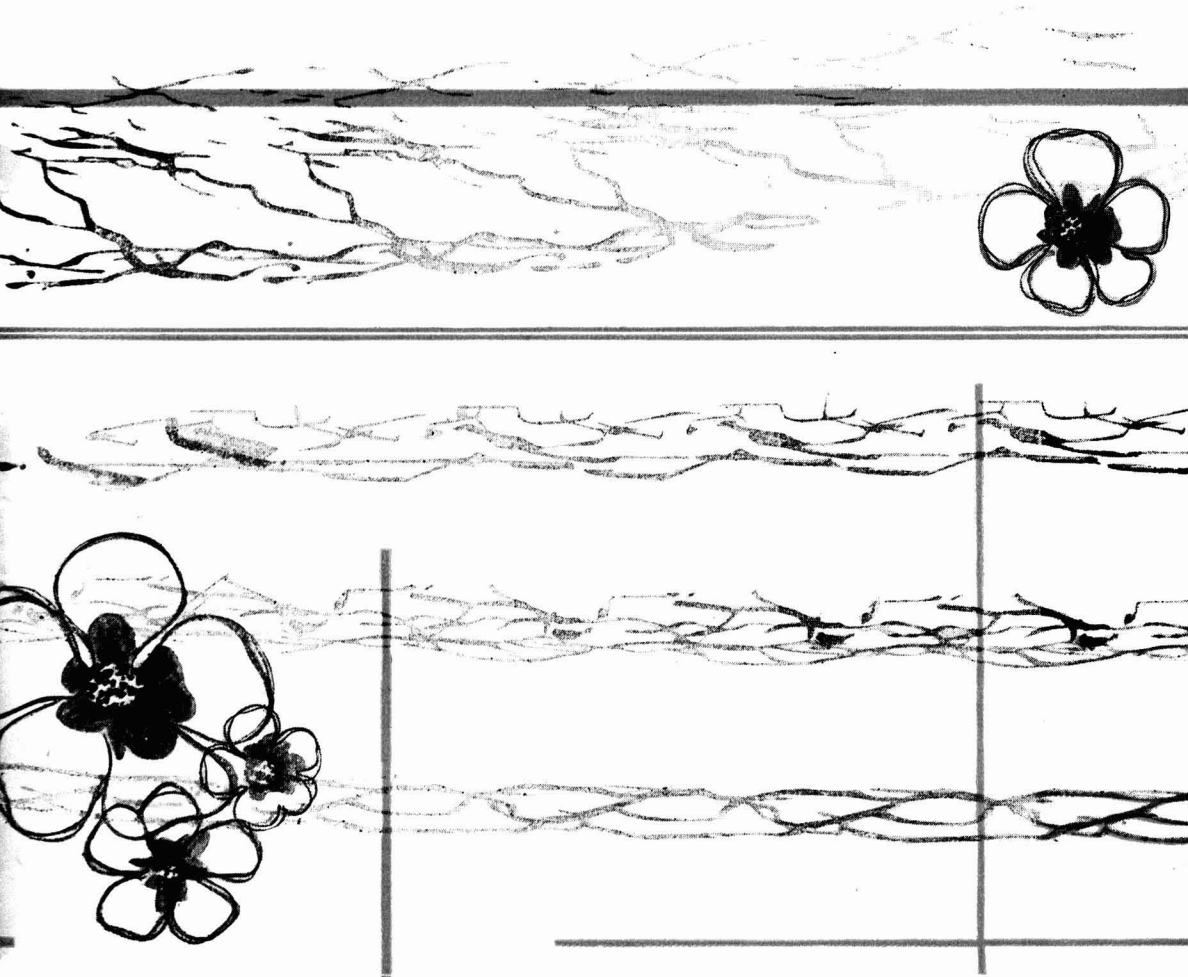
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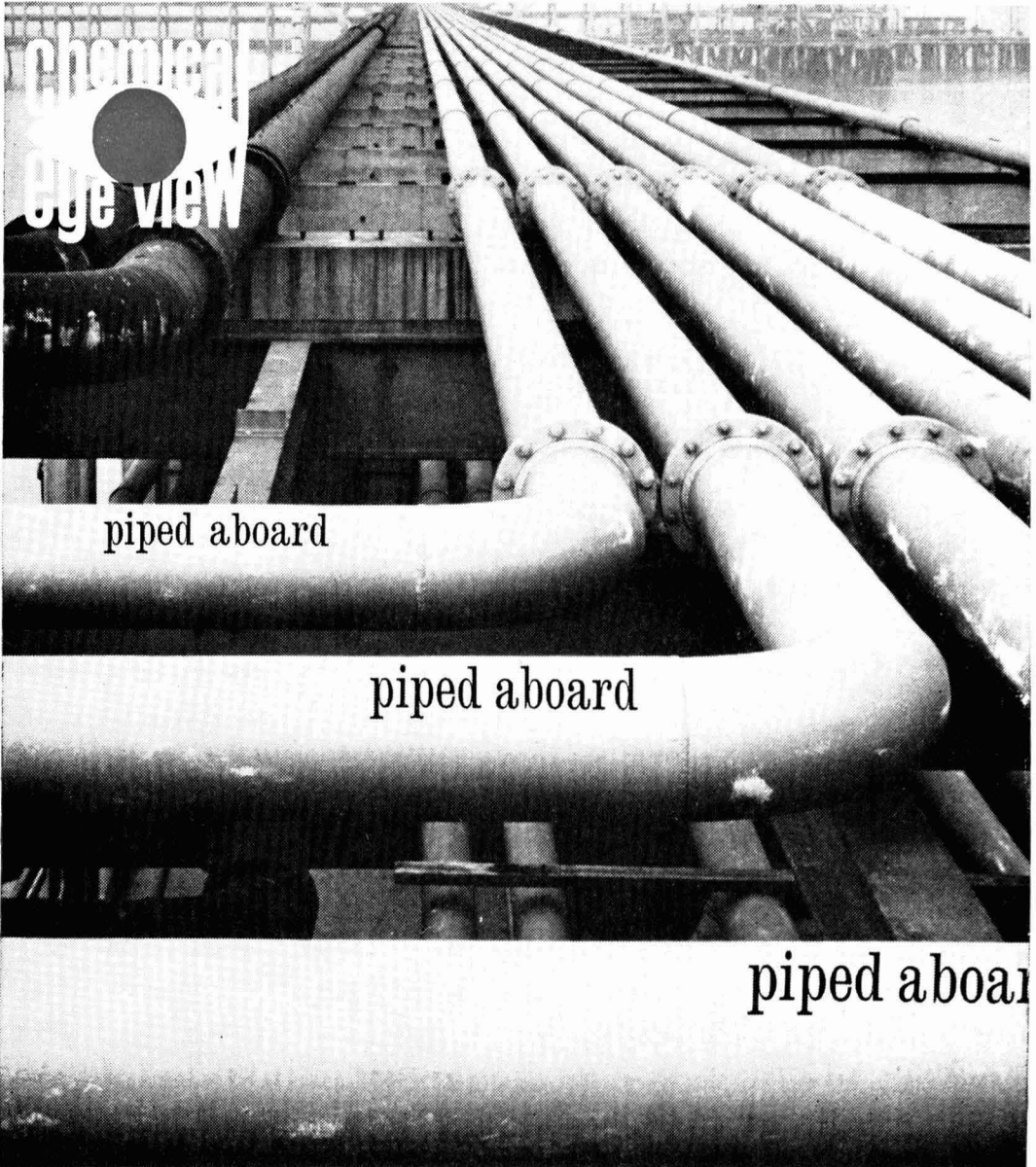
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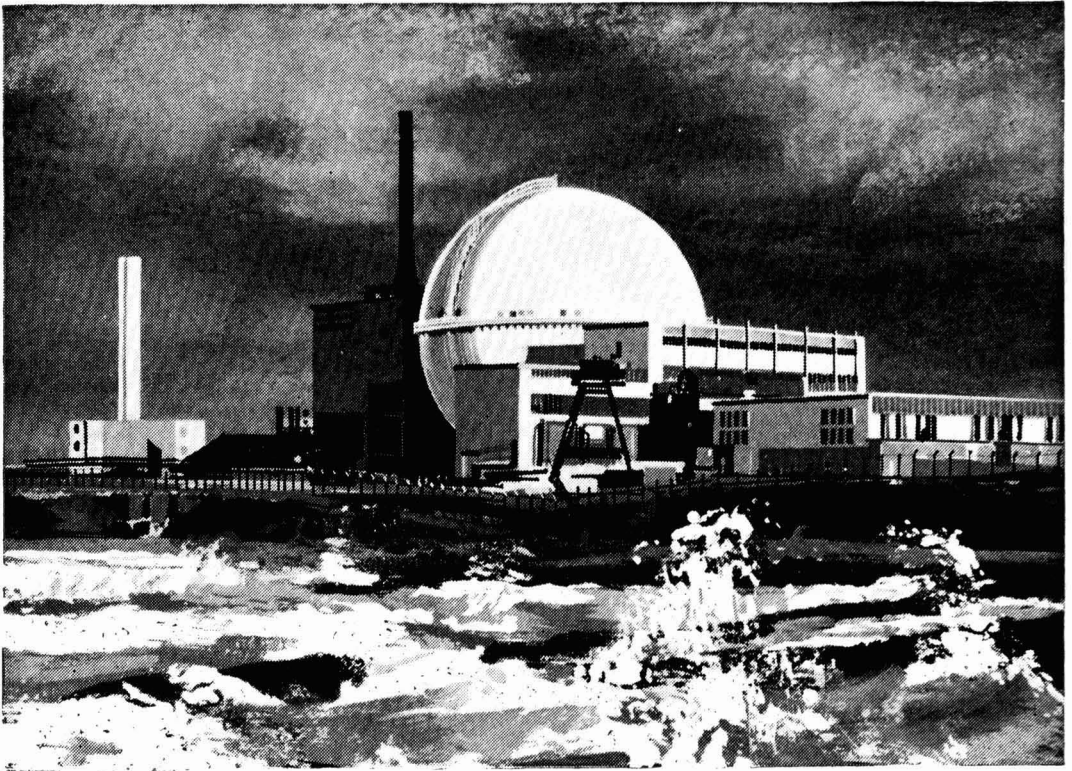
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Further investigation of short oil lactic pentaerythritol alkyds

By H. R. Touchin

180 Framingham Road, Brooklands, Sale, Cheshire

Summary

Further investigation has been made of short oil lactic modified pentaerythritol alkyds. The use of litharge as alcoholysis catalyst in place of sodium hydroxide has been found to give alkyds of better colour and colour retention on stoving. A study has been made of pigmented enamels using these alkyds both as air drying and stoving enamels and these have been found generally to give harder films than a conventional pentaerythritol alkyd not modified with lactic acid. The gloss of the enamels decreased as the oil length became shorter. Wrinkling on stoving was less prevalent with the lactic modified resins. In most respects the properties of the enamels are consistent with those previously reported for lactic modified alkyds.

Une investigation nouvelle des résines alkydes courtes en huile, modifiées à l'acide lactique

Résumé

L'emploi de litharge comme catalyseur de l'alcoolyse au lieu de soude caustique produit des résines de meilleur couleur et également de tenue de couleur après séchage au four. On a étudié le comportement de ces alkydes en peintures séchant soit à l'air, soit au four. En général la dureté de leurs films est supérieure à celle rendue par des alkydes conventionnelles pentaérythritoliques non-modifiées à l'acide lactique. Le brillant des films de peintures préparés des alkydes modifiées à l'acide lactique diminue tant que la longueur d'huile devient plus courte. Les peintures basées sur les résines modifiées à l'acide lactique présentent une tendance réduite concernant la formation de rides durant le séchage au four. Sous la plupart des rapports, les propriétés des peintures se conforment à ceux des alkydes modifiées à l'acide lactique déjà constatées.

Weitere Untersuchungen von Kurzöligen Milchsäure Pentaerythrit Alkyden

Zusammenfassung

Mit Milchsäure modifizierte Pentaerythrit Alkyde niedrigen ölgehaltes wurden weiterhin untersucht. Es stellte sich dabei heraus, dass bei Anwendung von Bleiglätte als Katalyst für die Alkoholyse an Stelle von Natriumhydroxyd Alkyde von hellerer Farbe und geringerer Neigung zum Nachdunkeln bei Ofentrocknung erhalten werden. Unter Verwendung derartiger Alkyde wurden pigmentierte Emaillacke, sowohl für Luft- als auch Ofentrocknung angefertigt und geprüft. Dabei stellte es sich heraus, dass ihre Filme im allgemeinen härter waren, als die eines herkömmlichen Pentaerithrit Alkydes, der nicht mit Milchsäure modifiziert worden war. Mit abnehmendem ölgehalt verringerte sich der Glanz der Emaillacke. Die Neigung zu Schrumpferscheinungen nach Ofentrocknung war geringer, wenn die Harze mit Milchsäure modifiziert worden waren.

Die Eigenschaften der Emaillacke stimmen in fast jeder Beziehung mit denen der mit Milchsäure modifizierten Alkyde überein, über die bereits berichtet wurde.

Introduction

A preliminary investigation of short oil pentaerythritol alkyds² showed that they could be made satisfactorily and to have interesting properties when lactic acid was incorporated. The conventional manner of facilitating production of such short oil resins is by reduction of the functionality by, for example, incorporating a monofunctional acid or a polyol of lower functionality. Both methods in principle tend to defeat the object of using pentaerythritol and, for example, alkyds based on suitable blends of pentaerythritol and ethylene glycol behave more as glycerol alkyds. A method of making short oil pentaerythritol alkyds without this limitation is hence of definite interest and this can be done using lactic acid as has been previously reported.

The purpose of this present work was to examine certain properties of such lactic modified resins in more detail, the main aspects being a comparison with a conventional pentaerythritol/glycol alkyd, certain features of the production of the resins and the examination of pigmented films, both air dried and stoved.

Resin preparation

Because of the wide differences in viscosity normally found between conventional and lactic modified resins, it has been the practice to cook them, using acid value as a criterion rather than viscosity. This gives resins of comparable degree of esterification.

This approach was similarly adopted to prepare a 55 per cent oil length linseed pentaerythritol alkyd. In the absence of some form of modification, difficulty is experienced in consistently preparing resins of this composition since there is always a danger of gelation before a sufficiently low acid value is attained and the product in any event might not be entirely stable on storage. Hence, for purposes of comparison, it was thought appropriate to modify the resin by incorporating a glycol since this not only gave a resin not liable to the disadvantages above but also enabled a direct comparison to be made of the two methods of achieving shorter oil lengths, namely, lactic acid modification and lowering functionality. The formulation and characteristics of the control resin are given in Table 1.

The alcoholysis was carried out using the linseed oil and pentaerythritol and 0.1 per cent NaOH as catalyst at 250°C. On reaching maximum methanol tolerance, the temperature was dropped to 150°C, the ethylene glycol and phthalic anhydride added and esterification carried out at 220°C azeotropically, using xylol as the entraining agent.

Two 45 per cent oil length lactic modified resins were prepared essentially as described previously. It had been found³ that improved colour of lactic acid modified resins resulted if litharge were used as alcoholysis catalyst in place of sodium hydroxide, but no direct comparison of the two catalysts was made. Accordingly, this was included in this programme, preparing two otherwise identical resins, except that litharge was used in one, sodium hydroxide in the other. The method of manufacture was as described previously², except that it has been found possible to add both the lactic acid and phthalic anhydride to the monoglyceride at 150°C and pursue the esterification normally. Details of these resins are given in Table 2.

Table 1
55 per cent glycol modified pentaerythritol alkyd T815

Alkali refined linseed oil	53.4
Pentaerythritol	14.3
Phthalic anhydride	29.3
Ethylene glycol	3.0
	100.0
<i>Properties</i>	
Theoretical water	3.5
Oil length	55%
Excess hydroxyl	20%
Colour (PRS scale)*	2
Viscosity (poises)*	0.6
Acid value	16.1

*60 per cent in xylol.

Table 2

	<i>T670</i>	<i>T671</i>
Alkali refined linseed oil	41.5	41.5
Pentaerythritol	16.0	16.0
Phthalic anhydride	25.2	25.2
Lactic acid BP	17.3	17.3
	100.0	100.0
<i>Properties</i>		
Theoretical water	8.1	8.1
Oil length	45%	45%
Excess hydroxyl	20%	20%
Alcoholysis catalyst	NaOH	PbO
Colour (PRS scale)*	3	2
Viscosity (poises)*	0.5	0.6
Acid value	14.9	15.2

*50 per cent in xylol.

White enamels

Six white enamels were prepared using the three resins described here and three selected from those previously reported². The six resins were :

T79

55 per cent oil length linseed/lactic/pentaerythritol.

T80

50 per cent oil length linseed/lactic/pentaerythritol.

T670

45 per cent oil length linseed/lactic/pentaerythritol (catalyst, NaOH).

T671

45 per cent oil length linseed/lactic/pentaerythritol (catalyst, PbO).

T171

40 per cent oil length linseed/lactic/pentaerythritol.

T815

55 per cent oil length linseed/pentaerythritol/glycol.

All were dissolved to give 60 per cent solutions in xylol and used in this form. The paints were prepared by grinding overnight in a ball mill at high pigment concentration and subsequently adding the balance of resin and thinner. The details are given in Table 3.

