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Papers from the South African Symposium

The design of resins for electrodeposition

H. R. Crawford

Equipment aspects and quality control of electro-painting plants

R. L. Nicolay

Developments in marine paints

K. S. Ford

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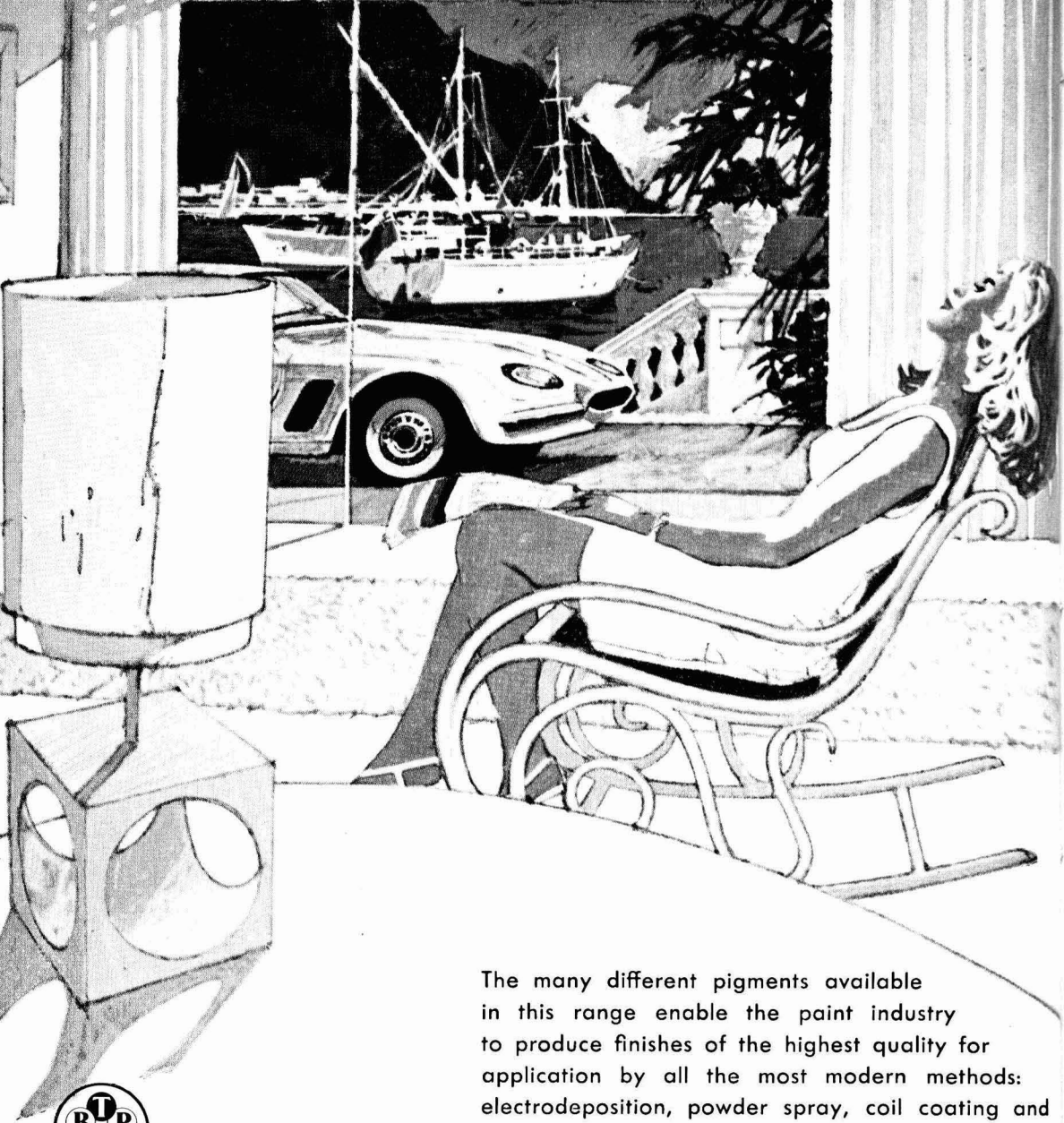
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JOURNAL OF THE OIL & COLOUR CHEMISTS' ASSOCIATION

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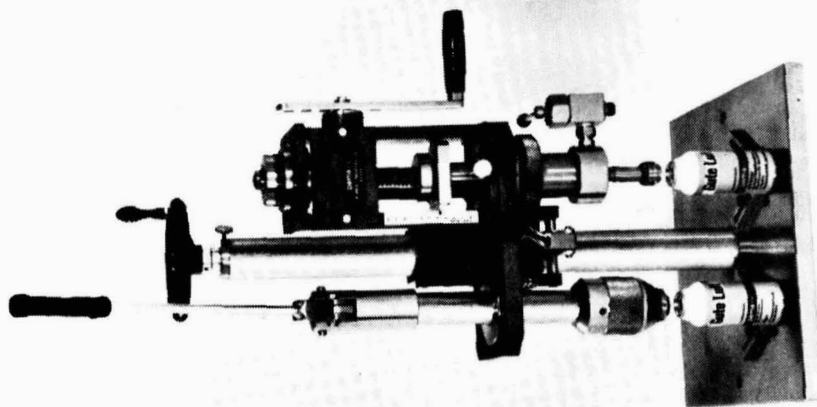
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Transactions and Communications

The design of resins for electrodeposition*

By H. R. Crawford

Cray Valley Products (SA) Pty. Ltd., PO Box 211, Mobeni, Natal

Summary

Although electrodeposition techniques of application offer many advantages, problems may be posed for the resin supplier. It is important that details of the application process are decided beforehand, and the choice of resin made with reference to four resin parameters: polarisation, throwing power, coulombic efficiency and stability.

Although most development work has been into water soluble resins, emulsion types may be of use where high build is required; the main advantages and disadvantages of both types are discussed.

Future developments in electrodeposition are outlined, including gloss finishes and deposition on to substrates other than phosphate pretreated steel, and the possibilities of cathodic deposition processes.

Keywords

Processes and methods primarily associated with application
electropainting

Resins, binders etc.
thermoplastic resin

La création des résines destinées pour être appliquées par électrodéposition

Résumé

Bien que les techniques de l'électrodéposition possèdent beaucoup d'avantages, en même temps elles posent des problèmes au fournisseur de résines. Il est important que les détails du moyens d'application sont établis au début et que l'on base la choix de la résine sur quatre paramètres: polarisation, pouvoir de projection, rendement coulombique, et stabilité.

Bien que la plupart des études de développement se soient confinées aux résines solubles dans l'eau, les types émulsionnés peuvent offrir des possibilités dans le cas où il faut les couches épaisses. On discute les avantages et les inconvénients de tous les deux types.

On trace les grandes lignes des développements à l'avenir dans le domaine de l'électrodéposition, citons, les finitions brillantes et la déposition de peintures sur des subjectiles autres que l'acier traité au phosphate, et enfin les possibilités des processus de déposition sur la cathode.

Der Entwurf eines für Elektrophorese Geeigneten Harzes

Zusammenfassung

Die Anwendung von Elektrotacklackierungsmethoden bietet viele Vorteile, dem Harzlieferanten können sie allerdings viele Probleme stellen. Wichtig ist, dass die Einzelheiten des Verfahrens zuvor entschieden werden, und die Auswahl des Harzes unter Bezugnahme auf vier Parameter getroffen wird:

Polarisation, Umgriff, Coulomb-Nutzeffekt und Stabilität.

Entwicklungsarbeiten wurden hauptsächlich auf dem Gebiete wasserlöslicher Harze vorgenommen, wenn aber Dickschichtung verlangt wird, können Emulsionstyps von Nutzen sein; die wesentlichen Vor- und Nachteile beider Typs werden besprochen.

*Presented at the Third National Convention of the South African Section, held 11-13 September 1970 at Winterton, Natal.

Künftige Entwicklungen auf dem Gebiete der Elektrotauchlackierung werden skizziert, einschliesslich der von Glanzlackierungen und Niederschlag auf andere Substrate als phosphatisiertes Eisen, und ausserdem werden die Möglichkeiten kathodischer Elektrotauchverfahren besprochen.

Формуляция смол для электролитического осаждения

Резюме

Хотя технология применения электролитического осаждения включает в себе ряд преимуществ, она все же предъявляет трудности для поставщика смол. Важно чтобы детали применяемого процесса решались заранее и чтобы выбор смолы делался учитывающая следующие четыре параметра смолы: поляризацию, рассеивающую способность, кулоновскую продуктивность и устойчивость.

Хотя большинство исследовательских работ производилось с водорастворимыми смолами, эмульсионные типы могут оказаться пригодными, когда требуется высокая плотность. Обсуждаются основные преимущества и недостатки обоих типов.

Обзревается будущее развитие в области электролитического осаждения, включая гляцевитые отделки, осаждения в субстратах различных от стали предварительно обработанной фосфатом, и возможности катодных процессов осаждения.

Introduction

The electrophoretic deposition (electrodeposition) of resins was pioneered in the United Kingdom in the 1930's by Crosse & Blackwell Ltd., who in 1936 were granted a patent for the internal lacquering of food containers¹. The heavy duty hot dipped tinplate used in that period to fabricate foodcans had good exterior corrosion resistance, but sulphur staining of the interior surfaces was a major problem with certain foodstuffs. Crosse & Blackwell devised a system whereby drying oil varnishes emulsified in water, using ammonia as the stabilising base, were deposited at high current densities for very short deposition times—three to ten seconds. Electrodeposition of rubber from latices for the manufacture of rubber gloves was also reported, both for deposition on specially shaped articles² and also as a method of concentrating rubber latex in the vicinity of a semipermeable membrane without actual coagulation³. These early applications, however, did not progress to pigmented paint systems and it was not until considerably more work on water dilutable and water dispersible resins for use as film formers had been carried out that the process was taken further. Some time in the 1950's, teams working independently in the UK and USA both saw the potential of the electrodeposition process, particularly for improvements in the painting of automobiles and their components. In America the Ford Motor Company, in conjunction with several leading paint companies, carried out a considerable amount of research and development on new resins systems, which would deposit electrophoretically in pigmented form, and would give paints with superior performance to those applied by existing methods of application. The success of this work led to the first electrodeposition of primers on car body shells in the early 1960's⁴. In this development work, new resins systems were devised to meet the demands of this innovation in paint application. The British development which was carried out jointly by ICI Ltd. and Pressed Steel has been described⁵. In this work advantage was taken not only of new types of resin but also included the use of resins which had already been developed for application by conventional dipping and spraying techniques. Since these early developments, the process has progressed rapidly, a diversity

of articles on the subject have been published, and a bibliography of articles and patents has been produced^{6, 7}.

Resin design

Advantages of the process

Before considering the factors affecting resin requirements, it is necessary to establish why electrodeposition should be preferred to any other coating methods, and what parameters should be met in resin development, since far more emphasis will be based on the electrical characteristics of the resins, and less on the traditional features of solvent type and content, acid value, and viscosity, etc., except in so far as they affect electrical performance.

Electrodeposition is a dipping process, in which the article to be coated, on immersion in the paint, is made one of the electrodes in an electric cell and current is passed between this and other electrodes, causing a coating to be deposited. The paint in the dip tank is usually a low solids, low viscosity, aqueous system, whereas the deposited film has a high solids content, high viscosity and is relatively insoluble in the surrounding medium. The following advantages can be gained from using such a process:

Good control of film thickness, since the weight of paint deposited is in direct ratio to the quantity of electricity passed.

Even deposition can be expected on edges and surfaces, since the main criterion for deposition is a surface of good electrical conductivity, and the shape of the article does not materially affect the amount of resin deposited, unless certain surfaces are shielded from the oppositely charged electrodes.

The bath is maintained at low solids, and therefore the amount of paint lost through "drag out" is minimal, giving efficient paint utilisation.

The deposited film is at high solids content, so "flash off" times before stoving may be significantly reduced.

Resin structure

From these advantages it is possible to decide on the electrical properties required by the resin system in order to obtain optimum results. The thickness of film deposited being directly proportional to the quantity of electricity passed shows that measurement of the coulombic yield will give a comparison of film thicknesses obtained with different resin types.

Since an advantage is shown by the ability to coat internal surfaces, then a measure of throwing power is necessary. The throwing power of a resin is its ability to deposit on surfaces remote from or shielded from the oppositely charged electrodes. Although throwing power is easy to demonstrate, it is difficult to define in terms of electrical characteristics. The hypothesis put forward by Tawn and Berry⁸ seems basically sound; this lays down the essential property of high conductivity and the relationship of throwing power to the rate of change of film resistance with film thickness, which is itself a function of time. In order to obtain satisfactory working in large dip tanks containing resin solutions or dispersions at low solids, good stability at these low resin concentrations is a necessity. Under the heading of stability, two types must be considered:

static stability—stability of the system at low solids;
turnover stability—the ability of this low solids system to withstand the electrical conditions imposed upon it, and also the intermittent replenishment of paint removed by deposition.

An additional feature which it is important to measure and which is allied to coulombic yield is the polarisation, since this will give an indication both of the efficiency of deposition and also the rate of build-up of film resistance.

In any resin development, it is therefore desirable to examine four basic properties; polarisation, coulombic yield, throwing power and stability.

Examination of basic parameters

In looking at these four basic properties, there are two approaches to be considered. The first is to take a single resin and to examine the effect of variations in the environment on the basic parameters. The second is to examine the effect of variations in a resin type on these same properties. In the development work already carried out, it has been seen that, once the effect of environment has been considered, certain trends may be taken as general and will therefore assist in explaining some of the differences which occur with varying resin types.

The effect of environmental conditions on a water thinnable alkyd phenolic complex Resydrol P411 will be considered. In this work, variations in resin concentration, pH, temperature, neutralising base and solvent type and content are examined.

Polarisation: Two types of polarisation are considered, the first is the rate of change of voltage at constant current deposition, the second the rate of

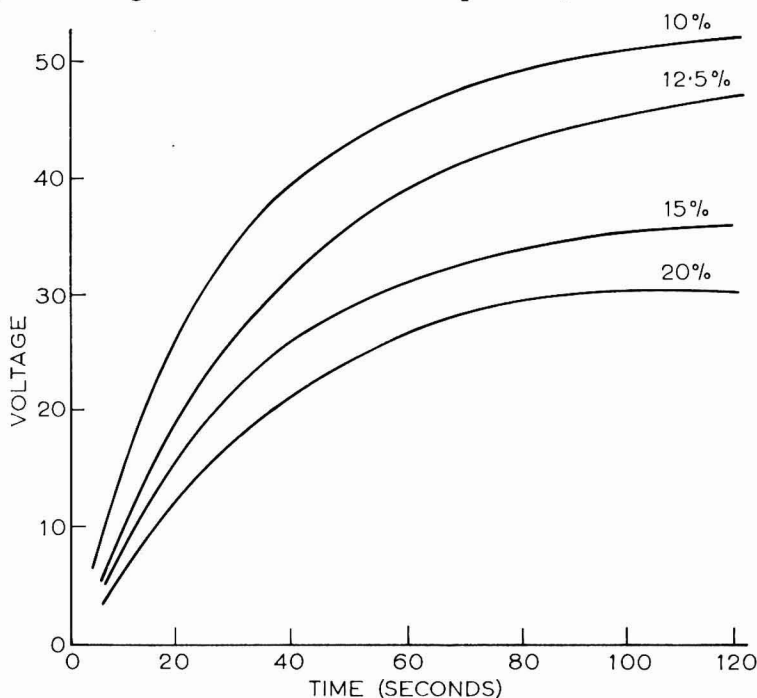


Fig. 1. Effect of resin concentration on polarisation

change of current at constant voltage deposition. Fig. 1 shows the constant current deposition at 2 milliamps per square centimetre for 120 seconds. This graph shows that, as the solids is reduced, the polarisation becomes better, which indicates that the film resistance is higher at lower solids, but coulombic yield will be reduced.

