

JOURNAL OF THE OIL AND COLOUR CHEMISTS' ASSOCIATION



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Some factors affecting the brightness and opacity of emulsion paint films—1: The Stereoscan electron microscope
J. Fairless

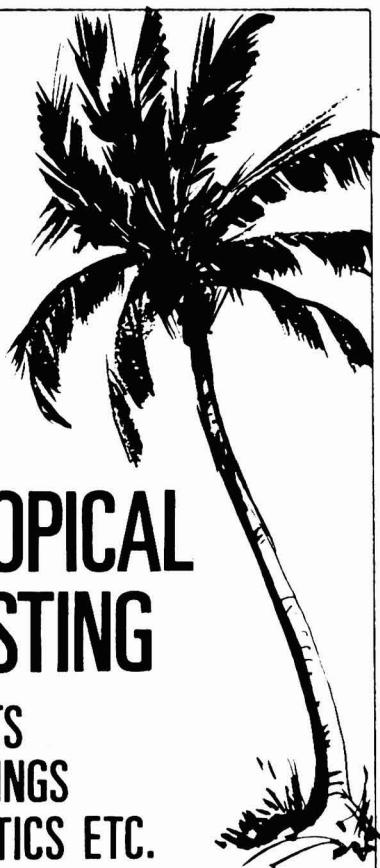
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Polarographic study of the effect of additives on the aggregation of dyes
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AGM, Eastbourne, 20 June

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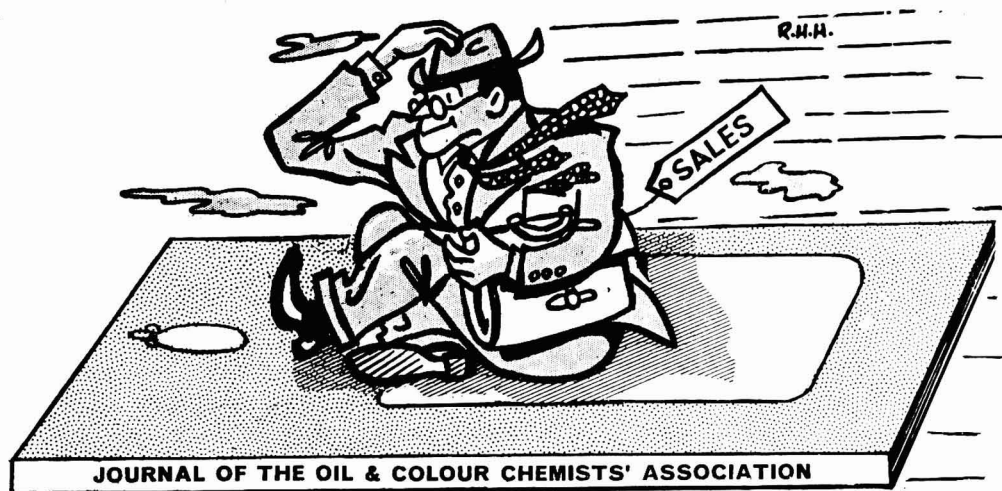
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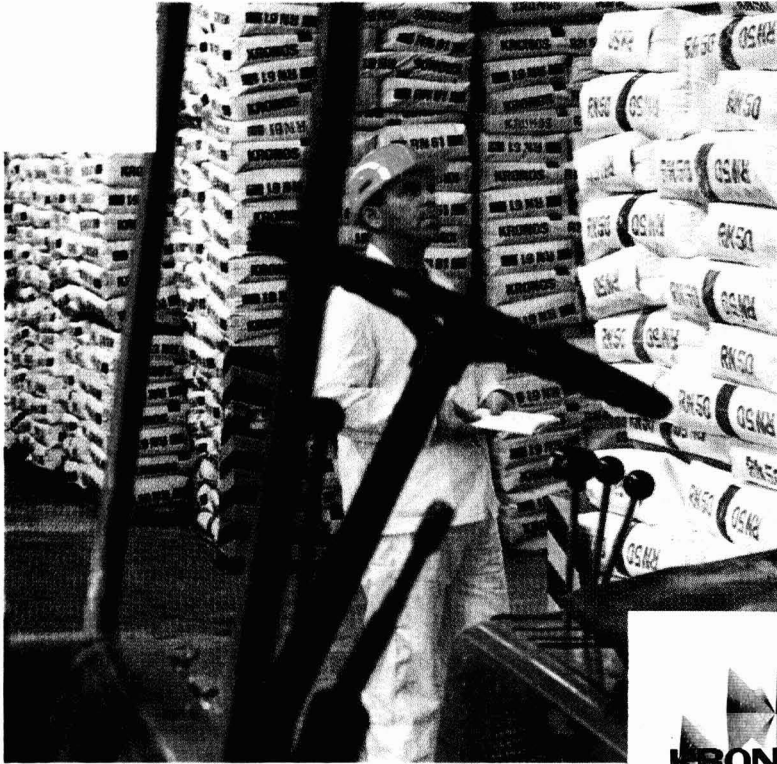
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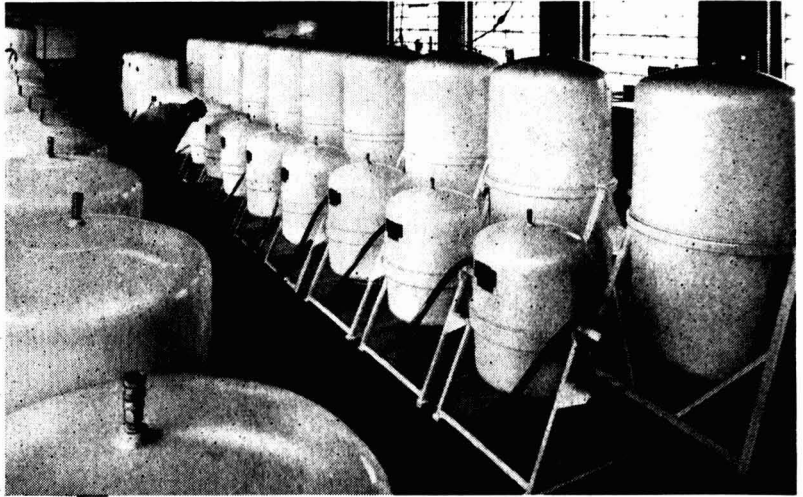
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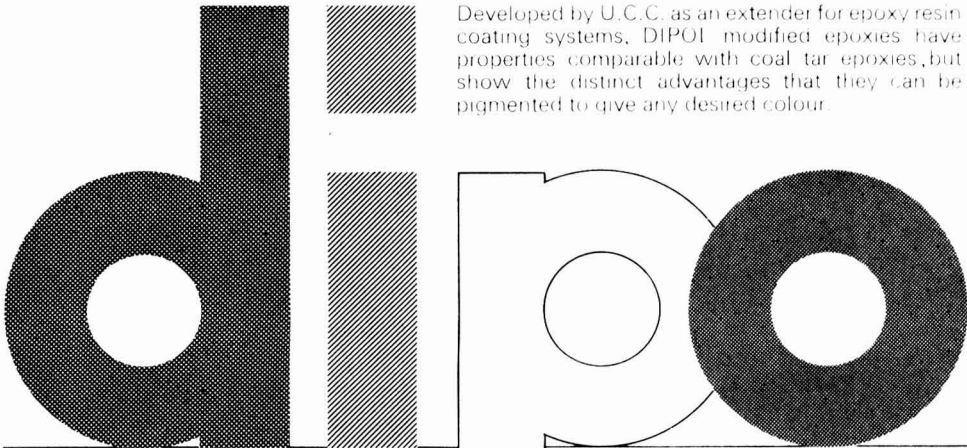


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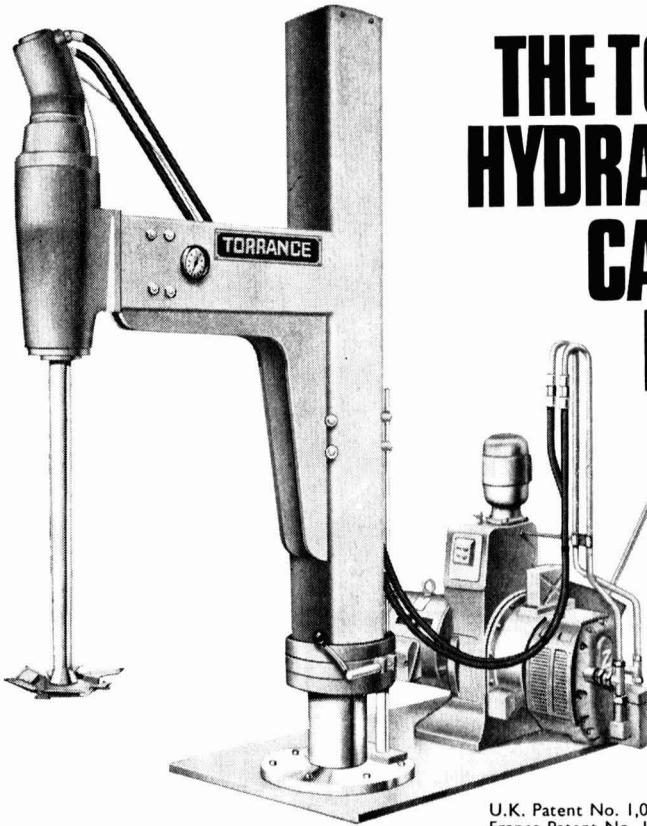
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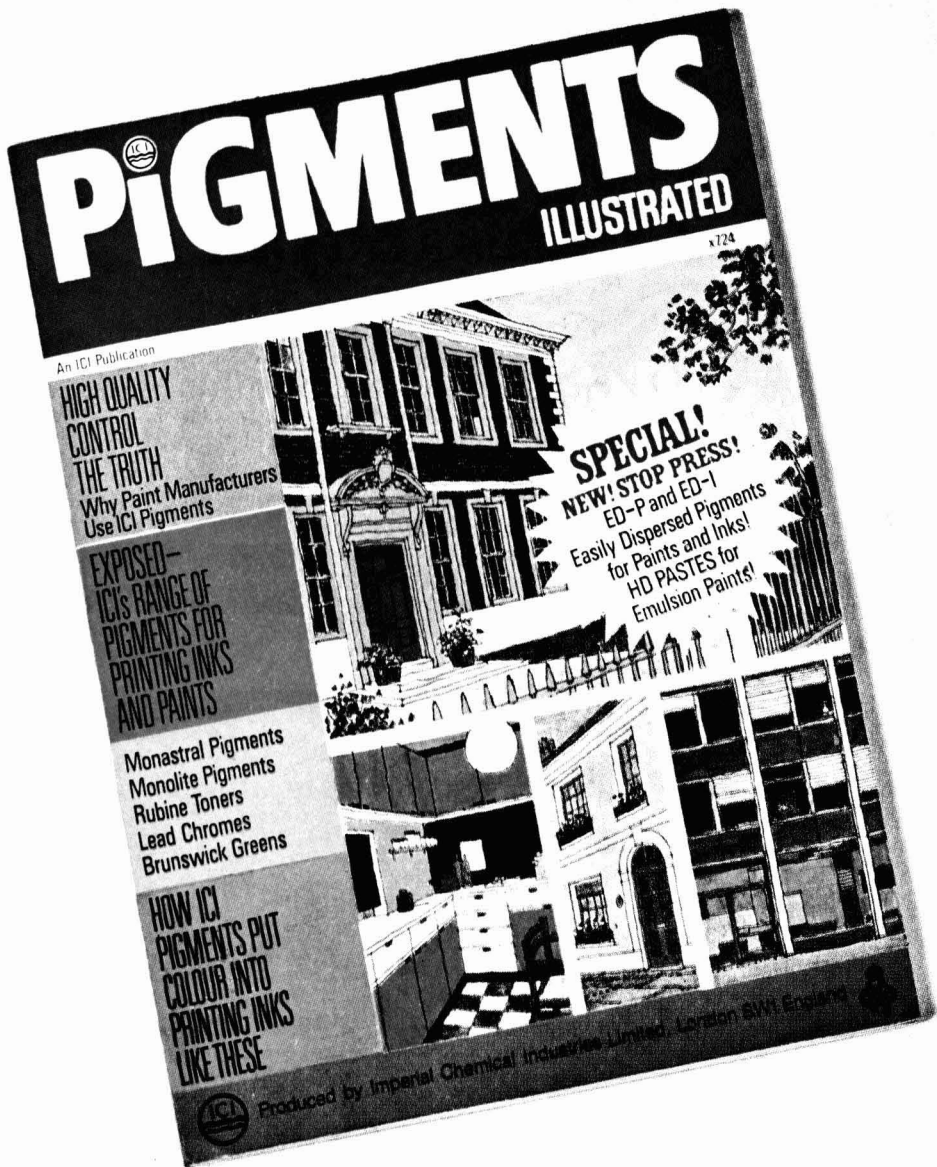
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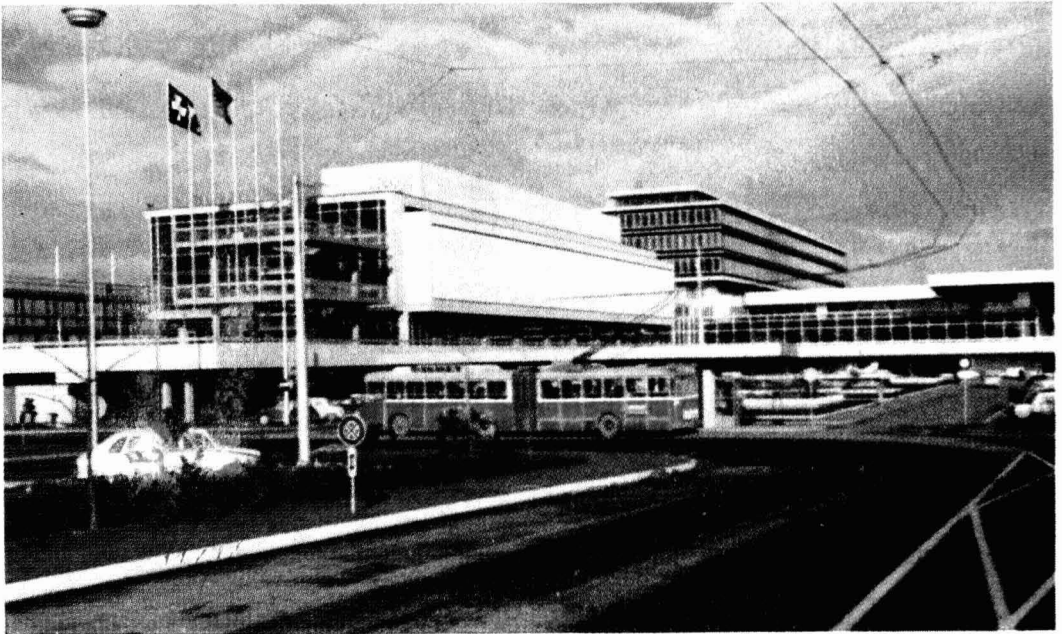
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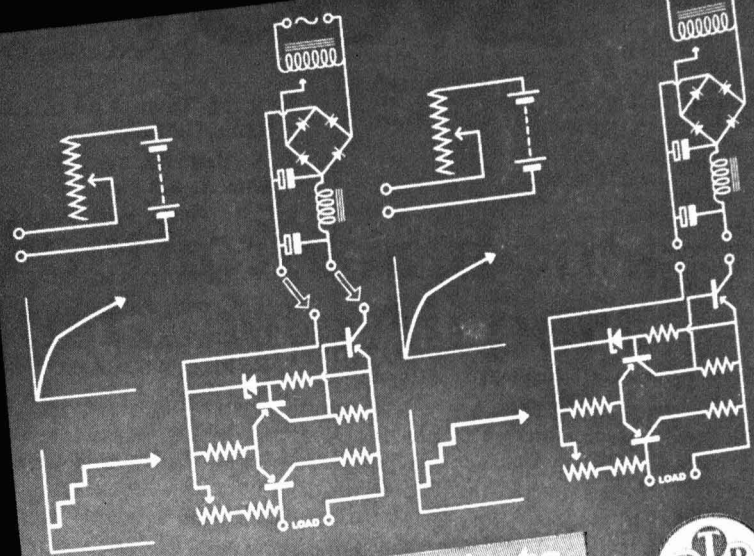
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Transactions and Communications

Some factors affecting the brightness and opacity of emulsion paint films—I: The Stereoscan electron microscope*

By J. Fairless

English China Clays Lovering Pochin Co. Ltd., St. Austell, Cornwall

Summary

This work represents a study of the surfaces of emulsion paint films, using the Stereoscan electron microscope. Paints have been prepared at 50 per cent and 70 per cent total pigment volume concentration, incorporating a coated titanium dioxide grade as prime pigment and a selected range of commonly used mineral extenders.

The latex used was a co-polymer of vinyl acetate and versatic acid (Veova 911) which was prepared experimentally in three particle size ranges: (a) average 0.25 microns, (b) average 0.50-0.75 microns and (c) average 1.25 microns.

Effects of pigment/extender packing in emulsion paint films, pigmented above and below the critical pigment volume concentration, have been studied and a tentative relationship drawn between emulsion paint film formation and the properties of opacity and brightness, under the influence of varying emulsion particle size.

Key words

Prime pigments

titanium dioxide

Extender pigments

calcined clay
calcium carbonate
clay

Binders-resins etc.

polyvinyl acetate
versatate resin

Apparatus primarily associated with analysis and testing

electron microscope

Quelques facteurs ayant une influence sur la brillance et l'opacité de peintures-émulsions

Résumé

Cet exposé comprend une étude sur des surfaces de peintures-émulsions au moyens du microscope électronique "Stereoscan." Des peintures ont été préparées à 50% et à 70% totale concentration pigmentaire en volume, avec un type de dioxyde de titane enrobé en tant que le pigment effectif et une gamme sélectionnée de matières de charge usuelles.

On a utilisé un latex-copolymère de l'acétate vinylique et de l'acide versatique (Véova 911), préparé expérimentalement en les trois séries suivantes de grandeurs particulières: (a) 0,25 microns moyen, (b) 0,50—0,75 microns moyen, (c) 1,25 microns moyen.

*Presented to the Bristol Section on 13 December 1968.

On a étudié les effets du tassement pigment/matière de charge en feuillets des peintures-émulsions, pigmentées au dessus et au dessous de la concentration pigmentaire critique en volume, et l'on a proposé un rapport tentatif entre la formation de feuillets en peintures-émulsions et les caractéristiques d'opacité et de brillance, sous l'influence de diverses grandeurs particulières des émulsions.

Einige die Helle Farbe und Opazität von Dispersionsfarben Beeinflussende Faktoren

Zusammenfassung

In dieser Arbeit wird das Studium von Dispersionsfarbfilm-Oberflächen unter Benutzung des Stereoscan—Elektronenmikroskopes behandelt. Farben mit 50 und 70% Gesamt PVK, enthaltend als Hauptpigment eines der umhüllten Titandioxide, sowie eine Auswahl gebräuchlicher mineralischer Füllstoffe wurden untersucht.

Als Latex wurde ein aus Vinylazetat und Versaticsäure (Veova 911) hergestelltes Mischpolymer eingesetzt, welches experimentell in drei Teilchengrößen präpariert worden war:

- (a) durchschnittlich 0,25 Mikrons
- (b) „ 0,50-0,75 Mikrons
- (c) „ 1,25 Mikrons

Die Auswirkung der Pigment/Streckmittel-Packung in Dispersionsfarbfilmen, höher und niedriger als die KPVK pigmentiert, wurde untersucht, sowie versuchsweise Schlüsse wurden gezogen hinsichtlich Beziehungen zwischen der Bildung von Dispersionsfarbfilmen und der Opazität und Hellfarbigkeit in Abhängigkeit von den verschiedenen Teilchengrößen in den Emulsionen.

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Резюме

Настоящая статья исследует поверхности эмульсионных красочных пленок, применяя стереоскопический обзорный электронный микроскоп. Приготавливались краски с общей пигментной объемной концентрацией в 50% и 70%, включая покрытие двуокиси титана в качестве грунтовочного пигмента и избранное число обычно применяемых минеральных наполнителей.

Применяемый латекс состоял из сополимера из винилацетата и версатовой кислоты (Veova 911), который приготавливался экспериментально в трех средних размерах частиц:—(а) 0.25 микрон (б) 0.50-0.75 микрон и (в) 1.25 микрон.

Исследуется влияние пигментных и наполнительных уплотнений в эмульсионных красочных пленках, пигментированных выше и ниже критической пигментной объемной концентрации и формулируется экспериментальная зависимость между образованием пленок и свойствами непрозрачности и яркости, под влиянием вариации размера эмульсионных частиц.

Introduction

This paper represents the first stage in a study to determine the factors which affect the brightness and opacity of emulsion paint films.

For some time now, chemists have been well aware of the differences in paint properties which occur in the region of the critical pigment volume concentrations of both solvent- and water-based paints. Oil-bound paints have been thoroughly examined, particularly with regard to opacity and gloss changes occurring in this region^{1,2,3}, and, while emulsion-bound paints have received

similar attention, it can be argued that many of the "rules" of opacity applying to oil-bound paints just do not necessarily apply to the emulsion-bound types.

For example, in the author's determination of the opacity of alkyd flat paints, pigmented at critical pigment volume concentration, importance was centred on a graph in which $10 \times \log_{10}$ contrast ratio is plotted against the spreading rate of the paint under consideration⁴.

No matter what the extender system, it was found that, with thinner paint films, the opacity steadily increased with increase in volume concentration of titanium dioxide. With thicker paint films of the same paints, however, measured at 98 per cent contrast ratio, in accordance with Munk's equation⁵, the hiding power increased to a maximum with increase in titanium dioxide volume concentration, and then fell away. In fact, opacity increased to a maximum at a concentration of 25 to 27 per cent titanium dioxide, independently of the extender used, but the amplitude of the peak was higher in the case of a lamellar extender than with a nodular one, due to more regular spacing of the titanium dioxide. (See Fig. 1.)

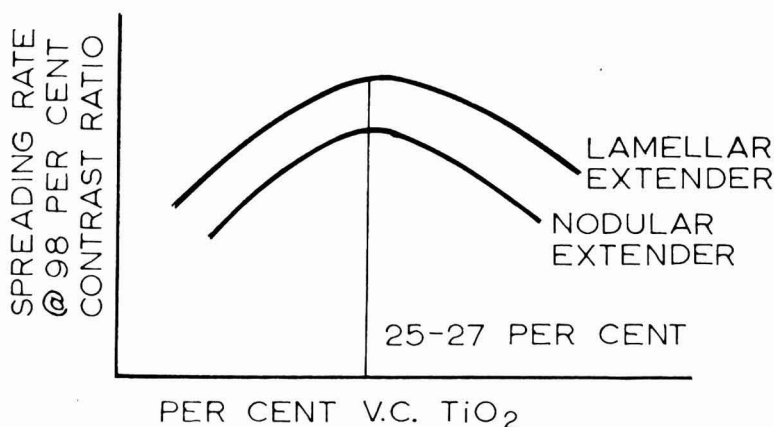


Fig. 1. Effect of extender on opacity

Now, if the same approach is made to latex paints, it is found that, in the plotting of the original opacity graph, discrepancies occur in the 98 per cent contrast ratio region. Contrast ratio measurements of paint films made at a spreading rate of 100sq yd per gallon, and below, lead to the premature crossing of the lines on the graph. In other words, dry hiding is in evidence, and sensible results have not been obtainable with this method, which is practically regarded as the most satisfactory in this type of work, in the region of "maximum opacity" at 98 per cent contrast ratio. In fact, results following any sensible pattern can only be obtained in the region of 95 per cent contrast ratio.

It was this problem that led the writer to take a closer look at the factors affecting the opacity of latex paints with particular regard to the influence of the extender, and the particle size of the latex itself.

The work, as a whole, studies the effects of particle shape and size of mineral extenders, their brightness, the effects of pigmenting above and below the

critical pigment volume concentration with a new type of treated titanium dioxide and, finally, the effects of varying latex particle size ranging from 0.25 micron to 1.25 micron.

The paint films so produced are being examined for opacity and brightness with the Hardy and Elrepho spectrophotometers. However, this will form the second stage of the work.

At this point, the results of the initial investigations to discover just what the surface of the emulsion paints look like are presented.

The technique that has been used involves the scanning electron microscope, perhaps better known as the Stereoscan. The reason why it was used was, because above all others available, it provided a convenient means of producing accurately, and relatively quickly, images of paint films at high magnifications. By producing such images, it was hoped that an idea could be formed as to the actual type of packing, between pigment and extender, and the distribution of the latex binder in emulsion paint films.

Description of the instrument

The Stereoscan was first developed at Cambridge by Professor Oatley, and is now produced and marketed by Cambridge Scientific Instruments Ltd.

It produces an image of the surface of any specimen at a range of magnifications from about 20 to 50,000 times, with an ultimate resolution of at least 300Å and with an exceptional depth of focus which can be of the order of millimetres at lower magnifications. It will accept quite bulky specimens, with no need for replication of surfaces, provided only that the surface can be made conductive, usually by coating with a thin gold-palladium layer, and that the specimen withstands the high vacuum and the electron bombardment. Consequently the Stereoscan can produce micrographs of paint surfaces of unprecedented clarity and at much higher magnifications than are obtainable with an optical microscope.

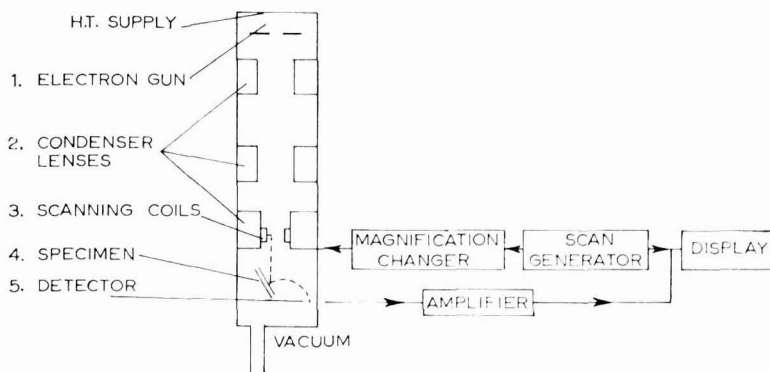


Fig. 2. The Stereoscan

The instrument is briefly described. (See Fig. 2). A beam of electrons emerges from the electron gun (1) under the influence of an accelerating voltage of from 1 to 30 kV, and is focused by a series of electromagnetic lenses (2) into a small spot on the specimen surface (4). The incident electrons are partly reflected and partly absorbed, with some re-emission of lower energy secondary electrons.

The reflected primaries or the emitted secondaries are collected by a scintillator (5) and the strength of the signal received is dependent on the surface topography at the point where the electron beam strikes the specimen.

By applying a scanning motion to the electron beam, using the scanning coils (3), the signal strength will vary, and the amplified signal can be displayed on a cathode ray tube, using a synchronous scanning motion on the cathode ray tube display. Magnification is changed merely by altering the amplitude of the scan on the specimen, and the display is recorded photographically.

In the following illustrations, the specimen surface is in each case at 45° to the direction of view, and the quoted magnification applies only to lateral distances. The field of view at 4,000 times is thus about 25μ (laterally) 35μ (vertically) and at 13,000 times, about $8\mu \times 11\mu$; and for other magnifications in inverse proportion.

Each sample has been prepared and made conductive by the use of an evaporation deposited film of gold-palladium up to 500\AA thick.

Experimental

In the study, two levels of pigment volume concentration were considered at (a) 50 per cent and (b) 70 per cent. The PVC of TiO_2 was kept constant at 22.5 per cent and the differences made up with single extenders, which were Speswhite natural china clay, M100 calcined china clay and a calcitic calcium carbonate.

The experimental emulsion paints used were prepared especially for the programme by Dunlop Chemical Products Ltd. and were polyvinyl acetate/VeoVa 911 copolymers at particle size range of 0.25 microns, 0.5-0.75 microns and 1.25 microns. (Formulae—Table 1.)

Method of manufacture

The paints were prepared by dispersing the pigment and extender portions in all the deflocculant and sufficient water to form a working slurry with a Cowles dissolver. The residence time in each case was five minutes.

▶ The remaining constituents were successively added with the latex being last to be incorporated.

Finally, the paints were brought to 82 Krebs units before application and examination.

Table 1
Composition of emulsion paints

	1	2	3	4	5	6	7	8	9
50% PVC total									
RN 44	82.1	82.1	82.1	82.1	82.1	82.1	82.1	82.1	82.1
Speswhite	58.5	—	—	58.5	—	—	58.5	—	—
M100	—	58.5	—	—	58.5	—	—	58.5	—
Calcite	—	—	60.75	—	—	60.75	—	—	60.75
Sodium hexametaphosphate (10% Sol ⁿ)									
Sodium polyacrylate (10% Sol ⁿ)	7.03	7.03	7.14	7.03	7.03	7.14	7.03	7.03	7.14
Sodium hydroxide (10% Sol ⁿ)									
Sodium benzoate (10% Sol ⁿ)	14.1	14.1	14.3	14.1	14.1	14.3	14.1	14.1	14.3
Latex A (average 0.25 micron)	116.5	116.5	116.5	—	—	—	—	—	—
Latex B (average 0.5-0.75 micron)	—	—	—	95.75	95.75	95.75	—	—	—
Latex C (average 1.25 micron)	—	—	—	—	—	—	85.75	85.75	85.75
Hydroxyethyl cellulose (5% Sol ⁿ)	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0
Butyl cellosolve acetate	2.4	2.4	2.4	2.0	2.0	2.0	1.7	1.7	1.7
Fungicide	1.2	1.2	1.2	1.0	1.0	1.0	0.9	0.9	0.9
Anti-foam	1.1	1.1	1.1	1.0	1.0	1.0	1.0	1.0	1.0
Water	102.5	97.5	123.5	140	112	111	116	122	113

Table 1 (continued)

	10	11	12	13	14	15	16	17	18
70% PVC total									
RN 44	82.1	82.1	82.1	82.1	82.1	82.1	82.1	82.1	82.1
Speswhite	123.5	—	—	123.5	—	—	123.5	—	—
M100	—	123.5	—	—	123.5	—	—	123.5	—
Calcite	—	—	128.2	—	—	128.2	—	—	128.2
Sodium hexametaphosphate 10% Sol ⁿ at 0.25%									
Sodium polyacrylate 0.05%	10.28	10.28	10.51	10.28	10.28	10.51	10.28	10.28	10.51
Sodium hydroxide 0.20%									
Sodium benzoate 10% Sol ⁿ	20.6	20.6	21.0	20.6	20.6	21.0	20.6	20.6	21.0
Latex A (average 0.25 micron)	70.1	70.1	70.1	—	—	—	—	—	—
Latex B (average 0.5-0.75 micron)	—	—	—	57.4	57.4	57.4	—	—	—
Latex C (average 1.25 micron)	—	—	—	—	—	—	51.5	51.5	51.5
Hydroxyethyl cellulose (5% Sol ⁿ)	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0
Butyl cellosolve acetate	1.4	1.4	1.4	1.2	1.2	1.2	1.0	1.0	1.0
Fungicide	0.7	0.7	0.7	0.5	0.5	0.5	0.5	0.5	0.5
Anti-foam	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Water	175.5	131.5	181	171.5	172	117	168.5	145	135

Table 2
Raw material data

RN 44	Kronos Titanium Pigments Ltd., York House, 199 Westminster Bridge Road, London SE1. TiO ₂ content 84.8% Specific gravity 3.65 Oil absorption 40-42		
M 100 Speswhite } Nature	English China Clays Ltd., St. Austell, Cornwall.		
	<i>Speswhite</i>		<i>M100</i>
	Natural aluminium silicate hydrate		calcined china clay
Specific gravity	2.60		2.60
pH of 10% slurry in water	5.5 ± 0.5		6.5 ± 0.5
300 mesh residue (max)	0.05%		0.10%
Finer than 10 microns	99.5% (minimum)		90% (minimum)
Finer than 2 microns	80 ± 3%		50%
Brightness at 4580Å	89 ± 0.7		91.5 ± 1.0
Oil absorption (spatula rub out)	42		45
Latex A } Latex B } Latex C }	Dunlop Chemical Products Ltd. Erdington, Birmingham 24.		
	<i>Latex A</i>	<i>Latex B</i>	<i>Latex C</i>
	Polyvinylacetate/Neova 911, 75%/25% copolymer		
Specific gravity of solids	1.06	1.06	1.06
% solids	45.5	55.4	61.8
Particle size	0.25 microns (somewhat wider in spread than B or C)	0.5-0.75 microns (Narrow cut)	1.25 microns (Average)
Calcite		<i>Ground calcitic calcium carbonate</i>	
Specific gravity		2.70	
Oil absorption (spatula rub out)		15-16	
pH of 10% slurry in water		9-9.5	
Mean diameter		2.5 microns	
300 mesh residue		0.44%	
Finer than 10 microns		96%	
Finer than 2 microns		19%	
Brightness at 4580Å		92.1	

Application

The paints were applied to "Sheen" hiding power charts No. 102, and Melinex polyester film with a 0.0032in (80 microns) wire wound applicator bar.

Before subjecting the paints to examination all films were allowed to age for 48 hours approximately.