Table 3

	<i>P1</i>	<i>P2</i>	<i>P3</i>	<i>P4</i>	<i>P5</i>	<i>P6</i>
Titanium dioxide (<i>Tioxide R.CR</i>)	28.2	28.2	24.9	28.2	26.2	26.6
<i>T79</i> solution	63.3	—	—	—	—	—
<i>T80</i> solution	—	63.3	—	—	—	—
<i>T670</i> solution	—	—	56.1	—	—	—
<i>T671</i> solution	—	—	—	63.3	—	—
<i>T171</i> solution	—	—	—	—	59.1	—
<i>T815</i> solution	—	—	—	—	—	60.1
Xylol+driers*	8.5	8.5	19.0	8.5	14.7	13.3
	<u>100.0</u>	<u>100.0</u>	<u>100.0</u>	<u>100.0</u>	<u>100.0</u>	<u>100.0</u>
Viscosity (BS flow cup at 20°C seconds)	40	60	122	119	30	118

*Driers equivalent to 0.05 per cent Co on base resin.

These paints were then applied to glass and mild steel panels by a doctor blade set at 3/1000 in and to tin plate panels by brushing. The films were examined in the following manner.

Colour, wrinkling and blooming were assessed subjectively after seven days' drying, 10=excellent, 0=poor.

Gloss was assessed after 24 hours' drying using a visual glossmeter¹, in which the maximum angle at which reflection is visible is recorded. The higher the angle, the greater the gloss.

Hardness was measured by rocker hardness and by pencil hardness, in which a sharpened round point is gently pushed obliquely into the film.

Adhesion was evaluated by making two series at right angles of parallel cuts spaced 2 mm apart through the film, applying adhesive cellulose tape and removing this by a sharp pull. The percentage of the film area remaining on the substrate is a measure of the adhesion.

Flexibility was examined after 168 hours' drying by $\frac{1}{8}$ in bend test.

Water resistance was tested by allowing glass panels prepared as above to dry at room temperature for 48 hours and immersing in water at room temperature for 48 hours. The extent of recovery of film properties was noted 24 hours after withdrawal. The observations are summarised in Table 4.

Table 4
Air dried films

	P1	P2	P3	P4	P5	P6
Touch dry time (hours) ..	3	1 $\frac{3}{4}$	1 $\frac{1}{2}$	1 $\frac{3}{4}$	1 $\frac{1}{2}$	3 $\frac{3}{4}$
Hard dry time (hours) ..	3 $\frac{3}{4}$	2 $\frac{3}{4}$	2 $\frac{3}{4}$	2 $\frac{3}{4}$	1 $\frac{3}{4}$	5
Gloss	80°	80°	70°	80°	70°	80°
Colour	8	7	8-9	9	8	8-9
Wrinkling	Nil	Nil	Nil	Nil	Nil	Nil
Blooming	V. sev.	V. sev.	V. sev.	V. sev.	V. sev.	V. sev.
Pencil hardness						
24 hours	B	B	2H	2H	H	HB
48 hours	HB	HB	3H	3H	2H	2B
168 hours	6H	6H	6H	4H	6H	H
Rocker hardness						
24 hours	24%	25%	30%	31%	29%	16%
48 hours	32%	32%	35%	39%	40%	16%
168 hours	54%	55%	53%	46%	52%	27%
$\frac{1}{8}$ in bend test	Pass	Pass	Pass	Pass	Pass	Pass
Adhesion :						
Glass						
48 hours	72%	100%	48%	90%	32%	100%
168 hours	100%	44%	100%	100%	100%	90%
Mild steel						
48 hours	92%	100%	100%	100%	100%	100%
168 hours	90%	100%	100%	100%	100%	100%
Tin plate						
48 hours	100%	100%	100%	100%	100%	100%
168 hours	50%	100%	100%	100%	100%	100%

Water resistance

P1

Severe micro blistering overall, moderate softening.

Recovery : overall blistering, very slight bleaching, moderate loss of gloss, physical properties excellent.

*Water Resistance**P1*

Severe micro blistering overall, moderate loss of gloss, moderate softening.

Recovery : collapsed blisters visible under $\times 10$ magnification, otherwise excellent.

P2

Severe micro blistering overall, severe loss of gloss, moderate softening.

Recovery : collapsed blisters visible under $\times 10$ magnification, moderate loss of gloss, otherwise excellent.

P3

Severe micro blistering overall, moderate loss of gloss, moderate softening.

Recovery : collapsed blisters visible under $\times 10$ magnification, very slight loss of gloss, otherwise excellent.

P4

Severe micro blistering overall, moderate loss of gloss, moderate softening.

Recovery : large number of collapsed blisters visible under $\times 10$ magnification, moderate loss of gloss, otherwise excellent.

P5

Severe micro blistering overall, moderate loss of gloss, moderate softening.

Recovery : collapsed blisters visible under $\times 10$ magnification, otherwise excellent.

P6

No blistering, very slight loss of gloss, slight wrinkling, moderate softening.

Recovery : excellent.

A brief practical examination of the paints was then made by thinning, where necessary, with additional xylol to a viscosity of 30-35 seconds, BS flow cup, Type B4, at 25°C. In view of the wrinkling experienced on stoving with *P4* and *P6*, an attempt was made to eliminate it by adding to these paints zinc naphthenate to give 0.1 per cent Zn on base resin. The modified paints were then sprayed on tin plate panels and air dried or stoved for 30 minutes at 120°C. The observations made on the dried films are reproduced in Table 6.

Table 6
Sprayed films

	<i>P1</i>	<i>P2</i>	<i>P3</i>	<i>P4</i>	<i>P5</i>	<i>P6</i>
<i>Air dried</i>						
Gloss	80°	75°	75°	80°	45°	80°
Colour	7-8	8	8-9	9	8	8
Flow	8	6	10	10	10	10
Pencil hardness	HB	4H	4H	4H	5H	2B
<i>Stoved</i>						
Gloss	75°	75°	75°	80°	60°	80°
Colour	6	7	7-8	8	7-8	7
Flow	6	8	10	8	9	7
Wrinkling	Nil	Nil	Nil	Nil	Nil	F. sev.
Pencil hardness	4H	4H	5H	6H	5H	2B

Skinning and settling

The paints were stored in partially filled but closed containers for 28 days, when the following observations were made on their condition :

P1

No skinning, slight soft settlement, slight syneresis.

P2

No skinning, no settlement, slight syneresis.

P3

Thin rubbery skin, no settlement or syneresis.

P4

Thin skin, slight soft settlement, slight syneresis.

P5

No skinning, no settlement, no syneresis.

P6

No skinning, moderate settlement, slight syneresis.

Discussion of results

The effectiveness of lactic acid in reducing resin viscosity is well demonstrated by the comparative readiness in which short oil pentaerythritol alkyds can be prepared. This has only been possible hitherto by reducing the average functionality of the resin formulation in some manner. However, the results quoted here show that only 3 per cent ethylene glycol was sufficient to effect the resin properties significantly, whereas lactic acid, at considerably higher percentages, does not produce such marked changes in film properties. This is consistent with the postulate that lactic acid modifies the structure of the polymer chain without affecting functionality.

The colour of lactic acid modified resins is significantly improved by replacing sodium hydroxide as alcoholysis catalyst by litharge. It is believed that the darkening previously observed with these resins was occasioned by caramelisation of small amounts of sugars as impurities in the lactic acid by the alkali.

Consideration of the film properties leads to the following conclusions, which are presented separately for air dried and stoved films.

Air dried films

The drying time of the lactic modified alkyds in general became shorter as the oil length decreased while the films were initially harder, though this difference disappeared after seven days' drying. The rate of hardening is slower with pigmented films than with the clear films previously reported.

Gloss was generally good, except at the shortest oil length (*P5*), when the films were slightly hazy. There was no wrinkling and the films bloomed characteristically for pentaerythritol alkyds.

Flexibility was satisfactory and adhesion to mild steel and tin plate was good, except at the longest oil length (*P1*).

Comparison of *P3* and *P4* reveals that the replacement of sodium hydroxide by litharge as alcoholysis catalyst occasioned somewhat improved gloss and colour, but the films were slightly softer.

There is a marked difference in rate of drying and hardening between the lactic modified resins and the control pentaerythritol/glycol resin (*P6*), which was slower drying and gave much softer films.

On water immersion, all the paints formed a large number of very small blisters, which did not disappear entirely after withdrawal. There was also, in the case of the lactic modified resins, some loss of gloss, although it is thought that this is partially accounted for by the smooth surface of the film being disrupted by the blisters. Some improvement in colour of the immersed area was also found at the longer oil lengths, and this may suggest leaching out of the coloured component, which is, presumably, water soluble. Another tendency was the slight wrinkling of some films on immersion, although the control was considerably worse than the others in this respect. No essential differences appeared to arise due to change in oil length or alcoholysis catalyst.

Stoved films

All the lactic modified resins gave approximately the same hardness on stoving and in all cases this was of a satisfactorily high order. Adhesion was satisfactory except for the longest oil length on tin plate. Flexibility was also satisfactory. Gloss tended to decrease slightly as the oil length decreased, while colour was fairly good for a stoving finish on a linseed alkyd. Wrinkling was found to a slight extent on one or two panels, but *P4* using litharge was much more prone to this defect and some modification to the paint formulation was necessary in this case to overcome it.

The most striking feature of the results is the considerable improvement in hardness of the lactic modified resins over the control. The control was also the worst resin for wrinkling.

On water immersion, all the lactic modified alkyds blistered and lost gloss and were inferior to the control in both respects.

As with air dried films, the use of litharge tended to give improved gloss and colour of the stoved film.

On storage, only two paints developed skinning, i.e. those based on the 45 per cent oil length resins described here. Pigment settled more rapidly in the paint using the control resin than in those with the lactic modified resins.

Conclusions

The promise of short oil lactic modified pentaerythritol alkyds noted previously is generally confirmed by the present work. White enamels prepared from such resins exhibit fast drying to give hard flexible films of good gloss and appearance. Adhesion is satisfactory. Notably hard films are obtained on stoving without giving inadequate flexibility, while gloss and appearance were also good.

The improved colour of and gloss given by lactic acid modified resins consequent upon replacing sodium hydroxide by litharge as catalyst in the alcoholysis has been confirmed, although this did occasion some difficulty with wrinkling on stoving.

The water resistance of both air dried and stoved films was somewhat inferior due to the formation of a large number of blisters and some loss of gloss.

A most significant feature is the generally considerable enhancement of the mechanical properties of the films of the lactic acid modified resins over the control using ethylene glycol. This would seem to demonstrate plainly the difference between using lactic acid and a method of reducing functionality in order to control the manufacture of reactive alkyd resin systems and would further suggest that lactic acid is technically preferable in almost all respects.

[Received 15 April 1965]

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Pit corrosion in internally painted cargo and cargo/ballast tanks of ocean-going crude oil tankers

By P. Voogel

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Summary

This paper suggests an electro-chemical explanation of pit corrosion in internally painted cargo and cargo/ballast tanks of crude oil tankers.

La venue de corrosion en forme de piqûre dans les réservoirs à charge ou à lest—revêtus intérieurement de peinture—à bord des navires-citerne au long cours propres à pétrole brut

Résumé

Cet article propose une explication électro-chimique à l'égard de corrosion en forme de piqûre dans les réservoirs à charge ou à lest—revêtus intérieurement de peinture—à bord des navires-citerne au long cours propres à pétrole brut.

Loch-Korrosion an Gestrichenen Innenwänden von Lade und Lade/Ballast Tanks in Hochsee-Tankschiffen für Rohes Erdöl

Zusammenfassung

In der vorliegenden Arbeit wird der Versuch gemacht, Lochkorrosion an mit Anstrich versehenen Innenwänden von Lade und Lade/Ballast Tanks in Rohöl-Tankschiffen auf elektrochemische Vorgänge zurückzuführen.

Introduction

During the inspection of crude oil tankers with fully or partly painted internal tanks, the following fact has become evident.

Pit corrosion occurs in all horizontals, both high up in the tank and far down on the bottom. This pit corrosion is very serious in cargo/ballast tanks, causing a large number of rather deep pits.

In "cargo only" tanks the same pattern occurs, but, to a less extent, both as regards number and depth of the pits. In permanent ballast tanks this pit corrosion is not encountered, neither was pit corrosion detected when inspecting painted tanks in white product carriers. All tanks inspected were not protected cathodically.

It was also found that such surfaces as had been very carefully painted and holiday detected (among others the painted test sections in the *Ondina* and the painted tanks in the *Doelwijk*) suffered from pit corrosion after $\frac{1}{2}$ -1 year on the horizontals; the number of pits, however, was much smaller, but the depth of the pits was greater.

In general this pit corrosion is considerably more serious in painted tanks as compared with unpainted tanks of vessels in the crude oil trade.



Fig. 1. Examples of pit corrosion

In collaboration with a Netherlands tanker-owning company an investigation has been made into the occurrence of this serious pit corrosion, and it was found that this type of corrosion was evident in all tank coating systems applied so far, viz. :

- (a) Zinc-rich epoxy paint coat with 92 per cent zinc (about 25 microns) + micaceous iron oxide epoxy paint coat (about 50 microns).
- (b) Zinc-rich epoxy paint coat with 92 per cent zinc (about 25 microns) + high built epoxy paint coat (about 200 microns).
- (c) Epoxy coal tar paint coat (about 200 microns).
- (d) Zinc-rich epoxy paint coat with 92 per cent zinc (about 25 microns).
- (e) Four coats epoxy paint (with a total layer thickness of about 150 microns).

The above systems were applied in cargo/ballast tanks. For the cargo tanks the same systems were applied with the exception of (e).

Absolutely poreless layers do not, in practice, exclude the occurrence of one or more pores or damages.

It has been ascertained whether or not the galvanic corrosion damage or pores had been caused by copper or cast iron lines, but as in a number of coated tanks such lines were not present and these tanks still suffered serious pitting corrosion ; this is out of the question.

The " Max Planck Institut für Eisenforschung " (Max Plank Iron Research Institute) some ten years ago investigated this field at the request of some tanker shipping companies.¹

The problem concerned pit corrosion in tanks alternately filled with crude oil and ballast water ; the tanks, however, were not internally coated. In this work the crude oil film on the tank wall was regarded as a protective coating when the tank was filled with ballast water.

From this publication it appeared that the electrochemical reaction of this oil film was thought to be the cause of the pit corrosion at the bottom of the tank. The cathodic currents should pass through the oil film practically unimpeded, whereas the anodal solubility would be practically nil. This would imply long cell action between the top and bottom part of the tank if the oil film in the tank bottom was disturbed. The tank members near the surface of the water became cathodic and at the bottom the anodic spots occur where the oil film was disturbed. The substantial cathodic action was amplified by the movements of the vessel when the oil film was washed from the surface in the sea water filled tank, which was not completely full. Recent pit corrosion in some tanks coated with a 200 micron epoxy film can hardly be primarily attributed to long cell action.

Should, in some way or other, long cell action be the cause, the question remains why this pit corrosion occurs on the horizontal top and bottom surfaces and hardly ever on the vertical bottom surfaces.

In crude oil tankers permanent ballast tanks differ from cargo/ballast tanks in that the water under the crude oil on the horizontal surfaces of the latter has a high acidity (pH values of 2 and 5 have been measured). A laboratory has further investigated the influence of the acidic watery medium on the pores and damaged areas in the coating. The watery substance present in the permanent ballast tanks is nearly always alkaline, so behaviour of the various types of tank coatings were investigated in buffered electrolytes at various pH values.

Methods of test

Small steel plates were grit blasted and completely coated with some usual types of tank coating. All plates were tested one week and one year after coating. The trials consisted of measuring the potential difference in millivolts between the coated plate and a saturated calomel electrode after submersion in an electrolyte with a certain buffered pH value. The potential difference between an uncoated grit-blasted plate and a saturated calomel electrode in the aforementioned solutions was also measured.