Table 1
Effect of pH on coulomb yield

pH		Coulomb yield (mg q ⁻¹)	
Resin concentration		Resin concentration	
10%	15%	10%	15%
7.20	7.20	9.55	9.34
7.45	7.40	8.50	8.39
7.60	7.60	7.73	7.01
7.80	7.85	6.39	6.02
8.10	8.10	5.27	4.77
8.30	8.35	4.22	3.58
8.55	8.50	3.55	2.94

Constant voltage depositions confirm this effect and the measured film thicknesses at constant voltage deposition of 50 volts for one minute show that the film thickness can be halved while reducing the resin solids from 15 to 12 per cent. Variation of pH at constant resin solids shows that, as the pH is reduced, so the polarisation is improved and Table 1 shows the effect of pH on deposition efficiency.

The effect of temperature on polarisation shows that, over the normal range of working temperatures, polarisation is reduced as the temperature increases. Although the change in coulombic yield is not very great, this is almost certainly due to the effect of the temperature on bath conductivity (Fig. 2).

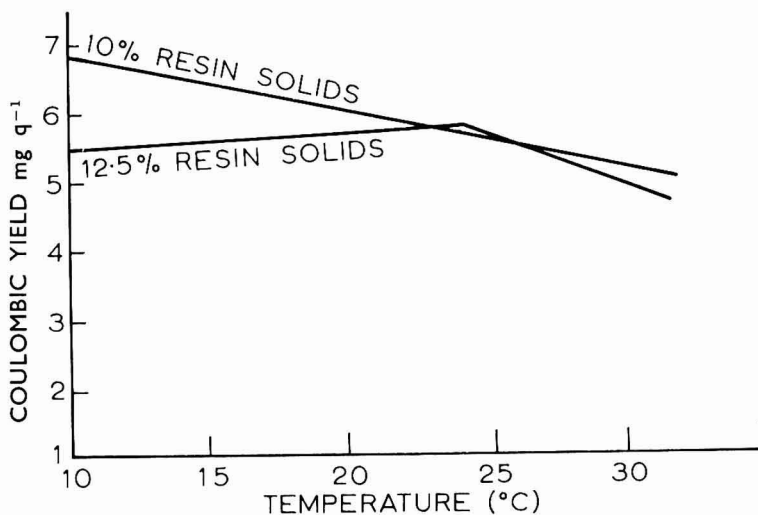


Fig. 2. Effect of temperature on coulombic yield. Deposition at 4mA cm⁻² for 240 seconds

Specific conductivity or its reciprocal, specific resistance, is an important factor in many resin systems, and in addition to being affected by temperature, it can also be changed materially by choice of neutralising base. Figs. 3 and 4 show the change of specific resistance with resin concentration for two types

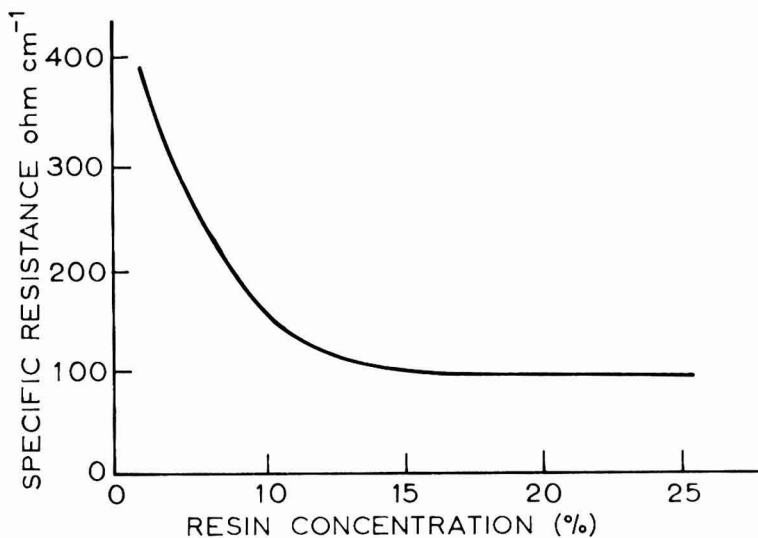


Fig. 3. Effect of resin concentration on bath resistance using ammonia as neutralising base

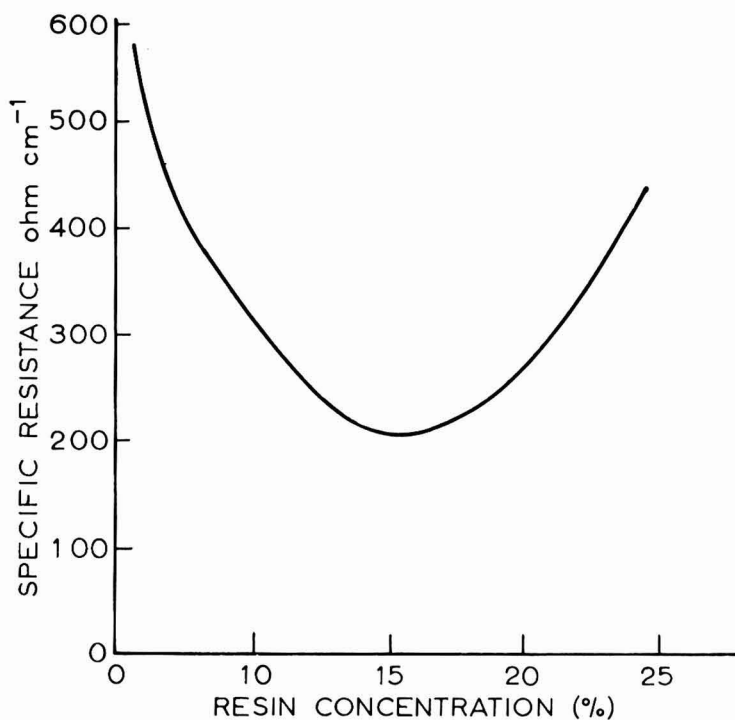


Fig. 4. Effect of resin concentration on bath resistance using triethylamine as neutralising base

of base—ammonia, and triethylamine. It can be seen that their effects are somewhat different, and that the solids range required to obtain optimum deposition conditions with triethylamine, all other effects being ignored, is much smaller than with ammonia.

Solvent content and type can have a large effect on polarisation, and Fig. 5 shows the film resistance curves obtained after the addition of a number of different solvents. From this work, it can be seen that the ethyl ether of ethylene glycol has least effect on polarisation, and from this property alone it should be a valuable solvent in resins designed for the electrodeposition process. Most of the other water miscible solvents cause a serious fall-off in film resistance.

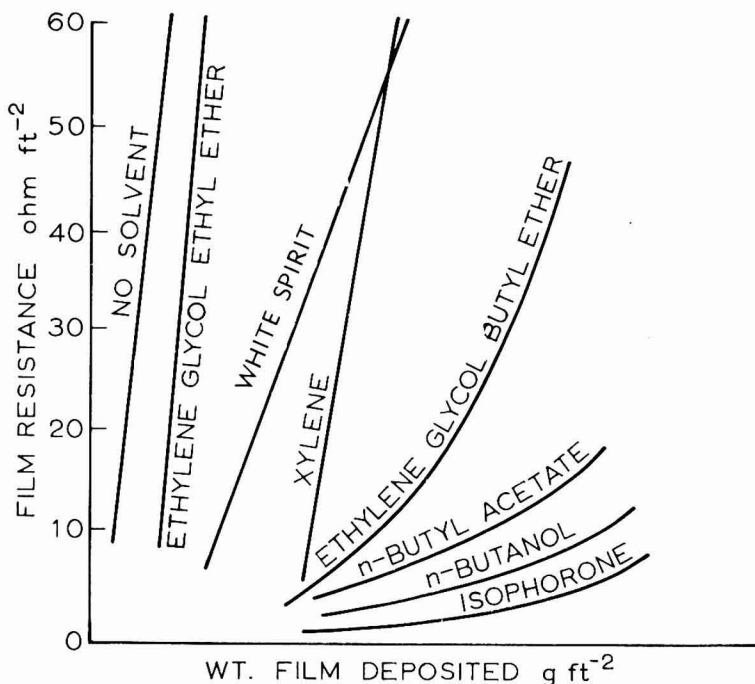


Fig. 5. Effect of 5 per cent added solvent on film resistance of maleined linseed oil

Throwing power: In order to obtain the best throwing power, it has already been seen that it is necessary to obtain a high film resistance and a high bath conductivity. The high bath conductivity can obviously be obtained with the strongest bases, and inorganic bases, such as sodium and potassium hydroxide, will be extremely useful in this respect, but care must be taken that sodium and potassium salts are not retained in the final film, since these could lead to a decrease in film performance, particularly water and corrosion resistance. Next to these inorganic bases, ammonia gives higher conductivity than most of the organic amines and is the preferred base where good throwing power is required; there is also no danger of these volatile bases being retained in the final stoved film.

In order to obtain maximum throwing power, many workers have aimed at deposition at high voltages in order to obtain the high film resistance necessary

to give good throwing power. However, Tawn and Berry⁸ have shown that throwing power is a dynamic function, and film thickness requirements can drastically alter the electrical characteristics necessary to obtain good throwing power. They were able to show that at very low film thicknesses high current densities are preferable for throwing power, but as the film thickness required is increased the converse becomes true. Fig. 6 illustrates this.

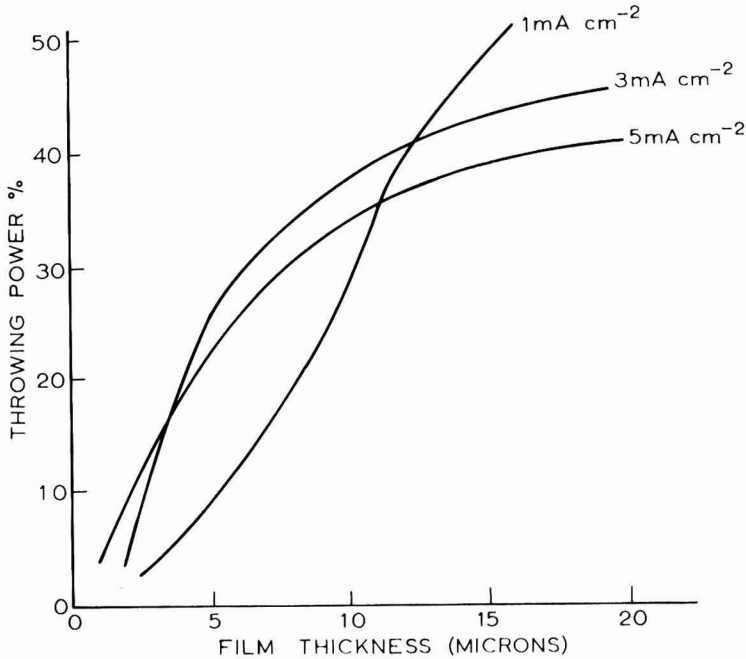


Fig. 6. Effect of current density on throwing power

From the previous section, it can be seen that good polarisation and good film resistance are obtained at reasonably low solids, low pH and moderate temperatures, and these effects should be borne in mind when designing resins for use in applications where throwing power is of prime importance.

Coulombic efficiency: Since Faraday's laws apply only to primary electrode reactions, the quantity of resin deposited for every coulomb of electricity passed is defined as coulombic efficiency or coulombic yield, rather than by the electrochemical equivalent, and is simply the number of milligrams of resin solids deposited per coulomb under standard conditions of measurement. The factors affecting polarisation will also have a similar effect on coulombic yield, and figures shown in Table 1 are relevant. The measurement of coulombic yield is, of course, liable to considerable error if care is not taken in the technique employed. The normal procedure when depositing resin solutions is to remove the deposited film from the dip tank after the specified time, and wash off the dip coat with water before drying the film in order to measure the weight of resin deposited. When working at high pH's, there is considerable danger that, if there is a delay in washing off the dip coat, redissolution of the deposited film will occur owing to the relatively high pH of the dip film, and much lower

apparent coulombic yields are obtained. Fig. 7 shows the rate of redissolution of deposited films at pH 8.5.

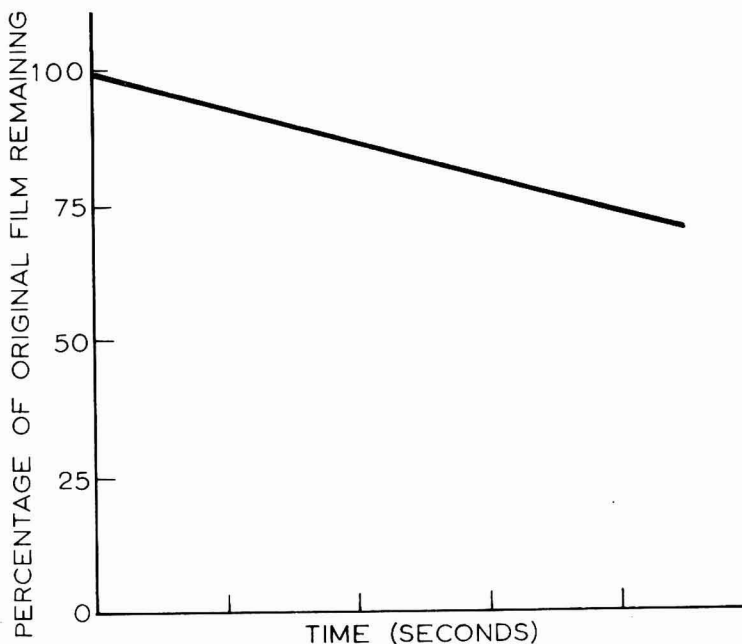


Fig. 7. Rate of redissolution of deposited film

Stability: With Resydrol P411, static stability tests show that below pH 7.6 the resin rapidly loses solubility in water, the effect being accelerated as the solids content is reduced. If satisfactory pH/resin concentration conditions are maintained, the turnover stability is excellent, no significant changes in electrical characteristics being noticed after 20 turnovers.

Variation in resin type

As stated in the introduction, the earliest resins used in the electrodeposition process were oleoresinous materials emulsified in water using ammonia as stabiliser. These were followed by rubber latices, shellac emulsions and bitumen emulsions. Advances in emulsion polymerisation techniques made available polyvinyl acetate, polyvinyl chloride, copolymers of these two materials, styrene-butadiene copolymers and many more high molecular weight polymers in emulsion form. The development of water soluble or water thinnable polymers posed somewhat greater problems, since their use tends to involve conflicting principles: the molecular weight of the polymer must be high enough for it to have good film forming properties and film performances, but if the molecular weight is too high then solubility in water will be poor, and the polymer solution will have a very high viscosity. This high viscosity is of far less significance in electrodeposition than in other applications but the basic research work on this type of resin was carried out prior to the advent of electrodeposition. Although water solubility is required for the polymer, it is necessary for the resin to be insoluble in water after application.

Many approaches have been made towards obtaining water soluble polymers, and Table 2 lists the most common types. Most of these suffer from the defect that either they are not of themselves good film formers, or else they do not develop water insolubility after application. With the useful resins, high molecular weight and water insolubility is usually developed by some form of cross-linking mechanism, such as oxidation at ambient temperatures or, more commonly, reaction on stoving at temperatures between 120 and 180°C.

Table 2

Water soluble polymers

Polyacrylic acids
Polyvinyl alcohols
Modified celluloses, e.g. Hydroxyl ethyl cellulose Carboxyl methyl cellulose
Styrene/maleic anhydride copolymers
Styrene/acrylamide copolymers
Poly (ethylene oxide)
Styrene/acrylate/hydroxy acrylate copolymers
Polyesters
Modified alkyd resins
Polyester allyl ethers
Styrene/allyl alcohol copolymers reacted with fatty acids
Phenolic and melamine formaldehyde condensates

The electrodeposition process does give the formulator both additional assistance and additional problems, since there is a possibility of electrode reactions taking place which may alter the characteristics of the resin.

Most of the resins used in the electrodeposition process are based on unsaturated fatty acids or drying oils and many are polycarboxylic acids.

