# JOURNAL

OF THE

# OIL AND COLOUR CHEMISTS' ASSOCIATION

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WAX CHANDLERS' HALL,
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# introduction to paint technology

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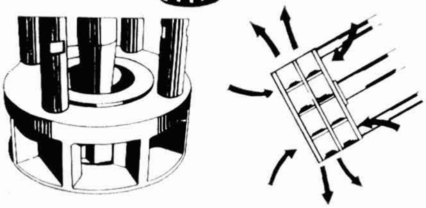

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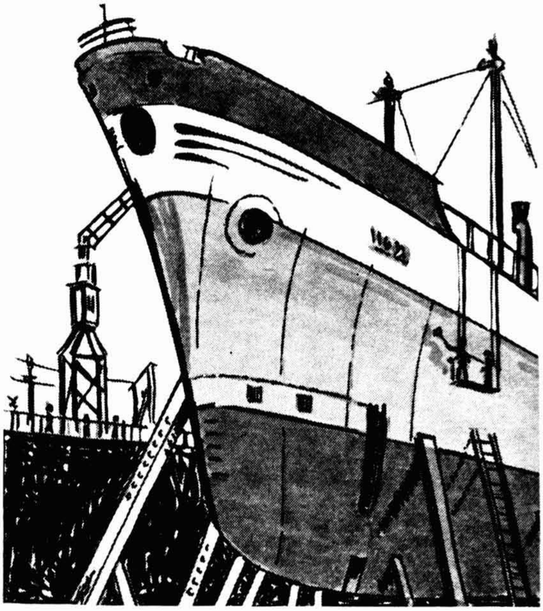

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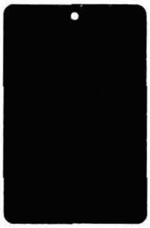

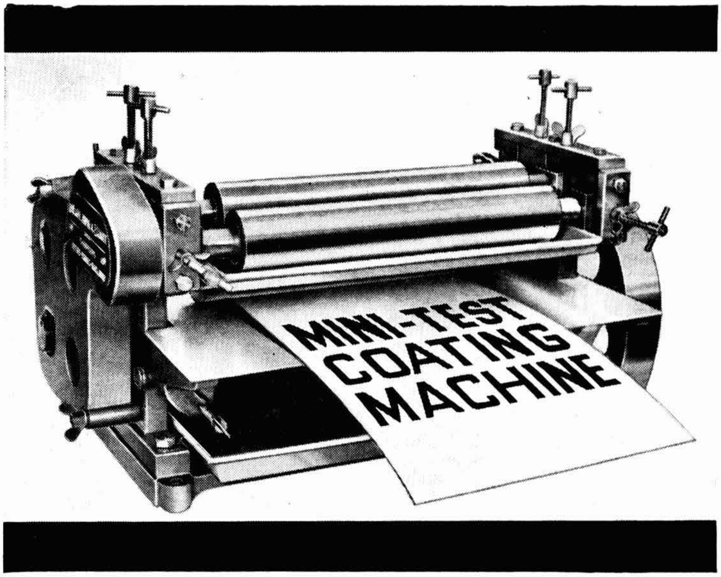
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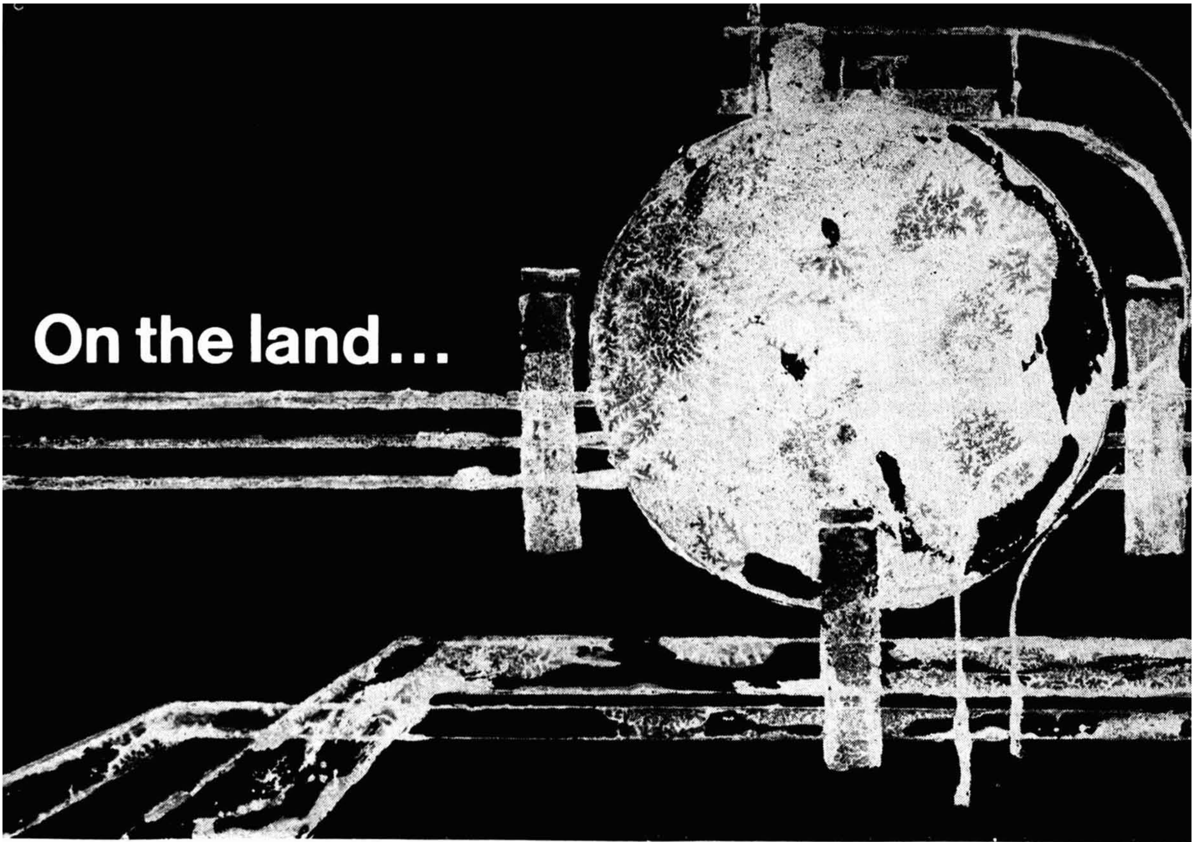

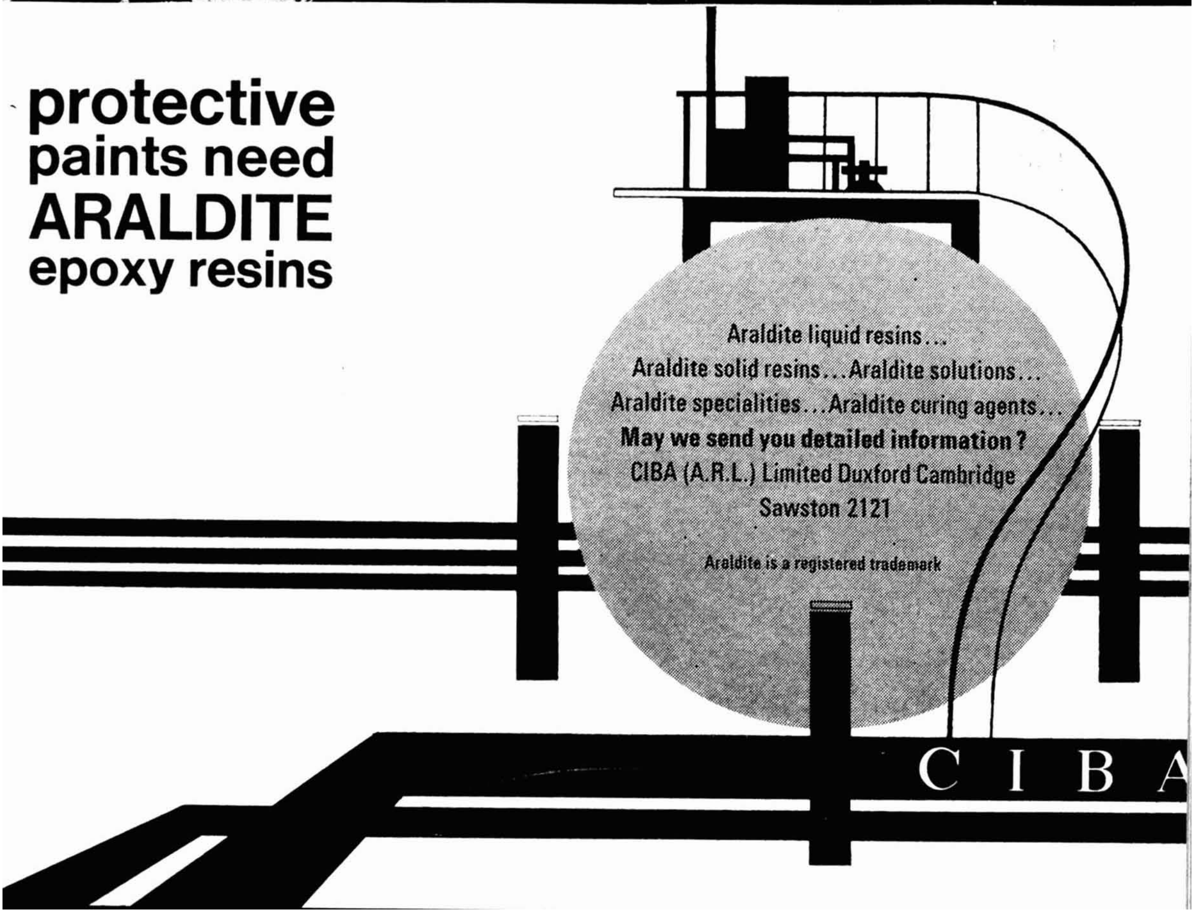

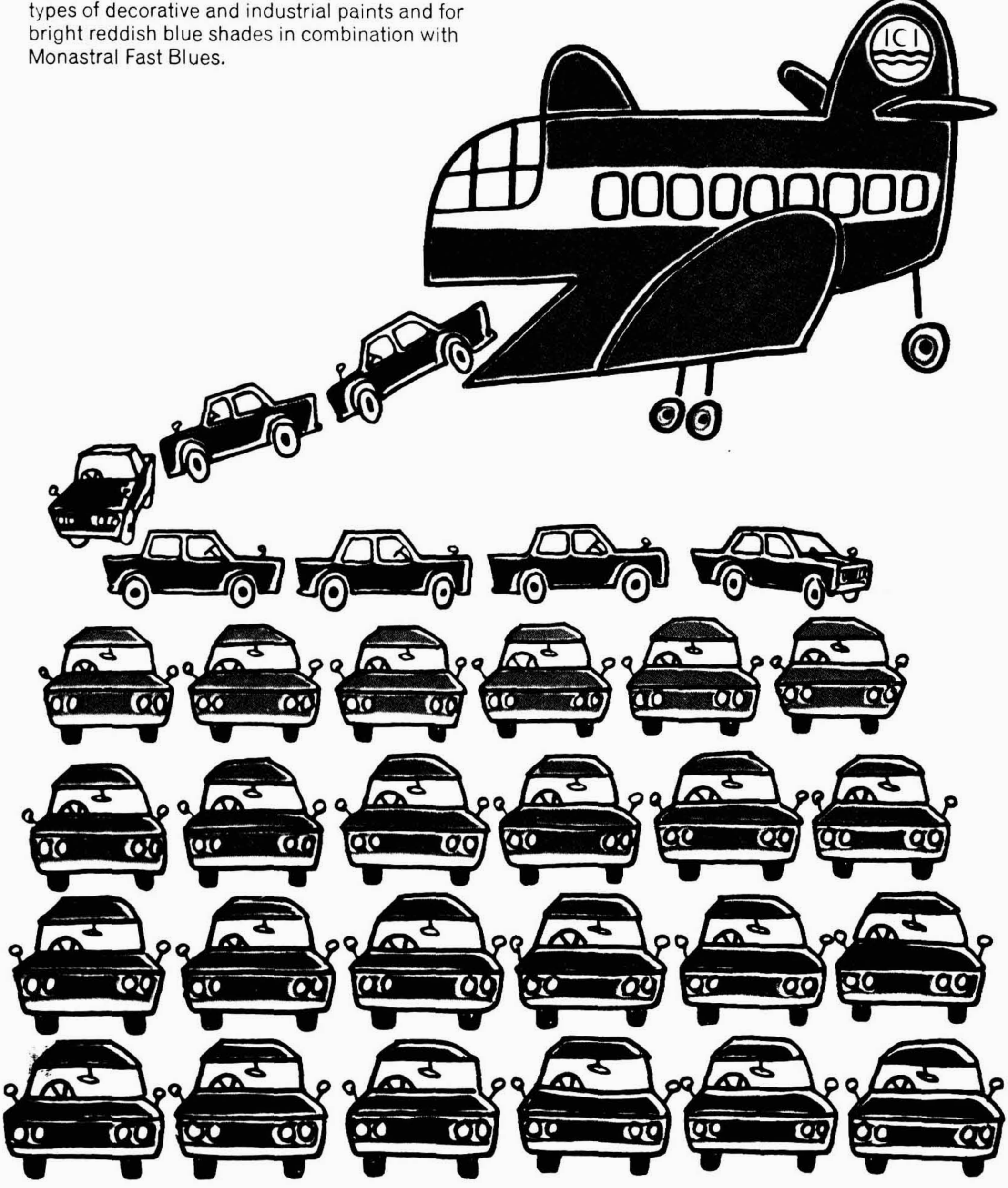
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Editorial correspondence should be addressed to the Hon. Editor, *JOCCA*, Cray Valley Products Ltd., St. Mary Cray, Kent.

General correspondence should be addressed to :

R. H. Hamblin, M.A., F.C.I.S., F.C.C.S.,
Director & Secretary,
Oil & Colour Chemists' Association,
Wax Chandlers' Hall, Gresham Street,
London, E.C.2. (Tel. : 01-606 1439)

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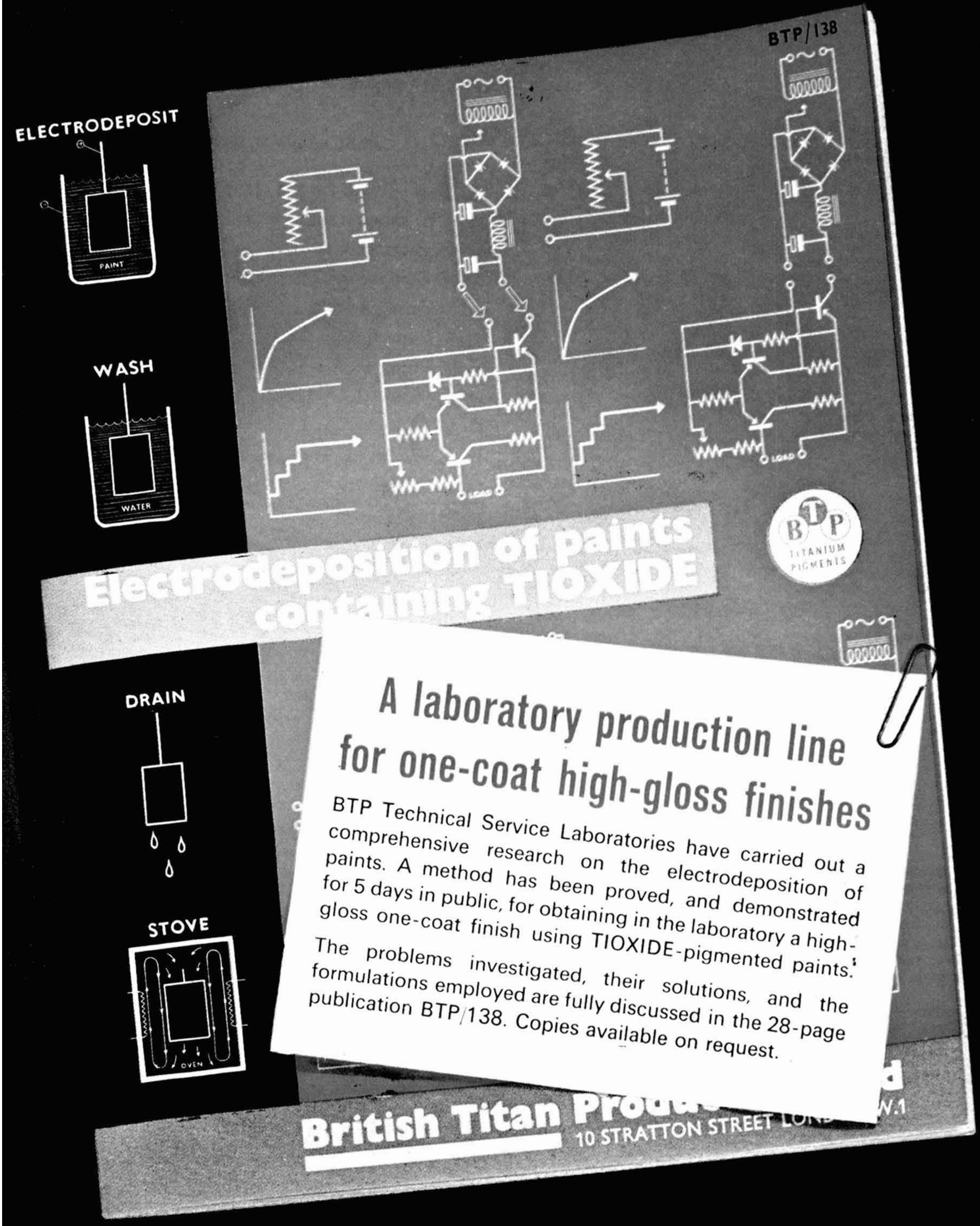

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*Transactions and communications*

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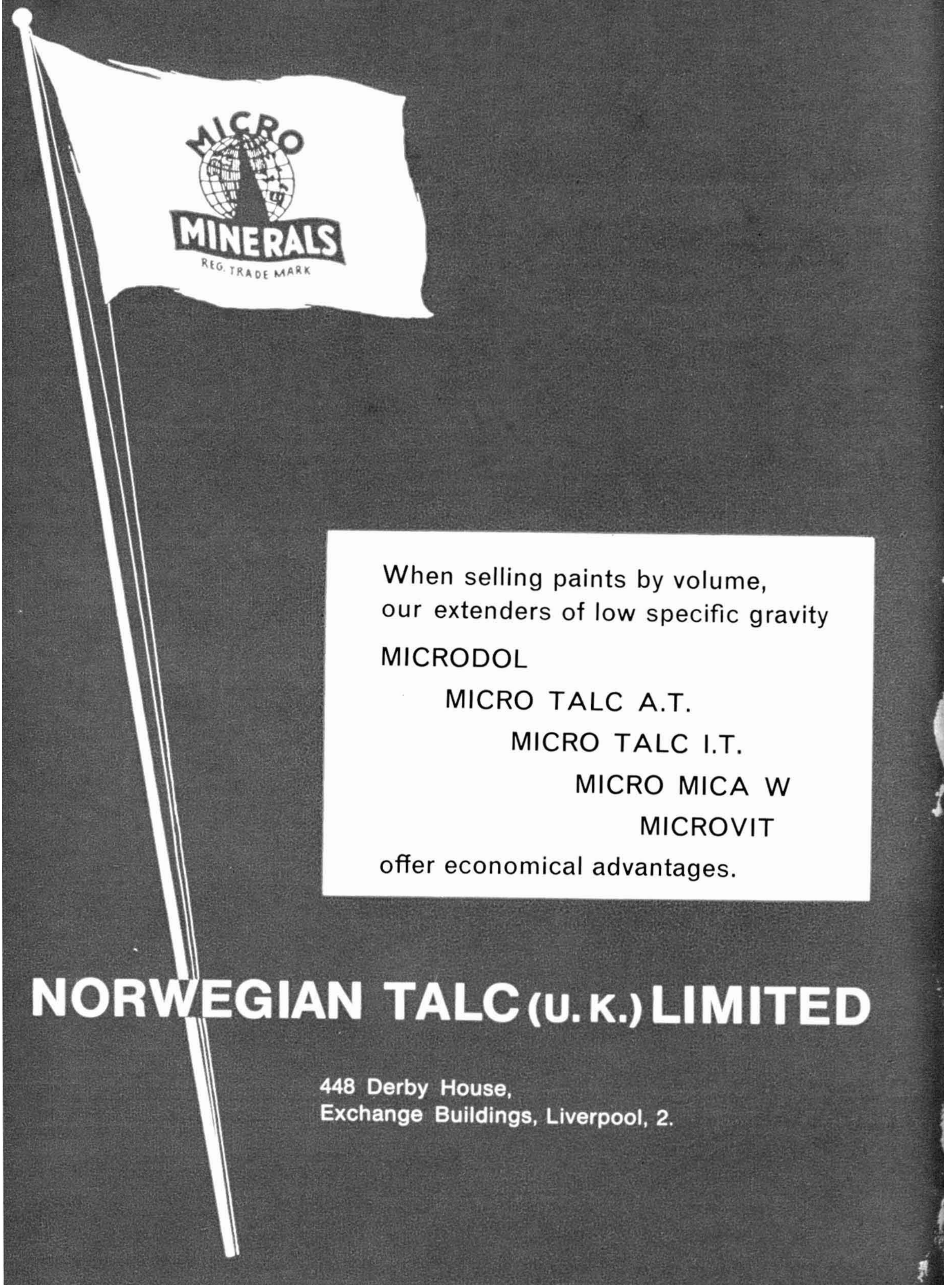
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*J. Oil Col. Chem. Assoc.* 1968, **51**, 287-304

## *Transactions and Communications*

# Some features of ship painting

**By P. J. Gay**

Hangers Paint Ltd., Stoneferry Works, Hull

*Summary*

A number of features of impact cleaned surfaces are considered, with particular reference to their influence on the performance of paint coatings. The energy aspects of impact cleaning are analysed and the differences between impeller and air blast processes outlined, and an attempt is made to relate impact energies with surface texture. Similarly the mechanical aspects of spray application are discussed. The much greater impact velocity in airless spraying compared with compressed air spraying is demonstrated and the serious effects of tip wear are emphasised. It is shown that in the combined automatic blasting and spray priming of ship plate, the speed of the plate in relation to rate of traverse of the gun and fan width is critical.

The second part of the paper outlines a number of features which influence fouling and draws attention to the effect of changing patterns of shipping and the local warming of port waters. Considerations of the chemistry of sea water and of copper compounds at high dilution indicate the inadequacies of a simple leaching theory of antifouling action of copper based compositions.

## Quelques aspects de la peinture maritime

*Résumé*

On considère plusieurs caractéristiques des surfaces nettoyées par impact à l'égard particulier à leur influence sur le rendement des revêtements de peinture. On fait une analyse des aspects de l'énergie de nettoyage par impact et l'on décrit brièvement les différences entre les procédés se servant des courants d'air et ceux aux couronnes mobiles. On essaie de relier l'énergie d'impact à la texture superficielle. De même manière on discute les aspects mécaniques de pistolage. On démontre que le pistolage " airless " provoque une vitesse d'impact beaucoup plus élevée en comparaison du pistolage par air comprimé et l'on appuie sur les effets graves en provenance de l'usure des bouts du pistolet. Dans les procédés combinés et automatiques de sablage avec de peinture, on démontre que la vitesse de trajet de la tôle par rapport à la vitesse transversale du pistolet et également à la largeur de l'éventail est tout à fait critique.

Dans la deuzième partie de l'exposé on trace les grandes lignes du plusieurs caractéristiques qui exercent une influence sur la croissance des salissures marines, et l'on concentre l'attention sur les effets des changements de la distribution de transports maritimes, et sur l'échauffement local des eaux de port. Un examen de la chimie des eaux marines et des composés de cuivre aux concentrations faibles révèle les insuffissances de la théorie d'action anti salissures conçue en termes de la dissolution simple des enduits cuivreux.

## Einige beim Schiffsanstrich zu Beachtende Gesichtspunkte

*Zusammenfassung*

Es werden einige Merkmale der mittels Prall gereinigten Oberflächen betrachtet unter besonderer Bezugnahme auf die hinsichtlich Dauerhaftigkeit des Anstrichsystems ausgeübten Einflüsse. Prallreinigung wird vom Gesichtspunkt des Energieverbrauchs aus analysiert, und die Unterschiede zwischen dem Gebläserad- und dem Luftstrahlverfahren werden aufgezeight. Es wird auch versucht Beziehungen zwischen Aufprallenergie mit Oberflächentextur herzustellen. Die mechanischen Gesichtspunkte, die sich aus der Farb-Spritzmethode ergeben, werden in gleicher Weise besprochen. Die viel grössere Aufprallgeschwindigkeit beim luftlosen Spritzen verglichen mit der beim Spritzen mit Druckluft wird aufgezeigt und auf die nachteiligen

Auswirkungen hinsichtlich Düsenabnutzung hingewiesen. Es wird weiter gezeigt, dass bei kombiniertem automatischen Strahlen und Spritzprimerauftrag auf die ankommenden Schiffsplatten die Geschwindigkeit der Platten im Verhältnis zu der sie kreuzenden Spritzpistole und zu der Weite des Spritzwinkels kritisch ist.

Im zweiten Teil des Vortrages werden einige Gesichtspunkte kurz aufgezeigt, die Faulen beeinflussen, und es wird auf die Folgen der dauernd wechselnden Wirkungen, welche von Schiffsrouten und der jeweiligen Wärme der Hafenwässer ausgehen, hingewiesen. Betrachtung der Chemie des Seewassers und der Kupferverbindungen in starker Verdünnung zeigt die Unzulänglichkeit einer einfachen Auslaugtheorie der Antifoulingwirkung von auf Kupfer basierenden Kompositionen auf.

## Некоторые аспекты окраски судов

*Резюме*

Обсуждается ряд особенностей динамической очистки поверхностей, в особенности по отношению к их влиянию на характеристики красочных покрытий. Анализируются энергетические аспекты динамической очистки и отмечается разница между импеллерным процессом и процессом обдувки сжатым воздухом и делается попытка согласовать ударную энергию с поверхностной текстурой. Аналогично обсуждаются механические аспекты применения опрыскивания. Демонстрируется значительно более высокая скорость столкновения в безвоздушном опрыскивании по сравнению с опрыскиванием сжатым воздухом и подчеркивается важное влияние износа конечностей. Показано что в совместной автоматической обдувке и грунтовочном опрыскивании судовых плит, скорость плиты по отношению к скорости хода распылителя и ширине вентилятора, является критической. Вторая часть статьи описывает ряд факторов которые влияют на засорение и обращает внимание на влияние различных стилей в судостроении и на местное прогревание портовых акваторий. Соображения по отношению к химии морской воды и медных соединений в высоко-разбавленном состоянии указывают несоразмерность простой теории выщелачивания определяющей активность против оплеснения соединений на медной основе.

## Introduction

This paper is intended neither to be a treatise on ship painting nor to describe developments in the subject which have taken place in recent years. These matters have been dealt with fully elsewhere by the present author and many others. It is rather an analysis of some factors involved in two important aspects of the subject, viz. the preparation and protection of ship plate and the battle against fouling. In no way is an attempt made to answer the many questions which the subject raises, though it is hoped there may be some pointers to further improvements.

## The steel

Steel supplied in the " as-rolled " condition initially has a smooth surface, free from rust but covered with mill scale. The scale varies in thickness, is brittle and usually begins to crack or break up in a short time. The steel at a shipyard usually has a varied surface with large areas of rust-free mill scale and considerable rusty areas, mainly around the edges of the sheet. This is an important difference from the old time condition when plate was stored for a long time in the open and was freed from scale, becoming fairly uniformly covered with rust. Nowadays the relatively short, though variable, periods of storage cause great variations in the surface condition of sheets. The amount of rusting depends upon such matters as the thickness of the plate, the amount of handling and the length and condition of storage.

## The significance of cleaning

The variations in surface condition are not altogether removed by present-day cleaning processes. Defects in the steel, such as lamination, occlusions, pits, etc., are features which are more often revealed than removed by cleaning, but revealing them does at least give the opportunity for dealing with them. Apart from this, however, there is no certainty that cleaning the surface by the methods now known does remove contaminants ; indeed there is evidence that the corrosion pattern on steel persists and may reappear even after impact cleaning to white metal and painting. De Vlieger[1] has demonstrated on well charted steel specimens the reappearance of original corrosion patterns after impact cleaning and painting, with a new pattern sometimes superimposed. This phenomenon has also been observed on ships' hulls, which have been impact cleaned before maintenance painting.

The above remarks indicate the nature of the problem in the cleaning of ship plate, and, indeed, of steel for other uses. All the known methods are imperfect, but nowadays it is generally accepted that impact cleaning is the most practicable for heavy steelwork. The process became established and the original standards were accepted as a basis for the metal spray coating of steel, and the high standards of cleanliness necessary for metal spraying were found to be excellent for receiving paint, though the texture of the surface was not necessarily the most suitable. It is, however, unfortunate that whereas a small departure from the standards of cleanliness will dramatically affect the adhesion and performance of metal coatings, poorer surface condition under paint coatings is revealed more slowly and the relationship between breakdown and surface condition is less clear and has been less persuasively demonstrated. There is thus a tendency to skimp the cleaning of plate for painting, and for inadequate inspection. At the present time standards of cleanliness and methods of inspection are not defined, although much work is in hand and much progress has been achieved in this direction. Present day terminology defines surface cleanness in such terms as, " white metal finish," " commercial finish " and the like. Attempts to standardise involve applying optical measurements to these subjective optical terms and when they are finalised they will represent a marked step forward. It is to be doubted, however, whether optical terms alone will ever be sufficient to define surface cleanness.

The fact that original corrosion patterns can reappear on plates that have been impact cleaned and repainted implies that the process has left a corrosive influence on or in the surface of the steel, which subjective optical examination at least fails to recognise. It is possible that the latent pattern is retained, because rust on the originally corroded areas is folded or hammered into the surface in the manner described and illustrated by Wilson and Zonsveld[2] although any significant amount of rust would be apparent as a colour pattern. Where such a colour pattern cannot be seen it is likely that chemical contaminants in and under the corrosion layer removed by blasting have persisted in the microstructure of the steel. Evans and Taylor[3] have demonstrated the significance of such materials on rusting surfaces. It is therefore likely that no commercially acceptable method of surface cleaning will remove all possibility of previous corrosion stimulating further corrosion and the responsibility for preventing any adverse performance from this cause must rest with the primer applied.

This is mainly a formulation matter, but, as will be shown later, application technique also needs to be taken into consideration. A study of the relationship between corrosion inhibitive systems and the contaminants likely to be met is outside the scope of this paper and has been adequately dealt with by a number of workers. At the present time, failure to recognise the significance of the

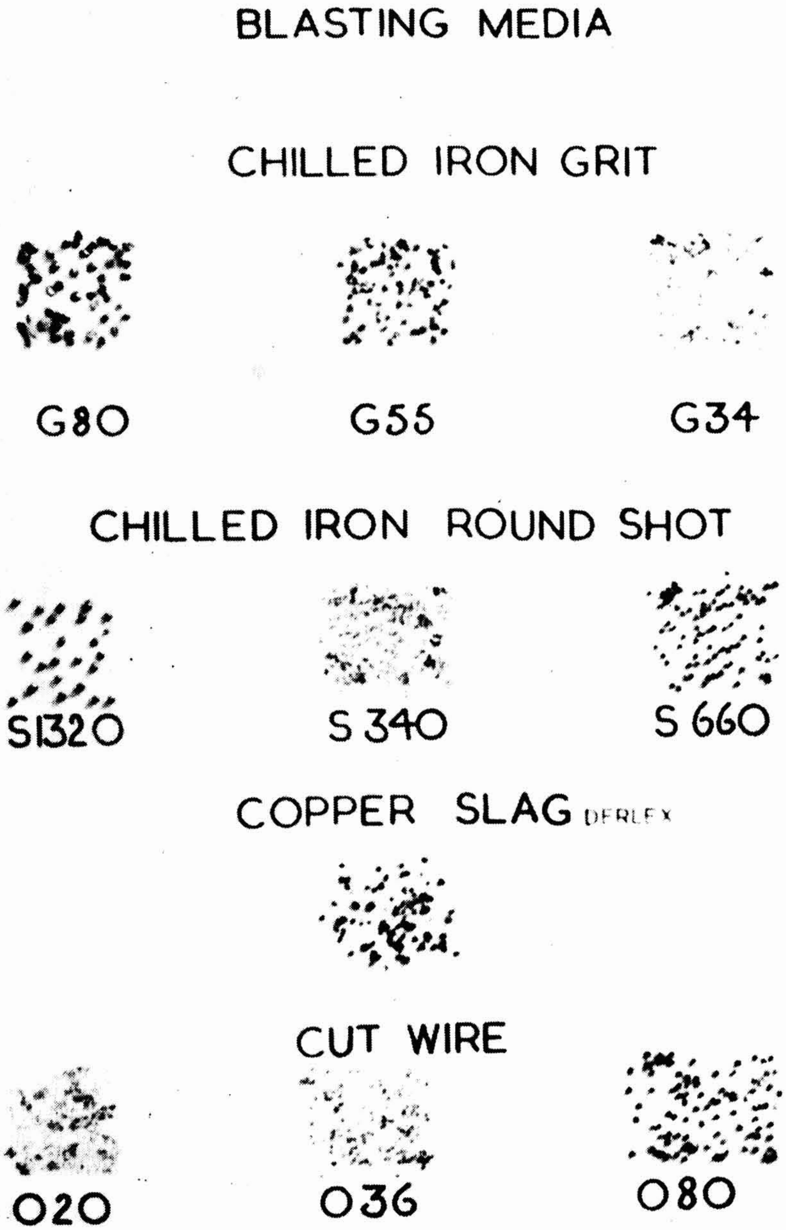

Fig. 1. Grades of blasting media

pre-rusting pattern on the performance of subsequent protective coatings is an important omission from ship painting codes. The wide acceptance of low quality " temporary primers " or " holding primers " for ship plate shows that this factor is not appreciated. It is a particularly dangerous practice to use a primer which allows rusting during construction if the ship is not to be reblasted before painting, since manual or even power driven wire brushing does little to remove the later influence of the early corrosion and has been shown to leave considerable quantities of dangerous salts on the surface[4].

## An analysis of impact cleaning processes

The texture of steel surfaces after impact cleaning has been the subject of considerable study, though of little analysis. This is probably because there are known techniques for measuring and recording the shape of a surface even though they have little relationship to work in a shipyard. Except for considerations of steel left in primer only, it is the author's opinion that the importance of texture has been much over-emphasised, particularly in view of modern painting procedures involving the use of protective coatings of much greater thickness than was common up to a few years ago. Truelove[5], considering primed steel only, concluded that the profile of the surface is important but his work gave a lead to the recognition of the importance of thick coatings, since his ideal relationship $\frac{\text{thickness over peaks}}{\text{thickness over troughs}} = 1$ is nearer to achievement the greater the overall thickness of coating becomes.

Texture can be controlled by the choice of abrasive, particularly hardness and sharpness, as well as by procedure. Unfortunately, the various published works on the relationship between size and type of medium, time, etc., and the profile produced cannot be correlated because they do not give essential information about the velocity and angle of impact of grits, and other similar mechanical factors.

The impact energy of an abrasive particle on a steel surface varies as $(\text{velocity})^2$ and directly as weight, and the effect of the impact will also depend upon the area of contact. There is thus an essential difference between the behaviour of air jet and impeller type of equipment. In general, heavy particles are projected more slowly than light particles from air jet equipment because they do not accelerate so rapidly on being caught up in the air stream. Consequently there is greater cleaning efficiency from fine than coarse particles of the same type and the less dense particle media tend to be more efficient than denser ones. With impeller equipment the case is different. Then particle velocity is determined entirely by the peripheral speed of the impeller (with some loss of speed in flight) and is independent of the size and weight of particles except so far as these influence speed loss in flight. In such apparatus the impact energy of grits is proportional to weight, and larger, heavier particles have the greater abrasive effect. If the particles break down under impact, energy is lost, and is not effective in cleaning. In practice the impact energy for any given weight of grit used is constant for impeller type of equipment, since the greater impact energy of individual heavy particles is balanced by their smaller number. This statement is strictly true for sliding vane impellers but is not quite true for batter type impellers where an elastic impact effect between the vane and the grit has to be taken into account.

It is these considerations which explain the differences in published results of impact cleaning studies. Thus Bigos[6] reported that crushed iron grit of 72 mil maximum particle size used in a jet blast under defined conditions cleaned at the rate of 0.48 square feet per minute (0.045 $m^2$ $min^{-1}$) whereas at 20 mil maximum particle size the rate was 1.56 square feet per minute (0.14 $m^2$ $min^{-1}$) and that, for a given abrasive, maximum profile height increased with maximum particle size. Malleable iron shot and silica sand gave similar results. There appears to be a contradiction in the results since, if larger particles have lower impact energy, they would be expected to roughen the surface less and penetrate less deeply. Large particles might be expected to have some levelling action on high peaks. Wilson and Zonsveld, using impeller type equipment, found no evidence either for the higher rate of cleaning with finer abrasive or for the coarser profile with larger grits. There does not appear to be any study of the influence of particle size range in a working abrasive mixture often used in automatic equipment. An initial mixture of sizes is continually de-sintered and recirculated and a wide mixture of particle sizes results. Wilson and Zonsveld state that there is some evidence in favour of using a small percentage of coarser particles in a predominantly fine abrasive.

The author, analysing the results of Wilson and Zonsveld, has shown that in their examples profile size bears no resemblance to the particle size of the abrasive. Indeed, in the example analysed, the size of the trough, peak-valley-peak, was only about 1/100-1/50 the size of the grit particles used. It is therefore difficult to see how grit particles could become embedded unless there is break-down to fine dust. It is also of interest to note that whereas Wilson and Zonsveld state that with impeller type machines the abrasion travels approximately normal to the plate, the evidence of the trace analysed is that impact has occurred at an angle of incidence of 60° or 30°. A further inference of these observations is that the greater the number of impacts by grit particles, the finer is the profile produced. Number of impacts is a function of the volume of grit used, its particle size and the speed of the throughput of the plate. This is in line with the observation of many users of impact cleaning equipment. There is a natural desire for maximum speed of throughput and speeds up to 14 ft (4.5 metres) per minute are frequent, whereas a maximum speed of 9-10 ft (3-3.25 metres) is better for producing a fine profile and a clean surface. Some people prefer even slower speeds.