For the results see the accompanying graphs depicting the values measured in millivolts set out against the numbers of the trial plates, which tally with the following table :

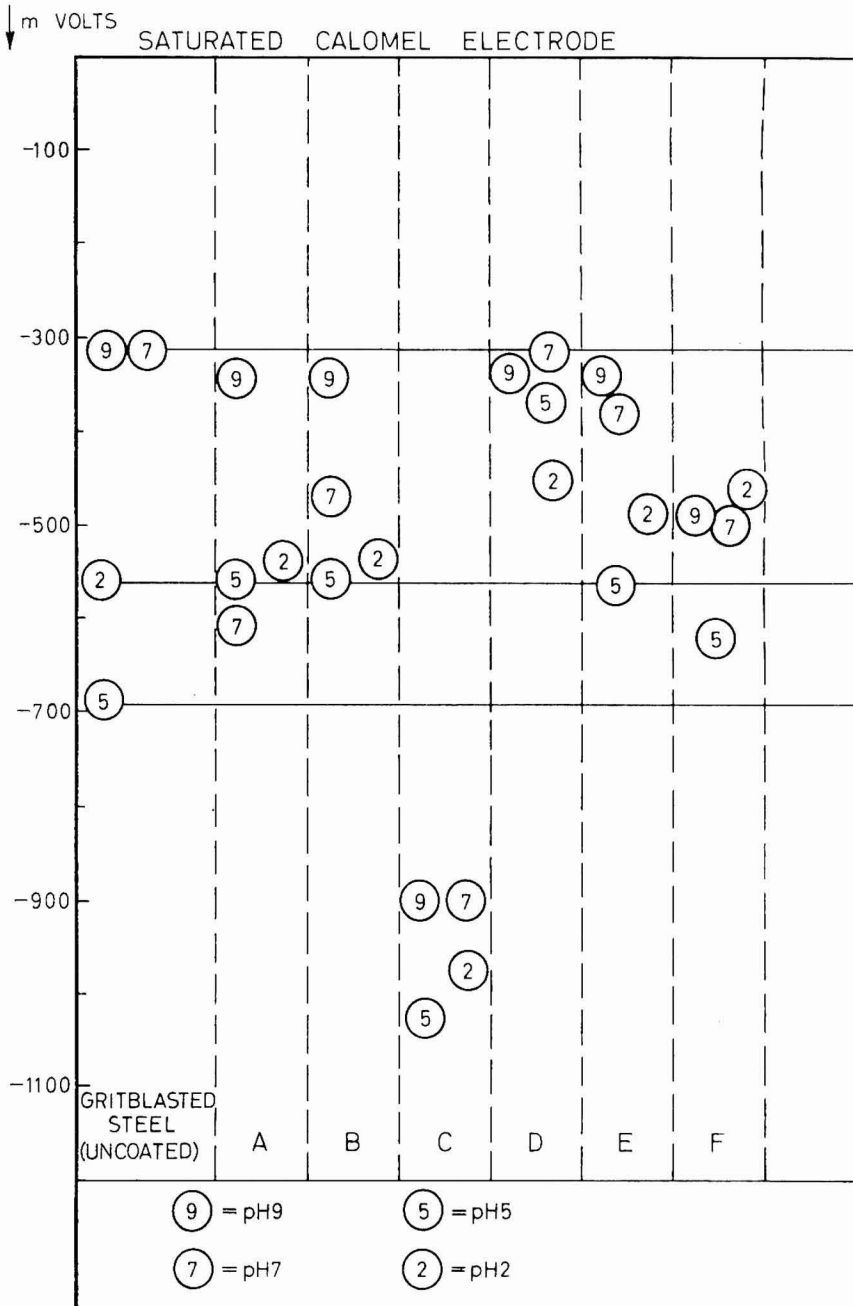


Fig. 2.

Plate	Type of coating	Film thickness (microns)	Ageing
<i>A</i>	“ High build ” epoxy paint film	About 200	1 week
<i>B</i>	Epoxy coal tar paint film	About 200	1 week
<i>C</i>	Zinc epoxy paint film (92 per cent zinc) + “ High build ” epoxy paint film	About 230	1 week
<i>D</i>	Zinc epoxy paint film (92 per cent zinc) + “ High build ” epoxy paint film	About 230	1 year
<i>E</i>	Zinc epoxy paint film (92 per cent zinc)	About 30	1 year
<i>F</i>	Zinc silicate paint film (92 per cent zinc)	About 30	1 year

Observations show that with a pH value below 7 the entire coated plate, with or without zinc primer (92 per cent zinc in the solid film), acts as a cathode towards an uncoated grit-blasted plate if the coating has aged one year. Even only one zinc primer coating of more than 92 per cent zinc in the solid film acts likewise after ageing one year.

It is a well-known phenomenon that such a zinc paint film, after some ageing, no longer cathodically protects the steel surface, although when this coating is damaged, the cathodic action may be more or less restored. In a neutral and in an alkaline environment the painted surface mostly behaves anodically towards uncoated grit-blasted steel.

If the painted surface is cathodic towards grit-blasted steel, the anodic solution of the steel could cause pit corrosion. If the painted surface is anodic towards grit-blasted steel, no pit corrosion will occur.

From the factual observations it can be deduced that the acidic water under the crude oil cargo acts as a catalyst in the pit corrosion process as far as the horizontal surfaces are concerned.

This deep pitting is not the normal attack of rather mild acid on the steel, but is far more severe. This may have been brought about by the painted surface around a pore or damaged spot, which acts as a cathode towards that pore or damaged spot. This explanation would also account for the pitting in zinc compound coated tanks as, after ageing, this paint coating on shot-blasted steel is also cathodic towards the uncoated pore or damaged spot.

Conclusions

The entire phenomenon of pit corrosion on horizontal surfaces at the top and bottom of a tank, whether completely or partly coated, could be due to the low pH value of the water under the crude oil during the laden voyage.

The latest data collected by a Netherlands tanker company support this hypothesis as :

- (a) It was clearly evident that no pit corrosion occurs in permanent ballast tanks.
- (b) Pit corrosion was worst in tanks containing ballast water and crude oil alternately.
- (c) Besides the acid in the water under the oil, the ballast water left in the tank also plays a part as this lowers the electrolytic resistance of the water.
- (d) The electrolyte content of the acid water under the crude of " cargo only tanks " is less, so that these tanks should have less pit corrosion, which is corroborated by the factual observations.

[Received 3 May 1965]

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Phthalocyanine pigments and their application*

By R. F. Hill

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Summary

The paper surveys the history, manufacture and applications of phthalocyanine pigments.

Les pigments de Phthalocyanine et leurs applications

Résumé

L'exposé considère l'histoire, la fabrication et les applications des pigments de phthalocyanine.

Phthalozyaninpigmente und deren Anwendung

Zusammenfassung

Diese Arbeit gibt einen grossen Überblick hinsichtlich Geschichte, Fabrikation und Einsatz von Phthalozyaninpigmenten.

History

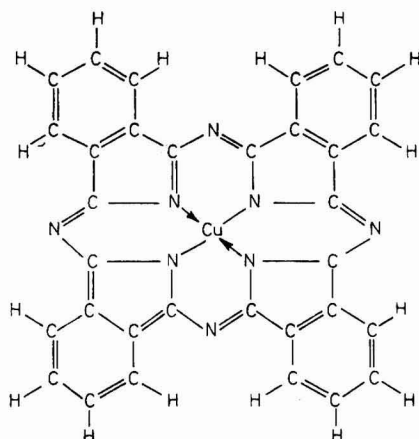
The introduction of the first phthalocyanine blue pigment was welcomed by all concerned in the colour industry, especially the paint chemist and the pigment manufacturer. Previously blue pigments had consisted of ultramarine, prussian blue, indigo derivatives, some azo compounds and some basic dyes-toners. However, they all suffered from defects and, in general, these had poor resistance to chemical attack in alkaline or acid medium, poor lightfastness and instability at high temperatures, decomposition taking place in some cases. Phthalocyanine pigments may be described as the most outstanding organic pigments, in that they show remarkable resistance to chemical attack, good fastness to heat and light, combined with brightness and cleanliness of shade. They will be oxidised by some oxidising agents to phthalic residues such as phthalimide.

The earliest discovery of phthalocyanine was by Braun and Tcherniac in 1907, who found a trace of a blue compound when preparing cyanobenzamide from the reaction between phthalamide and acetic anhydride. They did not recognise the importance of their discovery, and the next observation of a phthalocyanine compound was by de Diesbach and von der Weid, who in 1927 obtained a blue compound in 23 per cent yield when attempting to prepare phthalonitrile from the reaction of cuprous cyanide on *o*-dibromobenzene. They remarked on its stability to chemical attack, but like Braun and Tcherniac they did not recognise its potential as a pigment.

*This paper was awarded first prize in the Scottish Section's essay competition.

In 1928 at Scottish Dyes, during the preparation of phthalimide by the reaction of ammonia on molten phthalic anhydride in a glass lined iron vessel, a blue impurity was observed in the reaction mass. This impurity, iron phthalocyanine, was formed by the reaction of phthalimide with the iron lining in a flaw of the glass lining of the vessel. Dunworth and Drescher remarked on the crystalline form of the iron compound, its stability and the fact that it contained iron which was not removed when the compound was treated with sulphuric acid. One year later in 1929 a patent was granted to Scottish Dyes for the preparation of phthalocyanine. The process comprised the reaction between molten phthalic anhydride, ammonia and a metal salt. Many patents have been published since then and it has been possible to prepare metal derivatives for most of the metals of the periodic table. A metal-free derivative has also been prepared where the central metal atom is replaced by hydrogen.

Preliminary investigations into this new class of compound revealed that the empirical formula was $C_{32}H_{16}N_8M$ (where M is a metal). More careful investigation by Linstead enabled him to propose the following structure for a metal phthalocyanine :



Robertson, who carried out extensive X-ray studies, was able to confirm Linstead's proposed formula and to show that the molecule was planar rather than three-dimensional. Although it would appear that there is one *o*-quinonoid ring present, all the carbon bonds are equivalent owing to resonance of the molecule. The central metal ion is joined to two of the nitrogen atoms by covalent bonds and to the other two by co-ordinate bonds. From the skeletal representation of the molecule it is obvious how effectively the metal atom is protected within the interior of the molecule. Other properties which may be mentioned are the symmetry of the molecule, the essentially covalent bonding which contributes to its stability, and the lack of an appreciable dipole moment. There are several crystalline forms of phthalocyanine, the most important of which are the α and β forms.

Manufacture

Commercially the most important phthalocyanine is copper phthalocyanine (CuPc) and its derivatives, as they possess many of the properties of the "ideal"

pigment : stability to chemical attack, fastness to heat and light in combination with cleanliness and strength of shade.

Broadly speaking the preparation of CuPc can be divided into two classes, that of the "dry baking" process and the "solvent" process.

In the one form of the "dry baking"¹ process a copper conveyor belt is enclosed in a cylindrical shell to which a hopper is attached. The copper belt is electrically heated. A mixture of phthalonitrile and cuprous chloride is charged through the hopper and allowed to fall on to the belt, which has already been heated to 160°C. An exothermic reaction occurs and the temperature is thereby raised to approximately 280°C. Conversion of the phthalonitrile and cuprous chloride to copper phthalocyanine takes place, phthalimide being obtained as a by-product. The CuPc is collected in a discharge hopper. The process is advantageous in that the reaction reaches completion rapidly and can be carried out continuously. It suffers from the disadvantage that yields are low (70 per cent) and purification is costly. Slight chlorination will also take place which is not always desirable. The equation for the reaction is as follows :



The solvent process² involves the reaction between phthalic anhydride, urea and cuprous chloride in the presence of a small amount of catalyst. Trichlorobenzene is used as solvent and the reaction mass is stirred continuously over 16 hours at about 150°C. When the reaction is complete the trichlorobenzene is removed either by distillation or filtration. The disadvantages of this process are the slow reaction time and the high cost of solvent recovery. Both processes are widely used in the preparation of CuPc, but generally speaking the phthalic anhydride/solvent process is used if only CuPc is desired. Phthalonitrile will favour the formation of $\text{CuPcCl}_{0.5-1.5}$ and its use is confined primarily to the preparation of this derivative. The crude CuPc obtained from the above processes is mainly in the β -form and is greenish-blue in shade. The β -form is the most stable form of CuPc and the coarse crystals formed in the preparation may vary in size from the micron range to needle-like crystals, 2 cm in length. As such the crude CuPc has no pigmentary value and must be conditioned by further treatment.

The most favoured process is that known as "acid pasting" in which the CuPc is dissolved in sulphuric acid. The resulting solution is then precipitated into a large volume of water. The product is the α modification of CuPc, which is somewhat redder and brighter in shade than the crude β starting material, but less stable. The α form is of suitable particle size for use in pigment-consuming industries.

Applications

Having obtained a phthalocyanine in pigmentary form, it may have been concluded from the foregoing discussion that the pigment can be used in all applications with very little difficulty. However, copper phthalocyanine has its own defects. These are (i) poor dispersibility, (ii) poor flow, (iii) poor resistance to flocculation, (iv) crystal growth. The defects indicated above can

be ascribed to the physical form of phthalocyanine, in particular particle size and shape, and state of its surface.

In the early chemistry of phthalocyanines, crystallisation was often mistaken for the defect known as flocculation. Crystallisation involves the different arrangements of the molecules in the crystal lattice and the various shapes of the crystals can only be elucidated from X-ray diffraction studies or more recently from infrared spectrophotometric measurements. Since these are relatively modern techniques, it can be understood why the polymorphism shown by CuPc was not at first realised.

Crystallisation of phthalocyanine takes place in what are known as crystallising solvents, among which may be mentioned 1-chloronaphthalene, toluene, xylene and white spirit. When the α -form of CuPc was incorporated in a paint medium and stored for a period, the colour strength of the pigment was found to have deteriorated from that of the original product. Microscopic examination revealed the presence of crystals which were long and needle-like, and somewhat larger than the original α modification. The larger crystal size accounts for the strength difference, but what was more important was that the crystals were in the β -form. Slow conversion from the less stable α -form to the more stable β -form had taken place on storing. The stability of the β crystals so formed is indicated by the fact that no amount of regrinding would restore the original colour strength to the paint.

Phthalocyanines are soluble, although to a very slight extent in some solvents and crystallisation is attributed to this. A dynamic equilibrium is set up between dissolved and undissolved molecules. The stable β -form is formed by those molecules emerging from solution and these being larger crystals will develop more rapidly than the smaller, the process being known as Ostwald ripening.

Since most CuPc paint systems involve the use of crystallising solvents, the crystallisation defect had to be overcome, and many methods have been devised for producing a non-crystallising CuPc. One of the most favourable of these is to prepare a pigment solely in the β -form, which is of such a particle size as to produce good colour strength. This is achieved by grinding "the crude pigment" in a ball mill in the presence of a crystallising solvent and a water soluble salt. In this process there are two conflicting tendencies. Grinding with a salt, e.g. NaCl, will give the α -form CuPc, while if solvent alone were used a β -form would be produced, but without pigmentary value. A careful balance must be struck in order to give correct particle size and also the desired β modification. The salt is removed from the pigment by leaching with water. When used to pigment a paint system good colour strength was obtained and moreover no loss of strength was observed on prolonged storing in solvents. If, however, a mixture of crystals exists some loss in colour strength may occur, the loss of strength increasing with increasing α content.

A stabilised α -form can also be obtained which is not subject to recrystallisation. Such a product contains a substituent usually in the 4-position of the phthalocyanine molecule. Many substituents have been used, but the one which is most favoured is the chlorine atom. The chlorinated α -form is most easily prepared from 4-chlorophthalic acid as in the phthalic anhydride/solvent process or by using phthalonitrile in the "dry baking" process. The presence

of the chlorine atom in the 4-position upsets the symmetry of the molecule and for steric reasons crystallisation is prevented. (Although a chlorine atom in 3-position upsets the symmetry of the molecule, it does not prevent crystallisation.)

A mixture of a small amount of monochloro CuPc in CuPc is sufficient to confer crystallisation resistance just as effectively as if only monochlorinated CuPc had been used. The stable α -form is much redder in shade than the β -form. Other methods of preventing crystallisation are to use mixtures of CuPc with small amounts of AlPc, SnPc and MgPc, but the chlorinated derivative is most widely used.

The problem of crystallisation has been overcome by most pigment manufacturers, but there remain three major problems which have defied complete solution; these are flocculation, flotation and flooding. The attention of many phthalocyanine chemists has been directed towards overcoming these defects and they have benefited much from their experiences in that field. Flocculation is not peculiar to phthalocyanine blue alone, and is known in some other pigments, for example, Dioxazine Violet and some red and yellow pigments. Because of its nature, flocculation does not present such a difficult problem with red or yellow pigments, the shade difference between flocculated and unflocculated not being so great.

Flocculation in a paint system may be defined as the formation of aggregates in the can, which can be broken up by mechanical forces. The mechanical forces used may not break the aggregates into individual particles, only into flocs of about 1 micron in diameter, but these are sufficiently small to maintain the tinctorial properties of the paint. The aggregates can be broken up by brushing vigorously or by applying the paint from a spray gun and involve work being done on the paint system. If instead a paint panel is prepared merely by dipping, virtually no work is involved, and in the case of this paint panel, flocculation is very bad. As a consequence, a panel prepared by spraying will be stronger tinctorially than one prepared by brushing and both will be superior to one prepared by dipping.

The motor car industry was one of the major industries which suffered most from the defect of flocculation. If the same paint was used to coat the various components of a car body, various shade differences could be obtained according to whether the part were sprayed, brushed or dipped.

What causes flocculation in phthalocyanine paint systems? The answer is not readily given for in a phthalocyanine blue pigmented paint system there are three other variables which contribute to the defect, namely, solvent, resin and white pigment. If, for example, two paint panels are prepared using CuPc, the only difference being that titanium dioxide is used as white pigment in one and zinc oxide in the other, it will be noted that flocculation is considerably worse in that panel where titanium dioxide is used.

In their efforts to provide flocculation resistance, pigment chemists turned their attention towards the physical form of copper phthalocyanine. In a hypothesis put forward by these workers, they suggested that the clusters or flocs formed were caused by the planarity and symmetry of the molecules and to a larger extent by the lack of a significant dipole moment. To overcome

the latter defect, work was carried out to try to introduce a charge on to the phthalocyanine molecule.