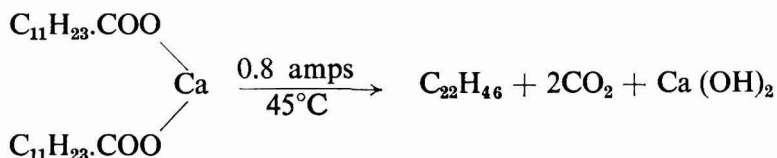
The unsaturated acids or drying oils contain vinyl double bonds which could polymerise in the presence of free radicals. Some authors have mentioned this reaction's taking place, and even proposed that films applied by electrodeposition are harder because of it¹⁰. There has been no conclusive proof to date of the occurrence of vinyl polymerisation during the deposition process, although some resin systems have been developed which, from their structure, appear to have no mechanism for self curing and show poor film properties on conventional application, but when applied at high current densities give demonstrably better film performance, indicating that the application method has contributed to the curing mechanism.

Polycarboxylic acids can suffer decarboxylation during deposition.

In 1849 Kolbé discovered a hydrocarbon synthesis which consisted of the electrolysis of an aqueous solution of an organic acid salt. Electrolysis of a solution of sodium acetate yields ethane:



Another example of this reaction is the electrolysis of calcium laurate to form n-Docosane¹¹:



Other reactions of this type are also known to occur, particularly the Crum-Brown and Walker synthesis of dicarboxylic acids and the Hofer-Moest reaction. A survey of these reactions has been made by Fichter¹². If these reactions do take place, then carbon dioxide will be liberated at the anode. Analysis of the gases liberated at the anode during electrodeposition of a paint based on a polycarboxylic acid showed that carbon dioxide was in fact liberated¹³. However, the paint was not degassed before the experiment was carried out, so the results were not conclusive. Another method of checking whether decarboxylation had taken place would be measurement of acid value, which should show a lower value for the deposited film compared with that of the unneutralised resin prior to deposition. It has been shown that some loss of acid value can be measured¹⁴ although the results of Tawn and Berry suggest fractionation of the component species of the resin during deposition rather than decarboxylation.

It is felt that, although vinyl polymerisation could be a significant factor, decarboxylation does not occur to any extent under present application conditions, but may become more significant if high current densities are used in an attempt to improve throwing power.

Therefore, two basic types of polymer can be considered for use in the electrodeposition process: the emulsion or dispersed system and the water soluble or water thinnable system. The advantages and disadvantages of each type will be considered.

Emulsion types: Returning to the basic parameters, it can be shown generally that emulsions have poor polarisation, low film resistance and, as a consequence, virtually no throwing power. The stability of emulsion types will, of course, vary considerably with the type of polymer in question and no general conclusion can be drawn. It can be seen from the above that emulsion systems are to be preferred where high build is required, and where throwing power is not a prerequisite. If two electrodes are placed face to face and current passed, good deposition will occur on the opposing faces, but virtually no deposition will occur on the side of the anode which is remote from the cathode. One of the problems with low solids emulsion systems which have been pigmented is that, when replenishing the paint which has been removed from the bath by deposition, difficulties can arise because of flocculation or even breakdown of the emulsion if the "let down" procedure is not controlled extremely carefully. This, in itself, may be no problem if the plant is designed for this type of procedure, but it can affect the general use of emulsion systems.

A novel application of electrodeposition of emulsions has been described by Hill and Cronberger¹⁵, where the technique is used to apply bituminous coatings to the exterior well casings, in situ, in the ground. Coatings ranging from

$\frac{1}{16}$ in to $\frac{1}{4}$ in may be obtained, depending on the conductivity of the adjacent soil.

Water soluble types: Since the major use for this type of process was considered to be coatings on articles which by their shape were difficult to coat by other methods, the preponderance of development work has been on solution rather than on emulsion types, since there are many other methods which will allow for a high build to be obtained on flat surfaces.

The types of resin which have been developed have generally been aimed at obtaining optimum throwing power at a level of build sufficient to give good protection. In this respect, throwing power requirements are contrary to those for good film build to obtain the best protection, and it has been necessary to choose polymer types which give inherently good protection even at low film thicknesses in order to ensure that satisfactory throwing power can be achieved. One way around this is to use water thinnable rather than water soluble systems. The distinction here is that the resin at low solids is neither a true solution nor an emulsion, and by using this system at pH's around 7.0 it is possible to get slightly higher build, whilst maintaining the throwing power requirements.

Most of the resins currently used in the electrodeposition process on a large scale are either modified maleinised oils, modified alkyds or epoxy esters. Since the process is limited to one-coat applications, the design of resins for decorative as well as protective finishes has been seen to be a worthwhile requirement. However, there are certain limitations in the design of resins for this purpose and there has not been the success in this field that there has with primers. A number of resins have been developed for one-coat finishes and these are predominantly modified alkyds or thermosetting acrylic resins, where the accent is more on build and flow, so as to get good build, gloss and appearance in one coat, than on a high throwing power. Here the throwing power requirements are not as stringent as for car body shells, so that solvents may be used to improve build and flow. (See Fig. 5.)

Future developments

Although the process has been operating on a commercial scale for about the last decade, there are still considerable developments taking place in the field of electrodeposition. At present the primer field has been most fully investigated owing to the large volume demand of the motor car and allied industries. The basic design of resins has been aimed at obtaining sufficient corrosion resistance and adequate throwing power. In general, the substrate for this type of work is either zinc phosphate or iron phosphate arising from pretreatment of steel.

In the field of gloss finishes, there is more of a problem in that the resin must deposit on a wider variety of substrates, including phosphated steel, aluminium and Mazak. Deposition on copper, brass and alloys is also of interest, but work done so far has failed to overcome the discoloration which occurs owing to reaction between the copper ions and the neutralising base. One problem which is still difficult to overcome completely with one-coat finishes applied by electrodeposition is that of secondary flow. The ability of the electrodeposition process to give an even film thickness over the entire surface and also on the edges can also be a disadvantage because the coating

reproduces the surface imperfections in the metal, and unless there is sufficient secondary flow on stoving an apparently lower gloss is achieved than by conventional applications. The careful use of organic solvents goes some way to providing an answer, but so far coatings have not been produced which completely equal the flow and gloss of spray-applied solvent-borne coatings.

From this it can be seen that, even in the narrow field that has already been investigated, there are still some problems to be overcome; however, work has been limited mainly to stoving systems and all the plants currently in operation use anodic deposition. An indication of future trends and an insight into the much wider scope which could be achieved for the electrodepositon process has been given by North¹⁶ who has investigated the electrodepositon of a two-component paint system that gives a room temperature curing deposited film, the paint being deposited on the cathode using an organic acid dispersing agent. A further novelty is that the disadvantages of a reactive two-component system have been overcome by working at such a low solids content that the paint is virtually exhausted at the end of a day's work, and the solids remaining in the tank at the end of the day may be discarded without materially affecting the economics of the process. There are obviously a number of factors to be considered here, of which one is that satisfactory deposition would have to be obtained over a very wide range of solids contents so that comparable results were obtained throughout the day. However, this does indicate that resin development for the electrodepositon process is still in its infancy and there is still plenty of scope for research workers to develop new types of protective polymers which will add impetus to the techniques of electrophoretic deposition.

Conclusions

From this discussion, it can be seen that, in designing a resin system for the electrodepositon process, it is necessary to decide on the details of the application—there is no one resin type which will suit all requirements. Once the application has been defined, it is necessary to formulate a resin which will have the necessary polarisation, throwing power, coulombic yield and stability to meet the conditions laid down. These parameters can be met not only by resin design, but also by control of the environment.

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Equipment aspects and quality control of electropainting plants*

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Summary

The main objective of this paper is outline plant requirements for the electrodeposition of paint and to indicate where control tests are necessary. The different trends in current thinking and how they affect plant design for the electropainting process will be described. The term "electropainting" is used in preference to "electrophoresis", since the process of electrodeposition of paint involves not only electrophoresis but also electrolysis, electrocoagulation and electro-osmosis.

Keywords

Processes and methods—

*primarily associated with application of coatings
electrocoating*

Equipment—

electrocoating equipment

Les installations pour l'électropeinture, leur matériel, et le contrôle de leur production

Résumé

Le premier objectif de cet exposé c'est de tracer les grandes lignes des besoins au point de vue du matériel des installations pour effectuer l'électropeinture et également de donner une indication des essais de contrôle, le cas échéant. On décrit les tendances qui existent actuellement parmi les divers points de vue à l'égard de la conception des installations pour l'électropeinture. On utilise le terme "électropeinture" au lieu de l'électrophorèse, puisque le processus d'électrodéposition entraîne non seulement l'électrophorèse mais aussi l'électrocoagulation et l'électroosmose.

Beachtenswerte Gesichtspunkte für die Ausrüstung von Elektrotauchanlagen mit Qualitätskontrollen

Zusammenfassung

Der Hauptzweck dieser Abhandlung besteht darin, die Erfordernisse einer Tauchlackierungsanlage darzulegen und darüber Angaben zu machen, wo man am zweckmässigsten Kontrollpunkte einschalten soll. Verschiedene diesbezügliche Ideen werden besprochen, und wie sich diese auf das Planen von Elektrophoreseanlagen auswirken. Die Bezeichnung "electropainting" (Elektrotauchlackierung) wird "electrophoresis" (Elektrophorese) deshalb vorgezogen, weil dieses Verfahren bei Lacken nicht nur Elektrophorese, sondern auch Elektrolyse, Elektrokoagulation und Elektroosmose einschliesst.

Оборудование и контроль качества установок для электролитического осаждения красок

Резюме

Главной целью настоящей статьи является дать обзор требований предъявляемых установкой для электролитического осаждения красок и указать где необходимы контрольные испытания. Описываются различные современные направления и подходы

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к этому вопросу и их влияния на расчеты и конструкцию установок для процессов электролитического осаждения. Потребление термина «электролитического осаждения» красок предпочитается термину «электрофореза», так как процесс электролитического осаждения красок включает в себе не только электрофорез, но также и электролиз, электрокоагуляцию и электроосмос.

The advantages of electropainting

Before anyone considers installing an electropainting plant, there must be a prospect of advantages of some kind over their existing paint or coating process. It is possible that the potential user will find that one or more of the following advantages apply.

Electropainting may solve the problem of painting “difficult to paint” items.

Electropainting could give an improved protection and finished appearance compared to the existing process, at little or no extra cost.

Electropaint would give a satisfactory coating at a reduced cost compared to the existing application.

Electropainting, since it is based on a waterborne system, could reduce and, in fact, almost eliminate fire hazards. However, it should also be remembered that this would also be true for waterborne dipping applications.

It is interesting to elaborate on the first three points. First, electropainting may solve the problem of painting “difficult to paint” items. The interior of the box-section on the underside of motor vehicles has always been such an item. It is difficult to apply paint uniformly in these box-sections by conventional methods and even if a paint film is applied by, for example, conventional dipping, solvent washing occurs on stoving and parts of the box-section are left bare. With electropaint, no such solvent washing takes place and a reasonably uniform thickness of coating can be obtained. Another example is the inside of a welded-up petrol tank. The only way to obtain a satisfactory coating inside such a tank is by the electropaint technique. Other difficult to paint items include grilles, dashboards, pipe or tubular sections, fans, electric motor housings and, in fact, any geometrically intricate designs.

The second possible advantage is that electropaint would give improved protection and finished appearance compared with the existing process, at little or no extra cost. The improved protection can be clearly seen when the sharp edges of electropainted parts are examined. They are evenly coated, since there is next to no runaway of paint as there is with conventional painting. In addition, there are no runs or nibs produced and it is therefore possible that the number of people employed in rubbing down prior to the next coating of paint can be reduced. Electropainting can thus show considerable reduction in labour charges at a later stage on the production line. This saving could well overshadow the slightly increased cost per square foot in terms of painting charges for electropainting.

The third point is that electropainting gives a satisfactory coating at a reduced cost when compared with other processes. In order to assess how the efficiency of electropaint applications compares with conventional methods, consider the usage of one gallon of paint at a solids content by volume of 35 per cent. Assuming an average film build of 0.001in (1 mil) over the work, a coverage of 600ft² would be expected by dipping, 300-350ft² by spraying, 500ft² by

electrostatic spraying and 600ft² by electropainting. These figures are, of course, approximate and will depend on the size and shape of items being painted. However, the deposition efficiency, in terms of weight applied, of electropainting and conventional dipping is shown to be similar. But, whereas the deposition of electropaint is nearly uniform over the whole surface of the item, especially over large vertical surfaces, with conventional dipping it is impossible to avoid large differences in the film thickness from the top to the bottom of the item. As the film thickness at its thinnest point must be sufficient to pass the paint specification, more paint than necessary must be applied in some areas in order to meet this requirement. This factor of uniformity of film thickness constitutes a major advantage of application by electropainting over application by dipping.

The fact that electropainting is the most modern technique of paint application carries a lot of weight from the prestige and advertising angles, but does not constitute a technical reason for any manufacturer to use the process.

No method or technique is perfect and electropainting is no exception to this rule. On the debit side, there is the high initial cost of installation. When compared with a normal dipping tank, it is obvious that, while the pre-treatment and curing plants are common to both, the electro tank requires considerable additional plant. This is mainly the electrical equipment and, since current generates heat, heat exchangers to keep the electropaint cool. The additional capital investment is anything from 50-100 per cent more than the cost of a dipping tank. The fact that electropainting is a complicated electrochemical process and, as such, the bath requires more servicing and adjustment than does a dipping tank, is another disadvantage of the process.

General electropaint plant outline

Fig. 1 illustrates schematically the flow diagram of an electropainting plant. It will be observed that the pre-treatment section shown is a six-stage process. This normally includes zinc phosphate treatment but, if iron phosphate is used, as it still is in some plants, then the pre-treatment section can be reduced to four stages. In either case, the last stage before electropainting is a demineralised water rinse. The subsequent optional dry-off zone is usually used when the work pieces are large articles, such as motor-car or truck bodies, but this will be discussed later. After pre-treatment, the work passes through the electro-

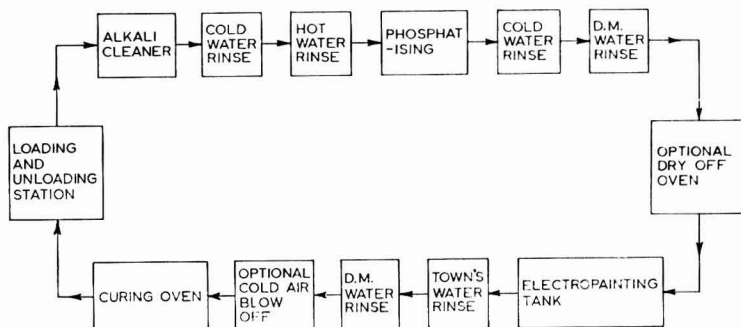


Fig. 1. Schematic flow diagram of electropainting plant

paint tank and then on to the water rinsing section, in which the dip-coat is removed. This section is usually in two stages, the first being a town's water rinse followed by a demineralised water rinse. The work then enters a cold air blow-off zone, after which it is conveyed to the oven and stoved.

Ancillary plant, which is usually required, includes some form of jig stripping facility, demineralised water plant and an effluent treatment plant.

The plant requirements of each stage of the process may now be considered in more detail.

Methods of conveying work-pieces

There are two main types of plant in use, either of which is peculiar to electro-painting plant. They are the flight bar or the mono-rail conveyor.

The flight bar plant consists essentially of the movement of long iron bars from which the items to be painted are suspended. Plants with flight bars up to 25ft long are in operation. These bars are moved at right angles to their lengths by means of chains attached to their ends, the chains being generally run on geared wheels. The loaded flight bars can be progressed either continuously or intermittently through the different process tanks. Boat-shaped tanks would be preferred in the case of continuous running, whereas rectangular or box-shaped tanks would be more suitable in the case of intermittent running.

The mono-rail conveyor type of plant operates continuously. The work is conveyed by means of an endless chain to which attachments are made at various points for hanging jigs. These hanging points are spaced to suit the work being processed.

It is possible, from the point of view of conveyance of work, to use a combination of the two methods. For instance, the pre-treatment section can have its own mono-rail conveyor from which the work is automatically transferred to a drop or dunking section for electro-painting and then to a second mono-rail conveyor for passage through the rinses and stoving.

Generally speaking, the flight bar type of plant will be shorter, but wider and higher than an equivalent mono-rail plant. It is eminently suitable for coating long objects such as chassis or long steel sections. It is also favoured by jobbing contractors because numerous small parts can be suspended from a grid-like flight bar and electro-painted in one dunking operation. The mono-rail conveyor, unlike the flight bar plant, can be so designed that horizontal bends are negotiable. The current trend towards automation certainly favours the mono-rail conveyor type of plant in that it lends itself well to automation, whereas, in general, the flight bar type requires more manual operation.