A study has been made of a number of standard type impacting media and velocity and kinetic energy under certain blasting conditions have been calculated. These cover sliding vane impeller equipment with impellers 20 in diameter revolving at 3,000 rpm.

In typical air blast equipment with $\frac{3}{8}$ in diameter nozzle, with air at 100 cu ft $min^{-1}$, the rate of air blast at the nozzle is 64,800 cm $sec^{-1}$ or eight times that of impeller equipment at the perimeter. The rate varies according to the actual amount of air passing. It is likely that the very small particles, such as S340 grades, are ejected at somewhere near the speed of the air, but the heavier grits, such as S1320, with a higher inertia, do not achieve the speed of the air during the short time they are in the blast. A small loss of speed means a much

*Impeller equipment*

| *Code* | *Av. wt. of particle (g.)* | *Av. radius of particle cm.* | *Velocity cm. sec$^{-1}$* | *KE per particle* | *KE per g.* |
|---|---|---|---|---|---|
| S 340M. Malleable Round Shot .. .. .. | 0.0037 | 0.05 | 8,000 | $92 \times 10^3$ | $32 \times 10^6$ |
| S 660M. Malleable Round Shot .. .. .. | 0.0242 | 0.09 | 8,000 | $60 \times 10^3$ | $32 \times 10^6$ |
| S 132M. Malleable Round Shot .. .. .. | 0.1238 | 0.15 | 8,000 | $3{,}070 \times 10$ | $32 \times 10^6$ |
| G 34. Chilled Iron Angular Grit .. .. .. | 0.0039 | 0.05 | 8,000 | $97 \times 10^3$ | $32 \times 10^6$ |
| G 55. Chilled Iron Angular Grit .. .. .. | 0.0320 | 0.10 | 8,000 | $800 \times 10^3$ | $32 \times 10^6$ |
| G 80. Chilled Iron Angular Grit .. .. .. | 0.0842 | 0.15 | 8,000 | $2{,}060 \times 10^3$ | $32 \times 10^6$ |
| G 24M. Malleable Angular Grit .. .. .. | 0.0015 | 0.033 | 8,000 | $37.4 \times 10^3$ | $32 \times 10^6$ |
| CR 80M. Malleable Angular Grit .. .. | 0.0716 | 0.07 | 8,000 | $1{,}790 \times 10^3$ | $32 \times 10^6$ |
| S 340. Cl Round Shot .. | 0.0057 | 0.06 | 8,000 | $143 \times 10^3$ | $32 \times 10^6$ |
| S 1320. Cl Round Shot .. | 0.1334 | 0.15 | 8,000 | $4{,}670 \times 10^3$ | $32 \times 10^6$ |
| O 20. Cut Wire .. .. | 0.0026 | 0.025 | 8,000 | $65 \times 10^3$ | $32 \times 10^6$ |
| C 36. Cut Wire .. .. | 0.0063 | 0.04 | 8,000 | $155 \times 10^3$ | $32 \times 10^6$ |
| O 80. Cut Wire .. .. | 0.0352 | 0.03 | 8,000 | $87.5 \times 10^3$ | $32 \times 10^6$ |
| Derlex .. .. .. | 0.0273 | 0.125 | 8,000 | $68 \times 10^3$ | $32 \times 10^6$ |

greater reduction in kinetic energy, since this varies as (velocity)$^2$. It would be valuable to obtain some figures of relative speeds for different particle sizes, but these have not been available to the writer.

It is usual to define profile in terms of amplitude from valleys to peaks and there is reason to believe that this is an important feature, particularly when the surface is coated only thinly, i.e. with primer only and with traditional paint coatings up to the oft-quoted 5 mil thickness. At such thicknesses the amplitude is of the same order as coating thickness and, when impact cleaned steel is left in primer only, as in usual shipbuilding practice, coating thickness is much less than valley to peak amplitude. Whereas Truelove considers the ratio $\frac{\text{thickness over peaks}}{\text{thickness over troughs}}$ to be of greatest significance, Wilson and Zonsveld stress the importance of avoiding the peaks of exceptional height, which are not likely to be covered adequately by coatings. The author is of the opinion that of probably greater importance is the increase in surface area caused by blasting, and has calculated that this may be as much as 32-44 per cent for a grit blasted surface. Moreover, any lateral strain at the interface due to shrinkage forces in the film is virtually eliminated by this configuration, and this must account for much of the improved performance. It is felt that a measure of surface area would be a useful parameter in defining a blast cleaned surface. It is probably here that the significance of the shape and sharpness of the blasting medium is greatest. Round shot tends to produce a smaller number of peaks and valleys per unit area than grit, with a consequently smaller surface area.

From published traces it has been calculated that the increase in area for shot blasting is rather less than half that for chilled iron grit blasting, i.e. of the order of 15 per cent increase. Round shot is used for peening, i.e. the repeated impacts relieve stress in the surface and greatly increase fatigue life, and it has been reported that high tensile maraging steel used in spacecraft is improved in corrosion resistance by the annealing action of the repeated impacts. It is probable that the annealing effect is a significant factor in the corrosion behaviour of ship steel.

**Fig. 2. Gritblasting steel bars, Rotterdam**

It is thus seen that impact cleaning is no simple process and there is no straightforward way of assessing the surface produced. Cleanliness alone, even if definable, is not sufficient. Texture involves more complex factors than trough to peak amplitude. It is, however, important to note the fundamental energy differences between impeller cleaning and air jet cleaning. Since in practice the former equipment is almost universally used in shipyards for new building and the latter in repair yards and dry docks for hull and tank cleaning, these differences are important. It would seem to be appropriate to use high density and possibly mainly relatively large particle medium in the impeller type equipment in the fabrication sheds, but lower density smaller sized media, such as non-metallic abrasives, with air jet equipment in the repair yards and dry docks. This distinction also has the advantage that the lower cost material is used where efficient recovery and re-use are most difficult.

### Priming impact cleaned steel

Steel plate cleaned by blasting is likely to rerust rapidly and it is important to apply a protective coating immediately. British Standard Code of Practice CP 2008, and other similar codes, recommend priming within four hours of cleaning, but this is too long an interval. It is best to apply the primer immediately after cleaning and before the surface has cooled. In a fixed plant in fabrication shops this is easily arranged by including a dust remover at the exit from the cleaning chamber and spray equipment immediately afterwards. The cleaned steel thus passes under the spray guns in controlled conditions and the slightly warm surface helps to flash off solvent and dry the primer. When flat plate is being treated, conditions are relatively simple, but with sections the geometry of the steel adds greatly to the complications. Hand spraying cannot be controlled and leads to wide variations in performance.

The aim in applying primer is to produce a uniform coating of minimum thickness to achieve the protection required. With some types of primer too great a thickness causes trouble. It is not the purpose of this paper to discuss types of primer but to examine the application process.

In automatic equipment the spray gun, held normally to the steel, moves at high speed at right angles to the direction the plate is moving, and coats a band across the plate of width dependent on the fan angle of the spray. In hand spraying the gun is seldom held vertically, the movement being in an arc. It is important that the spray be held normally to the surface, particularly with a coarsely textured surface, or there may be a " shadow " effect.

It is essential, if good results are to be obtained in the automatic plant, that the speed of the plate be related to speed of gun and fan width. With a completely uniform fan pattern, the ideal speed is such that the plate moves forward half a band width in the time the gun takes to traverse the plate. Then a completely uniform cover of primer is obtained. Too slow movement of the plate produces overlaps of the spray bands, with excessive thickness of primer in strips, leading to complaints of slow drying and sometimes to poor adhesion and other troubles. Too rapid movement of the plate produces thin strips and premature rusting during construction. In practice spray fans are not uniform, but tend to be thin at the edges, so that a slightly slower speed than that indicated above is desirable. Bad setting of the gun or obstructions in the tip cause " fingering " of the paint and uneven coatings. Probably the best way to obtain a uniform coating on flat plate would be to use a reverse rotating roller, but this would involve enormous engineering problems, and would have only limited use. With sections, H girders and the like, a uniform coating cannot be obtained by conventional methods, and probably here a system of electrostatic spraying will be necessary. It is worthy of note that hand spraying is not capable of giving uniform coatings and, since marginal thicknesses are being considered, this is a serious drawback. Thus, when hand spraying, it is often found that there is excessive thickness of primer on the webs of girders, but the inner faces of flanges are deficient.

The velocity of the paint issuing from the spray nozzle and, more important, the velocity on reaching the surface, influence the wetting of the steel and penetration of paint into the " valleys " on the surface. At present there is much to be learned about this aspect of application, but it is possible to calculate certain mean nozzle velocities. For instance, it has been calculated that paint applied by airless spray through a 15 mil diameter tip is projected through the orifice at a mean rate of 2,180 ft $sec^{-1}$ (65,800 cm $sec^{-1}$) for each Imperial gallon per minute of paint applied. Such rates are by no means excessive. This represents a speed of 1,490 mph, well above the speed of sound, which accounts for the sound like a pistol shot as the paint breaks the sound barrier when spraying starts. The paint is thus subjected to great shear which warms and atomises it. Pigmented primer wears the tips and there is appreciable wear after a few days' use, even with the hard alloys used for tips. Inspection for wear, and discarding after a small increase in orifice size, are important. Thus for the conditions of the above calculations an increase of tip size through wear from 15-17 mil decreases the velocity of the issuing paint from 65,800 cm $sec^{-1}$ to 51,300 cm $sec^{-1}$, or alternatively if the same velocity is maintained paint consumption is increased by 28 per cent and to obtain similar atomisation paint consumption would rise by 45 per cent, which means an excessive thickness of coating, and slower drying. There is a misconception among some users that low pressures and large tip sizes (21 mil and over) giving the same paint throughput as high pressure and small tip size (15 mil and less) give comparable primer performance, but this is not so. All the evidence points to the desirability of using high delivery pressures (3,000 psi and above) and small tips. This places extra responsibility on the paint manufacturer to ensure freedom from bits likely to clog the tips.

From the above figures it can be calculated, on the basis that airless spray gives a " throw " of about 8 ft, that the velocity at which the paint meets steel plate 2 ft distant from the tip is about 545 ft $sec^{-1}$ (16,450 cm $sec^{-1}$) for each Imperial gallon/minute of paint consumed, which is much greater than the velocity of impact between blasting medium and the steel during cleaning in impeller equipment. The force of impact of a paint droplet of SG 2 is of the order of $17 \times 10^5$ g $cm^{-2}$ or 24,000 psi. These great speeds and enormous forces promote intimate contact between paint and metal, and clearly indicate the tendency to penetrate into valleys and spread over the surface. They also show clearly the industrial hazards involved in airless spraying. The force of paint issuing from the gun, and for some distance from the gun, is sufficient to penetrate clothing and the skin and inject paint into the bloodstream with serious consequences. The recoil on a manually held gun is sufficient, unless there is a firm grip, to cause wild aim with hazard to nearby people.

The forces involved and speeds of paint droplets in compressed air spraying are much lower. The rate of consumption of paint is several times less ; the paint issues through a generally much larger annulus area. On the other hand droplets are accelerated by the rapid expansion of the propelling air after leaving the gun, and this acceleration is the main cause of atomising. Generally paints are atomised to smaller droplet sizes in compressed air spraying than in airless spraying. Calculations suggest that the velocity of impact on the steel at 2 ft distance is only of the order 16-17 ft $sec^{-1}$ (500 cm $sec^{-1}$) for compressed air spray and it may be much less. These figures may not be accurate, since there is no direct relationship between rate of consumption of paint and velocity after leaving the gun annulus, but they do indicate the order of velocity. There are also other factors which influence the coating produced. The large rapid expansion of the propellant air promotes evaporation of solvent and cooling of the paint to a much greater extent than with airless spray. Unless the temperature and humidity of the ambient air are controlled there is a danger of falling below the dew point, with the formation of water droplets, with compressed air spraying.

The wide difference between the impact forces of paint on steel for airless and compressed air spray have a great bearing on the nature of the coating laid down on the textured surface of impact cleaned steel, and this difference is revealed in performance. This particularly applies to the behaviour of steel in primer only, as used in shipyards, and where the primer coat is usually of 1 mil calculated thickness, or less. Coatings of primer produced by high pressure airless spray at 3,000 psi or above show markedly superior performance to those of the same primer produced at 1,500 psi and below with larger tips at the same thickness as calculated by spreading rate, and these in turn are superior to coatings given by compressed air spray. These observations are related to the fact that the velocity of paint at the same rate of consumption when using a 21 mil tip is only half that when using a 15 mil tip and the impact energy on the steel only a quarter. For a 30 mil tip, the velocity is only a quarter and the impact energy one sixteenth as great. For compressed air spray, the energy is still lower, as indicated above. The general appearance of the coatings, their integrity and cohesiveness and general structure, follow the same pattern, which is borne out by the electrical conductivity in wet conditions of those primer coatings free from conductive pigments such as zinc. Electrical conductivity under wet conditions is a good test of film continuity and gives a good qualitative or semi-quantitative evaluation of the primer for the steel.

The above conclusions are drawn from considerations of automatic plant used in controlled conditions. It is not possible to obtain this measure of control by manual operations, as in ship repairing or the cleaning and priming of fabricated tanks, but it can be assumed that the same considerations apply and the conclusions drawn above are relevant to these conditions.

## Marine fouling

Another matter of great importance in ship painting, and which is highlighted by changing conditions in the shipping industry, is that of marine fouling.

Fig. 3. Incorrect practise in hand spraying

There are many unknown factors in this matter and changes in shipping usage have added to the number. As an example of significant changes, mention can be made of refrigerated ships on the one hand and bulk carriers with hot cargo on the other. In spite of internal lagging it is not uncommon to notice a lower hull temperature in the vicinity of refrigeration spaces on ships. In dry dock this shows as areas of condensed moisture on an otherwise dry hull. A large oil tankship containing many thousands of tons of heated oil cargo can raise hull temperature by a few degrees C and so stimulate the growth and development of specific organisms. For instance, there is evidence that some types of barnacle (Balanus) do not thrive below about 13°C (55°F), which is approximately the water temperature around much of the British coastline during summer. An organism of this type carried on the hull of a heated tanker from hotter waters would continue to thrive, whereas on a vessel with unheated cargo it would either remain static or die. On the other hand, it seems that Balanus balanoides, common in European waters, thrives in the areas where the winter temperature does not exceed 7°C. Another factor which influences the fouling of ships in specific harbours is the local warming due to the discharge of hot water from power stations and industrial plants, which sometimes increases temperatures by several degrees and encourages local colonies of fouling organisms not native to the locality.

Various workers in Australia have pointed out the relationship between fouling environment and the surface at the time of initial immersion. Thus Wood and Allen[7] state that, if a ship is released from dock during heavy spawning, the bottom will be seriously infected and though the organisms may die they serve as a substrate for further settlement, whereas a ship released when there is no heavy spawning may stay clean for a long time. Wisely[8] found evidence that the rate of fouling at any time depended upon the concentration of larvae at that time, and that in turn was greatly affected, in Sydney harbour, by the number of living adults some weeks before. Dilution of the salinity, as by heavy rainfall, caused high mortality among adults, which led to a low concentration of larvae and low intensity of fouling some weeks later.

There appear to be several factors, some of them geographical, which affect the overall world pattern of the growth of fouling organisms, but superimposed on this are local factors of great importance. It is quite a complex matter to begin to unravel the various inter-related factors, among which may be identified the following :

(a) water temperature in relation to geographical situation,
(b) chemical composition of sea water, particularly concerning salinity and the availability of nutrients,
(c) ocean currents.

None of the above can be considered in isolation.

For some time now workers have been collecting information about fouling conditions in different ports and sea areas around the world. It is very difficult to obtain precise information, partly because nomenclature, particularly of marine organisms, is not clear, at least to the non-biologist. The OECD have published booklets giving information about a number of test stations, but these do not give sufficient world cover to help greatly in forming an overall picture. Evidence is accumulating, but is not nearly sufficient for an authoritative statement, that ocean currents play a considerable role in the incidence of fouling. The effect appears to be twofold, first in carrying organisms or their larvae from warm breeding grounds to cooler latitudes while maintaining a favourable environment, and secondly in determining both atmospheric and aqueous conditions which influence the behaviour of organisms. For example, sea isotherms for the North Atlantic run, for the greater part of the year, in a distinctly SW-NE direction from the New England coast (Eastern USA) to Spitzbergen, but during autumn they dip southward, starting to turn at 20°W and continuing approximately south east to 5°E as the warm current of the North Atlantic drift (Gulf Stream) is overpowered by the cold flow of melted polar ice flowing down the coast of Norway. Thus in October the 10°C (50°F) isotherm passes through the points 20°W 60°N and 5°E 70°N, passing close to

Newfoundland and almost to the Lofoten Islands. In November, however, it passes through the point 20°W 58°N i.e. very little different from October, but farther eastwards it dips markedly south, so that almost all British waters are below 10°C (50°F) and the whole North Sea north of a line approximately Kings Lynn-Jutland is markedly cooled. The effect on fouling of fishing vessels is noticeable, since, whereas those fishing south of Iceland may foul throughout most of the year, particularly with algae, in more easterly waters fouling is severely restricted. A similar but more permanent " dip " in sea water isotherms occurs along the Labrador Newfoundland coast, resulting from cold arctic water (Labrador current) flowing down from the Davis Strait. The cold current not only cools the water but sunlight intensity is greatly reduced because of the fog produced, with resulting effects on plant life. It is well known that vessels fishing around the region of southern Greenland will often foul heavily with algae as will those on the Newfoundland Bank south of Newfoundland, whereas those north of Newfoundland and in the vicinity of Labrador usually remain clean. This clean area lies between the two fouling areas but is in the main stream of the cold Labrador current, an area of cold water and frequent heavy fog.

There is less evidence that the warm tropical currents actually stimulate fouling, though there is little doubt that they do behave conversely to the cold currents, and places such as Miami and Abidjan, swept by warm tropical currents, are bad fouling areas.

In so far as ocean currents are an important feature in determining the growth of marine organisms it might be expected that the most severe fouling coasts swept by tropical currents would be :

1. Caribbean and USA eastern seaboard,
2. Eastern South America (Brazil and Argentina),
3. Guinea coast of Africa—Dakar to the Congo,
4. All Indian Ocean coasts from Timor Sea via Indonesia, Burma, India, Arabia and East Africa,
5. Oceania, China and Japan,
6. Eastern Australia and New Zealand,

and the less severely fouling coasts, swept by colder currents, would be mainly western coasts of land masses in the southern hemisphere, although it is probable that the main effect of the cool currents would be to enlarge the seasonal differences as in the case of North Europe mentioned earlier. Affected coasts would be :

1. South American west coast,
2. South West African coast,
3. Western Australian coast,
   and to a lesser extent
4. Northern Californian, Oregon and Washington coast.

It is unfortunate that up to the present there is no information available to give any real indication of the probable effects of these currents. Differences between Walvis Bay and Beira (Mozambique) and between Callao, Antofagusta and Valparaiso on one hand and Recife, Rio de Janeiro, Montevideo on the other might provide valuable information.

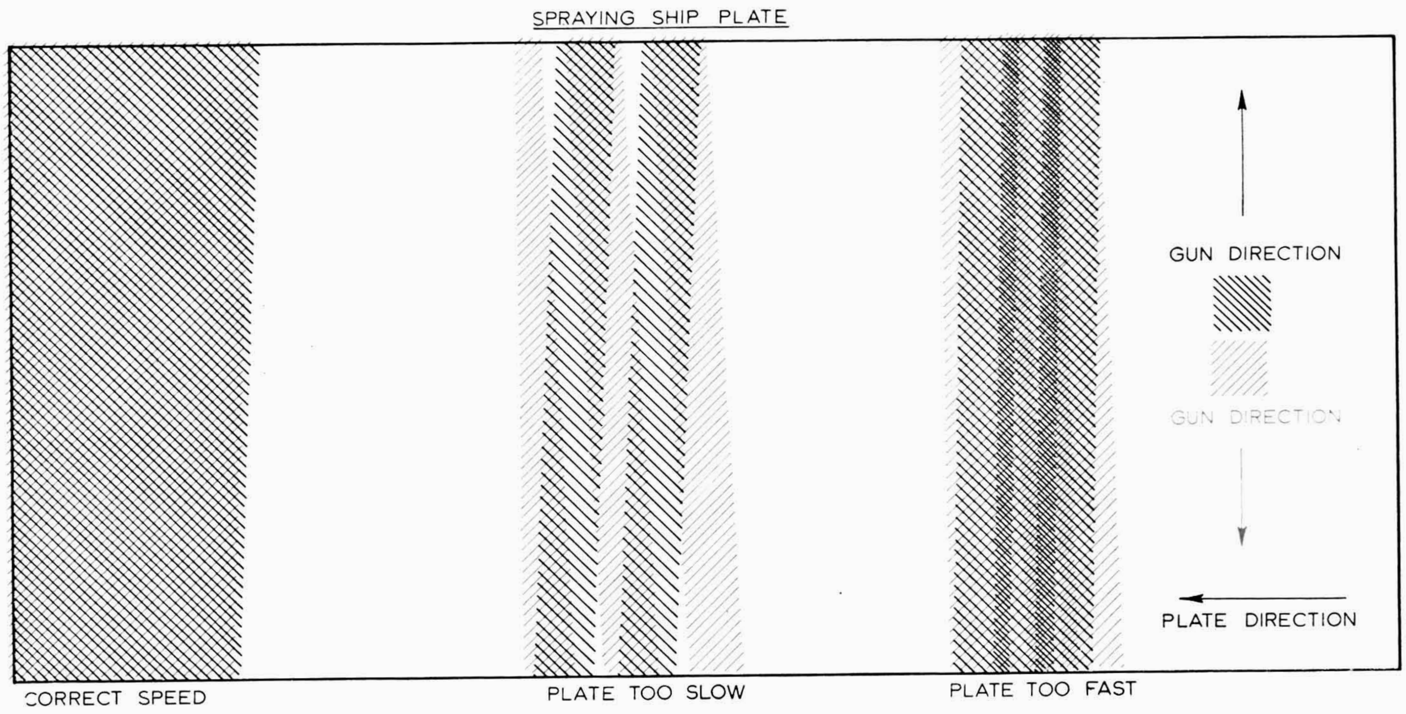

Fig. 4. Effects of incorrect spraying of ship plate

It is, however, not possible to give any world-wide picture of marine fouling. Local conditions vary too widely for that. For instance the annual Nile floods sweep along the coast of Palestine and the whole eastern Mediterranean, altering the salinity and providing a special seasonal biological variation. The Nile dam now being built may alter this.

The chemistry of sea water, particularly local chemistry, is a factor to be taken into account. There is considerable documentation of differences in salinity of the type mentioned above, but less is known about the nutrients and toxins in the sea and particularly in harbours, which are after all the places where most ships pick up their fouling. Armstrong and Butler[9] have studied the changes in sea water off Plymouth and have discovered among other things considerable seasonal changes in phosphate content, particularly in the surface layers to 20 fathoms depth, which are the parts of interest in ship fouling. Since phosphate is one of the important nutrients, particularly for plant life, it is significant that they found the highest seasonal concentration at all depths down to 60 fathoms during the period February to mid-March. Thereafter there is a rapid fall in concentration in the surface 20 fathoms until early May, with a reasonably steady, though low, concentration through the summer until early September. Whereas it cannot yet be said there is a connection, it is of interest to note that the period of relatively high concentration, though of rapid decline, corresponds with the period when algae tend to proliferate.

Of more interest, however, is the study of the copper content of sea water, since it is believed this can direct our thinking about the mode of action of copper-containing anti-fouling compositions. The limit of concentration of cupric ions in sea water of pH8 is much lower than the concentration lethal to marine plants and animals, which although varying according to species require a concentration of copper around 1,000 mg $m^{-3}$ for death. Small quantities of copper added to sea water actually stimulate the settlement of certain larvae and accelerate their metamorphosis to the adult form. Copper is found in the respiratory pigment of many marine invertebrate animals.

Sea water contains copper in solution. In general it seems that the concentration in normal salinity water is lower than in some low salinity waters. Thus in the English Channel copper concentrations of 10 mg $m^{-3}$ have been found. In the low salinity water off the mouth of the Mississippi concentrations of 15-25 mg $m^{-3}$ were measured and, with increasing distance from the shore, concentration in the upper layers dropped to 5 mg $m^{-3}$.

It is of the utmost significance to note that copper in solution in sea water is rapidly adsorbed on organic matter and in some cases combines with it. Thus Harvey[10] reports that when sea water enriched with copper to 50 or 100 mg $m^{-3}$ is shaken with plankton, organic detritus or mud the concentration falls markedly. Indeed, it has been found, in some water at least, that the relationship follows the Freundlich adsorption isotherm, and this implies that copper is concentrated at water/organic matter interfaces. Also, if enriched sea water is kept in contact with various insoluble organic acids, such as rosin or the acids of vegetable oils, a similar reduction in concentration is found. Moreover, the copper is found combined with the organic acid and can be extracted with carbon tetrachloride.

The chemical observations would appear to cast considerable doubt on the leaching theory of antifouling action as normally understood, firstly because of the inadequate solubility of copper in sea water and secondly because of the strongly adsorptive action of the organic surface of the antifouling composition. There is no doubt that the local environment effect of the organic component of the composition plays an important part. Thus in the immediate vicinity of this layer, that is within molecular distances, it is likely that the pH of the water is well below that of the open sea and this may allow a high concentration of copper ions to be held in solution locally. This in turn would lead to a high rate of adsorption on, or a possible reaction with, the organic layer according to the relationship of the Freundlich isotherm. It may well be that the interaction between adsorbed copper and insoluble organic acids is an explanation of why acidic media, such as those containing rosin, can generally be used satisfactorily in antifouling compositions and those of a non-acidic or basic nature, such as the cured epoxide resin coatings, have not been found satisfactory.

Copper-containing antifouling compositions are usually made with cuprous oxide, which, when dissolved initially, produces the highly unstable cuprous ions which are almost immediately converted to cupric ions and copper.

$$Cu_2O \rightarrow Cu_2\,Cl_2 \rightarrow 2\,Cu^{\cdot} + 2\,Cl'$$
$$2\,Cu^{\cdot} \rightarrow Cu^{\cdot\cdot} + Cu$$

We cannot be certain whether the free latent copper or the concentration of cupric ions on the organic surface is the lethal ingredient. At present no study of the matter appears to have been made. It is, however, significant that all manufacturers of antifouling composition seem to be agreed that cuprous oxide is a more effective toxic agent than cupric oxide. An alternative possibility is that the initially formed cuprous ion is immediately absorbed on the organic layer and stabilised. Because its equivalent is twice that of the cupric ion it presents a much richer and more toxic surface.

These adsorption and solubility studies do, however, show that a simple leaching and diffusion theory of antifouling action for copper based compositions is untenable. Electrical environment must be a significant factor, since all ions in solution are subject to the electrical environment and there is now sufficient evidence of the behaviour of antifouling compositions on test specimens and in use on ships to lend support to this conception. Thus it is observed repeatedly in tests that the nature of the anticorrosive or insulation system between the steel and the antifouling composition can profoundly affect performance, and the proximity of other metals and other systems influences it in the same way as the proximity of dissimilar metals influences corrosion. The parallel is exact. Moreover, an antifouling system which behaves well on a substrate of one metal may behave poorly on another metal, even though there is an apparently good insulating system.

The above analyses of some of the problems involved in ship painting are given to indicate the deep technical and scientific interest which can be involved in this subject, and to indicate the way in which the author believes our thinking should be directed in the years ahead.

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# Discoloration of paint films by traces of mercury, lead, and iron compounds

**By E. Hoffmann**

Division of Building Research, Commonwealth Scientific and Industrial Research Organization, Melbourne, Australia

*Summary*

Under suitable conditions stains on paint films can be caused by mercury, lead, or iron, even if present in the paint film in small traces. These metals therefore should be kept out as far as is possible.

## Les changements de couleur en feuils de peinture provoqués par des traces de composés de mercure, de plomb et de fer

*Résumé*

Sous les conditions appropriées, des taches en feuils de peinture peuvent être provoquées par mercure, plomb ou fer, même dans le cas où ils ne s'y trouvent qu'en traces. Ainsi on doit éliminer ces métaux autant que possible.

## Verfärbung von Anstrichfilmen durch Spuren von Quecksilber, Blei und Eisenver-Bindungen

*Zusammenfassung*

Unter geeigneten Bedingungen können in Lackfilmen durch Quecksilber, Blei und Eisen, selbst wenn darin nur in Spuren anwesend, Flecken verursacht werden. Deshalb sollten diese Metalle soweit als möglich vermieden werden.

## Обезцвечивание красочных пленок следами ртутных, свинцовых и железных соединений

*Резюме*

В известных условиях пятна на красочных пленках могут быть причинены ртутью, свинцом или железом, даже если они присутствуют в красочной пленке в ничтожных количествах. Эти металлы поэтому должны быть исключены по мере возможности.

## Introduction

In the overwhelming majority of cases encountered in Australia, the staining of surface coatings is due to the formation of mercuric sulphide, lead sulphide, or ferric hydroxide, in descending order of frequency.

It has been known for a long time that lead in paint can cause staining, but the small quantities of lead (about 0.1 per cent) which can cause trouble and the fact that lead can diffuse from one paint film to another in sufficient quantities to cause staining were unexpected findings[1, 2].

Staining occurred mainly on flat alkyd enamel paint films and, when the lead driers were omitted from the paint, which can be done without changing the drying properties of the coating significantly, the number of complaints was very much reduced. Nevertheless, occasional cases of lead sulphide staining still come to the attention of the Division and, in most of these cases, the amount of lead found in the paint film seemed to be too small to explain the intensity of the observed discoloration.

Organic mercury compounds were first used in oil-based paints to make the paint film fungus-resistant. With the advent of latex-based paints these additives were used for the dual purpose of protecting the water-based paints from spoilage and imparting mould resistance to the paint film.

It seems that the present author was the first to report on sulphide staining caused by the organic mercury fungicides[3] in dwellings. When further investigations showed that these compounds were very unsatisfactory as fungicides[4], their use for this purpose was much reduced by most manufacturers. They continued to be used as a preservative, and it was believed that quantities of the order of 0.01-0.02 per cent would not cause staining. This limit was estimated from laboratory observations, but even with these small amounts cases of staining were still encountered.

The author then pointed out[5] that the intensity of staining caused by a coloured compound in a paint film depends to a large degree on its distribution in the coating. A given amount of the coloured constituent, e.g. lead sulphide, will cause much more staining if it is concentrated in the top layer of the paint film than it would if it were distributed evenly throughout the thickness. The difference in the intensity of staining between an even distribution of mercury sulphide in the paint film and an uneven one (concentrated in 25 per cent of the film thickness) was also experimentally demonstrated[5].

For a full appreciation of the cases of staining encountered in the field it is necessary to have an estimate of the actual concentrations of the various compounds which cause discoloration of a surface coating. The present communication deals with this subject, and also refers to iron staining.

## Theoretical

As already mentioned the staining of surface coatings is mainly due to the formation of mercury sulphide, lead sulphide, or ferric hydroxide. The cause of the uneven distribution of sulphides has been discussed in detail in an earlier paper[5]. Ferric hydroxide could collect in the surface layer by the following mechanism : when iron rusts the first product is ferrous hydroxide, which being comparatively soluble (solubility product $1.64 \times 10^{-14}$) diffuses to near the surface where it can react with oxygen to form the much less soluble ferric hydroxide (solubility product $1.1 \times 10^{-36}$)[6].

A direct quantitative analysis of the stains on films is difficult because it is necessary to differentiate between metallic compounds which cause the staining and those in which the same metal is present in some other form. For instance, in staining by mercury compounds it would be necessary to determine the amount of mercury present as the sulphide, which would be very difficult. Similar considerations apply to the other metals.

The method chosen was as follows. Known amounts of mercury sulphide, lead sulphide, or ferric hydroxide were precipitated on to a bed of barium sulphate and the minimum amount of these compounds which could produce a distinct staining effect was determined. Since this method produces a stain confined mainly to the surface it might be considered that the discoloration would be exaggerated, but the following calculation shows that this is not the case.

In a previous paper[5] an equation was derived for the light $I_n$* reflected from a paint film containing a small amount of staining matter.

$$I_n = I_o \left[\frac{r}{r + 2nc} + \frac{2nc}{r + 2nc} \exp - \left(\frac{r}{n} + 2c\right) t - \exp - \left(r + 2c\right) t\right] \qquad (1)$$

$I_o$ = intensity of light falling on to the paint film.
$r$ = constant expressing the reflectivity of the pigment.
$c$ = constant expressing the absorption due to the staining substance.
$t$ = thickness of paint film.

To evaluate this equation it is necessary to prescribe some conditions to be able to calculate $r$ and $c$. These conditions are that $r$ is to have such a value as to reduce the light intensity reaching the substrate to 1 per cent of the original in a paint film of thickness $4 \times 10^{-3}$ inches free of colouring matter. $r$ is calculated from the equation

$$I = I_o \exp - 4 \times 10^{-3}\, r$$

from which $r = 1150$.

$c$ is to have such a value that the initial light intensity $I_o$ is reduced to $I_o \times 0.98$ on traversing the paint film in which the staining matter is suspended. The medium itself is assumed neither to reflect nor absorb light. $c$ can be calculated from the equation

$$I = I_o \exp - 4 \times 10^{-3}\, c,$$

from which $c = 5$.

The values obtained by substituting $r$ and $c$ in equation (1) are set out in Table 1.

*Table 1*

*Ratio $I_n/I_o$ if the staining substance is concentrated in $\frac{1}{n}$th of the film thickness*

| $n$ | $I_n/I_o$ | $\frac{\Delta I}{I_f} \times 100$ |
|---|---|---|
| 1 | 0.981 | 0.9 |
| 2 | 0.975 | 1.5 |
| 5 | 0.965 | 2.5 |
| 10 | 0.959 | 3.1 |
| 20 | 0.955 | 3.5 |
| $\infty$ | 0.951 | 3.9 |

$n$ = fraction in which the staining substance is concentrated.
$I_n$ = reflected light intensity if staining substance is concentrated in $\frac{1}{n}$th of film thickness.
$I_f$ = light reflected with no staining substance present, $0.990 \times I_o$.
$\Delta I$ = difference in light intensity between $I_f$ and $I_n$.

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*Denoted by $R_2$ in Ref. 5.

For $c = 0$, that is if no staining matter is present, $I_o$ would be reduced to $I_f = 0.990 \times I_o$. $\Delta I$ denotes the difference in light intensity between $I_f$ and $I_n$. As can be seen from Table 1 the difference in light extinction between the case $n = 20$ (staining matter concentrated in a 5 per cent layer of the paint film) and $n = \infty$ (staining matter on surface of paint film) is very small.† In Table 1 the difference between $I_f$ and $I_1 = 0.9$ per cent. The difference in light intensity which the eye can detect depends on the intensity of light ; at the lower end of the scale the difference is nearly 100 per cent, decreasing to 0.6 per cent at the highest intensity[7].

In a room at average illumination a weakening of 0.9 per cent in the intensity of the reflected light between two parts of a surface will be scarcely noticeable, but should the staining matter become concentrated in 50 per cent of the film thickness a stain will be noticed. The stain will intensify with increasing concentration of the staining substance in the top layer of the paint film.

## Experimental

A bed of barium sulphate 1 sq in in area was produced in a suitable tube by centrifuging. An aqueous solution (2 ml) containing the metal ion in a known concentration was carefully pipetted on top of the barium sulphate bed without disturbing it. A drop of a solution containing the precipitating agent (hydrogen sulphide for the production of mercuric sulphide or lead sulphide and ammonia for the precipitation of ferric hydroxide) was added. The precipitate was centrifuged and the discoloration of the barium sulphate was observed by comparing its surface colour with that of a second bed which was free of staining substance. The amount of each metal which caused noticeable discoloration by this method is shown in Table 2.

*Table 2*

*Amount of metal per sq in of surface which produces a noticeable discoloration*

| Metal | Amount to produce discoloration (mμ) |
|---|---|
| Mercury . . . . | 4 |
| Lead . . . . . . | 2 |
| Iron . . . . . . | 5 |

Assuming that 1 gallon of paint is spread to cover 500 sq ft and the weight to be 14 lb, it would need approximately 0.005 per cent mercury to produce a stain, provided that the formed mercuric sulphide were concentrated in the top 5 per cent of the paint film thickness. This will happen only on rare occasions, but mercury stains have been observed with paints which did not contain more than this amount.

Actually, the sensitivity to metal impurities may be greater than the foregoing data suggest. A white painted fibrous plaster ceiling showed a stain over the joint caused by mercuric sulphide, and a small rectangular piece of the

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†This means that the discoloration obtained with the method described here is approximately equivalent to the one which would be obtained if the same amount of colouring matter was contained in 1/20th of the thickness of the paint film.

joint was cut out. When the sample was inspected the discoloration was not apparent, indicating that the perception of a slight variation in colour depends on the size of the background.

## Conclusions

Stains on a paint film can be caused by mercury, lead or iron, even if they are present in concentrations of the order of only a few thousandths of 1 per cent. Mercury is usually introduced to the paint as a fungicide or as a preservative. It has been shown previously that mercury compounds are not of much value as fungicides and there is no point in adding them to the paint for this purpose. Mercurials are useful as preservatives for latex paints, but a great range of non-staining compounds is now available and there is no need to use mercurials. However, they are sometimes added to latices, and, although as far as the author can establish, the quantities seem to be of the order of 0.01 per cent mercury, which would give a paint containing $<0.005$ per cent mercury, it would be preferable to use some other preservative.

The use of lead driers has been discontinued in flat alkyd enamels, and complaints of lead sulphide staining have been greatly reduced in consequence, but a few are still received. In a few cases, analysis has shown that the quantity of lead was less than would be expected if the usual amounts of lead driers had been added. Lead can be introduced into paints unknowingly with certain pigments, e.g. zinc oxide, which often contains as much as 1 per cent of lead or even more. Another source of lead could be the alkyd resin itself. Lead oxide may be used as a catalyst in the production of these resins and, although the amounts normally used are unlikely to lead to staining in the paint film, larger quantities could be introduced by mistake. Control of the raw material used would therefore be desirable.

Iron stains are usually caused by small particles of iron contained either in the paint or in the substrate. Control of the raw materials used for paint and substrate to keep them free of iron particles is necessary.