Results

Raw materials

Before the paint films were examined, it was thought expedient to examine micrographs of the principal raw materials themselves, at increasing magnification.

All micrographs in this work were taken at an inclination of 45° , and optical density should be disregarded since these are micrographs of an electron beam and not an optical image.

Figs. 3 to 6: These represent increasing magnifications of our china clay grade Speswhite. The aggregates of hexagonal plates are clearly discernible.

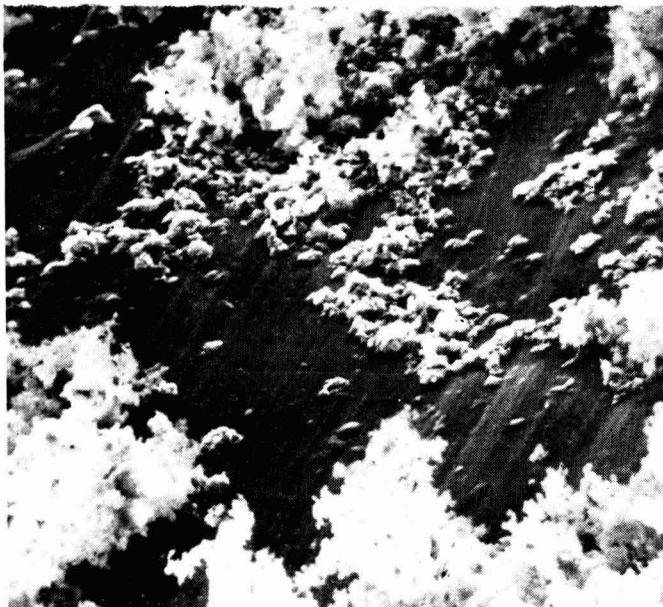


Fig. 3. Speswhite, $\times 360$



Fig. 4. Speswhite, $\times 1200$

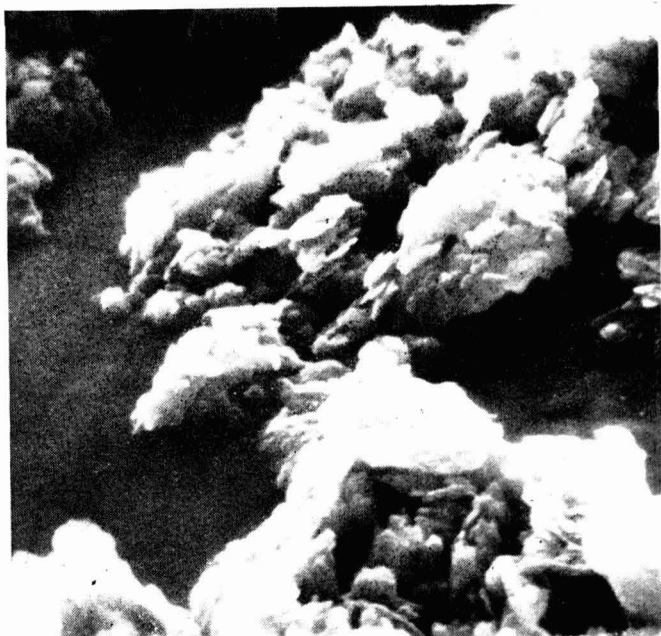


Fig. 5. Speswhite, $\times 3600$



Fig. 6. Speswhite, $\times 12000$

Figs. 7 to 9: This series represents our calcined china clay grade M100. Here it is interesting to note that while the product has been calcined and milled,

it still retains the plate structure of its crystal. The aggregates are somewhat larger than in the case of Speswhite.

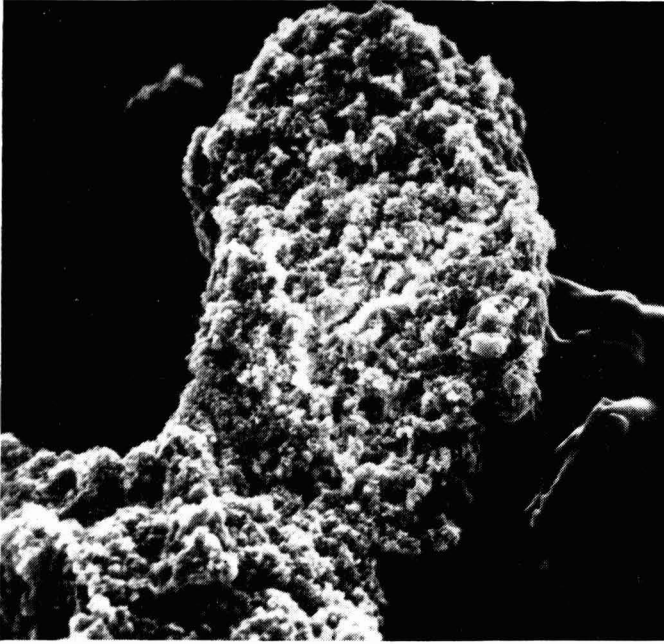


Fig. 7. M100, $\times 360$

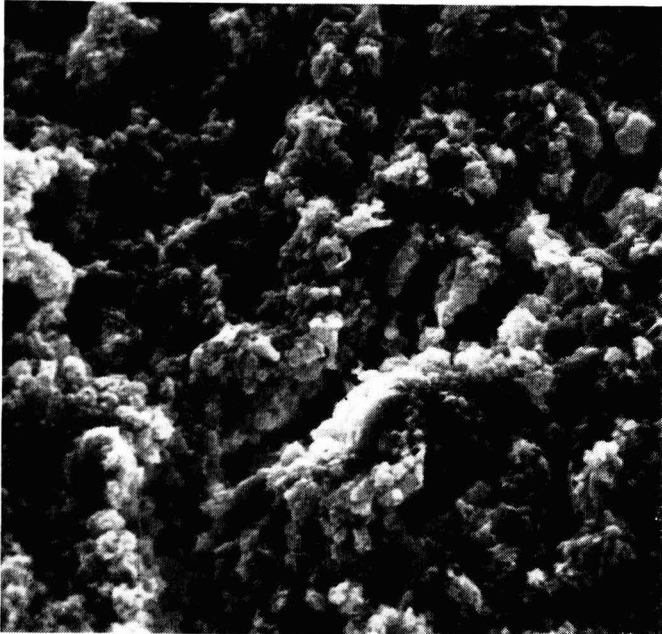


Fig. 8. M100, $\times 1200$

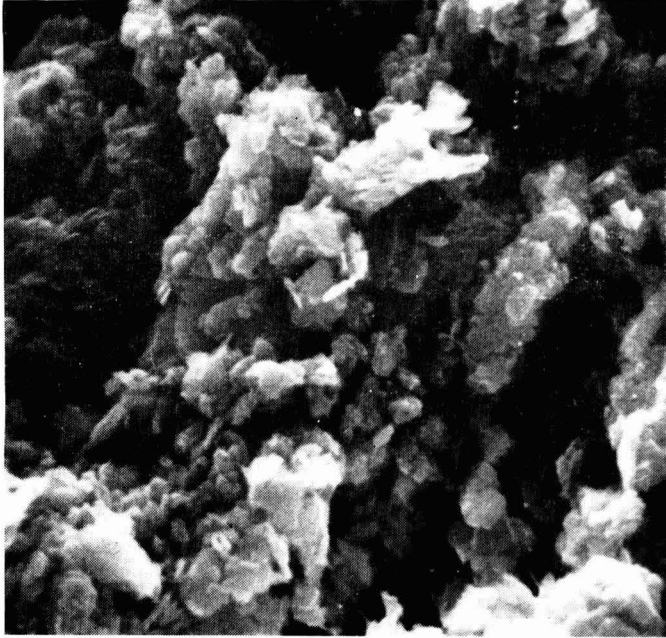


Fig. 9. M100, $\times 3600$

Figs. 10 to 13: These figures represent the ground calcite. The nodular or chunky shape is clearly in evidence and, at the higher magnification, one can see the cleavages in the crystal.

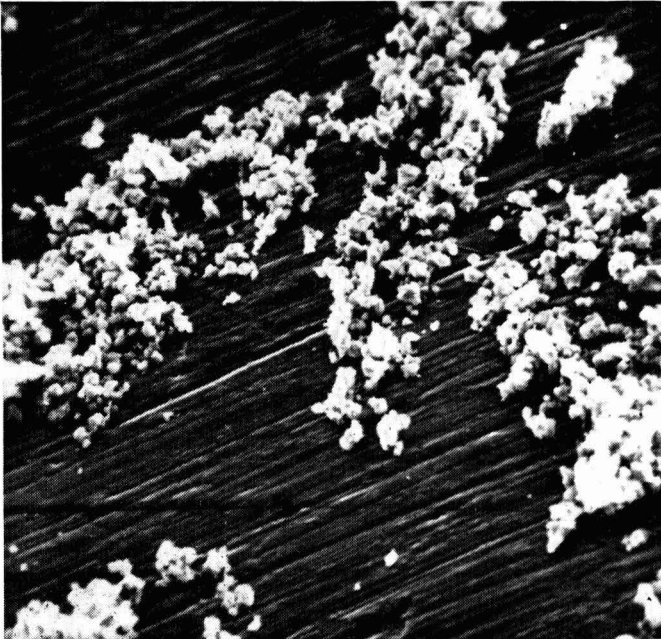


Fig. 10. Calcite, $\times 370$

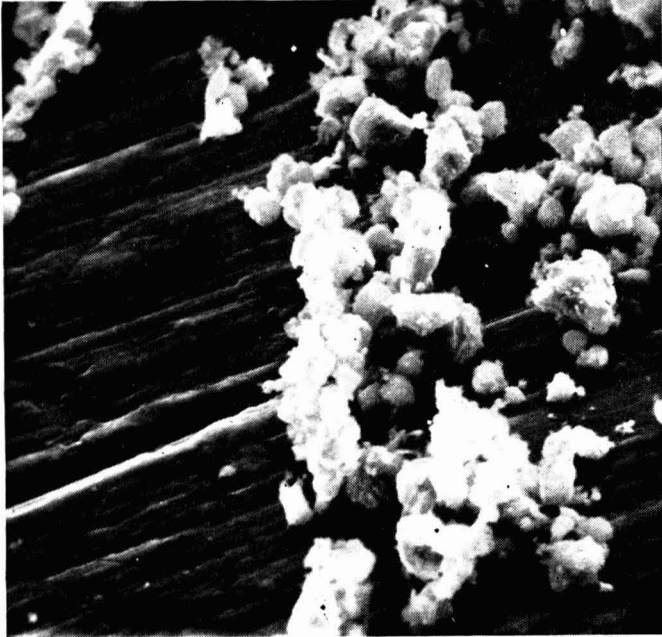


Fig. 11. Calcite, $\times 1250$



Fig. 12. Calcite, $\times 3700$



Fig. 13. Calcite, $\times 13500$

Figs. 14 to 16: These are micrographs of the titanium dioxide, and show the massive aggregation present. Unfortunately, it is difficult to draw any definite conclusions regarding the shape of the individual TiO_2 particles.

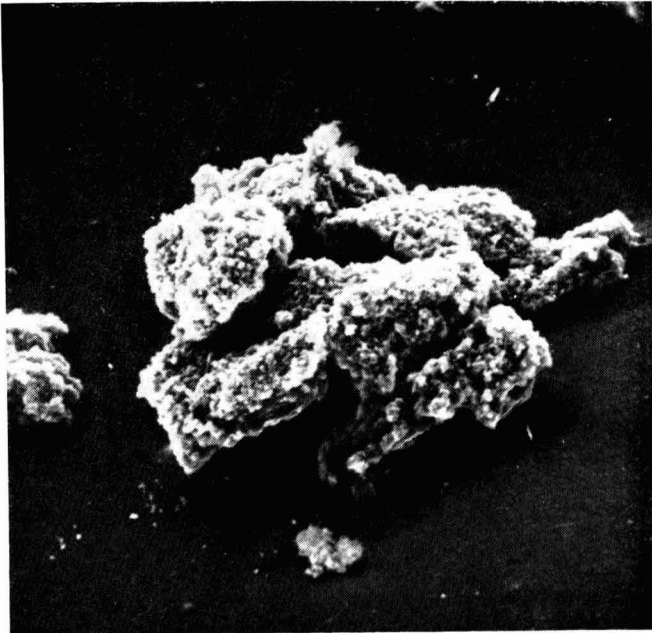


Fig. 14. RN 44 TiO_2 , $\times 370$

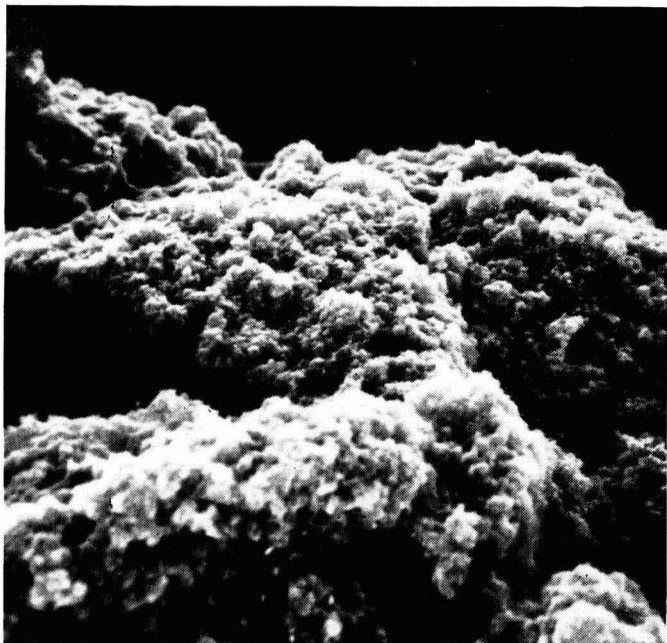


Fig. 15. RN44 TiO₂, × 1250

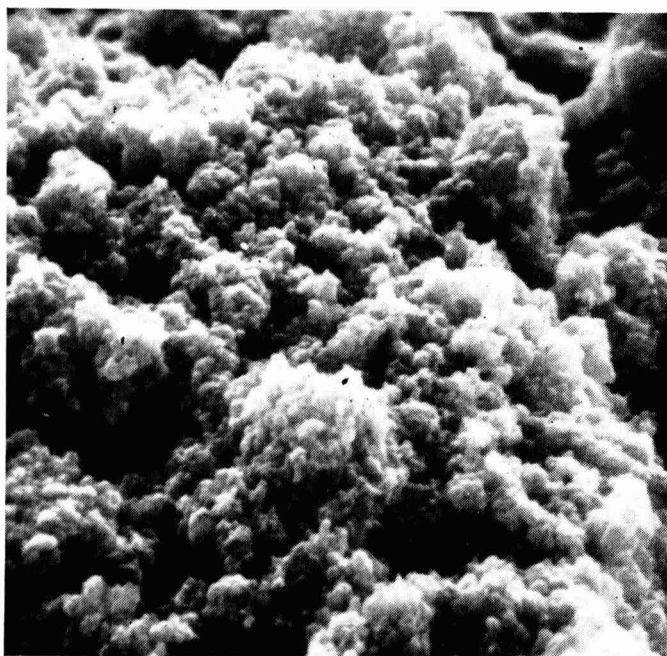


Fig. 16. RN44 TiO₂, × 3700

Figs. 17 to 20: This series represents simple dispersions of TiO_2 in the Latex A *i.e.* that with the bulk of particles of the order 0.25 microns, and several points of interest arise here.



Fig. 17. Latex A + RN44, $\times 360$



Fig. 18. Latex A + RN44, $\times 1200$

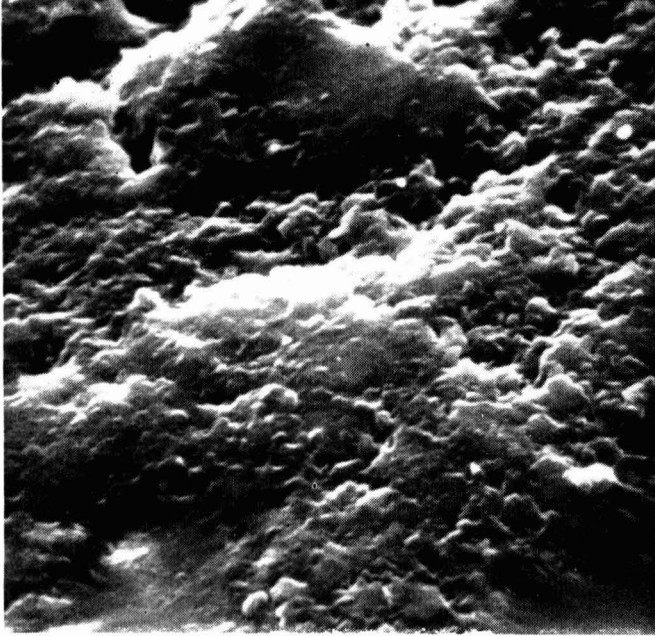


Fig. 19. Latex A + RN44, $\times 3600$

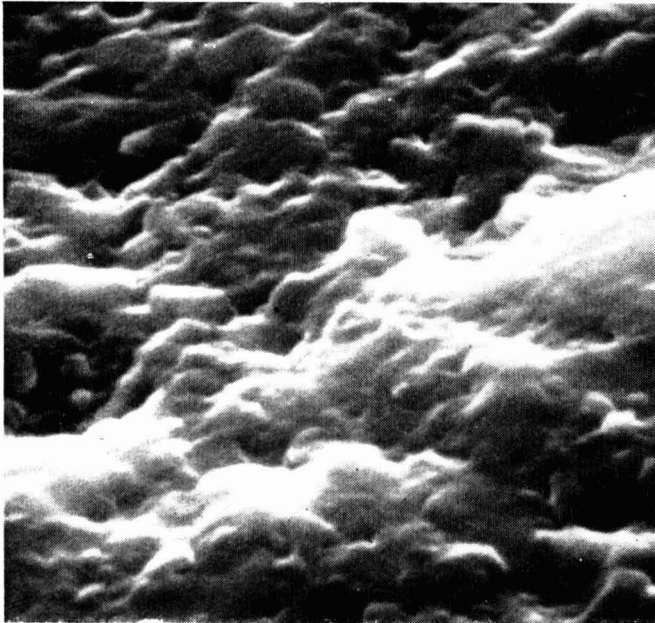


Fig. 20. Latex A + RN44, $\times 12000$

First of all the latex is well coalesced as a continuous film and no individual particles of polymer are seen. Secondly a "frame" has appeared due to the electron beam resting for too long a period of time upon the same area of the polymer film.

Figs. 21 to 23: Here the TiO_2 has been simply dispersed in the Latex C *i.e.* that of 1.25 micron nominal particle size.

These figures are similar to the previous series, except that less of the pigment is grinning through the surface. Certainly the film has coalesced well.



Fig. 21. Latex C + RN44, $\times 360$



Fig. 22. Latex C + RN44, $\times 1200$

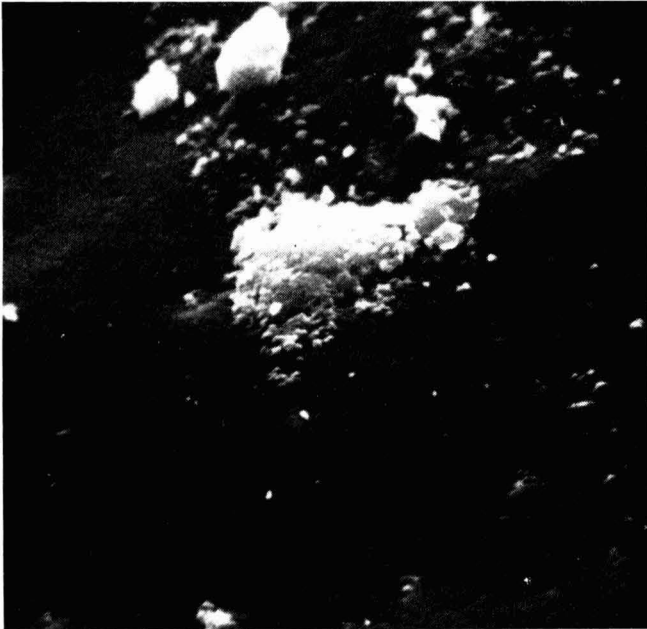


Fig. 23. Latex C + RN44, $\times 3600$

The paint films

The latex in each case is Latex A.

50 per cent PVC: Fig. 24. This represents the paint extended with M100. The aggregates of titanium dioxide and clay and parts of the latex film can be seen.

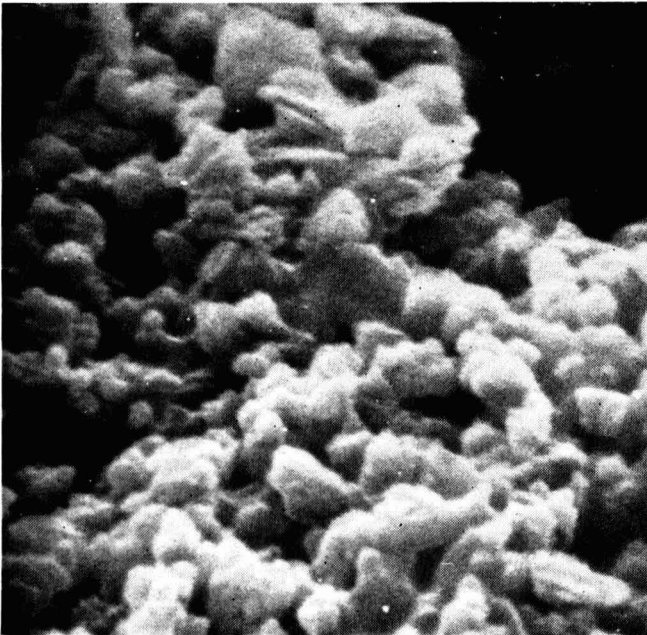


Fig. 24. M100, 50% PVC, $\times 12000$

Fig. 25. This one is calcite at the same magnification as Fig. 22. Here the aggregates of titanium dioxide and flakes of latex as well as fairly large patches are clearly seen. In addition, several particles of calcite are in the picture.

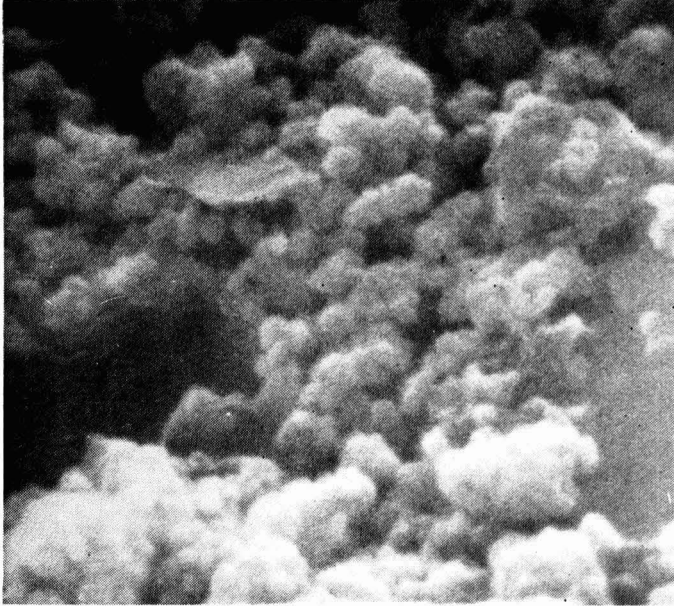


Fig. 25. Calcite, 50% PVC, $\times 12000$

Figs. 26 to 27. At these two magnifications the plates and aggregates of titanium dioxide are seen, and, once more an indication of the skin formed by the latex is in evidence.

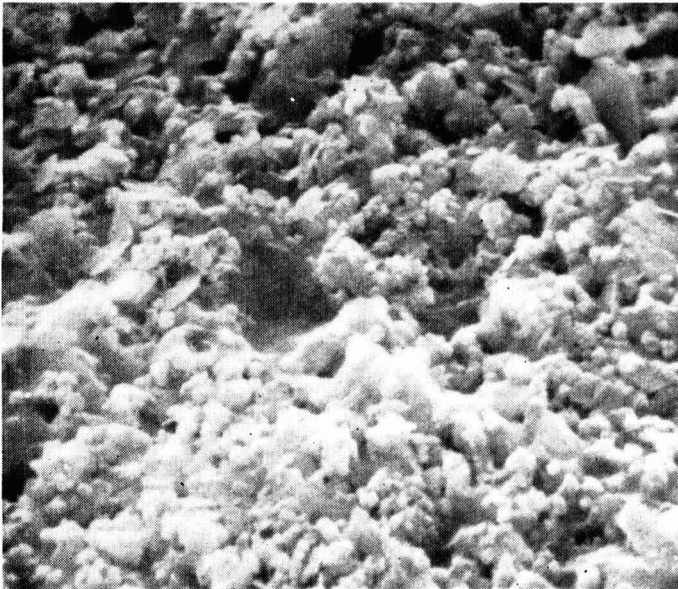


Fig. 26. Speswhite, 50% PVC, $\times 3600$

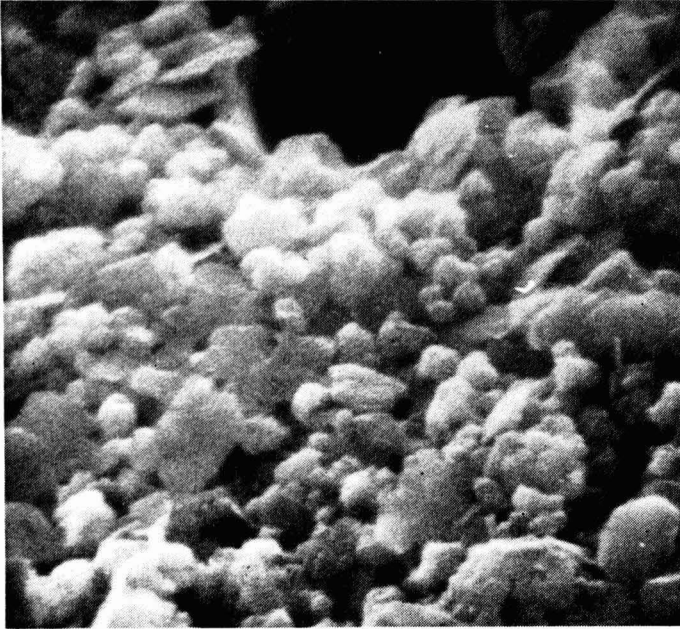


Fig. 27. Speswhite, 50% PVC, \times 12000

70 per cent PVC: Figs. 28 to 29. These are micrographs of M100 extended paint. One is struck by the general uniformity of texture of the surface and by the apparent absence of latex film. The aggregates of titanium dioxide and clay can be seen.

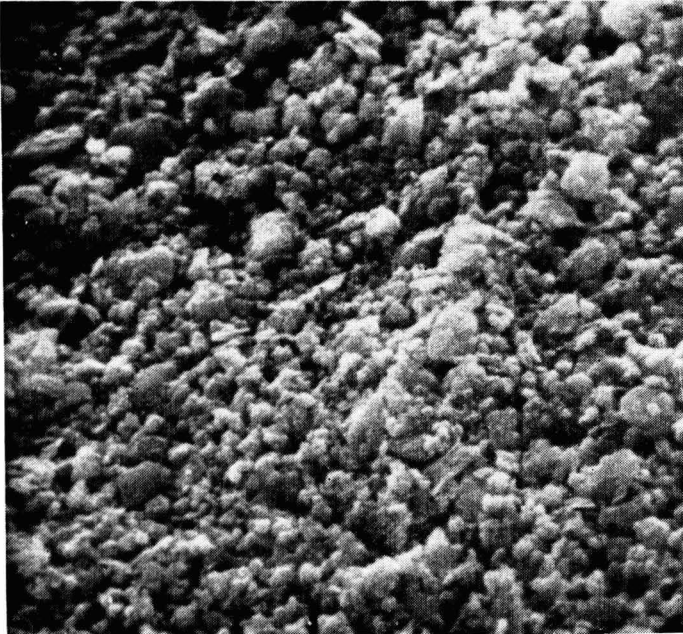


Fig. 28. M100, 70% PVC, \times 3600

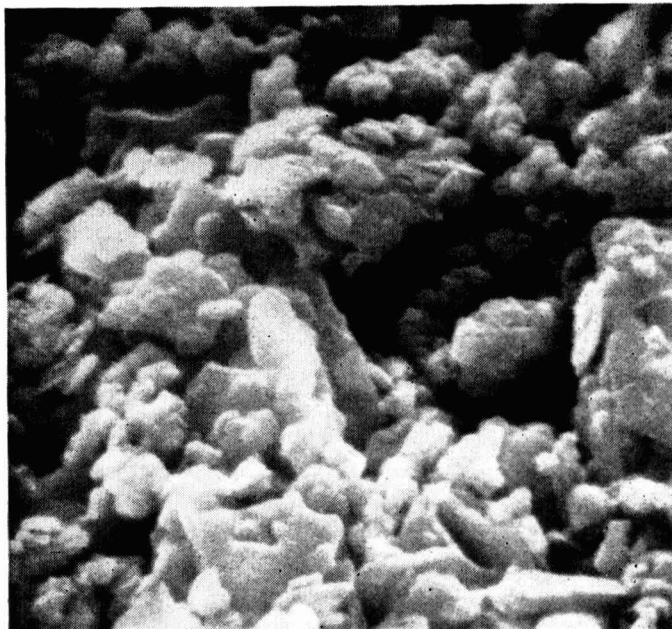


Fig. 29. M100, 70% PVC, $\times 12000$

Figs. 30 to 32. These represent increasing magnifications of the calcite extended paint, and the largest magnification perhaps is one of the most important in the whole series. In the bottom right-hand corner one can clearly see a

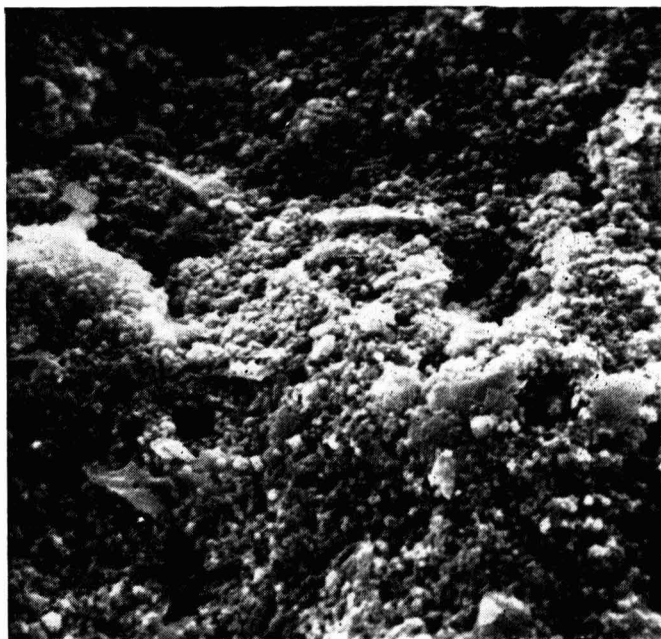


Fig. 30. Calcite, 70% PVC, $\times 1250$

flake of latex submerging an aggregate of TiO_2 . In the top right-hand corner one can see a twisted flake of latex on its side.

Apart from this, what look to be particles of calcite and aggregated titanium dioxide particles in a random distribution, are in evidence.

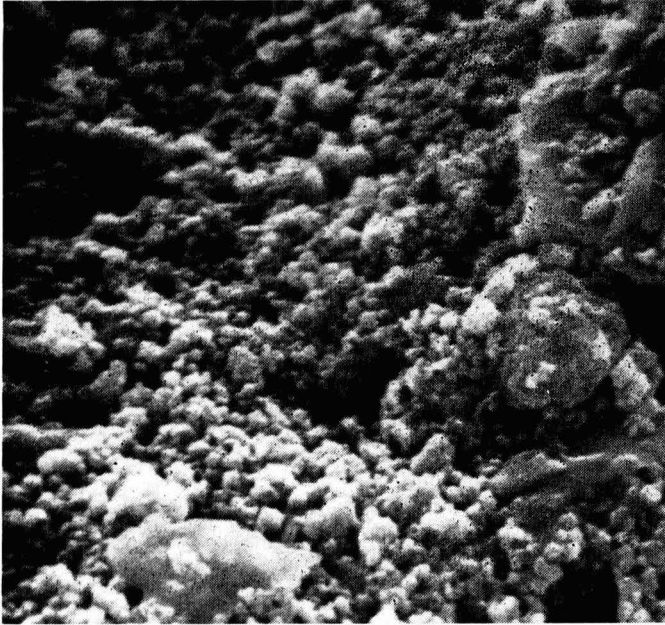


Fig. 31. Calcite, 70% PVC, $\times 3600$

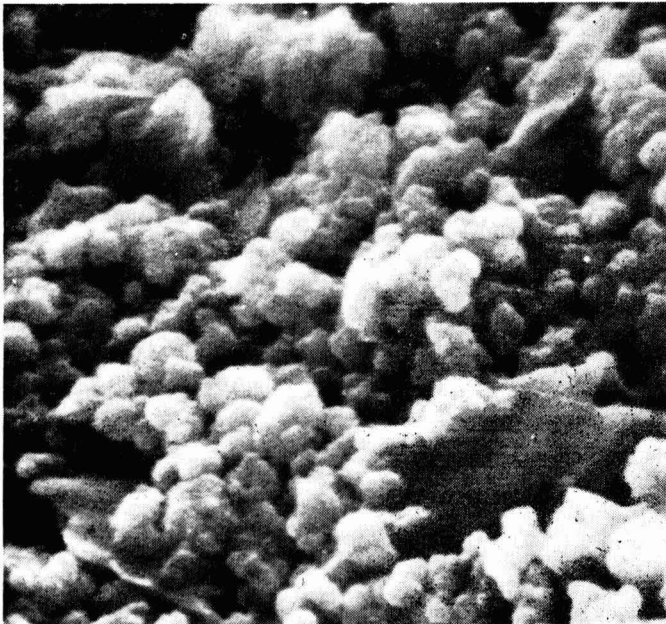


Fig. 32. Calcite, 70% PVC, $\times 12500$

Fig. 33. This is the final micrograph in the series and represents the paint extended with Speswhite. Immediately one sees a lamellar packing with aggregates of titanium dioxide randomly scattered over the clay plates. What are not so evident are the flakes of latex which were clearly seen with the calcite film. However, because they are a similar shape to the clay particles, perhaps they are there after all but blend too well to be easily seen.