Jigging

In some operations, such as the electrocoating of motor-car bodies, the bodies are designed so as to be specially suited to the electro-paint process. This means that there are no undrained tray-like areas in which the electro-paint can be trapped when emerging from the electro-tank, or areas in which air can be entrapped in the form of a large bubble and so prevent the electro-paint from coming into contact with the metal surface in this area. In such cases, the jigging or method of suspension of the work from the conveyor is

straightforward. However, this happy state of affairs does not always prevail, and one of the first things which should be investigated when an electropaint plant is being considered, is how to jig the work satisfactorily and economically. It is generally true to say that any work that cannot be jugged so as to avoid either excessive paint drag out or air trapping, cannot be economically or properly electropainted. Any object which is dipped will drag out small quantities of paint, especially in slightly recessed areas. This paint is wasted and indeed can give rise to a poor appearance of the finished product. Conventional dipping paint dragged out in this way would probably have a solids content of 30 per cent 40 per cent, whereas electropaint would only be of the order of 10 per cent solids content. Thus the weight of electropaint wasted due to dragout from recessed areas is only a third to a quarter of that wasted when using conventional dipping paint. Furthermore, since, in the electropainting process, such excess drag out paint is rinsed away and accumulated water from this rinsing process is in turn removed by rocking and/or blow-off, the appearance of the article is less likely to be spoiled.

An approximate figure for drag out of electropaint, when painting reasonably drained articles, is 15 per cent of the paint used when applying a 1 mil film. However, in plants processing car bodies specifically designed with electropainting in view, a 95 per cent usage of paint is not uncommon. From the above, it is clear that careful consideration of jugging can well constitute an important factor in the efficient functioning of an electropainting plant.

Pre-treatment

A characteristic of the electropaint film is that it follows the profile of the substrate exactly. Electropaint, like all types of painting, is not successful over grease or dirt. This means that the finish of the electrodeposited film can only be as good as the pre-treatment which has preceded it. Hence, the importance of good pre-treatment cannot be overstressed. The sequence of operations is quite clear in the schematic flow diagram, but some slight elaboration on two stages, viz., the phosphating tank and the demineralised water wash, is called for. The phosphating or, better, phosphatising (as the Americans call it) process can either be by immersion or by spray. The choice of process is influenced by the type of component to be treated, the service conditions to be catered for, the paint process subsequently to be used, the speed of treatment required, and last but not least, the cost of the treatment. In some car body plants, a combination is used—the bottom part of the body is immersed while the top part is sprayed. This process is expensive.

In the phosphatising stage of the surface treatment system, sludge has always presented a problem. Sludge removal equipment can only improve the quality of surface treatment and reduce maintenance and production costs. In one such piece of equipment, the phosphate solution is pumped from the phosphatising tank into a distribution header. From here the solution flows into four bags, each about six inches in diameter, which hang vertically from the distribution header. Solids remain in the bags while the filtrate flows through synthetic cloth and is collected in a reservoir at the bottom. To empty the bags, all that is required is to operate a lever so that the contents of all the bags drop into a container for disposal. The unit has its own circulating pump.

Current thinking and experience is that a zinc phosphate coating is preferable to iron phosphate. For electropainting, the zinc phosphate coating should be finely grained and uniform. The weight of zinc phosphate coating commonly preferred is of the order of 200mg ft^{-2} , but the use of higher weights is being considered. It is extremely important that there is no dragout of town's water (calcium contamination) or phosphating chemicals into the electropaint tank and, to minimise this possibility, a demineralised water rinse is inserted prior to the work's emerging from the pre-treatment section.

In some cases, especially in the so-called accelerated phosphatising bath, a final rinse with dilute chromate solution is specified. However, some electropaints are susceptible to soluble chromate contamination, so this stage is optional, depending on the type of electropaint to be used.

Dry-off after pre-treatment

This stage of the process is dependent on the items being processed and the electrical details of the electropaint tank. Large items such as motor car bodies can be put through a dry-off oven or, preferably, subjected to a hot air blow-off. The latter procedure is better, since a large volume of air at a relatively low temperature is used, resulting in drying without a high metal temperature. This means that less heat will be transferred to the electropaint tank. In some plants this dry-off stage is combined with a rocker device to remove water from recessed areas. In the case of small objects such as wheels, fans, etc., a cold air blow-off is generally used, or possibly there is no blow-off at all. In the latter event, of course, the articles enter the electropaint tank wet. Such articles must, of course, enter the electropaint tank as soon as possible to prevent rusting. In fact, even dried articles should not be left unpainted for any length of time, for example overnight, otherwise rusting might take place.

The electropaint tank (E-tank) and its accessories

The electropaint tank (E-tank) is illustrated in Fig. 2. Its accessories consist of: draught tube mixers (internal circulation), circulatory pumps (external circulation), filters, a transformer-rectifier unit, a heat exchanger, cathode boxes, and current collection equipment and busbars.

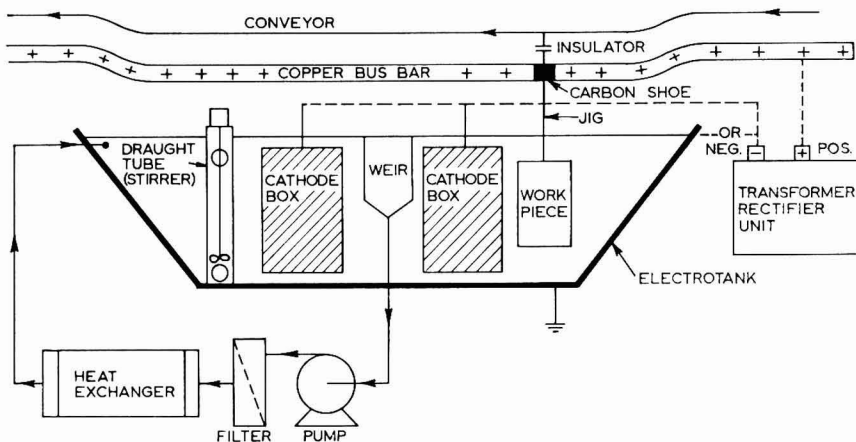


Fig. 2. Schematic diagram of electropainting tank and accessories

The electropaint tank

The E-tank itself is made of mild steel. This discussion will be restricted to a mono-rail conveyor type of plant, since translation of these principles to a dunk type of operation is a matter of calculation and simple engineering practice. The physical dimensions of the E-tank will depend upon the geometry of the work-pieces, the period of residence required to apply the desired paint thickness, and the conveyor speed.

Generally, a residence time of two minutes is sufficient to deposit 1 mil of paint. The rate of electrodeposition is governed, inter alia, by the ratio of anode surface area to cathode area. For some enclosed articles, such as petrol tanks and for screened areas in some car bodies, it is necessary to introduce secondary cathodes. These usually consist of suitably shaped steel rods, each covered with a plastic glove having many holes punched in it. Especially in the case of petrol tanks, it will be clear that the internal cathode area is by force of circumstance very much smaller than the anode area, and a residence time of 3-4 minutes is required to give the necessary paint thickness or build. Conveyor speed can be up to about 15 feet per minute, above which difficulties arise owing to wave formations.

For small objects, the tank depth should be such that they are submerged at least 9in below the surface level. For car bodies, a depth of 15in is usual. The distance between the cathodes and the nearest point on the work-piece should be 9in-12in for small objects and for car bodies 15in-18in.

Electropaints do tend to change with time, owing to oxidation, mechanical shear stresses and the almost unavoidable gradual build up of impurities. It is, therefore, essential that the E-tank should be designed to be as small as possible, but still in accordance with the above requirements, so as to achieve as fast a rate of usage of the E-tank contents as possible. For car bodies, a rate of E-tank turnover of four weeks is very satisfactory and eight weeks acceptable. Some small parts tanks operate well on a 12 week turnover.

The E-tank should have as few horizontal surfaces as possible. The bottom surfaces in the weir should be sloped to reduce fall-out, as static volumes can easily occur in weir boxes. For the same reason, cathode boxes should be flush up against the E-tank. In some plants, especially in the UK, the weirs are placed at the centre of the E-tank and the paint surface movement so arranged that the paint is forced from the ends of the tank towards the weir. This should ensure a clean paint surface at both the entry and exit ends of the E-tank. The present trend is to place the weir at the end of the E-tank with appropriate flow.

Finally, the E-tank is either internally coated with an electrically insulating material, such as a double coat of epoxy paint, or else the interior surface is kept as a clean steel surface. It is perhaps pertinent to elaborate on this difference at this stage, since it constitutes a major difference in E-plant thinking and design. Either the cathodes are enclosed in boxes, the faces being of semi-permeable or ion selective membranes, or else no boxes are used and the whole tank constitutes the cathode. In the former type, i.e. with boxed cathodes, the interior of the E-tank is insulated: this is commonly referred to as the membrane system. When the whole interior of the tank constitutes the cathode it obviously

cannot be insulated, and this system is generally known as the "base deficient feed" system. When an acidic ion with its entrained pigments is deposited on the anode, a base ion must be discharged at the cathode. This is, of course, true for both systems. Where the whole tank is the cathode, the pH of the bath will rise with the continuous discharge of base in the bath. This rising pH is adjusted periodically by means of addition of base deficient or acid electropaint, from which the system derives its name. In the membrane system, the cathode is isolated from the electropaint and only the base ions can penetrate the membrane. Hence the rise in pH is confined to the liquor within the membrane compartment, known as the catholyte. The pH of the tank is thus automatically kept constant and the pH of the catholyte is adjusted by flushing of the cathode box. There are pros and cons for each system. Clearly, by using the base deficient feed system a far greater area of cathode is available than is the case with the membrane system. Also, it is cheaper and saves space to build plant without cathode boxes. On the other hand, additional plant is required for a premix facility, as compared to the requirements for the membrane system premix facility. This counterbalances the economic advantage of the base deficient feed system with respect to plant. Further, the automatic pH control, except in cases where evaporation occurs because the solubilising base is volatile, is a clear advantage of the membrane system. A further advantage of the base deficient feed system is that excess base is re-used, whereas in the membrane system the excess base is another effluent which has to be disposed of. However, more control, as regards both pH and solids content, is required for an E-tank operating on the base deficient feed system. Both systems are in wide use and both operate perfectly satisfactorily.

Control tests on the E-tank

The pH value of the electropaint should be accurately determined at least daily and adjustments made to keep it at the required value. Solids content is usually determined twice weekly when a routine for fresh paint additions has been achieved in practice. Combined with solids content determination, the pigment to binder ratio is determined. The pH and conductivity of the catholyte liquor is determined and adjusted until correct rate of flushing keeps these values constant. Other parameters that are periodically determined are conductivity, electrical efficiency, which is the weight in mg deposited by the passage of 1 coulomb of electricity, the solvent balance, which is evaluated by means of gas liquid chromatography, and the total base content.

Samples are taken from the tank and test panels are electropainted to determine control characteristics such as wet film resistance, throwing power, evenness of the cured film and the salt spray resistance. Further tests on the film include the effects of drops of water and the redissolution of the electro-deposited film in the parent electropaint.

The stability of new consignments of electropaint should always be evaluated. This includes hot storage stability, stability under conditions of constant stirring and pumping, and maintenance of good electrodeposition characteristics under conditions of increasing contaminant equilibria. Such a control programme will usually give warning of trouble which might be developing in the tank. The necessary remedial action is then taken.

Electropaint circulation

Referring again to the schematic diagram of the E-tank (Fig. 2) it can be seen that circulation is effected by means of draught tube mixers, also called eductors, and a circulating pump with associated sparge pipes for re-entry of paint to the E-tank. As could be expected of a paint which is 85 to 90 per cent water, and thus of low viscosity, rapid agitation is necessary to avoid settling out of the pigment. Small installations often use external circulation only, but large E-tanks use both internal and external circulation. The rates of mixing required to keep the pigments in suspension will depend, to a large extent, on the pigment to binder ratio of the paint and on the density of the pigments used. Generally, for small installations which use only external pumps and sparge pipes, a pumping rate of between five and ten turnovers per hour of the tank volume is sufficient. It is essential that the sparge pipes be located so as to give uniform mixing within the tank, and special attention should be given to movement of paint at the base of the tank.

For large installations, most of the mixing is normally performed by draught tube mixers situated at the sides of the tank. Paint is drawn into the top of the draught tubes and ejected from the bottom. With this type of mixer, much smaller shear forces are involved than is the case with centrifugal pumps and, when properly installed, no vortices form. The outlet ports of the draught tubes should be so shaped and positioned as to give a good uniform scouring action to the base of the tank. As these mixers are placed on the sides of the tank, they are less efficient in giving uniform circulation than are sparge pipes. Thus their throughputs are usually in the region of 20 or more turnovers of the volume of the E-tank per hour. Where draught tubes are used, the circulation is supplemented by a secondary external circulation, the paint being re-introduced to the tank via sparge pipes, located to give surface flow towards the weir or weirs, and towards any point where poor agitation can be expected. The pumping rate used in the external circulation will depend on the size of the heat exchanger—it is, in fact, usually equivalent to about 2-3 tank volumes per hour.

External circulation is always required on an E-tank in order to pass paint through filters and a heat-exchanger or cooler. A flow rate of 8-10ft sec⁻¹ is normally required to prevent settling out in the pipes. Centrifugal pumps with a double mechanical seal are used. It is important that the pump seal is kept in good condition or aeration of the electropaint can result. The nature of electropaint is such that any aeration can cause considerable foaming problems. The double mechanical seal is cooled by either demineralised or tap water. If a recirculating water system is used for cooling, then the seal may be under pressure. In this case, demineralised water should be used, as, in the event of a seal breakdown, water will be injected into the paint. If tap water is used as a coolant, it should be sent directly to drain.

Filters

Filtration of the electropaint is normally carried out at two points. A coarse filter or screen is placed in the weir compartment to protect the pump by removing things like gum boots, etc., which somehow seem to find their way into an E-tank. An in-line filter is placed in the external circulating system on the output side of the pump. If it is placed on the input side and the filter be-

comes blocked, cavitation can occur in the pump. This in turn can result in air being sucked into the pipe circuit through the pump seals. Usually the filter is 80-100 mesh. If smaller sizes are used they tend to block up rapidly. Human nature being what it is, operators get tired of cleaning them and open the filter by-pass line, when no filtration at all takes place.

Heat exchanger

The process of electropainting requires the passage of current and thus energy is put into the system. This energy manifests itself in the form of heat. Consequently, if there is no means of removing this heat, the temperature of the electropaint will steadily increase. Since the operating temperatures called for by most paint suppliers fall between 20° and 26°C, a heat exchanger is required to remove heat continuously from the system.

The heat exchanger construction is normally of the shell and tube type. Cooling water is passed through the shell and the electropaint through the tubes. Rate of flow through the tubes should not drop below 5ft sec⁻¹. The amount of refrigeration of the cooling water and the size of the heat exchanger is governed by the power output from the transformer/rectifier and the heat input from pumps, mixers, etc.

Electrical connections

Figs. 3a and 3b show the electrical connections where cathode boxes are used, i.e. they represent a membrane system. However, in Fig. 3a the positive leg or anode is earthed, whereas in Fig. 3b the negative leg or cathode is earthed. There are reasons for and against earthing either the positive or negative side. If the negative side is earthed then, as the E-tank is earthed, it will become cathodic. If the electrically insulated coating inside the tank is chipped or broken at any point, then this point will act as a cathode and base will be discharged there. This base will be concentrated and thus act as a very good stripping solution, causing removal of the insulating coating. On the other hand, if the positive side is earthed the tank will be anodic and, if a break in the insulating layer occurs, it will be coated with electropaint. As long as it is not a large area this represents no problem. Whichever side of the DC supply is earthed, the other side will become live. As it is easier to insulate the cathode side when using cathode boxes, then it is preferred, for reasons of safety, to earth the positive side.