[*Received 30 October 1967*

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# The dehydropolymerisation and copolymerisation of drying oils and other reactive compounds exhibiting α-methylenic activity*

**By R. Lambourne**

Research Department, Imperial Chemical Industries Limited, Paints Division,
Wexham Road, Slough, Bucks.

## *Summary*

The use of dialkyl peroxides to abstract hydrogen from molecules containing active methylene groups, followed by the combination of the free radicals so produced, is a useful way of carrying out controlled " polymerisation," and has been termed " dehydropolymerisation " or the " polyrecombination reaction." The work reported confirms the stoichiometry of the reaction with respect to triglycerides and extends previous work with naturally occurring oils to free unsaturated fatty acids. It has been found that the reaction provides a novel means of producing esters of unsaturated hydroxy acids directly from unsaturated fatty acids and a scheme is put forward to explain this reaction.

The modification of drying and semi-drying esters by co-reaction with terpenes such as alloocimene and myrcene has been examined. The influence of structure on reactivity has been clearly demonstrated in the cases of alloocimene and myrcene. The former underwent the dehydropolymerisation reaction normally, whereas the latter, containing a terminal $CH_2 = C-$, gelled under conditions favourable to dehydropolymerisation, but could be used to " myrcenate " (by analogy with " styrenate ") an oil using a catalytic amount of peroxide.

## La déshydropolymérisation et copolymérisation des huiles siccatives et d'autres composés réactifs manifestant de l'activité α-methylenique

### *Résumé*

L'abstraction d'hydrogène, par des peroxydes dialcoylliques, à partir des molécules contenant des groupements actifs méthyléniques, suivi par la combinaison des radicaux libres résultants, a été nommée " déshydropolymérisation " ou la réaction de " polycombinaison." Celle-ci offrit un moyen utile pour effectuer la " polymérisation " contrôlée. Les recherches ci-décrites donnent confirmation à la stœchiométrie de la réaction où il s'agit des triglycérides, et elles suppléent les recherches précédentes sur des huiles naturelles par l'inclusion des acides gras non-saturés libres. On a trouvé que la réaction fournit un moyen nouvel pour produire les esters des acides hydroxylés non-saturés directement à partir des acides gras non-saturés. On propose un schéma pour expliquer la réaction.

On a examiné la modification des esters siccatifs et semi-siccatifs par co-réaction avec terpènes tels que allöocimène et myrcène. On a demontré nettement l'influence qu'exerce la structure sur la réactivité, dans les cas d'allöocimène et de myrcène. Celui-la subit de façon normal la réaction de déshydropolymérisation, tandis que celui-ci, contenant du groupement terminal, $CH_2=C-$ se gélifiait sous des conditions favorables à déshydropolymerisation, mais on pourrait s'en servir pour " myrcéner " (par analogie à styréner) une huile en présence d'une quantité convenable de peroxyde en tant que catalyseur.

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## Die Dehydropolymerisation und Mischpolymerisation Trocknender Öle und Anderer Reaktiver Verbindungen mit Methylen-Aktivität

*Zusammenfassung*

Es hat sich gezeigt, dass zur Durchführung einer kontrollierten " Polymerisation " die Verwendung von Dialkylperoxiden um Wasserstoff aus aktive Methylengruppen enthaltenden Molekülen zu entfernen, mit sich anschliessender Kombinierung der auf diese Weise erzeugten freien Radikale, nützlich ist. Dieses Verfahren wurde als " Dehydropolymerisation " oder als " Polyrekombinationsreaktion " bezeichnet. Die hier wiedergegebene Arbeit bestätigt die Stochiometrie der Reaktion hinsichtlich Triglyzeriden und dehnt vorangegangene, mit natürlich vorkommenden Ölen durchgeführte Arbeiten auf freie ungesättigte Fettsäuren aus. Es stellte sich heraus, dass die Reaktion eine neuartige Methode zur Erzeugung von Estern ungesättigter Hydrosäuren direkt aus ungesättigten Fettsäuren zur Verfügung stellt. Ein Schema zur Erklärung dieser Reaktion wird vorgelegt.

Die Modifikation von trocknenden und nichttrocknenden Estern durch gemeinsames Reagieren mit Terpenen, wie z.B. Allocymol und Myrcen, wurde untersucht. Bei ersteren ging die Dehydropolymerisationsreaktion normal vonstatten, aber letztere, die eine $CH_2{=}C$—Endgruppe enthält, gellierte unter Bedingungen, welche die Dehydropolymerisation begünstigten, konnte aber zum Myrcenisieren (Analogie zum Styrolisieren) eines Öles unter Benutzung von einer katalytischen Menge von Peroxid angewandt werden.

## Дегидрополимеризация и сополимеризация высыхающих масел и других реактивных соединений проявляющих α-метиленовую активность

*Резюме*

Применение диалкиловых перекисей для извлечения водорода из молекул содержащих активные метиленовые группы, с последующим соединением образовавшихся свободных радикалов, является полезным способом проведения регулируемой «полимеризации» и называется «дегидрополимеризацией» или «полирекомбинационной реакцией». Доложенная работа подтверждает стехиометрию реакции по отношению к триглицеридам и распространяет предыдущую работу с натуральными маслами в область свободных ненасыщенных жирных кислот. Найдено что реакция является новым методом получения эфиров ненасыщенных гидрокси-кислот непосредственно из ненасыщенных жирных кислот и предлагается план для объяснения этой реакции.

Рассматривается модификация высыхающих и полу-высыхающих эфиров посредством совместной реакции с терпенами, как например аллоцимен и мирцен. Демонстрируется влияние структуры на реактивность в случае аллооцимена и мирцена. Первый подвергался реакции дегидрополимеризации нормально, в то время как второй, содержащий конечный член $CH_2{=}C$—, желатинировался в условиях благоприятных для дегидрополимеризации, но мог быть применен для «мирценизации» (по аналогии с «стиренизацией») масла, применяя каталитическое количество перекиси.

## Introduction

During the past 15 years much experimental work has been carried out on the thermal decomposition of organic peroxides and the reactions of the primary radicals produced. In particular it has been shown that tertiary alkyl peroxides undergo homolytic scission of the -O-O- peroxide bond to yield peroxy radicals that in many cases are sufficiently energetic to abstract hydrogen from unsaturated hydrocarbons or other materials that have " active " hydrogen sites within their molecules. Hydrogen atoms that are sufficiently " active " to undergo abstraction are present in many molecular configurations, but specially active hydrogen atoms are those occurring in methylene groups adjacent to or between carbon-carbon double bonds, attached to tertiary carbon atoms, or adjacent to ether groups.

Rushman and Simpson[1] using the method of Kooyman have measured the " methylenic " activity of various drying oil esters and related compounds. The relative activities of a selection of these materials is shown in Table 1.

*Table 1*

*Methylenic activities of fatty esters and miscellaneous compounds determined by the method of Kooyman*[1]

| Compound | $10^2 \times Kp$ |
|---|---|
| Methyl palmitate .. .. .. | 0.0 |
| Methyl oleate .. .. .. | 8.1 |
| ,, linoleate (9 : 12) .. .. | 60.5 |
| ,, ,, (9 : 11) .. .. | 437.0 |
| ,, linolenate (9 : 12 : 15) .. | 110.0 |
| ,, elaeostearate .. .. | 445.0 |
| Dipentene .. .. .. .. | 217.0 |
| Tetralin .. .. .. .. | 7.1 |

Several workers[2, 3, 4] have shown that peroxy radicals react with hydrocarbons to yield dimeric and polymeric products. These were shown to be " dehydro-dimers " and " polymers " and not normal poly-addition products. The term " dehydropolymer " was introduced by Farmer[2]. (An alternative name for these types of product has been suggested by Korshak[5] who prefers to describe the abstraction and subsequent radical-radical addition the " polyrecombination " reaction.) Kharasch et al.[3] using diacetyl peroxide obtained *d*, *l* and *meso* 2:3 diphenyl *n*-butane from ethyl benzene, and dimethyl diphenyl benzene from isopropyl benzene. Similar experiments were carried out by Farmer and Moore[2] using ditertiary butyl peroxide with various aromatic and aliphatic hydrocarbons, and dehydropolymerisation was found to occur exclusively, except where the hydrocarbon under examination contained an unsubstituted terminal (vinyl) double bond. In the latter case addition polymerisation was initiated and a high yield of saturated polymers resulted. Olefins other than those containing terminal double bonds yield dehydropolymers without loss of unsaturation. There is evidence (ref. 2 footnote to text) that coupling of olefin and tertiary alkoxy radicals to give ethers can occur, but this happens to only a small extent.

The dehydropolymerisation of dialkyl benzenes (diethyl and diisopropyl benzene) to yield linear polymers has been the subject of patent literature[6]. The extension of dehydropolymerisation reactions to simple fatty acid esters was carried out by Clingman and Sutton[7] and by Harrison and Wheeler[8] who examined the reactivity of the methyl esters of stearic, linoleic and linolelaidic acids.

Clingman and Sutton proposed the following mechanism to explain the reaction between tertiary butoxy radicals and methyl linoleate :—

1. $(CH_3)_3CO^{\cdot} + R\,CH{:}CH\,CH_2CH{:}CH.R' \longrightarrow RCH{:}CH.\dot{C}HCH{:}CH.R' + (CH_3)_3COH$

$\{$ where $R = CH_3(CH_2)_4$ and $R' = -(CH_2)_7COOCH_3$ $\}$

2. $$\underset{(R_1)}{\text{R CH:CH.}\dot{\text{C}}\text{HCH:CH.R}'} \rightleftharpoons \underset{(R_2)}{\text{RCH:CH.CH:CH}\dot{\text{C}}\text{H R}'} \rightleftharpoons \underset{(R_3)}{\text{R }\dot{\text{C}}\text{HCH:CHCH:CH R}'}$$

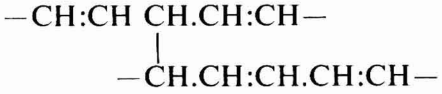
3. Dimerisation reactions :—

(i) $R_1 + R_2 \longrightarrow$ non conjugated dimer

(ii) $R_1 + R_2$ and $R_1 + R_3 \longrightarrow$ dimer with conjugation in one chain

(iii) $R_2 + R_2$, $R_2 + R_3$, $R_3 + R_3 \longrightarrow$ dimer with conjugation present in both fatty acid chains.

Ultra-violet analysis of the dimer formed indicated that about 40 per cent of the unsaturated groups were conjugated. Alkali isomerisation of the dimer resulted in no increase in absorption maxima at 235m$\mu$ and it was suggested that the dimers were mainly of the type given by the termination steps shown in 3(ii) above. Furthermore, it was suggested that the structures produced by this step,



$$\begin{array}{l}-\text{CH:CH CH.CH:CH}-\\ \qquad\qquad\quad |\\ \qquad\quad -\text{CH.CH:CH.CH:CH}-\end{array}$$

would be less susceptible to alkali isomerisation than one in which the active methylene group was unsubstituted.

Improvements in the drying rates of semi-drying oils after subjecting them to dehydropolymerisation has been claimed[6] and is reported in detail by Tess and Dannenberg[9].

The present work is concerned with the reaction of ditertiary butyl peroxide (DTBP) with commercially available refined vegetable oils and with mixtures of vegetable oils and other reactive materials.

The work (in part) has been the subject of patent applications[10].

## Experimental

### *Materials*

All materials were commercially available and were used as received.

| | |
|---|---|
| Ditertiary butyl peroxide (DTBP)<br>Assay : 95 per cent DTBP | —ex Shell Chemical Co. 5 per cent *t*-butyl hydroperoxide. |
| Linseed oil | —alkali refined oil ; $n_D^{25}$ 1.4792. Iodine value (Wijs), 182 cg.I/g. |
| Soyabean oil | —Alkali refined oil ; $n_D^{25}$ 1.4734. Iodine value (Wijs), 134 cg.I/g. |
| Tobacco seed oil | —alkali refined oil ; $n_D^{25}$ 1.4750. Iodine value (Wijs), 140 cg.I/g. |
| Tall oil | —a refined oil/containing 3 per cent rosin acids : acid value 183 mg.KOH/g. $n_D^{25}$ 1.4660. |
| Alloocimene | —2, 6 dimethyl 2, 4, 6 octatriene, 85 per cent + 15 per cent mixture of $\alpha$ and $\beta$ pinenes. |

| | |
|---|---|
| Myrcene | —" Myrcene 85 " ex Glidden Chemical Co. 7 methyl-3-methylene 1, 6 octadiene 75 per cent, remainder principally mixed monocyclic terpenes. |

### *Methods*

*Dehydropolymerisation* was carried out, unless otherwise stated, either by polymerisation of small samples sealed under vacuum in glass tubes or in bulk in conventional laboratory equipment. Thus (2g) samples for viscometry or molecular distillation were polymerised in sealed glass tubes, which were inserted into a metal block that was thermostated at 145°C ± 0.5°C. The samples were removed from the block after the required polymerisation time, cooled and stored until a series was complete before opening the tubes, removing volatile products under high vacuum on a vacuum manifold and determining viscosity and/or polymer content.

Polymerisations in bulk were carried out in a flask equipped with reflux condenser, inert gas bleed, and stirrer, and heated with an oil bath.

*Viscosity* determinations were made on the samples at 25.0°C, using a falling sphere technique, in the sample tubes in which the polymerisation was carried out, after removing volatile products on a vacuum manifold. The internal diameter of the tubes was kept constant at 1 cm and a 0.7 mm steel ball was timed falling vertically through the centre of the sample over 3 cms. The viscosity was calculated from the equation

$$\eta = \frac{g\, d^2 t\, (\rho - \rho')}{18S}\left[1 - 2.104\frac{d}{D} + 2.09\frac{d^3}{D^3}\right]$$

where $g = 981$ cm/sec.$^2$ $t$ = time in secs.
$\rho$ = density of ball. $\rho'$ = density of oil.
$S$ = distance over which the fall of the ball was timed.
$d$ = diameter of ball. $D$ = diameter of tube.

The equation was essentially that deduced from Stokes Law with a correction for the " wall effect " of the tube.

*Molecular distillation* was used to separate monomeric and polymeric triglycerides, the monomeric, dimeric and polymeric products from carboxylic acids and methyl esters. Quantitative determinations were carried out with a semi-micro still of the " vacuum hotplate " type at $10^{-4}$ mm Hg. Semi-quantitative and preparative separations were carried out in a falling film still (Quickfit & Quartz Ltd. Ref. No. IFSMP). Quantitative measurements were reproducible to within ± 5 per cent. The temperature at which the respective species were volatile was determined with pure $C_{18}$ methyl esters and dimer methyl esters; distillation was found to occur for monomeric $C_{18}$ esters and acids at 100-110°C, $C_{36}$ dimer acids and methyl esters at 190-200°C and for monomeric triglycerides 250-260°C.

## Results

### *Linseed oil*

The viscosity/polymerisation time and refractive index/polymerisation time data for linseed oil using various ratios of peroxide to oil are set out in Table 2.

*Table 2*

*Dehydropolymerisation of linseed oil at 145°C*

| Molar ratio peroxide/ oil | REACTION TIME (HOURS) | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 4 | | 5 | | 6 | | 8 | | 12 | | 16 | | 20 | |
| | Visc. (poise) | $n_D^{25}$ | Visc. (poise) | $n_D^{25}$ | Visc. (poise) | $n_D^{25}$ | Visc. (poise) | $n_D^{25}$ | Visc. (poise) | $n_D^{25}$ | Visc. (poise) | $n_D^{25}$ | Visc. (poise) | $n_D^{25}$ |
| 0.40 | 0.45 | 1.4776 | — | — | — | — | 1.3 | 1.4781 | 1.7 | 1.4789 | 2.0 | 1.4789 | 2.1 | 1.4795 |
| 0.60 | 1.5 | 1.4769 | — | — | — | — | 3.9 | 1.4778 | 9.0 | 1.4795 | 15.6 | 1.4786 | 16.4 | 1.4765 |
| 0.70 | 2.9 | 1.4774 | 6.1 | 1.4784 | 23.2* | 1.4750 | — | — | — | — | — | — | — | — |
| 0.80 | 3.6 | 1.4771 | — | — | gelled | — | — | — | — | — | — | — | — | — |

*Gelled in 6.5 hours

From the results shown in Table 2, there would appear to be a critical ratio of peroxide to linseed oil below which it is impossible to gel the oil by dehydropolymerisation alone. This limit is somewhat less than 0.70 moles DTBP per mol. of linseed oil but will vary from oil to oil depending on the fatty acid composition of the oil.

A bulk polymerisation of the same batch of oil was carried out, using 0.65 mols. DTBP/oil and heating at 145°C for six hours. Volatile products of the reaction (e.g. butanol) were removed by passing the oil through the falling film still at 120°C at 0.3 mm Hg pressure, and a pale yellow oil was isolated. The oil had a viscosity of 17.5 poises, iodine value (Woburn) 185 cg.I/g. and $n_D^{25}$ 1.4885. Ultra-violet spectroscopic analysis of the oil showed that approximately 10 per cent of its unsaturation was conjugated but no conjugated triene was present. Clearly the polymerisation had taken place without the loss of unsaturation, which was reflected in the improved drying of the oil (in the presence of 0.05 per cent cobalt metal catalyst, added as the naphthenate) compared to the untreated linseed oil or a thermally bodied oil of similar viscosity ($\sim$ 20 poise). The oil gave a dry rubbery film after about 2 hours, whereas the untreated oil and the stand oil gave soft tacky films after about 3-4 hours.

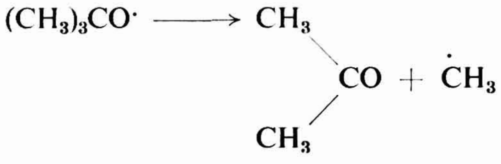
Since temperature is known to have a marked effect on the mode of decomposition of the peroxide (DTBP), two bulk polymerisations of linseed oil were carried out at 210°C. The purpose of the experiments was to determine whether or not rapid polymerisation would yield products comparable with those obtained at lower temperatures, provided that the peroxide could be decomposed in the reaction mixtures before it had time to distil out. The peroxide was blown dropwise into the heated oil and dispersed through the oil using a bell-type stirrer. The peroxide was added over a period of an hour. The properties of the products obtained are shown in Table 3.

*Table 3*

*Dehydropolymerisation of linseed oil at 210°C*

| Sample | Molar ratio DTBP/oil | I.V. (cg.I/g) (Woburn) | Viscosity (poises) | Polymer analysis (from methyl esters) | |
|---|---|---|---|---|---|
| | | | | | % |
| A | 0.5 | 157 | 5.3 | Monomer<br>Dimer<br>Higher polymer | 72.8<br>17.2<br>10.0 |
| | | | | | % |
| B | 0.65 | 157 | 32.4 | Monomer<br>Dimer<br>Higher polymer | 68.1<br>16.1<br>15.8 |

Above 160°C it is known that a secondary reaction of the *t*-butoxy radical takes place,



$$(CH_3)_3CO\cdot \longrightarrow CH_3COCH_3 + \dot{C}H_3$$

The methyl radical so formed may abstract hydrogen from the triglyceride, the net effect of such a reaction being no different from the action of the *t*-butoxy radical itself. Alternatively it may add to radicals formed on the fatty acid chain, thus interfering with the dimerisation steps through which polymerisation occurs. However, since a decrease in unsaturation occurred to the same extent in the samples (A and B, Table 3), it was not possible to establish whether this secondary reaction was significant. The loss of unsaturation and the relatively higher viscosities of the products compared with products obtained at 145°C (Table 2) indicates that polymerisation by a mechanism other than dehydropolymerisation occurs concurrently with the dehydropolymerisation. It is probable that the loss of unsaturation is due to the Diels-Alder addition of dimeric or polymeric species containing conjugated dimers at the higher temperature of reaction, since Diels-Alder addition of conjugated fatty esters is very slow at 145°C.

### *Soyabean oil*

The dehydropolymerisation of soyabean oil was carried out with low concentration of peroxide, in tubes sealed under vacuum, in vessels open to air and in vessels swept with carbon dioxide. For comparison samples of linseed oil were polymerised in tubes sealed under vacuum. The results are shown in Table 4. Low concentrations of peroxide were chosen in order to obtain low viscosity oils which are useful in the preparation of paint media. In order to improve drying and to reduce after-tack in semi-drying oil alkyds, thermally bodied oils (0.75-2 poises) may be used in place of unpolymerised oils. Replacement of these oils with dehydropolymerised oils of equal viscosity would be expected to improve the drying properties of the alkyd.

*Table 4*

*Dehydropolymerisation of soyabean oil at 145°C*

| Oil | Wt. % DTBP | Molar ratio DTBP/oil | Atmosphere | Viscosity (poises) | Polymeric triglycerides % |
|---|---|---|---|---|---|
| Soyabean .. | 2.0 | 0.12 | air | 0.932 | 20.0 |
| Soyabean .. | 2.0 | 0.12 | $CO_2$ | 0.775 | 16.1 |
| Soyabean .. | 2.0 | 0.12 | vacuum | — | 19.5 |
| Soyabean .. | 4.0 | 0.24 | air | 1.395 | 35.0 |
| Soyabean .. | 4.0 | 0.24 | $CO_2$ | 1.275 | 31.8 |
| Soyabean .. | 4.0 | 0.24 | vacuum | — | 31.4 |
| Linseed .. | 2.0 | 0.12 | vacuum | — | 22.5 |
| Linseed .. | 4.0 | 0.24 | vacuum | — | 32.9 |
| Soyabean .. | 0 | — | vacuum | 0.580 | 1.85 |
| Linseed .. | 0 | — | vacuum | — | 6.25 |

With low concentrations of peroxide the proportions of polymeric triglycerides formed with linseed and soyabean oils was comparable. When the polymerisation vessels were open to air, small but significantly larger quantities of polymeric triglycerides were present, possibly due to autoxidation.

However, the " critical gelation limit " for the peroxide/soyabean oil ratio was higher than that for linseed oil, and it was possible to react, under conditions for bulk polymerisation, soyabean oil and DTBP in the molar ratio 1 : 1 for six hours at 145°C without gelation occurring. The product was a pale yellow oil (viscosity 9.5 poises ; saponification value 188 mg KOH/g ; iodine value 130 cg.I/g), containing a minor proportion of conjugated unsaturation (5.9 cg.I/g determined as the maleic anhydride value). The difference in the " critical gelation limit " is clearly dependent upon the nature of the fatty acids that constitute the triglyceride. Thus linseed oil, which is rich in linolenic ester, would be expected to be more reactive than soyabean oil, which contains linolenic acid, since the linolenate ester has more active methylene sites per $C_{18}$ chain due to its triene structure.

### *Tall oil*

Tall oil consists principally of a mixture of oleic and linoleic acids. It was of interest to establish whether dehydropolymerisation would enable novel dimeric or polymeric acids to be prepared. Such products could, for example, be converted into polyamide resins but, in contrast to thermally polymerised products, would contain more readily autoxidisable groups and thus be capable of cross-linking.

The polymer analysis of the tall oil-DTBP reaction (using 0.25 mol peroxide per mol fatty acid) is given in Table 5.

*Table 5*

*Tall oil—DTBP reaction at 145°C*

| Polymerisation time (hours) | Polymer analysis | | |
|---|---|---|---|
| | Monomer (%) | Dimer (%) | Higher polymer (%) |
| 0 | 97.7 | 0.3 | — |
| 4 | 67.2 | 15.4 | 17.4 |
| 8 | 62.3 | 17.6 | 20.1 |
| 12 | 62.8 | 18.0 | 19.2 |
| 16 | 62.7 | 18.4 | 19.0 |
| 20 | 62.2 | 17.4 | 20.3 |

No significant change in polymer analysis occurs after eight hours since over 90 per cent of the peroxide was decomposed in this time. The results clearly indicate that the polymerisation is stoichiometric with respect to peroxide decomposition and that polymerisation other than by dehydropolymerisation is absent.

The product of a bulk polymerisation of tall oil using DTBP in the molar ratio 0.5 moles per mol of oil was fractionated on the falling film molecular still. Analytical data on four fractions obtained from 226 g of polymerised oil are given in Table 6.

Fractions 2 and 3 were both essentially dimeric. The fall in acid value with molecular complexity is significant. Since the saponification value of the polymeric

*Table 6*

*Fractionation of dehydropolymerised tall oil*

| Fraction | Wt. (g) | % | Acid value (mg.KOH/g) | $n_D^{25}$ | Iodine value (Woburn) cg.I/g | Sap. value mg.KOH/g | Remarks |
|---|---|---|---|---|---|---|---|
| 1 | 85 | 37.6 | 182.5 | 1.4663 | 120 | — | Pale yellow mobile liquid (monomer) |
| 2 | 25 | 11.1 | 168.5 | 1.4679 | 120 | — | Pale yellow liquid (dimer) |
| 3 | 10 | 4.4 | 166 | 1.4720 | 125 | 184 | Pale yellow liquid (dimer) |
| 4 | 75 | 33.2 | 124 | 1.4902 | 124 | 180 | Orange viscous oil (trimers and higher polymers) |
| Losses | 31 | 13.7 | — | — | — | — | |

fractions is similar to the acid value of the monomeric acid, the decrease in acid value must be due to esterification. Esterification of the fatty acids with *t*-butanol formed as a by-product of the decomposition can be discounted since such an esterification would involve the formation of water and should occur to the same extent with dimer or trimer acids. Experiment shows that this is not so and that there is a decrease in acid value with increasing molecular complexity.

Since the abstraction of a hydrogen atom from the carboxy group is energetically unlikely, the following radical-ion mechanism is proffered to explain the formation of the ester group :

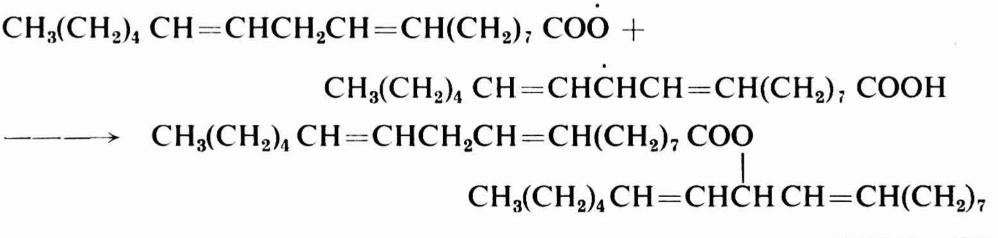
$$\mathrm{CH_3(CH_2)_4\,CH{=}CHCH_2CH{=}CH(CH_2)_7\,COO^- + (CH_3)_3\,C\dot{O}}$$

$$\longrightarrow \mathrm{CH_3(CH_2)_4\,CH{=}CHCH_2CH{=}CH(CH_2)_7\,CO\dot{O} + (CH_3)_3\,CO^-} \qquad \text{(i)}$$

$$\mathrm{CH_3(CH_2)_4\,CH{=}CHCH_2CH{=}CH(CH_2)_7\,COOH + (CH_3)_3\,C\dot{O}}$$

$$\longrightarrow \mathrm{CH_3(CH_2)_4CH{=}CH.\dot{C}HCH{=}CH(CH_2)_7\,COOH + (CH_3)_3COH} \qquad \text{(ii)}$$

followed by the termination reaction



$$\mathrm{CH_3(CH_2)_4\,CH{=}CHCH_2CH{=}CH(CH_2)_7\,CO\dot{O}} + \mathrm{CH_3(CH_2)_4\,CH{=}CH\dot{C}HCH{=}CH(CH_2)_7\,COOH}$$

$$\longrightarrow \mathrm{CH_3(CH_2)_4\,CH{=}CHCH_2CH{=}CH(CH_2)_7\,COO{-}CH(CH{=}CH(CH_2)_4CH_3)CH{=}CH(CH_2)_7COOH} \qquad \text{(iii)}$$

Isomerisation of the free radical produced by reaction (ii) can occur and mixed conjugated and non-conjugated products are formed.

Since hydrogen abstraction occurs at random with structurally similar monomeric and polymeric species, a product containing the esters of monomeric and polymeric hydroxy acids is obtained. Thus fraction 4 (Table 6) was essentially a $C_{18}$ unsaturated ester of an hydroxylated $C_{28}$ dimer.

Although ester formation due to the attachment of fragments from peroxides is well known (e.g. formation of benzoate esters during reactions involving benzoyl peroxide), the self-esterification of fatty acids as a result of hydrogen abstraction reactions has not been reported hitherto.

### *Dehydrocopolymerisation or " mixed polyrecombinations "*

The isomeric terpenes alloocimene (2, 6 dimethyl 2, 4, 6 octatriene) and myrcene (7 methyl 3 methylene 1.6 octadiene) were chosen for copolymerisation work because of the high $\alpha$-methylenic activity of terpenes as a class (see dipentene, Table 1).

*Alloocimene* : The methyl ester of linseed oil fatty acids, alloocimene and DTBP (molar ratio 1 : 1 : 1) were reacted for six hours at 140-145°C. Volatile matter was removed by distillation under high vacuum up to 130°C, which removed unreacted DTBP, *t*-butanol, alloocimene and alloocimene dimer. The residue material was molecularly distilled and fractions collected at 110°C, 160°C and 210°C. Saponification values and unsaponifiable matter were determined on each fraction and are recorded in Table 7.

The experiment was repeated, replacing the linseed esters with the methyl esters of tobacco seed oil fatty acids to enable the comparisons of reactivity of the latter linoleic rich esters with the linolenic rich esters. The results are similarly collected in Table 7.

Good agreement was not obtained between the total hydrocarbon content of the fractions (calculated from saponification value) and that determined from the total of " percentage unsaponifiable " and " percentage combined hydrocarbon " calculated from the acid value of the recovered acids. The former is probably more reliable since it involves only a simple analytical determination on the original fraction in each case. The saponification, separation and isolation of fatty acids and unsaponifiable matter required several operations ; losses, causing inaccuracy, can occur at each stage and could account for the discrepancy. The results obtained do, however, give an indication of the distribution of combined and uncombined hydrocarbon and enable an assessment of the relative reactivity of the linolenic rich and linoleic rich esters towards alloocimene to be made. From the table it appears that the linseed esters form approximately the same amount by weight of polymer (i.e. higher than dimer) as the tobacco seed esters, but the polymer contains a larger proportion of hydrocarbon. In addition, a larger proportion of the hydrocarbon is combined with the linseed esters, whereas in the case of the tobacco seed esters the hydrocarbon is present in approximately equal combined and uncombined proportions. In the volatile fractions the overall level of hydrocarbon content is higher in the tobacco seed esters than in the linseed esters and the ratios of combined and uncombined hydrocarbon are of the same order for both esters.

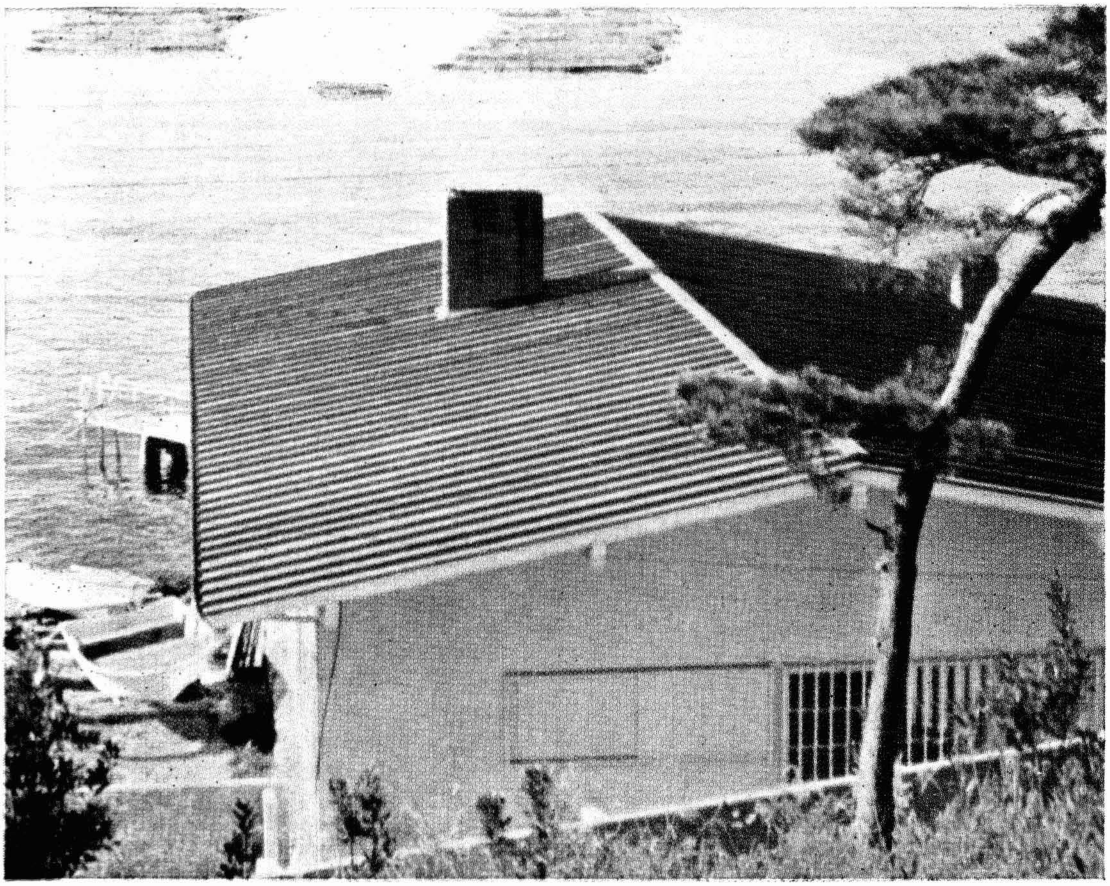



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*Table 7*

*Dehydrocopolymerisation of fatty esters and alloocimene*

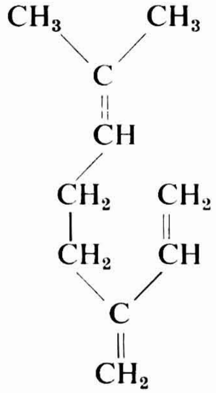
*Methyl esters of linseed fatty acids*

| Distillate at | % by wt. | $n_D^{25}$ | Sap. value mg KOH/g | % total HC calc. from sap. val. | % acids recovered after sap. | Av. of recovered acids (mg KOH/g) | % unsap. (uncombined HC) | % combined HC from acid value | Ratio $\frac{\text{comb.}}{\text{uncomb.}}$ |
|---|---|---|---|---|---|---|---|---|---|
| 110°C | 22 | 1.4667 | 192.0 | 0 | 93.4 | 170 | 2.6 | 14.3 | 5.5 |
| 160°C | 17 | 1.4850 | 143.6 | 25 | 87.9 | 128 | 7.75 | 34.3 | 4.43 |
| 210°C | 20 | 1.5010 | 119.0 | 38 | 82.6 | 112 | 13.1 | 41.9 | 3.2 |
| Residue | 41 | 1.5138 | 112.0 | 42 | 91.5 | 90 | 4.2 | 52.3 | 12.5 |

*Methyl esters of tobacco seed acids*

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 110°C | 30 | 1.4651 | 164.0 | 15.4 | 81.9 | 186 | 13.8 | 6.7 | 0.5 |
| 160°C | 19 | 1.4891 | 117.0 | 39 | 86.0 | 105 | 9.8 | 45.3 | 4.6 |
| 210°C | 13 | 1.4989 | 107.0 | 44 | 86.2 | 93 | 9.6 | 51.0 | 5.3 |
| Residue | 39 | 1.5037 | 128.0 | 33 | 76.6 | 150 | 19.2 | 23.8 | 1.2 |

*Myrcene* : Attempts to prepare dehydrocopolymers of myrcene and drying oil esters were unsuccessful, gels being obtained whenever the DTBP was used in stoichiometric proportions. From the structure of myrcene,



one would expect a poly addition reaction to take place involving the terminal $CH_2{=}C$— group. Clearly the structure provides an explanation of the gel formation experienced under the conditions used for dehydrocopolymerisation. However, it was found that useful air drying products could be obtained by polymerising myrcene in the presence of a drying or semi-drying oil, using a small proportion of peroxide as initiator. The products, low viscosity oils, may be dehydropolymerised further to give more viscous oils that dry rapidly to hard, glossy films. Dehydropolymerisation enables controlled cross-linking to take place and products varying over a wide viscosity range can be obtained, which may be used as lithographic varnishes, the binder for wood fillers, and in paints. In a typical experiment, alkali refined linseed oil was "myrcenated" by adding myrcene containing 1 per cent (by wt) DTBP to the oil heated to 145-150°C over a period of four hours. Heating was then continued for a further six hours. Thus linseed oil was myrcenated in the ratios 1 : 2, 1 : 1 and 2 : 1 (by wt), and the products were dehydropolymerised using DTBP (5 per cent by wt on total oil+myrcene) to give products in a 10-12 poise range. The myrcenated oils and the dehydropolymerised myrcenated oils were driered with cobalt (0.1 per cent metal as naphthenate) and lead (0.5 per cent metal as naphthenate) and their air drying properties compared with linseed oil, 20 poise linseed stand oil and a dehydropolymerised oil (17 poises), similarly driered. The myrcenated oils (both dehydropolymerised and untreated) were markedly superior to the linseed oil, the stand oil and the dehydropolymerised oil. They dried rapidly to hard glossy films, whereas films from the non-myrcenated oils remained soft. The best films were initially those formed from the dehydropolymerised myrcenated linseed oil (2 : 1 by wt, myrcene : linseed oil), but they embrittled subsequently on ageing.

Similar results were obtained with soyabean oil and in this case the improvement in drying rate and film hardness was even more marked than with linseed oil. Thus " myrcenation " with or without subsequent dehydropolymerisation provides a convenient means of up-grading the drying properties of semi-drying oils.

## Acknowledgments

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# Mechanical properties of alkyd resin varnish films and the effect of different weathering conditions on them

**By R. Vittal Rao, Mohd. Yaseen and J. S. Aggarwal**

Regional Research Laboratory, Hyderabad, India

*Summary*

Mechanical properties such as tensile strength, percentage elongation, toughness, flexibility, modulus of rigidity and bursting strength of films of alkyd resin varnishes of 66 per cent and 55 per cent oil length based on linseed oil/DCO—phthalic anhydride—glycerol/pentaerythritol have been determined. The pentaerythritol alkyd films have been found to have better mechanical properties than the films of other varnish compositions, even after exposing to different weathering conditions. Partial replacement of phthalic anhydride by maleic anhydride in the formulation of the alkyd resin varnish was found to improve the mechanical properties of the film.