Fig. 33. Speswhite, 70% PVC, $\times 12000$

Discussion

This series of micrographs is the result of what was considered to be thorough dispersion and preparation followed by careful application of the paint films, under standard research laboratory conditions.

If these micrographs are representative of emulsion paint film surfaces—and there is good reason to believe they are—then a study of the properties of brightness and opacity will be no easy task. Certainly, theories proposed and accepted by the majority for the study of those properties in oil based paints would be rather difficult to apply in the case of emulsion paints in the PVCs considered in this work. However, this will come to light, one hopes, in the second stage of the work.

This particular stage has illustrated several points.

The Stereoscan is a valuable instrument for high-lighting the inter-packing of pigment/extender particles at paint surfaces at high magnifications.

Certainly at 70 per cent, and in some cases at 50 per cent, pigment volume concentration, there is strong evidence that the surface of emulsion paint films consists largely of pigment/extender particles with flakes of latex randomly

scattered at intervals over the paint surface area. In the case of clay at 70 per cent PVC, the flakes are not easily seen. The fact that the latex is in flake form, generally merging with the adjacent pigment/extender particles, is shown by some of the flakes standing at an angle to the surface of the paint.

The distribution of nodular extenders with titanium dioxide appears to produce a rather more uneven paint surface than the distribution of platey extenders with titanium dioxide. This could well be a pointer to the question of why plates give a higher opacity than nodules or chunks as extenders in emulsion paints. In a lamellar paint surface, such as that produced by Speswhite, one could predict that the relatively even distribution of one of the variables, i.e. the clay, would lead to a more even distribution of the titanium dioxide leading in turn to a higher opacity, than in the case of the nodular extender. In other words, the film shown in Fig. 33 could predictably resist the transmission of light to a greater extent than the film shown in Fig. 32.

The latex films are coalesced.

The titanium dioxide is quite aggregated or flocculated in the cases studied.

Conclusions

The Stereoscan is a very direct method of observing paint film surfaces and, though the instrument is rather complex and expensive, it is extremely simple to use. The advantage of the instrument as compared to an optical microscope lies partly in the facility to achieve higher magnifications but probably of more importance is the very great depth of focus.

It is the author's belief that this instrument will play a valuable part in the future work of paint technology, in leading to a greater understanding of the factors affecting brightness and opacity, as well as many other properties of paint.

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Long term adhesion studies on multicoat systems exposed to natural weathering

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Summary

The adhesion of a range of organic coatings to various substrates has been measured under service conditions by the torque spanner technique. Measurements, carried out monthly over a period of four years, have shown that the adhesion of all the systems varied considerably over a very wide range of values. Observed losses in adhesion could be related to the moisture content of the ambient air.

Key words

<i>Types of coating</i>	<i>Types of surface</i>	<i>Binders</i>	
alkyd coating	aluminium	<i>Oils</i>	<i>Resins etc.</i>
epoxy coating	steel	linseed oil	amide cured epoxy resin
epoxy ester coating	wood	urethane oil	chlorinated rubber
primer			epoxy resin
rubber base coating	<i>Properties associated with</i>		urethane resin
undercoater	<i>dried or cured films</i>		
urethane finish	adhesion	<i>Prime pigments</i>	<i>Chemically active pigments</i>
zinc rich coating		red lead	zinc chromate
		white lead	

Etudes sur l'adhérence des systèmes de revêtements aux multicouches après leur exposition prolongée aux intempéries

Résumé

Sous des conditions effectives de leur utilisation, on a mesuré par la technique de "Torque Spanner" l'adhérence, aux divers supports, d'une gamme de revêtements organiques. Les mesures effectuées mensuellement pendant une période de quatre ans ont démontré que l'adhérence de tous les systèmes s'est variée fortement à travers une gamme très large de valeurs. On pourrait faire un rapport entre les pertes d'adhérence observées et la teneur en humidité de l'air ambiant.

Haftfähigkeitsstudien auf Lange Sicht von Natürlicher Bewitterung Ausgesetzten Mehrschichtensystemen

Zusammenfassung

Die Haftfähigkeit einer Anzahl organischer Anstrichstoffe auf verschiedenen Substraten wurde mittels der Torque Spanner Technik unter praktischen Bedingungen gemessen. Monatliche, vier Jahre lang durchgeführte Messresultate zeigten bei allen Systemen, dass die Haftung sehr wechselhaft war; die Werte schwankten sehr stark. Beobachtete Herabsetzung des Haftvermögens konnte mit dem Feuchtigkeitsgehalt der umgebenden Luft in Beziehung gebracht werden.

Длительные испытания адгезии многослойных систем подверженных естественному выветриванию

Резюме

Измерялась адгезия, в рабочих условиях, между рядом органических покрытий и различных субстратов, применяя технику момента кручения. Измерения, проводимые ежемесячно в течение четырех лет, показали что слипание всех систем значительно изменялось в широком диапазоне значений. Наблюдаемые потери в адгезии могут быть отнесены к содержанию влажности окружающего воздуха.

Introduction

Although there is generally great interest in the prediction of performance of organic coatings under service conditions, few workers have reported work carried out to assess the change in physical properties of paints during exposure to natural weathering. The little that has been reported has been concerned with changes in tensile strength and elongation at break^{1, 2, 3}. In his City and Guilds thesis, published in part in the open literature in 1965, Wright⁴ notes this deficiency and comments that, as far as he is aware, no information has been published on changes of adhesion of modern coatings during atmospheric exposure.

This is largely the case today: the author knows only of one paper covering adhesion changes on exposure, and this work was carried out on the specialised substrate cadmium plate⁵. It has been stated by several authors that the adhesion of a coating is of major importance^{6, 7, 8} since, to protect or decorate a surface, the coating must adhere. Bullett and Prosser⁹ justify work at the Paint Research Station on surface preparation, by stressing the paramount importance of the adhesion factor, particularly in the behaviour of the newer coating materials. In view of this agreement between workers, it is perhaps surprising that the lack of published data still exists. It may well be that lack of suitable quantitative test methods for measuring the adhesion of a coating to the substrate, particularly under service conditions, is responsible for this deficiency and, of course, work involving natural exposure is time consuming.

A test method, involving the use of a recording torque spanner, has now been developed,¹⁰ which is suitable for measuring changes of adhesion during exposure. This present paper describes work carried out to assess changes in adhesion of modern coatings during natural exposure, and to show to what extent the adhesion varies under actual exposure conditions.

Choice of paint systems and substrates

The choice of paint systems for exposure was made from those in current use within the establishment, and covered three of the major mechanisms of film formation. Thus, among the 12 systems tested were alkyds and styrenated epoxy esters representing those coatings curing by atmospheric oxidation, epoxides and polyurethanes curing by chemical reaction, and chlorinated rubber drying by solvent evaporation. All the coatings selected were exposed as part of a two or three coat system. The substrates chosen were 18 gauge EDDQ, mild steel, 18 gauge L16 aluminium in the half-hard condition, and 3/4 in edge grain western red cedar.

The complete systems exposed are shown below.

<i>System</i>	<i>Substrates</i>	<i>Coatings</i>
1	Steel and aluminium	Etch primer to DEF 1408 Cream chlorinated rubber undercoat to HR 852 Cream chlorinated rubber finish to HR 852
2	Steel and aluminium	Red oxide/zinc chromate primer to DEF 1035 Light grey undercoat to DEF 1156 Cream finish to DEF 1156
3	Steel and aluminium	Red oxide/zinc chromate primer to CS 8072 Light grey undercoat to CS 8072 Service brown styrenated epoxy ester finish to CS 8072
4	Steel and aluminium	Red oxide/zinc chromate polyamide cured epoxide primer White adduct cured epoxide finish
5	Steel and aluminium	Red oxide/zinc chromate polyamide cured epoxide primer White polyamide cured epoxide finish
6	Steel and aluminium	Red oxide/zinc chromate polyamide cured epoxide primer White aliphatic polyurethane
7	Steel and aluminium	Red oxide/zinc chromate polyamide cured epoxide primer White aromatic polyurethane
8	Steel and aluminium	Zinc-rich primer to DEF 1217 Cream chlorinated rubber undercoat to HR 852 Cream chlorinated rubber finish to HR 852
9	Wood	Red and white lead primer Light grey undercoat to DEF 1156 Cream finish to DEF 1156
10	Wood	Red and white lead primer Grey styrenated epoxy ester undercoat to CS 8072 Service brown styrenated epoxy ester finish to CS 8072
11	Wood	Linseed oil/T.D.I. urethane oil
12	Wood	Red and white lead primer Proprietary white alkyd undercoat Proprietary white alkyd finish

HR specifications are available from the Atomic Weapons Research Establishment, Aldermaston, Berkshire.

The formulations of the non-specification paints are given in Appendix I.

Panel preparation

All panels were cut from the same batch of material to a standard size of 2ft \times 1ft. The steel panels were carefully degreased with xylene and then burnished uniformly with emery cloth Grade 0 to BS 871. The burnishing operation was carried out as described in DEF 1053 method 2. On completion of this operation, the panels were carefully degreased by rubbing with a xylene soaked cloth until the cloth showed no trace of discoloration.

The aluminium panels, other than those to which an etch primer was to be applied, were prepared in the same manner. The panels to be etch-primed were carefully degreased by repeated swabbing with a xylene-soaked cloth. The wooden panels were carefully examined for shakes, knots etc., and only those panels free from defects were chosen. All panel edges were slightly rounded and the planed surface rubbed with No. 0 glass-paper. The prepared panels were then conditioned for 7 days at a relative humidity of 60-70 per cent and a temperature of 60-70°F.

The steel and aluminium panels were coated by spray to the film weight quoted in the appropriate specification, or at such a film weight as to give a dry film thickness of 1-1.5 mils. The wooden panels were coated by brush. All coatings were allowed to cure for 24 hr at room temperature and humidity before application of the next coat, except the etch-primed panels which were cured for 4 hr. On completion of the entire system, the coated panels were cured at room temperature and humidity for 14 days prior to exposure.

Exposure conditions

The complete programme was exposed in September 1964 at Aldermaston at an angle of 45° facing due South. Aldermaston is a rural area relatively free from atmospheric contamination, although there is a power station in the immediate vicinity and the prevailing wind blows from this direction.

Test schedule

The original intention was to measure the adhesion of the coating system on each panel at approximately monthly intervals irrespective of the weather conditions at the time. No attempt was to be made to pick specific dates or specific climatic conditions, and all tests would be performed, out of doors, so that the adhesion under the actual prevailing conditions would be measured. Preliminary tests indicated that, under extreme conditions of rain or low temperature, the adhesive used for the test would not cure satisfactorily, and this, coupled with the discomfort to the operator, suggested that particularly wet or cold days should be avoided. Because of this, the days selected for test were not always the wettest possible, although several tests were carried out in light rain or snowy conditions. This exterior *in situ* testing was carried out for a period of 30 months until July 1967. A further two determinations were carried out in

December 1967 and September 1968, when the programme was discontinued. The latter two tests were carried out indoors after the panels had been allowed to dry out for three days.

Test method

All adhesion measurements were carried out by the torque spanner technique which is described in detail in the original paper¹⁰. Briefly, cylindrical steel specimens were bonded to the test panel after gently abrading the surface with a nylon pad. The adhesive used was Eastman Kodak 910, a mixture of alkyl cyanoacrylates thickened with some polymeric cyanoacrylates, which sets by the base catalysed addition polymerisation of the cyanoacrylate monomers. This adhesive has the desirable property of curing to an acceptable bond strength within 15-30min at room temperature. After the curing period, the cylindrical specimens were twisted off using a supporting table and recording torque spanner coupled through a universal joint. The failing load for each specimen was recorded, together with the site of failure and an estimate of the percentage area of each type of failure. This was obtained by a careful examination of both the panel and the cylindrical specimen. Tests were carried out in quadruplicate.

To carry out the adhesion test, the panels were removed from the exposure racks and placed horizontally on a table adjacent to the racks. Where surface water was present, it was removed from the panel surface by dabbing with a paper tissue, and after abrading the surface, four cylinders were bonded to the panel. On completion of the test, the damaged areas were made good with a high quality quick drying primer and the panels replaced in the exposure racks. Except where stated, the panels were never brought indoors. The results obtained therefore represent, as nearly as possible, the actual adhesion of the paint system under the prevailing ambient conditions. In general, the determinations were completed within 2hr of removing the panels from the exposure racks.

Results

During the course of the four-year investigation, approximately 136 separate adhesion determinations were carried out on each of the 22 substrate/paint system combinations, making a good total of 3,000 values and sites of failure. It is obvious that the data accumulated are far too bulky to record fully in this paper and for this reason only selected data are presented in detail, although the variation in adhesion for all systems is shown graphically in Figs. 1 to 10. Only those values which represent some component of adhesion failure from the substrate or of intercoat adhesion have been included in the curves.

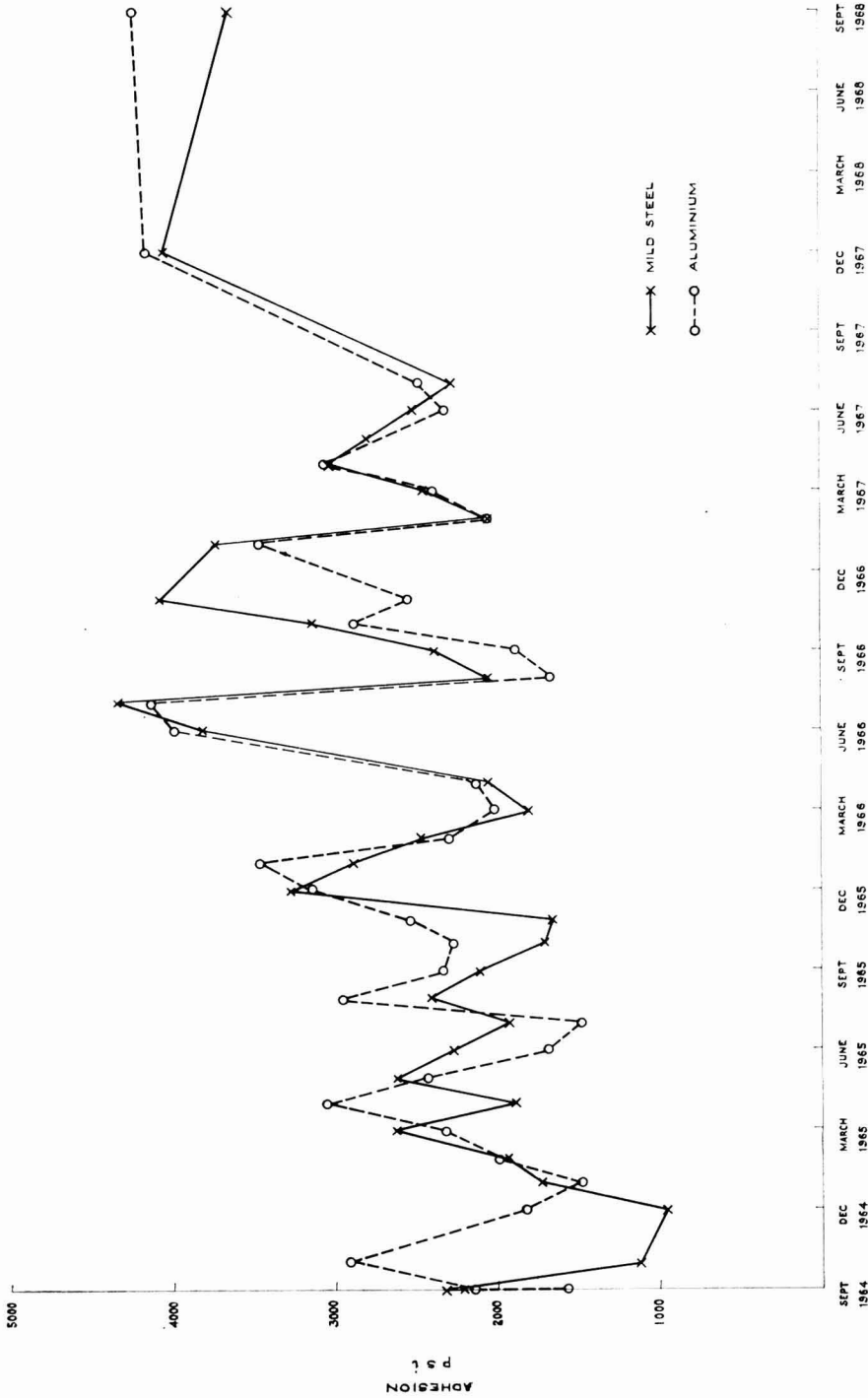


Fig. 1. Variation in adhesion on natural weathering. System 1: etch primer/chlorinated rubber

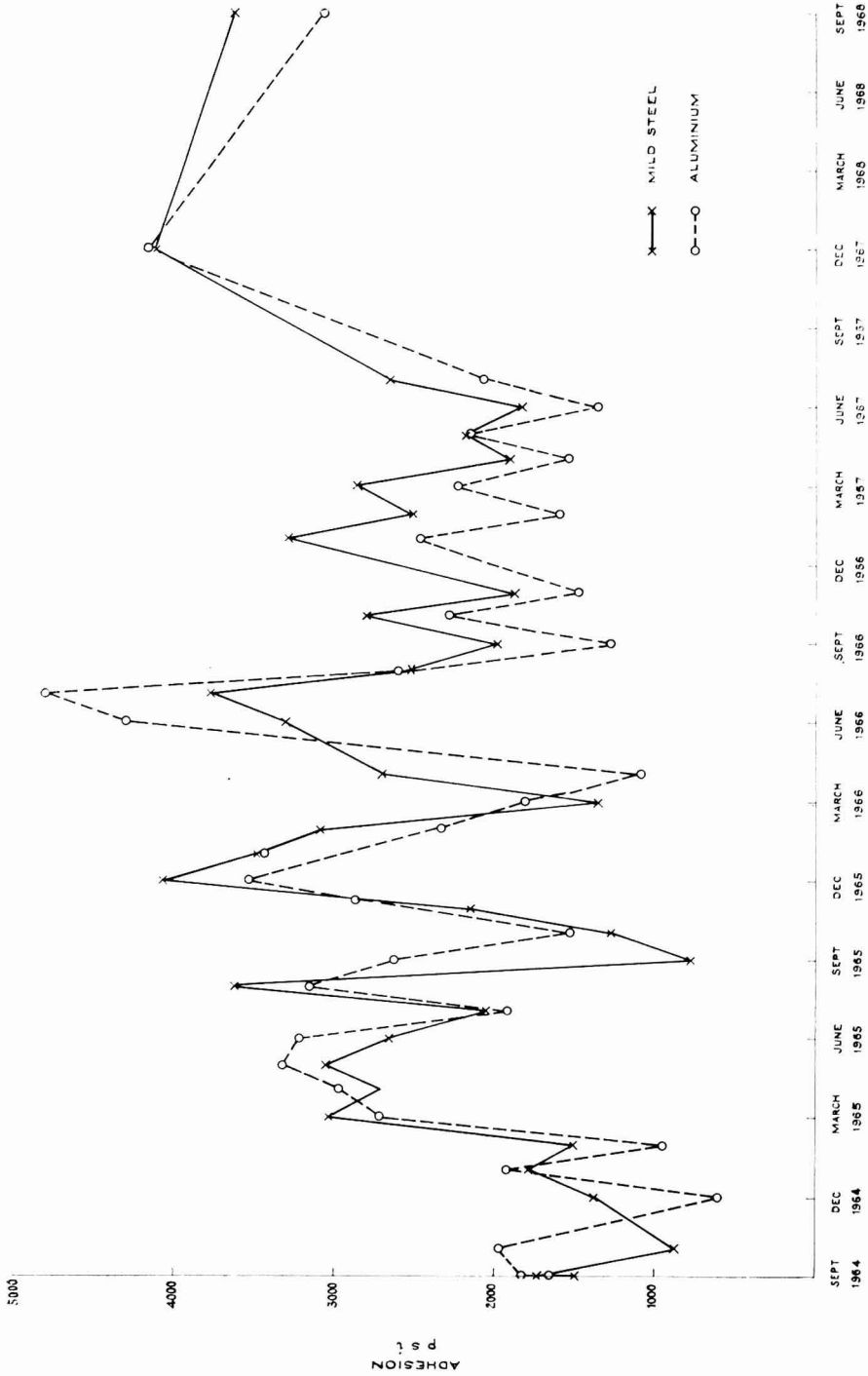


Fig. 2. Variation in adhesion on natural weathering. System 2: oleoresinous primer/alkyd undercoat and finish

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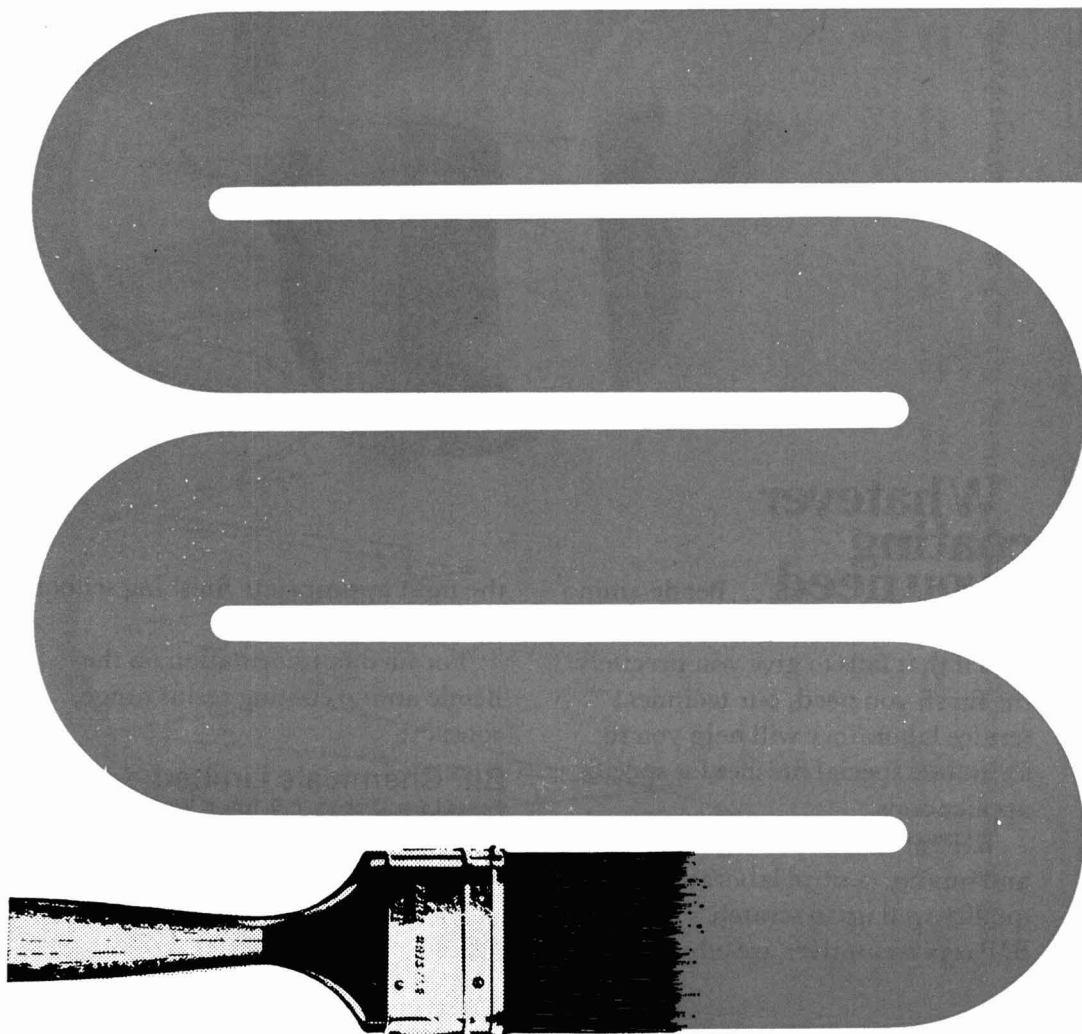
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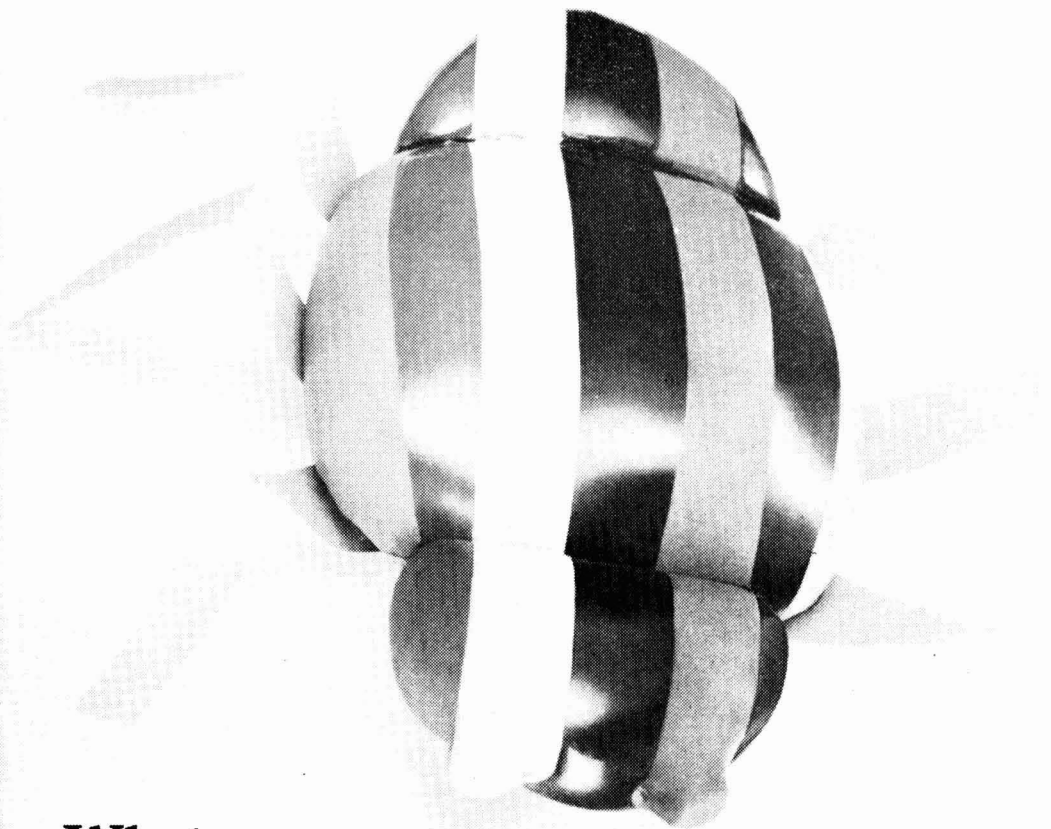
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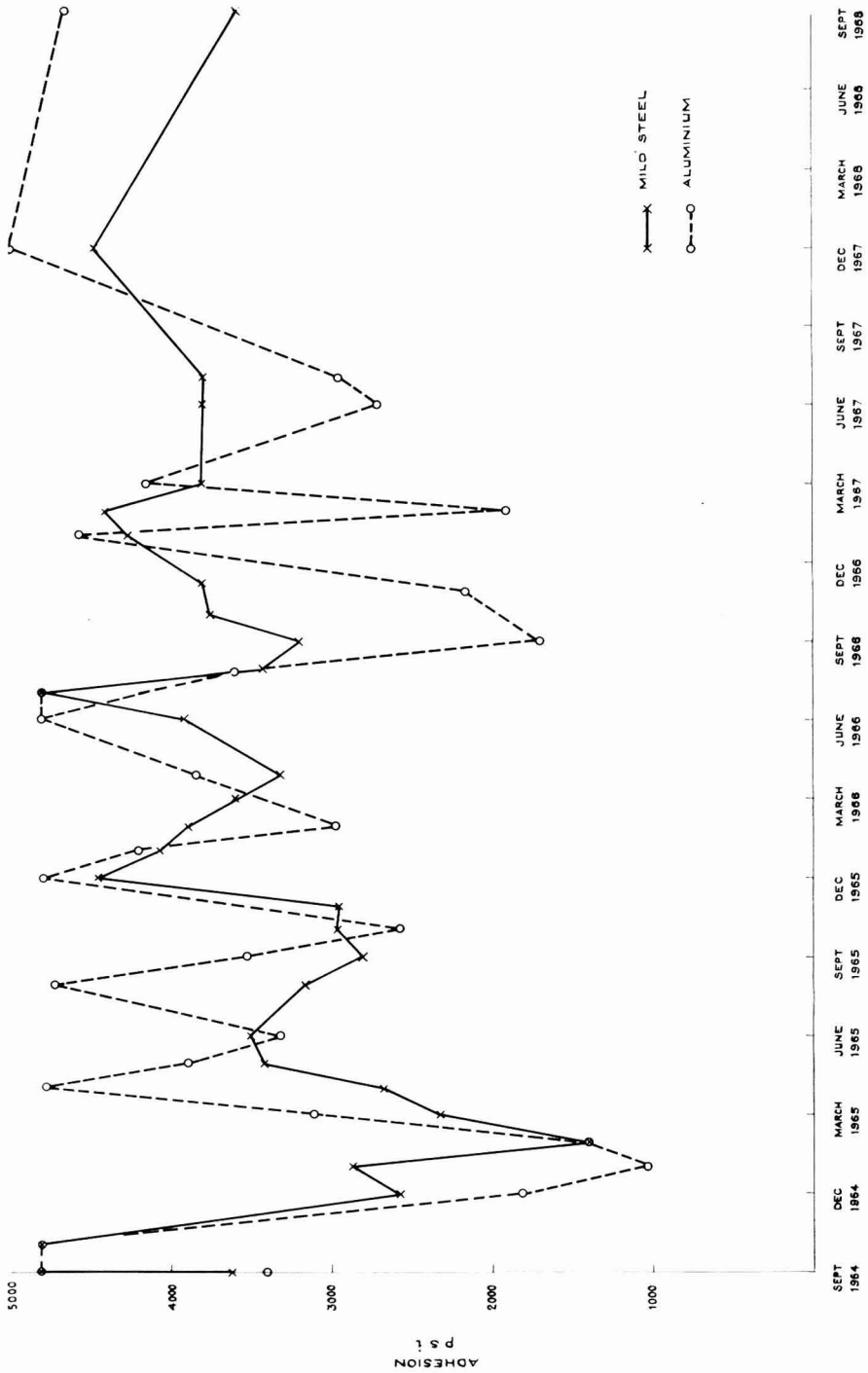


Fig. 3. Variation in adhesion on natural weathering. System 3: styrenated epoxide ester primer, undercoat and finish