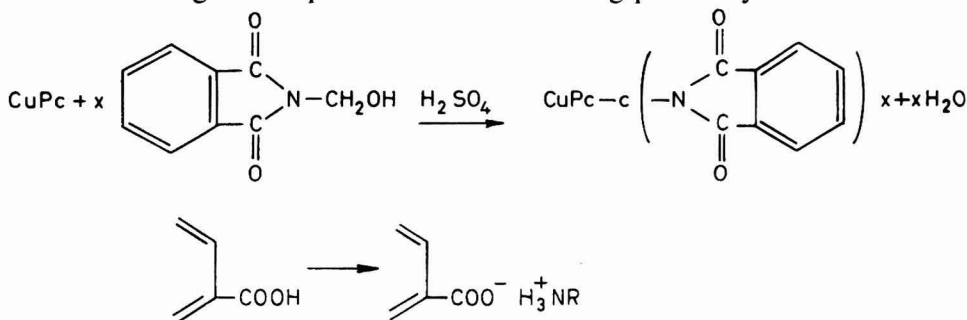
It has also been shown that flocculation is predominantly caused by the driving force resulting from the high free surface energy, which is a function of both nature of the surface and the size of the particles.

If a polar group was introduced on a CuPc molecule, then to confer flocculation resistance, the net repulsion of the charged molecules must be sufficient to overcome the van der Waal's and coulombic forces, causing the high surface energy. At this point it should be stated that flocculation had been overcome in other ways, but at the expense of some other property of the pigment, and as often as not this meant a reduction of tinctorial properties. Such methods involved the addition of large amounts of aluminium benzoate³ to the CuPc paste, or a baking process involving phthalonitrile and copper salts in the presence of equal parts zirconium or titanium oxides.

Other methods involved the preparation of the barium lake of the sulphonic acid derivative⁴ or by adding small amounts of SnPc to copper phthalocyanine⁵. Both were resistant to flocculation, but the former had poor alkali fastness and the latter proved undesirable due to its dirtiness of shade.

The synthesis of CuPc containing a negative polar group sufficiently charged to prevent flocculation was the aim of phthalocyanine chemists.

One method of obtaining such a product was to prepare an acid derivative of CuPc and form the corresponding ammonium or amine salt⁶. This was carried out during the acid-pasting stage by condensation between *N*-methylol-phthalimide and CuPc. The phthalimidomethyl derivative is then partially hydrolysed to *o*-carboxbenzomidomethyl derivative and then converted to the ammonium or amine salt by boiling with ammonium hydroxide or excess organic amine. The mono substituted derivative gave the best results and further by reacting this derivative with organic amines such as ethylene diamine the problem of crystallisation and flocculation could be largely overcome with comparative ease. The pigment obtained was of the desired shade and was somewhat stronger than previous non-flocculating phthalocyanine blues.



A non-flocculating pigment can also be prepared by heating phthalic anhydride, urea and cupric chloride with a small amount of 4-sulpho phthalic anhydride until reaction is complete¹⁴.

The above methods relating to the preparation of flocculation resistant pigments apply to what is known as "classical flocculation." Another type of flocculation is sometimes known as "dynamic flocculation" or flotation.

The effect is illustrated by allowing a drop of paint to run down a previously brushed panel which is still wet. The appearance of white striations or the formation of Bénard cells indicates the flotation effect. If a uniform colour change is noticed over the paint film, the phenomenon is known as flooding.

The nature of the solvent used in preparing a paint has an important bearing on flotation. Thus a quick drying paint will be more prone to flotation than a slowly drying paint. During the evaporation of the solvent it is considered that a "vortex effect" is taking place. As a consequence of these vortices there are centrifugal forces which carry the small pigment particles to the paint surface where flocculation may take place. It is the spiral effect of the vortices which causes the formation of the familiar Bénard cells and striations (which may be considered as elongated Bénard cells). In a paint exhibiting flocculation the flotation problem may not be so apparent, as the flocs will not be so mobile as individual particles. Thus in a phthalocyanine pigmented paint two opposing tendencies are at work, one in which individual particles are desired to overcome classical flocculation and the other in which larger particles are desired to overcome flotation. A very delicate balance has to be struck between the two and in general it is easier to tackle the two types separately.

The humidity of the atmosphere plays an important part in pigment flotation. This effect can be shown by exposing a phthalocyanine pigmented paint to different atmospheric conditions. Flotation will increase with increasing humidity if the pigment particles are sufficiently hydrophilic in nature.

Flotation may be overcome by incorporating some fatty acids or a suitable extender such as china clay. They have the effect of reducing the agitation or chaos in the vortices and so reduce the tendency of the pigment particles to "float" to the paint film surface.

The following methods will serve to distinguish between flocculation and flotation. The most severe test for flocculation is to prepare a paint panel by spraying and compare it with a dipped panel prepared from the same paint. No strength difference indicates the absence of flocculation. In testing for flotation, a brushed panel is supported at an angle of 30° to the vertical and a drop of paint allowed to run down the panel. The appearance of striations is observed if flotation is taking place.

There is no complete answer to flocculation and flotation/flooding, but the advances made towards finding a complete solution have allowed paint manufacturers to market paints which are suitable for practically all applications.

The particle size of CuPc is so small that it can only be determined by electron microscope. Taking the three pigments CuPc, TiO_2 and Toluidine Red, the corresponding particle sizes in microns are 0.052, 0.28 and 0.49. There will therefore be a proportionately greater number of particles in 1 gram of CuPc than in the other two, thus the specific surface of CuPc is greater. When introduced into printing ink media, the greater surface area of 1 gram CuPc will adsorb more of the media than, for example, the corresponding weight of Toluidine Red. The viscosity of a CuPc pigmented ink will be large compared with other inks and the flow will be inferior. Other factors influencing flow are the electrical properties of the particles (not the molecules), the

“loading” of the dispersion and the shape of the particles. The effect of the electrical charge can be reduced by coating the particles with suitable resins. The “loading” of the dispersion is further complicated by the fact that the viscosity-concentration relationship is exponential rather than linear and flow properties are best determined by careful experiments. Resins again may be used to improve dispersion. α and β phthalocyanine particles differ in shape and this will give different flow properties. In general the β modification will exhibit better flow characteristics than the α -form. It is assumed that “mechanical tangling” takes place in the α -form leading to increased resistance to shear.

Despite its inferior flow properties, when used as a printing ink, CuPc finds a wide market in this field. This is probably due to its non-bleeding in alcohols, esters, ketones, soaps, wax coatings and its non-toxicity.

The use of CuPc pigments is not confined to paint and ink manufacture and they are well known in rubber and plastics applications. The heat resistance of CuPc renders them specially useful, since they are not decomposed by the high moulding temperature required. It must be noted, however, that if a strong red shade is required a stabilised α -form must be used or a fast conversion to the β -form will occur. Shade differences can be introduced by using mixtures of α/β content, but in all cases the mixture will revert to 100 per cent β -form.

Although CuPc has been mentioned until now only in pigmentary applications, it is also an important dyestuff in the dyeing of cellulosic materials, e.g. cotton, wool and viscose rayon. The dyestuff can be prepared separately or within the pores of the material to be coloured by impregnation of the material with phthalocyanine precursors followed by suitable heat treatment.

In textile applications extensive use of resin bonded pigments is becoming important and the physical properties must be modified to meet the demands of the textile manufacturer. The major requirements are that the particles should be of suitable size to ensure satisfactory binding of the resin, the pigment dispersion should be stable and flocculation should not occur. In addition, the pigment must have an affinity for the fibre. The physical properties are controlled by suitable grinding and resination process.

Water soluble dyestuffs were prepared by sulphonation of phthalocyanine, a stage being reached where the sulphonation process has a maximum affinity for the fibre. Halogenated phthalocyanine disulphonic acid dyes having an increased affinity for cellulose fibres are prepared by reacting the disulphonic acids of CuPc or NiPc with a halogenating agent in the presence of an aluminium chloride melt. Best results are obtained when substitution by from 2 to 7 halogen atoms has taken place⁸. Another soluble dyestuff can be synthesised by preparing the quaternary salts of copper tetra-4-pyridyl phthalocyanine with dimethyl sulphate.

The advantages of CuPc were readily recognised and there was a general desire to extend the shade range to include red and yellow shades. Some measure of success was obtained when a related porphyrin was prepared in which the extracyclic nitrogen atoms were replaced by $-\text{CH}$ groups. Violet shades were prepared by this method, but they had very low solvent stability. The most

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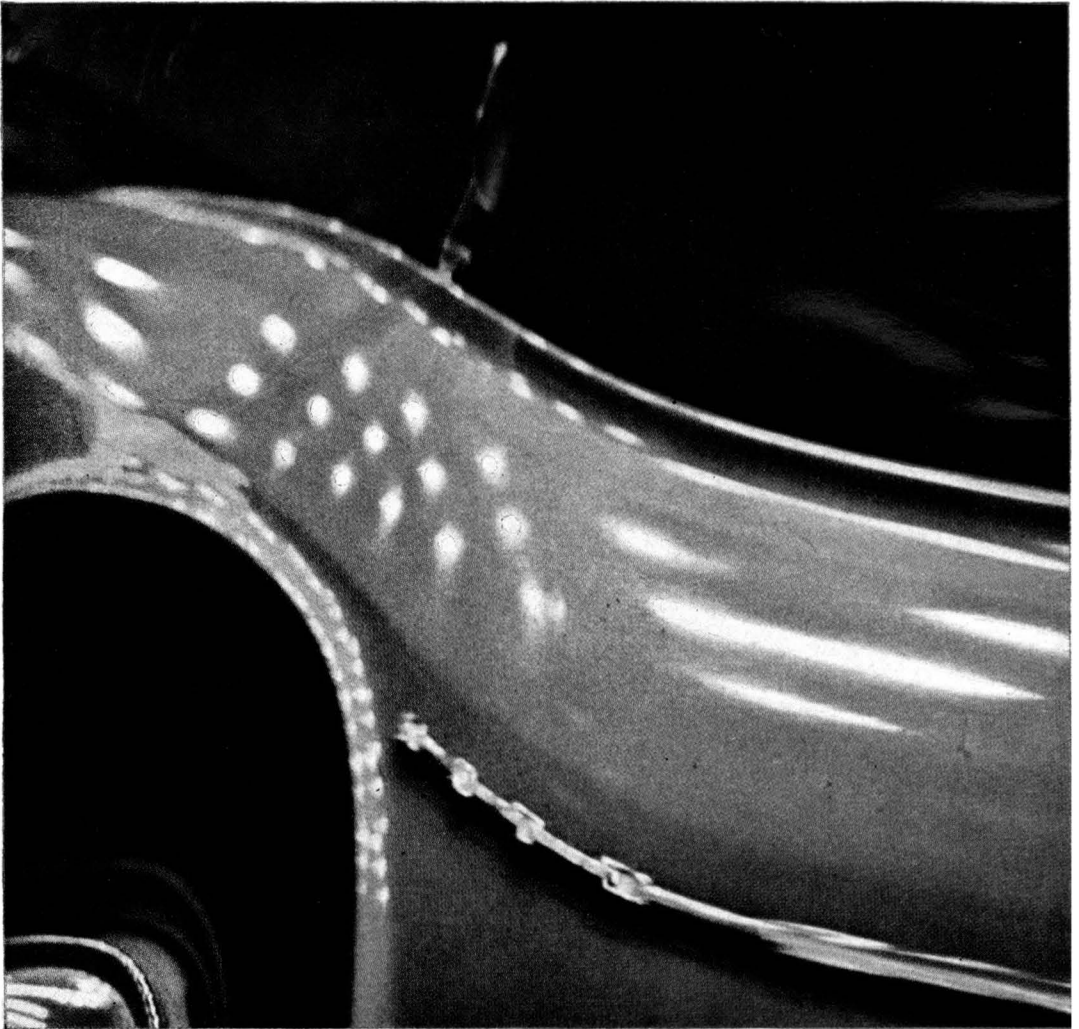
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successful attempts in extending the shade range produced phthalocyanine green.

Theoretically there are 16 available places for substitution in the benzene rings of phthalocyanine molecule. Substitution of 14-16 of these places by chlorine yields polychlorocopper phthalocyanine which is green in shade. The pigment obtained has all the outstanding properties associated with CuPc blue. Chlorination takes place readily and the substitution can be carried out in a great number of ways.

The most important method involves the use of a Friedel-Craft reagent. The process is best carried out using a eutectic mixture of aluminium chloride and sodium chloride, neither of which takes any part in the actual chlorination. Any metal phthalocyanine may be used, but CuPc gives the best results. Metal-free phthalocyanine can also be used, but substitution of the central hydrogen atoms may take place by aluminium. The following are two examples of methods which have been described for carrying out halogenation in the eutectic melt process. The first involves the use of pyrosulphuryl chloride an oxyhalide of sulphur. In this process aluminium chloride, sodium chloride, CuPc and pyrosulphuryl chloride are charged to a flask and reaction is then carried out at temperatures of between 120°-180°C over a period of three hours. The second reaction is similar, but instead of using pyrosulphuryl chloride, a mixture of sulphuryl chloride and sulphur monochloride is used. In each case the green pigment is obtained by precipitating the molten mass into cold water, and it is claimed that it can be used without further treatment.

In some cases phthalic anhydride¹¹ is used as a solvent for CuPc and the halogenating agent used is elemental chlorine. A catalyst must be used if a product containing more than 11 chlorine atoms is required. A method analogous to that for the preparation of Pc blue is also used¹².

In this case tetrachlorophthalic anhydride is used in conjunction with urea, cuprous chloride and an aromatic solvent, the mixture being heated until reaction is complete. The solvent is removed by steam distillation. It has been reported by some workers that for the above reaction to go to completion cupric chloride dihydrate must be used¹³. The reason suggested is that if anhydrous cuprous chloride is used an imide will be formed, which is the most stable compound formed. The crude green pigment obtained from the above processes can be used without further treatment. It is more usual for a finishing process to be employed as better results are obtained. An acid pasting process may be used, although it may be necessary to use stronger acid, e.g. oleum or chlorosulphonic acid, owing to the lower solubility of the green.

Only one crystalline form of CuPc green occurs, hence recrystallisation will not occur in solvents and as a result they can be used in the after-treatment of the green pigment. One method involves refluxing the green filter cake with an aromatic solvent in the presence of a fatty acid salt. The solvent is removed by distillation or filtration¹⁴.

A yellower product than that obtained by chlorination of CuPc can be prepared by chlorination of metal-free phthalocyanine or by substitution by bromine atoms. A brominated compound was not so readily prepared as the chlorinated compound and it is only recently that a bright yellow-shade green

has appeared commercially, although patents were published before the war. Alkali or alkaline earth metal bromides are used as brominating agents in a reaction similar to that for preparing the chlorinated compound. Elemental bromine may be used, depending on the degree of substitution required.

Experiments are still being carried out to extend the shade range of phthalocyanines outside the blue-green range.

More work will be done to produce pigments having these desirable red and yellow shades, but their synthesis would appear to be difficult. It is more likely that advances will be made in eliminating flow, flocculation and dispersion defects.

Phthalocyanine pigments have produced a major revolution in the pigment industry and chemists are striving daily to produce pigments (not necessarily of phthalocyanine structure) which will match, in general, their all-round properties.

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Photochemistry of vinyl chloride/ vinyl-iso-butyl ether copolymer : Part II

Crosslinking of the copolymer by light

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Summary

The relationship between gel formation and UV irradiation dosage has been studied using the vinyl chloride/vinyl isobutyl ether copolymer described previously. The results have been used to evaluate the ratio of quantum yields for scission and cross-linking by means of the Schultz equation solved iteratively on a digital computer. It is shown that this ratio, which is < 1 over the dosage range studied, falls as irradiation proceeds and there are indications that the quantum yields for both reactions are dosage-dependent. The mechanism of the degradation/cross-linking processes is discussed in the light of these and earlier infrared studies, and it is suggested that observations are consistent with a radical or partly radical mechanism similar to that induced by gamma radiation.

Photochimie du copolymère ether de chlorure de vinyle/vinyle- iso-butyle : 2ème Partie

Résumé

Le rapport existant entre la gélification et le dosage des irradiations ultraviolettes a été étudié à l'aide du copolymère d'éther isobutylique de chlorure/vinyle vinylique, décrit précédemment. Les résultats ont été utilisés afin d'évaluer le taux des rendements quantiques pour la scission et la copolymérisation grâce à l'équation de Schultz, résolue itérativement à l'aide d'un ordinateur numérique. Il est démontré que ce taux, qui est de < 1 pour l'ensemble des dosages étudiés, diminue au fur et à mesure que l'irradiation se déroule et certaines indications permettent de déduire que les rendements quantiques pour les deux réactions dépendent du dosage. Le mécanisme des phénomènes de dégradation/copolymérisation est commenté à la lumière de ces études et des études précédentes aux radiations infrarouges ; cet article décrit également les observations faites comme étant en harmonie avec un mécanisme radical ou partiellement radical, similaire à celui engendré par les radiations gamma.