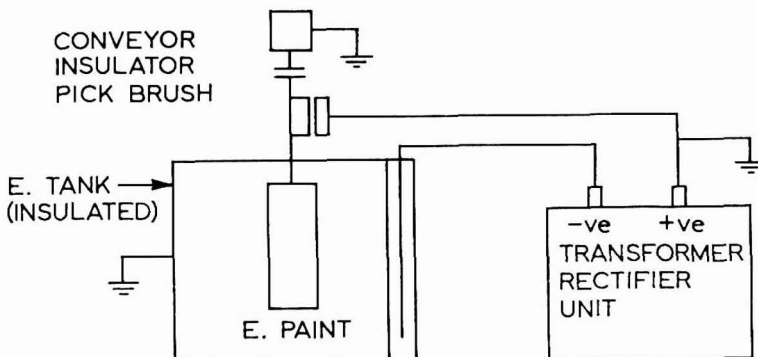


Fig. 3a. Positive earthing with cathode boxes

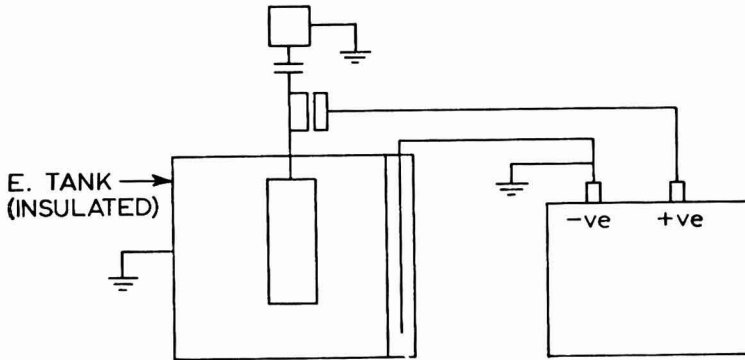


Fig. 3b. Negative earthing with cathode boxes

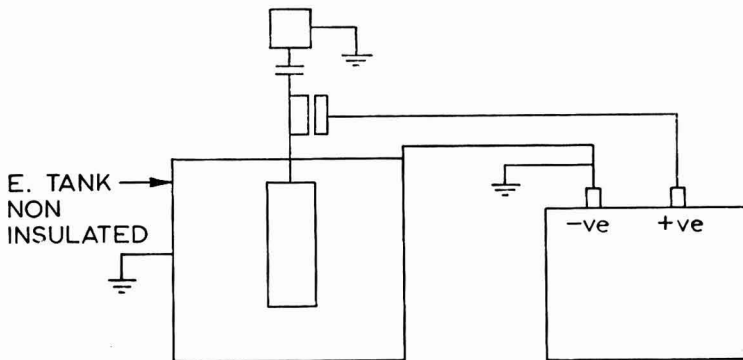


Fig. 3c. Negative earthing without cathode boxes

When cathode boxes are not used, the whole of the interior of the E-tank acts as the cathode. This is, of course, the base deficient feed system. In this case, for obvious safety reasons, it is necessary to earth the negative leg. This means that the work-piece or positive leg is live and thus it is essential for the jigs to be insulated from the conveyor, or a short circuit will result.

Cathode boxes: In membrane system plants, the negative leg of the rectifier is connected to stainless steel cathodes which are located in boxes along the sides of the E-tank. The box is usually fabricated from rigid pvc and must, of course, be leak-proof. It is closed at the front by means of a semi-permeable membrane which separates the paint from the catholyte liquor. The cathode can be placed either at the front or the back of the box, but, if placed at the front, it must be perforated. Demineralised water is forced in at the bottom of the box and flows out at the top. Thus the base is removed as it is discharged at the cathode.

The voltage available at the paint membrane interface is largely dependent on the conductivity of the catholyte. During electrodeposition most of the paint is deposited in the first 30 seconds or less. Consequently, the cathode boxes situated at the entry end of the slipper dip type of tank will receive far more base than those at the exit end. Hence, the conductivity of these boxes

will increase unless proper measures to keep them constant are taken. It has been found difficult to adjust individual flows of demineralised water to each box to effect this requirement. To offset this problem, on large installations, a recirculating circuit, linking all the boxes via a common reservoir, is used. By this means the conductivity of the catholyte is equalised throughout the boxes and demineralised water is introduced into, and catholyte overflowed from, the reservoir, to keep the conductivity at a constant value. This can be performed either manually or automatically by means of a conductivity bridge linked to an automatically operated valve in the demineralised water main. The conductivity of the catholyte should be approximately the same as that of the electropaint.

Positive connections and busbars: The positive side of the transformer/rectifier unit is connected to a copper busbar situated above the E-tank. On a continuous plant, the busbar is commonly split into a number of spring loaded sections. The sections are electrically connected by means of flexible braids. Connection to the work-piece is by means of a brush, usually made of carbon, carried on the jig and making contact with the busbar. In some plants the busbars are fixed and the brushes spring loaded. The jigs themselves usually act as current carriers in small plants. For car bodies, the electrical connections are usually made by means of leads from the brushes, which are fastened directly to the bodies. The length of each section of busbar is arranged so that only one pick-up brush is on a section at any given time.

On some small dunk type plants it is possible to have a permanent positive connection to the flight-bar and a remote controlled switch operating a contactor in the AC side of the transformer, instead of a current pick-up arrangement.

Making or completing of the electrical circuit: This can be effected by either the electrically live work-piece entering the electropaint surface, which is called live entry, or alternatively by the brush making contact with the busbar when the work-piece is already fully immersed, which is called dead entry. In the event of live entry being used, the work must be dried off after pre-treatment, otherwise water droplets on the substrate surface can result in the appearance of the electropainted work being blotchy. This is due to the initial coating being drawn from a very dilute solution of electropaint. If wet objects are to be painted, then it is usual to immerse them in the electropaint for about 15 seconds, so as to wet all the surface with the same concentration of electropaint prior to the circuit being made. For large objects, the preferred method of entry is dry live, as this limits the surge current and hence makes possible the use of a smaller transformer/rectifier unit.

Transformer/rectifier unit: A detailed electrical analysis of this very important component is perhaps beyond the scope of this paper. However, the principles involved will be discussed.

The application voltage of an electropaint, under a given set of conditions such as work-piece size and distance between electrodes, is a function of that particular electropaint. Hence, a transformer is required to produce the specified voltage. Since all electropainting is carried out under direct current, a rectifier bridge is essential to convert alternating current to direct current. A full wave rectifier is always employed. Rectification of a three-phase alternating supply

usually provides sufficient smoothing of the DC output, but in some plants further smoothing is carried out by means of chokes or coils.

It is perhaps appropriate to mention that there are two schools of thought as to which type of DC is best for electropainting. On the one hand there is the conventional DC, smoothed to a certain percentage of ripple. On the other hand, the DC is very rapidly switched on and off by means of electronic switch-gear. This results in a pulsating direct current in the form of an almost square wave. In this case, silicon controlled rectifiers are used in place of conventional solid state rectifiers. Switching is effected by applying a DC of the required square wave form as a triggering current to the gates of the silicon controlled rectifiers. This is generally known as the impulse system, and advantages claimed for it include greater film build, improved throwing power and elevated rupture voltage. The cost of such a plant is only fractionally higher than is that of a straight DC plant and the system is quite widely used in Europe.

The size of the transformer/rectifier unit in kVA will depend on the mean current demand and the surge current. The mean current demand is calculated from the square footage of the work-pieces being painted in a unit of time, the required paint thickness and the electrical efficiency of the particular electro-paint being used.

When painting small objects, such as car wheels, it is likely that, as a number of jigs will be operative in the E-tank at any given time, the surge on dead entry, or even live entry, will be small compared to the mean current. The surge will be dependent on the relative sizes of the wheels and the cathodes, the distance between them, the voltage applied, and the conductivity of the paint. The surge can be minimised by ensuring, in the case of dead entry, that the switch-on point is not opposite cathode boxes, thus increasing the inter electrode distances. Thus the transformer/rectifier unit size is decided by allowing a relatively small percentage, dependent on plant design, over and above mean current demand.

For car body plants, where the body is being immersed under live entry conditions, the rate of increase of current will largely depend on the voltage applied and the speed of entry of the body. There may be only $1\frac{1}{2}$ other bodies immersed in the E-tank at the time and, although the current is attenuated by live entry, if the speed of entry is high, a significant surge can be expected. In this case a relatively large safety factor over the calculated mean is allowed in terms of transformer/rectifier capacity.

A method also used in some plants to limit surge is to programme the applied voltage. In this case, the minimum voltage applied at the commencement must be above the so-called "threshold voltage" or minimum voltage, below which electropainting does not occur.

Rinsing

The time between the work emerging from the E-tank and entering the rinse zone should be kept to a minimum consistent with overspray running back into the electrotank. Rinsing is almost universally carried out by spray from suitably located ring-jets. If the application is a one-coat finish for which the appearance is not very important, then it is possible to use only tap or town's

water for rinsing. However, if the electropaint is required to be overcoated, then a demineralised water rinse is required after the town's water rinse. It is common practice for car bodies to receive an air blow off to remove excess water droplets.

Stoving

No flash-off time is required before the work is transferred to the oven. Stoving schedules, depending on the electropaint, are for periods of up to 30 minutes at up to 180°C effective metal temperature. It is possible that items which require a further coat of paint be stoved for, say, 15 minutes after electropainting and then a further 15 minutes after the next coat is applied.

Future of the electropainting process

In this age in which automation is playing an increasingly large part, the future of this technique, which lends itself so well to automation, seems well assured. It is impressive and suggestive to see a long line of vehicle bodies passing through the various stages of electropainting without any human intervention, except perhaps for the attachment of secondary cathodes. As new and better electropaints with higher throwing power are being developed and as bodies are being specifically designed for the electropainting process, so the need for secondary cathodes is disappearing. It seems probable that in the near future the entire electropainting process will proceed completely automatically, except for periodic tank control and adjustment—a prospect which adds additional realism to an optimistic outlook on the future of the process.

Because of the high initial plant costs, it does seem that the technique will be confined to the mass producer. No doubt with the current development of electroprimers to take white top-coats and with their increasing ability to meet exacting domestic appliance specification requirements, so more and more inroads into this market will be made.

It certainly seems that this relatively new technique is here to stay. It provides unique advantages representing an improved technology. Indeed, given normal progress and development, its role in the mass coating of metallic objects can only grow increasingly large.

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Developments in marine paints*

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Summary

Changes in shipping practice and economic factors that have affected the usage of marine paints, together with the performance factors involved in the painting of ships, are discussed. Technical and economic reasons are put forward for the development of modern high duty coatings, particularly those of the high build type.

Performance testing of marine paints by raft trials and atmospheric exposure is described and details given of the results of a series of experiments to assess the effect of formulation variables on the performance of chlorinated rubber high build marine paints.

The comparative performance after four years' underwater exposure of a number of paint systems over a wide variety of surface preparations is given. The paint systems comprised chlorinated rubber high build and low build primers, coal tar epoxy, bituminous, and vinyl; and the best overall performance was given by a chlorinated rubber high build primer.

Keywords

Types and classes of coating
high build coating
marine finish

Binders—resins etc.
chlorinated rubber

*Processes and methods primarily associated
with analysis, measurement and testing*
exposure testing
immersion testing

Développements dans le domaine des peintures marines

Résumé

On discute les changements dans les modalités de transports maritimes et dans les facteurs économiques qui exercent une influence sur l'utilisation des peintures marines, et l'on considère les aspects du rendement de celles-ci dont on doit tenir compte lors du peinturage des navires. On propose une explication au point de vue des raisons techniques et économiques du développement des revêtements modernes à haute résistance, surtout ceux du type "high build", c'est-à-dire ceux qui donnent des couches épaisses.

On décrit l'appréciation des peintures marines au moyens des essais sur radeau et par exposition aux intempéries, et l'on mentionne les résultats mis en évidence par une série d'expériences conçues pour apprécier l'influence sur leur rendement qu'exercent les variations dans la composition des peintures marines "high build" à base de caoutchouc chloré.

On donne le rendement comparatif, après une durée d'exposition sous-marine de quatre ans, de plusieurs systèmes de peinture, appliqués sur les subjectiles dont leurs surfaces ont été préparées selon une gamme étendue de possibilités. Les systèmes de peintures comprenaient des primaires "high build" ou "low build" à base de caoutchouc chloré, goudron de houille-époxyde, "bitumastic" ou vinylique. Le meilleur rendement était offert par le primaire "high build" à caoutchouc chloré.

Entwicklungen auf dem Schiffsfarbengebiet

Zusammenfassung

Eine Besprechung der Änderungen in den Gewohnheiten der Schifffahrt, sowie der wirtschaftlichen Faktoren, welche die Anwendung von Schiffsfarben und gleichzeitig die an diese gestellten Anforderungen betreffen. Technische und wirtschaftliche Gründe für die Entwicklung moderner hochwiderstandsfähiger Anstrichsysteme, besonders dickschichtiger, werden vorgebracht.

*Presented to the Midlands Section, 23 September 1971

Praktische Prüfungsmethoden für Schiffsfarben am Freiwasserstand und durch Bewitterung werden besprochen. Die Ergebnisse einer Reihe von Versuchen zu Bewertung von Varianten in der Rezeptur von Dickschichtchlorokautschuk Schiffsfarben werden vorgelegt, wobei in Einzelheiten gegangen wird.

Das Verhalten einer Anzahl von Anstrichsystemen über einer Anzahl verschieden vorbereiteter Oberflächen wird nach vierjähriger Exponierung unter Wasser aufgezeigt. Darunter befanden sich Chlorokautschuk-Dick- und Dünnschicht-, Steinkohlenteer-Epoxy-, Bitumen- und Vinyl-Primer; im grossen und ganzen verhielt sich Chlorokautschuk-Dickschichtprimer am besten.

Развитие судовых красок

Резюме

Обсуждаются изменения в судовой практике и экономические факторы которые повлияли на потребление морских красок и характеристики окраски судов. Предъявляются технологические и экономические соображения для развития современных красок высокого качества, в частности красок высокой плотности.

Описываются исследования характеристических свойств морских красок путем испытаний на плотах и выветривания на воздухе и прилагаются подробные результаты ряда опытов для оценки эффекта формулировочных переменных на характеристики хлорированных каучуковых морских красок высокой плотности.

Даются сравнительные данные эксплуатационных качеств, после четырех лет погружения в воду, ряда красочных систем в широком диапазоне поверхностных формулировок. Красочные системы включали хлорированные каучуковые грунтовки высокой и низкой плотности, каменно-угольные смольные эпоксины, битумные и виниловые. Наилучшие общие характеристики были получены для хлорированной каучуковой грунтовой краски высокой плотности.

Introduction

It is widely known¹ that chlorinated rubber paints can meet the general requirements for surface protection but, because of increasing interest in marine paints, data on their performance in that field was required.

In planning a programme to develop marine paints it was important to consider existing or envisaged changes in shipping practice, since many of these are linked with developments in marine paints. Some of the relevant changes are outlined below.

For example in the oil tanker field, with the closing of the Suez Canal the longer haul around the Cape of Good Hope was one of the factors affecting the move towards larger tankers, a development which has made rapid strides in recent years and has also extended to other types of cargo ships including coastal vessels. The present world economic situation has affected the finances of the shipping industry as much as, if not more than, other industries. Although ships have become bigger, crews have tended to become smaller, since the wages bill can be a major item in the overheads, and as an example of the expenses involved in shipping the running costs for a 10,000 to 12,000 ton ship can be upwards of £2,500 per day. There is a saying in the shipping industry that "a ship is only making a profit when the prop is turning" and as a consequence the target is to achieve faster turnrounds and fewer and shorter dry docking periods. Time at sea is a very important factor in ship economics.

In the ship-building sector, inflation has caused a rapid increase in the price of ships and the effect of fixed price contracts is readily evident in the difficulties

of many UK yards. Consequently, the trend in ship-building is towards increased efficiency and faster building techniques to offset the high cost of labour.

These shipping economics link up with marine paint development in a number of ways. The desirability of a greater proportion of sea time and less crew availability to carry out maintenance en route leads to the modern requirement for high duty marine paints which will have a long service life and which are readily touched up both during ship-board maintenance and during shortened dry dock periods.