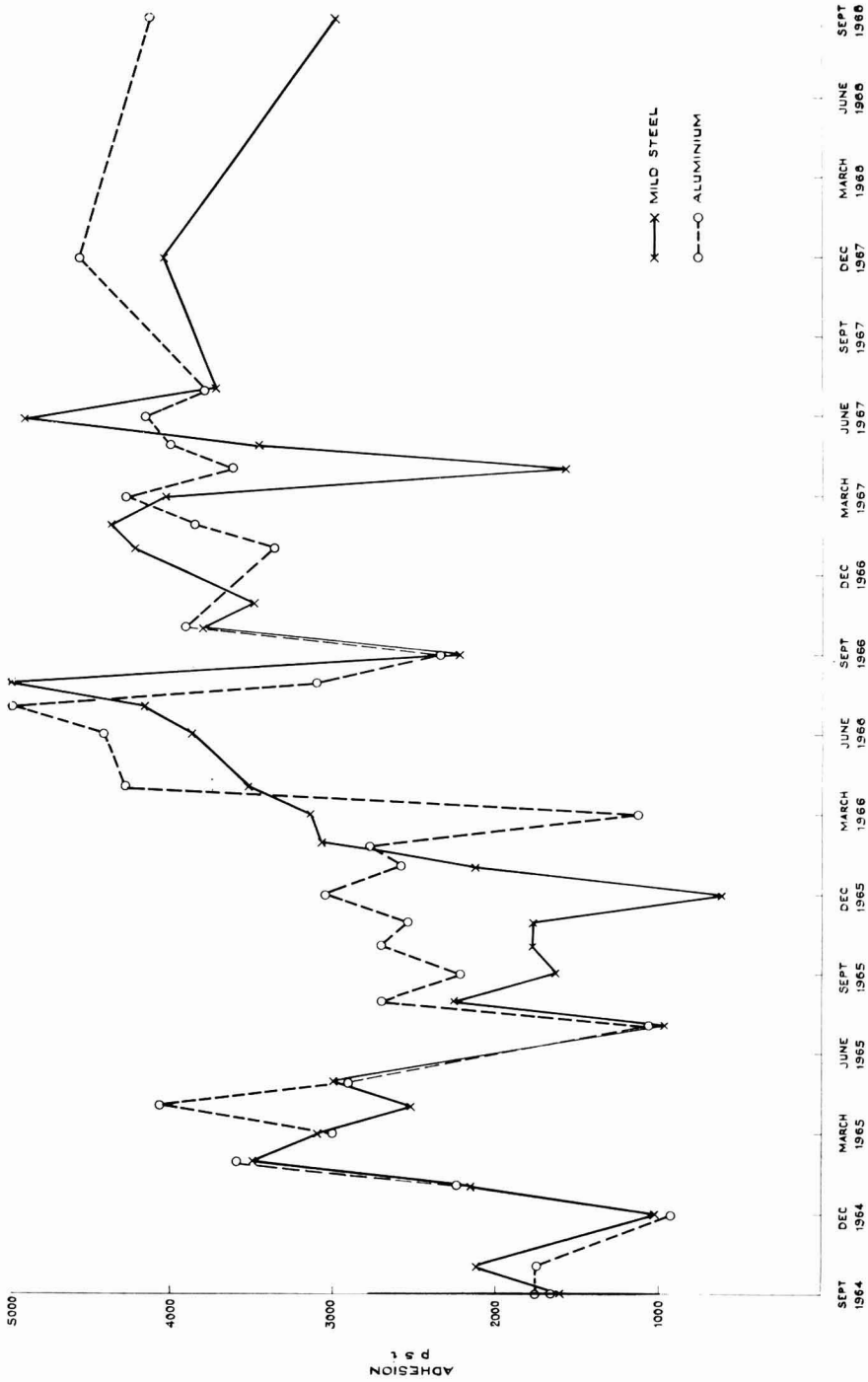


Fig. 4. Variation in adhesion on natural weathering. System 4: polyamide epoxide primer/adduct epoxide finish

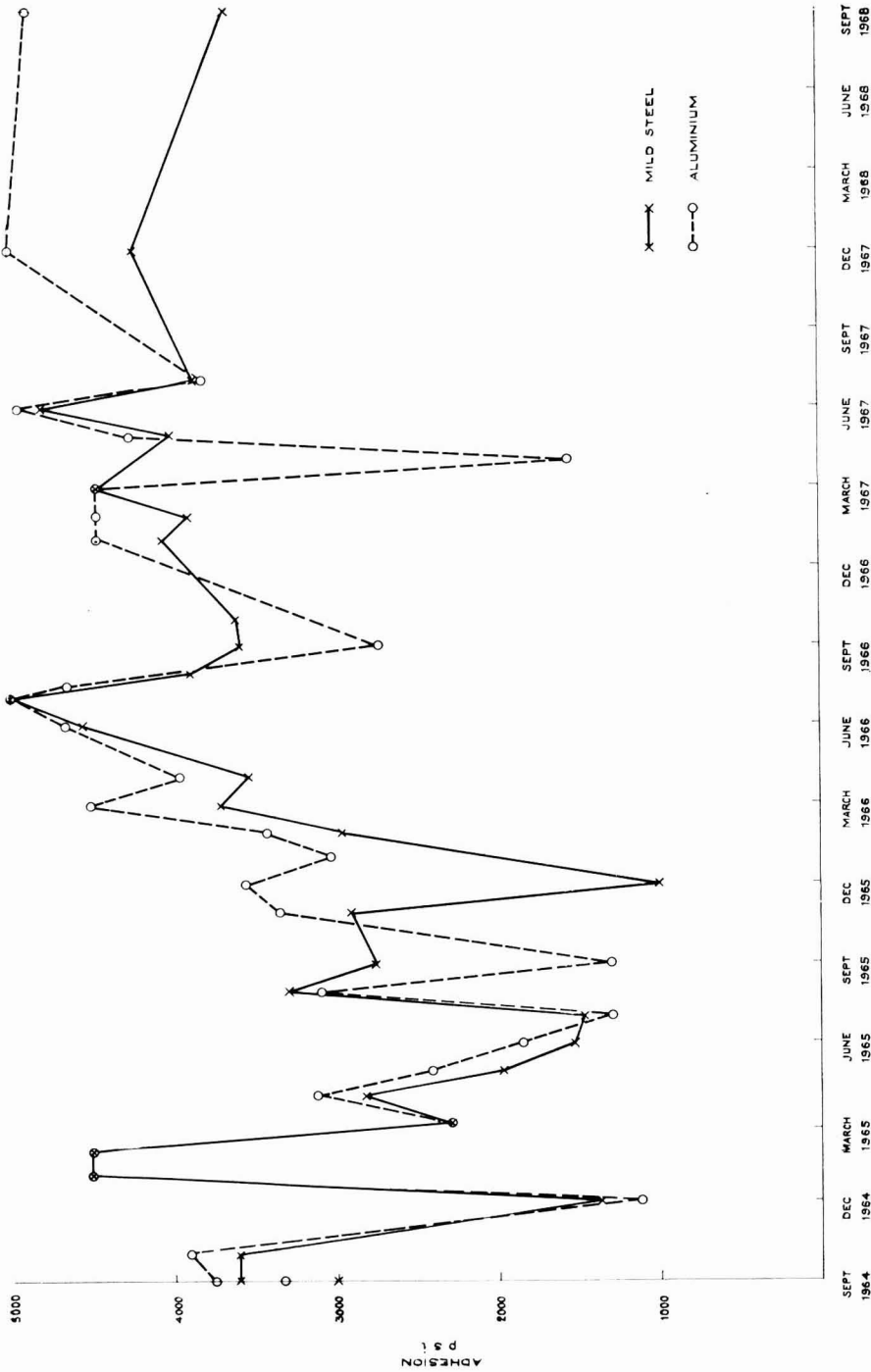


Fig. 5. Variation in adhesion on natural weathering. System 5: polyamide epoxide primer and finish

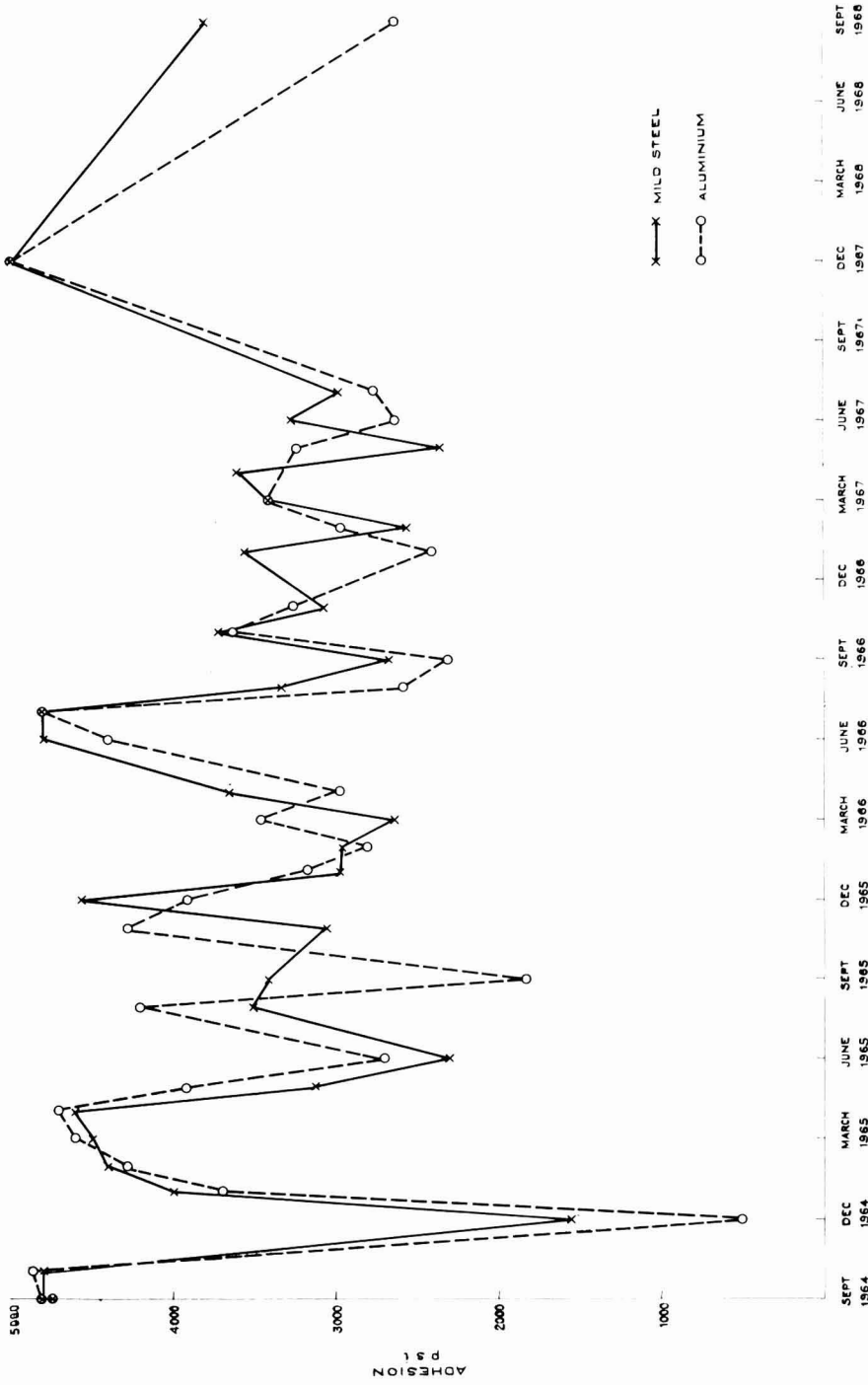


Fig. 6. Variation in adhesion on natural weathering. System 6: polyamide epoxide primer/aliphatic polyurethane finish

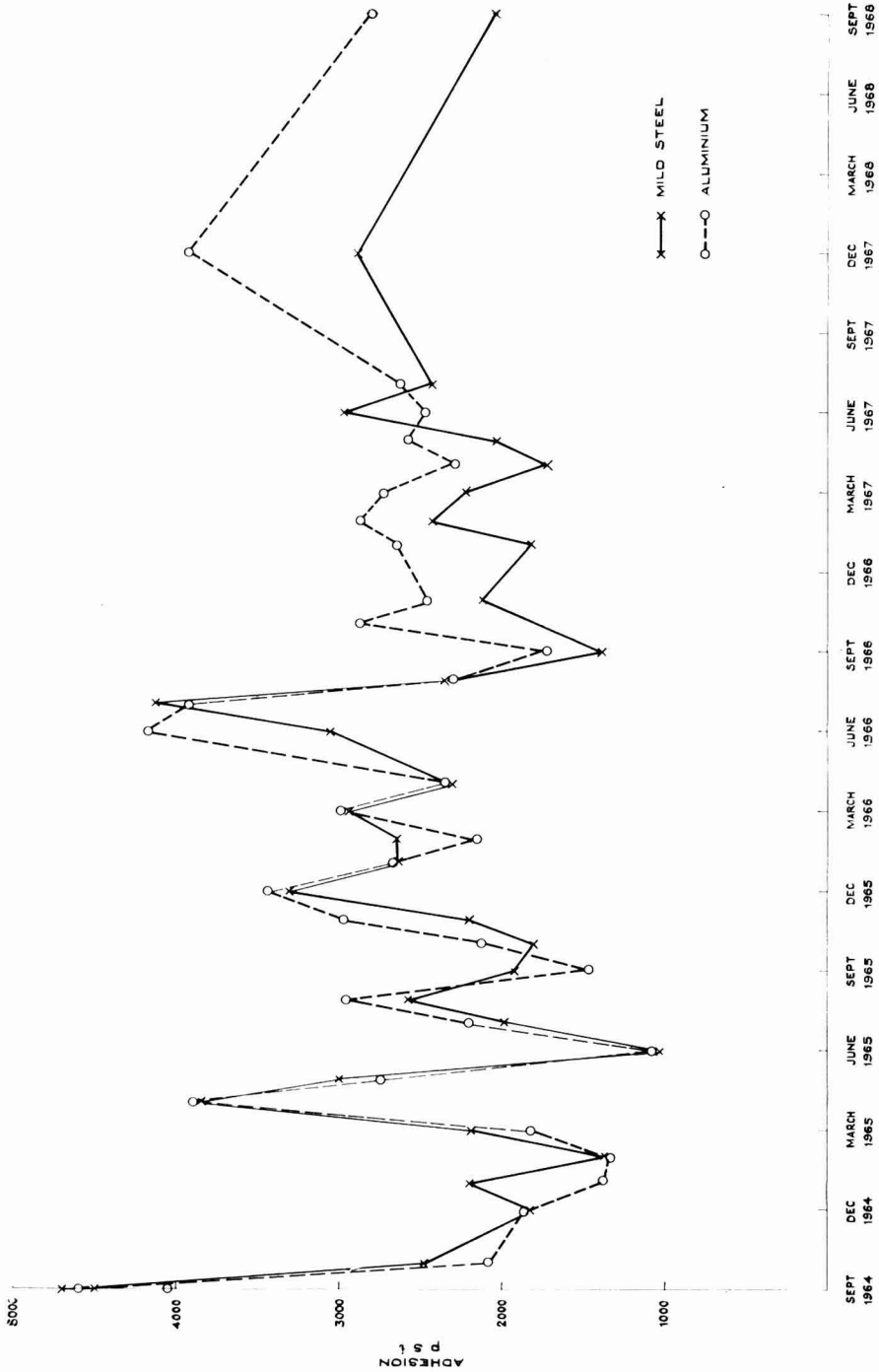


Fig. 7. Variation in adhesion on natural weathering. System 7: polyamide epoxide primer/aromatic polyurethane finish

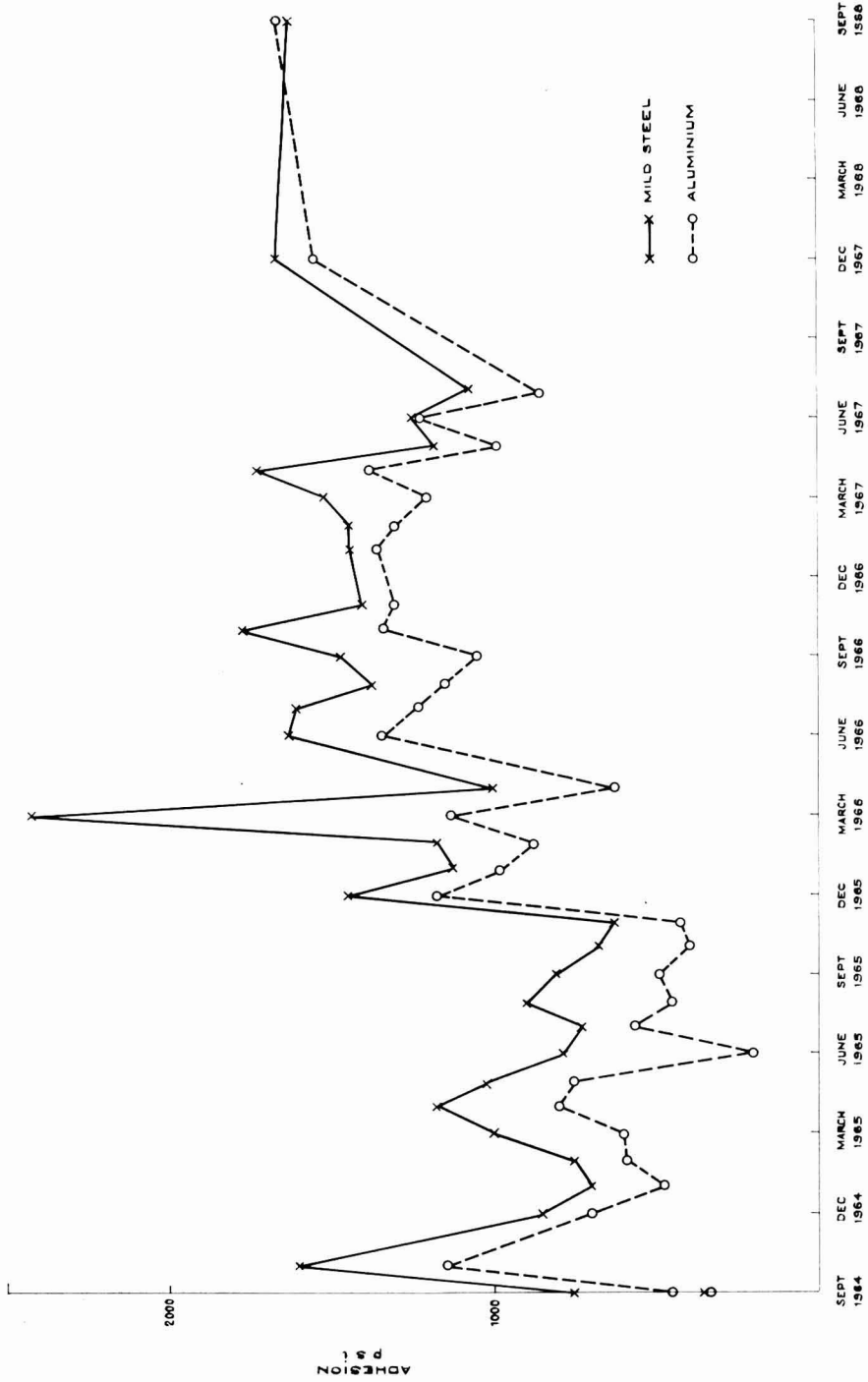


Fig. 8. Variation in adhesion on natural weathering. System 8: zinc rich primer/chlorinated rubber undercoat and finish

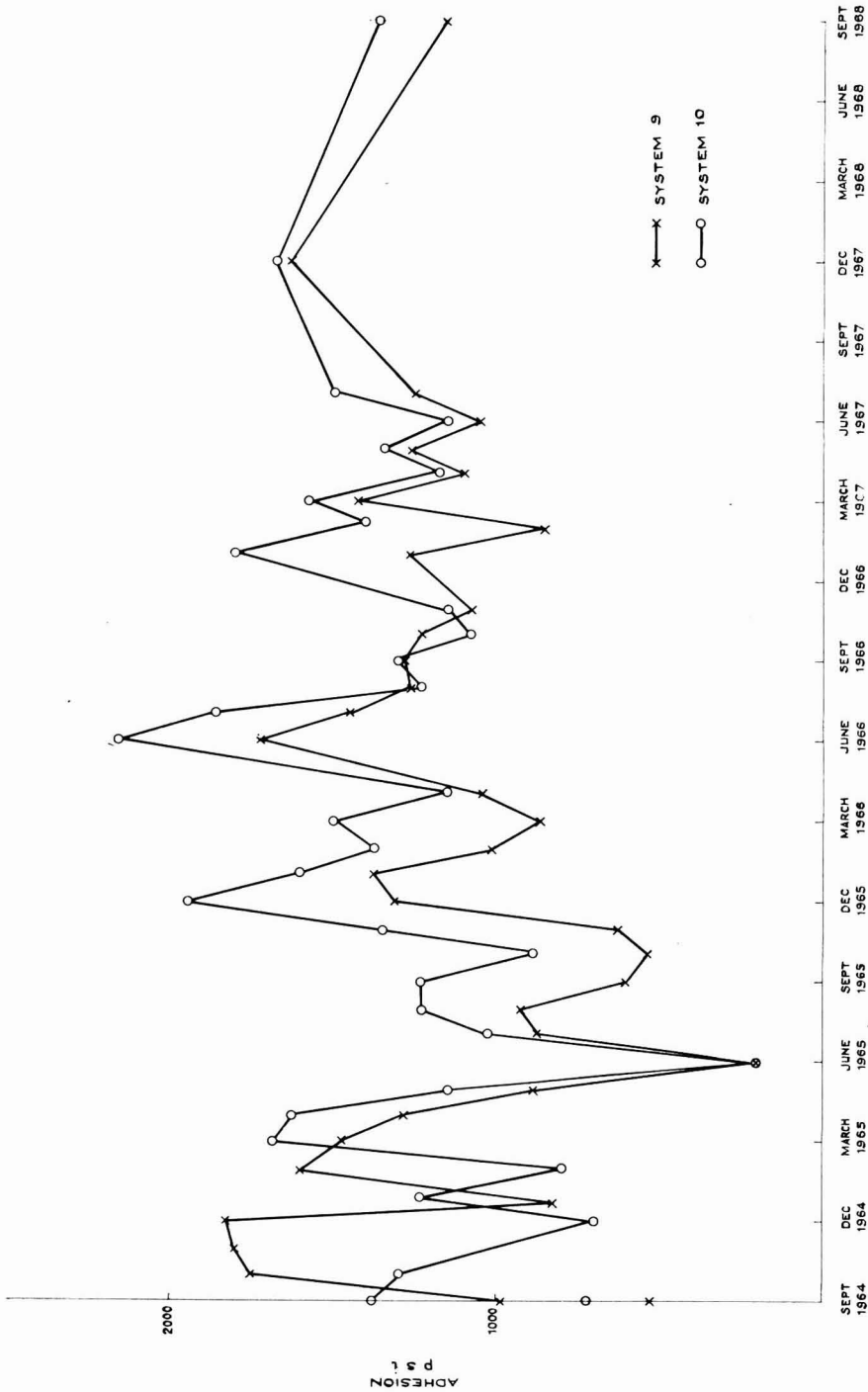


Fig. 9. Variation in adhesion on natural weathering. System 9: red and white lead primer/alkyd undercoat and finish. System 10: red and white lead primer/styrenated epoxide ester undercoat and finish

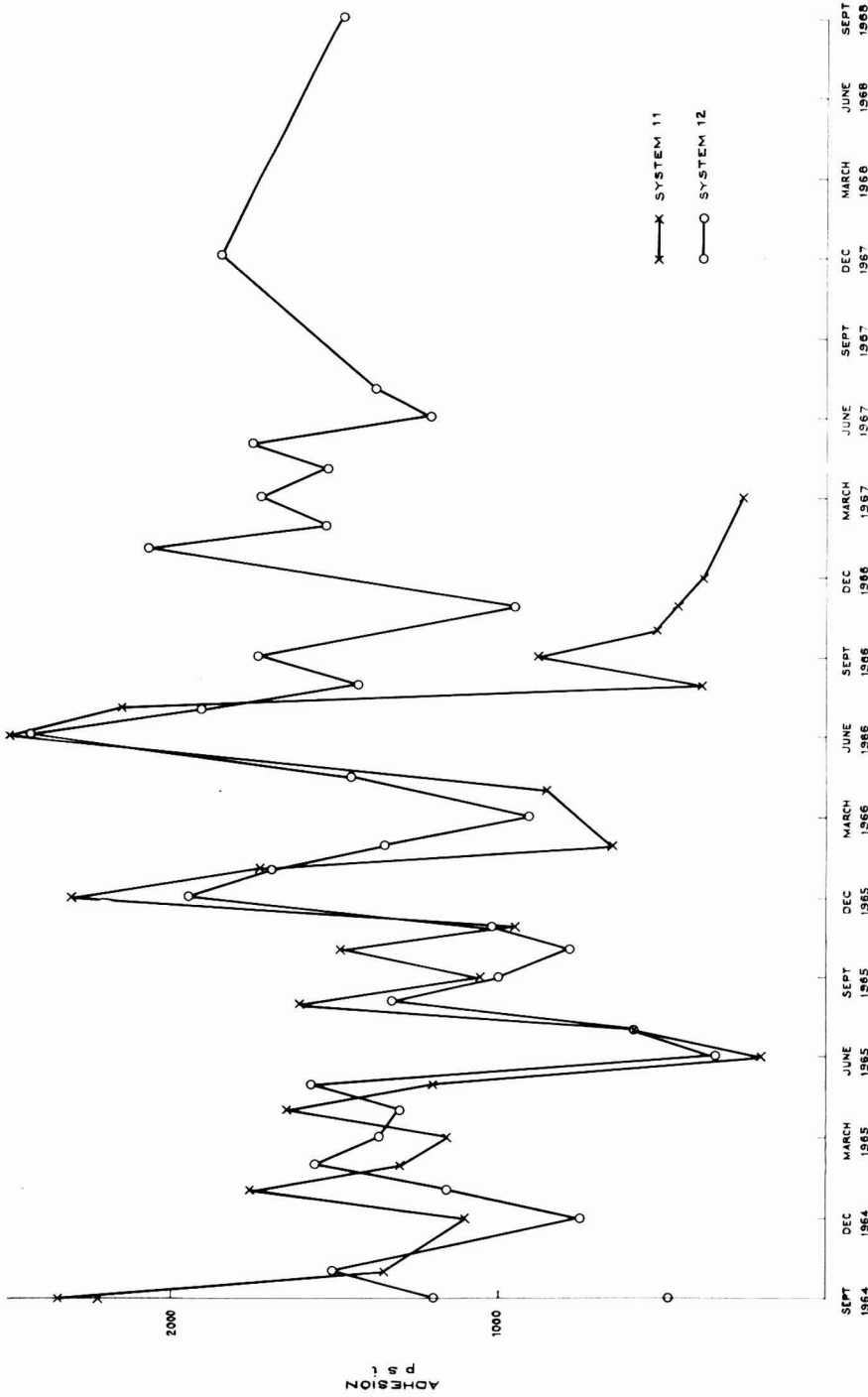



Fig. 10. Variation in adhesion on natural weathering. System 11: linseed urethane oil. System 12: red and white lead primer/proprietary undercoat and finish



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Reference to Table 1 will show the effect of natural weathering on the adhesion of the paint systems: the initial values quoted are for determinations made after panels had been conditioned for three days at room temperature and humidity, and the later results therefore tend to show changes in the intrinsic strength of the systems. It is apparent from the initial results and those after 36 months that only two paint systems were fully cured before exposure, and a drying period of 14 days before exposure is insufficient to achieve complete cure.

The two polyurethane systems, Systems 6 and 7, did not show an increase in adhesion on weathering; the remaining systems showed a considerable increase. The greatest increase in adhesion occurred with the chlorinated rubber systems, Systems 1 and 8, and the alkyd system, System 2. Almost all the systems showed a weakness in adhesion, in that failure occurred from the substrate or, in the case of System 1, from the etch primer. This intercoat failure observed in the original determination persisted throughout the exposure period, and most of the monthly tests showed failure of this type, although the actual values varied considerably.

It would be easy, therefore, to say that all the paint systems showed an improvement in adhesion on natural weathering, and in the short term this is no doubt true, but this is by no means the whole story. If the values for the test at 26, 38 and 48 months are compared, a somewhat different picture emerges. Systems 1 and 8 were the only coating systems to maintain their adhesion on both substrates, and there was no indication of failure from the metal with System 1, although System 8 failed consistently at the metal surface.

Systems 3, 4, and 5 showed no loss of adhesion on aluminium but did show a loss on mild steel, while Systems 2, 6 and 7 showed a loss of adhesion on both substrates. The coatings on wood, Systems 9, 10, 11 and 12 also showed a considerable loss. The overall picture then, is of a gradual fall in the adhesion of most systems on one or both metallic substrates, but only one system, System 11, failed by complete loss of adhesion during the course of the exposure programme.

Table 2 shows the maximum and minimum breaking loads recorded for each system during the four years exposure. The values recorded are for determinations carried out under the actual exposure conditions, and higher values obtained when the panels were allowed to dry out have not been included. The differences between the maximum and minimum values for each system are large, and represent a loss in strength of between 65 and 92 per cent.

It is not possible to calculate the actual change in adhesion of all systems, as several of the sites of failure were cohesive. However, where the failure occurred from the metal, it is possible to give a minimum value for the percentage change.

Tab.
Effect of natural weathering @

Paint system	Substrate	Initial adhesion psi \pm S.D.	Site of failure	Adhesion 26 months psi \pm S.D.	Site of failure
1	Aluminium	1570 \pm 162	100% adhesion from etch primer	4200 \pm 219	100% cohesion of finish
1	Mild steel	2200 \pm 139	100% adhesion from etch primer	4350 \pm 372	10% adhesion from etch primer 90% cohesion of finish
2	Aluminium	1500 \pm 211	20-60% adhesion from metal 40-80% cohesion of primer	4690 \pm 411	100% adhesion from metal
2	Mild steel	1820 \pm 155	60% adhesion from metal 40% cohesion of primer	3800 \pm 262	50-100% adhesion from metal 0-50% cohesion of primer
3	Aluminium	3400 \pm 271	40-60% adhesion from primer 40-60% cohesion of undercoat	4400 \pm 316	10-20% adhesion from metal 80-90% cohesion of finish
3	Mild steel	3620 \pm 317	50% adhesion from primer 50% cohesion of undercoat	4600 \pm 285	20-40% adhesion from metal 60-80% cohesion of undercoat
4	Aluminium	1660 \pm 118	100% adhesion from metal	4400 \pm 301	30-100% adhesion from metal
4	Mild steel	1640 \pm 92	100% adhesion from metal	4800 \pm	No failure
5	Aluminium	3340 \pm 230	100% adhesion from metal	4800 \pm 368	100% cohesion of finish
5	Mild steel	3000 \pm 147	100% adhesion from metal	4800 \pm 277	100% cohesion of finish
6	Aluminium	4800 \pm	No failure	4800 \pm	No failure
6	Mild steel	4800 \pm	No failure	4800 \pm	No failure
7	Aluminium	4050 \pm 362	60% adhesion from metal 40% adhesion from primer	3600 \pm 271	100% adhesion from metal
7	Mild steel	4500 \pm 287	60% adhesion from metal 40% adhesion from primer	4000 \pm 312	100% adhesion from metal
8	Aluminium	290 \pm 17	100% adhesion from metal	1700 \pm 54	100% adhesion from metal
8	Mild steel	310 \pm 43	100% adhesion from metal	1600 \pm 63	100% adhesion from metal
9	Wood	530 \pm 91	100% adhesion from wood	1400 \pm 48	100% adhesion from wood
10	Wood	720 \pm 24	100% adhesion from wood	2200 \pm 51	100% adhesion from wood
11	Wood	2200 \pm 112	100% adhesion from wood	1600 \pm 42	100% adhesion from wood
12	Wood	460 \pm 29	100% adhesion from wood	1800 \pm 49	100% adhesion from wood

Tab.
Variation in adhesion over 4 years

Paint system	Substrate	Highest mean adhesion \pm S.D. psi
1. Etch primer/chlorinated rubber	Aluminium	4130 \pm 217
1. Etch primer/chlorinated rubber	Mild steel	4330 \pm 260
2. Oleoresinous primer/alkyd	Aluminium	4800 \pm
2. Oleoresinous primer/alkyd	Mild steel	4080 \pm 178
3. Styrenated epoxide ester primer/styrenated epoxide ester	Aluminium	4800 \pm
3. Styrenated epoxide ester primer/styrenated epoxide ester	Mild steel	4800 \pm
4. Polyamide/epoxide primer/adduct/epoxide	Aluminium	4800 \pm
4. Polyamide/epoxide primer/adduct/epoxide	Mild steel	4800 \pm
5. Polyamide/epoxide primer/polyamide/epoxide	Aluminium	4800 \pm
5. Polyamide/epoxide primer/polyamide/epoxide	Mild steel	4800 \pm
6. Polyamide/epoxide primer/aliphatic polyurethane	Aluminium	4800 \pm
6. Polyamide/epoxide primer/aliphatic polyurethane	Mild steel	4800 \pm
7. Polyamide/epoxide primer/aromatic polyurethane	Aluminium	4600 \pm 212
7. Polyamide/epoxide primer/aromatic polyurethane	Mild steel	4700 \pm 259
8. Zinc rich primer/chlorinated rubber	Aluminium	1390 \pm 136
8. Zinc rich primer/chlorinated rubber	Mild steel	3145 \pm 261
9. Red and white lead primer/alkyd	Wood	1600 \pm 96
10. Red and white primer/styrenated epoxide ester	Wood	2160 \pm 121
11. Linseed urethane oil	Wood	2580 \pm 65
12. Red and white lead/alkyd	Wood	2400 \pm 135

Adhesion of multicoat systems

Adhesion 38 months psi ± S.D.	Site of failure	Adhesion 48 months psi ± S.D.	Site of failure
4150 ± 363	70-100% adhesion from etch primer 0-30% cohesion of finish	4220 ± 318	10-50% adhesion from etch primer 20-90% cohesion of finish
4040 ± 259	100% adhesion from etch primer	3640 ± 217	80%-130% adhesion from etch primer
4180 ± 304	90% adhesion from metal 10% cohesion of primer	3060 ± 196	50-90% adhesion from metal 10-50% cohesion of primer
4130 ± 272	90-100% adhesion from metal 0-10% cohesion of primer	2800 ± 220	50% adhesion from metal 50% cohesion of primer
5860 ± 391	20-60% adhesion from metal 40-80% cohesion of undercoat	4460 ± 335	10-50% adhesion from metal 10-90% adhesion from primer
4730 ± 326	10-30% adhesion from metal 70-90% cohesion of finish	3570 ± 336	20-50% adhesion from metal 10-20% adhesion from primer
4550 ± 380	40% adhesion from metal 60% cohesion of finish	4120 ± 350	50-100% cohesive failure in finish
4040 ± 384	20% adhesion from metal 40% adhesion from primer 40% cohesion of finish	2980 ± 284	20-30% adhesion from primer 70-80% cohesive
5030 ±	0-30% adhesion from metal 70-100% cohesion of finish		Failure in finish
3240 ± 339	100% cohesion of finish	3660 ± 251	20-30% adhesion from metal 70-80% cohesion in finish
4570 ±	100% cohesion of finish	2640 ± 160	100% adhesion from metal
4520 ±	10-60% adhesion from metal 40-90% cohesion of finish	3800 ± 315	100% adhesion from metal
440 ± 245	100% adhesion from metal	2800 ± 179	100-120% adhesion from metal
390 ± 197	100% adhesion from metal	2020 ± 77	100-120% adhesion from metal
550 ± 112	100% adhesion from metal	1670 ± 145	40-100% adhesion from metal 0-60% cohesion of finish
570 ± 94	100% adhesion from metal	1630 ± 98	100% adhesion from metal
530 ± 108	100% adhesion from wood	1150 ± 130	50-80% adhesion from wood 20-50% cohesion in primer
580 ± 152	100% adhesion from wood Panel failed	1360 ± 98	60-100% adhesion from wood Panel failed
340 ± 133	100% adhesion from wood	1480 ± 107	40-90% adhesion from wood 10-40% cohesion of primer 0-20% adhesion from primer

For exposure 45° due South

Site of failure	Lowest mean adhesion ± S.D. psi	Site of failure
100% adhesion from the etch primer	1460 ± 138	100% adhesion from the etch primer
100% Cohesional failure in finish	950 ± 103	100% adhesion from the etch primer
failure	870 ± 115	100% adhesion from metal
% adhesion from metal	600 ± 99	30% adhesion from metal
% cohesive failure in primer		70% cohesive failure in finish
failure	1000 ± 157	60% adhesion from metal
failure		40% cohesive failure in finish
failure	1400 ± 118	100% adhesion from primer
failure	930 ± 133	100% adhesion from metal
failure	970 ± 136	100% cohesive failure in general
failure	1030 ± 85	100% cohesive failure in finish
failure	1000 ± 87	100% adhesion from metal
failure	500 ± 132	100% adhesion from primer
failure	1550 ± 150	100% adhesion from metal
% adhesion from metal	1070 ± 137	100% adhesion from metal
% cohesive failure in undercoat		
% adhesion from metal	1020 ± 75	100% adhesion from metal
% cohesive failure in undercoat		
% adhesion from metal	200 ± 29	100% adhesion from metal
% adhesion from metal	640 ± 83	100% adhesion from metal
% adhesion from wood	200 ± 66	100% adhesion from wood
% adhesion from wood	200 ± 47	100% adhesion from wood
% adhesion from wood	200 ± 35	100% adhesion from wood
% adhesion from wood	200 ± 54	100% adhesion from wood

Variation in adhesion

Reference to Figs. 1-10 will show the actual variation in adhesion over the course of the exposure period for each paint system.