Die Photochemie von Vinylchlorid/vinyl-iso-butylester-copolymer: Teil II

Zusammenfassung

Die Beziehungen zwischen Gelbildung und UV Bestrahlungsdosis wurden untersucht, wobei die bereits beschriebenen Copolymere aus Vinylchlorid/Vinylisobutyläther benutzt wurden. Die Ergebnisse wurden dazu verwandt, um die Grösse der Quantenausbeuten hinsichtlich Spaltung und Vernetzung mittelst der Gleichung von Schultz, wiederholt mit Hilfe eines Digital-Computers aufgelöst, zu berechnen. Dass dieses Grössenverhältnis, welches < 1 oberhalb des untersuchten Dosierungs bereiches liegt, in dem Masse abfällt, in dem die Bestrahlung fortschreitet, wird aufgezeigt ; es sind ausserdem Anzeichen dafür vorhanden, dass die Quantenausbeuten für beide Reaktionen von der Dosierung abhängen. Der Mechanismus des Degradierungs/Vernetzungs-Prozesses wird im Lichte dieser und früherer infraroter Studien besprochen, und es wird weiterhin vorgebracht, dass die Beobachtungen mit einem radikalalen oder teiltradikalalen Mechanismus, entsprechend einem durch gamma-Strahlung induzierten, in Einklang gebracht werden können.

Introduction

The mechanism and kinetics of photolysis of vinyl chloride/vinyl isobutyl ether copolymer were described in a previous paper¹. It was found that the chlorine atoms are strongly connected with the main chain of the copolymer whereas isobutyl substituent yields to scission relatively easy. Also the change of the carbon chains' stereoregularity caused by the ultra-violet radiation was observed.

The problem of the crosslinking of the copolymer seems to be worthy of separate consideration because of its considerable practical and theoretical interest.

Generally the polymer network formation depends on the absorption of radiation energy. If the absorption coefficient k (cm^{-1}) of UV-light remains constant during the radiation period, the largest part of the energy is being absorbed at the incident surface. Energy absorbed in the inner laminus situated at the depth x below the incident surface is, readily expressed by the equation :

$$R_x = k.t.v . I_0 e^{-kx} = R_0 e^{-kx} \quad (1)$$

where t is radiation time (sec) with light of intensity I_0 (photons $\cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$) v is specific volume of polymer ($\text{cm}^{-3} \cdot \text{g}^{-1}$) and R_0 (photons $\cdot \text{g}^{-1}$) is the energy absorption at the incident surface.

The crosslinking of polymer molecules causes the formation of insoluble fraction (gel). The evaluation of the gel concentration of an irradiated polymer film allows the estimation of the quantum yield for polymer crosslinking.

In the case of the investigated copolymer, the crosslinking was associated with the scission of carbon chains. Thus, the gel formation should be regarded as the sum of simultaneous crosslinking and degradation effects, taking place at each laminus of thickness dx .

The quantity of gel (g) in the polymer sample of thickness (L), is evaluated by the definite integral :

$$g = L^{-1} \int_0^L L_0 g_x dx \quad (2)$$

where g_x is an implicit function of energy absorption at the incident surface (R_0); energy absorption in polymer film of thickness L (R_L); quantum yields for crosslinking and degradation, φ_c and φ_d respectively; and gelation dose (R^*). The last term is an auxiliary notion in photochemistry of polymers and represents the radiation dose producing incipient gel formation in the polymer.

Considering that :

- (a) the investigated copolymer contained no insoluble fraction before irradiation
- (b) the condition of experiments were arranged that $R_L > R_x$
- (c) $\varphi_c > \varphi_d$ because of big share of insoluble fraction, equation (2) can be developed to the trivial solution according to Schultz²:

$$g = \left(\frac{1}{2} - \frac{\varphi_d}{\varphi_c} \right) + C(kL)^{-1} \left(\frac{R^*}{R_0} - \frac{R^*}{R_L} \right) - 2(kL)^{-1} \left[\left(B + C \frac{R^*}{R_L} \right)^{\frac{1}{2}} - \left(B + C \frac{R^*}{R_0} \right)^{\frac{1}{2}} \right] \\ + 2B^{\frac{1}{2}}(kL)^{-1} \left[\operatorname{ctnh}^{-1} \left(1 + \frac{C}{B} \frac{R^*}{R_0} \right)^{\frac{1}{2}} - \operatorname{ctnh}^{-1} \left(1 + \frac{C}{B} \frac{R^*}{R_L} \right)^{\frac{1}{2}} \right] \quad (3)$$

where $B \doteq \left(\frac{1}{4} + \frac{\varphi_d}{\varphi_c} \right)$; $C \doteq \left(2 - \frac{\varphi_d}{\varphi_c} \right)$

The aim of the work was the evaluation by equation (3) of the ratio of quantum yield for scission to the quantum yield for crosslinking $\frac{\varphi_d}{\varphi_c}$, and the evaluation of how this ratio varies with dose.

Experimental

The properties of the copolymer, the method of irradiation, and the method of light intensity measurements were described in the previous paper¹.

The copolymer as $50 \pm 5\mu$ thick free film was irradiated over periods of 30.5 ; 41.0 ; 71.0 ; 87.5 and 145.0 hours.

The absorption coefficient, evaluated by actinometric measurements, was $k = 1.32 \times 10^2 \text{ cm}^{-1}$.

The amount of insoluble fraction (gel) was estimated by weight. The films, irradiated with various doses, were extracted in Soxhlet's apparatus with ethyl acetate for 4 hours.

The results of gel fraction determinations are shown in Table 1.

Table 1
Gel content [g] in copolymer after irradiation

Irradiation time—t [hours]	Incident energy— I_0 [erg . cm ⁻²]	Gel content—g [%]
30.5	2.6×10^{10}	20.8
41.0	3.5×10^{10}	20.1
46.0	3.9×10^{10}	20.6
71.0	6.0×10^{10}	23.1
87.5	7.4×10^{10}	24.3
145.0	12.3×10^{10}	36.5

Results and discussion

The solution of equation (3) i.e. the evaluation of the ratio $\frac{\varphi_d}{\varphi_c}$ from known values g , L , K , R_0 , R_L and R^* can be done by iteration method³. Regarding the long way (hyperbolic and exponential functions), the equation was solved by universal electronic digital computer UMC-1 (the type γ , 1963 y. f-m Elwro, Poland).

The values R_0 and R_L needed for solution of equation (3) were calculated for all exposure periods from equation (1). Under the prevailing experimental condition $RL=0.517 R_0$.

The gelation dose R^* was estimated graphically plotting the results from Table 1 on the graph: \log . of weight fraction sol s ($s=1-g$) versus \log . of energy absorbed by copolymer. (Fig. 1). The extrapolation of the curve to the value $s=100$ per cent gives $R=2.03 \times 10^{21}$ photons $\cdot g^{-1}$.

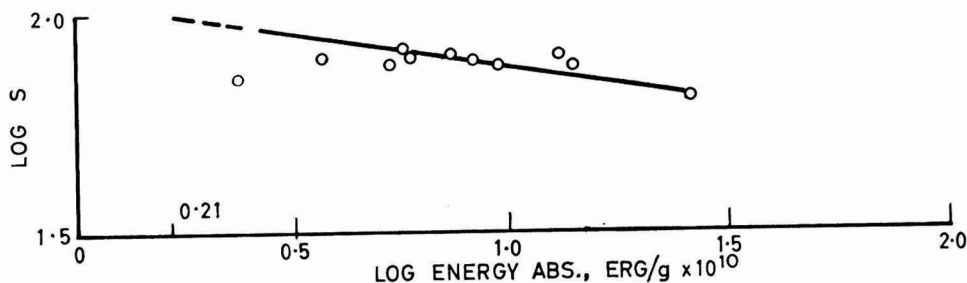


Fig. 1. Logarithmic plot of sol fraction concentrations against energy absorbed (erg. g^{-1})

The results of calculations of ratio $\frac{\varphi_d}{\varphi_c}$ at assumed accuracy of evaluation $\delta=0.00001$, and effective accuracy $e=0.001$ are presented in Table 2. In the last row of Table 2 the values gk are given, which are the control results of calculations received from substitution of values $\frac{\varphi_d}{\varphi_c}$ to the equation (3). The obtained values by this way are identical with those of g (the gel fraction established experimentally) continuing the great accuracy of iteration.

Table 2
Calculations of $\frac{\varphi_d}{\varphi_c}$ ratios for irradiated copolymer

Irradiation time— t [hours]	Energy absorbed [protons $\cdot g^{-1}$]	Gel content g	$\frac{\varphi_d}{\varphi_c}$	gk
30.5	3.39×10^3	0.208	0.265	0.208
41.0	4.55×10^3	0.201	0.279	0.201
46.0	5.11×10^3	0.206	0.277	0.206
71.0	7.89×10^3	0.231	0.257	0.231
87.5	9.72×10^3	0.243	0.248	0.243
145.0	16.1×10^3	0.365	0.129	0.365

The variation of values with dose absorbed by copolymer is shown in Fig. 2. The $\frac{\varphi_d}{\varphi_c} < 1$ found within entire range of applied radiation doses proves that crosslinking takes place faster than degradation. The character of the curve shown in Fig. 2 suggests that both quantum yield for scission and that for crosslinking are subject to change during the photolysis process.

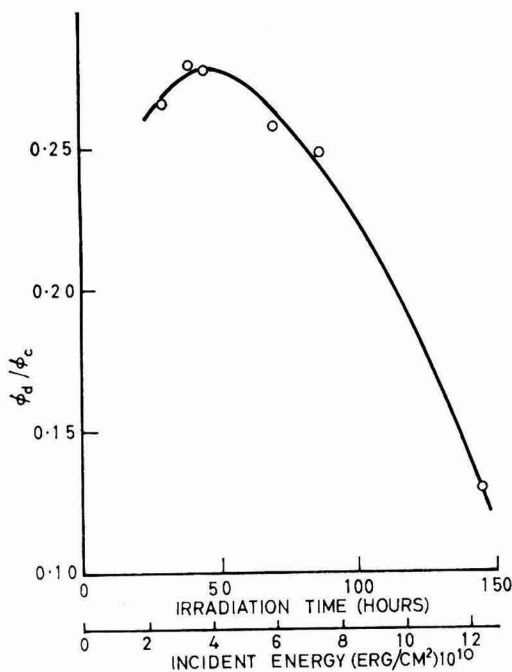


Fig. 2. Dependence of $\frac{\varphi_d}{\varphi_c}$ ratio on the energy absorbed

Assuming that the investigated copolymer characterises by random initial molecular weight distribution, the relationship of gel contents to the rate of crosslinking and rate of scission of the main chain for unit of dose can be established with the equation developed by Charlesby⁴, for linear polymer molecules with simultaneous crosslinking and scission :

$$s + \sqrt{s} = \frac{1 + p_0 u_1 r}{q_0 u_1 r} = \frac{p_0}{q_0} + \frac{1}{q_0 u_1 r} \quad (4)$$

where r is the dose, u_1 —number average degree of polymerisation. From the definition of p_0 (the rate of scission per unit of dose per mer) and q_0 (the number of crosslinked units per unit of dose per mer) results that the expressions φ_d and φ_c can be combined p_0 and q_0 , applying the relationships :

$$\varphi_d = p_0 \cdot w \text{ and } \varphi_c = q_0 \cdot w \quad (5)$$

where w —is the molecular weight of the basic unit (mer).

Inserting into equation (4) the expression for φ_d and φ_c from equation (5) $s + \sqrt{s}$ may be expressed in slightly different terms :

$$s + \sqrt{s} = \frac{\varphi_d}{\varphi_c} + \frac{w}{\varphi_c \cdot u_1 \cdot r} \quad (6)$$

Having the known values of s , $\frac{\varphi_d}{\varphi_c}$, r , w and u_1 (in this case $w=70$, $u_1=77.08$), φ_c can be calculated directly. The results of calculations are plotted in Fig. 3. The curve (1) representing the relationship φ_d against exposure time approaches

asymptotically to zero whereas the curve $2\phi_c$ vs. exposure time tends to the value 1×10^{-5} . The plot of this curve confirms the hypothesis that throughout the entire region of applied radiation doses the rate for crosslinking of the copolymer is greater than that for scission.

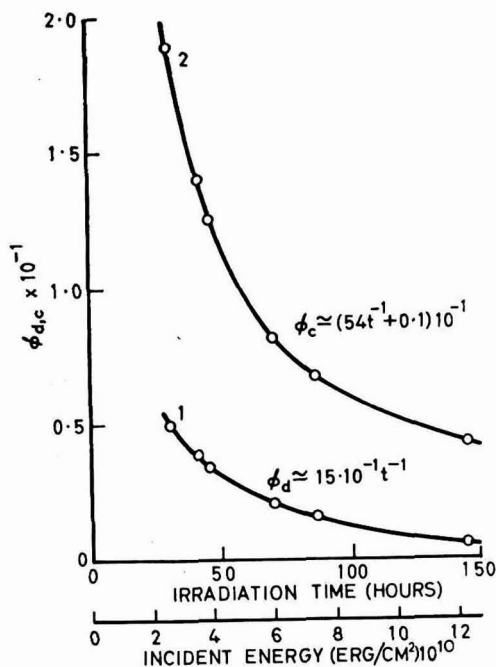


Fig. 3. Dependence of the quantum yield for scission, ϕ_d , and quantum yield for crosslinking, ϕ_c , on the energy absorbed

It could be supposed, that the extension of the exposure period would lead to the complete network formation throughout the film.

The curves (1) and (2) in Fig. 3 were made on assumption of the random initial molecular weight distribution. The data published by Bovey⁵ indicates, that even in case of initial uniform molecular weight distribution (if the thickness of irradiated sample $d < 125\mu$) just after about four chain scissions the molecular weight distribution may be regarded as random, and the use of the equation (4) can be applied without limitations.

Some conclusions of the mechanism of the degradation/crosslinking process can be drawn on the basis of infrared spectrum of gel fraction cited in the first part of the work. It would seem that in the case of vinyl chloride/vinyl isobutyl ether copolymer, UV-light brings about both scission and crosslinking, the latter might be accomplished with the participation of methyl groups in the isobutyl substituent. This is sufficiently confirmed by the almost total disappearance of the absorption doublet at 1370 cm^{-1} and 1383 cm^{-1} ($(\text{CH}_3)_2\text{CH}$ -structure) in gel fraction spectrum¹. Partial entries of isobutyl groups in copolymer crosslinking does not decrease the evolution of the volatiles (the fragments of broken side substituent), for the quantum yield of crosslinking is relatively

small, and the reaction of side groups splitting is of zero order, i.e. it does not depend on concentration but the light intensity.

It could be supposed that mechanism of the copolymer crosslinking is radical or partly radical. This conclusion is consistent with the observations on γ radiation induced changes of vinyl chloride/vinyl isobutyl ether copolymer⁶.

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Selection of research and development projects*

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Summary

As the method for choosing successful R and D projects is not reducible to an exact science, the paper concerns itself with trying to estimate the risk and returns involved in any venture.

The theory of the equitable game is discussed and then a method for estimating the probability of success is given.

It is noted that time may influence the results and that by introducing this factor into the argument some order of consistency in estimating the result can be obtained.

Selection de projets de recherches et de développements

Résumé

La méthode applicable lors de la sélection de projets de recherches et de développements susceptibles de réussite ne pouvant être ramenée à une science exacte, cet exposé se limite à tenter d'évaluer les risques et répercussions entraînées par toute entreprise.

La théorie du jeu équitable est commentée, puis une méthode est exposée dans le cadre de l'évaluation de la probabilité du succès.

Il est constaté que le temps est susceptible d'exercer une influence sur les résultats et qu'en incorporant ce facteur dans le raisonnement, il est possible d'obtenir un certain ordre d'uniformité lors de l'évaluation du résultat.

Auswahl von Forschungs- und Entwicklungsprojekten

Zusammenfassung

Da sich die Methode zur Wahl erfolversprechender Forschungs- und Entwicklungsprojekte nicht im Rahmen einer exakten Wissenschaft festlegen lässt, wird in diesem Beitrag versucht, die Risiken abzuschätzen und gegen die positiven Ergebnisse eines Projektes abzuwägen.

Die Spieltheorie wird erörtert, und ein Verfahren zur Einschätzung der Wahrscheinlichkeit eines Erfolges wird beschrieben.

Es wird eigens darauf hingewiesen, dass der Zeitfaktor die Ergebnisse möglicherweise beeinflusst, und dass zugleich durch Einführung dieses Faktors eine gewisse Folgerichtigkeit beim Einschätzen der Resultate erzielt werden kann.

Introduction

Success in selecting subjects for research and development which actually give rise to results—and the determination of how much to spend/invest in such work—is obviously not reducible to an exact science. Factors involved in the successful management of research and development include, for example :

- (i) Broad technical knowledge, (ii) commercial sense, (iii) imagination to foresee needs, (iv) imagination to foresee applications, (v) ability to size up actual or potential staff, both for technical adequacy and for qualities such as tenacity of purpose, intellectual honesty, willingness to do the hard work of analytical research, etc. (vi) Strength of character to undertake *calculated*

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risks and abide by the consequences ; to know when to admit defeat and terminate an unsuccessful/unprofitable line of work. (vii) Ability to convince laymen (who usually finance the project) of the desirability of a given proposal and of the probable utility of the results. (viii) Ability to secure teamwork and co-operation between various specialists.

Carrying out the function of research director in respect of all the factors mentioned above can be likened to a game, a game played with/against Nature and one's fellow men, with the object of ensuring a gain.

The outcome of any move is always in doubt until it has been irrevocably made : i.e. it is a gamble. This paper is concerned only with a single problem, that of putting a figure on the "gamble". In any gamble, one has first to know or have some idea of the possible "prize" which is being competed for.