Economies in running costs can also be achieved by the use of high duty paint systems on the hull, since in 1967 the Dutch TNO Research Institute² showed that the increase in roughness caused by corrosion and/or fouling of a hull is a very significant factor, and up to 10 per cent saving in fuel can be achieved by a smooth hull. The TNO also calculated that, although the cost of application of a sophisticated paint system could be twice that of a conventional paint system, this extra expenditure could be saved in two to three years owing to lower maintenance costs—and this is without allowing for savings due to “keeping the prop turning”.

In ship-building, the requirement of speed of application can be met by the use of high build coatings, which require fewer applications to achieve the requisite film build and are suitable for application under a variety of climatic conditions (e.g. low temperature). In addition, they should have good over-coating properties, including intercoat adhesion, a property which is of particular importance in block building. There is also an economic advantage in high build coatings as discussed by Bowerman⁴ and Gay⁵.

Performance factors

Turning from shipping economics and the move towards more advanced paint systems, the factors involved in the performance of ships' paints will be considered. Esso Research investigated the factors involved in paint failures on Esso's own tankers⁶ and showed that these are: application conditions, surface preparation and paint formulations. These factors were taken into consideration in the development programme shown below.

Application

This can be by brush, roller or spray. Brush application gives good wetting of the surface but for large areas is rather slow. Roller application is faster, but when repainting ships in dry dock it is not uncommon to find $\frac{1}{4}$ in deep corrosion pits in the hull. In such cases a roller can be unsatisfactory because it does not coat these pits properly, with the result that accelerated paint failure can occur.

Airless spray is probably the most efficient method of application, giving less overspray, high build and faster application rates (rates as high as 400 square metres per hour being possible). For this reason, suitability for application by airless spray was one of the requirements in developing a marine paint, and experiments showed that PVC (pigment volume concentration) was one of the factors affecting application properties, a PVC of 30 per cent or more being recommended.

Surface preparation

Blast cleaning is the recommended method for the preparation of ships' surfaces, grit blasting being widely used, and in many modern yards vacuum equipment is often employed for the purpose of dust control. In prefabricated systems, plates are often shot blasted in workshops, this being a very efficient cleaning process. However, it is important that, in order to obtain the maximum benefit from these treatments, the surfaces should be blasted to the correct standard of cleanliness, and the Swedish Standard SIS 05 5900—1967 can be used for control purposes⁷.

This standard gives pictorial representations of surface preparation standards for the painting of steel surfaces. Four rust grades are depicted, denoting the condition of the surface before treatment, varying from a steel surface covered with mill scale and no rust to a surface with all the mill scale rusted away, and on which considerable pitting is visible. Preparation grades are also listed.

The Sa grades for blast cleaning comprise:

- Sa 1 for light blast cleaning,
- Sa 2 for thorough blast cleaning,
- Sa 2½ for very thorough blast cleaning,
- Sa 3 for blast cleaning to pure metal.

For preparation by scraping and wire brushing, St grade is used. After blast cleaning, shop primers, generally of the zinc chromate/polyvinylbutyral or zinc rich epoxy types, can be applied to give limited protection to the blast cleaned plates during fabrication. Zinc silicate primers, which are claimed to give good protection to the steel, are also used.

Having considered blast cleaning mainly with reference to removal of surface contamination, there is another factor to be considered, namely the surface profile. For example, the Ship Research Institute of Norway specifies a maximum roughness of $75\mu^8$ and van Londen³ has also stressed the effect of surface roughness on ships' performance. Bullett⁹ has considered the problem of obtaining continuity with paint coatings on blast cleaned steel because of the peaks in the surface profile. The realisation of this problem was one of the motivating factors in the development of high build chlorinated rubber paints, and the problem is illustrated in Figs. 1 to 3.

In Fig. 1, a photomicrograph of a cross section of grit blasted steel plate coated with conventional low build paints shows how peaks in the surface profile can penetrate the primer film, an obvious point of weakness. Fig. 2 shows that, although peaks can still penetrate the low build primer, two 100μ coats of inert high build give added protection.

However, in Fig. 3, the use of two 100μ coats of high build primer or one coat of high build primer plus a coat of inert high build give protection in depth.

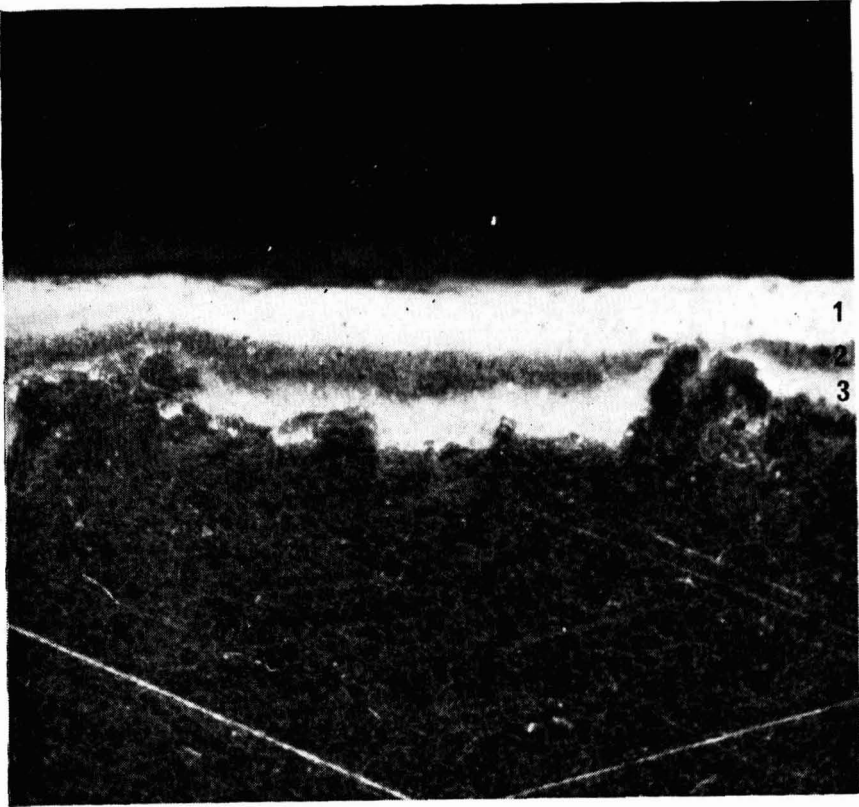


Fig. 1. Photomicrograph of grit blasted steel coated with conventional low build paints, primer (3) and two top coats (1 and 2). Total thickness approx. 100 microns

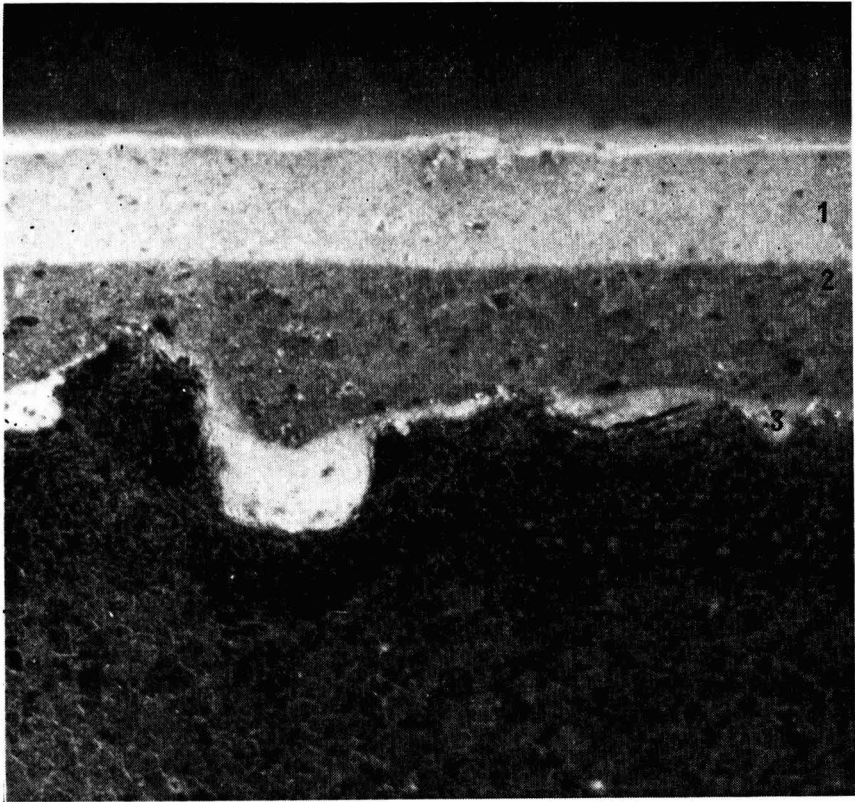


Fig. 2. Photomicrograph of grit blasted steel coated with low build primer (approx. 25 microns, 3) and two coats of high build paint (approx. 2×100 microns, 1 and 2)

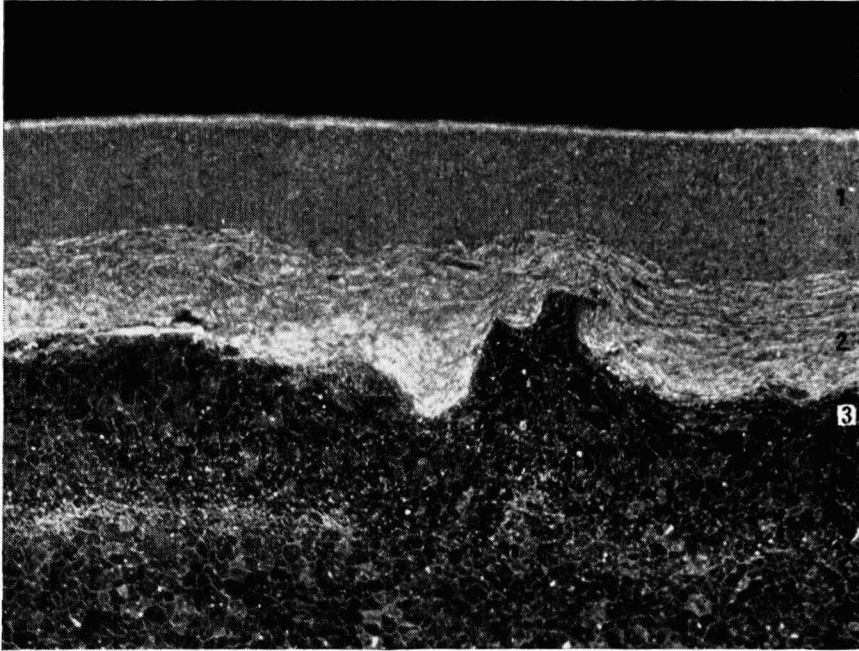


Fig. 3. Photomicrograph of grit blasted steel (3) coated with high build primer (approx. 100 microns, 2) and high build top coat (approx. 100 microns, 1)

Paint formulations

Fleet operators⁶ have stressed the advantage of using high duty paints having properties not offered by conventional drying oil paints. High build, as mentioned previously, is a useful attribute in such paints and in Alloprene chlorinated rubber media this is achieved by producing formulations with suitable rheological properties, normally by the use of thixotropic additives. A simplified presentation of the rheological requirements for a high build coating for airless spray application is given in the following table.

Two types of additives are normally used, namely modified bentonitic clay gellants and modified hydrogenated castor oil type thixotropes. Both additives produce non-Newtonian systems, the difference being that the former tend to

Table 1
Rheological requirements for a high build coating for airless spray application

Paint property	Relative shear rates	Relative viscosity requirements
Airless spray application	High (1,000-40,000 sec ⁻¹)	Medium
Sagging	Low (0.02-0.2 sec ⁻¹)	High
Flow out	Low (<1 sec ⁻¹)	Low
Pigment settlement	Very low	High

give pseudoplastic flow, whereas the latter give thixotropic flow, the difference between these being illustrated in Fig. 4.

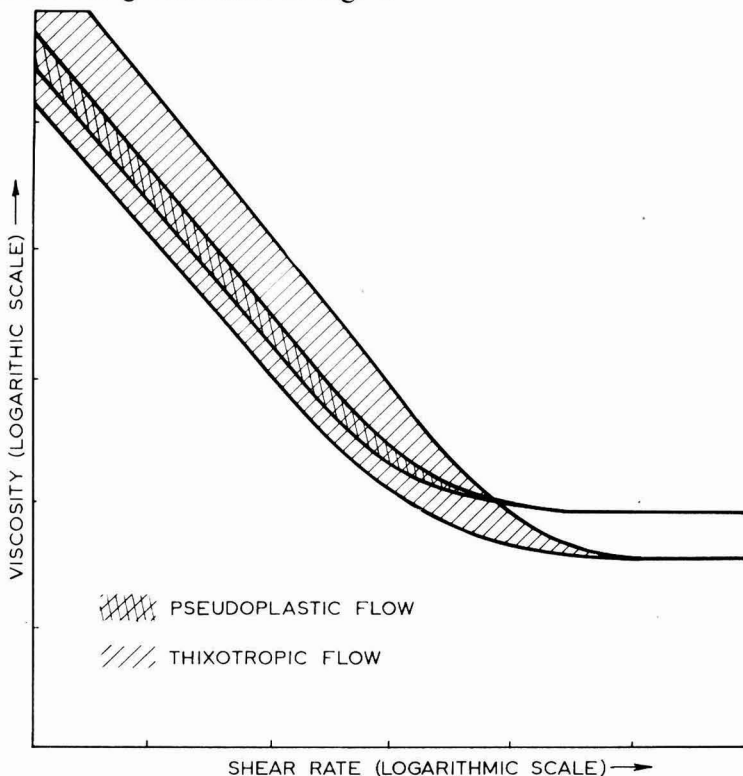


Fig. 4. Difference between thixotropic and pseudoplastic flow in high build paints

With pseudoplastic flow, as the shear rate increases the viscosity decreases and reaches a constant value which is dependent on the shear rate. However, with thixotropic flow the initial pseudoplastic flow is time dependent, and on shearing at a given shear rate a gradual reduction in viscosity occurs. The thixotropic change which occurs with thixotropes can be a factor in the control of flow out or sagging. The rheology of paint systems is dealt with in greater detail by Patton¹⁰. With these factors in mind, manufacturing techniques for chlorinated rubber high build paints were established¹¹, but detailed information about the effect of the formulation variables of such coatings on performance under marine conditions was required.

Performance tests

In order to carry out a programme of work to assess the various paint variables, a test raft based on the ROSCM (Research Organisation of Ships' Composition Manufacturers) design was built and then moored in the Menai Straits off the North Wales coast. Tests were also carried out on a similar raft moored in the Wych Channel of Poole Harbour in Dorset and owned by ROSCM, and in addition atmospheric exposure tests were carried out on selected systems at three land based sites. These include a marine atmosphere (Gladstone Dock Wall, Liverpool, overlooking the Mersey Estuary), an aggressive industrial

atmosphere (a Widnes chemical factory) and a rural atmosphere (Peckforton Castle, Cheshire).

The plates used for the underwater tests were 6mm thick steel plates size $60 \times 45\text{cm}$, to the ROSCM standard design. These were suspended from the raft by steel carriers (Fig. 5) to which they are attached by means of $\frac{1}{4}$ in bolts and Tufnol insulating washers in order to insulate the plates from the carriers and eliminate electrolytic effects, see Figs. 6 and 7.

The panels were assessed at regular intervals during the period of test, the assessment being based on the methods given in the American Exposure Standard Manual¹². As an extension to the methods, the percentage area of the plate on which failure had occurred was recorded. In order to obtain a simplified assessment for comparison purposes, these results were converted to a 0-10 scale (0 = complete failure, 10 = no failure) which was made non-linear in order to give greater emphasis to the earlier stages of failure.