System 1. Etch primer/chlorinated rubber undercoat and finish: It should be noted that all the values indicated on Fig. 1 are for intercoat adhesion between the etch primer and the chlorinated rubber undercoat, no adhesion failure from the metal occurred. It is perhaps for this reason that the difference between the mild steel and aluminium panels is small, although there are isolated instances where the values on the two metals diverged markedly. The curves demonstrate continuous change in adhesion over the period of exposure with well defined low points in December 1964, July 1965, March 1966, July 1966 and February 1967. There is a general tendency for the values to increase over the exposure period up to December 1966, followed by a slow decrease.

System 2. Oleoresinous primer/alkyd undercoat and finish: The values indicated on Fig. 2 are for adhesion to the metal in every case. The fluctuation in the values is considerable and in general the curves for mild steel and aluminium are very similar, although there are some small points of divergence. As in the case of System 1, there are well defined low points in December 1964, September 1965, March 1966, September 1966 and June 1967. There appears to be a tendency for the values to increase over the exposure period up to mid-1966 and then to decline slowly.

System 3. Styrenated epoxide ester primer/styrenated epoxide ester undercoat and finish: Reference to Fig. 3 will show that the curves indicate a considerable variation in adhesion, but at a generally higher level than those of the previous two systems. In general the adhesion to aluminium is higher than to mild steel, but the loss of adhesion tends to be greater on aluminium. Again there are well defined low points in January 1965, September 1966 and February 1967.

System 4. Polyamide epoxide primer/adduct epoxide finish: System 4 also showed a considerable variation in adhesion, ranging between 400 and 5,000 psi with a tendency for the adhesion on aluminium to be higher than that to mild steel. There are well defined low points in December 1964, July 1965, September 1966 and April 1967.

System 5. Polyamide epoxide primer/polyamide epoxide finish: System 5 showed a very similar pattern to that of System 4 with only one major point of divergence, in March 1966 when System 5 showed no loss of adhesion whereas System 4 showed a considerable loss. This similarity in behaviour is perhaps hardly surprising in view of the similarity of the two systems, which have a mutual primer. There are well defined low points in December 1964, July 1965 and April 1967.

System 6. Polyamide epoxide primer/aliphatic polyurethane finish: Although Fig. 6 shows curves which are very similar in general outline to those in Figs. 4 and 5, there are several points of divergence. In general the curves show a higher adhesion value over the period of exposure, with fewer steep inflections, indicating a more uniform level of adhesion. There are only three consistent low points, in December 1964, June 1965 and September 1966.

System 7. Polyamide epoxide primer/aromatic polyurethane finish: System 7 showed a marked variation in adhesion over the exposure period at a rather lower level than the aliphatic polyurethane System 6 which was on the same

primer. There are three well defined low points, in February 1965, June 1965 and September 1966.

System 8. Zinc rich primer/chlorinated rubber undercoat and finish: Reference to Fig. 8 will show that System 8 is perhaps unique in that it is the only system that consistently shows a higher adhesion on mild steel than aluminium, although this may not be surprising in view of the fact that zinc rich primers are not normally applied to aluminium. Once again the curves present a picture of a system that fluctuates wildly in adhesion over the period of exposure, but there is no indication of a progressive loss of adhesion with time. There are three well defined low points in January 1965, June 1965, and April 1966.

System 9. Red and white lead primer/alkyd undercoat and finish: Fig. 9 shows that the variation in adhesion of System 9 to wood on natural weathering is considerable, and fluctuates rapidly and reversibly within wide limits. There are several low points, the most pronounced of which are in June 1965, October 1965, March 1966 and February 1967.

System 10. Red and white lead primer/styrenated epoxy ester undercoat and finish: The variation in adhesion of System 10 is shown in Fig. 9, from which it can be seen that once again there is considerable variation in the adhesion, with three low points in December 1964, February 1965 and June, 1965.

System 11. Linseed urethane oil: System 11 was the only system which failed in adhesion during the course of the exposure programme, and no tests were possible after March 1967, a period of 30 months. The curve clearly shows this loss of adhesion during the last 3 months of exposure. This system also showed considerable variation in adhesion with low points in June 1965, February 1966 and August 1966.

System 12. Red and white lead primer/proprietary alkyd undercoat and finish: The adhesion curve for System 12 was almost identical with that for Systems 9 and 10, having the same low points.

Sites of failure

It is obvious that in the multilayer assembly panel/paint system/adhesive/specimen, many potential sites of failure exist, ranging from adhesion to the metal to cohesive failures within the paint layers. The sites considered the most important were those involving loss of adhesion either from the substrate or intercoat adhesion failures. During the course of the investigation every possible site of failure was recorded, either singly or in combination, although adhesion failures predominated.

Several typical failures are illustrated in Figs. 11-16. Fig. 11 illustrates the almost complete adhesion failure of System 8, zinc rich/chlorinated rubber, from the mild steel panel, note the jagged edge to the paint film indicating brittleness, and the tendency to lift. Cohesion failure of the red lead/white lead primer, System 10, on wood is shown in Fig. 12. Fig. 13 shows mixed adhesion failure from the metal and cohesive failure of the primer on the aluminium panel of System 7. A more complex failure occurring at different points within the paint system is shown in Fig. 14. In this case, the styrenated epoxide ester, System 3, on aluminium shows failure from the metal, cohesive failure of the undercoat, and cohesive failure in the surface layer of the finish.

A simpler failure pattern, although particularly interesting, is shown in Fig. 15, where the chlorinated rubber paint of System 1 has failed in adhesion

from the etch primer. This is a very good example of intercoat failure. A similar, though more complex, failure is shown in Fig. 16, which is of the styrenated epoxide ester, System 3, on aluminium, and is taken from the same panel as Fig. 14. The sites of failure here include intercoat adhesion between primer and undercoat, cohesive failure of the undercoat, and cohesive failure of the finish.

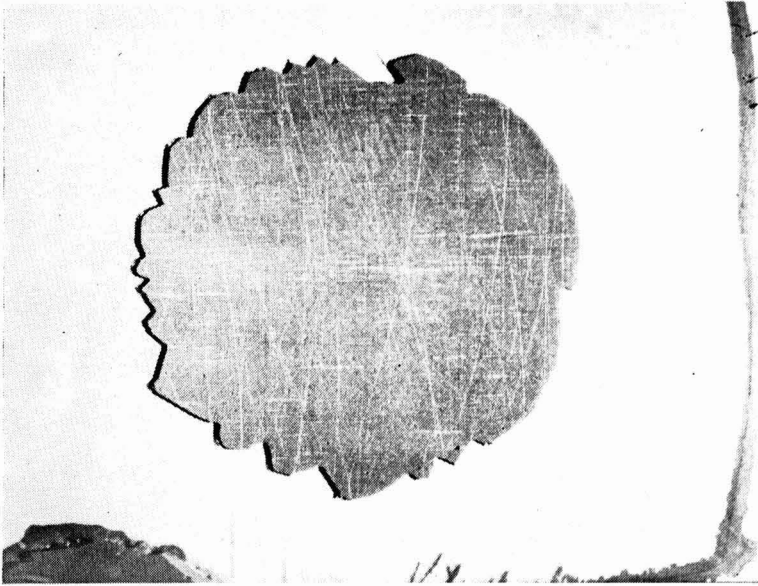


Fig. 11. Adhesion failure from the metal of System 8, zinc rich primer/chlorinated rubber, on mild steel. Mag. $\times 4$

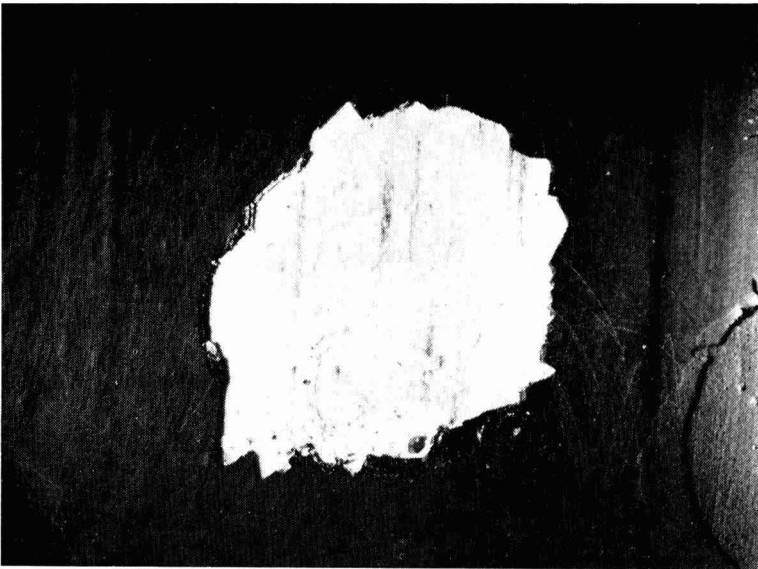


Fig. 12. Cohesional failure of System 10, red and white lead primer/styrenated epoxide ester, on wood. Mag. $\times 4$

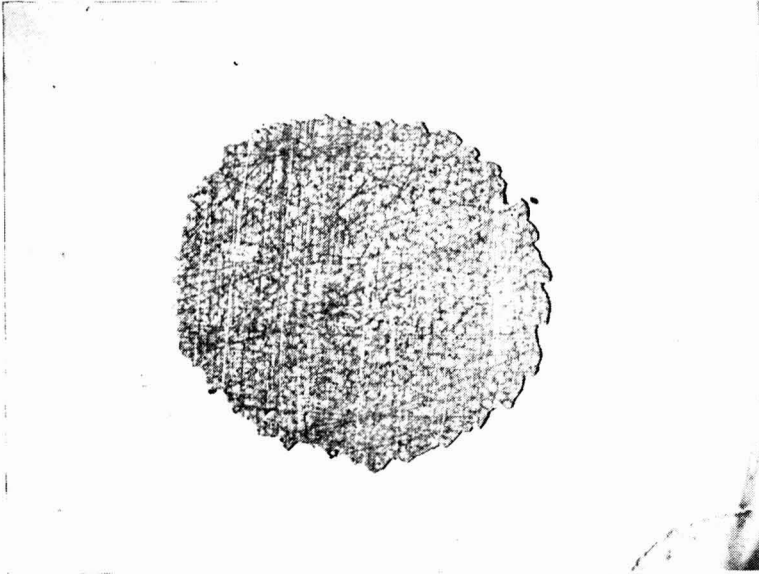


Fig. 13. Mixed adhesion/cohesion failure of System 7, polyamide primer/aromatic polyurethane, on aluminium. Mag. $\times 4$

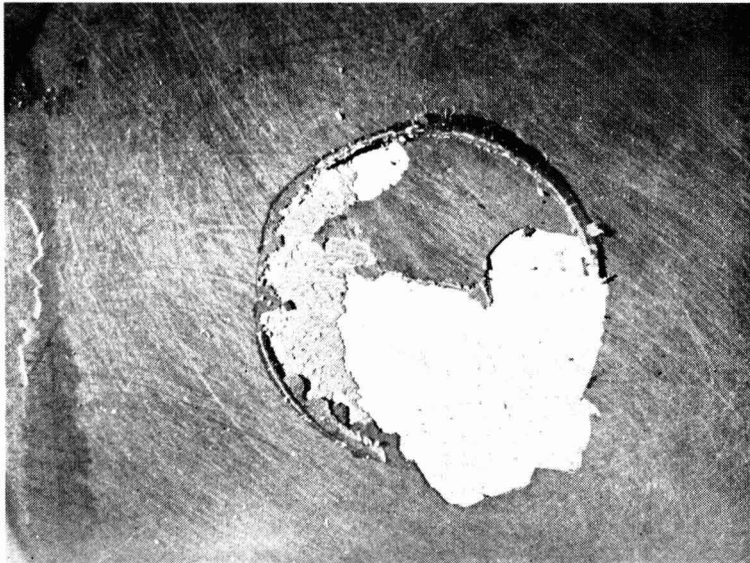


Fig. 14. Complex failure of System 3, styrenated epoxide ester, on aluminium showing intercoat adhesion and cohesive failure. Mag. $\times 4$



Fig. 15. Internal adhesion failure of System 1, etch primer/chlorinated rubber, on mild steel. Mag. $\times 4$

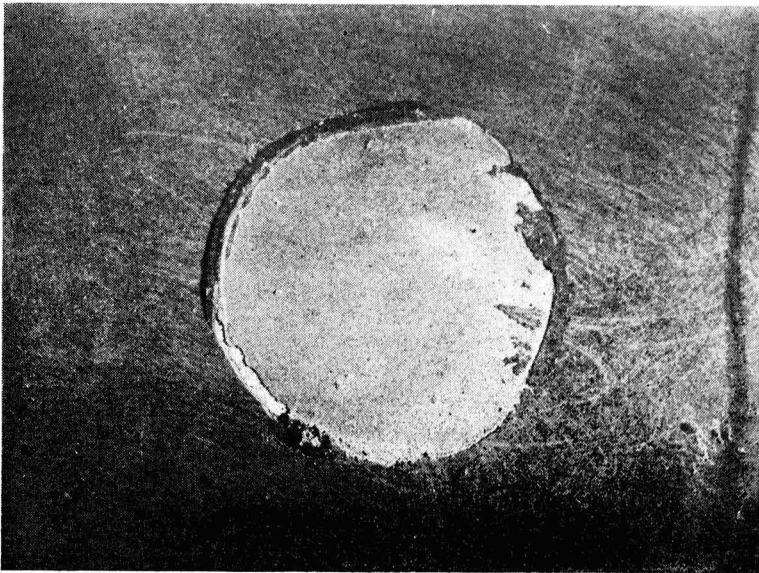


Fig. 16. Complex failure of System 3, styrenated epoxide ester, on aluminium, showing multiple points of failure. Mag. $\times 4$

Correlation of adhesion with external conditions

A limited amount of meteorological data was collected during the course of the programme, including precipitation, relative humidity, air temperature, and daily maximum and minimum temperature. The information relating to the day of the test was compared with the actual adhesion values recorded on that day. From Figs. 1-10 it can be seen that there were approximately 18 well defined low points in the adhesion curves. A well defined low point is defined as one at which the paint system showed a marked loss of adhesion on both substrates. The meteorological data for each of these days are shown in Table 3.

Table 3
Meteorological data for low point days

Date	Number of systems showing low point	Precipitation in 24hr	Relative humidity %	Air temperature °C
16.12.64	7 (1, 2, 4, 5, 6, 10, 12)	0.02	99	-5, -2
15. 1.65	2 (3, 8)	0.15	81-98	3-4
17. 2.65	3 (7, 10, 12)	0.02	89-95	3-4
10. 6.65	6 (6, 7, 9, 10, 11, 12)	0.29	64-95	12-17
15. 7.65	3 (1, 4, 5)	0.10	81-93	12-17
15. 9.65	1 (2)	Nil	83-93	16-17
19.10.65	2 (8, 9)	Nil	98-99	6-10
21.12.65	1 (4)	Nil	94-97	-1-2
27. 2.66	1 (11)	Nil	97-100	5-6
28. 3.66	4 (1, 2, 3, 9)	0.19	85-100	6-7
27. 4.66	1 (8)	0.04	76-98	10-12
6. 7.66	1 (1)	Nil	66-75	18-19
1. 8.66	1 (11)	0.46	50-82	9-12
5. 9.66	5 (2, 3, 4, 6, 7)	0.32	75-90	17-18
12. 2.67	3 (1, 9, 12)	0.02	80-95	4-5
18. 4.67	2 (4, 5)	Nil	60-80	12-14
12. 6.67	2 (2, 3)	0.01	55-95	17-18

From Table 3 it can be seen that, on every day on which the measured adhesion was low on several systems, precipitation had occurred. In all other cases the relative humidity was high. Thus, there would appear to be good correlation between the moisture content of the air or paint system and the measured adhesion. This however, was not always the case, as there were several occasions during the programme when precipitation was recorded during the 24hr but the measured adhesion was high. However, this may be explained in part by the method of measuring precipitation which records only the amount of rain falling within 24hr and not the time at which the rainfall occurred.

Final observations on panels after four years natural weathering

The final observations made on the panels after four years' exposure are shown in Table 4, from which it can be seen that only System 11 showed complete failure by loss of adhesion, cracking and flaking, Systems 3 and 4 showed a tendency to fail by checking and cracking, but this was not reflected in the adhesion results. The cracking recorded on the isolated blisters on System 10 is shown in Fig. 17.

Table
Final observations on panels after

Paint system	Substrate	Appearance	Chalking	Checking
1. Etch primer/chlorinated rubber	Mild steel	3	0	5
1. Etch primer/chlorinated rubber	Aluminium	3	0	5
2. Oleoresinous primer/alkyd	Mild steel	3	0	5
2. Oleoresinous primer/alkyd	Aluminium	3	0	5
3. Styrenated epoxide ester primer/undercoat and finish	Mild steel	3	0	4
3. Styrenated epoxide ester primer/undercoat and finish	Aluminium	2	0	4
4. Polyamide epoxide primer/adduct epoxide finish	Mild steel	1	0	2
4. Polyamide epoxide primer/adduct epoxide finish	Aluminium	1	0	3
5. Polyamide epoxide primer/polyamide epoxide finish	Mild steel	4	0	5
5. Polyamide epoxide primer/polyamide epoxide finish	Aluminium	4	0	5
6. Polyamide epoxide primer/aliphatic polyurethane finish	Mild steel	4	3	5
6. Polyamide epoxide primer/aliphatic polyurethane finish	Aluminium	4	3	5
7. Polyamide epoxide primer/aromatic polyurethane finish	Mild steel	3	0	5
7. Polyamide epoxide primer/aromatic polyurethane finish	Aluminium	3	0	5
8. Zinc rich/chlorinated rubber	Mild steel	4	0	5
8. Zinc rich/chlorinated rubber	Aluminium	4	0	5
9. Red and white lead primer/alkyd undercoat and finish	Wood	4	0	5
10. Red and white lead primer/styrenated epoxide undercoat and finish	Wood	3	0	5
11. Linseed urethane oil	Wood			
12. Red and white lead primer/proprietary alkyd undercoat and finish	Wood	4	0	5

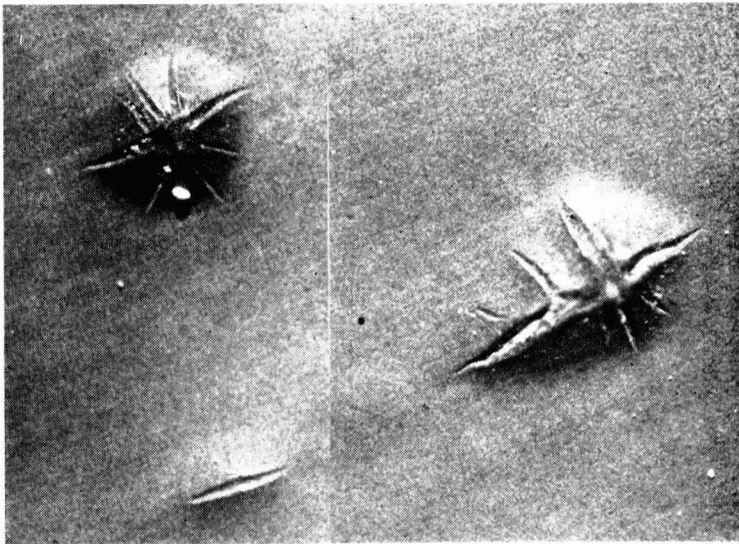


Fig. 17. Cracking of isolated blister caps on System 10, red and white lead primer/styrenated epoxide ester, on wood. Mag. $\times 30$

Discussion

It is apparent from the results and observations recorded that the adhesion of the systems tested, and by inference of many other conventional coatings, varied considerably during the period of exposure. Further, that the adhesion may fall to a small fraction of the original without major failure occurring, and this loss of adhesion may be recovered at a later date. The picture presented is of the property of adhesion to the substrate fluctuating rapidly and reversibly within very wide limits. All the coating systems tested showed this variation in adhesion on exposure, and many of them to the same extent. The least affected appeared to be the aliphatic polyurethane finish applied over a polyamide cured

4

four years' natural weathering

Cracking	Flaking	Coated	Corrosion stripped	Comments
5	5	ReO	ReO	Film in good condition but brittle
5	5	ReO	ReO	Film in good condition but brittle
5	5	ReO	ReO	Film in excellent condition
5	5	ReO	ReO	Film in excellent condition
5	5	ReO	ReO	Very pronounced colour change
5	5	ReO	ReO	Very pronounced colour change
3	5	ReO	ReO	Very poor appearance, cracked badly around repair points.
4	5	ReO	ReO	Poor appearance, cracked around the repair points
5	5	ReO	ReO	Badly yellowed but otherwise in excellent condition
5	5	ReO	ReO	Badly yellowed but otherwise in excellent condition
5	5	ReO	ReO	Film in good condition
5	5	ReO	ReO	Film in good condition
5	5	ReO	ReO	Scattered pin point craters to the primer, badly yellowed
5	5	ReO	ReO	Scattered pin point craters to the primer, badly yellowed
5	5	ReO	ReO	Film in excellent condition
5	5	ReO	ReO	Film in excellent condition
5	5	—	—	Film in excellent condition
5	5	—	—	Isolated small blisters showing cracking over blister cap.
Failed completely by checking, cracking and flaking				
5	5	—	—	Film in excellent condition

epoxide primer, although even in this case the measured adhesion changed rapidly within wide limits.

Although complete correlation cannot be claimed there is strong evidence that this variation in adhesion in the short term is directly relatable to the water content of the ambient air. This, of course, is not new; several authors have demonstrated that organic surface coatings lose adhesion under water-soaked conditions and the present author in his Roon Award paper has shown that adhesion may be lost under conditions of high humidity in the laboratory¹¹.

Experiments carried out within the laboratory with single coat or multicoat systems may not always be considered directly relatable to actual service exposure and are therefore bound to be accepted with reservations. The present results, however, show that, under conditions of natural weathering such as may be experienced by any paint system in the UK, the adhesion of these coatings is likely to be in a state of continual change, and this is in line with laboratory findings. The work also suggests that, under normal exposure conditions, typical surface coating systems are unlikely to fail by loss of adhesion, although some gradual loss of adhesion must be anticipated on ageing. It also suggests that this cyclic loss of adhesion may occur without allowing corrosion of the substrate to take place.

Acknowledgments

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Appendix

Formulation of non-specification paints

Red oxide/zinc chromate epoxide primer

	parts by wt
Red oxide	88
Zinc chromate	20
Asbestine	12
Epikote 1001 ¹	60
Methyl isobutyl ketone	30
Xylene	30
Versamid 115 ²	50
Methyl isobutyl ketone	18
Cellosolve	24
Toluene	8

White adduct epoxide finish

	parts by wt
Rutile titanium dioxide	200
Epikote 1001	200
Methyl isobutyl ketone	66
Cellosolve	33
Toluene	101
EDA 870 adduct ³	150
Cellosolve	120
Butyl alcohol	30
Toluene	75

White polyamide epoxide finish

	parts by wt
Rutile titanium dioxide	200
Epikote 1001	200
Methyl isobutyl ketone	100
Xylene	100
Versamid 115	120
Methyl isobutyl ketone	54
Cellosolve	72
Toluene	24

White aliphatic polyurethane finish

	parts by wt
Rutile titanium dioxide	300
Desmophen 650 ⁴	150
10% Solution $\frac{1}{2}$ second butyrate in methyl ethyl ketone	50
Methyl isobutyl ketone	114
Butyl acetate	29
Ethylglycol acetate	28
Toluene	28
Desmodur N 75% ⁴	183

White aromatic polyurethane finish

	parts by wt
Rutile titanium dioxide	200
Daltolac 1200 ⁵	200
10% Solution $\frac{1}{2}$ second butyrate in methyl ethyl ketone	40
Methyl isobutyl ketone	200
Cyclohexanone	50
Suprasec 4175 ⁵	226

1. Shell Chemicals.
2. Cray Valley Products.
3. Anchor Chemical Company
4. J. M. Steele & Co.
5. Imperial Chemical Industries.

Management by objectives in research and development*

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Summary

The value of management by objectives to the planning and conduct of R & D programmes is discussed and illustrated by examples.

Key words

Management

Gestion par objectifs dans les domaines de recherche et de développement

Résumé

On discute l'utilité de gestion par objectifs pour le planning et la conduite des programmes de recherche et de développement et l'on la démontre au moyens des exemples.

Geschäftsführung durch Zielsetzung für Forschung und Entwicklung

Zusammenfassung

Eine Diskussion anhand illustrierter Beispiele über den Wert der Geschäftsführung auf der Basis einer Zielsetzung für Planung und Durchführung von Forschungs- und Entwicklungsprogrammen.

Объективное управление в исследованиях и развитии

Резюме

Обсуждается значение объективного управления в планировании и проведении программ исследования и развития. Обсуждение иллюстрируется примерами.

Introduction

The shortness of human memory is a shelter behind which too many research and development managers hide. Scientists, brought up on the importance of measurement, are only too ready to divert attention from any attempt to measure their performance in terms of commercial or national profit related to effort input. Pursuit of knowledge *per se* is the all too frequent cry; also, "have not European scientists throughout the years proved their worth in new discoveries?" This is surely true but, when backs are against the wall, we should

*Presented to the London Section on 17 October 1968.

leave just the inspired few to this activity and divert the energetic many to profit-oriented pursuits. It follows that we should tell these energetic many what is wanted and measure their success. If Lady Luck really plays such a big part in the R & D process as serendipity believers (like pharmaceutical chemists) would have us believe, then, at the very least, we should try and identify the best gamblers in our ranks.

Here it is that management by objectives¹ can come to our aid. The concept is simple and this is its strength and, at the same time, its Achilles heel. It is said, "but this is only budgetary control dressed up in another name" and also, "but what's so new about that, we have always set clear objectives." And yet the author's colleagues to a man say they have yet to find a company where everyone has clear, unambiguous and verifiable objectives covering all their tasks and not just the financial aspects.

Management by objectives

Management by objectives is the name given to a way of managing or an attitude of mind with which one attempts to crystallise the key objectives of a company, a division, a subsidiary, a department, a section and an individual, and to build an integrated hierarchy of these objectives so that individual efforts are, like vectors in phase, all contributing to the corporate goals.

Certain functions in a business lend themselves to this approach more readily than others. They tend to be those functions where results are relatively easily measured and/or directly related to profit, e.g. production, marketing, finance. Other functions have only an indirect effect, or are separated from day to day profit by a time lag or some other transfer function of high inertia, e.g. personnel, research and development. Nevertheless, this does not mean that management by objectives is not applicable in the latter cases, but rather that it is more difficult and hence more challenging.

Applications

The application of management by objectives in research and development² can best be described by analysing it into its various phases as illustrated in Fig. 1.

Dominating all is the need for unit objectives. The days are past when any company can afford to maintain a R & D department as an act of faith or merely to "keep up with the Joneses." The present-day department must have goals that are a closely integrated part of the total company strategy. More and more companies have formally recognised Corporate Planning³ departments and it is their task to guide all concerned towards clear *corporate objectives*^{4,5,6}. The end-product of their work as far as R & D is concerned might be on the following lines.

New products

1. To develop two new products in the "X" line that will eventually replace "L" and "M" by 1974 and provide a minimum turnover of £1,500,000 p.a. and provide an internal rate of return of at least 18 per cent on capital employed of not more than £2,000,000.
2. Similar cases in other product areas.

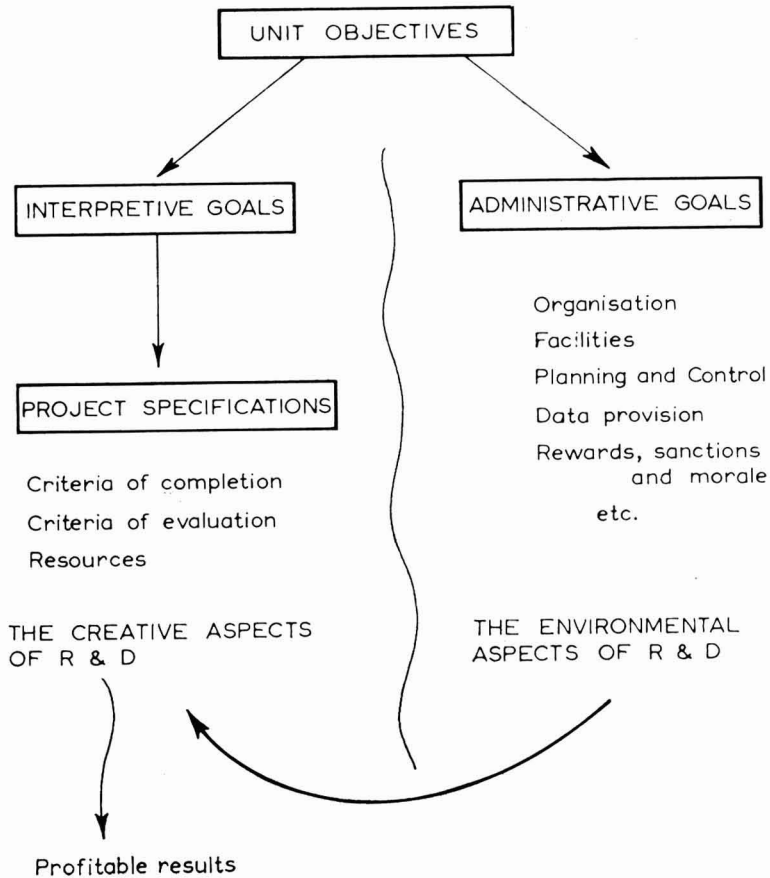


Fig. 1. Management by objectives scheme for research and development

New processes

1. To improve yield in the "Z" process from 74 per cent to 77 per cent by 1972 (in time for design of new plant in Northern England).
2. Similar cases for other processes.

Quality

1. To improve purity of "W" from 97.5 per cent to 98.5 per cent by 1971.
2. Similar cases for other products.

Management

Those responsible for managing the R & D function have two main roles. Firstly, they must act as interpreters between those who make corporate goal statements and the bench level research worker. Secondly, they must provide the best possible environment for the research workers to optimise the chances of success in every project.

These can now be examined in turn.