(Some points in relation to calculating the "prize", are made later, but this topic will not be studied very deeply.)

Assuming that one has calculated the "prize", there then come the problems of relating this to the "stake" which may have to be invested in order to take part in the game, and the difficult problem of estimating the probability of success.

This paper is principally concerned with finding an analytical function for relating these three things.

$$\text{Prize} = F(\text{Stake, Probability of winning Prize}).$$

The problem of commercial enterprise

It is common knowledge that any commercial enterprise is a gamble ; it is the concern of the *entrepreneur* to place his money in such an enterprise that his probability of a gain is maximised and the probability of a loss is minimised.

It is commonly true that the reward (multiplication of the original stake) is greater in proportion as the risk of loss is higher, and less in proportion as the likelihood of success becomes greater. It is in the nature of things that the general public cannot all become millionaires by betting on the "favourite" whereas a consistent heavy gambler on "outsiders only" will soon be bankrupt.

To make money in business, one has to choose an effective compromise between two extremes, *viz* :

(a) New enterprises which are almost certain to succeed, but for which the prospects of gain are only marginally higher than investing in fixed interest securities. The probability of success is high precisely because others have done the same or almost the same before with success, and hence competition is bound to be severe, and profits low.

(b) New enterprises in which the prospect of gain may be very high indeed, but the likelihood of success cannot be estimated at all reliably, by reason of the fact that no one has ever tried or succeeded in anything similar before.

It is clear that one will not make much money in the long run by concentrating on either of the above two classes of new enterprise. Hence, the best strategy is a mixture of the two, which contains a small number of gambles at "long

odds ” plus a sufficient number of “ short odds ” to enable one to be sure of paying one’s way and supporting the investment necessary on the “ long odds ” projects, one of which, in the end, will probably prove extremely profitable.

In attempting to evaluate possible projects, it is useful to have a definite concept or rule around which to organise one’s thinking. In this case there is the notion of the “ Expectation of a Game ” ; this was developed in connection with the mathematical study of the laws of probability in relation to games of dice, cards, etc. It cannot be claimed that it has full theoretical validity except in cases of many repetitions of a game all of whose “ laws ” are known (e.g. dice). However, the “ entrepreneurial game ” is played innumerable times and, especially when it involves the risks connected with technical innovation, exhibits a certain sameness on all occasions. Hence, this approach is useful as a guide, though it is not to be followed uncritically.

The expectation of a game

This section discusses, first, “ equitable games ” in which the chances of making a fortune or going bankrupt are small ; secondly, the advantages of being well-breeched with finance ; and, finally, the games which everyone would like to play where one would expect to win all the time.

An equitable game

An “ equitable game ” is defined as one in which, with an indefinitely large number of repetitions between two opponents, there is likely at the end to be a nett transfer of original funds from the loser to winner which is not large compared with the amounts staked per game or with the resources commanded by the participants ; i.e. “ the odds are even ”, and “ ruin ” is not expected or intended to be a common outcome of a run of games. Expressed more precisely, the definition of an equitable game is such that :

Expectation = prize \times probability of winning it — stake \times probability of losing it,
= a sum which is not great compared with the stake per game,

or, expressed in symbols :

Expectation = $p \times \text{Prize} - q \times \text{Stake} = E$, which is small.

$\therefore E = p \times P - q \times S = 0$, in the limit

where p = probability of winning, and q of losing (naturally $p + q = 1$ because one must certainly either win or lose in this type of game).

Notice that $P = \text{Prize} = \text{Total Return} - \text{Stake} = R - S$

$\therefore \text{Expectation} = \text{Total Return} \times p - \text{Stake} \times p - q \times \text{Stake}$

$= \text{Total Return} \times p - \text{Stake} (\because p + q = 1)$

$E = R \times p - S = 0.$

Now, a game is “ equitable ” if the “ Expectation ” is zero, i.e. Proper Stake, $S = \text{Total Return} \times \text{probability of winning it}$.

If one stakes a greater amount than the "proper stake", the expectation is negative; i.e. in the long run by repeating this game one stands to lose an indefinitely large amount. On the contrary, if the stake is smaller than the "proper stake", in the long run one stands to win an indefinitely large amount.

Generally speaking, Equitable Games are suitable for amusement between friends and for little else. In all games of chance played commercially (at casinos, etc.) the "Expectation" of the game is negative for the player, but positive for the "bank" because the rules of the game are designed to ensure this.

Pools promoters, race-course bookmakers, Crown and Anchor board proprietors, etc., or the Casino operators, all play games with you in which your value of expectation-stake is negative, their's positive. Hence, you become steadily poorer, they steadily richer. The theory of probability originated principally from the study by Pascal, Fermat, Bernoulli, Laplace of the problems put to them by noblemen whose main pastime was gambling.

There is the famous case of the Chevalier de Meré, who made a fortune by betting small favourable odds on getting at least one six in four tosses of a dice (probability is $1 - \left(\frac{5}{6}\right)^4 = 0.517 = \text{more likely than not}$) and lost it doing the same in favour of getting a double six in 24 double tosses (probability = $1 - \left(\frac{35}{36}\right)^{24} = 0.491 = \text{less likely than not}$).

This demonstrates that a calculation of prior probability is a formal necessity for those who gamble.¹

Life Assurance offices have a gamble with you, but your input to the game (premiums) is adjusted to be higher than the true mathematical expectation of your take-out; i.e. the "average" participator is bound to receive back less than he pays in; if this were not so the scheme would almost certainly become insolvent. Out of the margin thus accruing to the company, it pays its dividends to the holders of the equity capital, and bonuses on the sums assured. In broad terms, the Life Assurance business is very nearly an "equitable game".

The problem of "the gambler's ruin"—The difference between small and large firms
An extension of the theory deals with the case where the players have limited funds. Obviously, there exists the possibility of a player or the bank being without funds at a certain stage, as a result of a "run" of luck for either side. By continuing, either could and would have restored the probabilities appertaining to an indefinitely large number of games—but this series may be interrupted at any time when the nett transfer of funds happens to equal the total resources of one of the contestants.

It is worth noting that, if the game is equitable (zero discrepancy), the probability of ruin is inversely proportioned to the initial fortunes (resources) of each side.² Thus, as should be expected, the likelihood of coming out on the credit side "in the end" is greater for those with greater initial capital.

Hence, small firms tend to be successful as long as they are on an initial certainty—probably what they were founded to exploit. The danger comes when they start to diversify too much on things which are not certainties. On the

contrary, a big firm can afford to have more irons in the fire, knowing that sooner or later there will be a big pay-off to cover losses or failures.

“ *Non-equitable games—the discrepancy* ”

Naturally, in commercial enterprises, one desires to make one's stake smaller than the “ proper stake ”, in order to have a positive “ Expectation ”, i.e. Stake must be smaller than “ Total Return \times probability of winning it ”.

In general, $\text{Expectation} = R \times p - S + \text{“ Discrepancy ”}$ where the Discrepancy is the bias for or against the player contained in the “ odds ”, i.e. the amount he will win or lose, on the average, per “ throw ”.

The problem of the businessman is to decide what ratio of Discrepancy/Stake he is willing to accept, bearing in mind the value of p —the probability of success—which he assigns to a given project. Generally, if p is assessed low, then the ratio of Discrepancy/Stake should be taken as high—and vice versa.

These ideas can be used to estimate the worthwhileness of any given enterprise, provided one can calculate, estimate or assign arbitrarily, some value for p .

Estimate of probability of success

The General Problem

Separation of two probabilities: There are really two probabilities to be assessed, namely :

- (i) Given a particular expenditure of money on research and development, what is the probability of a *technical success* ? i.e. a success in the technical problems involved, a success which makes entry to the market feasible because it offers a new process, product or service.
- (ii) Given a technical success, i.e. given an ability to enter the market with a saleable product, what is the probability of the actual “ return-through-sales ” having any pre-assigned magnitude ?

What is wanted, evidently, is some analytical function F_1 which gives :

Probability of a technical success $= F_1$ (resources invested in Research and Development)

and also F_2 , such that :

Probability of a market success of a given magnitude (Total Return) $= F_2$ (resources invested in productive plant, materials, marketing activity, etc.)

If the form of such functions was known, it could be readily calculated how to maximise the “ Expectation ” and hence spend the right amounts on Research and Development and on advertising, etc., out of a “ best ” total invested in the new project.

The shape of the function for Research and Development expenditure : In seeking an analytical form for F_1 and F_2 , one is guided by certain things which seem “ obvious ” *a priori*.

- (i) As the expenditure on Research and Development increases from zero, the corresponding probability of success at first rises very slowly. The curve is asymptotic to the x -axis at $x=0$.

- (ii) For a given task, there is a fairly well-marked “ threshold ” of expenditure above which the probability of success ceases to be negligible and becomes interesting. This might be, for example, one PH.D’s salary for two years plus laboratory space, materials and overheads, i.e. a minimum investment “ quantum ”.
- (iii) Correspondingly, there is a “ ceiling ” of expenditure by exceeding which the probability of success can only be marginally improved.
- (iv) The curve approaches the line $y=1$ as x increases without limit (infinite expenditure produces certainty of success).
- (v) Over the “ practical range ” of expenditure and probabilities there is a roughly linear relationship with a positive slope, i.e.

$$\frac{dy}{dx} = \frac{dF}{dx} = \text{a positive quantity.}$$

Viewed “ from afar,” the slope is monotonic, i.e. a small increase in expenditure always increases the likelihood of success by some amount.

But, viewed in detail, at any point there may be a “ least significant quantum ” of extra expense which has to be added in order to achieve a definite increase in probability.

One of the purposes of a careful analysis of the probability of success as a function of expenditure is to locate correctly these discontinuities where, for example, one has to increase the Research and Development effort by one PH.D., by one electron microscope, etc., requiring a marked increase in expense.

These considerations lead to an “ S-shaped ” curve as shown in Fig. 1.

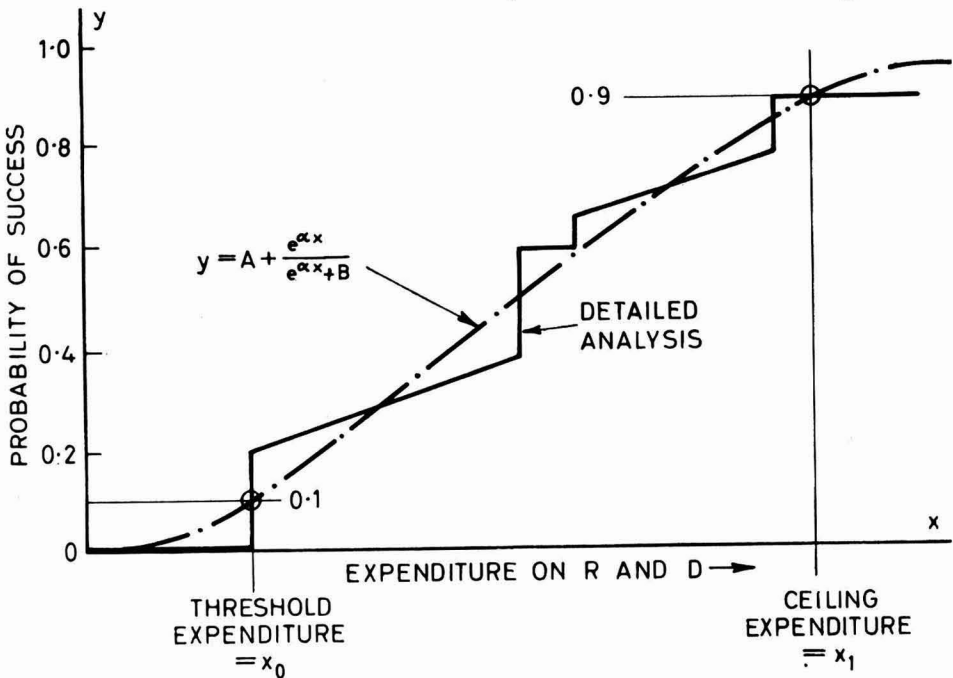


Fig. 1. Probability of success as a function of expenditure

The logistic curve of growth

There is a function well-known in biology and economics, called the "Logistic Curve of Growth," such that

$$y = F(x) = A + \frac{e^{\alpha x}}{e^{\alpha x} + B}$$

which has the required shape.

Arguments can be adduced for thinking that this model should be approximately true, but in any case the shape must be broadly correct.

It is contended that it should be possible, by study and experience, to assign reasonable figures for the "threshold" and "ceiling" expenditures in any given case. Having done this, we can fix A and B such that the curve passes through four points, viz:

- (i) $y = 0$ at $x = 0$.
- (ii) $y =$ the minimum probability of success which can be regarded as "interesting" (say 10 per cent, or $y = 0.1$).
 $x =$ the corresponding estimate of the "threshold" expenditure.
- (iii) $y =$ the maximum probability of success which can reasonably be aimed at (say 90 per cent or $y = 0.9$).
 $x =$ the corresponding "ceiling" expenditure.
- (iv) $y = 1$ at $x =$ infinity.

We now have a rule for interpolating between these points. As a check, we can calculate the expenditure required for a 50/50 chance of success. This should appeal to one's judgment; otherwise, the original assumptions should be reviewed.

Use of the model

It was stated before that :

$$\text{Expectation} = E = R \times p - S$$

$$\text{We have now assumed } p (=y) = F(x) = A + \frac{e^{\alpha x}}{e^{\alpha x} + B}$$

where $S = x =$ stake or investment.

$$\text{Hence } E = \left[A + \frac{e^{\alpha x}}{e^{\alpha x} + B} \right] \times R - x$$

Given an estimated value of R , which is the expected total return which will be made possible by the technical success (cost= x) and by the future employment of fixed capital resources, etc., to make and market the new product, an upper limit to the size of x can at once be calculated, because clearly E must not be less than or equal zero. Because $E = 0$ at $x = 0$ and also at

$$x_k = \left[A + \frac{e^{\alpha x}}{e^{\alpha x} + B} \right] R,$$

it follows that E must go through a maximum between $x = 0$ and $x = x_k$.

Thus, the value of x such that $\frac{dE}{dx} = 0$ gives us the “optimum” value of the investment in Research and Development, given the assumptions.

The exact shape of the curve and any discontinuities in the neighbourhood of E_{max} should be examined, as it ought to be a valuable help in decision-making. Fig. 2 shows diagrammatically the situation already described.

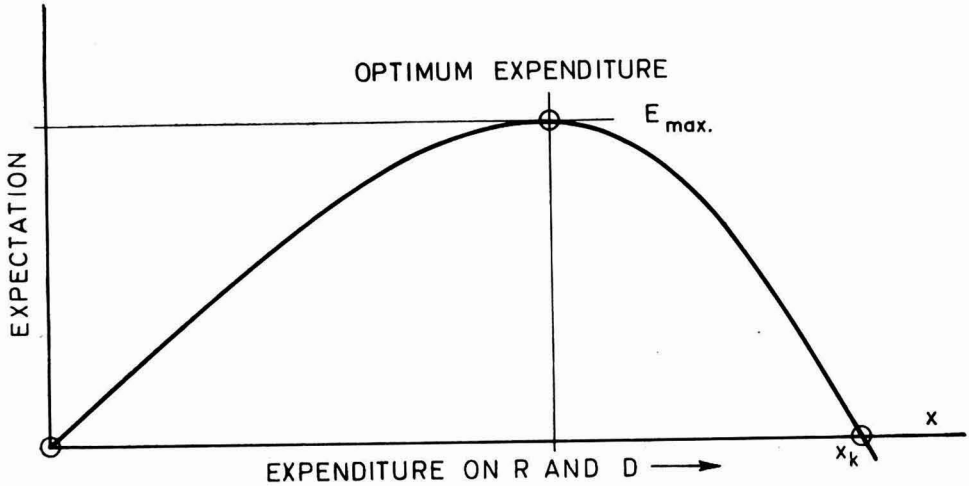


Fig. 2. Expectation v. expenditure

A practical suggestion

The effect of time

It is known, of course, that success in a Research and Development project is not a function only of money spent, but also of time. It is frequently necessary to take into consideration the fact that the ultimate Total Return will be highly dependent upon the calendar time expended (a competitor may scoop you).

Hence, the assessment of probabilities and their use in the model ought to be repeated for different assumed time scales.

Systematic guessing

The added dimension of time may be used to give “depth and self-consistency” to our estimates of probabilities, and for this purpose it is suggested that fruitful results can be obtained by drawing up a table on the following lines (see Table 1). The idea is to fill in this table in the following way.

For a given expenditure on the Research and Development project, assign probabilities of success as a function of time allowed. This should be done for several assumed values of total expenditure (rows in the table). Now the same should be done for constant assumed periods of time, assigning probabilities of success as a function of money expended in that time.