## Propriétés mécaniques de feuils de vernis à résine alkyde et les effets des conditions diverses de l'exposition aux intempéries

*Résumé*

On a déterminé des propriétés mécaniques telles que, résistance à la traction, élongation pour cent, tenacité, flexibilité, module de rigidité et résistance à la rupture des feuils de vernis à résine alkyde de longueur en huile de 66% et 55% contenant d'huile de lin/huile de ricine déshydratée, de l'anhydride phtallique et de glycérine/pentaerythrite. Les feuils de la résine alkyde à pentaerythrite démontrent des meilleurs propriétés mécaniques que celles des feuils d'autres vernis, même où ils ont été exposés aux conditions diverses des intempéries.

## Die mechanischen Eigenschaften von Alkydharzlackfilmen und die auf diese durch Verschiedene Bewitterungen Ausgeübten Wirkungen

*Zusammenfassung*

Die mechanischen Eigenschaften wie Zugfestigkeit, prozentale Dehnbarkeit, Zähigkeit, Biegefestigkeit, Starrheitsmodul und Bruchfestigkeit von Alkydharzlackfilmen mit einem Ölgehalt von 66% und 55% wurden bestimmt. Es handelt sich um Leinöl/Rizinusöl-Phtalsäureanhydrid-Glyzerin/Pentaerythrit Lacke. Es wurde festgestellt, dass die mechanischen Eigenschaften der Pentaerythrit Alkydfilme selbst unter verschiedenen Wetterverhältnissen besser, als die von Lacken anderer Zusammensetzung sind. Es stellte sich heraus, dass wenn in dem Rezept ein Teil des Phtalsäureanhydrides durch Maleinsäureanhydrid ersetzt wurde, sich die mechanischen Eigenschaften des Alkydharzlackfilms verbesserten.

## Механические свойства алкидно-смольных лаковых пленок и влияние на них различных условий выветривания

*Резюме*

Определяются механические свойства как например сопротивление разрыву, относительное удлинение, жесткость, гибкость, модуль сдвига и сопротивление продавливанию алкидно-смольных лаковых пленок 66% и 55% жирности лака на основе льняного масла/DCO — фталового ангидрида — глицерина/пентаэритрита. Обнаружено что алкидные пленки из пента-эритрита обладают лучшими механическими свойствами чем пленки из других лаковых соединений, даже после подвержения различным условиям выветривания. Найдено что частичная замена фталового ангидрида малеиновым ангидридом в формуляции алкидно-смольного лака улучшает механические свойства пленки.

## Introduction

The durability of a surface coating depends on the physical characteristics of its films, i.e. flexibility, tensile and bursting strengths, impact resistance, resistance to the permeation of water vapour, ions and gases, and its adhesion to the substrate. Generally, coatings fail in service by cracking and flaking due to the mechanical breakdown of their films, indicating that, at the time of failure, the magnitude of the stresses present in the film exceeds that of the cohesive forces. These stresses are set up as a result of the differential dimensional changes in the film and its substrate, and changes in the chemical structure of the film as a result of weathering. The stresses induced in the film and in the substrate are communicated to and resolved in the plane of the interface. The stress concentration and chemical changes lead ultimately to the breakdown of the film.

The stresses induced (or developed) on ageing are opposed to the forces bonding the coating to the surface of the substrate. In the process of drying, paints and varnishes are converted from the liquid to the solid state by oxygen-induced cross-linking. Since, under such conditions the paint film dries from the outside, rigidity will first develop at the exposed surface. To avoid stress concentration in the film, which will bring about cracking and flaking, a reasonably high order of mechanical properties is required. Thus, the determination of the mechanical properties of surface coatings under different weathering conditions is important in order to find out whether they will perform satisfactorily.

A close examination of methods available for measuring mechanical properties of paint and varnish coatings, such as rocker hardness, impact, bend and scratch tests, shows some limitations particularly with regard to their time dependence and reproducibility. Since these tests are normally carried out on films coated on metal surfaces, the values obtained may be affected by the nature of and adhesion to the substrate. An alternative approach based on measurements made on unsupported films could thus be advantageous.

A considerable amount of work has been done[1–6] on the stress-strain properties of paint and varnish films, and it has been found that tensile strength measurements are in many ways a far more reliable guide to film strength than the other methods. Film strength is related to the degree of cross-linking in the film-forming material. Cross-linking imparts rigidity, which shows itself in increased tensile strength and lower elongation[7–9]. The stress-strain curves can be used not merely to define the ultimate tensile strength and elongation of the material[10], but also to define its toughness, flexibility and hardness. Toughness is best measured by the total work required to break the film, as indicated by the area under the load elongation curve. In agreement with the definition of flexibility as extensibility or the ability to undergo deformation, the ultimate elongation can be considered as a measure of flexibility. The yield point on the load elongation curve is suggested as a measure of hardness.

The importance of physical specifications for film-forming materials has been emphasised[11] in connection with the relationship between the physical properties and the general durability of a coating. The initial values of the physical properties of the coatings vary with the composition of the film-forming materials. The durability depends more on the rate of change of physical properties than on their initial values[12]. Periodical determination of these properties during the course of ageing will show the extent of changes taking place in the film up to its ultimate failure. Such data will provide a classification of the film-forming materials with regard to mechanical properties.

Certain physical properties of varnish films on metal substrates have been measured by several workers[13-17] at definite ageing intervals. The flexibility of the coating was determined by bending a metal panel coated with the material under test around a mandrel. It was found[14] that exposure to continuous carbon arc light, in absence of water, had little visible effect on the films, hence the time of exposure required to crack the varnish film on bending over a mandrel of 3 mm rod was taken as a measure of durability of the films[17]. The progressive oxidation of oil in the course of ageing generally increases the tensile strength and decreases the flexibility of the film.

The function of the oil component of a varnish is to give the film the necessary extensibility to withstand the tensions caused by expansion, contraction, bending, etc., which would otherwise make it crack. In the present study a number of alkyd resin varnishes of the following compositions were selected for determining the mechanical properties :

(1) 66 per cent linseed oil—phthalic anhydride—glycerol alkyd.
(2) 55 per cent linseed oil—phthalic anhydride—glycerol alkyd.
(3) 66 per cent DCO—phthalic anhydride—glycerol alkyd.
(4) 55 per cent DCO—phthalic anhydride—glycerol alkyd.
(5) 66 per cent linseed oil—phthalic anhydride—pentaerythritol alkyd.
(6) 55 per cent linseed oil—phthalic anhydride—pentaerythritol alkyd.
(7) Alkyd (1) in which five parts of phthalic anhydride were replaced by an equivalent amount of maleic anhydride.
(8) Alkyd (1) styrenated with 33 parts of styrene per 100 parts oil.
(9) Alkyd (1) to which 30 parts cardanol-hexamine condensate was added (physical mixture).
(10) Alkyd (1) to which 30 parts cardanol-hexamine condensate was added during polycondensation.
(11) 66 per cent linseed oil—phthalic anhydride—glycerol alkyd by fatty acid-oil process[21].
(12) 55 per cent linseed oil—phthalic anhydride—glycerol alkyd in which ten parts of phthalic anhydride were replaced by a corresponding amount of styrenated rosin.

The work outlined here was undertaken to determine the relationship between the composition of alkyd resin varnishes and their mechanical properties, i.e. tensile strength, elongation, modulus of rigidity and bursting strength.

The studies also included the periodical determination of some of the above properties during the course of ageing by exposing the free films of the varnishes to (i) natural weathering, and (ii) carbon arc lamp.

## Experimental

The alkyd resin varnishes were prepared as described in Appendix I.

The free films of these varnishes were prepared by an amalgamation technique[18]. The thickness of the dry varnish film can be controlled by variation in the percentage of thinner in the varnish and by using strips of known thickness

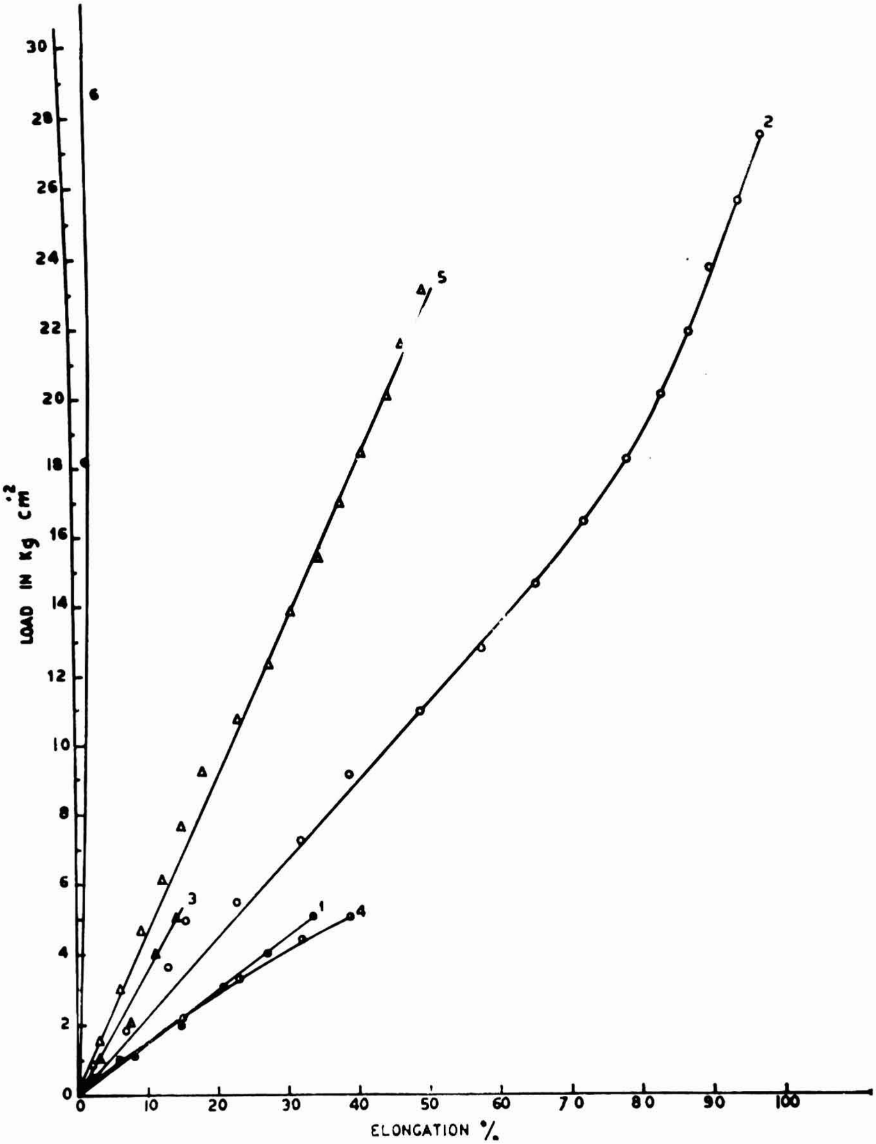


Fig. 1. Load elongation curves for varnishes 1-6

while applying the varnish film over the tin foil with the help of a film applicator. For proper comparison of data obtained by the measurement of various film properties, the thickness of the dried film was controlled at 60 ± 5$\mu$ as measured by dial gauge.

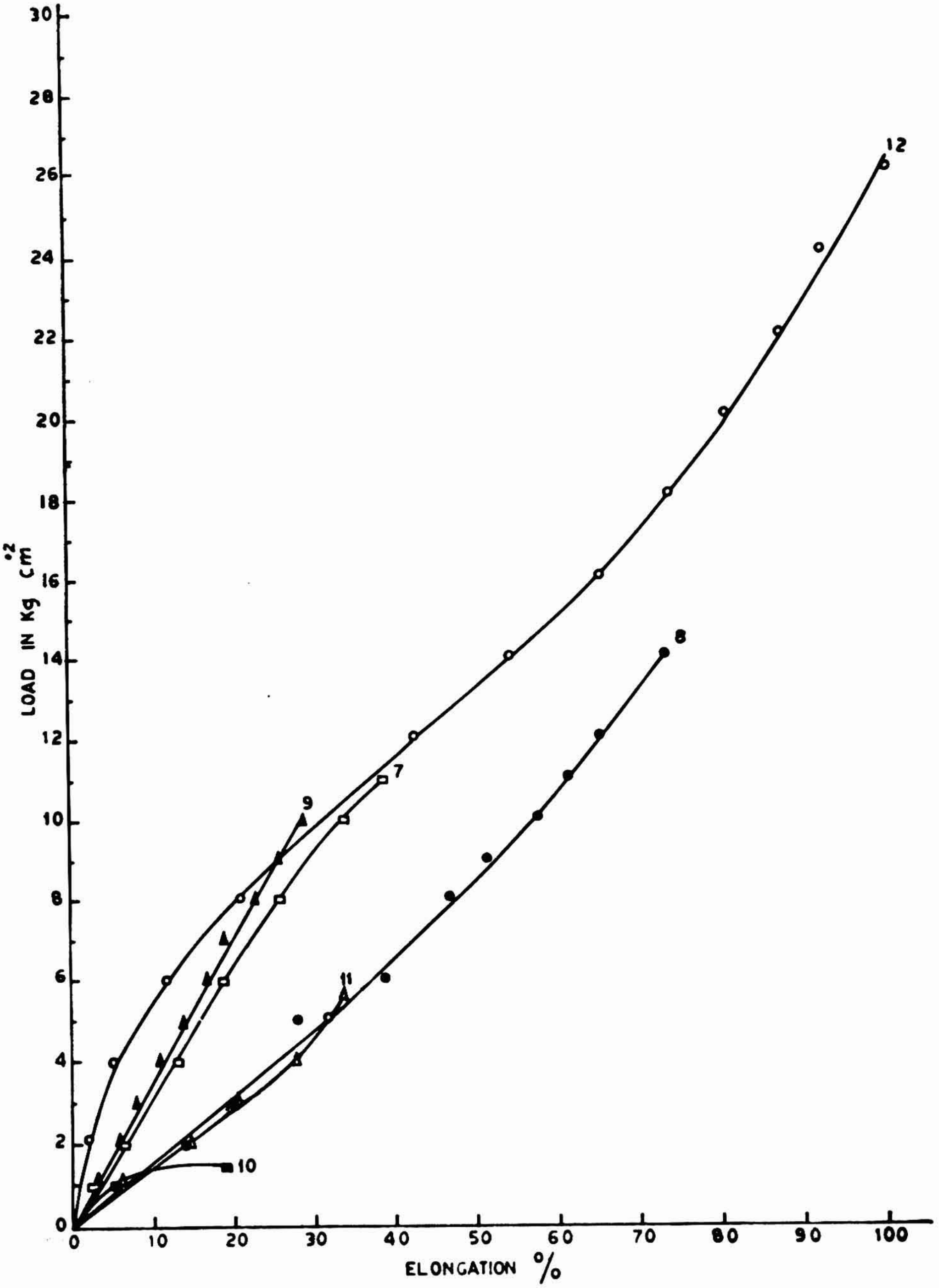


Fig. 2. Load elongation curves for modified varnishes 7-12

*Tensile strength and per cent elongation*

The electrically operated Gardner tensile strength and elongation apparatus was used for determining the tensile strength and percentage elongation of the varnish films. Films were cut into test pieces of 12 × 1 cm and fastened to

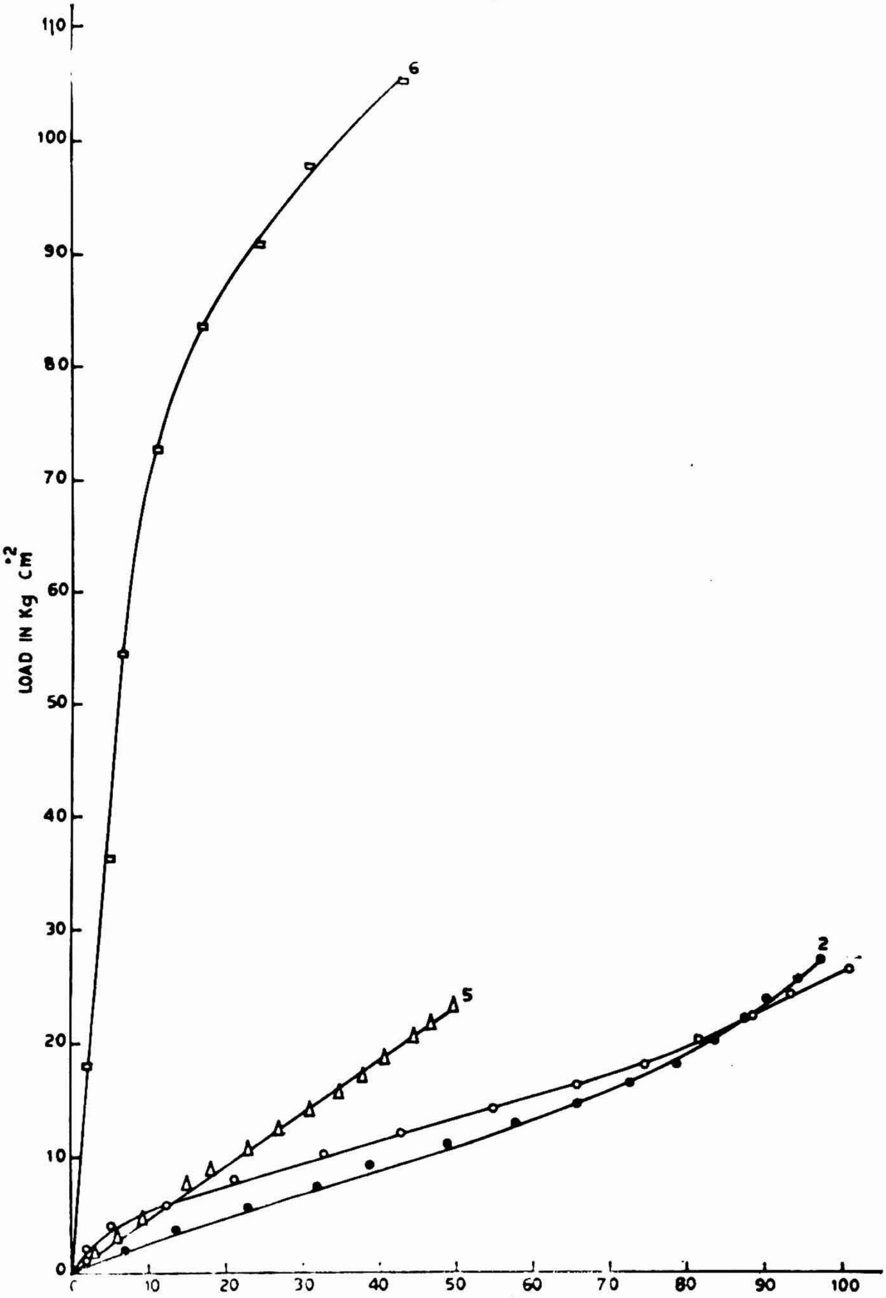


**Fig. 3. Load elongation curves for varnishes 2, 5, 6 and 12**

the upper and lower clamps of the apparatus so that the length of the film in between two clamps was 10 cm. The percentage elongation was noted for every reading of the load indicated by the scale and the observations were continued until the film failed. At least six determinations were made for each of the varnish films under test. The load values, calculated in terms of kg $cm^{-2}$, were plotted against percentage elongation (Figs. 1-2) and the area under each curve estimated for the determination of the toughness of the film. The load elongation curves of varnishes No. 2, 5, 6 and 12 which have high tensile strength are plotted separately in Fig. 3. The tensile strength, elongation and toughness data are given in Table 1.

*Table 1*

*Mechanical properties of alkyd resin varnish films*

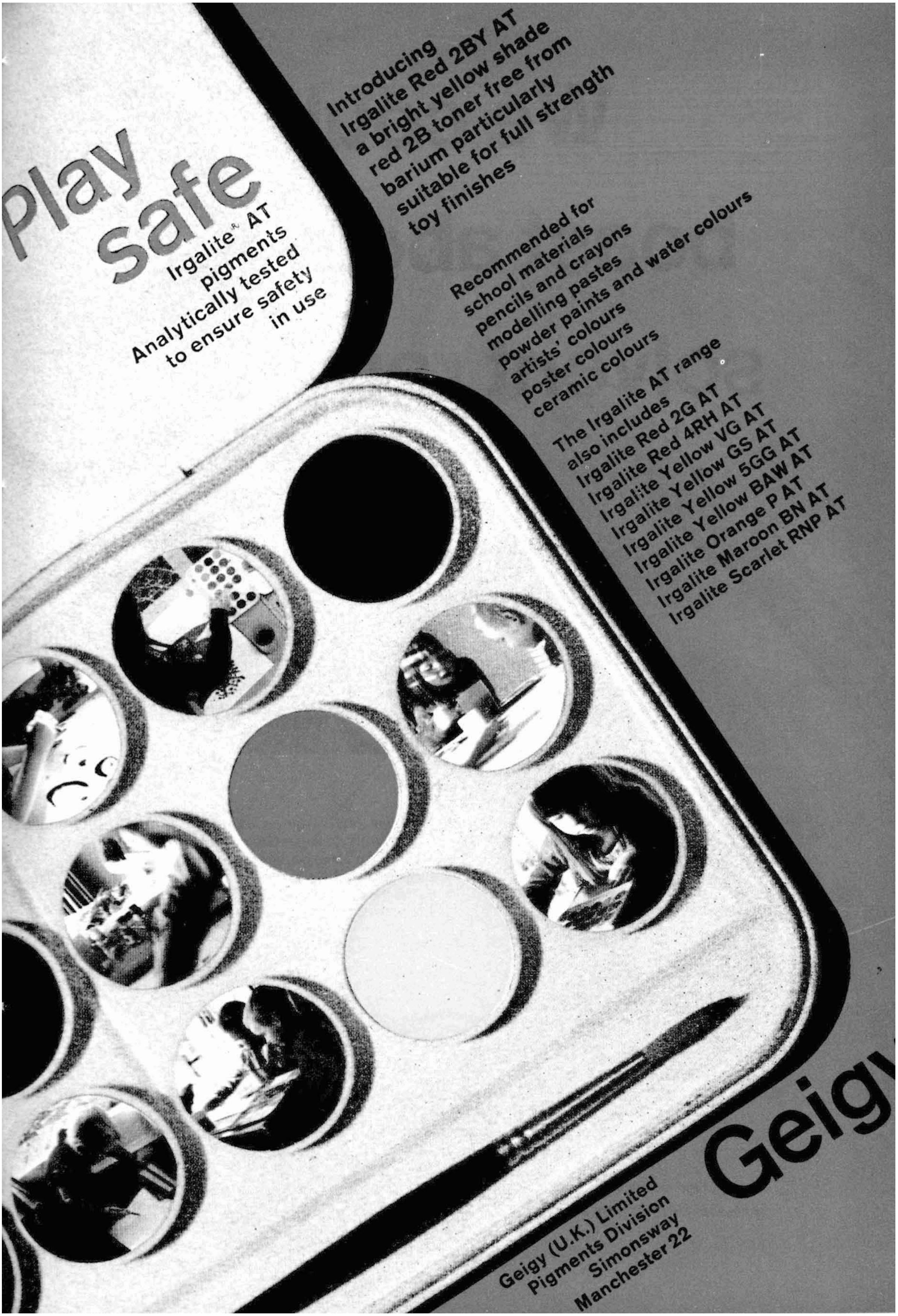
| No. of alkyd resin | Tensile strength kg $cm^{-2}$ | Elongation % | Toughness kg $cm^{-2}$ | Bursting strength mm Hg | Modulus of rigidity dyne $cm^{-1}$ $\times 10^9$ |
|---|---|---|---|---|---|
| 1 | 5.0 | 33.5 | 8.22 | 86 | 5.688 |
| 2 | 27.3 | 98.0 | 112.19 | 256 | 4.514 |
| 3 | 5.0 | 14.0 | 3.45 | 120 | 5.607 |
| 4 | 5.0 | 39.0 | 10.55 | 130 | 3.771 |
| 5 | 23.1 | 50.0 | 57.28 | 300 | 3.326 |
| 6 | 105.4 | 43.0 | 226.64 | 680 | 7.330 |
| 7 | 11.0 | 39.0 | 23.01 | 104 | 5.928 |
| 8 | 14.0 | 74.0 | 46.98 | 84 | 6.488 |
| 9 | 10.0 | 29.0 | 14.65 | 180 | 6.938 |
| 10 | 1.4 | 19.0 | 2.48 | 20 | 4.622 |
| 11 | 5.6 | 34.0 | 8.55 | 58 | 5.919 |
| 12 | 26.0 | 102.0 | 139.12 | 204 | 6.288 |

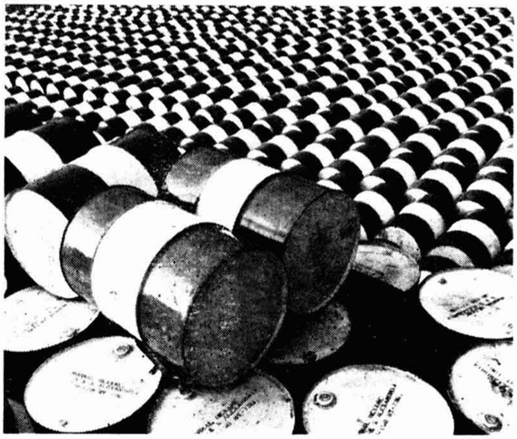
### *Modulus of rigidity*

The modulus of rigidity was also measured using the film as a torsion pendulum and results are reported in Table 1. These data were not useful in interpreting change of film properties and so are not further discussed.

### *Bursting strength*

The apparatus described in an earlier communication[19] was used for determining the bursting strength of the varnish film. Steadily increasing air pressure was applied to a known area of the film. The pressure was indicated by a mercury manometer and the pressure at which the film burst gave the bursting strength expressed in terms of the height of mercury in mm.





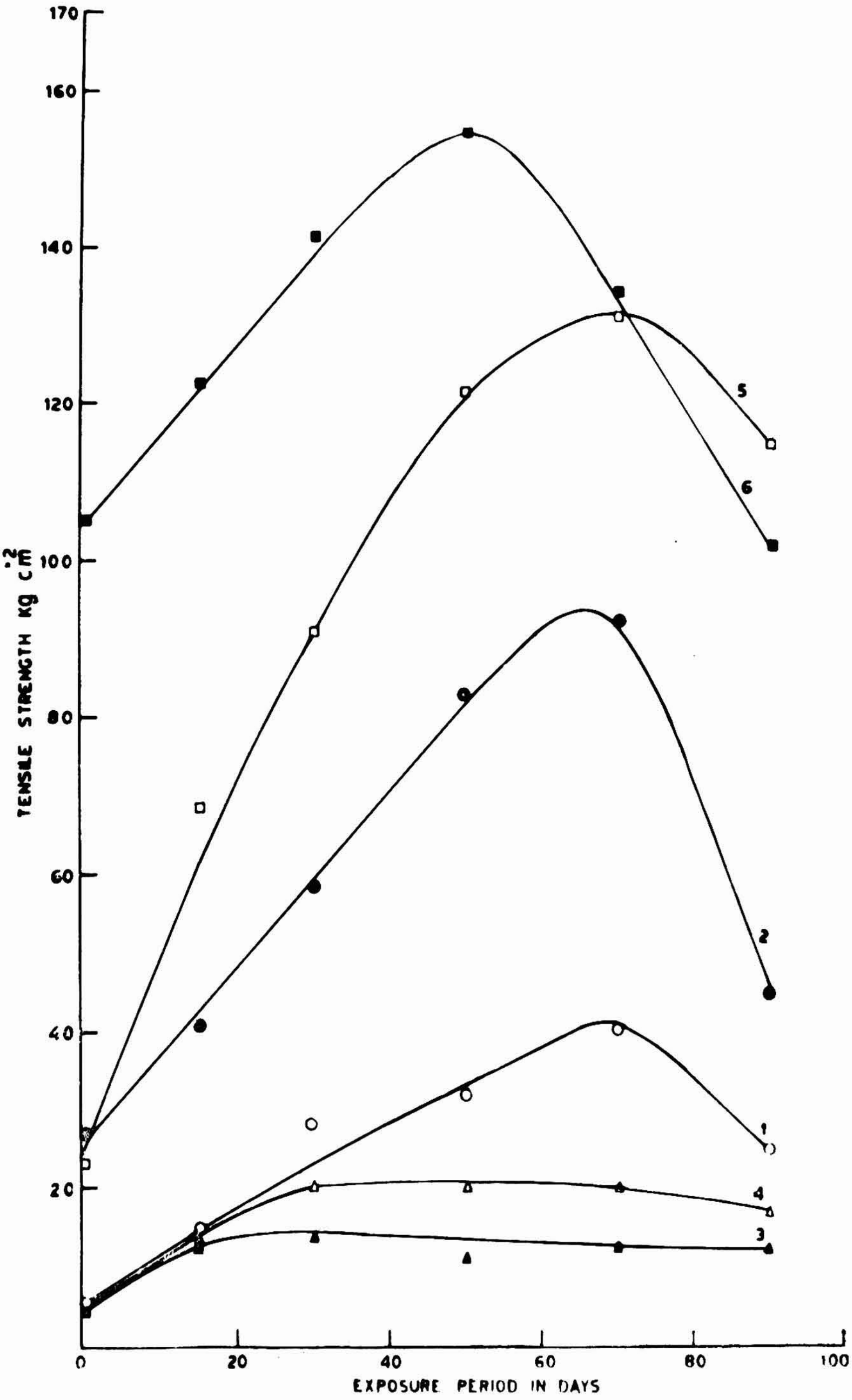


Fig. 4. Tensile strength vs exposure period for films exposed to natural weathering

*Natural weathering*

In order to study the effect of ageing on mechanical properties of alkyd resin varnishes, their free films, supported on glass plates by pasting at the ends with cellulose adhesive tape, were exposed to natural weathering on racks at 45° facing south.

The mechanical properties of the varnish films were measured after 15, 30, 50, 70 and 90 days' exposure. On completion of each exposure period, the films were removed from the exposure rack and kept in a room maintained at 25 ± 2°C for 48 hours and their tensile strength and percentage elongation were determined. The data are graphically represented in Figs. 4-7.

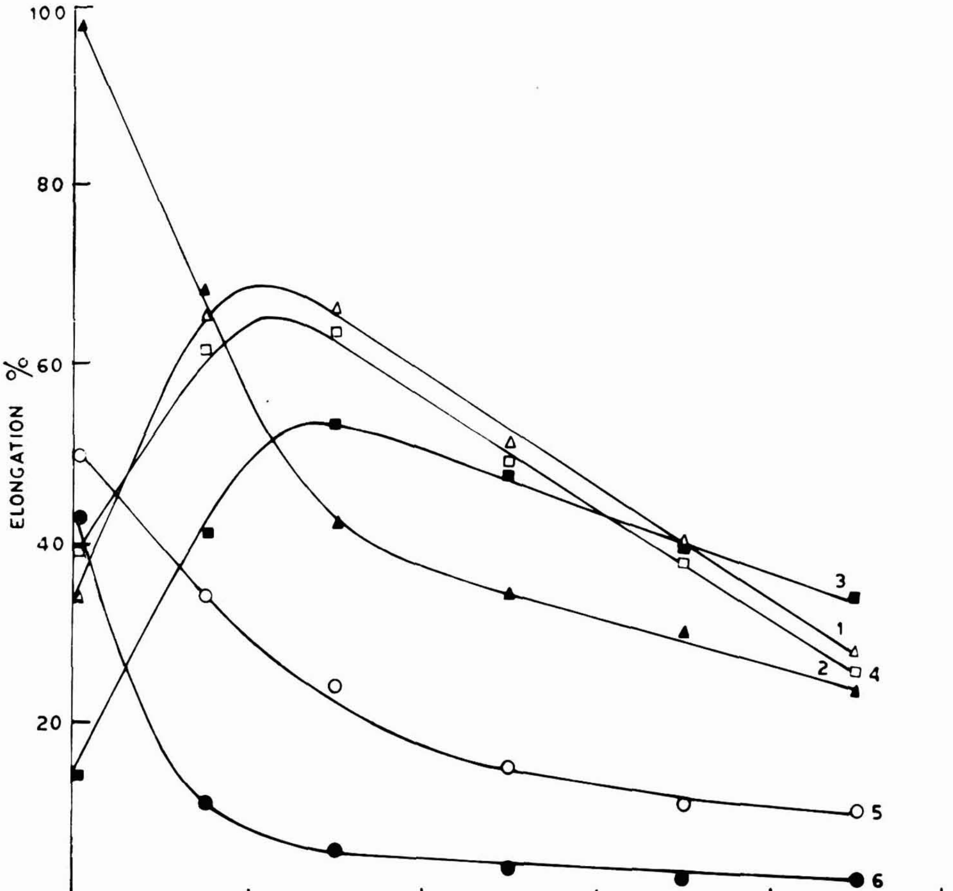


**Fig. 5. Percentage elongation vs exposure period for films exposed to natural weathering**

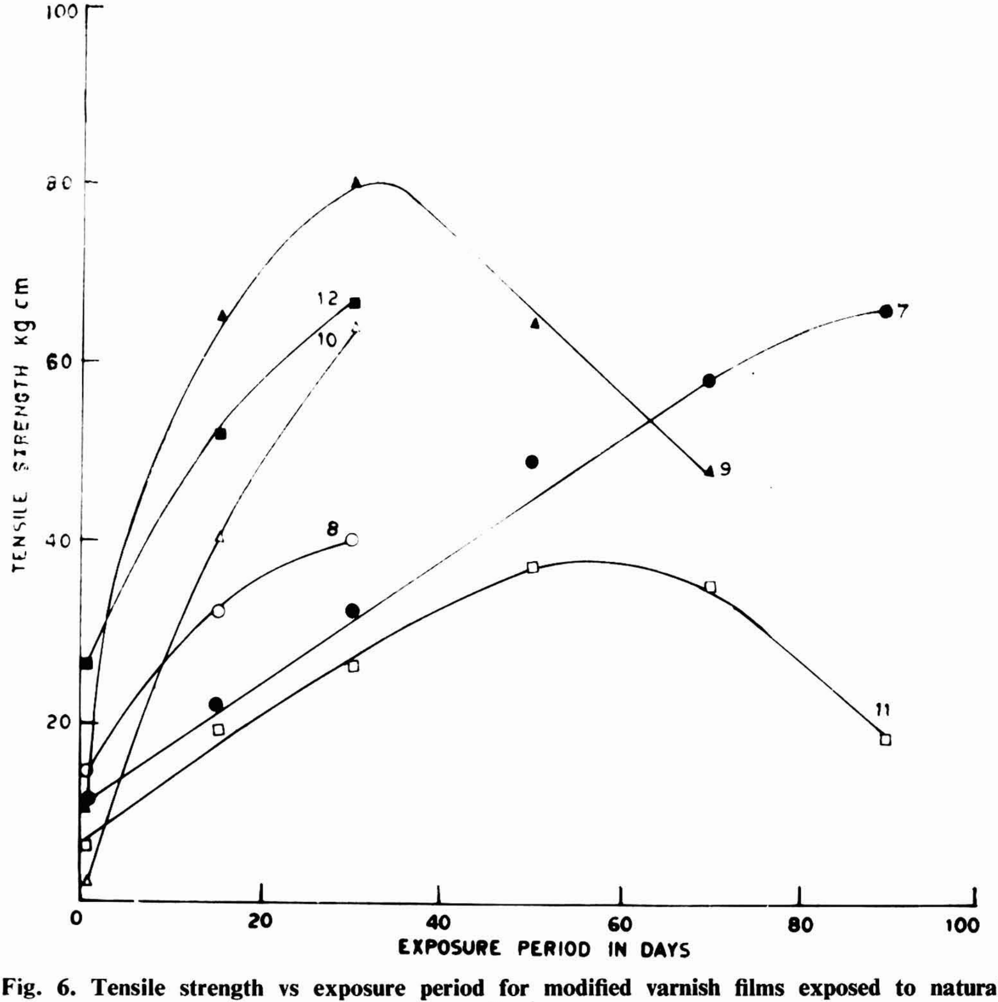


Fig. 6. Tensile strength vs exposure period for modified varnish films exposed to natural weathering

*Exposure to carbon arc lamp*

To study the effect of UV radiation on the mechanical properties of the films of alkyd resin varnishes under accelerated conditions, their free films were exposed to a carbon arc lamp in the Marr Fastness-to-light apparatus. The determinations of tensile strength and percentage elongation of the films were made after exposure periods of 30, 60, 100, 150, 200 and 300 hours and are graphically represented in Figs. 8 to 11. All determinations were carried out at 25 ± 2°C.