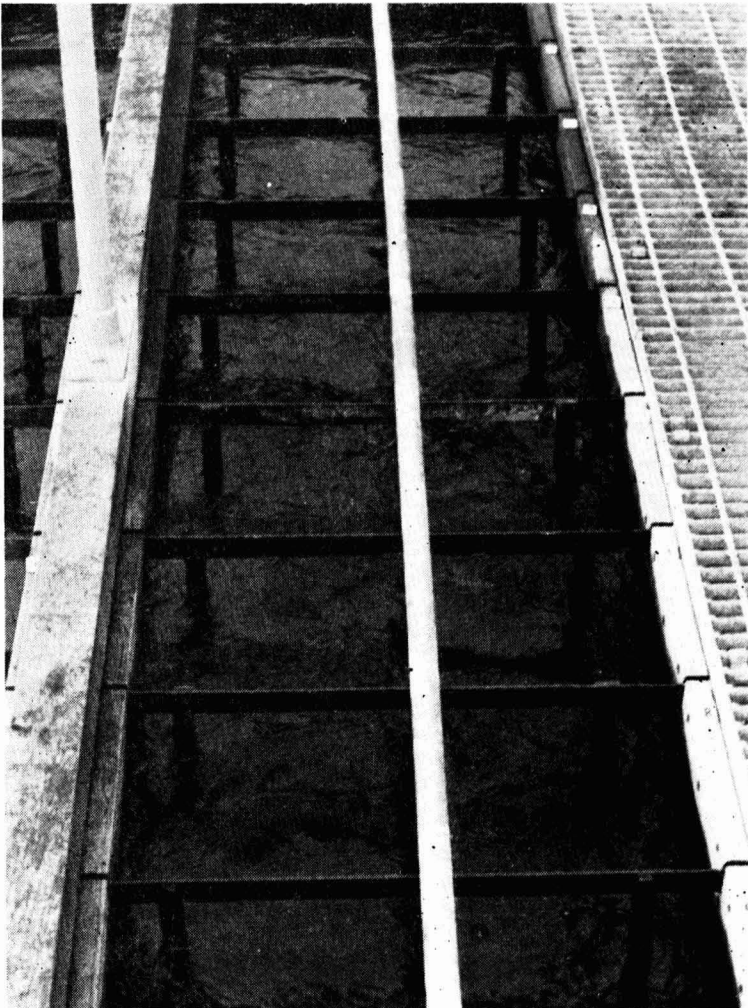


Fig. 5. Method of suspending plates from raft in an area of turbulent flow

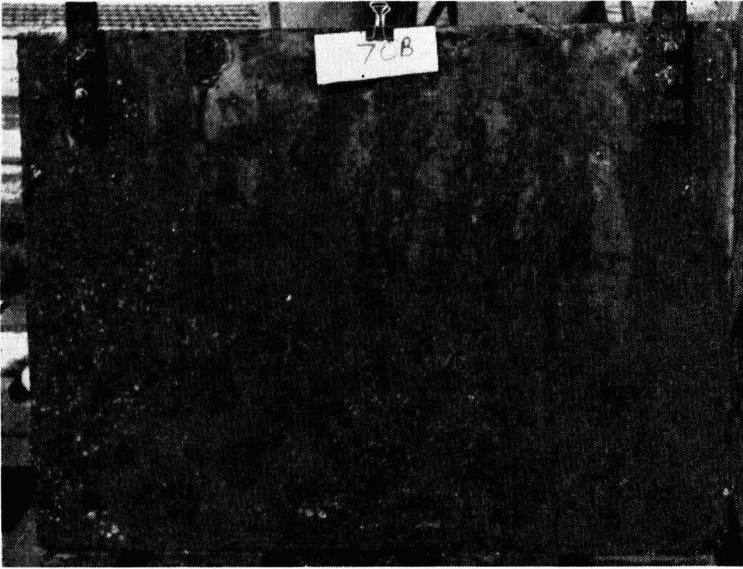


Fig. 6. Rear of ROSCM design raft test plate showing attachment of carrier

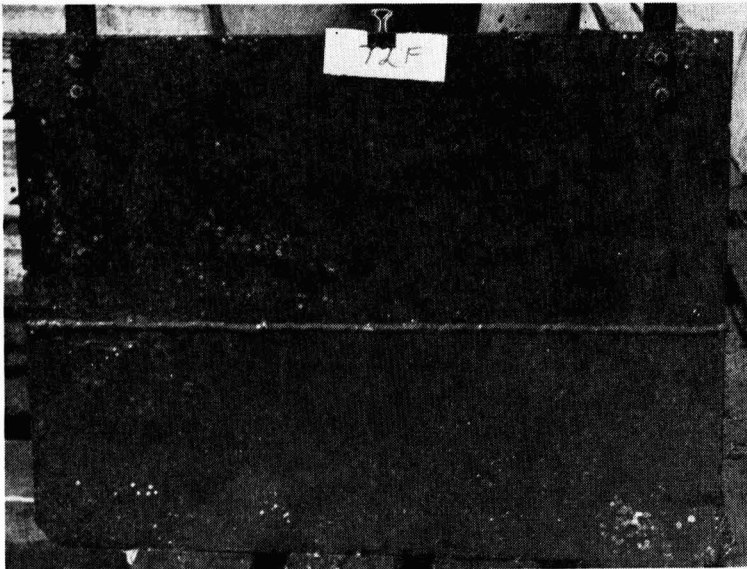


Fig. 7. Front of raft test plate used to simulate the effect of weld lines on performance

Based on the experience with the foregoing plates, a new type of carrier with smaller plates was evolved (Fig. 8). These were more convenient to use and eliminated the electrochemical effects that can occur when several systems are applied to the same plate.

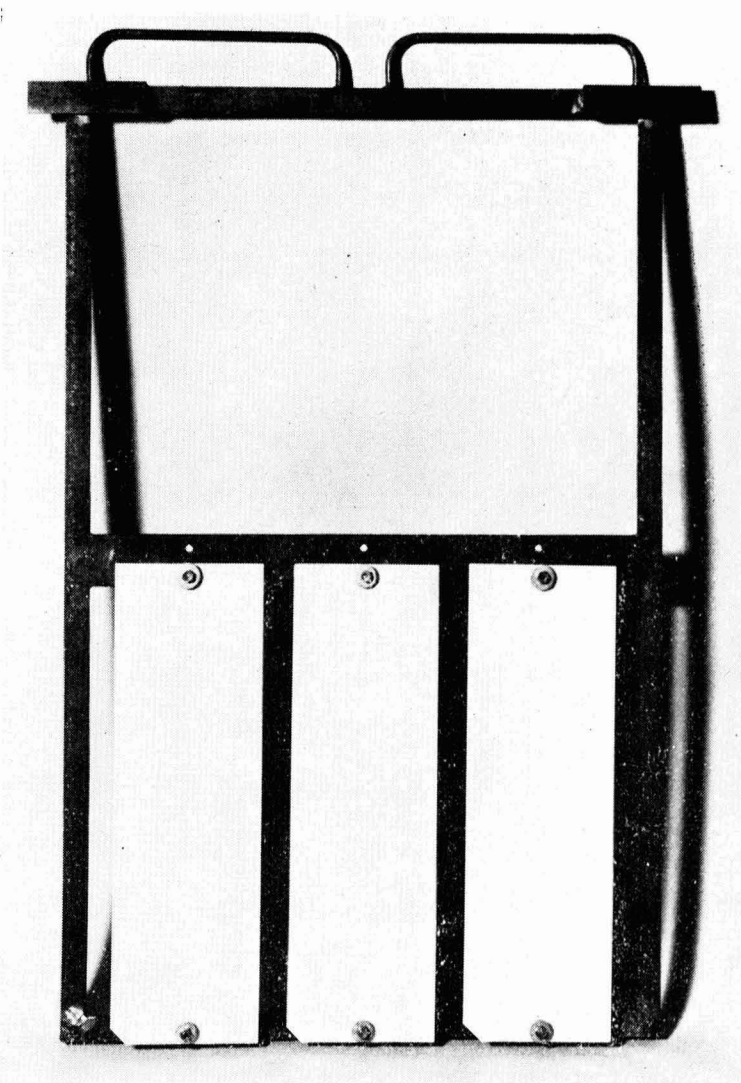


Fig. 8. Carrier designed to utilise 150mm × 450mm size marine test plates

Effect of formulation variables on performance

In the author's work on marine coatings in general, a large number of self-contained experiments have been carried out¹⁷. These included investigations into the effect of formulation variables of high build coatings and surface preparation on performance. The original series numbers have been retained for consistency, and details of the experiments are given in the following sections.

Investigation into effect of thixotropic agents and pigment volume concentration on performance (Series 3)

Experimental details

As mentioned, a thixotrope or a gellant is an important constituent of high build coatings, hence a programme of work designated Series 3 was initiated to investigate the performance underwater of high build paints containing either a modified bentonitic clay gellant (Bentone 34 from Berk Limited) or a modified hydrogenated castor oil organic type thixotrope (Thixatrol ST from Baker Castor Oil Co), made up at a range of pigment volume concentrations and with two different pigmentations, the variations forming a $6 \times 2 \times 2$ factorial design experiment¹³, plus a mixed system with alternate coats having different pigmentations.

The systems applied to shot blasted steel plates comprised:

primer coat (25 microns dry) applied by brush, which was either a commercial epoxy red oxide holding primer or a chlorinated rubber/metallic lead primer;

three coats of high build paint (3×100 microns dry);

commercial antifouling (1×25 microns dry).

The formulation variables of the high build paints are shown below.

Pigment volume concentration: Six levels of PVC—18.0, 26.0, 30.0, 34.0, 38.0 and 46.0 per cent (with thixotropic agents considered as pigments).

Pigmentation: Grey paint = titanium dioxide (Tioxide R-CR from Tioxide International Limited), barytes, carbon black: 49.5/49.5/1 by weight.

Red paint = natural red iron oxide/barytes = 50/50.

Thixotropic agents: Bentone 34 gellant (10 per cent by weight of binder); Thixatrol ST thixotrope (4 per cent by weight of binder).

Binder: The binder composition was a chlorinated rubber resin (Alloprene R10 from ICI Limited), a plasticising or extender resin (Cereclor 70, chlorinated paraffin wax from ICI Limited) and a liquid chlorinated paraffin wax plasticiser (Cereclor 42 from ICI Limited) in the ratios 50/33/17 by weight.

Solvent: Xylene/ethyl glycol ether acetate (Cellosolve acetate), 4/1 w/w ratio.

In addition to the systems with three coats of grey or three coats of red, a mixed system of red/grey/red was tested.

Test results

The results as given in Table 2 show that there are upper limits of PVC, formulations with Thixatrol being satisfactory up to PVC's of 38 per cent, whereas those with Bentone are satisfactory up to 34 per cent. However, if Thixatrol is considered as binder then the upper limit for this thixotrope is 34 per cent and the optimum range for each thixotrope would appear to be 30-34 per cent PVC. This is another reason, apart from rheological properties, why the two types of thixotrope should not be considered as directly interchangeable and that modified hydrogenated castor oils should be expressed as resins, as opposed to modified bentonitic clays which may be counted as pigments in pigment volume concentration calculations.

Table 2
 Test series 3—Simplified assessment of marine test plates after 3 years 8 months' immersion on Menai raft

Primer	Thixotropic agent	System	Pigment volume concentration*					
			18%	26%	30%	34%	38%	46%
Chlorinated rubber/ metallic lead	Thixatrol	Grey	M	10	10	10	10	5
		Red	M	10	8	10	10	5
		Red/grey/red	10	1	10	10	10	7
	Bentone	Grey	10	10	4	10	5	3
Red		10	10	7	10	10	2	
Red/grey/red		2	6	10	3	6	M	
Epoxy/red oxide	Thixatrol	Grey	M	10	10	8	10	5
		Red	M	10	10	7	6	5
		Red/grey/red	10	10	10	10	10	6
	Bentone	Grey	10	10	5	10	5	7
		Red	5	5	5	0	5	6
		Red/grey/red	5	3	3	3	3	M

*If Thixatrol is considered part of the binder the pigment volume concentrations are 13.3, 21.8, 26.1, 30.3, 34.5 and 44%, respectively, for systems containing Thixatrol.

The plates are assessed on the scale 10 = no failure
 0 = complete failure
 M = missing

In this series the pigment/extender ratio was kept constant. As the PVC increases in the grey paints, the cost reduction obtained by lower resin usage is offset by increases due to high titanium dioxide levels, which means that the raw materials costs stay fairly constant. However, as described in the following experiments, the volume of titanium dioxide can be reduced without affecting performance, which means that paints with high pigment volume concentrations will be cheaper. With regard to their performance as anti-corrosive systems, there seemed to be little difference between the high build pigment systems tested. The random failure observed is believed to be due to manufacturing variables.

Cross hatch adhesion tests, carried out on small sections of panels after 22 months' exposure, indicated that paints containing modified hydrogenated castor oil thixotrope are less brittle than those containing the modified bentonitic clay, and that paints with titanium dioxide as the main pigment can show a high degree of embrittlement. This may be reflected in the fact that the paints containing Thixatrol performed best on exposure.

Effect of binder composition on performance of high build paints (series 7)

Experimental details

The object of series 7 was to assess the effect of binder composition on underwater performance of high build paints, using two different primers, in addition to atmospheric exposure tests with only one of the primers, at the three land based sites. For underwater exposure, the systems were applied to shot blasted steel panels over two different primers. For atmospheric exposure they were

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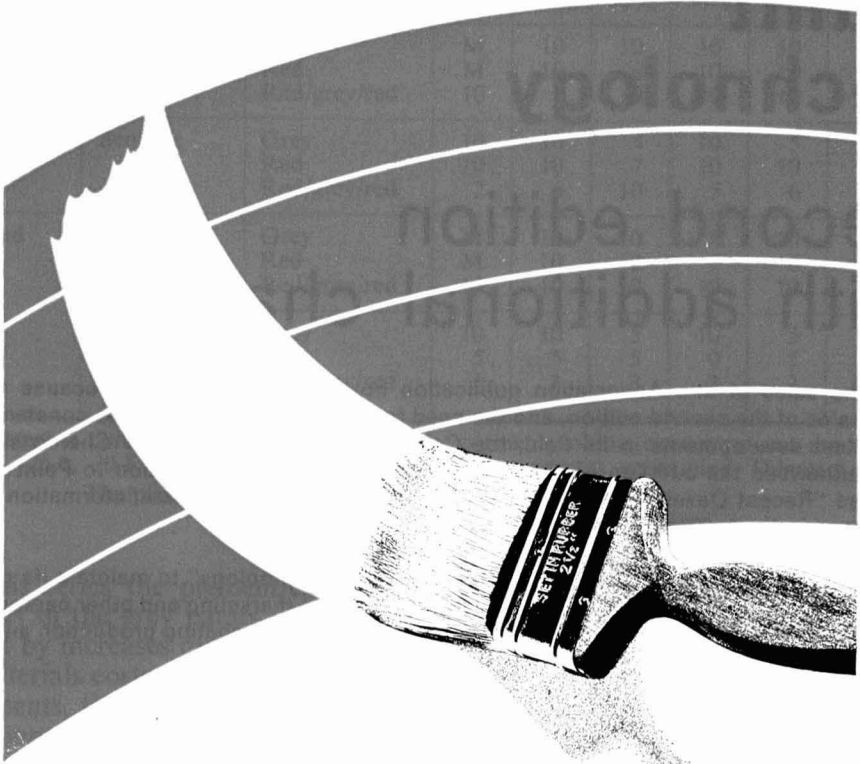
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applied over the zinc epoxy primer only, three sets being applied on standard 12in × 4in steel test panels (without an antifouling coating). The details of the systems are as follows:

- primer coat (25 microns dry);
- either a commercial zinc rich two-pack epoxy paint;
- or a chlorinated rubber/metallic lead primer;
- three coats of high build "Alloprene" paint (3 × 100 microns dry) in the sequence of red/grey/red pigmentations;
- commercial antifouling coat (1 × 25 microns dry).

The formulation variables for the high build paints were as follows.

Pigment volume concentration

Twenty pairs of high build paints were prepared, all having a PVC in the region of 30 per cent, but differing in binder composition.

Pigmentation

Each pair of paints had the same PVC and binder composition, but a different pigmentation, being

- either a red lead paint pigmented with barytes and natural red iron oxide at a w/w ratio of 2 : 1;
- or a grey paint pigmented with Tioxide R-CR, barytes and vegetable black at a w/w ratio of 50/49/1.