Clearly, there must be some degree of consistency in the results, such that the “probability surface” does not have cliffs, re-entrant angles, reversals of slope,

Table 1
Probability of success in terms of time and money

Total sum expended	Total time available for project										Rate of Expenditure per annum	Probability of success			
	Time no object	20 years	15 years	10 years	5 years	3 years	2 years	12 months	6 months	3 months					
£5,000	0	0	0	0	£1,000	0	0.1	£2,500	£5,000	£10,000	£20,000	0	0	£20,000	0
£10,000	0	0	0	£1,000	£2,000	0.2	0.3	£5,000	£10,000	£20,000	£40,000	0	0	£40,000	0
£25,000	0	£1,250	0.1	£2,500	£5,000	0.4	0.4	£12,500	£25,000	£50,000	£100,000	0.05	0.2	£100,000	0
£50,000	0.1	£2,500	0.2	£5,000	£10,000	0.6	0.5	£25,000	£50,000	£100,000	£200,000	0.1	0.25	£200,000	0
£100,000	0.5	£5,000	0.6	£10,000	£20,000	0.9	0.8	£50,000	£100,000	£200,000	£400,000	0.2	0.3	£400,000	0.1
£250,000	0.9	£12,500	0.95	£25,000	£50,000	0.85	0.75	£125,000	£250,000	£500,000	£1 million	0.3	0.4	£500,000	0.2

etc., which do not correspond with some assignable cause in the process of reasoning which led to the writing down of the figure in a local region of the table. Equally, a logical progression should be seen in any diagonal traverse of the table.

It will probably be found difficult at first to secure rationality in all parts and directions of the table, and in revising it to obtain internal consistency, attention will be focused on the reasons or assumptions originally put forward. This process will give valuable insight into the problem and will serve as an organising principle in reaching decisions.

In particular, one would expect to locate a region of combinations of time and money which shows the best chance of success ; if this is not very practicable or desirable (in terms of time or money) then the project is contra-indicated, or vice versa.

Bounds to the favourable region are also set by upper and lower rates of expenditure (£'s per annum) because there is a rate of expenditure below which nothing can be achieved (one man's salary, for example) ; also, there is an upper limit above which you cannot find the money or you have not the resources to employ.

Similar arguments limit the permissible times. There are some types of research where a relatively low rate of expenditure (e.g. the salary and requirements of one brilliant individual) can be expected to pay off handsomely in the end, time being available (fundamental work).

On the other hand, some things cannot be solved in less than a certain period whatever the absolute, or rate of, expenditure (e.g. soil treatment and agricultural methods).

Reservations

It is known that, in fact, the notion of the Mathematical Expectation of a game does not always accord with good sense. For example, if there was the choice between:

- | | | | |
|-----|-----------------|------------------|------|
| (a) | Receive £5,000 | with probability | 1 |
| (b) | Receive £25,000 | „ | 0.1 |
| | plus £5,000 | „ | 0.89 |
| | plus £0 | „ | 0.01 |

then it would be the unusual one who would exchange the certainty of £5,000 in (a) (Expectation=£5,000), for the uncertainty of (b), although the latter Expectation is in fact higher than in (a) (viz : £6,950).

$$\text{ration } E_b/E_a = 1.39$$

It is easy to construct paradoxes of this kind, which bring the utility of the concept of "Expectation of a Game" into some disrepute.

For this reason, it has been proposed* to use the logarithm of the amount of value as a measure of its utility—this is equivalent to saying that the marginal utility of a unit increase in a sum of money has a decreasing value; in other

*G. Bernard, Recherche Operationnelle, No. 27, p. 181.

words, an increase, to be equally significant, must be a constant percentage of the capital sum.

Our example would then give :

$$\begin{aligned} E_a &= \log 5 \\ E_b &= 0.1 \log 25 + 0.89 \log 5 = 1.09 \log 5 \\ \text{ratio } E_b/E_a &= 1.09 \end{aligned}$$

This manoeuvre reduces the degree of paradox, without removing it, because in each case common sense chooses the alternative with lower Expectation.

For this reason it has been proposed to define the utility of a sum of money, M , as :

$$p^\alpha \cdot M$$

If $\alpha=0$, this rule reduces to that of the classical rule, i.e. that Money measures Utility directly. For $\alpha=1$, a non-paradoxical result can usually be derived. In the example already given, with $\alpha=1$, we have :

$$\begin{aligned} E_a &= \log 5 \\ E_b &= 0.1 (0.1^\alpha \times 2 \log 5) + 0.89^2 \log 5 \\ &= 0.02 \log 5 + 0.7921 \log 5 = 0.8121 \log 5 \\ \text{ration } E_b/E_a &= 1/0.8121 = 1.23 \end{aligned}$$

This at last gives a measure of Expectation which leads to the same choice as common sense (but judgment has been improved by the use of quantitative instead of merely qualitative assessments.)

It may be found in some cases that the certainty, even of a much smaller gain, prevails in attraction over that of a larger but uncertain one. It is then necessary to use a higher value of α to restore common sense.

α may be regarded as a measure of the fear of the risk. Thus, for an affair of given magnitude, the calculation of Expectation in a small firm would be based on a different basis (higher value of α) than in a big firm. This accords with common sense.

Calculation of prize

This paper is not primarily concerned with this aspect of the problem, and it is mentioned here chiefly to emphasise the importance to the firm and to the Research Director of having an explicit, carefully reasoned estimate made of the commercial results (Total Return) to be expected if a given *technical success* is produced by Research and Development effort within a given time.

The preparation of this estimate will involve chiefly :

Finance, Marketing, Accountancy, Production
Costing, Commercial intelligence (competitors), etc.

A forecast will have to be made of the probable pattern of sales versus time, the life of the product on the market, the return to be expected by employing the capital elsewhere, the method of estimating present worth of future profits (discounted cash flow, etc.).

Logically, a different probability ought to be assigned to various absolute levels of Total Return, because the choice is not one merely between total

failure or total success—a modest success (in some fields) may be more probable than a large success—whereas in other fields (fashion trades) this may not apply.

Here again, is a paradox ; for the Expectations are the same (£10m.), whether :

- (a) Total Return of £100m. can be secured with probability 0.1
 or (b) Total Return of £20m. with p = 0.5
 or (c) Total Return of £10.1m. with p = 0.99

(to avoid the absurdity of “ certainty ”).

But these are clearly very different orders of success. A logarithmic measure would, on the other hand, give Expectations of :

- (a) $0.1 \times 8 \log 10$ = 0.8
 (b) $0.5 \times 1.3 + 0.5 \times 7 \log 10$ = 4.15
 (c) $0.99 \times 7 \log 10$ = 7.00

Obviously, a small or a large firm would view this situation differently, because the Total Return is a return on capital available and employed to exploit the technical success.

A small firm might be unable to finance even a virtual “ certainty ” to win £10m., whereas a big firm might prefer a gamble at the relatively long odds of 0.1, if it could contribute significantly to total turnover ; and the Research and Development expenditure required to buy entry to this “ game ” might appear relatively small to the big firm but impossibly large to a small one.

Evidently each situation requires careful study, in which the notion of Expectation can play a part.

Conclusion

The idea of “ Mathematical Expectation ” has been introduced, as applied to games of chance, as a concept which can play a useful part in helping to organise studies designed to estimate the worthwhileness of possible Research and Development enterprises.

As usual, the usefulness of mathematics depends not primarily upon its manipulations but upon the quality of thought put into the assumptions from which a calculation starts and also upon the quality of data available.

It is believed that the periodical literature shows a renewed interest in the application of Probability Theory to the decision-making process which precedes large capital expenditures—because the sums which have to be committed tend to become ever larger and hence every aid to crystal-gazing has to be brought into play.

Current theories are not altogether satisfactory in theory nor adequate in practice ; but something is better than nothing and those concerned should try their hand in this new field.

[Received 12 February 1965]

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Reviews

CHEMISTRY IN NON-AQUEOUS SOLVENTS

By H. H. SISLER. London : Chapman & Hall Ltd., 1965. Pp. 119. 10s. 6d.

Reactions in non-aqueous solvents have become an important field in the modern development of chemistry, and in this book, which forms part of a series of paperbacks, Professor Sisler, of the University of Florida, has provided a useful summary of recent work. Reactions in liquid ammonia, sulphuric acid and liquid oxide systems, e.g. dinitrogen tetroxide and sulphur dioxide, are discussed fully in separate chapters, followed by a short general review of other systems. This book is intended for use with teaching courses for second- and third-year students, and each chapter contains a short selected list of references to more comprehensive texts. It will also be of use as a concise introduction to the recent developments in this rapidly advancing field.

V. T. CROWL.

MODERN CHEMICAL KINETICS

By H. EYRING and E. M. EYRING. London : Chapman & Hall Ltd., 1965. Pp. 114. 10s. 6d.

This well produced paperback provides a useful review of modern aspects of reaction kinetics. The concepts of activated states and potential energy considerations are introduced in a straightforward manner, and these are followed by an account of the applications of statistical mechanics to rate theory. Transport mechanisms and thermodynamic aspects are discussed in the light of applications to particular processes. The book concludes with a chapter on rapid reactions in aqueous systems. The level of the book is that of second- or third-year students, for whom it would form a useful supplement to their teaching course, but it can also be recommended as a very readable means of bringing one's physical chemistry up to date.

V. T. CROWL.

AN INTRODUCTION TO MOLECULAR KINETIC THEORY

By H. HILDEBRAND. London : Chapman & Hall Ltd., 1965. Pp. 105. 10s. 6d.

This book forms part of a series of paperbacks covering a number of aspects of chemistry from an up-to-date standpoint. Concepts of molecular energy, the development of the gas laws and the perfect gas are followed by a discussion of real gases. This is followed by a brief chapter on condensed phases. Many of the chapters conclude with a series of problems, some with worked solutions, and the text is intended for use by first-year students.

V. T. CROWL.

CHEMICAL BONDING AND THE GEOMETRY OF MOLECULES

By G. E. RYSCHKEWITSCH. Chapman & Hall, 1965. Pp. 111. Price 10s. 6d.

This short book gives a simple, non-mathematical account of the application of orbital theory to the explanation of extra-nuclear atomic structure and to the formation and properties of molecules. A brief discussion of wave-mechanics is followed by an account of orbitals, energy levels and paired and unpaired spins. Compound formation is then taken up by way of ionisation potentials, electron affinity and orbital overlap. The discussion is well supported by tabulated data. The book ends with an account of the contribution of hybridisation and resonance energy to bond stability. In such a book the treatment must be selective, but the balance struck seems to be sensible and the material can be read and absorbed in a short time. It is recommended as a good introduction to a more rigorous treatment and it is also a very readable textbook for the non-specialist in its own right.

J. L. PROSSER.

INFRARED BAND HANDBOOK, SUPPLEMENTS 1 AND 2

Edited by H. A. SZYMANSKI. New York : Plenum Press, 1964. Pp. xii+259. Price \$15.

In our review of the original volume (*JOCCA*, 1964, 47, 43) we welcomed the principle which had been used in the compilation of the data. The book was, in fact, a list of compounds with infrared bands at specific frequencies.

The first two supplements, which are now to hand, have not added to the compounds listed in the original frequency range (617-3,610 cm^{-1}). They list, in fact, compounds with bands in the range 600-200 cm^{-1} (and a few bands below this range).

It is undeniable that an increasing number of laboratories are making use of instruments with KBr optics and grating instruments covering the far infrared region. Such workers will obviously welcome the present volume, since there is comparatively little published work on group frequencies in this range.

However, the reviewer feels that most workers in the conventional infrared region will be disappointed that the many important compounds omitted from the original volume have not yet been included in the series. It is recognised, however, that Dr. Szymanski cannot cope with every aspect of his chosen task at once, and we look forward to the growth of the series, which will only increase its usefulness.

I. T. SMITH.

Section Proceedings

Midlands

Trent Valley Branch

Student Group meeting

Prior to introducing the speaker, the Chairman, Mr. F. G. Dunkley, spoke briefly of the plans to form the Student Group of the Association attached to the Trent Valley Branch, saying that in the first place it was proposed to hold lectures similar to the one arranged for that day and held at times when attendance would not interfere with formal study courses. In some cases the meetings would be held during holiday periods at the Technical College. The Branch, he said, was anxious to provide some opportunities for the technological studies and called for two junior members to join the Committee responsible for the planning, and Messrs. V. Sercombe and R. Randle agreed to serve. In thanking these members, the Chairman said that their advice would be very valuable in ensuring that any future programmes would be attractive as well as instructive to those they were designed to serve.

After the speaker, Mr. A. T. S. Rudram, the well-known member of the Paint Research Station and the Association's Honorary Research Development Officer, had been introduced, the meeting adjourned to allow a tour of the Regional Scientific Service Laboratories to be made at the invitation of the Director, Mr. S. Bairstow.

Mr. Corbyn, of British Railways, demonstrated some of the latest instruments used for rapid analysis. Among them were the Direct Reading Emission Spectrometer (the Quantometer) and the Quantovac. An actual analysis of an alloy was carried out with the latter and the results were obtained in just over one minute. The X-Ray Spectrometer (the Fluorograph), also in the same laboratory, was shown to be particularly useful in the analysis of macro-quantities, and Mr. Rudram was able to give examples of the application to which a similar instrument was put at the Paint Research Station.

In another laboratory, Mr. Corbyn showed the workings of an infrared spectrometer with a range of up to 25 $m\mu$. This kind of instrument was also used at the Paint Research Station for the examination of adsorbents on pigment surfaces and for the tracing of chemical changes in paint films during ageing.

Other instruments examined, with the guidance of Mr. Tomlinson, included the Argon Gas Chromatograph and the Medium Quartz Spectrograph. The former was being used, among other things, for the analysis of solvent mixtures, and at the time of the visit the content of benzene in a sample of toluene was being determined—a very interesting case of its use in view of the recent publicity in connection with benzene and certain forms of leukaemia.

The Medium Quartz Spectrograph has been set up for the quantitative analysis of metal contaminants in diesel engine lubricating oils. A close estimation of the progressive wear on the bearings was obtained by this means and contributed to the safety and comfort of passengers by reducing the risk of engine breakdown. The instrument was demonstrated and the analysis took under two minutes—an enormous saving in time.

After a visit to the Chemical Laboratories, the meeting reassembled at the Lecture Theatre of the Engineering Research Laboratories (recently opened by the Duke of Edinburgh), where Mr. A. T. S. Rudram gave a very entertaining, instructive and lucid lecture, supplemented with slides, on the Paint Research Station, its history

with illustrations of the type of work it was carrying out for the service of the industry. It would be impossible, in the short space available, to do justice to Mr. Rudram's lecture, but a few salient points should be mentioned :

The Paint Research Station was a peculiarly British concept, quite unique in the world, not only from the point of view of finance but in the way it dealt with fundamental research for manufacturers.

The second Electron Microscope ever used in this country—the first was at the National Physical Laboratory—was designed and made by members of the Paint Research Station staff. It is still in constant use, although a larger model has been bought since. The Paint Research Station can also claim to be pioneers in section cutting for this class of microscope.

Mr. Rudram described how the proportions required of pigment mixtures for use in colour matching can be obtained, with a fair degree of accuracy in a matter of two minutes, with the help of a Colorimeter incorporating a computer.

Intensive studies were being carried out on adhesion problems. Studies involving the use of the Infrared Spectrometer have revealed, among other facts, that aged alkyd films tended to form compounds which in some respects resembled polyethylene in composition, and this probably explained the poor adhesion of freshly applied paint on old alkyd surfaces. New apparatus for estimating adhesive forces had already provided valuable information.

Chromatography, in its various forms, was being used extensively for complex organic reaction studies, and recent work with Thin Layer Chromatography had proved especially interesting.

Another branch of study was the cause of paint film breakdown by various micro-organisms such as fungi and algae, and methods of assessing the practical value of fungicides had been developed to a high degree.

Matters concerning corrosion were of vital importance to the paint manufacturers, and among the latest research work in this field. It had been demonstrated that paint films can act as ion exchanges systems. That this discovery may have very important practical application was one of the predictions which Mr. Rudram permitted himself to make.

Many other aspects of the work at the Paint Research Station were mentioned by Mr. Rudram, and in his concluding remarks he commented that approximately 1,000 inquiries from the industry were dealt with per annum.

Mr. H. J. Foot proposed a hearty vote of thanks, which was carried with acclamation.

J. L. P.

New South Wales

Fluidised bed coatings

United Kingdom Founder Member Mr. R. P. L. Britton and Mrs. Britton, during their private visit to Australia, attended the March technical meeting of the Section. After a welcome by the Section Chairman, Mr. Leahey, Mr. Britton addressed the meeting, outlining the events leading to the foundation of OCCA at the conclusion of the First World War and its growth into the world-wide organisation that it is today.

The first technical lecture in 1965 was presented by Mr. G. Ball and was entitled "Fluidised Bed Coatings."

One of the recently developed techniques for application of surface coatings was the fluidised bed coating of metals or other suitable substrates with powdered plastic materials.

Mr. Ball said that the process was discovered at Knapsack Griesheim in West Germany in 1952 in the course of an investigation into a particular method of plastics processing.

The speaker then discussed details of equipment which very simply consists of a container having a porous base plate and an air or nitrogen connection. The pressure below this porous plate caused continuous flow of gas which set the overlaying powder particles in motion. Each powder particle was surrounded by a cushion of air and the powder behaved in a similar way to a liquid. The coating of heated articles could be carried out by dipping in order to achieve a complete and uniform covering.

The plastics that were used in this process were many and varied and include cellulose acetate butyrate, polyamides, polystyrene, epoxies, phenolics, chlorinated polyethers and acrylics.

The speaker discussed various coating techniques in some detail, including the methods for obtaining a uniform thickness on complicated objects consisting of parts of varying heat capacity. For articles of very low heat capacity, such as wire mesh, application of induction heating in the bath overcomes heat retention problems. Going the opposite way, a material with low temperature resistance, such as zinc alloy die casting, could be coated by plastic being melted with radio frequency.