Interpretation of corporate goals

Management by objectives can do nothing to help the R & D manager directly to interpret corporate goals into project specifications, but it *can* help to clarify the interpretive responsibilities and measure the interpretive success rate.

A company in the fashion goods industry who were applying management by objectives realised that a key task of the R & D manager was to ensure that at least half the products were on a rising sales trend at any one time. As soon as this was appreciated and spelt out, the need to redesign the monthly sales analysis sheet to reveal this key measure became apparent, and the R & D manager soon got the idea of developing a new product in advance of sales decline of its predecessor. This company now stands high in its innovative reputation.

Clarity of thinking following management by objectives applications in this area is often directly responsible for:

- improved competitor intelligence,
- better cost benefit analysis,
- more appreciation of market needs,
- greater use of decision and risk analysis.

Environmental considerations

The second need for administrative goals is somewhat easier to tackle. The clarity of the organisation (particularly in those companies attempting to implant strong project loyalties in a basically functional structure), the adequacy and quality of the facilities, the value of the planning methods, the meaningfulness of the control procedures, the development and morale of the staff—these are all criteria which are relatively easily identified as being somebody's key tasks and are all relatively easily measurable in quantitative terms.

A medium sized engineering company, continually plagued by organisational misunderstandings and priority arguments, now sets goals for executive clarity for projects. Each R & D manager now knows that for every project he must discuss, agree and specify:

1. who is the project leader,
2. who composes the project team as:
 - i full-time direct subordinates of the leader
 - ii full-time secondments from other departments for duration of project only
 - iii part-time secondments for duration of project only,
3. who is the project leader's direct supervisor if it is not his own "boss,"
4. who composes the advisory team or "jury" that will judge the effectiveness of project execution and progress,
5. who is to convene the advisory team meetings and on what basis (calendar or project milestone?).

This company now finds it can muster and disband project teams with speed and facility, and has created some teams where the old prejudices of functional

role and status are completely forgotten within the team, and the authorities of the functional departmental heads are not usurped.

Introduction of management by objectives in the administrative areas of research and development has in many cases been directly responsible for:

- encouraging measurement of facility utilisation and hence factual data on which to base facility provision,
- improving project control statements,
- gearing the services of the library nearer to the needs of the R & D units,
- clarifying patent and publication policy,
- improving liaison with Research Associations and University facilities,
- revealing training needs,
- encouraging better project planning by using networks and other aids.

Conclusions

There is no substitute for "doing." If you are a R & D manager, get a piece of paper now and try to write down what are the six or seven *key* tasks that compose the hard core of your job, how you measure if you are performing these tasks well (or alternatively what condition will exist when you are performing well) and what controls or data you get that tell you how you are getting on. It will be very surprising if this does not either reveal enormous gaps in your understanding of your job or spur you on to thinking of all sorts of short and long term improvements you can make.

In one such case, a manager wrote down that he felt it was his task to try and see that 90 per cent of all the projects were completed within the original budgeted time and cost. When he came to consider controls he realised there was no regular feed-back of completion criteria against original estimate, so he introduced one. To everyone's horror, it was found that only 8 per cent of projects were completed on time, so the target of 90 per cent was obviously over-ambitious. A new target of 20 per cent was set and plans to improve performance were laid. This company now scores 50 per cent after several years of hard work. The financial savings are significant and the estimates for new projects much more realistic.

This last illustration highlights the difficulty of applying management by objectives. The concept is so deceptively simple that one is tempted to think "we will put it in next Tuesday." It is a discipline and attitude of mind that takes years to perfect.

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Discussion at London Section

DR H. WARSON asked whether management by objectives did not lead to excessive restraints to highly qualified personnel, whose professional requirements must be respected to some degree. Furthermore, did not management by objectives lead to an excessive stress on short term profits rather than long term objectives, of the order of ten years in our industry?

MR G. S. SANDERS did not agree that there would necessarily be excessive restraints on highly qualified personnel, which would restrict their activity. There were many examples, for instance, of sponsored research, where such constraints had to be applied. It was possible that many industrial research projects might benefit from a more careful watch on effort expended in relation to results achieved. He agreed, however, that the tasks and methods should not be too closely defined.

On the second point, he was firm in his belief that one should look more closely at the problem of achieving an increase in profitability in the short term. All too frequently had enterprising USA companies carried out applied development leading to profits based on long-term European basic research.

MR M. HEPHER asked how one equated the need for management disciplines and organisation in controlling R & D, with the encouragement of the entrepreneur. Looking back at the big men of industrial research, was it not true to say that many of them had been strong personalities with the ability to fire and stimulate activity in others?

MR SANDERS agreed with this point of view. Possibly a senior scientist could be linked-in under the research manager in the hope that "serendipity" would be achieved and he could have a positive role in maintaining contact with the universities and in every way furthering the company's image.

MR R. M. W. WILSON asked how the lecturer could reconcile his thoughts on the need for the consultant scientist or technologist, free to think clearly, with the fact that in so many organisations, advancement led to increasing multiplicity of paper work, telephoning and letter-writing, and often to the stifling of original thinking.

MR SANDERS agreed that this was a difficult problem and there seemed no easy way out of the situation. One could, of course, separate research from development, so that the research manager would be free to think solely of ideas for the future, e.g. five years ahead or more.

MR A. R. H. TAWN strongly supported the objective of the research function at corporate level, and also agreed broadly with that stated for development, i.e. market opportunity. But a real problem in selecting development projects arose from the existence of another dimension related to the probability of success. He could recall cases of a somewhat lower sales target (perhaps a much lower one) being a better development bet than a much larger target, purely because the one seemed readily attainable, whilst the other appeared infinitely remote. But this was a difficult idea to sell to the commercial departments.

MR SANDERS said that one solution was to have a portfolio of projects, some of which had a good chance of success, the others being of a more speculative nature. The portfolio should be subject to regular review, a point which emphasised the virtue of good management techniques to back up the "hunch." The most difficult task of the research manager was to pick the right projects.

DR M. BLOCK said that, in the schematic diagram of a research organisation, the senior scientist was shown out on a limb acting merely in an advisory capacity. Would it not be more effective if he acted in a position parallel to the chief chemist, physicist or engineer, with supporting staff to follow up his ideas?

MR SANDERS said that one could allow personnel in an advisory capacity to perform a task which was out of the ordinary, in other words, to give advice on matters over which they had no direct control. Their job was really to cajole and persuade others to accept their ideas.

MR P. E. WATSON asked whether the speaker knew of any companies which allowed a proportion of research time for projects chosen by the individual research workers and if so, what results had been obtained.

MR SANDERS said that this had produced very variable results in practice.

DR BLOCK said that a professor at an American university was R & D Director for a company for 20 years, at which the last hour each day could be spent by graduates and their assistants on their own projects, connected, however tenuously, with the company's interest. He found that the best ideas and patents resulted from this hour!

MR J. L. HAWKEY could not accept the idea of rationing time with R & D personnel in terms of so much on this project or that, short term or long term, and the idea of a period where imaginative and creative genius could be turned on like a tap. If the environment was right, the objectives clear, and the following of profitable side tracks and provocative observations was encouraged, the "genius" was likely to do the work without being conscious of the time ration. More important was the attempt to measure the efficiency of the market research. It would seem that all sorts of advice, good or bad, could come from personnel claiming to have undertaken market research.

MR SANDERS thought that it was necessary to apportion time if there were a number of minor projects.

Concerning the value of market research, good market research was essential. Even if a precise answer was not obtained, one was bound to get nearer to the truth each time.

MR H. ADLER asked how far should each level of management become involved in the level below? Was it not possible that each level became too compartmentalised by these schemes?

MR SANDERS said that there should be a smooth transition in the management chain. In the research and development department especially, there should be strong encouragement towards multilateral communications—not only up and down, but across boundaries. The idea of "project management" involving several departments was good in that it helped to break down resistance to change and provided a direction of effort for the future.

Polarographic study of the effect of additives on the aggregation of dyes

By Wahid U. Malik and S. M. Saleem

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Summary

By comparing the diffusion current of the two reducible dyes, *viz.* Orange G and Alizarin Red S, in the buffers of pH 7.0 and 9.0 respectively, with that of the equimolar solutions of Cd^{++} ions, their critical aggregation concentration and the aggregation numbers have been determined. The effect of various additives, *viz.* urea, formamide and methyl alcohol, has been studied as a function of their concentration, on the aggregation of these dyes. All these additives bring about a decrease in the tendency for aggregation of the dye ions. The results have been interpreted in terms of the loosening of the hydrophobic bonding by these additives.

Key words

Prime pigments and dyes

Alizarin red
orange dye

Properties associated with materials in general

polarity

Miscellaneous terms

aggregate

Apparatus primarily associated with analysis and testing

electrical equipment

Etudes polarographiques de l'effet des adjuvants sur l'état d'agrégation des colorants

Résumé

Par une comparaison de leurs courants de diffusion, on a déterminé les nombres d'agrégation des deux colorants réductibles, Orange G et Alizarine Rouge S, dans des solutions-tampons de pH 7.0 et 9.0 respectivement, auprès de celui des solutions équimolaires d'ions Cd^{++} . L'effet sur l'état d'agrégation de ces colorants qu'exercent de divers adjuvants, par exemple, urée, formamide, et alcool méthylique, a-t-il été étudié en fonction de leurs concentrations. Tous ces adjuvants réduisent la tendance d'agrégation des ions de colorants. On a interprété les résultats au point de vue du relâchement des liaisons hydrophobiques par ces adjuvants.

Polarographiestudien über den Einfluss von Zusatzmitteln auf die Aggregationen von Farbstoffen

Zusammenfassung

Durch Vergleich des Diffusionsstromes zweier reduzierbarer Farbstoffe, und zwar Orange G und Alizarinrot S in den Puffern von pH 7,0 bzw. 9,0 mit dem äquimolekularer Lösungen von Cd^{++} Ionen wurden ihre kritische Aggregationskonzentration und—zahl bestimmt. Der Einfluss verschiedener Zusatzmittel auf die Aggregation dieser Farbstoffe und zwar von Harnstoff, Formamid und Methylalkohol wurde als eine Funktion ihrer Konzentration untersucht. Alle diese Zusätze haben eine Minderung der Tendenz, Farbstoffjonen zu aggregieren, zur Folge.

Die Resultate wurden in dem Sinne interpretiert, dass durch diese Zusätze die hydrophobe Bindung gelockert wird.

Полярографическое исследование влияния примесей на скопление красок

Резюме

Путем сравнения диффузного тока двух редуцируемых красок — оранжевой Г и ализариновой С — в буферных растворах pH 7.0 и 9.0 соответственно, с диффузным током эквимольных растворов ионов Cd^{++} , определялись их критическая концентрация скопления и показатели концентрации. Исследовалось влияние различных примесей, как например карбамида, формамида и метилового спирта, как функция их концентрации, на скопление этих красок. Все эти примеси уменьшают тенденцию к скоплению красочных ионов. Результаты выражены в зависимости от ослабления гидрофобных связей этими примесями.

Introduction

The aggregation of dye ions in aqueous solutions has been studied by various workers through a number of experimental approaches, *e.g.*, absorption spectra¹, electrical conductivity², light scattering³, sedimentation⁴, etc. The merits of the various methods are described at length elsewhere⁵. However, all these methods are only applicable to highly purified dyes which are often not easy to obtain. Hilson and McKay⁶ have recently developed a polarographic method for determining the aggregation number of dyes in presence of electrolytes. In this paper the method has been extended to study the effect of urea, formamide and methyl alcohol on the aggregation of two textile dyes, *viz.*, Orange G and Alizarin Red S.

Experimental

Reagents

Orange G and Alizarin Red S were BDH products. All the other chemicals were of reagent grade. Methyl alcohol was the BDH product and was further purified by redistillation. The concentrations of urea and formamide are reported in moles per litre, while methyl alcohol is given by percentage.

The reduction of Orange G ($E_1 = -0.69\text{V}$ against standard calomel electrode) and Alizarin Red S ($E_1 = -0.60\text{V}$ against standard calomel electrode) was accomplished in Clark and Lubs buffer (pH = 7.0) and borax buffer (pH = 9.0) respectively. In the case of Orange G, a sharp acute maximum occurred in the current-voltage curve, which was not suppressed, and the measured diffusion currents correspond to the step height.

The polarographic measurements were carried out using a Heyrovsky polarograph (No. Lp55A) operated manually in conjunction with a "Scalamp" Pye galvanometer. Saturated calomel electrode was used as the reference electrode. All measurements were carried out at $30 \pm 0.1^\circ\text{C}$.

Procedure

For a non-aggregating species like Cd^{++} ions, the diffusion current is proportional to the molarity of the species. By comparing the limiting current given by a dye with that given by the same molar concentration of cadmium ions, the diffusion coefficient, D , of the dye can be compared with that of the (known) diffusion coefficient of Cd^{++} ions. In actual experiments, the difference in the logarithms of the diffusion currents of the equimolar solutions of dye ions and cadmium ions ($-\Delta \log_{10} i_d$) is plotted *vs* $\log_{10} C$ (C = concentration). Since the limiting current is proportional to the diffusion coefficient D , ($i_d \propto D^{1/2}$) the

plot of $-\Delta \log_{10} id$ against $\log_{10} C$ is also a plot of $-\Delta \log_{10} D$ (the difference between the logarithms of the diffusion coefficients of cadmium ion and dye ion). The plots remain horizontal up to a certain dye concentration and then an upward rise is observed due to the aggregation of dye ions (aggregated dye ions have a smaller diffusion coefficient). The molecular weight of the aggregate is determined from its diffusion coefficient by means of a linear empirical relationship between the logarithms of the molecular weight and the diffusion coefficient of a large number of substances. The molecular weight of the aggregate in turn gives the aggregation number. The details of the method are described elsewhere⁶.

Results and discussion

The logarithms of the diffusion current of cadmium ions and that of the dyes, *viz.*, Orange G and Alizarin Red S, were plotted against $\log_{10} C$, Fig. 1 (a, b). A linear plot is obtained with cadmium ions whereas those of the dyes show a downward deviation from linearity beyond a certain concentration of the dye. For the determination of critical aggregation concentration and the aggregation number, the plots of $-\Delta \log_{10} id$ vs $\log_{10} C$ are shown in Figs. 2 and 3. It is

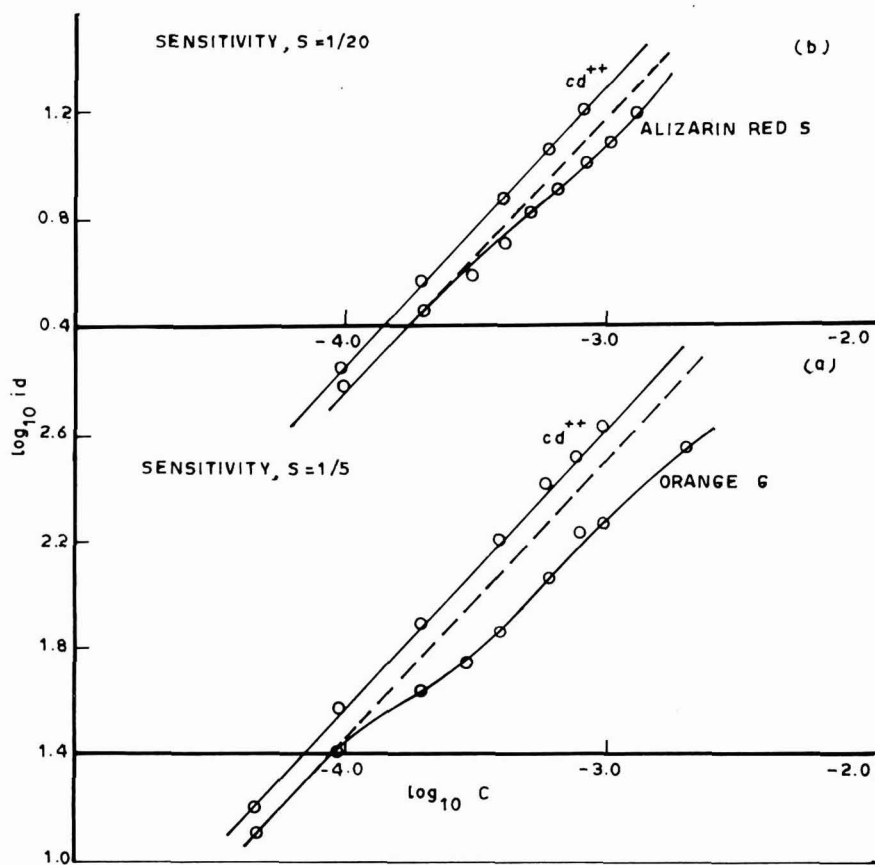


Fig. 1. Plots between $\log_{10} C$ and $\log_{10} id$

observed from Fig. 2 that Orange G starts aggregating after reaching a concentration of $7.9 \times 10^{-5}\text{M}$ and the aggregation number increases with further increase in dye concentration, and becomes almost constant after assuming maximum value of 25 at a concentration of $6.0 \times 10^{-4}\text{M}$. Thereafter, the curve again runs roughly parallel to the $\log_{10}C$ axis, thereby indicating that further increase in the dye concentration does not bring about any change in the aggregation state, but only the aggregates consisting of 25 dye ions increase. Similarly it is seen from Fig. 3, that Alizarin Red S starts aggregating at a concentration of $31.6 \times 10^{-5}\text{M}$ and a further increase in concentration causes very rapid aggregation. The aggregation number assumes the maximum value of 6 after reaching the concentration $39.0 \times 10^{-5}\text{M}$.

Similarly, the critical aggregation concentration and the aggregation number of both these dyes were determined in presence of different amounts of additives, viz., 1.0, 2.0, 4.0M urea, 0.5, 1.0, 2.0M formamide and 5.0, 10.0, 20.0 per cent methyl alcohol. The results are summarised in Tables 1 and 2. It is seen from Table 1, that the critical aggregation concentration of Orange G in presence of 4.0M urea is enhanced 2.5-fold as compared to that in absence of any additive. Formamide is still more effective, and brings about nearly 2.5-fold increase in the critical aggregation concentration when added in 2.0M concentration. Ten per cent methyl alcohol brings about a two-fold increase in the critical aggregation concentration of Orange G. It is also observed from Table 1. that the concentration required to form aggregates consisting of five dye ions increases

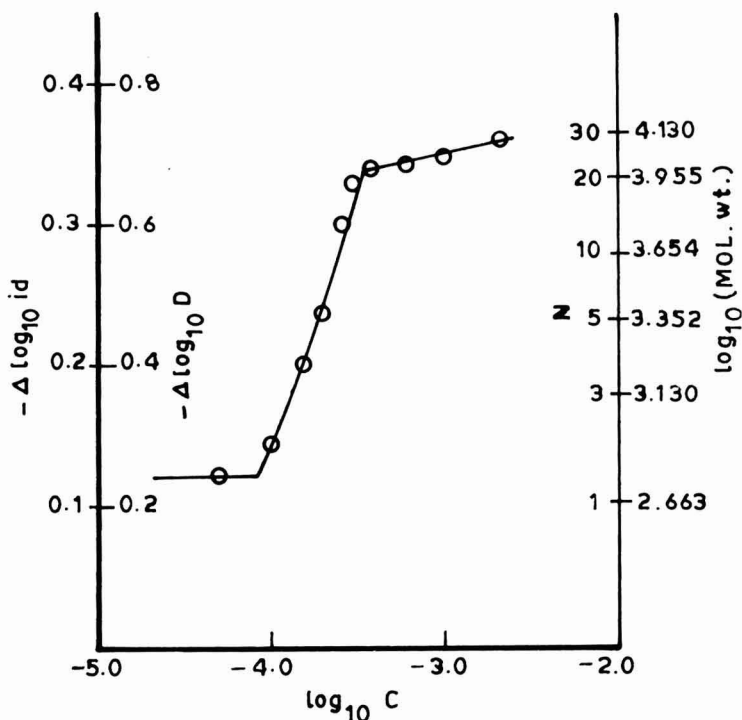


Fig. 2. The aggregation of Orange G

with the increase in the concentration of the additives. Similar results have been obtained in the case of Alizarin Red S.

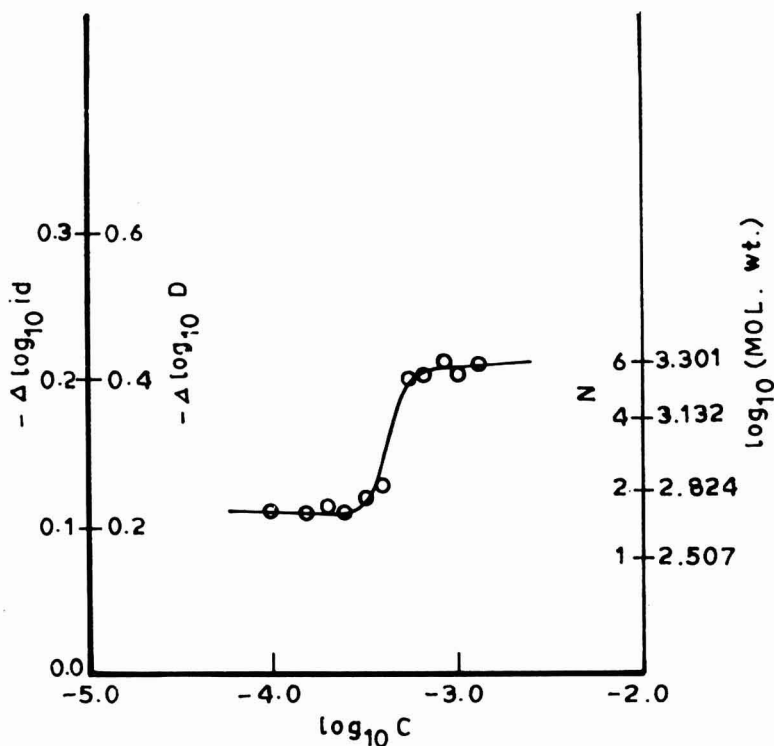


Fig. 3. The aggregation of Alizarin Red S

Table 1

Effect of urea, formamide and methyl alcohol on the aggregation concentration and concentration of the dye required to form aggregates of five-molecules

Additive	Additive concentration	Aggregation point ($\times 10^{-5}M$)		Concentration of dye (for $N=5$) $\times 10^{-5}M$	
		Orange G	Alizarin Red S	Orange G	Alizarin Red S
Urea	0.0	7.9	31.6	15.8	50.1
	1.0M	12.0	36.3	20.0	*
	2.0M	15.1	44.6	25.1	—
	4.0M	19.9	52.4	31.6	—
Formamide ..	0.5M	11.2	35.4	18.6	51.8
	1.0M	14.4	44.6	22.3	63.0
	2.0M	20.0	79.4	28.1	112.2
Methyl alcohol ..	0.5%	10.4	45.7	16.6	57.5
	10.0%	15.1	57.5	19.5	—
	20.0%	17.7	—	22.9	—

*Tendency of the dye to precipitate rendered the accurate measurements of aggregation concentration difficult.

Furthermore, it is observed from Table 2, that at a particular concentration of Orange G, increasing concentration of the additives brings about a diminution in the aggregation number.

Table 2

Effect of concentration of additives on the aggregation number of Orange G at different concentrations

Dye concn. $\times 10^{-4}M$	Aggregation number									
	Urea				Formamide			Methyl alcohol		
	0.0M	1.0M	2.0M	4.0M	0.5M	10M	2.0M	5%	10%	20%
1.0	1	1	1	1	1	1	1	1	1	1
2.0	4	4	3	1	1	4	2	3	2	1
3.0	15	10	8	5	3	8	7	13	12	8
4.0	20	20	20	18	12	12	12	15	15	15
6.0	25	20	20	20	15	15	15	15	15	15
8.0	25	20	20	—*	15	15	15	15	15	15
10.0	25	20	20	—	15	15	15	15	15	15

*Tendency of the dye to precipitate rendered the accurate measurement of the aggregation number difficult.

Effect of urea on the aggregation of dyes

The results can be explained in the light of current theories of water structure and its relation to hydrophobic bonding, *i.e.* the phenomenon in which the non-polar moieties or residues (usually hydrocarbon) in presence of water associate to form intermolecular aggregates, as in the case of native protein solutions or micelles in aqueous surfactant solutions^{7, 8}. According to Frank and Evans⁹, the water molecules become more ordered around a non-polar solute with an increasing extent of hydrogen bonding in this region. The hydrocarbon chain surrounded by water structure represents a comparatively low energy state, but the concomitant restriction of motion provides the driving force for aggregation¹⁰. It may therefore be anticipated that the water-structure-breaking substances would weaken the hydrophobic bonding. Being itself a good hydrogen bonding agent, urea partakes in the formation of mixed clusters and therefore reduces the ordered regions provided by another solute¹¹. In this way, urea shifts the equilibrium of hydrophobic forces by providing a more favourable environment for non-polar groups than provided by pure water. Consequently, the aggregation of dye ions which contain aromatic hydrophobic groups, becomes a disfavoured process.

Effect of formamide and methyl alcohol

Arvan and Zaitseva¹² have studied the aggregation of dyes in non-aqueous media of intermediate polarity such as methanol, and also in formamide, which has a higher dielectric constant than water. It was found that little or no association of the dye molecules is accomplished in these solvents. Therefore, water seems to be specifically favourable for hydrophobic bonding. The water-structure-breaking property of formamide has been demonstrated by Rupley¹³ on the basis of viscosity measurements on its aqueous solutions. Therefore, the greater effectiveness of formamide may be attributed to its being endowed with

the property of being less favourable for hydrophobic bonding which is further augmented by its water-structure-breaking property.

The same line of reasoning may be employed to explain the effect of methyl alcohol on the aggregation of these dyes. Moreover, the methyl alcohol, being less polar as compared to water, may penetrate into the aggregates, due to partition equilibrium, thereby bringing about disaggregation. Large amounts of additives may, however, influence the solvent properties, and precipitation of the dye takes place with the result that the aggregation point cannot be shifted to higher concentration.

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Acknowledgments

One of the authors (S.M.S.) is grateful to CSIR (India) for the award of a fellowship.

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Next month's issue

The Honorary Editor has accepted the following papers for publication, and these are expected to appear in the July issue.

"Aircraft finishes," by *J. A. Scott*.

"New concepts in polymer architecture," by *A. R. H. Tawn*.

"Analysis of vegetable oil mixtures by gas chromatography," by *M. Jernejcic and L. Premu*.

"Formulation of fungus-resistant paints. 5. Addition of salicylanilide," by *E. Hoffmann and A. Saracz*.

"Freeze-drying of soft polymer dispersions for determining their particle size by electron microscopy," by *F. H. de la Court and H. Vogt*.

Correspondence

SIR,—The very mention of Leonardo da Vinci and OCCA in the same paragraph is enough to induce in me a syndrome of some kind, but when no less an intellectual than our respected Dr Jolly selects him for our instruction and pleasure I simply must mount my hobby-horse—The Da Vinci Society as OCCA's new name by the time our diamond jubilee comes round. Merger Maniacs could have a wonderful time reorganising Associations, Societies, Royal and ordinary, Paint Manufacturers, Paint Chemists, Colour Chemists, Engineers and Architects under one glorious canopy of culture—The da Vinci Society!

Since Dr Jolly has admitted that he has the time, inclination and facilities for research may I suggest that he has found himself a job—Correspondent Extraordinary. He has a gift of literary style, pleasing on the eye and mind, so let us look forward to reading more of the fruits of Dr Jolly's gentle browsings.

Yours faithfully,

H. W. Keenan.

*Claremont, Stonnards Brow,
Shamley Green, Surrey.*

SIR,—We have read with interest the short communication in your issue of September, 1968, by D. R. Bush and M. Thompson¹ on the stripping of solvents from paints. The authors do not state the reason for isolation of the solvents, except for the general statement that it is for analysis.

If this analysis is carried out by GLC the methods adopted in these laboratories may be of interest. We find that the quantitative removal of solvents for coatings is almost impossible, especially in the case of nitrocellulose based lacquers, where the composition may contain materials varying in boiling point from ethyl acetate to butyl diethylene glycol ether. We find it satisfactory to inject the whole paint into the chromatograph. In order that the column itself shall not be contaminated, the injection port has been modified as in the accompanying sketch. A heated aluminium block which comprises the injection port can take one of two alternative liners. *A* is employed for ordinary solvent analysis, and *B* when whole paint is injected. The after part of *B* is bored out to take a plug of asbestos fibre. The needle of the syringe deposits the paint on the asbestos, from which the solvents appear to be released without difficulty, to give a normal chromatogram.

If the paint, as is usually the case, is too viscous to fill a syringe in the normal way, it could be diluted with a suitable diluent, e.g. CS₂, but we have never resorted to this expedient. Instead the clean dry syringe is held needle downwards, and a small drop of paint applied to the top of the barrel after removal of the plunger. The paint readily flows down the bore of the barrel displacing the air through the needle. When the bore is full the plunger is inserted and the paint forced through the needle to adjust to the required volume. Injection is then made normally.

It is also possible, and practised by us, to apply a suitable amount of paint to the asbestos plug on insert *B* while cold. *B* is then rapidly inserted into the hot zone followed by the silicone rubber septum etc. Carrier gas flow is then

established and time measured for commencement of gas flow. This amounts in fact to a type of interrupted elution and gives satisfactory results, particularly if an internal marker is added.

Yours faithfully,

G. M. Hamilton, Director, and
A. M. Milner, Senior Research Officer

*South African Paint Research Institute,
University of Natal,
King George V Avenue,
Durban, South Africa.*

(1) *JOCCA*, 1968, **51**, 824. Bush, D. R., and
Thompson, M.

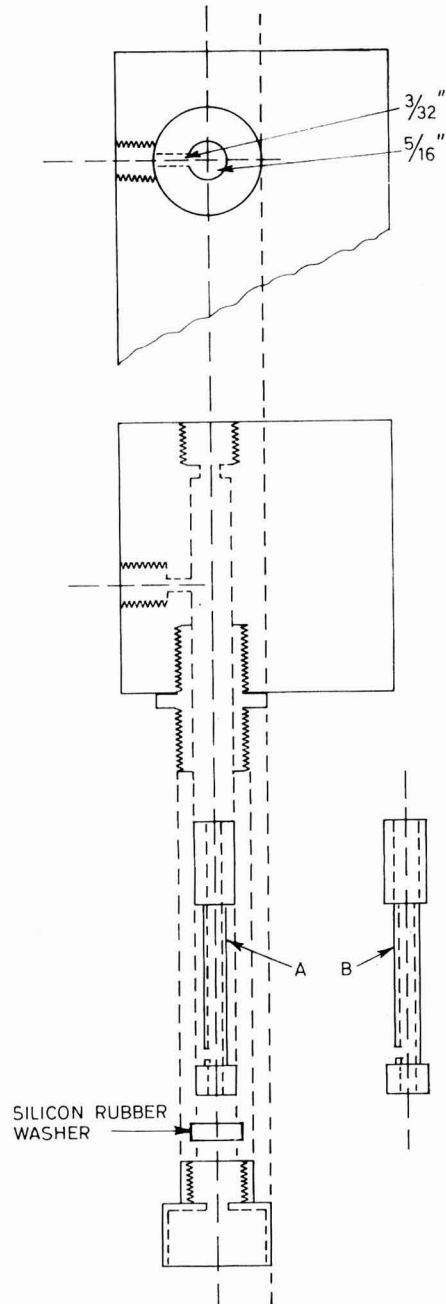


Fig. 1. Modified injection port

SIR,—Although many of us in, or associated with, the paint industry are involved in problems of potential lead toxicity to both man and cattle, few of us have the resources to study such biological problems. The paper published by J. C. Gage and M. H. Litchfield is, therefore, particularly welcome.

However, it would seem possible to the writer that some of the results they have obtained may have been affected by factors not mentioned by the authors. Whereas they find good correlation between diets containing lead nitrate and lead naphthenate, the same degree of correlation appears absent when lead-containing paints are incorporated into the feed.

May I suggest that in the first case the equal degree of lead migration obtained from the nitrate and the naphthenate is due to the rapid hydrolysis of the naphthenate.

Conversely, when using a naphthenate paint diet containing twice the lead concentration as present in the naphthenate solution diet the absence of a consistent higher migration rate with the paint is possibly attributable to

- (a) the limited water absorption of paint films, and
- (b) conversion of lead naphthenate in paint to water and oil insoluble lead compounds such as phthalate and stearate.

Further, the lower rate of migration of lead from a lead chromate paint in comparison with a lead naphthenate paint may be due to the fact that in the lead chromate pigment used, only part of the lead is present in "soluble" form; by "soluble" lead is meant that portion of the pigment soluble in dilute hydrochloric acid using the statutory analytical procedure.

If on this account the two paint diets contained a different percentage of "soluble" lead, then direct comparison between the diets would not be possible.

Other investigators have tried to produce a pattern of movement for the total lead in the feed by examining both the lead absorbed in the various organs and the lead excreted. It would be interesting to know whether there is any reason why the present authors limited their investigation to absorption.

Considering the relatively high migration of lead from paints in comparison with polymers, I would suggest that this does not result from the brittleness of a paint film permitting particle size reduction on mastication, but to the higher water absorption of paints in comparison with polymers. Furthermore it seems likely that mastication of a paint film results in sub-division in two planes only, there being little increase in surface area.