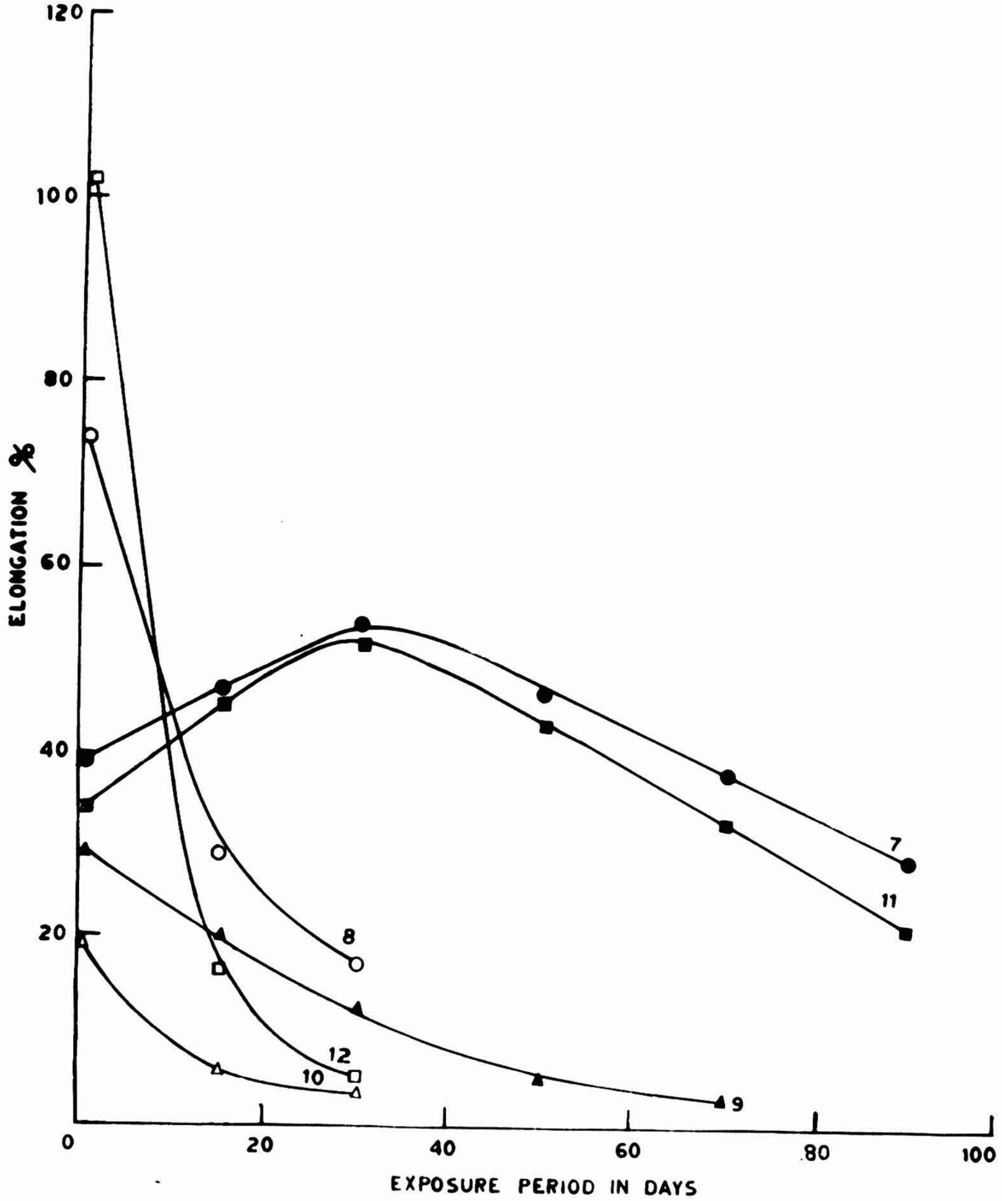


**Fig. 7. Percentage elongation vs exposure period for modified varnish films exposed to natural weathering**

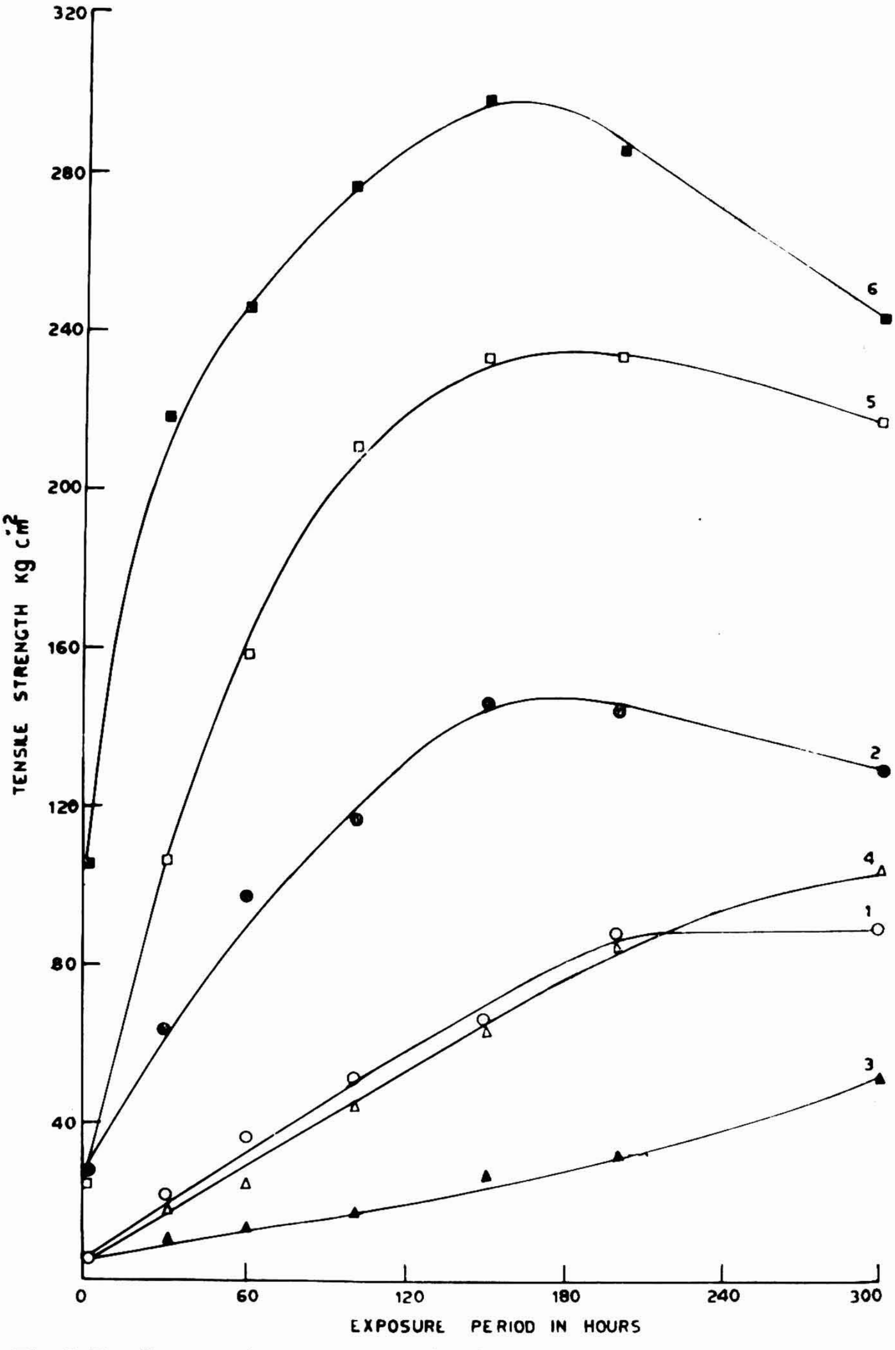


Fig. 8. Tensile strength vs exposure period for films exposed to the carbon arc lamp

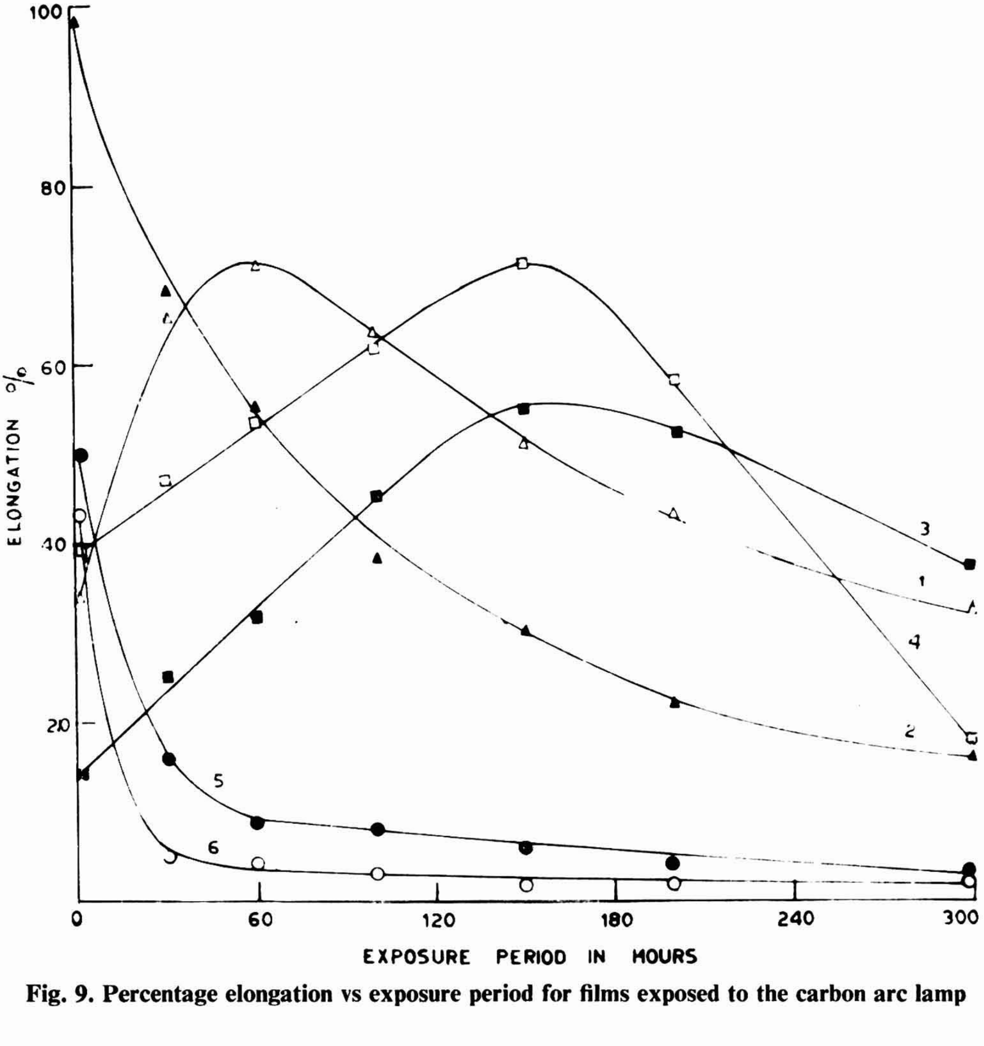


Fig. 9. Percentage elongation vs exposure period for films exposed to the carbon arc lamp

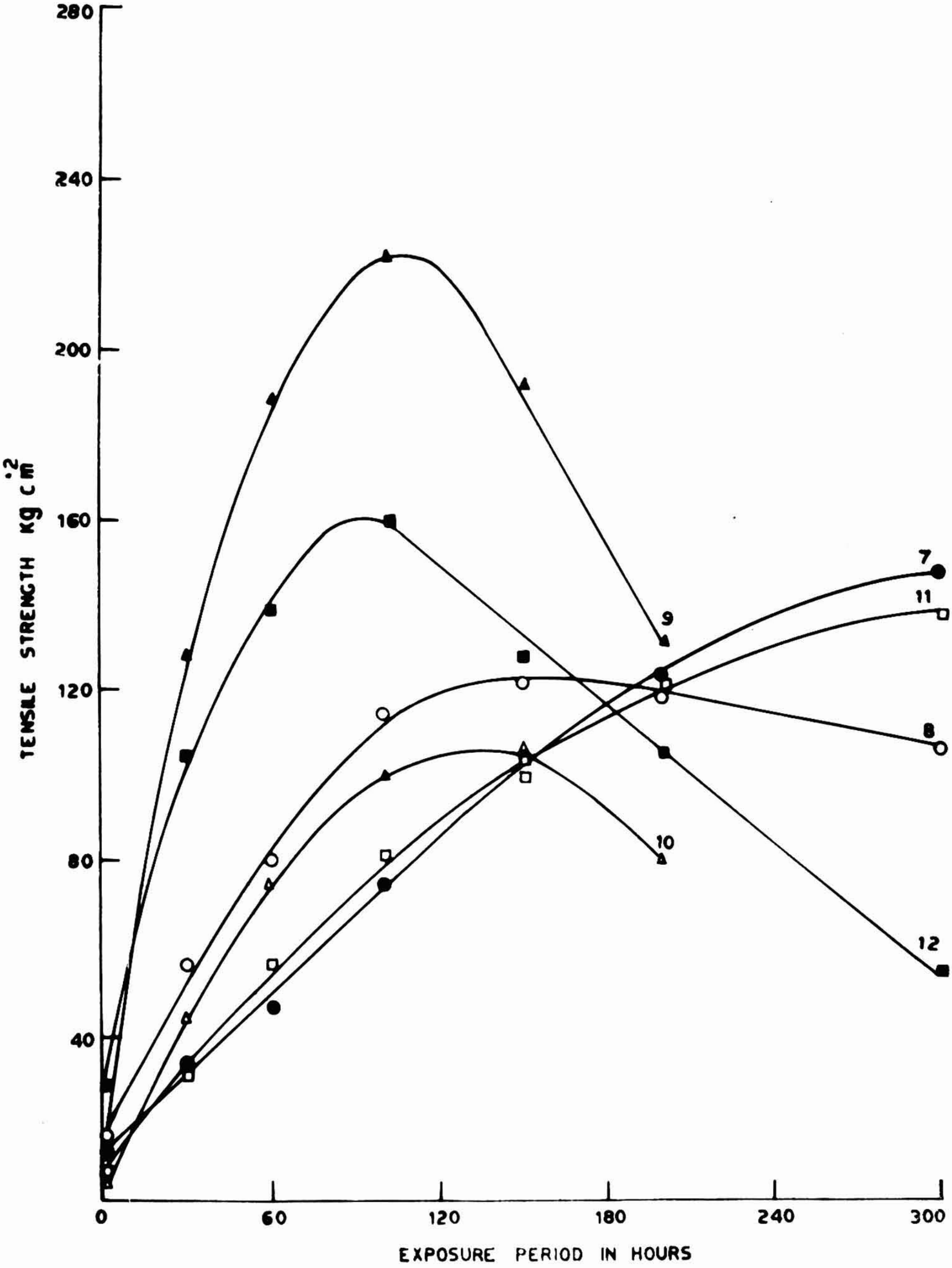


Fig. 10. Tensile strength vs exposure period for modified varnish films exposed to the carbon arc lamp

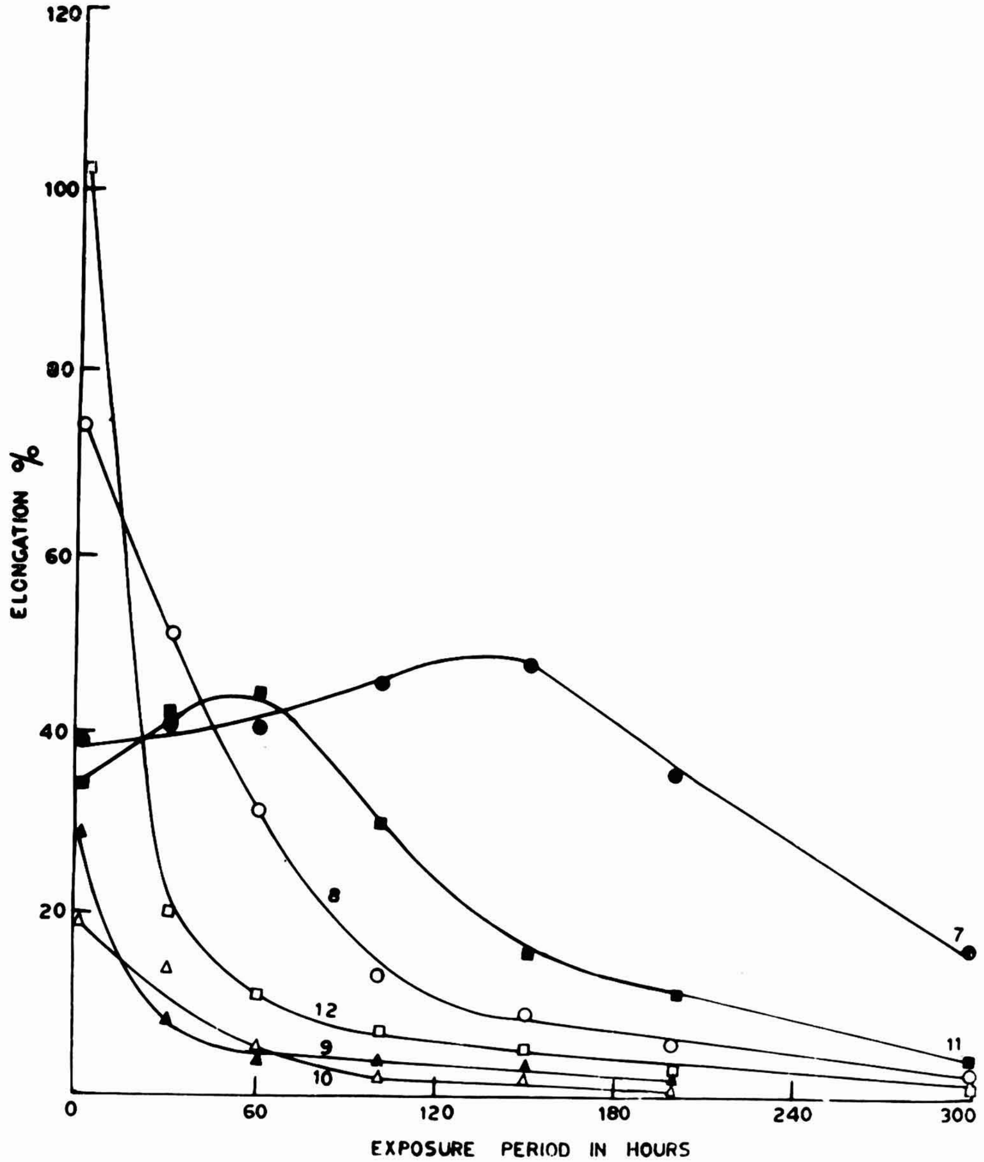


**Fig. 11. Percentage elongation vs exposure period for modified varnish films exposed to the carbon arc lamp**

## Results and discussion

### *Tensile strength and elongation*

The load elongation curves for the first six films are of similar form and are almost linear up to a certain value of stress (Fig. 1). This observation indicates that under low values of stress the extension of these varnishes is directly proportional to the load. The curves for the second set of films show slight variations in their form. These curves show that the extension of these varnishes is proportional to the applied load in a lower range of stress (Fig. 2).

From the observations of stress-elongation for the two groups of varnishes it may be concluded that there is a certain analogy between the behaviour of a varnish film and a strip of metal when subjected to tensile stress. The degree of recovery of varnish film depends mainly on the nature and extent of cross-linking in the surface coating material. The films differ from metals in that they are much affected by the duration of the stress or the number of times the stress is applied, and hence the ratio between stress and elongation fluctuates considerably with such factors and also changes with the age of the film and the type of exposure to which it is subjected.

Bosch et al.[20] have summarised the mechanical properties of paints and varnishes as follows : (1) low elongation and low tensile strength mean hard and brittle films liable to early failure, (2) low elongation and high tensile strength signify hard, tough films that are resistant to abrasion, (3) high elongation and low tensile strength result in flexible, soft and plastic films, (4) when both elongation and tensile strengths are high the film is flexible and tough and the film will have the best mechanical resistance.

In the case of linseed oil-phthalic anhydride-glycerol alkyds, both tensile strength and elongation increase considerably when the oil length is reduced from 66 per cent to 55 per cent. But in the case of pentaerythritol alkyds, the tensile strength increases from 23.1 kg $cm^{-2}$ to 105.4 kg $cm^{-2}$ and the elongation decreases slightly on reducing the oil length. The alkyds based on DCO do not show the same changes in their mechanical properties when the oil length is reduced from 66 per cent to 55 per cent.

The determinations of tensile strength and percentage elongation show that the oil lengths of the alkyds affect their general properties. The long oil length alkyd films are initially soft and flexible and have low toughness and hardness due to the high percentage of oil. The medium oil length alkyds appear to have a just sufficient amount of oil to impart a desirable flexibility, toughness and hardness, as is evident from the high initial values of their mechanical properties.

The load elongation curves for the second set of six alkyds are plotted in Fig. 2. Varnish no. 11 is very similar to varnish no. 1, except for the method of processing, varnish no. 11 being made by the fatty acid-oil process[21] and varnish no. 1 by the alcoholysis process. Thus they may be expected to have similar mechanical properties. Varnishes no. 7 to 10 are modifications of varnish no. 1 and varnish no. 12 is the modification of varnish no. 2. Varnish no. 10, in which the cardanol-hexamine condensate was cooked in, was found to be very much inferior to varnish no. 9, where the modification was by physical mixture. Varnish no. 10 was found to be inferior to varnish no. 1 also. Varnish no. 8 showed appreciable improvements in its properties as it attained high tensile strength and percentage elongation presumably due to the styrene modification. The modified varnishes no. 7 and 9 in general showed improvement in their mechanical properties (Table 1). The modification of varnish no. 2 by partial replacement of phthalic anhydride with styrenated rosin (varnish no. 12) was found not to have any appreciable effect on its mechanical properties.

### *Toughness*

The varnish films having high tensile strength and elongation were found to have high toughness as indicated by the area under the load-elongation curves. Amongst the varnishes studied, no. 6 was found to have the highest toughness.

### *Bursting strength*

Like tensile strength, elongation and toughness measurements, the bursting strength of varnish films can also be taken as one of the measures for the determination of the performance of a coating. The initial values of bursting strength are reported in Table 1. It has been found that increase of oil length of the alkyd results in a decrease of bursting strength. Modification of the alkyd by incorporation of maleic anhydride (varnish no. 7), styrene (varnish no. 8), cardanol-hexamine condensate as a physical mixture (varnish no. 9), and styrenated rosin (varnish no. 12) led to an increase in bursting strength. The pentaerythritol alkyds were found to have the greatest bursting strengths.

### *Natural weathering and exposure to carbon arc lamp*

Interesting information has been obtained from the data on the changes of the mechanical properties of alkyd resin varnish films subjected to natural weathering conditions and exposed to the carbon arc lamp.

The tensile strengths of varnishes no. 1 and 2 increase during natural ageing up to an exposure period of 20 days ; afterwards there was a decrease in these values. These observations show that, after attaining maximum mechanical strength, the film becomes brittle in the course of natural weathering and starts deteriorating. The tensile strength and the percentage elongation of 66 per cent linseed oil glycerine alkyd (varnish no. 1) films increase with ageing. Generally, in the course of ageing, the tensile strength of a coating increases and elongation decreases, but here both increase, showing that during ageing the toughness of the coating increases.

There is an improvement in the tensile strength of the 55 per cent linseed oil-glycerol alkyd film on ageing, but the percentage elongation sharply decreases. The films of this alkyd remained tougher than those of the longer oil length alkyds throughout the exposure period. The results as a whole, however, suggest a deterioration of properties on exposure. It would seem preferable to use a long oil alkyd as a medium for outdoor exposure as its mechanical properties improve on ageing. The pentaerythritol linseed oil alkyds have been found to possess better mechanical properties than linseed-glycerol alkyds.

In various mechanical properties, the medium oil length DCO alkyd (varnish no. 4) remained very similar to the 66 per cent linseed oil-glycerol alkyd (varnish no. 1), but it did not show as much improvement during ageing. The 66 per cent DCO alkyd (varnish no. 3) was much inferior to both of the above varnishes. Thus it may be concluded that, as far as mechanical properties are concerned, there is no particular advantage in the use of DCO in place of linseed oil in medium and long oil length alkyds.

Alkyd varnishes no. 7 to 9, which were obtained by modification of varnish no. 1, showed some improvement in the initial values of their mechanical properties. It was found (Fig. 6) that all the varnishes improved in tensile strength on weathering up to a certain period of time, after which the films became brittle and failed. Among the varnishes studied, varnish no. 7 showed the best performance and did not fail even after 90 days exposure. Varnish no. 11, which differed only in method of preparation from varnish no. 1, behaved similarly to varnish no. 1. Varnishes no. 8 and 10 attained the maximum tensile strength after 30 days ageing and failed immediately thereafter. Varnish no. 9, however, which also attained maximum tensile strength after 30 days, did not fail immediately, but slowly deteriorated and failed only after 70 days. Varnish no. 2 behaved similarly to varnish no. 9, the corresponding periods for maximum tensile strength and failure being 70 and 90 days respectively. On the other hand, varnish no. 12, which was a modification of varnish no. 2, behaved similarly to varnishes no. 8 and 10, failing immediately after attaining its maximum tensile strength at 30 days.

With regard to the change in the values of elongation of the varnishes on ageing, no uniformity is found. Varnishes no. 1, 3, 4, 7 and 11 showed increase in elongation up to 30 days, after which the elongation value decreased, but the elongation values of the other varnishes decreased continuously during ageing.

The weather data obtained from the meteorological department for the exposure period under study are given in Appendix II.

The free films were exposed in the fastness-to-light chamber around the carbon arc lamp with a temperature in the vicinity of the varnish films of about 85°C. Varnish no. 1 attained maximum tensile strength of 90.0 kg $cm^{-2}$ in 300 hours of exposure and varnish no. 2 attained a constant value of 146.6 kg $cm^{-2}$ after 150 hours with a tendency to slight decrease on further exposure, whereas the same varnishes attained maximum tensile strength of 40.70 and 92.5 kg $cm^{-2}$ respectively in 70 days under natural weathering. These observations show that the maximum tensile strength attained by the varnish films in natural weathering was comparatively less than that attained when exposed to carbon arc lamp. Both long and medium oil length DCO alkyds showed a constant increase in their tensile strength. Varnishes no. 5 and 6 showed better improvement in their tensile strengths, both in this test and under natural weathering conditions. Varnishes no. 1 to 6 followed a similar pattern with regard to their change of elongation in both the tests (Figs. 5 and 9).

The modified forms of alkyd no. 1, i.e. varnishes no. 7-10, and varnish no. 12, which was a modification of varnish no. 2, reached higher tensile strength values when exposed to the carbon arc lamp. Varnishes no. 1 and 11 behaved similarly in both the tests. Varnish no. 7 showed better performance than varnish no. 1 and varnish no. 9 attained higher tensile strength than varnish no. 1, but failed earlier.

## Conclusions

The present study on the mechanical properties of alkyd resin varnish films has led to certain interesting conclusions. Taking into consideration the overall mechanical properties, these may be summarised as follows :

(1) It has been found that pentaerythritol as the polyol in the preparation of the alkyd confers better mechanical properties on the films than does glycerol.

(2) Linseed oil appears somewhat superior to DCO as the alkyd modifier and, as expected, oil length has a considerable effect on mechanical properties.

(3) Modification of the alkyd resin by the partial replacement of phthalic anhydride with maleic anhydride improves mechanical properties.

(4) While modification of the alkyd with styrene appears to improve the initial mechanical properties of the films, the use of styrenated rosin as partial replacement of phthalic anhydride does not seem to affect these properties. Both these varnishes fail earlier on weathering than the unmodified varnishes.

(5) Modification of the alkyd with cardanol hexamine condensate appears to improve the initial film properties only if the modifier is present as a physical mixture. These varnishes, however, fail earlier on weathering than the unmodified alkyd.

(6) The use of the fatty acid-oil process for the preparation of the alkyd does not result in any appreciable change in the mechanical properties of the films.

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# Appendix I

## Preparation of alkyd resin varnishes

### *Varnishes no. 1-6*

The alkyds based on 66 per cent and 55 per cent of linseed oil and DCO were prepared with glycerol or pentaerythritol by the fusion process, using litharge (0.03 to 0.05 per cent) as alcoholysis catalyst. After completion of alcoholysis the temperature was lowered from 240°C to about 180°C and phthalic anhydride was added in small lots. Cooking was continued at 260°C until the final product of low acid value gave a string of 12 to 16 inches. The preparation was conducted in an inert atmosphere.

*Modified varnishes no. 7-12*

*No. 7.* The above procedure was followed except that five parts of phthalic anhydride were replaced by the equivalent amount of maleic anhydride.

*No. 8.* After adding phthalic anhydride to the alcoholysis product, the heating was continued till a string of 2-3 inches was obtained. Then 33 per cent on weight of oil of distilled styrene containing 5 per cent benzoyl peroxide as catalyst was added slowly and the heating continued under reflux till a low acid value product was formed which gave a string of 12-16 inches.

*No. 9. Cardanol-hexamine condensate* : The cardanol-hexamine condensate was prepared by heating cardanol and hexamine (7.5 per cent on the weight of cardanol) at 120-130°C with constant stirring. When the smell of ammonia ceased the temperature was raised to 180°C and the heating continued till a string of 6-8 inches was obtained.

This condensate was physically mixed with 66 per cent linseed oil alkyd in the required proportion.

*No. 10.* To the alcoholysis product the required amounts of cardanol and hexamine were added. Heating was continued at 150°C till the smell of ammonia ceased. Phthalic anhydride was then added and the product was processed by heating at 260°C to a low acid value and to give a string of 12-16 in.

*No. 11.* Linseed oil fatty acids, phthalic anhydride and glycerine, in the proportion of 26, 15.8 and 9.4 parts respectively, were heated at 260°C for one hour. 13.5 parts of linseed stand oil (25 poises) was then added in three instalments and heating continued until a stringy bead was obtained.

*No. 12.* Styrene, 20 per cent on weight of rosin, was added gradually to rosin at 120°C with constant stirring. The temperature was then raised to 150°C and the material was refluxed for three hours. In the preparation of the 55 per cent linseed oil alkyd, ten parts of phthalic anhydride were replaced with an equivalent amount of the styrenated rosin.

All the above alkyd resins were thinned to the required consistency by the addition of a mixture of white spirit and xylene (1 : 1). In each of the resins no. 1 to 8 and 11, 12, a mixture of cobalt naphthenate (0.02 per cent metal) and lead naphthenate (0.5 per cent metal) was used as driers. In the resins no. 9 and 10, a mixture of cobalt naphthenate (0.02 per cent metal) and manganese naphthenate (0.02 per cent metal) was used.

# Appendix II

**Weather data at Hyderabad during the exposure period**

| Month and year | Temperature, °C | | Relative humidity, % | | Rainfall mm |
|---|---|---|---|---|---|
| | Maximum | Minimum | Maximum | Minimum | |
| April 1966 .. | 38.0 | 24.3 | 50 | 25 | 20.0 |
| May 1966 .. | 39.2 | 25.6 | 37 | 19 | 5.9 |
| June 1966 .. | 35.7 | 24.1 | 66 | 41 | 37.8 |
| July 1966 .. | 31.8 | 23.3 | 72 | 58 | 134.4 |

*J. Oil Col. Chem. Assoc.* 1968, 51, 344-346

## *Short Communications*

# The non-ohmic nature of conduction in the electrodeposition of paint films

**By B. A. Cooke and T. A. Strivens**

I.C.I Ltd. (Paints Division) Slough, Bucks

In investigating conduction through electrodeposited films of surface coatings derived from aqueous resin dispersions, we have found deviations from Ohm's law of a larger magnitude than is to be expected as a normal consequence of field-induced dissociation in weak electrolytes.

Typically, the electrodeposition of paint entails the electrolysis of a dilute (say 10 per cent) aqueous solution of pigment and resin.[1, 2, 3] Carboxylic resins, e.g. maleinised drying oils, maleinised alkyds, acrylic or phenolic compositions etc., with a carboxyl content in the region of 1 m eq $g^{-1}$ are generally used in dispersions in which they are partly or completely neutralised by a base. On steel or other metallic substrates, anodic films 10-40$\mu$ thick can usually be obtained in 0.5-5 min using applied voltages in the range 50-300V. The films, though comprised primarily of destabilised resin and co-deposited pigment, always contain some residual water and base (and organic solvent, if present in the dispersion). As the conductivity of the film is much lower than that of the parent aqueous dispersion, most of the applied voltage is present across the film once an appreciable film thickness has built up ; as a result average field strengths reaching the order of 100kV $cm^{-1}$ may develop across a film. Electrodeposition can be induced with simpler substances than the usual waterborne surface coating dispersions, e.g. from amine, ammonia or alkali metal soaps of oleic acid or of the fatty acid mixtures yielded by the splitting of drying oils.

We have found that electrodeposited paint or varnish films deviate markedly from Ohm's law in their response to voltage variations imposed during deposition, the effect of increased voltage being always to increase the observed film conductivity. For example, if the applied voltage is abruptly doubled the current passing rises, typically, by a factor of four or more, implying a twofold or greater increase in film conductivity (deposition conditions being so arranged that the film is the dominant resistance in the circuit and that the voltages employed greatly exceed overpotentials acting at the electrodes). A tendency for the specific conductivity of electrodeposited paint films to vary with application conditions has been observed by Tawn and Berry[4], who found a variation with current density in the same sense as that observed by the authors, and by Holzinger[5], who found a decrease in film conductivity with the progress of deposition at constant voltage (i.e. with decreasing current density) which he tentatively ascribed to progressive electro-osmotic dehydration. It does not seem to have been appreciated that the deviations from Ohm's law are considerable nor that they can occur rapidly and reversibly.

To study the non-ohmic effect and its time-dependence, we have determined current-voltage oscillograms using a sinusoidal voltage sweep provided by full-wave rectified a.c. ; Figure 1 is such an oscillogram obtained on a 29.2$\mu$ thick film from a 10 per cent dispersion of the waterborne resin Resydrol P411* deposited over a degreased mild steel anode. In this case the voltage sweep from 0-70V (traced as abscissa) occurred in 5 msec (50 Hz a.c. source frequency) ; the slope at low voltage corresponds to a specific conductivity for the film of $0.85 \times 10^{-7}$ ohm$^{-1}$ cm$^{-1}$ while at the peak voltage the conductivity was $2.4 \times 10^{-7}$ ohm$^{-1}$ cm$^{-1}$. (The film thickness value mentioned was ascertained after removing the coated steel panel, washing it in running water and stoving it at 165°C for 30 minutes.) We have found non-ohmic behaviour of the type illustrated to occur with a wide range of waterborne film-forming systems as well as with such materials as oleic acid or linseed oil fatty acid, though the latter materials show rather less pronounced non-ohmic behaviour than do the polymeric film-forming resins. Similar behaviour has been found using various substrate materials including phosphated and zinc phosphate coated steel, zinc, copper, platinum and a cation-exchange membrane in the hydrogen form

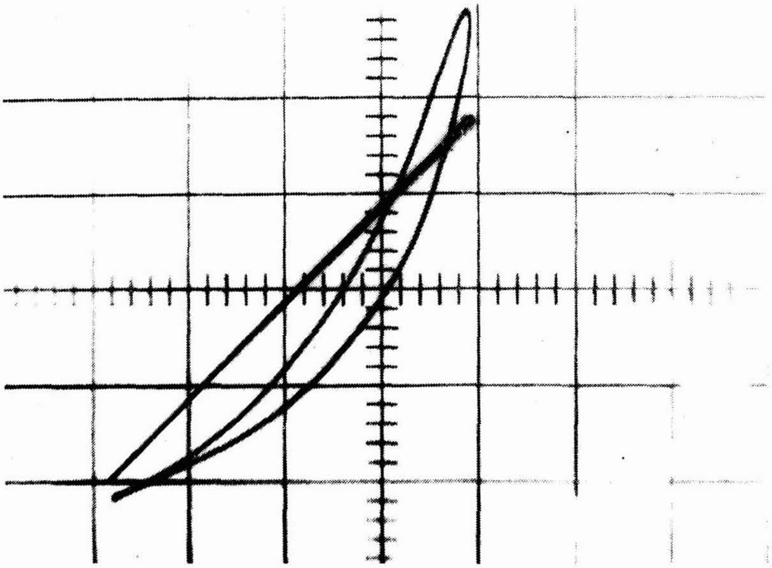

**Fig. 1. Current-voltage oscillogram obtained when full-wave rectified a.c. at 50 Hz source frequency was applied to a 29.2$\mu$ thick electrodeposited film over untreated mild steel sheet (as anode) from 10 per cent aqueous Resydrol P411. The straight line shown illustrates ohmic conduction through an ordinary resistance used for calibration**

Voltage traced as abscissa, 1 major div. = 20V
Current as ordinate, 1 major div. = 1.30 mA cm$^{-2}$
The upper side of the loop shows the effect of falling voltage

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*Cray Valley Products Limited, St. Mary Cray, Kent, England. This resin is an ammonia-neutralised phenolic-modified alkyd of acid value *ca* 85 mg KOH/g (1.5 m eq g$^{-1}$) which is suitable for the formulation of electrodepositable paints. Butanols and 2-butoxyethanol are normally present in addition in the proportion of *ca* 20 per cent of solids.

(arranged in a suitable electrodialysis train to function on passage of current as a source of hydrogen ions). The membrane provides an interesting case, in that oxide films are absent and deposition is not accompanied by electrolytic gas evolution ; these factors are, therefore, not responsible for the observed behaviour over metals. The non-ohmic behaviour appears also to be unaffected by pigmentation.

Current/voltage oscillograms obtained at 50 Hz source frequency on electrodeposited paint films have proved nearly always to be loops, such as that illustrated, in which the upper line represents the effect of falling voltage. It follows that although the film responds rapidly to voltage fluctuations it does not do so instantaneously ; the time constant of the response process is evidently of the order of a millisecond.

On the basis of the thickness of the cured film whose current/voltage oscillogram is shown in Fig. 1, the mean electric field across the film was 24.0 kV $cm^{-1}$ at the peak voltage used. Direct application of the theory of field-induced dissociation,[6, 7] assuming the film to behave as a weak uni-univalent electrolyte, indicates that the high field conductivity could exceed the low field value by a maximum of *ca* 50 per cent in the extreme case envisaged if its dielectric constant is only 2.5 (the value for oleic acid). This may be compared with an observed enhancement of *ca* 180 per cent. The magnitude and continuity of the variations in film conductivity as well as the observed speed of response have led to the suspicion that concentration polarisation, causing a concentration gradient in the film affecting neutralising base (and with it probably also water and alcohol solvents), gives rise to a marked concentration of the electric field in the region close to the substrate. The field acting over the most resistive part of the film then exceeds the average value, giving rise to an enhanced field-induced dissociation effect. The authors are examining this hypothesis by observing the effect of brief polarity reversal, by combining the theory of field-induced dissociation with observations on the self-capacitance of the electrodeposited films and by studying the impedance of the films. All the results obtained support the polarised film " structure " and consequent enhancement mechanism suggested, and the authors plan to publish the experimental methods and results more fully.

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# Curcumin reaction for the checking of curing of crosslinked films

## By M. Hess

Curry powder in water or alcohol has been used on the Continent for checking whether a cross-linking film has been properly cured. It has been reported in the literature that, owing to the quality differences of curry powder, such tests are not reliable enough. Since the colouring matter in curry is curcumin, tests have now been carried out to ascertain whether a solution in water or alcohol of this yellow dyestuff can give more reliable results. Some improvement has been observed but variations in the spreading of the solution due to differences in the wettability of surface finishes have been found to affect results.

The following experiments were carried out after it had been established, using a constant dyestuff concentration, that the test worked in principle, i.e. that the greater the degree of cure the fainter the yellow mark caused by the absorption of the dyestuff into the paint film surface. A thoroughly cured glossy film hardly absorbed any colour in the procedure described below.