After discussing advantages and limitations of fluidised bed coating technique, Mr. Ball concluded by posing a question to the audience—whether the use of the fluidised bed method and its ancillary techniques could mean the end of conventional surface coating materials for coating metals.

An interesting and lively discussion followed the lecture and the questions regarding special coating techniques, the prospects for market development, the cost of powders and the durability on outside wall surfaces were covered in some detail.

The vote of thanks was proposed by Mr. B. Clarke for an interesting and certainly a provocative lecture.

A. A.

OCCA 18

OCCA Eighteenth Technical Exhibition

In view of the considerable success of the OCCA Seventeenth Technical Exhibition, the Exhibition Committee is pleased to announce that the preliminary arrangements for OCCA 18 (Eighteenth Technical Exhibition) have been made on similar lines to those for 1965. The Exhibition will again be held at Alexandra Palace, London, and will be open on five days ; the dates and hours of opening will be as follows :

Monday 14 March	3.00 p.m.-6.30 p.m.
Tuesday 15 March	10.00 a.m.-6.00 p.m.
Wednesday 16 March	.. 10.00 a.m.-6.00 p.m.
Thursday 17 March	10.00 a.m.-6.00 p.m.
Friday 18 March	10.00 a.m.-4.00 p.m.

The Seventeenth Exhibition in March 1965 was visited by 11,000 people, including representatives from 27 overseas countries.

Visitors and exhibitors alike commented favourably upon the larger Exhibition area, which allowed for a more attractive lay out of the stands and seating, the ease of access to Alexandra Palace by Underground line and the coach service provided by the Association, and the ample free car parking facilities. Exhibitors also found the longer build-up and dismantling periods advantageous.

A map will be included in the Official Guide showing main line and Underground services, together with suggested routes for those travelling by car.

There are adequate catering facilities at Alexandra Palace and there are two restaurants with full dining facilities, together with two buffets and several bars.

The Exhibition Committee wishes to make known as widely as possible the

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

- (a) New products ;
- (b) New knowledge relating to existing products and their use ; or
- (c) In suitable cases, existing knowledge which is not generally available in the consuming industries.

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

Copies of the Invitation to Exhibit and application forms have already been dispatched to companies both in the United Kingdom and on the continent of Europe ; applications for stand space must be returned to the General Secretary by **Friday 3 September 1965**.

There will be no charge for admission and copies of the Official Guide will be available without charge both prior to the Exhibition and at Alexandra Palace. All members of the Association, wherever resident, will be sent a copy of the Official Guide as soon as these are available early in 1966. It is felt that members appreciate receiving copies of the Official Guide well in advance of the Exhibition dates in order that they can

plan their itineraries. Copies of the Official Guide will also be sent to paint and printing ink companies in the United Kingdom and individually to scientists and technologists on the continent of Europe. Any non-member, company or organisation wishing to receive a copy of the Official Guide before the Exhibition should notify the General Secretary before the end of the year.

A feature of the Exhibitions, which will be repeated at the Eighteenth Technical Exhibition, has been the stand devoted to Technical Education, on which information on technical courses and careers will be available. The Committee has decided once again to invite parties of sixth form science students to visit the Exhibition, when they will be given

short introductory lectures by members of the Association.

An Exhibition Luncheon will be held at the Savoy Hotel, London, W.C.2, on Monday 14 March, prior to the Opening Ceremony. So popular has this function become in recent years that it has not been possible to accommodate all the requests for tickets. A form of application for Luncheon Tickets will be enclosed with each copy of the Official Guide.

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

Manchester Section

Symposium on the recent technology of emulsions and emulsion paints

The Manchester Section are proposing to hold the above symposium in the spring of 1966. They are at present considering the list of subjects and lecturers and would be interested to hear from any company or speaker who would like to contribute to this symposium.

The amount of review material will be kept to a minimum and the aim is to cover the present state of knowledge and

where possible include new experimental work. The broad headings being considered are :

- The stability of emulsions
- Emulsion design
- Pigment selection
- Water phase composition
- Paint design

For further details please contact the Honorary Research Liaison Officer, Manchester OCCA Committee, Dr. F. M. Smith, c/o The Geigy Company Ltd., Simonsway, Manchester, 22.

Advances in polymer science and technology

The second Conference to be organised jointly by the Plastics and Polymer Group of the Society of Chemical Industry, the Plastics Institute and the Institution of the Rubber Industry will be held in London in September 1966. The Oil and Colour Chemists' Association and the Society of Dyers and Colourists will also participate on this occasion. The purpose of the Conference is to provide a forum for discussion between scientists and technologists whose work is concerned with polymers.

Papers will be preprinted and presented in summary form at the Conference. Ample time will be given for questions and discussion.

The Conference will discuss, in particular, the following topics :

- (i) The Macro and Micro Structure of Solid Polymeric Systems. Polymer morphology, polymer-additive interactions (excepting those in polymer-plasticiser systems), polymer blends and polymer-reinforcement interactions will be included under this heading.

(ii) Chemical Reactions in Polymer Films.

Cross-linking reactions in polymer films, chemical interactions with substrate and adhesion will be included under this heading.

(iii) Physical and Chemical Changes in Polymers with Particular Reference to Long-Term Ageing and Load Bearing Properties.*(iv)* Practical Implications of Rheological Measurements.

Offers of papers are invited and should be made to Joint Conference Hon.

Secretary, Society of Chemical Industry, 14 Belgrave Square, London, S.W.1. Summaries for consideration should be submitted by 1 September 1965 and should be no longer than 250 words. Complete manuscripts of papers accepted will be required by 1 March 1966.

News of members

Mr. S. Duckworth, an Ordinary Member attached to and Honorary Treasurer of the Manchester Section, has been promoted to Production Manager of the Walpamur Company Limited.

Register of Members

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

Ordinary Members

- ALLCOCK, STANLEY, B.SC.TECH., 28 Oakwood Avenue, Audenshaw, Nr. Manchester, Lancashire. (*Manchester*)
- ANSTEAD, DOUGLAS FREDERICK, B.SC., F.S.D.C., F.R.I.C., 99 Victoria Road, Romford, Essex. (*London*)
- COYNE, ANTHONY JOHN, 22 St. Olams Close, Luton, Bedfordshire. (*London*)
- EVANS, MICHAEL JOHN, B.SC., 37 Empress Avenue, Ilford, Essex. (*London*)
- FISHER, PETER, B.SC., Midland Silicones Ltd., City House, New Station Street, Leeds, 1, Yorkshire. (*West Riding*)
- HAMMON, ANTHONY JOHN, 26 Balmoral Road, South Harrow, Middlesex. (*London*)
- HOULTON, JOSEPH GERARD, 9 Pine Walk, Healing, Nr. Grimsby, Lincolnshire. (*Hull*)
- HUEY-WILLIAMS, RICHARDSON SPENCER, 18 Shelley Street, Firlie, South Australia. (*South Australian*)
- LAMB, ALAN ALFRED, Pioneer Chemicals Pty. Ltd., 91 Montague Road, South Brisbane, Queensland, Australia. (*Queensland*)
- NEALE, DAVID JOHN, B.SC., 78 Forest Approach, Woodford Green, Essex. (*London*)
- SEVESTRE, JEAN HENRI LOUIS, 85 Bel Brune, Paris, France. (*London*)
- SMITH, HENRY BARCLAY, B.SC., c/o Vinyl Products Ltd., 159 Deanston Drive, Glasgow, S.1. (*Scottish*)
- SMITH, JAMES ROYSTON, 19 Clee Road, Cleethorpes, Lincolnshire. (*Hull*)
- SMITH, THOMAS GEORGE, B.SC., 82 Broadway, Glenelg, South Australia. (*South Australian*)
- TUCKER, DOUGLAS RAYMOND, B.SC., Waverley, Westfield Road, Maidenhead, Berkshire. (*London—Thames Valley Branch*)
- TURNER, JAMES, 8 Cell Farm Avenue, Old Windsor, Berkshire. (*London*)
- UNSWORTH, ALFRED KENNETH, M.SC., F.R.I.C., F.P.I., 1 Court Downs Road, Beckenham, Kent. (*London*)

- VALENTINE, RAYMOND BRUCE, Expandite (Aust.) Pty. Ltd., Doonside Crescent,
Doonside, New South Wales, Australia. (*New South Wales*)
- VESSEY, CLIFFORD ALFRED, B.SC., M.I.CHEM.E., 12 Rossett Green Lane, Harrogate,
Yorkshire. (*West Riding*)
- WALKER, RONALD ANTHONY, B.SC., 26 Nile Street, East Perth, West Australia.
(*West Australian*)
- WALTER, ALEXANDER H., Roenneholmsv, 11B, Malmoe, Sweden. (*Overseas*)
- WEEDEN, ERNEST, 14 Eaton Drive, Collier Row, Romford, Essex. (*London*)
- WHOWELL, FREDERICK, B.SC.TECH., A.M.C.T., Bradite Ltd., Bethesda, North Wales.
(*Manchester*)

Associate Members

- CARROL, GEORGE DAVID ELLIS, c/o Smith & Walton SA Pty. Ltd., PO Box 46, Jacobs,
Natal, South Africa. (*South African*)
- ELLIS, GEORGE DAVID, c/o Smith & Walton SA Pty. Ltd., PO Box 46, Jacobs, Natal,
South Africa. (*South African*)
- FOURIE, DESSEDEIROUS HADLEY, 810 Arnleigh, Victoria Embankment, Durban, South
Africa. (*South African*)
- HUNT, STUART JAMES, CSR Chemicals Pty. Ltd., 172 Flinders Street, Adelaide, South
Australia. (*South Australian*)
- NATHAN, OVE, Ahlefeldtsgade 18A, Copenhagen K, Denmark. (*London*)
- SEXTY, DAVID WILLIAM, 21 East Hill, Woking, Surrey. (*London*)
- TAGGART, NEVILLE JAMES, c/o Pioneer Chemicals Pty. Ltd., 91-97 Montague Road,
South Brisbane, Queensland, Australia. (*Queensland*)
- WILLIS, WILLIAM ROSS, 51 Drylaw Crescent, Edinburgh, 4. (*Scottish*)
- WINTER, THOMAS PIERSON, 13 Balmont Road, Juniper Green, Edinburgh. (*Scottish*)

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Oil and Colour Chemists' Association

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

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

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

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

PUBLICATIONS

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

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

Paint Technology Manuals

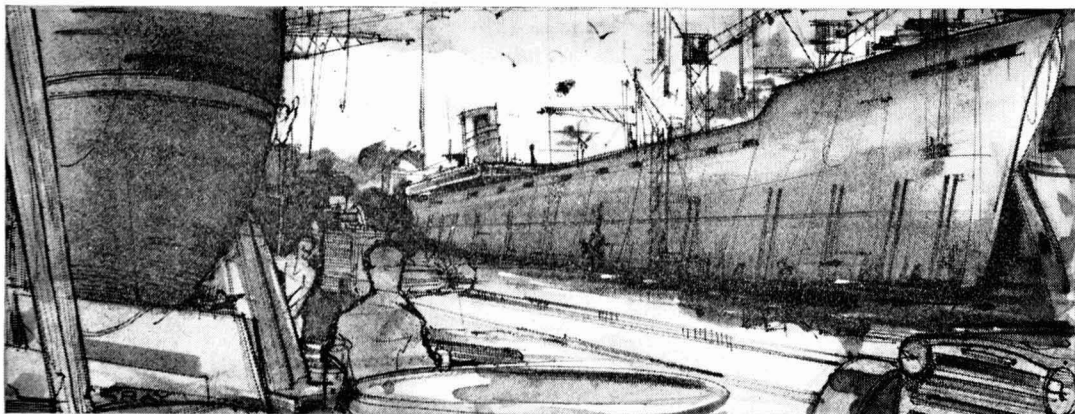
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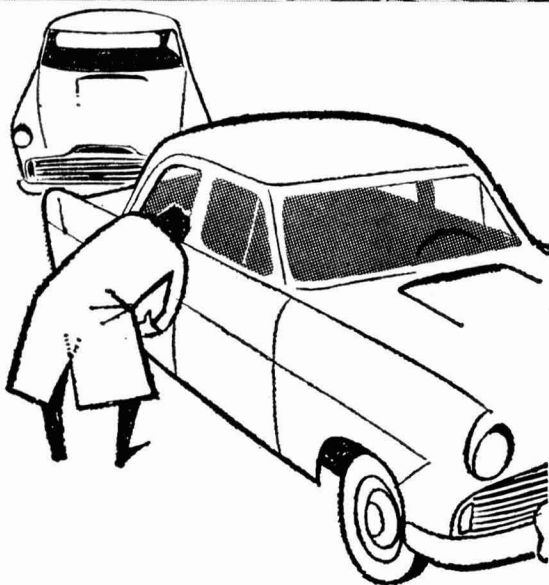


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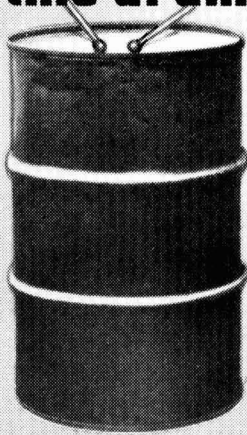


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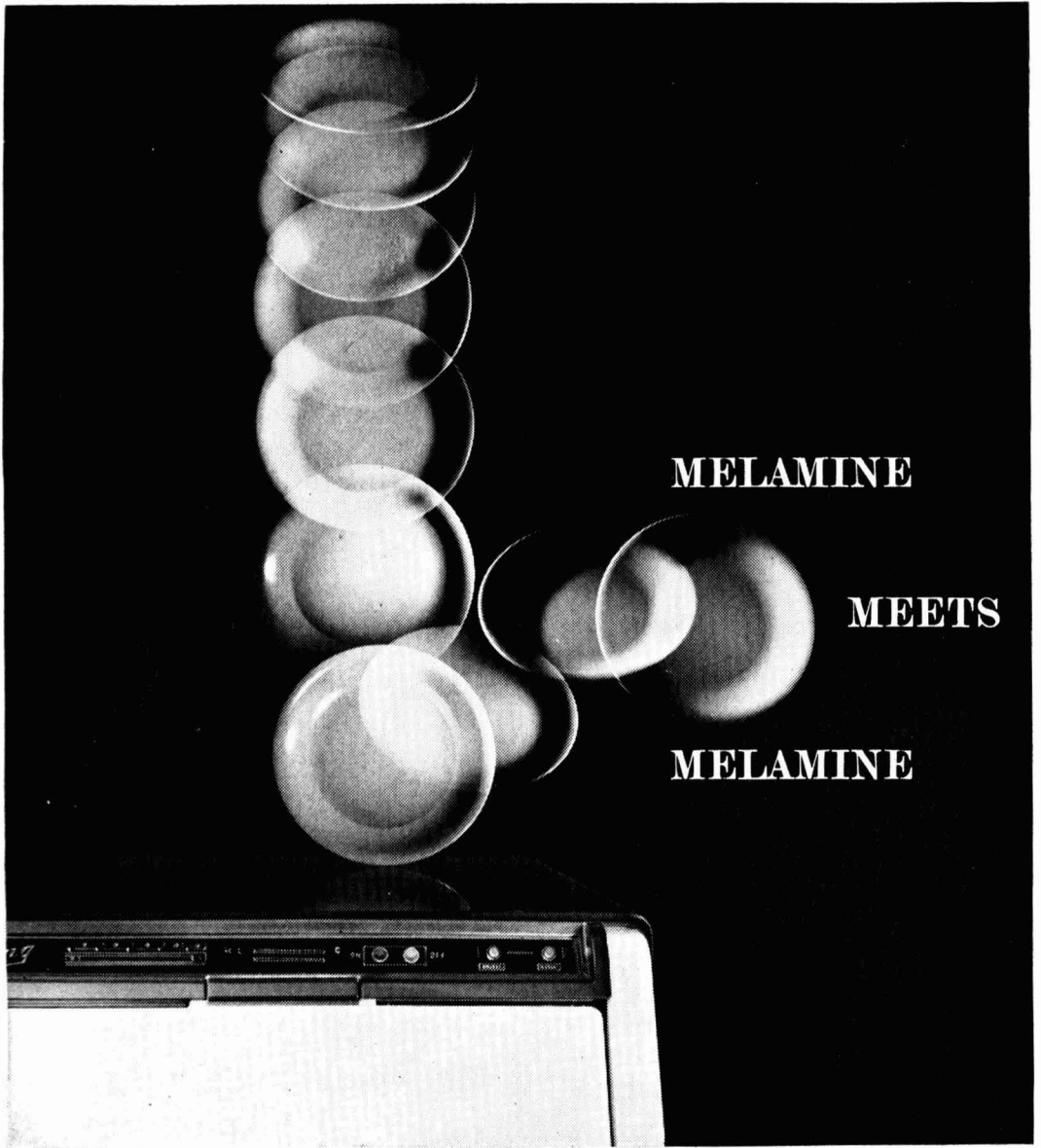
Revised by A. A. Drummond, M.Sc., A.R.I.C., under the Editorship of I. C. R. Bews, B.Sc., A.R.I.C., in consultation with T. E. Johnson, A.M.C.T., F.R.I.C.

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