Yours faithfully,

H. A. Newnham, Director

*Spelthorne Metals Limited,
Church Street,
Rickmansworth, Herts.*

SIR,—Commenting on Mr A. R. H. Tawn's article "The theory of functionality: Part I," printed in your issue, March, 1969, I should like to point out the logical shortcut being made there. The author states: "This means that union of two molecules to make a bigger one can only occur end-to-end. Hence the polymer molecules must always have a linear chain-like structure." Must they? What about cyclisation?

It seems that the W. H. Carothers theory of polymer formation, at least for alkyds, is insufficient and in view of recent data, a bit outfashioned. Since the average molecular weights always are smaller than calculated, R. W. Kilb has introduced a term for intramolecular condensation in his formula.

R. T. Blackiston's ingenious work on alkyds (*J. Paint. Tech.* October, 1967) shows that the model of alkyd polymer formation is more complex. We should adjust our views to these facts. Otherwise we are left with "approximations, simplifications" etc., compiled to calculate the values, which suit the theory not reality. (e.g. T. C. Patton: "Alkyd Resin Technology" p. 86-87).

Yours truly,

Eugene Beres

Gliwice
ul. Nowotki 15a/16,
Poland.

SIR,—I have been wondering how long it would be before I had to doff the editorial hat and write a letter to myself. The time has arrived, for I cannot let Mr Beres's letter go unanswered. He really should have noticed that the review of which he complains was headed "Part 1," and might have been wiser to wait and see what followed. I will resist the temptation to argue his interpretation of a sentence which seems unambiguous to me; for, if he has been misled, so perhaps have others.

It is true that cyclisation can occur, and this will have been made clear to the student by the time this letter is published. It is also true that the Carothers theory is insufficient for some purposes and that other treatments, like that of Kilb, are often preferable. It depends what you are trying to do with the theory and, unless I have mis-read my own words, this has not yet been discussed.

Much ill-informed criticism has been directed at the Carothers theory by workers who have failed to appreciate its fundamental logic *and its limitations*. It is only when wrongly applied that it gives the wrong answers—and that is not the fault of Carothers—hence my initial caveat about knowing your chemistry first. It is also an unfortunate fact that many examiners in coatings technology still expect candidates to have no more knowledge of functionality theory than a scant awareness of the Carothers equation (without even formal proof), notwithstanding the essential truth of Mr Beres's remarks.

My approach no doubt seems laboured to one with a thorough grasp of functionality theory in all its aspects; but Student Reviews are not addressed to the experts. After many years' experience of dealing with students' difficulties in this field, I have found it expedient, as have other teachers, to start with something simple and within the compass of the students' attainment, and to develop on from there. It is entirely possible to jump in at the deep end with Flory-Stockmayer statistics but except, perhaps, at the graduate level, this does more to confuse than to enlighten.

A. R. H. Tawn

Reviews

ADDITION POLYMERS: FORMATION AND CHARACTERIZATION

Edited by DEREK A. SMITH, London: Butterworths 1968. Pp. vii + 492. Price: 110s.

The preface states that the book is primarily intended for those who elect to specialise in polymer studies during their undergraduate course or after their first degree. It is also hoped that it will prove useful to practising polymer chemists and technologists in industry.

The first three chapters represent a general introduction to the field of polymers and the mechanisms which are operative in polymer formation (110 pages).

There follows a brief chapter introducing the industrial aspects of polymer technology, including a section indicating the industrial synthesis of some of the more common monomers.

The remaining chapters cover: molecular weight determination (89 pages) including description of the actual instruments, their operation and background theory; polymer fractionation (43 pages); polymer microstructure (75 pages). The last is a very well set out chapter giving a clear indication of the sources of structural variations in the polymer chain and the means whereby the structure can be elucidated.

A short chapter covers the crystallinity of polymers both on the micro- and macro-scale, including means of achieving crystallinity and estimating the degree of crystallinity (26 pages).

The chapter on degradation as a polymer characterisation technique, includes sections on the degradation of specific polymers (47 pages).

The final chapter reviews the known relationships between structure and bulk properties and compares predictions deduced from theoretical models with properties of real polymers.

This is an eminently practical book, well illustrated throughout, though examples tend to be biased towards those interested in *high* polymer technology, particularly the rubber industry.

An extensive use of italics, particularly in the first chapter, could confuse rather than clarify. The impression is given that these are key words in the particular context being discussed. Such a treatment for "pure" (page 12) even though in the course of defining this vague term in terms of polymer technology and again, "sharpness" (page 14) when referring to polymeric thermal transitions, is unnecessary.

Generally, there are very few references after 1961 and this will restrict its usefulness to specialists in other areas of polymer technology who wish to keep abreast of this rapidly advancing field.

Three typographic errors were noted by the reviewer. On page 6, Figure 1.2b is referred to as head to tail/tail to tail structure though it is referred to

correctly as head to head/tail to tail in the text. There is a mis-spelling of syndiotactic under the figure 7.7c (page 291) and on page 363 there is a reference to "power samples" under figure 8.10 (powder).

These are only very minor criticisms of a book which achieves its primary aim of bringing to the technological student an understanding of the major developments by the academic workers in this field.

J. L. ORPWOOD

QUARTERLY LITERATURE REPORTS: SURFACE ACTIVITY

Edited A. J. B. SPAULL, London: Kogan Page Publications, 105s per annum. Vol. 1, No. 1. Pp. 35.

This first number of a series of quarterly literature reports contains a selective review and critical examination of what the author considers to be the most important papers and patents in the field of surface activity which appeared during the three months immediately prior to publication i.e. in this case October to December 1968. One must remember that this means only journals that appeared in the British libraries during that period could be covered, and hence it is not strictly a review of the literature of that period. Provided continuity in reviewing is maintained despite the fact that certain relevant foreign journals might be received in this country somewhat spasmodically, then the value of the service provided will be ensured. This issue also contains reviews of some of the papers presented at the 5th International Congress of Surface Activity held in Barcelona in September 1968, and are therefore taken from the preprints. Such early reviewing of conference papers in the future is obviously a chancy business, depending on availability to the author. So the papers and journals that are destined for review in future issues cannot be anticipated, and the author will need to be strict in his survey if the reports are to provide the comprehensive coverage which would seem desirable.

Naturally, as the author suggests, the selection must be highly subjective. He claims to have selected two types of publication: "those which connect items of information and present explanations of known phenomena within the compass of the subject, and those which contribute some new knowledge which illuminates fundamental aspects of the subject or opens the way for practical advances." The papers are divided into sections covering (separately) the physics of surface activity, synthesis of surface active substances, analytical methods, and both technical and industrial applications. There are 107 reviews of average length about 60 words, and 63 papers that are considered worthy of note are also listed.

The value of such a publication depends on individual taste and urgency. Available computer methods give titles but titles are often misleading. Perhaps a set of selected reviews partly solves the increased problem of keeping up with the literature, but will the reader be satisfied with what Dr Spauld thinks is important?

G. D. PARFITT

DYES AND THEIR INTERMEDIATES

By E. N. ABRAHART. London: Pergamon Press, Pp. xvi + 335, 45s.

This book gives a very good overall view of the dye-making industry and is one of a series of teaching manuals for senior students interested in applied chemistry. Chapter 1 deals with colour physics and the related aspects of organic chemistry. Much of the theoretical aspects here could have been assumed rather than given a very scant treatment. Also, Chapter 2 compresses the methods of classification of dyes, the chemistry of textile fibres, dye application processes and fastness properties into one short chapter. Separate chapters cover various aspects of the subject, such as intermediates, dyes, pigments and fluorescent brightening agents. The final chapter gives some account of dye-making plant, typical manufacturing processes, dye testing and the requirements of the Alkali and Factories Acts. The book also includes a very useful bibliography and lists the principal dye and pigment manufacturers in the United Kingdom. As a whole, the book is very interesting to read and well presented.

Dr Abrahart has tackled a very difficult task in trying to compress a large range of subject matter into a small book. He has succeeded excellently in this objective and the book should be very acceptable to readers engaged in a preliminary study of the subject and others whose technical interest necessitates some working acquaintance with dyestuffs chemistry. The book is well illustrated and the many structural formulae are clear and useful. The book has, of necessity, a practical bias but sufficient theoretical treatment has been introduced to make it interesting. It is perhaps a pity that it was not possible for the author to restrict the amount of space given to old classes of dyestuffs such as triarylmethane dyes, many of which are no longer in great commercial use, and used the space for newer developments.

As is natural in a first edition of this sort, a few minor points require correction. Although the earlier methods of stabilising diazo compounds are referred to, no mention is made of the neutral-developing printing mixtures of the Rapidogen or Neutrogen types. Also, many of the coupling components given on page 165 are of only minor importance.

In comparison with the space taken up by some obsolete dyes, or dyes which are rapidly becoming obsolete, the nine pages given to reactive dyes is far from adequate, especially since this is the most revolutionary development in dyestuffs chemistry in the last twenty years. The omission of adequate reference to the modern development of instrumental match prediction is also regrettable.

Many of the structures given for metal complex dyes and pigments can be very misleading. For example, on page 268, Pigment Green should be clearly represented as being a chelate of ferrous iron. The azo metal complexes, for example see page 154, are disconcertingly represented with the centre of the bond from the metal to the azo link poised between the two azo nitrogens. The uninformed might be misled by this to consider the linkage to be that of a π complex.

The author deserves congratulating on the successful outcome of what must have been a mammoth task. The book deserves a place in any good technical library and will be invaluable to those wishing to learn something of a very complex and interesting subject.

R. R. DAVIES

The theory of functionality, Part IV

By A. R. H. Tawn

Cray Valley Products Ltd., St. Mary Cray, Kent, and
The Borough Polytechnic, London SE1

Reaction between complementary functions, one present in excess

If one wants to make linear polymers of very high molecular weight, suitable, for example, as fibre formers, it is necessary to have complementary functions present in exactly equal numbers since, as already stated, excess of one function will limit the growth of the polymer molecules. Extreme precautions to this end are taken in the manufacture of fibre-forming polyesters and polyamides.

Resins for convertible coatings are invariably made to much lower molecular weights than the fibre-formers, because of the need to compromise between viscosity and application solids. The requirement of convertibility is, moreover, usually enhanced by making branched molecules, necessitating the employment of polyfunctional monomers. In many of these resins a stoichiometric excess of one reactant (e.g. polyol in an alkyd formulation) is used to control the growth of the polymer molecules by regulating the relationship between molecular weight and degree of reaction. A knowledge of how to extend functionality treatment to such systems is therefore of value.

Consider the reaction between two moles of adipic acid and three moles of ethylene glycol. Reaction must clearly cease when all four carboxyl groups have reacted, at which point two hydroxyl groups will be left with nothing to react with. The *average* product molecule may be depicted as $\text{HO}[\text{C}_2\text{H}_4\text{OOC}_4\text{H}_8\text{COO}]_2\text{C}_2\text{H}_4\text{OH}$.

When both reactants are bifunctional, and are initially present in proportions a moles of A, b moles of B, and $b > a$, where a and b are integers, the ultimate average product molecule contains a moles of A and $(a + 1)$ moles of B. Hence, $2[b - (a + 1)]$ B functions remain unreacted. When all A functions have reacted ($p_A = 1$), we have $x = 2a + 1$. This clearly indicates the action of an excess of one reactant as a chain-stopper, reducing the attainable molecular weight of the polymer. It also demonstrates the absurdity of calculating f on the foregoing lines for a mixture of reactants, when one function is present in excess. If this is done for a mixture of 3 moles glycerol and 3 moles adipic acid, one obtains, total functions = $(3 \times 3) + (3 \times 2)$, total moles = $3 + 3$, $f = 15/6 = 2.5$, which is higher than the functionality of an equivalent mixture (2 moles glycerol, 3 moles adipic acid, $f = 2.4$)! This is contrary to what has gone before, and to general experience, since it would imply that excess polyol increases functionality and leads to higher molecular weight at a given degree of reaction; this is manifestly nonsense.

The solution to this superficial dilemma is very simple; so simple, indeed, that it seems to have escaped those who consider that functionality theory must of necessity be difficult. The mathematical solution has been given by Pinner (*J. Polymer Science*, 1956, **21**, 153) but, stripped of its mathematics,

it is simply that we should consider only those functions which are *reactable* in a given system; *i.e.* excess functions are not reactable because they have nothing to react with, and they should not therefore be counted. Hence, in the system three moles glycerol and three moles adipic acid already mentioned, we have

$$\begin{aligned} 3 \times 3 &= 9 \text{ OH functions} \\ 3 \times 2 &= 6 \text{ COOH functions} \\ 3 + 3 &= 6 \text{ moles.} \end{aligned}$$

The 6 COOH functions can react with only 6 OH functions, so the *reactable* functions number $6 + 6 = 12$. Hence, *reactable* functions per mole = $12/6 = 2$. The functionality of the system is 2 and this is the value of f to be used in the Carothers equation.

Also, it is necessary to be quite clear about the meaning of p in this situation. It was previously defined as the fraction of functions which have reacted. It must now be defined as the fraction of *reactable* functions which have reacted. Thus if, in an alkyd, OH is present in excess, all the OH groups are not reactable, whereas all the COOH groups are. The fraction of total reactable functions (COOH + an equal number of OH) which have reacted is the same as the fraction of minority functions (COOH) which have reacted; so, in calculating p , we need only consider those complementary functional groups which are in the minority.

Hence, we still have the familiar Carothers equation, but with modified definitions for f and p , thus:

$$p = \frac{2}{f} - \frac{2}{fx}$$

where p = fraction of reactable functions which have reacted
 = fraction of minority functions which have reacted
 f = reactable functions per mole
 x = degree of polymerisation (number average as before)

Example:

An alkyd is made by alcoholysis of 200lb linseed oil with 100lb glycerol and subsequent esterification with 200lb phthalic anhydride.

First, the weights must be converted into moles. The molecular weights of glycerol and phthalic anhydride are 92 and 148 respectively. That of linseed oil may be calculated from its saponification value, but the molecular weights of the mixed fatty acids from C18 oils do not differ widely and, as a first approximation, may be taken as 280, corresponding to a triglyceride molecular weight of $3 \times 280 + 92 - 3 \times 18 = 878$.

Thus, there is present $100/92$ moles glycerol as such, $200/148$ moles phthalic anhydride, and $200/878$ moles of oil, equivalent to $200/878$ moles glycerol plus $3 \times 200/878$ moles of fatty acid.

The overall composition is thus

glycerol	1.315 moles	3.945 OH functions
phthalic anhydride	1.351 moles	2.702 COOH functions
fatty acid	0.683 moles	0.683 COOH functions,

and we have

$$\begin{aligned} \text{total OH functions} &= 3.945 \\ \text{total COOH functions} &= 3.385 \\ \text{reactable functions} &= 2 \times 3.385 = 6.770 \\ \text{total moles} &= 3.349; \end{aligned}$$

therefore,

$$f = \frac{6.770}{3.349} = 2.02$$

An illogical extension of the Carothers theory

Readers who worked through Exercise 2 of Part 3 may have encountered difficulty in interpreting the behaviour of the system at $p = 0.9$. It will be recalled that the system comprised 1 mole pentaerythritol, 1.5 moles phthalic anhydride and 1 mole stearic acid, which is easily seen to have a functionality of $8/3.5 = 2.286$. The Carothers equation then rearranges to

$$x = 0.8749/(0.8749 - p),$$

whence the answers to the exercise are:

p	0.2	0.4	0.6	0.8	0.9
x	1.30	1.84	3.18	11.7	?

At $p = 0.9$, x apparently has a negative value, which is absurd. Look at what happens as p is increased by small steps above the value 0.8:

p	0.82	0.84	0.86	0.87	0.874	0.8748
x	15.9	25.1	58.7	178.9	972.1	8749

At $p = 0.8749$, we have

$$\begin{aligned} x &= 0.8749/(0.8749 - 0.8749) \\ &= 0.8749/0 \\ &= \infty \end{aligned}$$

i.e. the value of x apparently becomes infinite.

This has been *erroneously* identified with the point of gelation and from this false premise it is possible *erroneously* to extend the Carothers theory thus:

$$p = \frac{2}{f} - \frac{2}{fx}$$

If at the gel point, $x = \infty$, $2/fx = 0$, hence

$$p_{\text{gel}} = 2/f.$$

It follows that complete reaction without gelation is just possible when $f = 2$ and that gelation will occur before $p = 1$ in any system for which f exceeds 2.

Calculation of gel points in this way is wrong

It is true that, when only bifunctional reactants are present, gelation cannot occur because no cross-links can be formed. Only in this sense can a limiting condition be stated. When individual reactants having functionalities greater than 2 are present, gelation invariably occurs (assuming no loss of functions by ring formation) at a value of p less than $2/f$. Conversely, in this situation, systems having functionalities somewhat less than 2 *can* gel. Just how much less than 2, depends on the functionality of the branch units present; systems containing pentaerythritol gel more readily than those containing glycerol even when they have the same average functionality. The explanation is to be found in the random nature of the reaction; some molecules grow to "infinite size" before others, and their contribution is reflected in the weight average degree of polymerisation rather than the number average represented by Carothers's x . The weight average in a polydisperse system is higher than the number average at all stages of the reaction. It reaches an infinite value at a lower level of p and it is at this level of p that gelation occurs.

The Carothers theory as a useful approximation

Weight average cannot be predicted by a number average theory, so the Carothers treatment is at best an approximation when used in the prediction of gelation. What it can do, is to provide relationships between degree of reaction and number average degrees of polymerisation, and within the limitations of its basic assumptions (all functions equally reactive; random reaction; no ring formation; no loss of reactants) it does this unequivocally. Unfortunately, these conditions are rarely if ever met with in practice, so, from the viewpoint of the practical resin formulator, it is *always* an approximation. Its beauty is its simplicity, and for this reason it is often pressed into service as a rough guide, even when gelation is being considered. Thus, the teaching of experience is that a conventional alkyd performs best when processed to a degree of reaction approaching the gel point (say about 5 acid value units short of the gel point). Moreover, there is usually some desirable acid value specification for the product, perhaps in the region of 10 or 20 mgKOH/g. It is known that gelation will occur in systems of functionality a little under 2, say 1.95, and using this as a working basis one can calculate a starting point formulation containing approximately the right hydroxyl excess for a given oil length, which can be adjusted if necessary in a second or third experiment. When adjustment is required, the Carothers theory will indicate the direction in which the adjustment should be made (upwards or downwards in terms of functionality), and this is particularly useful when one is considering changing several formulating variables, like oil length, excess hydroxyl, use of different polyols, or incorporation of chain stoppers like rosin or benzoic acid.

The theory can be applied with equal facility to other poly-condensation resins, like polyamides and phenolics, provided the nature of the reaction taking place is known. It can be applied, albeit with difficulty, to addition polymerisations but its practical value in such cases is minimal.

In view of the foregoing, other functionality treatments have been developed. Some, like the "Alkyd Constant" concept, are no more than algebraic variations of the Carothers theory and, in the writer's view, serve only to complicate a picture which is basically simple. Others are concerned with predicting molecular

weight distribution and weight average, and hence with providing a more complete picture of the factors affecting gelation. Yet others extend these treatments to take account of ring formation and unequal reactivity of functions. These will be briefly discussed in the final part of this series, with particular reference to their practical utility.

Exercises

1. A conventional long oil penta alkyd is made from
386lb linseed oil
80lb pentaerythritol
142lb phthalic anhydride.
Calculate its functionality.
2. A plasticising alkyd prepared from lauric acid 205lb, glycerol 145lb and phthalic anhydride 255lb was found to gel prematurely during reaction. What weight of glycerol should have been used, assuming the target functionality for such a resin to be 1.95
3. A certain epoxy resin has a molecular weight of 1350 and the average molecule contains 7.75 hydroxyl groups (including the hydroxyls equivalent to the terminal epoxy group each of which is considered in esterification as a diol). 100lb is esterified with 40lb of soya fatty acids (mol. wt. 280) and 10lb of a commercial dimeric acid containing 6 per cent monomeric acid (mol. wt. 280), 73 per cent dimeric acid (mol. wt. 560) and 21 per cent trimeric acid (mol. wt. 840). What is the functionality of the system? Is it likely to gel before esterification is complete?

Answers to exercises in Part 3.

1. (a) 12/5 or 2.40. (b) excess carboxyl. (c) 10/4.5 or 2.22. (d) 8/3.5 or 2.29. (e) 16/6 or 2.67.
2. See text.

Manchester Section

New polymers for emulsion paints

At a meeting held at the Manchester Literary and Philosophical Society on 2 April 1969, Mr K. Geddes of J. Ferguson & Sons Ltd. gave a lecture, "New polymers for emulsion paints", to the student members of the Section under the chairmanship of Mr J. Mitchell.

Due to the illness of Mr A. C. Fletcher, of Vinyl Products Ltd., the original lecturer, Mr Geddes was asked to stand in at short notice to deliver the lecture. He proved to be more than an able deputy and for his talk used the same title as, but not the identical subject matter of, the original lecture.

Developing his lecture, the author introduced the concept of monomer polymerisation and then discussed briefly the techniques involved in emulsion

polymerisation. Using vinyl acetate as the basic monomer, it was shown that it was possible to modify the properties of the polymerised form by the addition of a range of carefully selected co-monomers during the reaction stage. The main effect of the co-monomer was to act as an internal plasticiser for the "hard" monomer. This was demonstrated by pointing out the differences in molecular structure between the various monomers and variations in glass transition temperature of various copolymers.

By careful choice of co-monomer, it was also possible to modify the performance of the resultant copolymer and thus in turn to affect the performance of the final paint film. The effect of co-monomers on wet-scrub resistance, opacity, alkali resistance, durability, flow, and gloss, was discussed and it was concluded that it was now possible to "tailor-make" emulsions for particular outlets, *e.g.* gloss paints, systems of high PVC, *etc.* Suitable co-monomers for vinyl acetate were stated to be vinyl esters, acrylic monomers, VeoVa 10, ethylene and α -olefines.

The use of styrene/acrylic combinations to produce fine particle size emulsions for paints of high PVC was discussed. Variation in the properties of a resin emulsion was also stated to be possible by the modification of the physical characteristics of the resin emulsion. This could be achieved by varying the particle size distribution of the resin or by adopting the "hard centre/soft shell build-up technique" during the polymerisation process.

The lecture closed with an indication of the relative costs of the various systems which had been discussed. It was shown that a very low cost monomer did not necessarily mean a low cost final product due to the extremely high manufacturing charges involved.

In conclusion, it was stated that the paint manufacturer now had a wide range of resin emulsions from which to choose and ultimately it was his selection which would determine the systems which would become widely used in the next few years.

Following a short discussion period, the meeting closed with a vote of thanks proposed by Mr D. Dean.

W.I.W.

Information Received

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

Vinyl Products Limited have recently published a booklet giving advice on bulk delivery and storage of *Vinamul* and *Vinacryl* emulsions.

The booklet, "Technical Service Report GI," is based on the company's accumulated experience of handling and storing polymer emulsions in bulk, and is intended not as an engineering manual but primarily to help firms approaching the question of bulk storage for the first time. Nevertheless, all major items of equipment are covered.

A new metal decorating laboratory was opened on 31 March at the Silvertown works of **Pinchin Johnson Paints**, the Industrial Division of **The International Paint Company Limited**. The laboratory, which will have a staff of 25 chemists, is extensively equipped with facilities for application, stoving and evaluation of all types of metal decorating coatings, together with general research.

Sachtleben AG has recently issued two new leaflets on its range of white pigments and extenders. One of the leaflets describes the full range, while the other gives more specific data on the pigments and extenders for use in printing inks.

The Under 21 lawn tennis championship of Great Britain, to be held at the Didsbury club, Manchester from 11-17 August 1969, is to be sponsored by the **Anchor Chemical Company Limited**, it was recently announced.

The company, whose roots are in Manchester, and with a predominantly Mancunian board, is said to have made the gesture in order that the event will remain in the Manchester area.

A curing agent for epoxide resins, which is said to avoid the problem of skin irritation, has recently been introduced by Anchor. Known as *Ancamine LO*, the new hardener is claimed to function at low temperatures, and to be free from the strong phenolic odour associated with previous low-temperature curing agents. A primary irritation index of 0.3 was obtained from tests at the Huntingdon Research Centre.

A new water wash spraybooth, the *Maxi-Booth*, was recently demonstrated to the Press by **Mechanical Coatings Limited**. The booth is claimed to be the first major step forward in design for many years, being a compromise between the conventional type of spraybooth and the pump-less type. It has a water curtain covering the whole of the back of the booth, with wash-down sheets of white vitreous enamel. The patented design of the scrubbing chamber means that the air is washed six times before being emitted to atmosphere. It is claimed that the water level is not critical, and that maintenance is lower and servicing simpler than in other types of spraybooth.

Dynamit Nobel AG has recently issued three booklets on its products. The booklets describe, with full technical details, the *Icdal TE* range of terephthalates, *Icdal TI 40* terephthalate resin, and *Dynapol L 203* thermoplastic polyester.

A range of high density blow-moulded containers has recently been announced by **Harcostar Limited**. The containers, for which ease of handling and cheapness of "turn-round" costs are claimed as advantages over conventional containers, are available from stock as 25, 40 and 45 gallon barrels, and a 45 gallon drum. For special applications, Harcostar can make any kind of container, to the customer's requirements from 5 to 125 gallons.

Microscal Ltd. has recently issued a new application data folder giving information on the use of *Flow Microcalorimetry* for the determination of the amount and rate of adsorption. Copies of the leaflet, number DL4, are available from Microscal.

An addition to the *Microlith-K* range of pigment dispersions has recently been made by **Ciba Clayton Limited**. The new dispersion, *Microlith Brown 5R-K*, produces bright copper brown shades, and is claimed to have excellent heat, light and migration resistance, superior to other available organic brown pigment dispersions. It is recommended for use in vinyl and acrylic applications.

In order to meet the Government's Statutory Instrument 310 (Consumer Protection: The Electrical Appliances (Colour Code) Regulations 1969) which concerns changes in the standard cable colours for flexible domestic cables, and which comes into effect on 1 July 1969, **Geigy (UK) Limited** have developed pigments for the new shades, with the required electrical characteristics. In particular a new standard, *Irgachrome Brown CB'E*, has been produced for use in insulation on the positive wire. It is claimed that the pigment has characteristics which tend to improve the electrical properties of the insulation.

A new type of flooring formulation, based on a flexible *Araldite* solvent-free resin and hardener system, has been developed by **Ciba (ARL) Limited**. It is claimed that compounds of this type give seamless floors with a resilient and decorative surface finish, which are also easy to clean.

Ciba Limited, Basle, and **J. R. Geigy SA**, Basle, have recently disclosed that their respective boards have decided to examine the possibilities of a future closer collaboration within the fields of mutual interest, in order to achieve a world-wide strengthening of their position. As is known, both companies already carry on common activities in various countries.

Hythane urethane modified alkyd resins are the subject of a new booklet produced by **Plastanol Limited**. Full specifications are given, together with suggested applications and formulations.

It has been announced that, as from 1 April, **Castrol Industrial Limited** has been renamed **Burmah-Castrol Industrial Limited**, following the merger, in 1966, of the **Castrol Group** with the **Burmah Oil Company Limited**. The trading policies of the company are to remain unchanged.

The Pyrene Company Limited has recently published an up-to-date booklet on its range of derusting and degreasing preparations.

The Carborundum Company Ltd. and **Scott Bader Ltd.** have reached an agreement whereby Carborundum will take over the production and marketing of Scott Bader's *Crestalkyd* range of alkyd resins, retaining the trade name *Crestalkyd*, it was recently announced.

This range of resins for the surface coatings industries will complement Carborundum's *Vincit* range of resins and adhesives.

Wright Hargreaves Tulloch Ltd., agents for the **Rannie Machine Works Ltd.**, has recently announced that technical papers on homogenisation of fluids using *Rannie* homogenisers are now available. It is claimed that the *Rannie* machines incorporate a

unique self-grinding head system which lasts up to five times as long as conventional heads.

The latest technical bulletin issued by **Armour Hess Chemicals Limited**, "L-20/1," deals with the use of the company's products for pigment coating and flushing. Copies are available from Armour Hess on request.

To commemorate the Tenth Anniversary of the development of the *Ransburg No. 2 Process* electrostatic spray gun, the first commercial hand gun was presented to the Department of Arts and Manufacturers of the Smithsonian Institution by the **Ransburg Electro-Coating Corporation**.

It has recently been announced that the **Calmic Engineering Company Limited** has completed agreements with the **Hayward Filter Company** of California, for the sole United Kingdom manufacturing and selling rights for Hayward's range of filtration equipment.

This range, which has previously only been manufactured in the USA, comprises units of the wire-wound candle type and high velocity sand filters, of filtration areas from 7 to 522 square feet. The filters will now be entirely of British manufacture, with the exception of the candles, which are made under an exclusive patented process.

Laporte-Synres Limited has recently introduced a new resin, *Synedol 1515 UF*, for coil coating applications. Samples of the resin, a silicone modified thermosetting acrylic, are expected to be available in the near future, and introductory data and further information are available from Laporte-Synres.

Primal AC-490, a new 100 per cent acrylic emulsion designed for higher gloss emulsion paints, is now being made in Britain, announce **Lenig Chemicals Limited**. It is claimed that the product offers many advantages over the previous *Primal AC-22* based system, including higher gloss and print resistance and greater binding capacity, while maintaining excellent flow and adhesion.

An agreement for the exchange of technical information has recently been completed by **International Colloids Ltd.** and **Carbon Dispersions, Incorporated**, of New York. Both companies are engaged in the manufacture and sale of pigment dispersions for the coatings, ink, plastics and paper industries. The exchange is intended to provide both companies with the benefit of the technical advances occurring in the USA and Europe, while maintaining their independent ownership and operation.

Rentokil Laboratories Ltd. has recently announced the issuing of an Agrément Certificate for its cavity wall filling method using *Hermeseal Rockwool*. It is claimed that this is the only cavity wall filling material to hold a Certificate.

It has recently been announced that **ICI Ltd.** has been awarded the Queen's Award to Industry for the fourth consecutive year. Three Divisions, Dyestuffs, Paints and Pharmaceuticals, received the 1969 Award for technological innovation, and Dyestuffs and Pharmaceuticals also gained the Award for export achievements.

Dyestuffs Division gained the technological award for the invention and development of a new catalytic hydrogenation process used in aniline manufacture, Paints Division, cited for the first time, for technological innovation in non-aqueous polymer dispersions, and Pharmaceuticals Division for the discovery and development of drugs used in the treatment of ischaemic heart disease.

The Chemical and Allied Products Industry Training Board has recently issued "Bulletin No. 7," giving details of various important aspects of training, including training of instructional staff.

It was recently announced that, following discussions between the boards of **Monsanto Chemicals Ltd.**, **Monsanto Textiles Ltd.** and the US parent company, **Monsanto Company**, it has been decided that the world-wide development of Monsanto, particularly in the United Kingdom, would be facilitated if Monsanto Chemicals became a wholly-owned subsidiary of Monsanto, as Monsanto Textiles now is. At present the whole of Chemicals Preference capital, and one-third of its equity capital, is held by the public.

In order to achieve this change, the boards of the two British companies have submitted a Scheme of Arrangement involving the shares of both companies and Common Shares of Monsanto Company, for which it is hoped a market will develop on the London Stock Exchange.

Abrex Speciality Coatings Ltd., of Canada, has recently introduced a piece of apparatus designed to help those developing systems for electrophoretic painting methods. The *Abrex Depletor* is said to simulate exactly the bath conditions which occur on an electrophoretic production line, thus facilitating examination of the change of composition of the paint through a number of coating cycles. It is essential that this information be obtained, so that suitable feedstock can be formulated, or methods of controlling build-up of non-depositing ingredients evolved.

The *Depletor* operates by the continuous coating of a flat-faced wheel, from which the paint film is immediately removed by a doctor blade. Great savings in time and cost are claimed over previous methods, which involved coating of large areas of substrate, which were then either stripped by hand or disposed of as waste.

Section Proceedings

London

Progress in electrodeposition in Europe

The European Liaison Lecture was given on 27 March 1969 by Dr K. H. Frangen of Lackwerke Wulfing GmbH, West Germany. For the first time the lecture was held at the OCCA Exhibition at Alexandra Palace, and to mark the occasion Mr R. N. Wheeler, the Chairman of London Section, was joined on the platform by the President, Mr F. Sowerbutts, and by the Chairman of the Exhibition Committee, Mr A. W. Blenkinsop. An audience of over two hundred gathered to hear Dr Frangen's paper.

Dr Frangen said that interest in electrodeposition started about ten years ago, and five years ago the first industrial plant was installed at the Ford factory in Cologne. There had been a very rapid growth, and there were now over 400 plants in operation throughout the world. With such a new technique, practical developments were ahead of theoretical explanations, but in general baths with solids contents of 7 to 8 per cent were used, with direct current voltages of 100-300V, resulting in the use of 30-100 coulombs per gm of paint deposited. Working temperature of the baths was 25-35°C, and continuous agitation was necessary to bring the particles near to the substrate surface, and to remove the reaction products from the area near the anode. The region where electrophoresis occurred was considered to extend only 100-1,000 microns from the surface, and the diffusion gradient was working in the same direction as the electrodeposition.

He then described the reactions occurring at the anode; the main reactions were the dissolution of metal, causing coagulation of the resin, decomposition of the carboxyl groups by the Kolbe reaction, and electrolysis of water. The most important reaction was the dissolution of the metal, as was shown by the presence of iron in the coating. Dr Frangen then described the layout of typical plants, illustrated by numerous slides.