0.15 per cent curcumin, crystalline, laboratory reagent quality (British Drug Houses) is dissolved in a mixture of 68 parts ethyl alcohol 61 OP and 24.65 parts distilled water, the latter in order to reduce possible attack of the solvent on the paint film, and this solution thickened with 7.20 parts of the low viscosity powdered methyl ether of cellulose, " Cellacol M20 " (British Celanese). In this condition a drop of the 0.15 per cent curcumin jelly can be applied with an eye dropper from a (preferably) brown glass bottle. The jelly will not flow out on smooth surfaces, and at room temperature forms a circle of always approximately the same diameter and dye concentration. The drop should be thoroughly wiped off, e.g. with dry cotton wool, exactly five minutes after application at room temperature, and the intensity of colour of the resulting mark is then compared with a standard. An alternative method is to let the jelly dry (approx. three hours) and make the comparison after removal of the film-disc formed. Staining in this case is much stronger, and distinction may be more difficult to make.

Curcumin is not very fast to light.

This test might be useful for routine checks and works control.

Where curing is slow or incomplete, distinctions between various stages of stoving or curing may not be marked enough. However in numerous tests, so far only on films of white thermosetting acrylic and thermosetting amino/alkyd types, the differences of curing could very definitely be made visible. It may be that this test works better with some types of surface coatings than others. It must also be borne in mind that some systems harden further after stoving.

Matt films accept the dyestuff curcumin mechanically, and when a glossy film turns more matt due to overstoving, the intensity of staining is bound to increase, in spite of the film being cured and having previously given a satisfactory reaction in the test.

Most coloured films respond to the test, but there are obviously colours on which differences of yellowness would not be distinguishable, e.g. dark blues.

If, due to low temperature, the jelly becomes too immobile, warming on a water bath will help.

Iron containers and tools should not be brought in contact with the curcumin reagent, to avoid staining.

[*Received 22 January 1968*

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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 May issue :

"**New oils and fatty acids for surface coating resin manufacture,**" *by K. B. Gilkes and T. Hunt.*

"**Calculation of paint formulations by computer,**" *by E. Hoffmann and J. Spencer*

# Editorial

## Accidents do happen

The publication of the Carcinogenic Substances Regulations 1967 caused something of a stir in the coatings industry, but now the dust has settled one wonders how many practitioners of the art are really going to treat them with the respect they deserve. There is an enormous temptation to pass the buck to the raw material supplier on the one hand or to say " we should be exempted by the wording of para. so and so " on the other. Just how far can one hide moral responsibility for safety in all its aspects behind rules and regulations or the findings of the Courts in specific instances?

We recall reading last year's report of HM Inspectors of Explosives, who stated that they could do no more than give " a brief account of the more important and technically interesting accidents." What makes an accident " interesting," technically or otherwise? HM Inspectors thought it " interesting " to record the death of two children, each after an " improbable " chain of events on Guy Fawkes Night. It was also " interesting " to note that a youth discovered too late the hazards of trying to dissolve red lead in picric acid heated over a portable gas burner in a bedroom, and that it is not a very good idea to rekindle sluggish fires with cellulose thinners. So, you say, you cannot cater for fools or for the million to one chance. But who is a fool and how do you know the odds?

What about the explosion in the laboratory where cellulose nitrate was being dried in an oven which overheated due to thermostat failure? Somebody had evidently never heard of thermal cut-outs. A recent issue of the *Quarterly Safety Summary* recorded the death of a chemical worker who fell into a barrel containing 20 gallons of liquid phenol. It was estimated that not more than 15 per cent of his body surface was immersed, and that for a mere minute. Despite immediate first aid and subsequent treatment at the medical centre, he was dead in 49 minutes. There is no known antidote for phenol poisoning after absorption has occurred. Didn't you know?

Everybody nowadays is well aware of the toxic hazards associated with the handling of benzene, are they not? In his report on industrial health for 1965, HM Chief Inspector of Factories recorded the death of a laboratory worker due to leukaemia following persistent use of small quantities of benzene as a reagent. Incidentally, BS 684 (Methods of analysis of oils and fats) recommends benzene as one of two solvents to be used in the determination of acidity in polymerised oils. The alternative offered is diethyl ether, well known for its explosion hazard. What is wrong with the much less hazardous toluene?

Reverting to HM Inspectors of Explosives, they note that the inspection of vehicles carrying petroleum spirit by road is " very casual." This must be somebody's fault; not yours or ours, of course, but somebody's.

Finally, elsewhere in this issue we show, by courtesy of the Manchester Section, something of the tastes of our members. A wide range of interests is displayed, but it does not embrace safety.

Accidents do happen and they are always somebody's fault. Some element of responsibility devolves upon everyone within sight or sound of one, so don't let us kid ourselves. They are seldom interesting, but they are always deplorable. Whilst there is no shortage of literature on the subject, we would recommend as a primer to all our readers *The Manager's Responsibility for Safety* (The Industrial Society, 1966, price 7s. 6d.).

# Reviews

## ADVANCES IN COLLOID AND INTERFACE SCIENCE

Published quarterly. Amsterdam : Elsevier Publishing Co. Volume 1, No. 1, 1967. Pp. 110. (Price quoted in issue £7 10s. per volume, but since devaluation it has risen to £8 14s. 6d.)

In these days when new journals appear so frequently and the number of scientific papers published is increasing at a phenomenal rate, the scientist with limited time at his disposal and average powers of literature digestion, but with a deep desire to keep abreast of developments in his field, is increasingly relying on authoritative review articles. It is therefore with some satisfaction and anticipation that we welcome the appearance of *this* new journal. It is to contain reviews of topics in surface and colloid chemistry which, to quote the editors, " should be of value not only to colleagues of the authors, but students and scholars entering a segment of the field should find these texts a fruitful compendium of theory and techniques. They will be of considerable value to interdisciplinary efforts such as those breached by the materials scientist and molecular biologist. Engineers and applied scientists involved in subjects such as nucleation, fuel cells, organic coatings, filled plastics, air pollution, pigment manufacture, catalysis and metal processing should find useful contributions in these volumes." This being the aim of the editors (Overbeek, Prins and Zettlemoyer) means that readers of *JOCCA* will be well advised to be aware of this journal and its contents.

The first number contains two review articles on widely different topics ; one is on the physical adsorption of gases on solids by W. A. Steele, and the other (in French), by Antoine Skoulios, reviews the structure of concentrated soap solutions.

The area chosen by Steele mainly concerns the theoretical aspects most relevant to the interpretation of experimental data and also the experiments leading to thermodynamic data from which the character of the solid surface and the adsorbed phase may be deduced. The advances discussed are those made since 1961 as the literature up to that date has been adequately reviewed elsewhere. Equations of state for monolayer adsorption and the simplifications and approximations to take account of multilayer adsorption, surface heterogeneity and the nature of the adsorbed film (mobile or localised) are discussed. The evaluation of the Henry's law constant, the potential energy of an adsorbed molecule and of the virial coefficients as well as their interpretation are critically reviewed. In the experimental section, Steele considers a large number of adsorbents, including carbon blacks (in particular the graphitised form as representative of a homogeneous surface), surfaces containing pre-adsorbed gases to produce a homogeneous surface, e.g. argon pre-adsorbed on rutile, organic surfaces, e.g. Teflon, ionic solids, zeolites (molecular sieves) with regular but heterogeneous surfaces, and the oxides with highly irregular heterogeneous surfaces. The last section of the review contains a discussion on multilayer adsorption and the application of the Polanyi potential theory, capillary condensation in porous materials and the associated hysteresis of adsorption. Some 360 references are quoted in this well-written and critical review. After studying it the reader is aware that significant advances in this field have been made during the five or six years.

The article on soap solutions is significantly shorter and not as comprehensive. It reviews the subject and not specifically the recent literature. All the various phases which exist in alkali metal soap solutions at different concentrations are discussed in a concise manner. To a large extent the data quoted originate from the author's laboratory and the article is liberally illustrated.

We hope that there will be a continuous flow of good review articles so that the journal will maintain the high standard of its first and subsequent issues.

G. D. PARFITT

## TECHNOLOGY OF ENAMELS

By V. V. VARGIN. Translated and edited by K. Shaw. London : Maclaren & Sons, 1967.

It is often stimulating to examine the other man's technology and to discover how he overcomes the practical day-to-day problems which are encountered. Professor Vargin's book on vitreous enamels provided a suitable opportunity for indulging in this pursuit. The translator's preface states that the book is written for the technologist, the manager and the student, with the emphasis on practicalities ; this is a good thing since, like the paint industry, the vitreous enamel industry has been said to be " a lot of art surrounded by a little science." Viewed as an entity it can be described as covering the whole field of the art (technology ? science ?) with the chapters on the chemistry of the crystalline state, the physics and physical chemistry underlying the behaviour and properties of enamels and the raw material employed. The latter subject, however, is dealt with more on the lines of a dictionary of chemistry and could usefully be enlarged. The problem of matching enamel and substrate are dealt with in several chapters and these certainly invoked sympathetic thoughts from your reviewer—remembering that organic surface coatings can at least be flexible enough to accept some degree of expansion and contraction.

The manufacture of frits follows the accepted lines for reduction of particle size by ball milling, although the diagram on p. 155 appears to invoke a repulsion due to gravity rather than an attraction.

Chapters on the metallurgy of steel and iron and their preparation for enamelling again have parallels in our industry. Mistakes are few ; p. 14 (bottom) invokes some mixed composition which can easily be corrected in the next edition, whilst on p. 88 reference is made to a " mono mineral barytes." This may be an error of translation, but these small errors do not in any way detract from the value of the book.

Concluding, this is a very readable and instructive publication which any surface coating (organic type) could read with benefit—he will certainly not go unrewarded.

D. S. NEWTON

## ORGANIC CHEMISTRY OF SYNTHETIC HIGH POLYMERS

By R. W. LENZ. New York : Interscience Publishers, 1967. Pp. xvi+837. Price 120s.

Reviewing this book was an infuriating experience owing to the lack of informative running heads. It is not until chapter titles are omitted from the top of every page that one realises how much use is made of them by the reader skimming through in search of interesting topics or using the work more seriously as a reference. Accordingly, this is a difficult book to " get to know " and if the seeker after knowledge chooses to take the easier path of looking elsewhere for his information, the publishers will have only themselves to blame.

The approach is strictly academic ; style and production are impeccable, and the level is above that of most introductory texts. It *could* be studied by one with no previous knowledge of polymer chemistry, but would then be rather hard going ; in our opinion it is more suitable for the serious student who has already been initiated.

An introductory section deals with the classification of polymer reactions and with the rudiments of structure-property relationships. The former deserves careful study as the author departs in principle from the classical division of the subject into polycondensates and addition polymers. There then follows a detailed treatment of the organic chemistry of polymers under the headings Step-growth Polymerisation, Homogeneous Chain-growth Polymerisation, Heterogeneous Chain-growth Polymerisation, and Polymer Reactions. Synthesis and structural chemistry are well presented and reaction mechanisms are amply discussed, generally in the light of very recent work. Emphasis on *organic* chemistry, however, leads to occasional omission of physico-chemical topics where their inclusion would be helpful to the student. The inclusion of many of the newer polymers and procedures, hitherto scarcely revealed outside the original literature, is to be commended. Polybenzimidazoles, interfacial polymerisation, carbodiimide and polymerisation in clathrates are examples of such entries. The treatment accorded ionic polymerisation in general and Ziegler-Natta polymerisation in particular is the most satisfying ever encountered by the reviewer outside the specialised literature.

Notwithstanding the general excellence of this work we would ill serve our readers did we not call attention to a most serious deficiency—the almost complete lack of any reference to industrial aspects of polymer chemistry, let alone coatings technology. Thus, we learn a lot about the *chemistry* of the nylons, poly (ethylene terephthalate) and the more well-defined condensation products of phenol and urea with formaldehyde, but nothing about alkyds, polyamides of polymeric fatty acids, cresylics, resorcinol glues or alkylated MF resins. Professor Lenz is now an academic, but he confesses in his preface that the book was written when he was in industry and was largely based on lectures to industrial scientists. This makes his treatment of a multi-million pound industry with such contumely as surprising as it is unforgivable.

A. R. H. TAWN

## PRINTING AND LITHO INKS

By H. J. WOLFE. New York : MacNair-Dorland Company, 1967. Sixth Edition. Pp. 537. Price £5 15s.

The first edition of this classic was published in 1933, and few entrants to the printing ink industry during the last 30 years can have failed to profit by it. It had the advantage for many years of being the only significant book on ink technology, and edition followed edition. Now we are faced with the sixth, some ten years after its predecessor. This edition is " in co-operation with a group of specialists " and the list contains some distinguished names. The effect of these contributions has not, however, been very marked : additions and deletions have been made, but the text is fundamentally that of the original author. In a work which has enjoyed esteem for a number of years, it is probably difficult to be ruthless with out of date material. Nevertheless, what justification can there be for devoting nearly two pages each to vermilion and zinc oxide, but only three to titanium dioxide and two (which do not include mention of $\alpha$ and $\beta$ forms) to phthalocyanines? The pigment chapters retain their addiction to an alphabetical arrangement, in spite of a new systematic table of organic pigments. This results in methyl violet being sandwiched between lithol rubine and naphthol reds. If ease of reference is the object, why cannot the index be used for this?

The chapter on " Printing Ink Vehicles " is little changed, except for the inclusion of a paragraph on urethane oils, and one on functionality theory which is marred by a reference (p. 69) to linoleic acid as dibasic. The chapter on " Driers and Drying " avoids all reference to free radicals.

The formulations in the letterpress and litho ink chapters are still mainly based on linseed stand oil vehicles, in spite of the information given elsewhere on synthetic resins.

Flexographic inks now have a chapter to themselves, instead of forming a section of that entitled " New Types of Printing Inks," but moisture-set and quick-setting inks are still " new." Neither of the chapters on gravure or flexographic inks contains much information on formulations for packaging films and foils, but the chapter on " Ink Troubles and Remedies " contains new sections on these inks.

Food-wrapper inks receive rather curious treatment. The pigment sections do not point out the potential hazards of lead chrome or cadmium pigments, and a brief reference to the F and DA regulations (p. 281) is immediately followed by a formulation for a parchment red based on molybdate orange. Vermilion comes close, on p. 142, to being recommended as a pigment in butter-wrapper inks.

Enough has been said to indicate that Mr. Wolfe and his collaborators have, for this sixth edition, done another piece of patchwork. The question must be asked whether the time has not come for " Wolfe " either to go into honourable retirement, or to undergo a much more thorough " revision." One does this with regret, not unmindful of past benefits.

The presentation is, as usual, excellent, and this edition is enriched with some new and instructive photographs. The text has apparently been re-set, and contains a number of " literals " : few of these are likely to mislead, except perhaps the generalised formula for ketones on p. 77, and the date of 1706 associated with Senefelder (p. 299).

Dr. Stoyle, in an interesting Foreword, compares the trends in ink-making practice in the USA and elsewhere, and puts forward some reasons for the differences.

F. A. ASKEW

# 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.)*

**Mitchell Craig Pumps Limited** have recently introduced two new brochures, dealing with the *Milton Roy* range of metering pumps and the *Mitchell Craig* ceramic lined pumps respectively.

A new electron curing process has been patented by **Tube Investments Limited** and was recently demonstrated jointly by Tube Investments and **Porter Paints Ltd.**

The new apparatus, *TIGER* (Tube Investments Generator for Electron Radiation), produces a stream of electrons, accelerated by a charge of 125,000 volts, which promotes cross-linking in the liquid paint film. Drying times of less than one second are claimed.

The process is expected to find immediate application in the furniture, industrialised building, and other timber-using industries, and possibilities exist for the paper packaging industry and, as suitable coating materials are developed, the metal industry.

**BP Chemicals (UK) Limited** has recently published a booklet entitled *Solvents for Industry*, giving brief details of the BP range of solvents and methylated spirits.

**Kronos Titanium Pigments Limited** has recently announced that copies of the Joseph J. Mathiello Memorial Lecture for 1967, entitled *Particle size as a formulating parameter*, are now available on request. The lecture was given to the Federation of Societies for Paint Technology by Fred B. Stieg Jr., of **Titanium Pigments Corporation.**

**United $CO_2$ Limited** have recently developed a new fully automatic compressed air drier. This unit provides a continuous supply of dried compressed air for use in instruments or pneumatic equipment. One model, the ST20, is in current production and, it is claimed, is capable of drying up to 20 scfm air at 100 psig.

A new brochure recently issued by **John & E. Sturge Limited** describes the advantages of precipitated calcium carbonate as a pigment for paper-coating, and at the same time demonstrates them by being printed on paper treated in this way.

The brochure, printed letterpress in two colours and black, is a revised and extended version of *Sturge Technical Bulletin No 7* describing *Calopake PC*. Both cover and text paper are coated with slips containing this material.

A new grade of *Vitrathene* polyethylene is now available from **Stanley Smith & Co.** The new grade, *Vitrathene UHMW*, is a polyethylene with molecular weight in excess of one million. This is the first time, it is claimed, that a polyethylene of this type has been available from a British source in such a range. Sheets, rods and blocks are available, and outstanding impact properties, good tensile strength, abrasion resistance, and low co-efficient of friction and creep are claimed.

**English Metal Powder Company Ltd.**, who are in the process of revising their literature, have recently produced *Folder No 2*, which describes the range of *EMPCO* aluminium paste pigments. Copies are available from EMPCO on request.

The availability of a new rapid set adhesive has recently been announced by **Ciba (ARL) Ltd.** The adhesive, *Eastman 910*, is a one-component cyanoacrylate monomer, developed in the USA by **Eastman Kodak Company.** Using a thin layer of adhesive, bonding times of seconds, with tensile strengths of 5,000 psi and shear strengths of 3,000 psi, are claimed.

**British Celanese Limited** have recently published a revised edition of their booklet dealing with the use of Celanese Colloids *Celacol* and *Courlose*, in water based paints and surface coatings.

Copies of the booklet, Ref : CC130, are available from British Celanese.

**Farbenfabriken Bayer** AG have recently announced commercial production of an α-naphthylamine containing less than 0.5 per cent of β-naphthylamine. The new product, α-naphthylamine pure extra, is said to reduce toxicity hazards to a minimum. Further information is available from Bayer's UK agents, **J. M. Steel & Co. Ltd.**

Two new booklets are now available from **Plastanol Limited.** The first deals with the range of *Plastanol* resins for trichloroethylene based paints, and the second with *Plastoprene* isomerised rubber resins.

A list of the metal indicators currently available has recently been produced by **Hopkin & Williams Ltd.** A selected bibliography for general reference purposes is provided for each reagent.

The range of **Bausch and Lomb** spectrophotometers available in Britain has now been increased by the addition of the *Precision Spectrophotometer*, announce **Applied Research Laboratories Ltd.** The instrument is a single beam spectrophotometer with a built-in galvanometer covering the range of wavelengths from 190 nm - 700 nm. Quick nitrogen purging and rapid servicing are design features, together with modular construction. Readout devices include a log/linear flat bed recorder, or log/linear digital readout.

Full details are available from ARL, who are main agents for Bausch and Lomb in Britain.

**Henry W. Peabody (Industrial) Limited** announce that in accordance with the terms of a Judgment dated 8 February 1968 of the House of Lords, British Letters Patent No. 710,852 owned by the **Ransburg Electro-Coating Corporation** of Indianapolis, Indiana, USA, was held to be valid and infringed by the operation of the *Statron* electrostatic hand gun equipment manufactured by **Societe Anonyme de Machines Electrostatiques (SAMES).** This patent has now expired but it is the subject of an Application for Extension of Term.

It is suggested that all purchasers of *Statron* electrostatic hand gun equipment in the United Kingdom who wish to regularise their position in respect of use during the lifetime and any extension of the Patent should contact **Henry W. Peabody (Industrial) Ltd.,** who are sole licensees for the United Kingdom for the Ransburg Electro-Coating Corporation.

# Manchester—Membership survey

**By W. G. Topham**

Goodlass Wall & Co. Ltd., Technical Department, Goodlass Road, Speke, Liverpool 24

**Co-workers: C. Barker and G. T. Williams**

## Introduction

In order to further interest in the Association's activities and attempt to increase, if possible, the meeting attendance which has recently averaged around 70, the Manchester Section Committee agreed in October 1966 to carry out a survey of the section members. It was hoped that the data, comments, criticisms and suggestions obtained in this way would be valuable when planning future programmes.

This report describes how the questionnaire was produced, how the survey was carried out and summarises the results. Some of the questions put to members, for instance views on future lecture subjects, produced varied and interesting ideas. These views are being studied by the Committee and are reproduced in full in the report.

## Questionnaire and survey

Membership surveys have been conducted in the past by various bodies and the Committee's attention was recently drawn to a survey carried out by the North-Western Section of the Plastics Institute and reported in their August 1966 *Journal*.

Details of this survey, which aimed at gathering the type of information which the Committee had in mind, were willingly made available to us by the Plastics Institute. In this survey considerable attention had been paid to the design of the questionnaire, which served, with suitable modification, as the basis for the present survey.

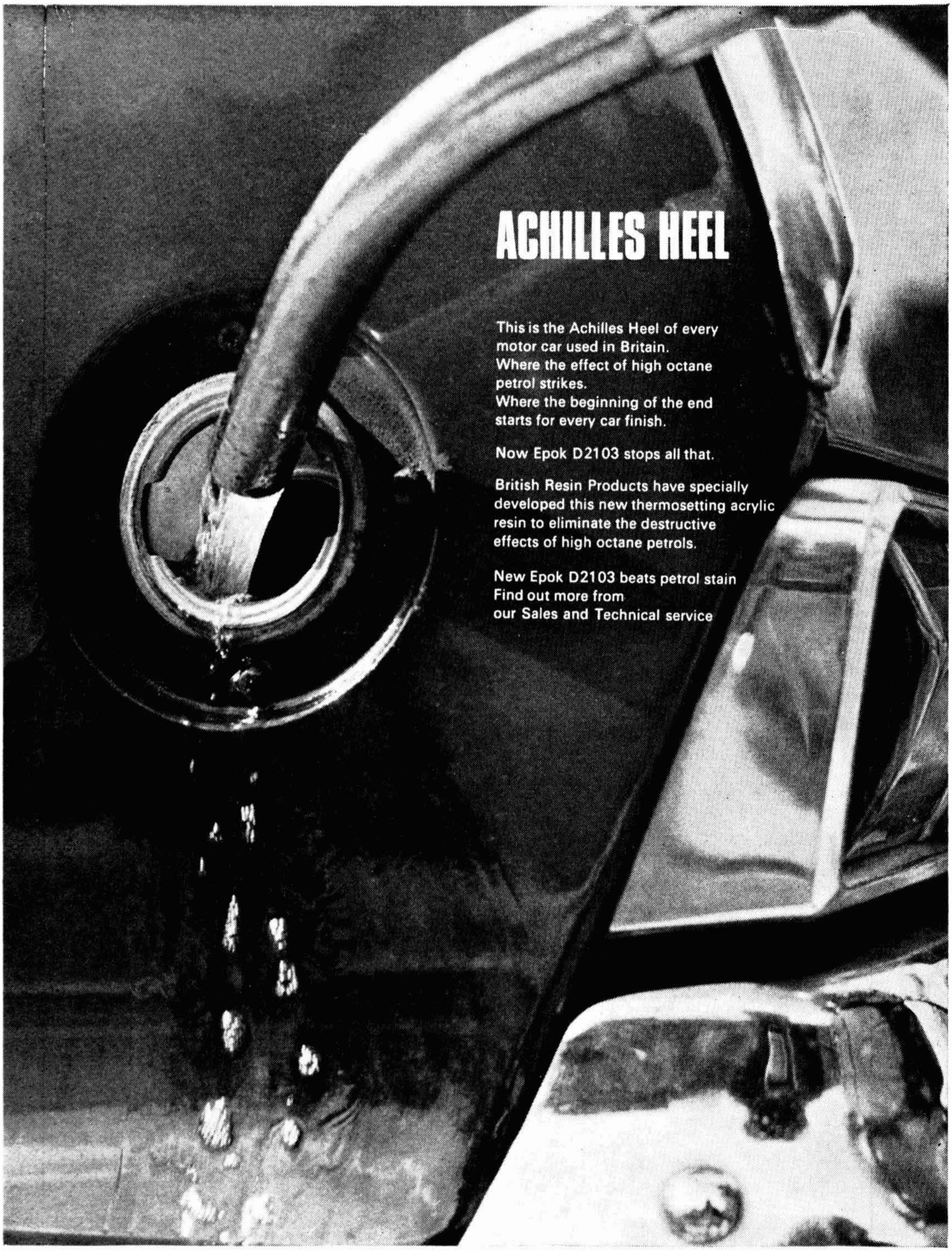
The sub-committee responsible accordingly prepared a draft questionnaire which called wherever possible for the marking of alternative answers, and was divided into the following sections :

Section A. Personal and company details
Section B. Programme organisation
Section C. Programme content
Section D. Social programme

The draft was circulated to the whole Committee in November 1966, when minor modifications were made, and the final questionnaire was sent out to members on 31 January 1967, accompanied by a covering letter from the section Chairman and a stamped return envelope. Return of completed questionnaires was requested by 20 February, and on 27 February a reminder was circulated to all members. By mid-March a 60.5 per cent response had been obtained, although in a few cases page four was, by error, left blank, and consequently some members' replies to this part of the questionnaire were not obtained.

In the absence of punched card facilities, sorting of the replies was carried out by hand, and written answers and comments were also obtained by individual examination of the returns.

Valid conclusions can only be drawn from a survey of this type if the replies are representative of the section membership as a whole. The bar diagrams provided clearly show that this is the case as far as class of membership is concerned, where an analysis of section membership shows figures virtually identical to those given



by the survey. In the case of age distribution, comparison of the results obtained from the survey and from a substantial sample from section membership records shows less precise but still good agreement, and it is concluded, therefore, that the replies are in fact fully representative.

Further bar diagrams illustrate the replies to other questions, and the detailed results are shown in the Appendix.

**Summary and conclusions**

The questionnaires distributed to members totalled 430, and 260 fully or partly completed questionnaires were returned. This represents a 60.5 per cent return which was judged excellent. Members were given the option of returning questionnaires anonymously, but in fact only 5.8 per cent of those replying chose to do so.

Company details, shown under Section A, illustrate the wide range of members' interests, and indicated that membership is high in some organisations, particularly those concerned with paint, pigment and resin manufacture. In the case of 15 firms, three or more members replied to the questionnaire (107 replies), and, of these, 68 replies were from five firms each showing more than ten returns. The remaining 119 members replying were from 100 different organisations.

The proportion of older members in the section is high, thus only some 15 per cent are aged under 30, the largest membership (35 per cent) being in the 30-40 year age group, followed by 28 per cent in the group 40-50 years. This distribution is confirmed by the fact that student membership is very low (4.6 per cent), and the fact that most members have been associated with the industries served by OCCA for a considerable number of years (22 per cent up to ten years, 36 per cent between ten and 20 years, and 40 per cent over 20 years). In this respect the paint industry differs greatly from the plastics industry. As far as function in the company or organisation is concerned, research and development accounts for the largest group (31 per cent), followed by technical service (24 per cent), and sales and marketing (16 per cent). A considerable percentage hold management posts or are directors or owners (36 per cent), while representatives form another substantial group (17 per cent). Laboratory technicians and assistants are not well represented (2.7 per cent).

As was to be expected, the majority of members are concerned with the manufacture or supply of paint, varnish and lacquers (30 per cent). Pigments and resins are also well represented (22 per cent and 18 per cent), followed by printing ink, intermediates and ancillary chemicals with 7 per cent each.

More than twice as many companies encourage OCCA membership as hold an indifferent attitude (67 per cent compared with 30 per cent), but rather fewer pay members' fees.

Companies and organisations gave varying assistance towards specific OCCA activities, ranging from time for meetings or symposia of direct interest (84 per cent), to time and expenses for the Biennial Conference (26 per cent).

The replies under Section B showed that the majority of members (43 per cent) attended one or two meetings per session and a smaller number attended 3-4 meetings. Of the remainder, roughly equal numbers (15 per cent) attended either none or most meetings. Most members attended only lectures of direct interest (33 per cent), while a similar number (30 per cent) could not spare the time to attend more meetings. A minority (about 5 per cent in each case) found either the time, date or venue of present meetings inconvenient. An overwhelming majority of members preferred after-lecture bar facilities.

Nearly all members (86 per cent) preferred the present arrangements whereby lectures are held in Manchester and Liverpool, but some alternative centres were suggested. Of these, Wigan, Preston, Warrington and Bolton were most frequently requested.

Friday evening was preferred by nearly half of the members (46 per cent), followed by Thursday evening (15 per cent), and a similar majority (43 per cent) found 18.30 hours, as at present, most suitable. Quite a large group (26 per cent), however, suggested a 19.00 hour start. The present frequency of meetings, one per month, was clearly favoured (81 per cent of members).

In Section C the programme content was approved by a substantial majority (70 per cent against 19 per cent). The general opinion was that more lectures should be held on fundamentals, materials, manufacture, application and organisation/management. Many members (45 per cent) thought that panel evenings would prove attractive, while 32 per cent suggested film evenings. A considerable number of suggestions for future lectures were made.

The answers to Section D showed that only half of the members attend OCCA social functions, but this apparently suits the majority of members, as 66 per cent felt that the present arrangements were adequate. However, 12 per cent of members thought that additional purely social events were needed, and golf, bowling, informal dances, cricket matches and car rallies, as well as a junior social event, were suggested. Far fewer members (27 per cent), however, regularly attend the Annual Dinner and Dance, and some 100 reasons (not all different) for not attending were given. Cost was clearly an important item, but some members felt strongly that commercial interests were unduly favoured.

Comments made under Section E showed that distance from Manchester was one reason why members did not participate more fully, but lack of spare time was also a factor.

Other comments made by members were of a varied nature, and are given in full in the Appendix.

## Analysis of questionnaire results

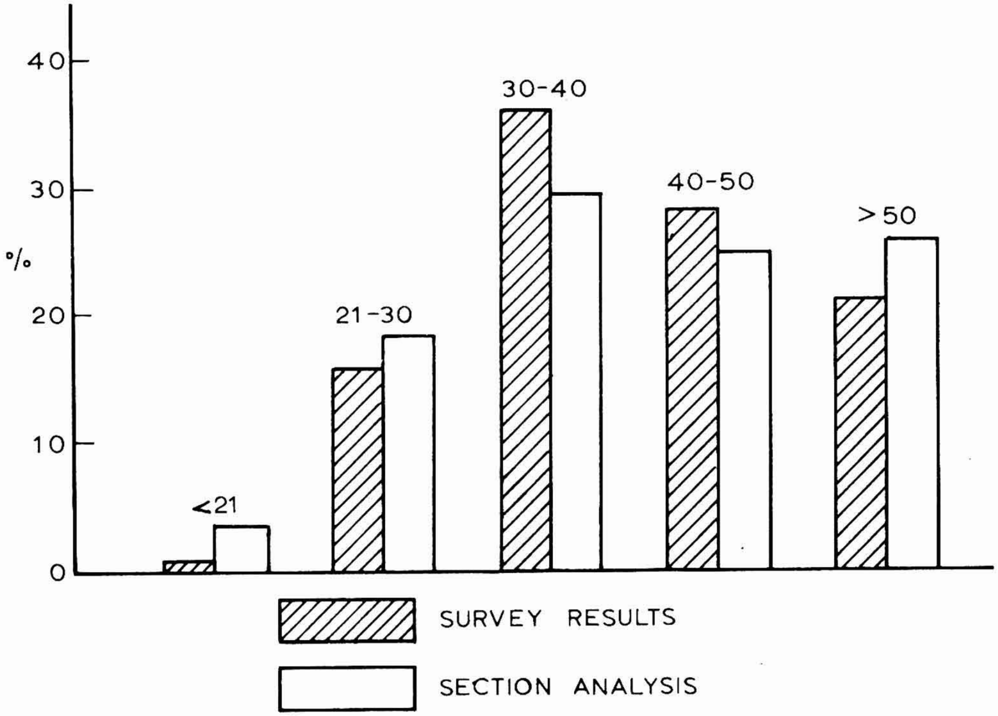
Questionnaires sent out = 430.

Questionnaires returned fully or partly completed = 260 (60.5 per cent).

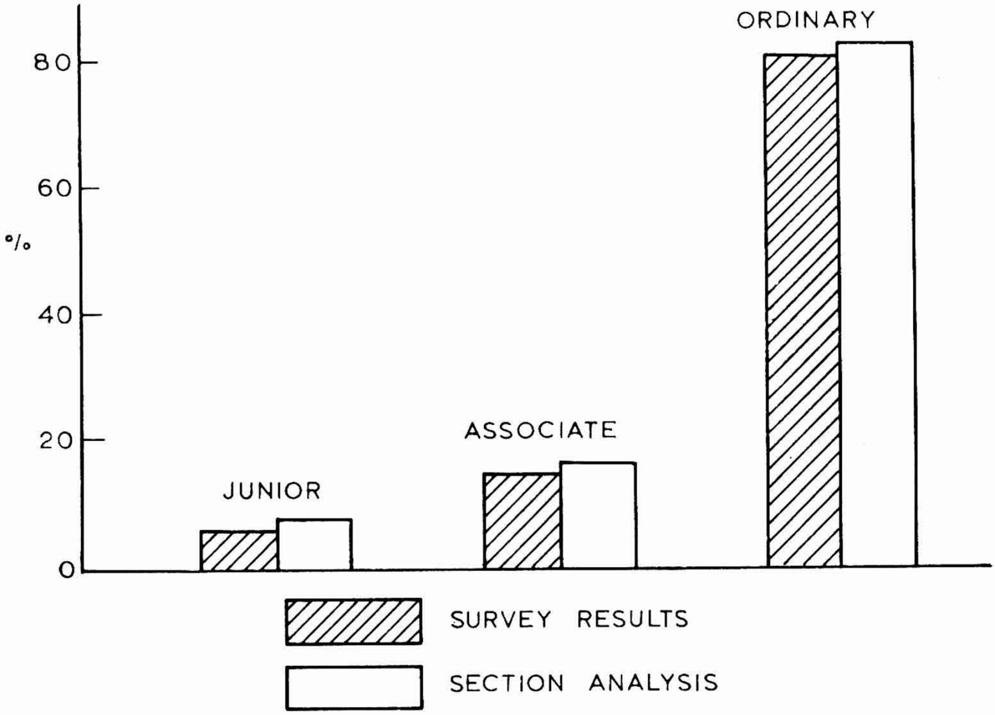
*Section A. Personal and company details*

| *Question and alternative answer* | *Question number* | *Alternative answer* | *Numbers returned* | *Percentage of returns* |
|---|---|---|---|---|
| Name | 1 | | 245 | 94.2 |
| Home address | 2 | | 245 | 94.2 |
| Company/organisation name and address | 3 | | 226 | 87.0 |
| Into which age-group do you fall? | 4 | | | |
| Under 21 | | 1 | 4 | 1.5 |
| 21-30 | | 2 | 36 | 13.8 |
| 30-40 | | 3 | 90 | 34.7 |
| 40-50 | | 4 | 74 | 28.5 |
| Over 50 | | 5 | 55 | 21.1 |
| Not classified | | | 1 | 0.4 |
| | | | 260 | 100.0 |
| In which function of your company are you engaged? | 5 | | | |
| Research and development | | 1 | 117 | 30.9 |
| Production | | 2 | 39 | 10.3 |
| Technical service | | 3 | 91 | 24.2 |
| Quality control | | 4 | 33 | 8.7 |
| Analysis | | 5 | 16 | 4.2 |
| Sales and marketing | | 6 | 62 | 16.4 |
| Other, please specify (See Appendix) | | 7 | 20 | 5.3 |
| | | | 378 | 100.0 |

QUESTION 4 AGE GROUP



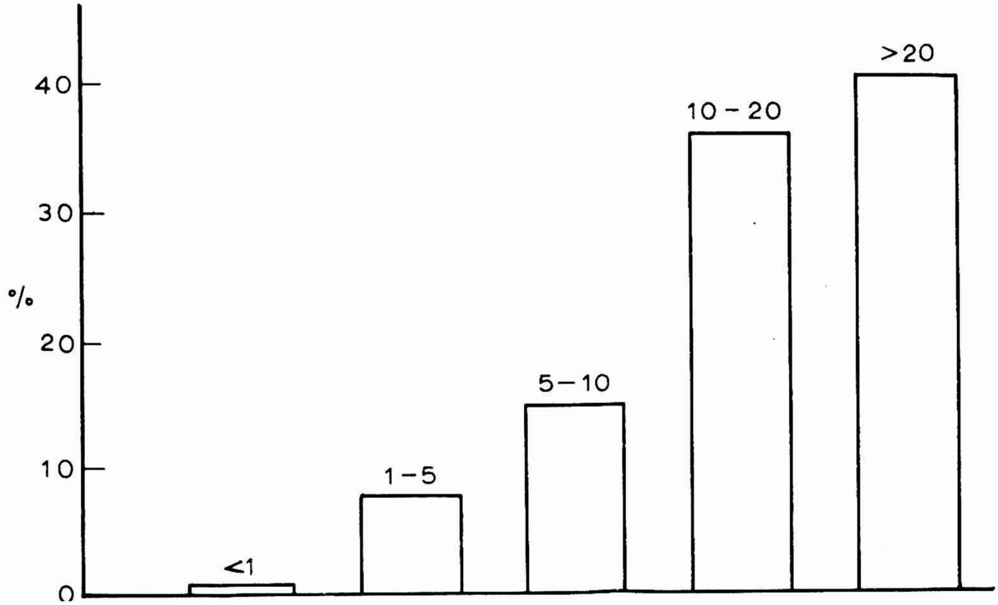
QUESTION 7 MEMBERSHIP CLASS



| *Question and alternative answer* | *Question number* | *Alternative answer* | *Number returned* | *Percentage of returns* |
|---|---|---|---|---|
| What type of position do you hold? | 6 | | | |
| Laboratory assistant/technician | | 1 | 7 | 2.7 |
| Chemist/physicist/technologist | | 2 | 55 | 20.9 |
| Section head/group leader | | 3 | 56 | 21.3 |
| Management | | 4 | 58 | 22.1 |
| Director or owner | | 5 | 36 | 13.7 |
| Representative | | 6 | 45 | 17.1 |
| Lecturer | | 7 | 3 | 1.1 |
| Not classified | | | 3 | 1.1 |
| | | | 263 | 100.0 |
| What is your class of OCCA membership? | 7 | | | |
| Student | | 1 | 12 | 4.6 |
| Associate | | 2 | 39 | 15.0 |
| Ordinary | | 3 | 206 | 79.3 |
| Not classified | | | 3 | 1.1 |
| | | | 260 | 100.0 |
| In which branch(es) of industry is your company engaged? | 8 | | | |
| Paint, varnish, lacquer manufacture or supply | | 1 | 111 | 29.8 |
| Printing ink manufacture/supply | | 2 | 26 | 7.0 |
| Resin manufacture/supply | | 3 | 68 | 18.3 |
| Pigment, extender manufacture/supply | | 4 | 81 | 21.8 |
| Equipment manufacture/supply | | 5 | 4 | 1.1 |
| Intermediate manufacture/supply (oils, solvents, basic chemicals) | | 6 | 27 | 7.3 |
| Ancillary chemicals | | 7 | 25 | 6.7 |
| Other, please specify (See Appendix) | | 8 | 30 | 8.0 |
| | | | 372 | 100.0 |
| How long have you been in the industries served by OCCA? | 9 | | | |
| Less than 1 year | | 1 | 1 | 0.4 |
| 1-5 years | | 2 | 20 | 7.7 |
| 5-10 years | | 3 | 35 | 13.5 |
| 10-20 years | | 4 | 95 | 36.5 |
| Over 20 years | | 5 | 104 | 40.0 |
| Not classified | | | 5 | 1.9 |
| | | | 260 | 100.0 |
| Does your company encourage, or is it indifferent to OCCA membership? | 10 | | | |
| Encourages | | 1 | 173 | 66.6 |
| Indifferent | | 2 | 76 | 29.2 |
| Discourages | | 3 | 0 | — |
| Not classified | | | 11 | 4.2 |
| | | | 260 | 100.0 |

| *Question and alternative answer* | *Question number* | *Alternative answer* | *Number returned* | *Percentage of returns* |
|---|---|---|---|---|
| Does your company or organisation pay your OCCA subscription? | 11 | | | |
| Yes | | 1 | 151 | 58.0 |
| No | | 2 | 102 | 39.3 |
| Not classified | | | 7 | 2.7 |
| | | | 260 | 100.0 |

QUESTION 9 YEARS IN INDUSTRIES SERVED BY O.C.C.A.



| *Question and alternative answer* | *Question number* | *Alternative answer* | *Number returned* | *Percentage of returns* |
|---|---|---|---|---|
| Does your company allow you time and/or expenses for the following OCCA functions? | 12 | | | |
| Technical meetings/symposia of general interest | | 1 | | |
| Time | | | 168 | 64.5 |
| Expenses | | | 127 | 48.8 |
| Technical meetings/symposia of direct interest | | 2 | | |
| Time | | | 218 | 83.8 |
| Expenses | | | 180 | 69.2 |
| Works visits | | 3 | | |
| Time | | | 147 | 56.5 |
| Expenses | | | 112 | 43.0 |
| Social functions | | 4 | | |
| Time | | | 119 | 45.7 |
| Expenses | | | 90 | 34.6 |
| Biennial Conference | | 5 | | |
| Time | | | 72 | 27.7 |
| Expenses | | | 65 | 25.0 |

*Section B. Programme organisation :*

At present our meetings are held monthly, October-March, on Fridays. Generally four meetings are held at the Manchester Literary and Philosophical Society, and the remaining two at the Strand Hotel, Liverpool. In addition, one or two Junior Meetings are arranged in Manchester.

| *Question and alternative answer* | *Question number* | *Alternative answer* | *Number returned* | *Percentage of returns* |
|---|---|---|---|---|
| How many meetings do you usually attend in the year's programme? .. .. .. | 13 | | | |
| None .. .. .. .. .. | | 1 | 44 | 16.9 |
| A few (1-2) .. .. .. .. | | 2 | 111 | 42.7 |
| Some (3-4) .. .. .. .. | | 3 | 68 | 26.2 |
| Most (5-6) .. .. .. .. .. | | 4 | 36 | 13.8 |
| Not classified .. .. .. .. | | | 1 | 0.4 |
| | | | 260 | 100.0 |
| Why do you not attend more meetings? .. | 14 | | | |
| Lectures are of insufficient interest .. | | 1 | 32 | 9.6 |
| Attend only lectures of particular interest | | 2 | 109 | 32.6 |
| Time of meetings inconvenient .. .. | | 3 | 17 | 5.1 |
| Dates of meetings inconvenient .. | | 4 | 26 | 7.8 |
| Venue of meetings inconvenient .. | | 5 | 20 | 6.0 |
| Meetings insufficiently publicised .. | | 6 | 0 | — |
| Insufficient spare time .. .. .. | | 7 | 98 | 29.3 |
| Other reasons .. .. .. .. (See Appendix) | | 8 | 32 | 9.6 |
| | | | 334 | 100.0 |
| Which of the following venues would you prefer? .. .. .. .. .. | 15 | | | |
| Meeting room without after-lecture facilities .. .. .. .. .. | | 1 | 41 | 15.8 |
| Meeting room with refreshment facilities (bar) to hand .. .. .. .. | | 2 | 178 | 68.4 |
| Not classified .. .. .. .. | | | 41 | 15.8 |
| | | | 260 | 100.0 |
| We now hold meetings in Manchester and Liverpool, the majority in Manchester. What are your views on these arrangements? .. .. .. .. .. | 16 | | | |
| Broadly satisfactory .. .. .. | | 1 | 225 | 86.5 |
| Unsatisfactory, in which case suggest a *third* major centre .. .. .. (See Appendix) | | 2 | 9 | 3.5 |
| Not classified .. .. .. .. | | | 26 | 10.0 |
| | | | 260 | 100.0 |
| Which is the most suitable evening of the week for you? .. .. .. .. | 17 | | | |
| Monday .. .. .. .. .. | | 1 | 25 | 9.6 |
| Tuesday .. .. .. .. .. | | 2 | 23 | 8.9 |
| Wednesday .. .. .. .. | | 3 | 31 | 11.9 |
| Thursday .. .. .. .. .. | | 4 | 38 | 14.6 |
| Friday .. .. .. .. .. | | 5 | 120 | 46.1 |
| Not classified .. .. .. .. | | | 23 | 8.9 |
| | | | 260 | 100.0 |

| *Question and alternative answer* | *Question number* | *Alternative answer* | *Number returned* | *Percentage of returns* |
|---|---|---|---|---|
| What is the most suitable time? .. .. | 18 | | | |
| 18.00 hours .. .. .. .. | | 1 | 36 | 13.9 |
| 18.30 hours .. .. .. .. | | 2 | 112 | 43.0 |
| 19.00 hours .. .. .. .. | | 3 | 67 | 25.8 |
| 19.30 hours .. .. .. .. | | 4 | 33 | 12.7 |
| Not classified .. .. .. .. | | | 12 | 4.6 |
| | | | 260 | 100.0 |
| How frequently would you like meetings to be held? .. .. .. .. .. | 19 | | | |
| Less than 1 per month .. .. .. | | 1 | 19 | 7.3 |
| Monthly (6 per year) .. .. .. | | 2 | 210 | 80.7 |
| More than 1 per month .. .. .. | | 3 | 9 | 3.5 |
| Not classified .. .. .. .. | | | 22 | 8.5 |
| | | | 260 | 100.0 |

*Section C. Programme content*

Our programme is planned to be a balanced one, e.g. this year's contains lectures on the following types of subject : evaluation, application, materials, general interest.

| *Question and alternative answer* | *Question number* | *Alternative answer* | *Number returned* | *Percentage of returns* |
|---|---|---|---|---|
| Do you find the existing balance of programmes largely satisfactory? .. .. | 20 | | | |
| Satisfactory .. .. .. .. | | 1 | 182 | 70.0 |
| Unsatisfactory .. .. .. .. | | 2 | 50 | 19.2 |
| Not classified .. .. .. .. | | | 28 | 10.8 |
| | | | 260 | 100.0 |
| Would you like to see more lectures on one or more of the following subjects? .. | 21 | | | |
| Fundamentals .. .. .. .. | | 1 | 74 | 14.7 |
| Materials .. .. .. .. .. | | 2 | 80 | 15.7 |
| Manufacture .. .. .. .. | | 3 | 61 | 12.0 |
| Machinery .. .. .. .. | | 4 | 24 | 4.7 |
| Application .. .. .. .. | | 5 | 77 | 15.1 |
| Organisation/management .. .. | | 6 | 93 | 18.3 |
| Education/training .. .. .. | | 7 | 21 | 4.1 |
| General interest .. .. .. .. | | 8 | 47 | 9.2 |
| Other subjects .. .. .. ..<br>(See Appendix) | | 9 | 32 | 6.2 |
| | | | 509 | 100.0 |
| Which of the following additional ideas do you favour? .. .. .. .. .. | 22 | | | |
| Debates .. .. .. .. .. | | 1 | 46 | 14.2 |
| Panel evenings (several speakers on a given topic) .. .. .. .. | | 2 | 147 | 45.6 |
| Film evenings .. .. .. .. | | 3 | 105 | 32.5 |
| Ladies' evenings .. .. .. .. | | 4 | 25 | 7.7 |
| | | | 325 | 100.0 |
| Are there any particular subjects on which you would like to hear talks? .. ..<br>(See Appendix) | 23 | | — | — |

*Section D. Social programme*

Our social programme consists of a Hot Pot Supper (after the AGM), and an Annual Dinner and Dance.

| *Question and alternative answer* | *Question number* | *Alternative answer* | *Number returned* | *Percentage of returns* |
|---|---|---|---|---|
| Do you attend any OCCA social functions? | 24 | | | |
| Yes | | 1 | 134 | 51.5 |
| No | | 2 | 111 | 42.7 |
| Not classified | | | 15 | 5.8 |
| | | | 260 | 100.0 |
| Do you think the social content of the present programme is: | 25 | | | |
| Unnecessary? | | 1 | 19 | 7.3 |
| Satisfactory? | | 2 | 171 | 65.7 |
| Needs more social events, in which case suggest additional activities (See Appendix) | | 3 | 31 | 11.9 |
| Not classified | | | 39 | 15.1 |
| | | | 260 | 100.0 |
| Do you regularly attend the Annual Dinner and Dance? | 26 | | | |
| Yes | | 1 | 70 | 26.9 |
| No (See Appendix) | | 2 | 169 | 65.1 |
| Not classified | | | 21 | 8.0 |
| | | | 260 | 100.0 |

*Section E. Other comments*

| | |
|---|---|
| Please state any other reasons for not attending meetings (See Appendix) | 27 |
| Are there any other alterations which if undertaken would make you personally attend? (See Appendix) | 28 |
| Have you any further comments to add? (See Appendix) | 29 |

# Appendix

*Question 5. Function in company.* Replies under alternative 7

| | |
|---|---|
| Administration | 11 |
| Education | 2 |
| Advisory | 2 |
| Consultancy | 2 |
| Market research | 1 |
| Purchasing | 1 |
| Design, construction | 1 |
| | 20 |

*Question 8. Company activity.* Replies under alternative 8

Container manufacture.
Fabric coating.
Plastics conversion.
Floor coverings.
Leather finishes.
Surfactants.
Adhesives, sealants.
Polish manufacture.
Steel manufacture.
Paint user.
Marketing.

*Question 14. Reasons for not attending more meetings.* Replies under alternative 8

Company's demands on time.
Changed interests.
Moved from area.
Personal reasons.
Illness.
Advancing age.

*Question 16. Suggestions for a third centre for meetings*

| | |
|---|---|
| Wigan | 6 |
| Preston | 5 |
| Warrington | 4 |
| Bolton | 4 |
| Chester | 3 |
| Blackburn | 2 |
| St. Helens | 2 |
| Birkenhead | 1 |
| Blackpool | 1 |
| Bury | 1 |
| Crewe | 1 |
| Macclesfield | 1 |
| Stoke-on-Trent | 1 |
| Widnes | 1 |
| More Liverpool meetings | 3 |

*Question 21. Suggestions for further lecture topics.* Replies under alternative 9

Literature survey techniques.
Information filing and retrieval.
Problem solving behaviour.
Laboratory techniques.
Development work techniques.
Formulation of inks and paints (2).
Planned experimentation.
Statistics.
Marketing and market research.
Dispersion.
Aqueous dispersions.
General paint papers.
Survey papers on subjects of importance.
Modern analytical techniques.
Pigment/vehicle interactions.
Quality control.
Relation of physical properties and performance.
Foreign paint industries.
Foreign languages.
Economic aspects of the paint industry.
Large scale industrial application of paints and inks.
Production of paint raw materials.
Protection of electrical components by encapsulation

*Question 23. Further suggestions for future lectures*

Resin development, fundamentals and experimental procedures (2).
Alkyd resins.
Driers.
Glyceride oils and fats in general applications.
Solvent manufacture and oil refinery operation.
Pigment manufacture and uses.
Applied rheology.
Application and control of acrylic paints.
Ink dispersion techniques.
Gravure ink technology.
Developments in dispersion plant.
Colour and colour matching (2).
Marine paints.
Quality control of raw materials and finished products.
Training of staff.
Use of epoxy resins in flooring, theory and practice.
Chemistry of colour films as an aid to better photography.
Surface phenomena—emphasis on pigmentation of new resin systems.
New materials, instruments and machinery.
Thermal degradation of polymers and paints.
Pigment dispersion.
Wetting, adhesion.
Polyurethane coatings (2).
Decorative schemes, colour appreciation.
Epoxy and urethane coatings.
Metal finishing techniques.
Thermosetting acrylics.

*Marketing, economic*

Balance of payments and UK economy with emphasis on the chemical industry.
Effect of the European Common Market on the surface coating industry.
Balance sheet reading.
Operational research.
Costing systems.
Raw material purchasing.
Role of technical salesman in product development.

*Miscellaneous*

Restore Annual Academic Lecture.
General interest lectures from other Societies.
History of surface coatings.

*Question 25. Suggestions for further social events*

Golf, section or inter-section (8).
Bowling (4).
Informal dances (3).
Cricket matches (3).
Car rally (2).
Junior Social event (perhaps cheaper) with Committee present (2).
Social event in Liverpool.
Informal dinner.
Informal social meeting.
Summer outings to places of interest.
Continental tour.
Better means of holding members together after meetings.
Better bar facilities after meetings.

*Question 26. Reasons for not attending Annual Dinner and Dance*

Excessive cost (24).
No interest in such a social event (13).
Too expensive and formal (10).
Lack of time (9).
Difficult domestic circumstances (8).
Too formal (6).
Lengthy speeches (3).
Dislike of venue (2).
Personal reasons (2).
Clashes with other functions and commitments (2).
Too crowded and hot (2).
Prefer not to combine technical and social events.
New members of Section.
Poor dancing facilities.
Too lazy to attend.
Lack of late transport.
Temporary company policy.
Company pays for Sales, but not Technical Staff.
Lack of contact with other members.
Domination of event by organised parties.
Excessive distance from Manchester.
Poor health.

*Question 27. Any other reasons for not attending meetings*

Distance from Manchester (5).
Lack of time (2).
Frequent absence from area.
Not technically inclined.
New to area.
Too many raw material suppliers.
Too much sales promotion.
Only loosely connected with industry.
Meetings clash with other activities.
Illness.
Advancing age.

*Question 28. Are there any other programme alterations which would make you personally attend?*

Two works visits each season (2).
Change date of works visit from late September.
An annual Symposium.
More Liverpool meetings.
More topics for production personnel.

*Question 29. Have you any further comments to add?*

There should be more lectures on fundamentals by research workers and university lecturers (2).

Some OCCA Conference lectures should be given locally for those members unable to attend.

The link between OCCA and the Universities should be strengthened.

Co-operative research programmes could be initiated, or study groups formed, by non-committee members, in order to encourage active membership.

A Symposium on printing inks should be arranged.

Closer co-operation is needed between the various organisations concerned with the paint, varnish and allied industries.

More frequent meetings, rather than the type of meeting, would induce wider participation in activities.

OCCA Exhibition should be held in the North every three years.

Formation of a Liverpool Section should be considered.

Printing ink industry is not adequately served.

A future President should come from a provincial Section.

Social content of the programme should not be extended at the expense of the technical side. The two interests could be informally combined after meetings.

Committee and Officers do not circulate among younger members.

Need for a permanent social secretary.

After-meeting bar facilities should be maintained.

# Hull

## Pigment/vehicle relations in emulsion paints and its influence on film properties

A paper entitled "Pigment/vehicle relations in emulsion paints and its influence on film properties " by Messrs. J. Clark and P. D. Aronson, of British Titan Products Co. Ltd., was given at the 4th ordinary meeting of the session, held at the Kingston-upon-Hull College of Technology on 8 January 1968. Mr. L. W. Wynn was in the Chair and the paper was presented by Mr. J. Clark.

The mechanism of film formation in unpigmented films was briefly considered. When pigment was present the basic problem was whether there was initial coalescence of emulsion droplets to form a network into which the pigment fitted, or whether there was initial flocculation of pigment, these agglomerates being later bound together by emulsion driven to coalescence by capillary forces. In an idealised emulsion, consisting of uniform spheres, on coalescence the maximum void volume would be 26 per cent, so that any paint containing more than this volume of pigment would be considered to be underbound. Conversely, if the system was considered to consist of uniform spherical pigment particles, PVC values of up to 74 per cent could be obtained with fine particle emulsions before underbinding became apparent.

These idealised conditions did not exist and pigment loading of much more than 26 per cent could be achieved without much falling off of film properties, although 74 per cent was rarely claimed. The normal concept of critical pigment volume concentration could not readily be applied to emulsion paints because of the discontinuous nature of the polymer.

An examination of the hardness, tensile strength, elongation, scrub resistance, opacity change on drying and chalk resistance in relation to the pigment volume present had been made in the hope of finding an abrupt change at a point corresponding to the critical value. Such determinations were tedious to perform and difficult to assess quantitatively.

Liberti and Pierrehumbert proposed a calculation of CPVCs based on the water demand of a pigment, and work had been carried out by the authors to see whether a correlation exists between water demand and the CPVC as determined from the film properties. Four grades of titanium dioxide were used in the work, differing in the coating present and in their water demands. Two extenders, whiting and china clay, were used, which also differed in their water demand.

Numerous slides were shown, from which it was evident that some correlations did exist but that the type of emulsion in use, the nature of the extender and the water demand of the titanium dioxide might have marked influences.

The change in opacity, as judged by the reflectance over a black background, on drying had given some most interesting results. With a lightly pigmented emulsion paint the opacity would continue to fall as the film dried, but with a highly pigmented paint the opacity would fall at first and then begin to rise due to the onset of " dry hiding." The concentration of pigment at which the opacity just began to rise on drying might therefore be related to the CPVC. The higher the water demand of the $TiO_2$ or extender, the lower the PVC at which the effect was observed. It was suggested that this dry hiding effect could be used as a guide to the resistance of a film to cracking and chalking on outside exposure.

A discussion in which Messrs. Robinson, Brown, Wenham and Finn took part followed the meeting. A vote of thanks was proposed by Mr. J. S. Geary and was well supported by those present. Forty members and 13 visitors attended the meeting.

S.R.F.

# London

### Conversazione : Paint and printing ink testing

The London Section Conversazione on " Paint and printing ink testing " was held at the Charing Cross Hotel, London, W.C.2, on 15 February 1968, with over 130 members and guests present. Mr. R. N. Wheeler, after welcoming those present, handed over the chair for the meeting to Dr. S. H. Bell, Immediate Past President of the Association.

The first paper was by Dr. F. Wagener of Titangesellschaft m.b.H., Leverkusen, on " Suitable tests to ensure the economic use of titanium dioxide in emulsion paints." Dr. Wagener described various tests which had been developed for the evaluation of existing and new grades of pigments. Good water-dispersibility was essential, but because of the use of substantial amounts of larger-sized extenders in formulations it was not possible to make an assessment based on the use of the Hegmann gauge. For this reason the surfactant demand was used as a criterion of dispersibility of the titanium dioxide, and a titration method based on wet point and flow points was used with a range of solutions of varying concentrations of the surfactant, sodium polyphosphate. As the concentration of surfactant increased, the wet and flow points decreased and converged, and at this point it was considered that the pigment was fully dispersed.

These tests were illustrated with a comparison between a special grade of titanium dioxide developed for emulsion paints and a normal grade, and showed that the special grade had the higher surfactant demand, due to the after-treatment.

Optical properties were measured by means of tinting strengths with a black pigment (Helio Fast Black), determined over a range of pigment/extender ratios at a constant partial volume concentration of titanium dioxide pigment. The extender mixture used was 90 per cent microdolomite and 10 per cent talc. These paints were applied to white cardboard substrates with an automatic applicator, and dried under standard conditions, before instrumental colour measurement on a tristimulus reflectance photometer.

Other optical measurements made were of hiding power and of tone. The latter was determined from instrumental readings on the grey drawdown as a " blueness index ." A further property which had proved useful was the porosity of the film, which was determined by a staining test with a solution of gilsonite. The solution was brushed across a white film and rinsed off immediately with white spirit. The intensity of discoloration remaining was an indication of the degree of porosity of the film. The last testing method described was scrub resistance.

In the lively discussion after the paper, the view was expressed that while titanium dioxide pigment manufacturers were endeavouring all the time to produce improved grades, paint manufacturers were at the same time being forced to produce cheaper types of emulsion paints, with lower proportions of titanium dioxide pigment, and under these conditions the improved grades did not show to special advantage. Other points discussed included the rheology of the mill bases produced, and the effects of varying size ranges of extenders. Dr. Wagener said that while extenders of similar size to the titanium dioxide pigment were ideal, their water demand was too high. With the new improved grades of titanium dioxide, the improvements produced by fine particle extenders were much less than with the standard grades.

The second paper was by Mr. C. J. H. Monk of ICI Paints Division Ltd., entitled " Some recent developments in paint testing instruments." Mr. Monk had brought along on display a wide range of the instruments which had been developed at Slough.

Mr. Monk discussed the philosophy of measurement of paint properties, and listed a number of design factors which should be considered. These were ; property to be measured, units of measurement, ease of use and cleaning, " paint proofness " and reliability and cost. These last three factors were of great importance in the economics of testing in the laboratory, and under the cost factor one should also consider costs of operation and cleaning as well as the initial cost of instrument.

Mr. Monk then described a number of instruments which had been developed by ICI over the last few years, with these considerations in mind. The first example was a weight per gallon cup, which operated by compressing the entrapped air under standard conditions to about a tenth of its volume. Viscosity measurements were next discussed, and a simple and robust cone and plate viscometer, which operated at a single rate of shear of 10,000 $\sec^{-1}$, under controlled temperature was described.

Gel strength measurements were measured with a blade attachment for the Rotothinner, fitted with a low speed motor (2 rpm) and with the rotating table calibrated in g.cm.torque. The standard Rotothinner had also been modified with a spherical bob for use with high viscosity materials (e.g. adhesives), of up to 340 poise.

A new block applicator was described, with automatic operation by means of a coil spring ; the speed of application could be varied. An ingenious feature was that all the mechanism was above the panel, so that spillages, etc. did not affect the mechanism.

A new drying time recorder was described, using standard 12 in x 4 in test panels which carried out three different tests at once on the same panel. A recent addition was a flock dispenser, used to assess the time at which the paint film would no longer pick up dust.

In a stoving oven the actual surface temperature of a massive object might differ appreciably from the air temperature, and consequently the actual temperature cycle attained by the paint film might differ appreciably from what would be expected. To investigate these effects a stoving temperature recorder had been developed. This consisted of a miniature multi-channel recorder, which could travel through the stoving oven (protected from temperature by enclosure in a Dewar vessel), and by means of which up to six small platinum resistance thermometers could be used to record surface temperatures on different parts of the object being stoved. This instrument was found in practice to be sufficiently robust to be attached to car bodies, etc., passing through a stoving oven, and on one occasion when a conveyor stopped the Dewar vessel gave complete protection to the recorder in the oven for 2 hours.

Mr. Monk finally described the measurement of film hardness with the ICI micro-indentation instrument. In the discussion after the paper questions were asked concerning the applications of the instruments described.

The third paper was by Mr. C. C. Mill of PIRA on " Physical testing of printing ink " and covered the measurement of the flow properties of inks. Mr. Mill discussed the theoretical treatment of the use of the Ferranti-Shirley cone and plate viscometer to produce a rheogram, in which the material was taken through a complete cycle of measurement. The second instrument described was the falling rod viscometer. Good agreement had been obtained between the Laray and the Ferranti-Shirley instruments provided that one did not go to too high rates of shear on the Ferranti-Shirley. Finally, the various types of tackmeter were discussed, and the results of experiments with the Inkometer, the Metal Box–Churchill, and the PATRA instruments were described. It was concluded that provided one took due note of the characteristics of the instrument used, there was reasonable correspondence between the various standard tests used for printing ink.

The final paper was by Mr. T. R. Bullett of the PRS on " The assessment of the durability of paint films." Mr. Bullett referred to the development of the standard procedure for accelerated weathering described in BS3900 Part F3, and considered some of the factors involved in film degradation and how methods of assessment might be improved. It would be very desirable to be able to produce standardised " imperfect " substrates, which would typify the real surfaces encountered in practice but be free of the gross lack of reproducibility encountered in surfaces exposed to natural contamination.

Mr. Bullett then considered various modes of failure. Chalking breakdown could be assessed simply by measuring the loss of weight of films exposed to artificial weathering cycles. Complications occured with natural exposure tests. It had also been found that a reliable indication could be obtained from the first few hundred hours exposure. Breakdown due to checking and cracking was more difficult to reproduce, since almost all paints were viscoelastic materials in which stresses could be relaxed by flow. The stresses developed in a coating depended in a complicated manner on the history of the coating and the nature of the substrate. The present tendency was to concentrate on measurements of changes in the mechanical properties of films, e.g. second order transition point, tensile strength, and extension at break. Mr. Bullett also considered the merits of testing on attached as well as detached films. The former seemed to be more relevent to practical performance than tests on free film.

The meeting concluded with a general discussion in which all four authors took part. A vote of thanks to the speakers for their excellent lectures covering the broad spectrum of paint and printing ink testing, and to Dr. Bell for his chairmanship of the meeting was proposed by Mr. R. N. Wheeler.

V.T.C.

### Characterisation of blast cleaned surfaces and its relation to paint performance

A meeting of London Section was held on 17 January 1968 at University College, London, W.C.1, with Mr. R. N. Wheeler in the chair. Mr. T. R. Bullett and Mr. D. Dasgupta, of the Paint Research Station, gave a paper on " Characterisation of blast cleaned surfaces and its relation to paint performance."

Mr. Bullett said that the work had been sponsored at the PRS by the Civil Engineering Research Association (now expanded to Construction Industry Research and Information Association) in view of the vital importance of surface preparation to the life of the coating and thus to long-term protection of structural steel. Chemical methods of surface preparation were unsuitable for structural steel. With hot rolled steel, three distinct layers of oxide existed in the millscale, $Fe_2O_3$, $Fe_3O_4$, and FeO.

On exposure the FeO was converted to voluminous hydrated ferric oxide, causing layers of the millscale to come away. This was not an even process, however, and consequently after a short period of weathering the surface was covered with islands of millscale and bare patches. The residual millscale was cathodic to bare steel and corrosion pitting occurred. This illustrated the danger of relying on weathering to remove millscale.

Blast cleaning was used to dislodge the millscale and oxide. Mr. Bullett described the types of equipment and abrasives used. The non-metallic abrasives were used mainly for on-site cleaning where recovery was not possible. The construction industry tended to favour angular grit, while shot, or shot/grit mixtures, were used mainly in shipyards. While large particles, having a greater kinetic energy, might have individually a great cutting power, smaller particles, because of their greater number per unit weight, had a greater effectiveness, and it was found in practice that cleaning rates increased markedly with decrease in particle size. Examination of grit blasted surfaces on the Stereoscan electron microscope showed the remarkably rough and irregular surface produced, and smaller sized grit produced a much finer textured surface.

Initially, it had been thought that a rough textured surface was necessary to provide sufficient key for the coating, with peak height of 3-4 thou. Such surfaces would require a very thick film for adequate coverage of peaks. The Swedish pictorial standards were of considerable value in evaluation of surface preparation, but there was need for an instrumental method. The PRS had developed two instruments. One of these was an optical method of measuring surface cleanliness. The second was a pneumatic gauge for measuring surface texture. Both of these instruments had been developed in conjunction with SIRA, and prototype models were now undergoing evaluation by users. Surface profiles were normally described in terms of Centre-Line Average figures obtained from instruments such as the Talysurf. Peak-trough heights could also be measured ; these were frequently considerably greater than the CLA figures.

Mr. Dasgupta then continued by describing the instruments which had been developed. The pneumatic gauge, operated from a small cylinder of compressed air, was a means of applying a known pressure of air to the surface *via* a head which was supported on a neoprene ring. Leakage of air occurred underneath the ring, and the resulting pressure drop through the head was a measure of the roughness of the surface. Examination of a number of blast cleaned surfaces had shown good agreement with CLA figures obtained using the Talysurf. There was also good agreement with average peak-trough heights, as measured by examination of cross-sections of surfaces on a projection microscope. The degree of roughness increased with the abrasive size, and was related to the increase in surface area. The paint required, however, had no direct relation with the increase in surface area, and was probably related to the increase in effective volume of the surface profile. It was of interest that there was a direct relation between the measured pressure drop and the change in volume.

The reflectometer, which was designed for mild steel surfaces, employed 45° illumination, through a blue filter, and the photocell was normal to the surface. A standard grey surface was used for calibration. It had been found that, on blast cleaning, the reflectance increased asymptotically to the white metal stage ; this might vary from one steel to another, and also depended upon the abrasive used (i.e., the type of surface produced). Comparisons had been made using the instrumental technique with a surface contaminated with labelled stearic acid, with metallographic examination, and with adhesion measurements on surfaces cleaned to varying extents, and in each case good agreement was obtained.

Various studies had been made on the blast cleaning process. It had been found that efficiency increased as one decreased the abrasive size, and that small angular particles produced the best removal of millscale. With rusty steel, blast cleaning did not remove all the rust, even when the white metal stage was reached. Crystals of ferrous sulphate had been found in the pits in the surface, and painting over this would lead to corrosion and under-rusting, with subsequent destruction of the paint film.

There was need for further work to decide how much residual ferrous sulphate could be tolerated. It had been shown that it was better to paint the surface immediately after blast cleaning (say within four hours), than to allow the surface to weather.

The paper was followed by an extensive discussion, contributions being made by Mr. J. F. D. Warren, Mr. D. E. Steed, Mr. A. G. Robinson, Mr. G. A. Newell, Dr. R. R. Bishop, Mr. J. K. B. Burke, Mr. L. G. Blackledge, Mr. K. J. Day and Mr. D. A. Bayliss. A vote of thanks for an extremely interesting paper in which highly scientific methods had been applied to a very practical problem, was proposed by Dr. H. R. Hamburg.

V.T.C.

# Manchester

## Synthetic resin manufacture

A Junior lecture was given on 24 January, at the Manchester Literary & Philosophical Society's premises, by Mr. C. Barker. The subject was " Synthetic resin manufacture " and 98 members, junior members and guests were present.

Mr. Barker based his talk on the reactions occurring in resin manufacture, and connected these via the conditions under which they occurred, with the type of plant required. He took examples from alkyds, solution vinyls and isocyanates by way of illustration.

Alkyd reactions took place around 250°C with a low heat of reaction. Vinyls reacted at about 120°C with 14-18 K cal/mol$^{-1}$ evolved exothermically—vinyls also had a low specific heat. Polymerising 2 tons of methyl methacrylate could evolve 150 kilowatts in a fairly small volume. Alkyds needed a high heat input for initial temperature raising, but little cooling during the reaction. Vinyls had opposite requirements, e.g. lower heat input, but cooling was essential to maintain the temperature during reaction.

The typical process sequence was—charge, heat to working temperature, hold at reaction temperature, stop reaction, cool, dissolve in solvent, filter and analyse.

Plant, originally of 2-500 gallon capacity, was now frequently 5-6,000 gallons, equivalent to 15 tons. The reaction pan, of stainless steel, or stainless clad, was jacketed for heating and cooling, and was followed by a dissolving tank twice its capacity. Direct heating by oil or gas had been superseded by indirect methods using heat transfer fluids, but electrical resistance and induction heaters could also be used. Where low temperatures only were involved, electrical or steam heating could be employed. Temperatures constant to ± 2°C were especially necessary for vinyl resins.

Since agitation affected heat transfer and therefore constancy of temperature, and achieved shorter reaction times, vane disc agitators were employed where the inert gas flow also assisted in water removal.

Mr. Barker concluded with a review of analytical methods used in ensuring consistency of manufacture.

After a valuable period for discussion, the vote of thanks was proposed by Mr. R. Handley.

D.A.P.

# Midlands

## Electron curing of paint films

The January meeting of Midlands Section was held at Winston Restaurant, Balsall Heath Road, Birmingham, on 19 January. The venue had been selected so that members could take dinner together, before the lecture. An excellent meal was provided and members appreciated the innovation. The lecturer was Dr. F. L. Dalton and his subject was " Electron curing of paint films."

Dr. Dalton said that electron beam processing provided a high concentration of free radicals, and thus the possibility of bringing about any reaction initiated by free radicals. Most work had been carried out with polyethylene sheet and with unsaturated polyesters on flat surfaces, but the problems associated with modifying the process for curved surfaces were not difficult. Compared with normal thermal methods of curing, there was higher power utilisation and reduced heat consumption, no limitation of substrates, the plant occupied much less space and higher throughputs were possible.

The electrons were produced by a thermally heated element, then accelerated by means of a potential difference, and finally scanned through a thin window on to the film to be cured. Potential differences of 300 kV were suitable for coatings of 20-50 thou and could be achieved with transformer-rectifier sets. Insulating core transformers had been developed in the United States and were very suitable for higher voltages but the capital cost was much greater. Capital cost was greatly influenced by the voltage selected, and for thin coatings the voltage should be low. However, the window, which had to withstand a vacuum and be free from pin-holes, imposed a limitation on how low the voltage could be. The power wastage with thin films was not critical, since the total power required was less than 1/5th of that required for conventional ovens.

When unsaturated polyesters were cured by electron beams, no catalysts nor accelerators were required, and thus they became single-pack systems. The rate of cure was so rapid that air did not diffuse into the surface and so there was no surface tack. The method offered scope for the formulation of highly flexible polyesters to be used on paper.

Acrylics and vinyls, which were normally applied in solvents, had been cured with electron beams by replacing the solvent with monomer. Polyurethanes and epoxides were not susceptible to free radicals, but blends were possible.

In classical kinetics, high intensities of free radicals led to low molecular weights. This did not seem to apply with electron curing of polyester-styrene systems. Some monomers obeyed classical kinetics at low voltages but not at higher voltages.

Turning to possible developments, the speaker said that he expected a growth in basic understanding of the process, optimisation of formulations for flexibility and more work on blending with epoxides and with urethanes. Wider types of materials should become available for coatings because functional groups were not required for electron curing. There was a need for better electron-guns and improved windows. If the window could be dispensed with, this would revolutionise the method, especially for thin coatings. Using techniques already developed for vacuum spluttering, the critical factors would seem to be the cost of pumping equipment and the development of suitable seals.

During the ensuing discussion period Dr. Dalton ably answered questions raised by Messrs. C. H. Morris, D.E. Yates, R.F. Hill, H. J. Clarke, S.E. Canning and R. McD. Barrett. Mr. D. J. Morris suitably conveyed to the lecturer the thanks of the meeting for a most interesting and well presented paper.

L.R.S.

## Polybutadienes in mastics and surface coatings

At a meeting of the Midlands Section, held on 16 February at Birmingham Chamber of Commerce, Mr. M. Artson gave a talk on " Polybutadienes in mastics and surface coatings."

Mr. Artson said that polybutadiene had been developed primarily for the tyre industry, where its use gave good abrasion resistance. Butadiene was a gaseous monomer obtained from cracking hydrocarbons and was cheap and in plentiful supply. When polymerised in hydrocarbon solvents, using lithium alkyl catalysts, it produced an elastomer of high purity, good colour and a narrow molecular weight range. The chain units were 45 per cent cis 1:4, 46 per cent trans 1:4 and 9 per cent of 1:2 vinyl type. Having no crystallinity, it showed good flexibility and, with no chain branching, it was readily soluble in a wide range of solvents. It was compatible with many surface coating materials and its possible applications to surface coatings have been examined.

When polybutadiene was incorporated in linseed oil putty it improved flexibility, ageing and storage properties and gave good alkali and acid resistance. The putty was particularly useful as a sealant for porous surfaces because there was no diffusion of oil into the substrate.

Polybutadiene was not compatible with alkyds, but was compatible with vegetable oils. It could be coupled with drying oils by reacting at 250°C, and the adduct could then be made into an alkyd. The alkyd had good through-dry, flexibility and some alkali resistance.

By using the double bonds present in polybutadiene, functional groups could be introduced. Perbenzoic acid or peracetic acid gave epoxidised products which could be cross-linked in the presence of $BF_3$ compounds. Halogenation, hydrogenation and hydrochlorination were also possible. Carboxylation gave a compound which could be cross-linked with epoxy-compounds.

Oxidative scission of the chain produced a low molecular weight polybutadiene. This was carried out in aromatic hydrocarbons, at high temperatures, in the presence of catalysts capable of forming hydroperoxides. The product was a viscous liquid with a molecular weight of 5000-7000 and had about 4 -OH groups per chain. It could be reacted with diisocyanates to give tough rubbers and novel urethanes suitable for carpet backings. It could be cross-linked with sulphur and lead peroxide and underwent partial cure with certain epoxy resins. A three component system comprising low molecular weight polybutadiene, epoxy resin and an amino-resin cured to give films with good abrasion resistance and suitable for can linings. Low molecular weight polybutadiene could also be cured with some substituted phenol-formaldehyde resins to give coatings with good chemical resistance and excellent deep-draw characteristics.

Attempts to react low M.Wt. polybutadiene with fatty acids produced gels due to the high reactivity of the polybutadiene. However, low M.Wt. polybutadiene was found to have good compatibility with many alkyds and when post-added to suitable alkyds gave coatings with good abrasion resistance, useful as car-primers and primer surfacers.