Metal preparation was an important stage, and this was followed by a rinse with demineralised water. The bath contents were circulated 2-3 times an hour, through filters and a heat exchanger. In addition there was a vigorous internal circulation in the bath, 20-30 times an hour, to prevent sedimentation. It was important to remove all of the dip coat, by rinsing with demineralised water, otherwise some of the benefits of electrodeposition were lost, and this should be done within two minutes of the material leaving the bath.

Discussing the various problems which had to be dealt with, the speaker stressed the importance of adequate pretreatment. Water drops left on the surface could lead to local dilution and hence a poor deposit, since about 90 per cent of the coat was deposited in the first 20 seconds. If for any reason the line was stopped, it was necessary to maintain a low voltage to prevent re-dissolution.

Although there were restrictions on the pigments which could be used, almost all colour shades could be produced. A one-coat aluminium paint was used successfully on automobile wheel rims. Three main types of medium were in use, phenolic resin drying oils, acrylics, and epoxy resins for primers. Dr Frangen described the methods used to control the bath stability; with daily checks on pH and solids contents, and more elaborate analytical control at central laboratories on a weekly basis. Finally, he gave some statistics on the use of electrocoating throughout the world; it was estimated that about two million square metres per day was being electrodeposited, and by far the greatest proportion of this was in the automobile industry.

Following the lecture, Messrs. A. T. S. Rudram, R. A. Oswald, J. R. Taylor, J. S. Boroky, R. H. E. Munn and P. L. Gollop took part in the discussion. A vote

of thanks for an extremely interesting and comprehensive lecture was proposed by Mr A. T. S. Rudram, who had been Chairman of London Section during the period when European Liaison lectures were first planned.

V.T.C.

Midlands

The Newton Friend Lecture: The contribution of science to design and fashion

The 1969 Newton Friend Lecture was held at Birmingham Chamber of Commerce on 21 March. The Chairman, Mr D. J. Morris, welcomed the lady visitors and introduced Mr M. W. Alford, who was to speak on "The contribution of science to design and fashion."

Mr Alford said that the natural fibres, wool, cotton, jute and silk had been used since prehistoric times. In 1664 Hooke speculated on the possibility of making synthetic fibres, but it was not until the 19th century that the first synthetic fibre, a cellulose derivative, was developed commercially. This was also the period of the colour chemists, Fischer and Perkin, and in 1884 a process for direct dyeing of cotton was developed. In 1904 the viscose process was introduced. A process for making cellulose acetate followed in 1907 but there were difficulties with dyeing and it was not until 1924 that the dispersed dyeing technique provided a method of dyeing.

Mr Alford then briefly summarised properties and applications of the wide range of synthetic fibres now available. These included acetate, acrylics, alginates, carbon fibres, elastofibres, glass fibres, metal fibres, nylons, polyesters, polypropylene and polyethylene, rayons, triacetate and tricelcon.

The fibres were processed as spun yarns for suits, as filaments for dresses, as textured filaments for knitwear or as speciality filaments for crinkle finishes and similar effects. Fabrics could be woven, knitted, nets, or felts, and nowadays many machines were able to combine these processes. Modern machines were capable of processing 40 to 120 yards per hour in double width of six feet.

A film entitled "Palettes of fashion" was then shown. Besides showing in a whimsical manner some of the striking colours available with synthetic fibres, there was a diagrammatic explanation of the processing of Trevira polyester.

During the discussion period Mr Alford and Miss A. Stein answered a number of questions, mainly from the lady visitors. Mr D. J. Silsby proposed a vote of thanks.

L.R.S.

Trent Valley Branch

Plastic coatings—techniques and recent developments

The fourth technical meeting of the Trent Valley Branch, held at Loughborough University on Thursday 27 February 1969, incorporated a lecture entitled "Plastic coatings—techniques and recent developments," by Mr E. R. Westmore of Aquitaine-Fisons Ltd.

Powder coating, when used for corrosion prevention, had the advantage over paints of being a solvent-free system with versatility, powder recovery, adaptability to automation and coating thickness control, said Mr Westmore. Polyethylene was first used for this application in 1948, as subsequently, after 1956, were cellulose acetate butyrate, polyvinylchloride and polyamide (Nylon 11). Use of epoxy powders, polyamide (Nylon 12) and chlorinated polyether (Penton) had followed since 1960.

For maximum chemical resistance, articles should be shot-blasted and coated with a conventional solvent-based epoxy primer followed by the powder coating.

Application methods for powders were flame spraying, electrostatic spraying and fluidised bed dipping; the latter was illustrated with colour slides showing industrial operational uses. Flame spraying, used for heavy industrial castings, was considered operator sensitive, and 15 thou was the usual minimum film thickness. Electrostatic projection, whereby the powder was given a strong negative electrical charge, gave coating thicknesses between 10 and 20 thou. The powder had sufficient cohesion to the surface to allow for curing on stoving.

Preheating gave heavier build. Since nylon powders were positively charged, a method of positive electrostatic projection was being developed. Epoxy powders also responded favourably to positive projection.

Mr Westmore, assisted by Mr Cunliffe, demonstrated a fluidised bed, which comprised a 1cu ft tank fitted with a porous base (9in square), containing a pale blue nylon powder. The large volume of air at low pressure required to pass through the base to "activate" the powder was amply provided by an ordinary cylinder type vacuum cleaner operated from the blower end. Objects preheated in an oven were immersed in the powder and gave a satisfactory coating. Quenching in water gave a gloss finish, cooling in air gave a matt finish.

After the demonstration, members of the audience were able to examine many objects from an industrial selection. Numerous questions were raised, among which were: comparative cost of powder coating against chrome plating and the durability against vitreous enamel.

Mr H. F. Clay thanked Mr Westmore for an interesting paper and demonstration, congratulated the committee on choice and the Chairman for keeping quiet.

Twelve members and eight visitors attended.

J.R.B.

Scottish

Acrylic resins

The last technical meeting of the current season for the Scottish Section was held on 13 March in the Whitehall Restaurant, Glasgow, and was addressed by Messrs. R. H. E. Munn and A. R. H. Tawn of Cray Valley Products Ltd., who chose as their subject "Acrylic resins."

Mr Tawn spoke first on the principles underlying acrylic polymer design. Acrylic resins were derived from alkyl acrylates or methacrylates, polymerised usually by free radical methods in solution or emulsion; copolymerisation was straightforward both with different acrylic monomers and with styrene. The relationship with vinyl polymers was close, the main carbon-carbon chain being similar, but in the acrylics the pendant groups were acid derivatives such as $-\text{COOH}$, $-\text{COOR}$, $-\text{CONRR}'$, $-\text{CN}$, $-\text{CHO}$, $-\text{COCl}$, which offered a wide range of chemical reactions for exploitation in curing by cross-linking. The chemical stability of acrylic polymers was ascribed to the non-hydrolysable nature of the main chain composed of C-C covalent bonds, combined with the low reactivity of the pendant ester groups. This conferred both high resistance to chemical attack and to discoloration on exposure.

Mr Tawn then considered likely future developments in acrylics. He predicted that costs relative to alkyd/MF resins would fall as a result of the high labour content of the latter and economies of scale resulting from capacity increases planned for acrylics and related materials. Over the next three years, the European installed capacity for acrylic monomers would increase by 620,000 metric tons per annum, and while this would not all be for coating use, its effect on price levels would be significant.

Chemical modifications at present under development included allyl derivatives where the unsaturated side chain gave air drying without discoloration, epoxy derivatives which had already led to cold curing resins for space research, and a two-pot acrylic system with polyisocyanate. In the thermoplastic field, increased understanding of factors influencing solubility had enabled resins soluble in ethanol for packaging inks to be prepared, and had also made cold compatibility of acrylic with alkyd resins possible. A number of other developments were described by Mr Tawn, including reactions with chlorosilanes to give outstanding durability, with amino-anthraquinone to give a "self-coloured" resin, with phosphoric acid to give flame retardance, and the introduction of ionic groups for use in electrodeposition methods.

He then went on to discuss block and graft copolymers and described a technique for their unambiguous preparation, starting from a polymer containing one or more reducible groups. After treatment with a salt of cerium this provided precisely located free radicals for the formation and attachment of new polymer chains without the possibility of unwanted homopolymerisation. The "comb" and "ladder" types of graft polymer were described, the former having side chains all of equal length while the latter consisted of two parallel chains rigidly cross linked at many points. The "ladder" polymers could be extended in two dimensions to give a "sheet" polymer which, on aromatisation, gave rise to a graphite-like structure, with high stability but low solubility. Stereospecific polymerisation had been achieved by the use of an asymmetric solvent. Mr Tawn concluded by mentioning ionomers, where cross-linking was by ionic bonds, and whose ceramic-like properties could open up a whole new field to coating technologists.

Mr Munn then reviewed the performance of existing acrylic resins in various applications, dealing first with thermoplastic types. The achievement of alkyd compatibility had led to acrylic modified alkyds which had improved hardness, exterior gloss retention and drying times over earlier types. Illustrations showed the proportionate improvement with increasing acrylic content. Acrylic resins were now tailor-made with appropriate properties for such applications as mastics and sealants, lacquers for metallised plastics, and inks for high speed printing of plastic films. Acrylics also found use in modern labour-saving polishes, where specific stripping properties (e.g. by ammonia) could be built in. Wood primers based on acrylic emulsions were exposure resistant to such an extent that they could be undercoated and finished after six months exterior exposure.

Turning to thermosetting resins, Mr Munn classified these according to the cross-linking mechanism employed—*via* acrylamide, hydroxy or acid groups. Polymers in the acrylamide group were self cross-linked at curing temperatures around 150°C, their chemical resistance was outstanding, and was combined with good gloss retention and mechanical properties. The hydroxy group was usually cross-linked with amine resins at conveniently low curing temperatures (80-120°C) to give coatings of excellent gloss retention but with chemical and mechanical properties inferior to the other groups. The acid group, cross-linked with epoxy resins at the relatively high temperature of 180°C, showed the best mechanical properties, good chemical resistance, but less satisfactory gloss retention.

Acrylics for automotive finishes had originally been of the acrylamide type, used to modify alkyds, but it was now commoner to use a straight hydroxy-type acrylic, melamine cross-linked, which was especially suitable for metallic finishes. This was the main field of use of the hydroxy types, which were notable for the ease with which imperfections could be polished out and their suitability for the modern "bake-sand-bake" or reflow processes. A wide tolerance of reflow temperatures from 80 to 100°C and sufficient hardness to permit sanding before reflow were required. Acrylamide types now found their chief outlet in the finishing of domestic appliances, where their high chemical and stain resistance was required. Few acid types were in commercial

use at present but their excellent mechanical properties would probably lead to their increased use in the field of strip pre-painting.

Mr Munn then described and illustrated the properties of cold-cure acrylics which were approaching commercial development. Their stable carbon chain backbone meant that comparatively little cross-linking was needed for chemical stability, so that mechanical properties remained unimpaired. Their colour retention was better than that of conventional systems. Cross-linking was by aliphatic or aromatic isocyanates, the former giving better durability and colour, while the latter gave lower cost; the acrylic resin had to be designed for use with the intended curing agent. He closed by touching on water-soluble thermosetting systems, which had good potential for electrodeposition in the motor industry. Colourless finish, good mechanical properties and ease of application directly to steel surfaces were required here, and it was felt that developments in this field were likely soon.

In discussion after the lecture, the speakers expanded on various points raised. The problem of odour in food packaging inks was partly one of solvent release, partly of monomer residues, and partly of polymer degradation if very high sealing temperatures were used; attention to all of these was necessary. The high exposure resistance of acrylic wood primers arose from chemical stability which preserved the integrity of the film. The cold-curing acrylic polymerised with aromatic isocyanate showed poorer colour retention than that with aliphatic isocyanate because coloured aromatic decomposition products arose in the former case. Cold curing took place at temperatures as low as 6°C, but the lower limit had not been determined.

The meeting closed with an enthusiastic vote of thanks to the speakers, proposed by Mr G. Hutchinson.

J.D.E.

Eastern Branch

Spray application of surface coatings

The fourth ordinary meeting of the Session, with Mr G. H. Hutchinson in the chair, was held in the Wee Windaes Restaurant, Edinburgh, on Wednesday 22 January, when Mr D. I. Muirhead, of Wm. Sim & Sons (Paints) Ltd., spoke on "Spray application of surface coatings."

Mr Muirhead described the various types of spraying equipment used at the present time. During his talk he made reference to the many examples of spraying equipment he had brought with him.

Conventional spraying

This method used a conventional spray gun coupled to compressed air at a pressure of 50-80lb per sq in. The spray guns were of four types: suction cup, pressure cup, pressure pot and gravity cup. In practice this was the most common method of spraying. The equipment was easy to transport and handle, but as the paint viscosity must be very low, the method had the drawback of not giving a very high film build.

Airless spraying

In this method a hydraulic system built up the compressed air pressure from 80lb per sq in to 2,000lb per sq in. This allowed higher viscosity paints to be used and therefore gave higher film builds.

Hot airless spraying

The principle of this method was the same as the previous system, except that the paint was heated to 180°F. This allowed even higher film builds, up to 1/32in.

Electrostatic spraying

This was the most efficient method of spraying (up to 80 per cent of the paint was deposited on the article being sprayed). The most common equipment was the Ransburg gun, which was bell shaped and charged the paint particles at 100-150 thousand volts.

Hot spraying

This method made use of conventional spray equipment but higher film builds were possible because, as the paint was hot, a higher solid content could be obtained at spraying viscosity.

Low pressure hot spraying

This method was another adaptation of conventional spraying, but allowed the use of compressed air at lower pressures to give the same performance.

Mr Muirhead also briefly described steam spraying (used in USA), automatic spraying (for articles on a conveyor belt), and multiple head spray guns (for fibreglass). Finally he discussed spraying faults. There were four main faults: misting, dusting, orange peel, and pinholing.

After a lively question period, Mr C. Cochrane proposed the vote of thanks.

J.H.S.

Thames Valley

Recent developments in the field of polyurethane finishes

The above lecture, by Dr Blomeyer, of Farbenfabriken Bayer AG, was given before a large audience at the Royal White Hart Hotel, Beaconsfield, on Tuesday 18 February.

The speaker began by outlining early developments in the industry and stressing how the considerable advances were made possible by the development of reaction products of toluene diisocyanate (TDI) which overcame its deficiencies of high vapour pressure and toxicity. The main part of the lecture consisted of a description of these main reaction products and an outline of their possible combinations with polyols, polyoxy compounds and so on.

Polyisocyanate 1 was the reaction product of TDI with triols. It might be used with a number of polyoxy compounds such as polyalcohols, polyether alcohols, epoxy resins, alkyds and silicone resins. The resulting combinations were either one-pack moisture curing or two-pack systems. Generally, they did not give good colour or gloss retention on exposure, although their rate of erosion was very slow.

Polyisocyanate 2 was the reaction product of hexamethylene diisocyanate (HMDI) with water. Its merit was excellent gloss retention, provided certain polyester alcohols (derived from phthalic acid) or certain acrylic resins with pendant hydroxy groups, were used. It was interesting to note that the maximum film life on exposure had not yet been established, since exposures in Central Europe were still continuing after eight years.

Polyisocyanate 3 performed a useful function where rapid speed of drying in the combination was important. It was a polymerisation product of TDI. Extremely fast drying combinations with polyester alcohols and alkyds could be evolved because of the high functionality of polyisocyanate 3.

Polyisocyanate 4 was a reaction product of TDI and HMDI. It enabled fast drying finishes to be formulated with good resistance to light and weathering, which were particularly suitable where corrosion resistance was required.

Polyisocyanate 5 was a preformed polymer of TDI and a high molecular weight divalent alcohol, and it offered extremely rubber-like films which were elastic enough to bridge the gaps that formed in concrete.

This concluded the description of the numbered products, but Dr Blomeyer reminded the audience that stoving electrical insulating varnishes could be formulated using phenol blocked isocyanates, and also described other media that could benefit from the presence of isocyanates, e.g. N/C finishes containing polyoxy compounds had their mechanical properties and gloss improved by the addition of about 10 per cent of polyisocyanate 2.

Moisture curing systems containing free isocyanate were described. He pointed out that they had unsurpassed abrasion resistance and good resistance to alcohol, water and solvents. Their pigmented forms presented problems owing to the presence of moisture in the pigments. This moisture could be effectively removed by the introduction of monoisocyanates to the formula together with auxiliary B, whose composition was not disclosed.

Finally Dr Blomeyer outlined some of the principles involved in the formulation of polyurethane/tar one-pack compositions which could completely harden at temperatures as low as 0°C.

Throughout the lecture Dr Blomeyer interspersed his material with slides which classified very well the chemistry of polyisocyanates and their reaction products. He also showed colour slides of various forms of transport which pointed to the excellent outdoor life of polyurethanes.

The vote of thanks was given by Committee Member Mr D. Horne.

R.E.G.

West Riding

Solubility parameters and other solvent topics

At a meeting of the West Riding Section on 14 January 1969, Mr C. J. Nunn, of Shell Research Ltd., gave a lecture with the above title.

In opening his lecture Mr Nunn commented that the title was rather a misnomer, as he was going to refer to only one other solvent topic, that of solvent retention, but he would do his best to answer any questions touching on other aspects relating to solvents which might be put to him after the lecture.

His first topic, solubility parameters, he divided into two parts. In the first of these he reviewed briefly those papers previously published on the subject; the second part was devoted to examples of applications of the solubility parameter approach to actual problems encountered in the surface coatings industry, thus giving an idea of the usefulness of the technique.

Several charts were used in the course of the lecture, e.g. to illustrate a few representative resins in increasing order of polarity, to show solubility parameters for the swelling of individual resins in ranges of solvents, and to compare solubility data obtained using only the Hildebrand parameter both with that obtained using the Burrell system which incorporated hydrogen bonding as an additional parameter, and with the later system incorporating dipole moment. Mr Nunn then went on to discuss the most recent modification by Hansen who, in the last year or so, had tackled the subject from perhaps a more satisfactory theoretical viewpoint. Hansen had reasoned that it would be more logical not to use a constant which referred to all three types of intermolecular force and then arbitrarily select two, but rather to select three parameters which were measures of each of these forces and which were then

correlated to give a total parameter, *i.e.* the parameter measuring polar forces δ_P , that which measures hydrogen bonding forces δ_H , and the parameter measuring dispersion forces δ_D .

Epoxy resins were a very suitable subject for calculations based on solubility parameters, since there was a wide range of solvents which were marginal in their solvency for epoxy resins, in that they would dissolve epoxy resins only to a certain minimum concentration and below this the resin would "kick out." Mr Nunn gave a few examples of the application of solubility parameters in determining optimum solvent blends.

For nitrocellulose there was much information available on limiting blends, *i.e.* dilution ratio data. As specific examples he selected methyl ethyl ketone and ethyl acetate, and as diluents an aromatic, toluene and an aliphatic, heptane. Here one could check not only the precise figures for the limiting blends, but also the rather strange reversal effect. While MEK had a much higher dilution ratio than ethyl acetate when toluene was the diluent, when one switched to a pure aliphatic the reverse was the case and the MEK solution precipitated the nitrocellulose first.

On solvent retention, Mr Nunn remarked that this subject had shown increasing importance in recent years in the fields of paint and printing ink. There was currently no generally accepted theory of solvent retention but it seemed that factors additional to solvent volatility and molecular shape were involved and the subject could well be linked with solubility parameters in that a good solvent for a particular resin would tend to remain with it when the film dried.

In the discussion which followed questions were submitted by Messrs McKean, M. J. Cochrane, Silver, Hargreaves, Gray, DuRieu, Smith and Milne, and Mr D. R. Gray proposed the vote of thanks, stressing that the thanks of the listeners should be threefold for they had been treated to three papers in one.

J. N. MCK.

Protective action of paint on metals

To one of the largest attendances of the Session 1968-9, on 11 February, Dr J. E. O. Mayne, of Vinyl Products Ltd., gave a very interesting and extremely lucid exposition on the physico-chemical factors involved in the electronic protection of metallic surfaces by metal-rich paints. Dr Mayne did not confine himself to the traditional metallic zinc approach but also covered the effects of using aluminium and lead as well as stainless steel on the appropriate substrates.

Despite the oppressive atmosphere of a hot and overcrowded room, he held the attention of all his listeners and the lively discussion period which followed took almost as long as the lecture itself. Contributors to the discussion were Messrs Duligal, Cochrane, DuRieu, T. R. Smith, and Gray. Since the new and original work discussed in the paper was the basis of a student's thesis for his doctorate, Dr Mayne regretted that he could not as yet provide a complete paper for consideration for publication but said that the Section's interest would be borne in mind.

The vote of thanks was proposed by Mr J. N. McKean.

J. N. MCK.

Manchester Section

Symposium: Recent advances in water-borne coatings

A symposium (1½ days) entitled "Recent advances in water-borne coatings" will be held at the University of Manchester Institute of Science and Technology on 24-25 September 1969. The meeting is being organised by the Manchester Section.

The technical programme will be divided into two related sections covering:

- (1) Emulsion-based coatings, with emphasis on new media;
- (2) Water-soluble/dispersed systems.

Some 12 papers will be given by

authors from UK, Western Europe and USA.

Specific lectures will deal with new copolymer media, gloss water paints, polyurethane ionomers and developments in electrodeposited coatings.

Advance information on the programme and arrangements for the symposium, including accommodation, may be obtained from:

C. Barker, Manchester Section OCCA,
c/o AR.TS Department,
ICI Ltd., Dyestuffs Division,
Hexagon House,
Blackley,
MANCHESTER M9 3DA.

News of Members

Mr W. Woodhall, an Ordinary Member attached to the London Section, has been appointed Vice-Chairman of the Board of Laporte Industries (Holdings) Ltd., and Adviser on Planning.

Mr A. G. Collings, an Ordinary Member attached to the London Section, has recently been appointed Scientific Adviser to London Transport Board. Mr Collings, who was previously Assistant Director of Research for London Transport, attained this position on the retirement of the previous Director of Research, the post being redesignated to denote its wider responsibilities.

Mr F. Lewis, an Ordinary Member attached to the Manchester Section, has recently been appointed Deputy Managing Director of Colour and Adhesives Ltd.

Mr P. D. Sutcliffe, an Associate Member attached to the West Riding Section, has recently taken over as Sales Manager of the Chemical Division of Nopco Hess Limited, following the dividing of the company's selling activities into Chemical and Textile Divisions.

FSPT Semi-Annual Index to Coatings Literature

The Federation of Societies for Paint Technology is to publish the Semi-Annual Index to Coatings Literature, a reference volume which presents a consolidated view of the latest six months of technical literature collected from about 100 periodicals. Articles relating to development, manufacturing and testing of organic coatings will be covered.

The Index will be published in January and July each year, at an annual subscription of \$50.00. The first issue is now available, covering the period July to December 1968, and contains 64 pages.

Courses at the Borough Polytechnic, SE1

6 June. One-day seminar, The physical chemistry of surface coatings, Part 3: "Physicochemical principles of electro-deposition."

9-10 June. "Principles of surface coatings technology," a short, intensive course for representatives and newcomers to the industry.

30 June-2 July. "Summer school in paint analysis"; an intensive course with practical work, the accent being on modern methods.

A. H. Whitaker—An appreciation

H. N. writes—I first met A. H. W. on the rugger fields of the West Riding, and later, when he moved from Huddersfield via London to Glasgow. He had taken part in the very active Manchester Section of OCCA and was determined to provide Scotland with a similar section. This was in 1934. I recall our first Chairman, J. A. Wilson; John Crombie, James Milligan, N. V. Crossley, James Bruce, D. B. F. MacAndrew, F. O. Holmes and myself were members of the first committee. Whitaker, as secretary, was the driving force behind this new section and he made a great success of it, both from a technical and social aspect.

At this time he had joined James Anderson and Co. (Colours) Ltd., of Glasgow, a small pigment manufacturer which he built up under extremely difficult conditions, at the factory in Florence Street, to a sizeable business. Although regarded by his subordinates as a stern disciplinarian, it was notable that he would go to considerable pains to help them if in personal trouble. Later Anderson was taken over by the Geigy Co. and this gave A. H. W. a great

deal more scope. This business is now probably the largest organic pigment manufacturer in the country. A. H. W. was an extremely pleasant and stimulating companion and a very able and competent technologist and administrator, who certainly contributed a great deal to the organic pigment industry of this country.

Joint Conference 1970

The Institution of the Rubber Industry in conjunction with the Plastics Institute, The Society of Chemical Industry (Plastics & Polymer Group), The Oil and Colour Chemists' Association and The Society of Dyers and Colourists are organising a conference on "Advances in polymer science and technology No. 3: Chemistry of liquid and thermoplastic copolymers". This is to be held on 29 September-1 October 1970 at the Institution of Electrical Engineers, London, and offers of papers and synopses are required by **30 June 1969**.

Further details are obtainable from the Secretary, The Institution of the Rubber Industry, 4 Kensington Palace Gardens, London, W.8 (Telephone: 01-229 9101).

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

DOHERTY, LIONEL F. M., Triton Chemicals, PO Box 78, New Germany, Natal, South Africa. *(South African)*

JACKSON, WALTER, AIRI, c/o Geigy South Africa (Pty.) Ltd., PO Box 829, Johannesburg, South Africa. *(South African)*

SMITH, PETER BARRIE, ICI (South Africa) Ltd., 1 Leyds Street, PO Box 11270, Braamfontein, Johannesburg, South Africa. *(South African)*

TAYLOR, ALAN PHILLIP, BSc, 33 Glen Road, Ranmati South, New Zealand. *(Wellington)*

Associate Member

KAYE, ANTHONY PHILIP, Plascon Paint and Chemicals Industries, PO Box 10, Luipaardsalei, Transvaal, South Africa. *(South African)*

Forthcoming Events

Details are given of meetings in the United Kingdom up to the end of the month following publication, and in South Africa and the Commonwealth up to the end of the second month where available.

Tuesday 17 June-Saturday 21 June

Association Biennial Conference, to be held at The Grand Hotel, Eastbourne, "Film Formation and Curing."

Saturday 21 June

Newcastle Section: Annual Golf Match for the British Titan Cup, to be held at Brancepeth, Co. Durham.

Friday 20 June

Annual General Meeting. To be held at the Grand Hotel Eastbourne.

Oil and Colour Chemists' Association

President : F. SOWERBUTTS, B.SC.TECH.

The Oil and Colour Chemists' Association was formed in 1918, to cover paint, printing inks, pigments, varnishes, drying and essential oils, resins, lacquers, soaps, linoleum and treated fabrics, and the plant, apparatus and raw materials useful in their manufacture. In 1924 it absorbed the Paint and Varnish Society. The stated purpose of the Association is to promote by discussion and scientific investigation the technology of the industries concerned with the above-mentioned products, and to afford members opportunity for the interchange of ideas. This is achieved by the regular holding of ordinary meetings at which papers are presented, and the organisation of annual technical exhibitions, biennial conferences, educational activities and practical co-operative experimental work. Details of these activities are given in the *Journal of the Oil and Colour Chemists' Association*, which is published monthly, and whose pages are open to receive communications and other pronouncements on scientific and technical matters affecting the members of the Association and the industries concerned. The Association's meetings also afford opportunities for members to meet informally and socially.

There are Sections of OCCA in Auckland, Bristol, Hull, Ireland, London, Manchester, the Midlands (with a Trent Valley Branch), Newcastle upon Tyne, Scotland (with an Eastern Branch), South Africa (with Branches in the Cape, Transvaal and Natal), Thames Valley, Wellington, 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).

The five Sections previously maintained by the Association in Australia formed (1.1.68) the Oil and Colour Chemists' Association Australia, having the same aims and activities as, and working in close liaison with, the parent body.

Ordinary Membership is granted to scientifically trained persons, and Associate Membership to others interested in the industries covered. Student 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 five guineas, except for Student Members whose subscription is one guinea. 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 Director & 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 with additional chapter). Pp. 187, illustrated, with index, £1 (including postage).

Paint Technology Manuals

Part 1 : " Non-convertible Coatings," Second Edition, Pp. 343, 36s.

Part 2 : " Solvents, Oils, Resins and Driers," Second Edition, Pp. 268, 36s.

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

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

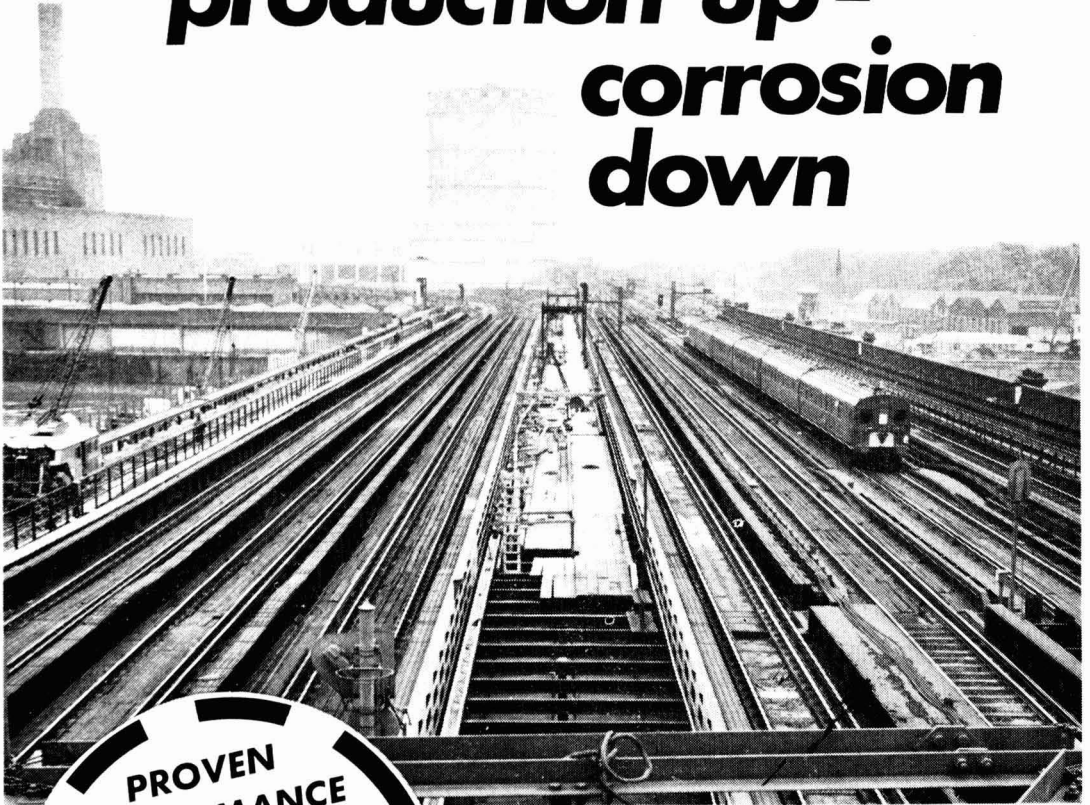
Part 5 : " The Testing of Paints," Pp. 196, 35s.

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

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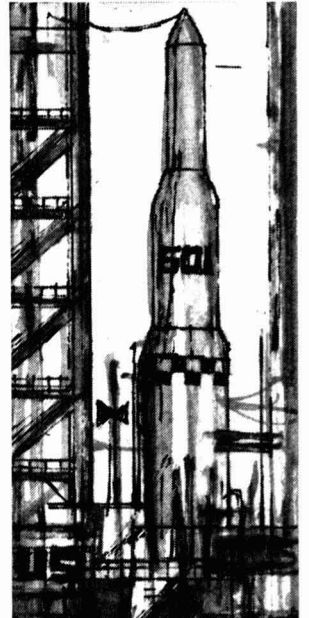
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Five day week and leave allowance starting at 3 weeks, 3 days (A.E.O.) and 4 weeks 2 days (E.O.) in addition to the usual public holidays.

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Further information and application forms on telephone or written request from:

**Scientific Personnel Officer,
Chemical Inspectorate (Ministry of Defence),
Headquarters Building,
Royal Arsenal East,
Woolwich,
London, SE18
Phone: 01-854 4261 Extension 55**

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The Secretary, PIRA, Randalls Road, Leatherhead, Surrey, quoting ref: PR/CH/269.

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

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Well known Paint Manufacturers situated in the Midlands wish to appoint a Representative to develop their existing business in the north Midlands and northern counties. This is a new appointment and the applicant will be resident on the territory and have considerable experience in selling industrial finishes to substantial users in the automotive, electrical and light engineering industries. The Company operates a brand new plant and "our man" will receive more than adequate support from a versatile and enthusiastic team. Write to: Thomas Howse Ltd., P.O. Box No. 57, Cakemore Road, Rowley Regis, Warley, Worcs.

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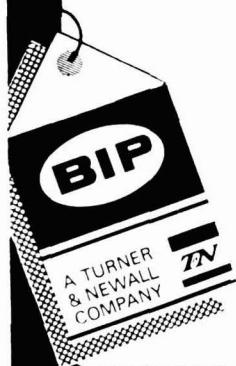
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Personnel Manager,
BIP Chemicals Ltd., Popes Lane,
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121 South Broad Street, Philadelphia, Pennsylvania 19107, USA**