During the subsequent discussion period Mr. Artson and Mr. V. Dando answered questions about stoving schedules, contact adhesives, weathering in view of the unsaturation of polybutadiene, the mechanism and types of phenolic resins which would cross-link, the possibility of using polybutadiene with unsaturated polyesters, the behaviour of phenolic cured systems on prolonged heating and the stability of treated alkyd systems. The meeting concluded with a vote of thanks proposed by Mr. D. E. Hopper.

L.R.S.

## Trent Valley Branch

### Industrial finishing in the cycle industry

The second technical meeting of the Trent Valley Branch was held at British Rail School of Transport, Derby, on 9 November 1967, when members listened to a talk by Mr. J. L. Barlow entitled " Industrial finishing in the cycle industry."

Mr. Barlow traced the history of the bicycle back to the 17th century, outlined the different types of finishes used on bicycles since that time and gave various reasons for the types used. In the 18th century, linseed oil paints were used, followed in the 19th century by high gloss black japans based on bituminous/Congo copal/linseed oil which were stoved in crude box ovens. It was interesting to note that over 40 per cent of bicycles produced today were still finished in black.

The 20th century saw the advent of coloured finishes used on bicycles, starting with the popular Raleigh Green. Some of these were adorned with solid gold lining and family crests. These finishes were still based on linseed oil and their application remained something of an art and individual skill.

The introduction of the air atomised spray gun and its commercial adoption by the cycle trade in the late 1920s also made it possible to supply a much wider colour range. About the same time phosphate pre-treatments were introduced and provided the means of reducing the number of coats of paint whilst still achieving the desired appearance and corrosion resistance.

In the 1930s there was an increased demand for bicycles, particularly in export markets, and this was responsible for the introduction of mass production methods using conveyors. The protection system used then, and for several years after, was a black primer based on bitumen/linseed oil followed by alkyd amino finishes. More recently finishes based on epoxy, acrylic and polyurethane resins have been more extensively used. Much development work had been carried out to find new lightfast pigments and dyes to produce unusual or improved colours for polychromatic and flamboyant finishes, since decorative appeal was a big factor in the selling of bicycles.

A further breakthrough in mass production finishing of bicycles came in 1956 with the introduction of the Ransburg reciprocating disc electrostatic equipment.

Mr. Barlow enumerated the various requirements for a modern cycle finish as good coverage, colour and gloss and excellent durability. Durability was normally tested by salt spray and accelerated weathering to DEF 1053 as well as natural exposure 45 South, hardness was tested to 2H - 3H, scratch resistance to DEF 1053 2,000 grms, and abrasion resistance to 100 cycles with 6 S 10 wheel 250 gm load in a Tabor Abrader.

For the future Mr. Barlow thought that large manufacturers would be using fully automatic plants based on electrophoretic priming.

The talk was very well illustrated with slides and samples and provoked a lively discussion afterwards.

J.R.B.

### Progress in polymer emulsions in the paint industry

The third technical meeting of the Trent Valley Branch was held at the British Rail School of Transport, Derby, on 11 January 1968, with Mr. R. S. Law in the chair.

Mr. E. Swales (Vinyl Products Ltd.) reviewed the various emulsion types available for paint manufacture and went on to consider their relative cost/performance characteristics with particular reference to pigment binding efficiencies.

Mr. Swales traced the history and growth of polymer emulsions for paints and then dealt specifically with vinyl acetate copolymers using acrylates, VeoVa 911 and grafted ethylene as plasticising comonomers, and all-acrylic and styrene-acrylic copolymers. In comparing the performance of these emulsions he pointed out that not all paint properties had been considered in the tests and that generalisations relating solely to polymer type, as opposed to other emulsion constituents, could be misleading. Wet scrub and wash resistance tests were taken as the basis of his comparisons and graphs and slides of the results were shown.

There was unfortunately no generally accepted standard method for evaluating scrub resistance but two types were in common use ; in one of these, ultimate failure was due to lack of adhesion, particularly with paints of low PVC, and in the other failure occurred by erosion. There was a lack of reproducibility with the first type of method and the second was therefore used for the paper. The wash test was adapted from the CS 2863B specification, but using a glass substrate.

Taking an 85/15 vinyl acetate/2-ethylhexyl acrylate copolymer as the control, the emulsion binders were evaluated in paints at 50 per cent and 70 per cent PVC.

After scrubbing, the paint panels were weighed to determine loss by erosion : at 50 per cent PVC the differences between the majority of polymers were so small as to be within experimental error; at 70 per cent PVC the polymers not based on vinyl acetate gave significantly better results than the control. In the wash tests the styrene-acrylics, the all-acrylic and one of the two VeoVa 911 copolymers were better than the standard at 50 per cent and 70 per cent PVC; the graft ethylene copolymer was equivalent and the remaining systems inferior to the standard.

The five polymer types were then tested for scrub resistance over PVC range, with slight formulation changes at the higher PVC levels; the results confirmed those obtained previously.

Mr. Swales then considered the raw material costs of the paints at equivalent performance ; the costings were, however, pre-devaluation and some emulsions, particularly those containing acrylic monomers, were likely to be increased more than others. He concluded that although all-acrylics were particularly suitable for specific applications, it was difficult to justify their use in normal emulsion paints ; styrene-acrylics would seem to offer a cheaper and possibly better alternative. At the present state of development, ethylene grafted vinyl acetate coplymers were a better proposition than conventional ethylene copolymers. VeoVa 911 copolymers could show better cost efficiency than vinyl acetate-acrylate copolymers, but the considerable differences between the two types examined in his paper emphasised the danger of discussing emulsions in terms of polymer type only. The water phase of the emulsions and the paint formulation also exerted a major influence.

After a short discussion on several aspects of Mr. Swales' paper the meeting closed with a vote of thanks proposed by Mr. Eric Hare.

J.R.B.

# Scottish

### Future surface coatings

The February meeting of the Scottish Section was held as usual in the Lorne Hotel, Glasgow, on the 8th of the month, when Mr. R.A. Brett of the Research Association of British Paint, Colour and Varnish Manufacturers spoke on "Future surface coatings."

Mr. Brett first considered the likely trends in types of paints and general requirements in properties that would be demanded. An increased swing to water based materials seemed likely from experience in the USA. Rising labour costs of painting would lead to a demand for longer life maintenance paints. The increase in mass production and " factory building " would emphasise quick and hard drying coatings, while the consequent better surface preparation would enable a wider range of formulations to be used.

Modifications to well established media were then considered. In the polyester field, the oil modified alkyds seemed likely to continue in use for many years, particularly in view of their versatility, as was exemplified by the silicone modified alkyds, with their good heat resistance. " Oil free " alkyds, when silicone modified, were particularly resistant to exterior exposure, and without such modification possessed the good flexibility, adhesion and impact resistance needed for coil coating ; the future for this type of material seemed bright. The recent development of the electron beam technique for curing paint films by irradiation would give a stimulus to the use of unsaturated polyester materials, and Mr. Brett described the technique in some detail. Methods of curing by visible or UV light were also discussed.

Turning to water thinnable paints, Mr. Brett considered that in the air drying field pva/ethylene copolymers had a particularly promising future. The production of an acceptable full gloss water thinnable paint remained the big prize in the decorative market, and some possible routes to it were considered. In stoving systems the electrodeposition process for water thinned paints would demand one coat finishes of good colour retention, thus favouring acrylics, perhaps with cationic properties. It seemed reasonable to suppose that solvent based acrylics would continue to replace traditional systems in car body and domestic appliance fields. In the field of epoxy resins, high build coatings of long life would be particularly suitable for the textured finishes now popular in the building industry. Developments in polyurethanes might lead towards increasing " one pack " use, the aliphatic type of diisocyanate, and perhaps polyurethane latices.

Mr. Brett then discussed some newer media and their properties and possible outlets. Much work had been done in the inorganic and organometallic fields, inspired by the success of the silicones. Hydrolytic instability was the danger here, but silicate coatings originally developed for space research seemed promising and were being evaluated at the PRS. Aluminium polyphosphates also looked encouraging, but the whole field of inorganic polymer science required much work to exploit its potentialities. Returning to organic materials, new techniques such as ultrafine powder handling had made polyethylene more versatile as a coating material. Its known defects of poor adhesion and exterior durability could be overcome by fluorination, and fluorocarbons had been given a terrific boost by the discovery of techniques for using them as coatings, for example on non-stick frying pans. The types of fluorocarbons available were described, and it was noted that such coatings were increasing rapidly in use in the USA, and that guarantees were being talked of for up to 20 years outdoor exposure.

A wide range of aromatic polymers had appeared in the patent literature, and some of these were described. Many phenylene compounds had been developed, including phenoxy-compounds, polyxylenols, poly-*p*-xylylene, polysulphones, polysulphonates and polycarbonates. Among the hetero-aromatic polymers, mostly developed with thermal stability in mind, polypyromellitides and polybenzimidazole were specially mentioned. Mr. Brett concluded by describing the principle of "ladder" polymers, whose molecular chain was much less liable to instability through bond breakage.

During discussion, Mr. Brett was able to expand on some of the points which he had made, and the meeting closed with a vote of thanks from Mr. G. Hutchinson.

J.D.E.

## Student Group

The February meeting, which was the penultimate meeting of this session, proved to be very interesting to the members. The meeting opened with a film which traced the history of the paint industry from the time of cave-dwellers to the present time.

The various types of pigments used by our ancestors were illustrated, as were the beginnings of the varnish and resin industries.

There followed a short talk on epoxy resins by Mr. Brockman of Egham Laboratories, who indicated the several outlets for epoxy resins other than the paint industry.

The meeting closed with another short film illustrating the use of epoxy finishes in the marine industry.

Mr. Ian McCallum cordially thanked Mr. Brockman for giving such an interesting lecture and also Mr. Alex Smith who once again favoured us with his services as projectionist.

Following the meeting there took place the A.G.M. of the section. A report of the Section's activities was read by Mr. P. Birrell, the Student Group Liaison officer, who also indicated that the preparation of next year's programme of lectures was virtually completed.

Mr. McLean, the Hon. Education Officer for the Scottish Section, then indicated that despite repeated attempts by the Scottish Section to persuade the City and Guilds Examination Board to continue the Paint Technician Advanced Certificate, all efforts had failed due to lack of support.

The following members were elected to office for session 1968-69 :—

| | |
|---|---|
| Hon. Vice-President .. .. | Ian McCallum |
| Hon. Secretary .. .. | Raymond F. Hill |
| Hon. Publicity Officer .. | Morton Devine |

*Members of Committee*

Alistair McMaster
Alex McKenzie
John Dunlop
Jim Devine

There being no further business, the meeting was closed.

R.F.H.

# Association's 50th Anniversary Celebrations

Members are reminded that the closing date for receipt of applications for tickets for the various functions arranged for the 50th Anniversary Celebrations on 9-10 May will be **25 April.**

### Commemorative Dinner-Dance

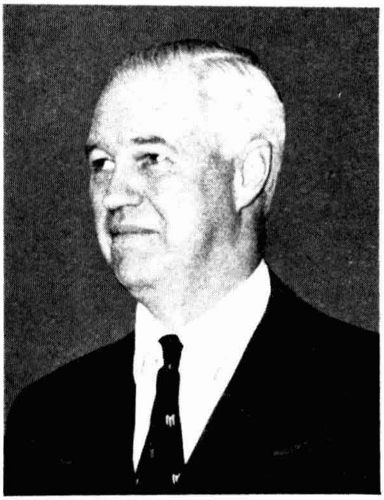
Already applications for the Dinner-Dance on 10 May have been very heavy. Applications can be accepted from members and non-members, and those wishing to attend should complete the form circulated on 1 January and return it as soon as possible. Further copies are obtainable from the Association's offices. Single tickets are priced at £3 13s. 6d. each.

### History and Register of Members

As already announced a copy of the History of the Association will be sent to all members early in May, and, at a meeting of Council on 28 February, it was further agreed to send to members a copy of the Register of Members, showing each member's name, with his present classification of membership, the Section to which he is attached and his current mailing address. Those attending the celebrations will be provided with a 24-page booklet showing various aspects of the growth of the Association, together with information in connection with the programme of events and places in which these are held.

### Commemorative Lecture and Dinner

Members are reminded that the Commemorative Foundation Lecture (instituted in 1963 in memory of the late H. A. Carwood, Esq., the first Hon. Secretary of the Association) will be given in the Court Room at the Painter Stainers' Hall, Little Trinity Lane, London, E.C.4, by Lord Todd, F.R.S., Chairman of the Advisory Council on Scientific Policy, 1952-64, Chairman of Royal Commission on Medical Education, Professor of Organic Chemistry at the University of Cambridge, and Master of Christ's College. The title he has chosen is "Science and Society." Admittance to the Lecture will be by ticket only and will be followed by a short reception. Dinner will be taken in the Dining Hall of the Painter Stainers' Company at 8 p.m. Informal dress will be worn.



**Lord Todd,** F.R.S.

The inclusive charge for the Dinner, together with wines and aperitifs at the reception, is £2 17s. 6d., and application should be made as soon as possible and in any case not later than 25 April.

Members who wish to attend the Lecture only should inform the Association's offices.

### Commemorative Service

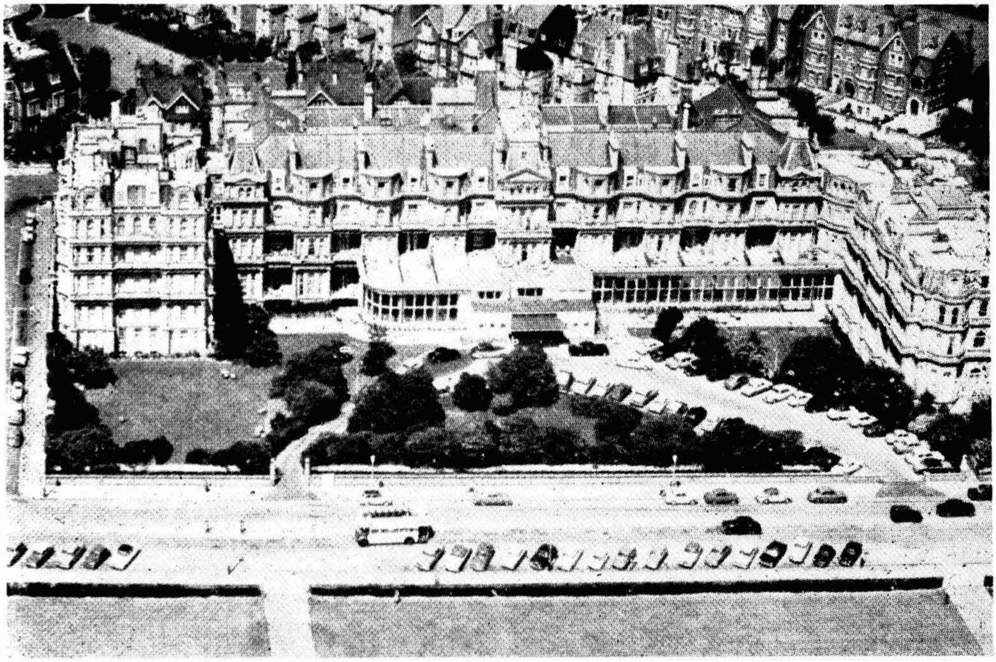
Places are still available for the Commemorative Service, to be held at 6 p.m. on 9 May at the Parish Church of

St. Vedast alias Foster. Members wishing to be present should write to the Association's offices.

**Receptions and Exhibition**

It will be recalled that two receptions will be held in conjunction with a small exhibition of Association activities at midday on 9 and 10 May. On Thursday 9 May the President and Council will welcome Founder Members, Past Presidents and Past Honorary Officers of the Association and Presidents of other societies, and on the following day they will be meeting the Press, together with the Presidents of other societies who were not able to attend on the previous day. Commemorative scrolls presented by other societies will be displayed at the Savoy Hotel on the occasion of the Dinner-Dance on 10 May.

# OCCA Biennial Conference



**The Grand Hotel, Eastbourne**

**17-21 June 1969**

The headquarters for the Eastbourne Conference will be in the Grand Hotel, shown above, where the majority of the delegates will be accommodated, and the Technical and Workshop Sessions and Official Functions held. The remainder of the delegates will stay at the nearby Burlington Hotel.

The theme of the Conference is to be " Film formation and curing," and it is hoped that four Technical Sessions and three Workshop Sessions will be held, as in 1967.

There will be a full social programme, including a Civic Reception on the Wednesday, and the Association's Dinner-Dance on the Friday evening. Trips to places of interest will be arranged, and there will be opportunities for delegates to take part in various sporting activities.

Details will be circulated to members early in 1969. Others wishing to receive details should write to the Director & Secretary at the Association's offices.

# Jordan Award

The Committee appointed by Council to consider the applications received for the Jordan Award met in February and, after long and careful consideration, decided that it was not possible to make the Award on this occasion.

It is intended, therefore, to invite further applications to be received in 1968, and the Committee will consider these early in 1969, with a view to making the Award at the Eastbourne Conference, which will be held 17-21 June 1969. The rules of the Award are appended below for the benefit of new members.

1. The Award will be made for the best contribution to the science or technology of surface coating by a member of any nationality working in either the academic or industrial field who is under the age of 35 at the date of application.
2. The final date for submission of applications will on this occasion be 1 January 1969.
3. The selection of the recipient of the Award will be made by a Committee under the Chairmanship of the Association's Hon. Research and Development Officer.
4. There will be two methods of application. First, by the submission of a paper describing original work by the candidate which is offered for publication in the *Journal* or has been so published during the two years prior to the closing date for application. The alternative method will be by recommendation by a superior for work which for reasons of commercial secrecy cannot be published ; in this case the candidate will be expected to submit a dissertation on a topic relating to his work and demonstrating his superior knowledge of the principles thereof. The Award is for *individual* merit and clear evidence of the candidate's own contribution will be required if a paper is offered under joint authorship.
5. Applications should be addressed to the Director & Secretary at the address shown on the front cover.

# Association Annual General Meeting

As members have already been informed, the Annual General Meeting of the Association for 1968 will be held in Bristol on 28 June. The programme will be as follows :

| | |
|---|---|
| Afternoon : | Coach Tour across the Severn Bridge to the Wye Valley. Tea will be provided. |
| 6.00 p.m. : | A film of the building of the Severn Bridge will be shown at the Royal Hotel, Bristol. |
| 7.00 p.m. : | AGM at the Royal Hotel, followed by the Dinner. |

Full details and application forms will be circulated with the Annual Report and the voting paper for the three elective members of Council, early in May.

Members are reminded that forms for nomination for the elective places were circulated on 1 January, and that the closing date will be 3 May.

# Scottish Section

**The Chairman of the Scottish Section, Mr. I. S. Hutchison (left), with Mrs. Hutchison, and the President, Mr. F. Sowerbutts (right), with Mrs. Sowerbutts, at the Scottish Section Dinner-Dance**

**Dinner Dance**

Following a custom originating as far back as January 1967, the menu for the Scottish Section Annual Dinner Dance was once again printed in the Gaelic. To the 240 members and guests who attended this function in the Kintyre Suite of the Central Hotel, Glasgow, on 12 January 1968, the problem of translating the Gaelic into edible courses added a definite Scotch piquancy to the early part of the meal.

In introducing the section's principal guest, the President, Mr. F. Sowerbutts, Mr. I. S. Hutchison, Chairman of the Scottish Section, referred in particular to the long and distinguished service that Mr. Sowerbutts had given to the association. Other principal guests were Mrs. F. Sowerbutts, Mr. and Mrs. C. H. Morris (Midland Section) and Mr. and Mrs. G. H. Hutchinson (Scottish Section, Eastern Branch). Unfortunately, due to a last-minute accident, Mr. and Mrs. L. W. Wynn (Hull Section) were unable to attend.

Mr. Hutchison also proposed the toast to " Our Guests " on behalf of the Scottish Section. In reply to the toast Mr. Sowerbutts stated that he did not wish to say again what had already been said by others about the Scottish Section, no doubt on several occasions. He felt that the activities of the section, particularly those of the juniors, spoke for themselves and he could only wish the section continuing success in this and other directions.

Again according to custom, the haggis was " piped in " by Pipe Major Lawrie of Glasgow Police Pipe Band and presentation made of a small haggis to each of the ladies among the principal guests.

To mark the departure of Mr. Arthur McGuire to take up an appointment south of the border, a presentation, on behalf of the section, of a set of crystal glasses and decanter, was made to him by Mr. I. Hutchison. In addition to holding a number of offices in the Scottish Section Committee, culminating in that of Hon. Programme Officer, Arthur had in his nine years with the section made himself one of the best-liked " characters " in it.

Shortly thereafter the informal part of

the evening was entered upon and it was immediately obvious that the section was going to " chalk up " another extremely successful evening. To prove that the Scots are " gluttons for punishment " Pipe Major Lawrie was kept busy and no doubt dry providing the music for the Eightsome Reel and other such energetic gyrations.

The evening was concluded with the singing of Auld Lang Syne and a vote of thanks to the organiser of the dinner dance, Mr. J. Miller.

# OCCA Australia

## Jubilee convention

Preliminary programme details for the 10th Oil and Colour Chemists' Association Australian Jubilee Convention have now been finalised.

*Venue :* Hotel Florida, Terrigal, New South Wales.

*Date :* 13-16 June 1968.

*Programme and Official Functions :*

*Thursday 13 June*

5.00 p.m. Registration of delegates.

7.00 p.m. Buffet Dinner.

*Friday 14 June*

9.15 a.m. Official Opening.

9.30 a.m. " Corrosion inhibiting properties of the polyamide-epoxy vehicle."

Author and Speaker H. Wittcoff, PH.D., A.B., Director, Chemical Research, Central Research Laboratories, General Mills Inc., USA.

11.00 a.m. " The use of acrylic polymers in the formulation of caulks and sealants."

Author and Speaker R. A. Wedemeyer, B.S., Sales Manager, Primal Chemicals Pty. Ltd., Australia.

2.00 p.m. " Further studies in heterogeneous polymerisation."

Author and Speaker A. E. Alexander, SC.D., PH.D., M.A., B.SC., F.A.A., Professor of Physical Chemistry, University of Sydney.

3.30 p.m. " New polymers for emulsion paint."

Author and Speaker A. C. Fletcher, B.SC., F.R.I.C., Technical Service Manager, Vinyl Products Ltd., UK.

*Saturday 15 June*

9.30 a.m. " Structure and properties of phthalocyanine pigments."

Author and Speaker H. Schroeder, DIP. PAINT TECH., Chief Technical Adviser—Paint and Printing Ink Industries, BASF AG, Germany.

11.00 a.m. " Organic pigments for automotive finishes."

Author and Speaker E. Chartrand, B.S., Technical Sales Manager, Harmon Colour Division, Allied Chemical Inc., USA.

2.00 p.m. " Paints, patents and the chemist."

Author and Speaker D. W. Berryman, B.TECH., Leader Patents and Information Section, Central Research Laboratory, BALM Paints Limited, Australia.

3.30 p.m. "National questions in Australian development."

Author and Speaker H. D. Black, M.EC., Senior Lecturer in Economics, University of Sydney.

6.30 p.m. Cocktails.

7.00 p.m. Jubilee Dinner.

Guest Speaker Mr. R. Y. Hillman, B.A., Assoc. Director, George Patterson Pty. Ltd., Australia.

*Registration Fee :* $A17.50.

*Accommodation :* Hotel Rates.

Application Forms are in April "Proceedings and News," or from State OCCAA Secretaries.

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**"Surface Coating Resin Index"**

The British Plastics Federation and the Surface Coating Synthetic Resin Manufacturers Association are currently preparing a revised edition of the *Surface Coating Resin Index*, which was last published in 1965.

All contributors to the last edition have been circularised for amendments and additions for the new *Index*, and any other British manufacturers of film forming polymers who wish to have their products included should contact the Editor :

Mr. J. Bridle,
Cray Valley Products Ltd.,
St. Mary Cray,
Kent.

The new *Index* is to be distributed widely overseas, in order to assist exports.

**New coatings symposium**

North Dakota State University is to hold its tenth Annual Symposium from 3 to 6 June 1968, with the title "New coatings and new coatings raw materials." The symposium will be held at the Fair Hills Resort, Pelican Lakes, Minnesota. Further details are available from :

Polymers and Coatings Department,
College of Chemistry and Physics,
North Dakota State University,
Fargo, North Dakota 58102.

**Detergent symposia**

The 59th Annual Spring Meeting of the American Oil Chemists' Society is to be composed of two symposia, one on trends in detergents and textiles and one on methodology and research in detergents, organised jointly with the American Association of Cereal Chemists.

Further details are available from the AOCS, 35 East Wacker Drive, Chicago, Illinois 60601.

**Alton E. Bailey Award**

The North Central Section of the American Oil Chemists' Society has named Dr. H. J. Dutton, of the USDA Northern Regional Research Laboratories, as winner of the Alton E. Bailey Award for 1968, for outstanding research in compositions, reactions and techniques in lipid chemistry.

## News of Members

Mr. N. Ashworth, Ordinary member and Committee Member of Manchester Section, has been appointed Chief Chemist, Leyland Paint & Varnish Co., Leyland, Lancs.

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Dr. A. Bowman, an Ordinary Member attached to the General Overseas Section, has been appointed a Director of British Titan Products Company Limited. Dr. Bowman will continue as President-Director-General of Tioxide SA, the Company's French subsidiary.

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Mr. H. A. Holden, an Ordinary Member attached to the London Section, has been appointed a Director of The Pyrene Company Limited.

Mr. G. A. Newell, an Ordinary Member attached to the London Section, has left his position as Chief Chemist at Thos. Hubbuck & Son Limited to join BIE (Anti-Corrosion) Ltd. Mr. Newell will act in a technical capacity with protective system selection and specification.

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Mr. W. A. Rutherford, an Ordinary Member attached to the Hull Section, and Chairman of the Section in 1950-52, has resigned his post as Regional Technical Adviser with Blundell-Permoglaze Limited.

For health reasons Mr. Rutherford is to take up residence in Tenerife in the Canary Islands, where he will become the British Technical Associate of The Canary International Import-Export Agency of Santa Cruz de Tenerife. As this agency handles Blundell-Permoglaze products in the Province of Tenerife, he will not be completely severing his 27-year-old connection with the paint industry.

**Mr. J. H. A. Quick**

Mr. J. A. Quick, Immediate Past Chairman of the Irish Section, has on retirement from Preston & Hadfields Ltd., Dublin, left Ireland to reside in Malaga. He joined Hadfields (Merton) Ltd. at their Mitcham Works in 1928, leaving in 1936 to take up the position of Production Manager in the Dublin factory, Preston & Hadfields Ltd., Rathfarnham. He later became Works Manager and joined the Board of Preston & Hadfields in 1962.

Although he had conveyed his intention of early retirement to his associates over a year ago, John Quick's departure from the paint industry and from Ireland leaves a real sense of loss amongst his colleagues and friends in Ireland. He intends to live in Spain, but his many friends in the Irish Section will be glad to know that he and Mrs. Quick hope to visit Dublin from time to time, where their younger son will continue to reside.

All members of the Irish Section wish John and Elsie the best of good health and fortune during their retirement.

# 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**

HENDERSON, DONALD STEWERT, 151 Orchard Park Avenue, Thornliebank, Glasgow. (*Scottish*)
LIFF, DENNIS, B.SC., A.R.I.C., Egham Industrial Chemicals Laboratory, Shell Research Ltd., Whitehall Lane, Egham, Surrey. (*London*)
ROBSON, GORDON REGINALD, B.SC., A.R.I.C., 71 Avondale Avenue, Hazel Grove, Stockport, Cheshire. (*Manchester*)
TURNER, KENNETH GEORGE, B.SC., 65 Rockdale Avenue, Westville, Natal, South Africa. (*South African*)
WALLINGTON, RAYMOND HENRY, B.SC., 8 Stratford Avenue, Hillingdon, Uxbridge, Middlesex. (*London*)
WATSON, ROBIN JOHN MONRO, Horse Heath Cottage, Leyhill Common, Nr. Chesham, Buckinghamshire. (*London*)

**Associate Members**

GILES, RONALD KEITH, Flat 1, 80 Hutchinson Avenue, New Lynn, Auckland, New Zealand. (*Auckland*)
MAGEE, PATRICIA ANN, " Cabra Villa," Cabra Road, Phibsborough, Dublin, 7. (*Irish*)
PERRY, ANTHONY, Hoechst Cassella Dyestuffs Ltd., 1 The Gatehouse, Lemyngton Street, Loughborough, Leicestershire. (*Midlands*)
WILLIAMS, STANLEY ERROL, Dow Chemical Africa (Pty) Ltd., PO Box 9170, Johannesburg, South Africa. (*South African*)

**Junior Members**

EASTWOOD, PETER KILBURN, 54 Bennett Lane, Dewsbury, Yorkshire. (*West Riding*)
GIBB, SAMUEL, 437 Carmunnock Road, Glasgow, S.5. (*Scottish*)
McKAY, DAVID MICHAEL, Quentsplass Limited, Thorp Arch, Trading Estate, Boston Spa, Yorkshire. (*West Riding*)
NICOL, ALEXANDER B., 74 Quarrywood Road, Barmulloch, Glasgow, N.1. (*Scottish*)

# 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.***

**Tuesday 2 April**

*Hull Section.* Annual General Meeting, to be held at the Queens Hotel, George Street, Hull, at 7 p.m.

**Wednesday 3 April**

*Manchester Section—Junior Members.* " Organic Pigments for Paint," by Mr. G. T. Williams (Geigy (UK) Ltd.), to be held at the Manchester Literary and Philosophical Society, at 4 p.m.

**Thursday 4 April**

*Midlands Section—Trent Valley Branch.* Annual General Meeting, to be held at the British Rail School of Transport, London Road, Derby, at 7 p.m., followed by a social evening for members and their ladies.

*Newcastle Section.* Annual General Meeting.

*Hull Section.* Symposium—" Industrialised Building : Surface Coating Problems," to be held at the Department of Chemistry, The University, Hull, 9.30 a.m. to 4.30 p.m.

**Friday 5 April**

*Irish Section.* " Wallpaper Manufacture," by Mr. S. K. Weir and Mr. M. Burke, preceded by the Annual General Meeting, to be held at the Clarence Hotel, Dublin, at 7.30 p.m.

*Scottish Section.* Annual General Meeting, to be held at the Lorne Hotel, Glasgow, followed by the annual " smoker," to be held in the Eglinton Arms Hotel, Eaglesham.

**Monday 8 April**

*London Section—Southern Branch.* Annual General Meeting.

**Tuesday 9 April**

*Thames Valley Section.* Annual General Meeting, to be held at the Royal White Hart Hotel, Beaconsfield, Buckinghamshire, at 7 p.m.

*West Riding Section.* Annual General Meeting.

**Thursday 18 April**

*London Section.* Annual General Meeting at the Criterion-in-Piccadilly, London, W.1, at 6.30 p.m.

*Manchester Section.* Annual General Meeting at the Lancashire County Cricket Club, Old Trafford, at 6.30 p.m.

**Wednesday 24 April**

*Scottish Section—Eastern Branch.* Joint Lecture with Society of Dyers and Colourists. Subject to be decided, to be held at The ICI Recreation Hall, Grangemouth.

**Friday 26 April**

*Bristol Section.* Annual General Meeting.

*Midlands Section.* Annual General Meeting, to be held at the Winston Restaurant, Balsall Heath Road, at 7 p.m., followed by a social evening.

**Saturday 27 April**

*Scottish Section.* Annual Golf Outing at Aberdour, at 2 p.m.

**Friday 3 May**

*West Riding Section.* Luncheon Lecture at Astoria Restaurant, Roundhay, Leeds.

Please note that the Manchester Section AGM will now be held on Thursday 18 April and not Friday 19 April as shown in the March issue of the *Journal.*

# 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 1923 it absorbed the Paint and Varnish Society. The stated purpose of the Association is to promote by discussion and scientific investigation the technology of the industries concerned with the above-mentioned products, and to afford members opportunity for the interchange of ideas. This is achieved by the regular holding of ordinary meetings at which papers are presented, and the organisation of annual technical exhibitions, biennial conferences, educational activities and practical co-operative experimental work. Details of these activities are given in the *Journal of the Oil and Colour Chemists' Association*, which is published monthly, and whose pages are open to receive communications and other pronouncements on scientific and technical matters affecting the members of the Association and the industries concerned. The Association's meetings also afford opportunities for members to meet informally and socially.

There are Sections of OCCA in Auckland, Bristol, 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).

Ordinary Membership is granted to scientifically trained persons, and Associate Membership to others interested in the industries covered. Junior Membership, which is intended primarily for students, is open without restriction to persons under the age of 21 and to those up to 25 who are following a course of technical study. The annual subscription in each case is five guineas, except for Junior 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 editions this year.
Part 2 : " Solvents, Oils, Resins and Driers" }
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.

Director & Secretary : R. H. Hamblin, M.A., F.C.I.S., F.C.C.S., Wax Chandlers' Hall,
Gresham Street, London, E.C.2.

## CLASSIFIED ADVERTISEMENTS

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 General Secretary, Oil & Colour Chemists' Association, Wax Chandlers' Hall, Gresham Street, London, E.C.2. Telephone: Monarch 1439

### SITUATIONS VACANT

# OIL TECHNICIAN

Laporte Industries Ltd., Organics & Pigments Division, requires an Oil Technician to work in the Technical Department at its Fullers' Earth Works, Redhill, Surrey.

The work involves the analysis and testing of a wide variety of vetegable oils from all over the world and also investigation of refining problems.

The successful candidate will be aged 22 - 39 and have either ONC or 3 ' A ' levels including chemistry and two from maths, physics or English. He will have spent at least two years in an oil refinery laboratory, carrying out routine tests on vegetable oils e.g. ffa, iodine value, peroxide, Lovibond colour etc.

Salary according to age and experience. Day-release facilities. Active Sports & Social Club. Non-contributory Pension-Scheme.

Applications giving brief details of experience, qualifications, age and present salary, should be sent to the

**Personnel Manager,**
**LAPORTE INDUSTRIES LIMITED,**
**Fullers' Earth Works,**
**Redhill, Surrey.**

LAPORTE

# OCCA BIENNIAL CONFERENCE

**17-21 June 1969 at the**

**Grand Hotel, Eastbourne**

## BRITISH INDUSTRIAL PLASTICS LTD.

(A Turner & Newall Company)

## Technical Service Representative
## Surface Coating Resins

B.I.P. Chemicals Ltd., Oldbury, have a vacancy for a Technical Service Representative to promote the sale of Surface Coating Resins. Applicants should have a sound technical knowledge of the paint industry and, in particular, the field of industrial stoving finishes. Training will be arranged at the Company's Laboratories at Oldbury. The Company offers excellent conditions of employment including a contributory Pension and Life Assurance Scheme. A Company car will be provided. Application should be made in writing, giving full details of age, experience and other relevant information, to the Personnel Manager,

**B.I.P. Chemicals Ltd., Popes Lane, Oldbury, P.O. Box No. 6, Warley, Worcs.**

BIP

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### BLUNDELL-PERMOGLAZE LIMITED
### LABORATORY STAFF

Applicants are invited for the following positions :

GROUP LEADER with experience in water-based finishes. This is a senior position and requires a paint chemist/technologist of wide experience, capable of planning development projects and controlling staff.

SECTION LEADER to work in a group engaged in development work on general decorative paints.

If you are interested in joining a company where staff at all levels are encouraged to use initiative, and put forward their own ideas, please apply in writing to :

**The Chief Chemist (decorative division),**
**Blundell-Permoglaze Limited,**
**Sculcoates Lane,**
**Hull.**

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### DEVELOPMENT CHEMIST

**Berger J & N Paints Limited**

require a qualified PAINT TECHNOLOGIST for their DECORATIVE LABORATORY

The work is concerned with the development of new and improved coatings and applicants should preferably have experience in this field. Prospects of early promotion are excellent and appropriate training will be given.

PREFERRED AGE : About 25

QUALIFICATIONS : B.Sc., A.R.I.C. or equivalent.

Salary and working conditions in modern laboratories are good.

Please apply giving details of age, qualifications and experience to :—

Staff Personnel Officer
Berger J & N Paints Limited,
Freshwater Road,
Dagenham, Essex.

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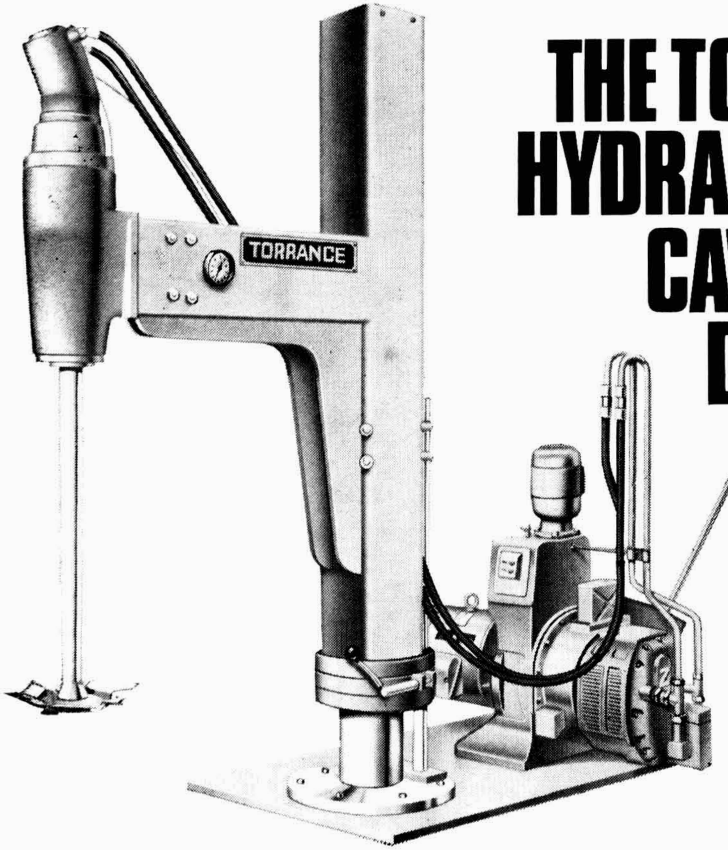
## FIFTIETH ANNIVERSARY CELEBRATIONS DINNER

**10 May 1968 at the**
**Savoy Hotel, London, W.C.2**


TORRANCE