Thixotropic agents

A mixed system was employed consisting of equal parts of a Bentone gellant and a modified hydrogenated castor oil thixotrope, each at 4 per cent by volume on the solids content. There was also the requisite amount of industrial methylated spirits calculated on the weight of the Bentone present.

Binder

The binder variables of the high build paint were:

- Grade of Alloprene chlorinated rubber being either R5, R10, R20 or a blend of R5/R20 to produce a viscosity of 10 cP.

(Alloprene chlorinated rubber is graded by reference to the viscosity of a 20 per cent w/w solution in toluene, e.g. R5 has a viscosity of 5 cP.)

A range of plasticiser and resin ratios was used.

In all the 50/33/17 plasticiser/resin ratios, four grades of Alloprene were used, whereas in the other ratios only the stated Alloprene grades were employed.

Alloprene/Cereclor 70/Cereclor 42	50/33/17
Alloprene/Cereclor 70/Cereclor S52	50/33/17
Alloprene/Cereclor 70/Aroclor 1254	50/33/17
Alloprene/Coumarone resin/Cereclor 42	50/33/17
Alloprene (5cP only)/Cereclor 70/Cereclor 42	60/25/15
Alloprene (10cP only)/Cereclor 70/Cereclor 42	50/25/25
and	40/35/25

Alloprene (20cP only)/Cereclor 70/Cereclor 42 40/25/35
(Cereclor S52 is a chlorinated paraffin and Aroclor 1254 is a chlorinated diphenyl from Monsanto Limited).

The paints with the 50/33/17 binder ratios formed a 4×4 factorial experiment¹³.

Solvent blend

The solvent blend used in these high build paints was xylene/Cellosolve acetate in an 80/20 ratio.

The underwater test panels were immersed in March 1967 on the rafts at Menai and Poole, and the atmospheric exposure tests at the three land exposure sites were commenced at the same time.

Test results

Marine exposure: The exposed plates were examined periodically for all the normal defects, blistering, rusting etc. by reference to the Exposure Standard Manual¹² and the results recorded in detail.

A simplified presentation of the evaluation results obtained after 3½ years exposure on the two rafts is given in Tables 3 and 4, whereby, in order to ease interpretation, detailed results have been converted to a non-linear numerical scale as described earlier.

Table 3

Series 7—Effect of binder variation. Simplified assessment after 3½ years' immersion on Menai raft

Binder	Binder ratio	Chlorinated rubber grades			
		R5	R10	R20	R5/R20
Primer = metallic lead					
A/C70/C42	(50/33/17)	2	6	7	1
A/C70/CS52	(50/33/17)	9	8	9	2
Λ/C70/Ar1254	(50/33/17)	10	9	10	10
A/C5/C42	(50/33/17)	3	7	8	8
A/C70/C42	(60/25/15)	10	—	—	—
Λ/C70/C42	(50/25/25)	—	8	—	—
Λ/C70/C42	(40/35/25)	—	9	—	—
Λ/C70/C42	(40/25/35)	—	—	1	—
Primer = zinc/epoxy					
A/C70/C42	(50/33/17)	10	10	10	10
A/C70/CS52	(50/33/17)	10	10	10	10
A/C70/Ar1254	(50/33/17)	10	10	10	10
Λ/C5/C42	(50/33/17)	10	10	10	10
Λ/C70/C42	(60/25/15)	10	—	—	—
A/C70/C42	(50/25/25)	—	10	—	—
A/C70/C42	(40/35/25)	—	10	—	—
A/C70/C42	(40/25/35)	—	—	10	—

0 to 10 scale (10 = no failure)

Table 4
 Series 7—Effect of binder variation. Simplified assessment after 3½ years' immersion on Poole raft

Binder	Binder ratio	Chlorinated rubber grades			
		R5	R10	R20	R5/R20
Primer = metallic lead					
A/C70/C42 (50/33/17)	7	10	M	5
A/C70/CS52 (50/33/17)	5	5	7	4
A/C70/Ar1254 (50/33/17)	M	9	10	7
A/C5/C42 (50/33/17)	M	M	5	7
A/C70/C42 (60/25/15)	8	—	—	—
A/C70/C42 (50/25/25)	—	9	—	—
A/C70/C42 (40/35/25)	—	10	—	—
A/C70/C42 (40/25/35)	—	—	2	—
Primer = zinc epoxy					
A/C70/C42 (50/33/17)	10	10	M	3
A/C70/CS52 (50/33/17)	5	4	8	3
A/C70/Ar1254 (50/33/17)	M	9	10	10
A/C5/C42 (50/33/17)	M	M	10	10
A/C70/C42 (60/25/15)	10	—	—	—
A/C70/C42 (50/25/25)	—	8	—	—
A/C70/C42 (40/35/25)	—	10	—	—
A/C70/C42 (40/25/35)	—	—	2	—

0 to 10 scale (10 = no failure)

M = missing

A = Alloprenne, C = Cereclor, Ar = Aroclor and C5 = coumarone resin.

One plate was lost at Poole and therefore a careful examination of the results was needed in order to reach a decision on the findings. Also, as in previous series, there appeared to be some random failures.

As regards the primer, the systems with the metallic lead primer had a worse performance with respect to corrosion inhibition at Menai than at Poole. By contrast, in the case of the systems with the zinc rich epoxy primer the reverse was true (this is confirmed in series 8). There are also indications that the conditions at Menai produce greater differences between primers than do the Poole conditions. However, on the basis of other work, the metallic lead primer used in this series has now been superseded by another formulation.

Conclusions about the 50/33/17 binder combinations are that the Alloprenne/Cereclor 70/Aroclor 1254 combinations gave the best performance and that the other three binder systems gave similar results. It was also observed that the blend of Alloprenne R10/Cereclor 70/Cereclor 42 in the ratio 40/35/25 had given promising results, indicating that a more highly plasticised film could be

used. However, the poor results with the 40/25/35 ratio film are indicative of a plasticisation limit, with this film being in the overplasticised region.

Consideration of the performances of the paints containing the various viscosity grades of chlorinated rubber reveals that the 10cP and 20cP grades gave the best results, both being slightly superior to the 5cP grade with 5cP/20cP mixture giving the worst results. Since polymer viscosity is generally linked with molecular weight this latter observation could possibly be related to the findings of other workers,^{14, 15} namely that the mechanical properties of a polymer film comprising a mixture of polymers of different molecular weights can be inferior to those of a single polymer with a smaller molecular weight range.

Atmospheric exposure: The detailed evaluation results after 3½ years' exposure of the panels exposed at the three land sites are given in Table 5. In order to obtain valid conclusions, an analysis of variance was carried out on the results obtained, taking a 1 per cent level of difference as significant and a 0.1 per cent as highly significant.

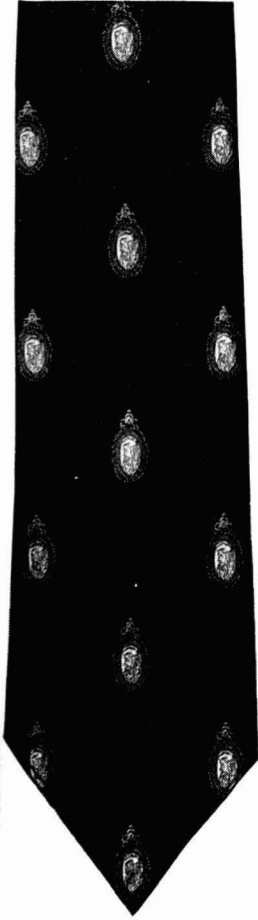
With the four binder compositions at the 50/33/17 ratio the order of performance from best to worst was Alloprene/Cereclor 70/Aroclor 1254; Alloprene/Cereclor 70/Cereclor S52; Alloprene/Cereclor 70/Cereclor 42; Alloprene/coumarone resin/Cereclor 42.

The difference between the first three binder systems is marginal and shows that in temperate climates Cereclor S52 can replace Cereclor 42. The coumarone resin system tested was unsuitable as a high build paint for atmospheric exposure, and this confirms the author's experience that the Cereclor 70 plasticising resin is an important constituent of the Alloprene/Cereclor system.

As in the raft trials, the Alloprene R10/Cereclor 70/Cereclor 42 (40/35/25 ratio) binder system gave excellent results, indicating that further exposure trials of paints based on this binder system should be considered.

With regard to the effect of the grade of chlorinated rubber used on performance, it was observed that the performance decreased with increasing viscosity, and, as in the case of the raft trials, the mixed grade gave the worst results. It is believed that airless spray application properties may be a factor here. A detailed analysis showed that the overall trend was observed with respect to checking, pinholing and dirt retention, and that cracking was more prevalent with the lower grades. Chalking was similar for each grade.

An interesting observation from these atmospheric exposure tests is that the three different sites affect paints in a different manner and the significance of this difference has been confirmed statistically as shown in Table 6.



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Table 5
 Test series 7—Effect of binder variation. Detailed evaluation of atmospheric exposure panels after 3 years' 9 months' exposure

Film defect	Ratio, % w/w	Location† Alloprene grade	Checking			Cracking			Pinholing			Chalking			Dirt collection		
			G	W	P	G	W	P	G	W	P	G	W	P	G	W	P
A/C70/C42	50/33/17	R5	10	10	10	5	10	10	10	6	8	8	9	9	7	7	8
		R10	10	9	10	5	10	10	10	6	5	8	9	9	7	7	8
		R20	10	8	10	5	10	10	10	8	2	2	9	9	6	6	8
		R5/R20	8	8	10	5	10	10	10	8	3	4	8	9	9	7	5
A/C70/CS52	50/33/17	R5	10	8	10	6	10	10	10	9	9	8	9	9	8	7	8
		R10	10	9	10	7	10	10	10	8	7	9	9	9	8	6	8
		R20	9	9	10	7	10	10	10	6	3	4	9	9	7	6	8
		R5/R20	10	9	10	10	10	10	10	2	3	5	9	9	7	5	8
A/C70/Ar1254	50/33/17	R5	10	9	10	10	10	10	8	9	9	9	9	9	8	7	8
		R10	10	8	10	10	10	10	8	4	8	9	9	9	8	6	8
		R20	10	7	10	10	10	10	2	4	5	9	9	9	7	6	8
		R5/R20	10	7	10	10	10	10	5	3	6	9	9	9	7	5	8
A/C5/C42	50/33/17	R5	0	0	1	10	10	10	5	3	1	7	9	9	6	3	8
		R10	0	0	1	10	7	10	7	4	2	6	9	8	6	2	8
		R20	0	0	1	10	8	10	4	1	1	6	9	8	5	2	8
		R5/R20	0	0	1	10	5*	1*	6	5	1	7	9	8	5	2	8
A/C70/C42	60/25/15	R5	10	5	10	10	10	10	8	7	6	8	9	6	7	8	
A/C70/C42	50/25/25	R10	10	8	10	10	10	10	4	6	8	9	9	7	7	8	
A/C70/C42	40/35/25	R10	10	8	10	10	10	10	9	8	8	9	9	8	7	8	
A/C70/C42	40/25/35	R20	10	9	10	10	10	10	6	5	4	8	9	8	2	8	

The panels are assessed on the scale 10 = intact, 0 = complete failure.

*Cracking through to grey middle layer.

†Location: G = Gladstone, W = Widnes, P = Peckforton

Table 6
Series 7—Difference in severity of Mond Division land exposure sites

Defect	Degree of severity of site		Level of significance of differences from variance analysis
	Most severe	Least severe	
Chalking	Gladstone	Peckforton/Widnes, similar	1%
Checking	Widnes	Gladstone/Peckforton, similar	0.1%
Pinholing	Widnes/Peckforton, similar	Gladstone	1%
Cracking	Gladstone	Widnes/Peckforton, similar	0.1%
Dirt retention ..	Widnes	Gladstone/Peckforton, similar	0.1%
All defects	Widnes/Gladstone (industrial) (marine)	Peckforton (rural)	0.1%

0.1% level: very significant.

1% level: significant

Effect of pigment variation in high build paints (series 8)

Experimental details

The experiment was designed to investigate the effect of pigment variation on underwater performance and atmospheric exposure of chlorinated rubber high build paints. The various high build paints, after application to shot blasted steel panels, using two different primers, were subjected to underwater exposure. For atmospheric exposure, the same high build paints were applied to standard 12in × 4in steel test panels using only the zinc rich epoxy primer.

The general system comprised:

Primer (1 × 25 microns dry)
commercial zinc rich epoxy primer

or Alloprene/metallic lead primer

High build; 3 coats (3 × 100 microns dry)

Antifouling (underwater exposure only) (1 × 25 microns dry)

Pigment volume concentration: 30 per cent PVC

Pigmentation: The pigment was either titanium dioxide or natural Spanish red oxide combined with one or more extender pigments.

Thixotropic Agents: Thixatrol ST thixotrope, 4 parts by weight per hundred parts of binder.

Binder: A blend of Alloprene R10 chlorinated rubber/Cereclor 70 plasticising resin and Cereclor 42 chlorinated liquid paraffin plasticiser in the ratio 50/33/17.

Solvent: Xylene/Cellosolve acetate 4/1.

Test results

In Tables 7 and 8, details of the various pigmentations used are given, together with an assessment of the degree of internal film bubbling formed during application and, with regard to the latter, indications are that the paints with dense crystalline pigments show less tendency to give a "honeycomb" film than those containing laminar mineral pigments. By contrast, however, laminar metallic pigments give dense films with no "honeycomb" structure.

Table 7

Details of pigmentations of white paints used in series 8 experiments

Pigmentations	Vol/Vol ratios	Internal film bubbling
TiO ₂ /china clay (Supreme)	20 : 10	2
TiO ₂ /whiting	15 : 15	8
TiO ₂ /Winnofil S	15 : 15	6
TiO ₂ /Microvit I	15 : 15	0
TiO ₂ /slate powder	15 : 15	0
TiO ₂ /Barytes RS	15 : 15	—
TiO ₂ /whiting	10 : 20	0
TiO ₂ /Microdol Extra	10 : 20	10
TiO ₂ /Barytes RS	10 : 20	8
TiO ₂ /china clay	7.5 : 22.5	0
TiO ₂ /Barytes RS	7.5 : 22.5	4
TiO ₂ /china clay/Microtalc	7.5 : 19.5 : 3.0	2
TiO ₂ /china clay/Micro Mica	7.5 : 19.5 : 3.0	0
TiO ₂ /china clay/Dicalite WB	7.5 : 19.5 : 3.0	4
TiO ₂ /Microdol/Microtalc	7.5 : 17.5 : 5.0	0
TiO ₂ /Microdol/Micro Mica	7.5 : 17.5 : 5.0	0
TiO ₂ /Microdol/Dicalite WB	7.5 : 17.5 : 5.0	2

0 to 10 scale: 10 = good

Table 8

Details of pigmentation of red paints used in series 8 experiments

Pigmentations	Vol/Vol ratios	Internal film bubbling
Red oxide/Tioxide A-LT (anatase)	15 : 15	8
Red oxide/china clay (Supreme)	15 : 15	4
Red oxide whiting	15 : 15	8
Red oxide/Microvit I	15 : 15	8
Red oxide/Barytes RS	15 : 15	—
Red oxide/Asbestine 3X	15 : 15	2
Red oxide/lithopone	15 : 15	2
Red oxide/basic lead carbonate	15 : 15	10
Red oxide/basic lead sulphate	15 : 15	10
Red oxide/whiting	10 : 20	0

0 to 10 scale: 10 = good

A detailed assessment of the series 8 performance underwater was made after approximately four years' exposure, and examination of the results showed that, as with series 7, the systems with the zinc rich epoxy primer performed better on immersion at Menai than the same systems with the chlorinated rubber/metallic lead primer, and again Poole was the more severe of the two sites.

Generally better results were obtained with the titanium dioxide paints than with the iron oxide ones, the latter systems showing greater incidence of failure attributed to the grade of natural Spanish red oxide used, a grade which is no longer available. Unfortunately, there was a fair degree of random failure, believed to be due to the problems of manufacture, which can occur in the production of high build paints using the high temperature method for the incorporation of the hydrogenated castor oil thixotrope. Later work showed that, with this method, "seeding" can occur; and these "seeds" can be a cause of film weakness.

Most pigmentations performed adequately, but those of greatest interest were TiO_2 /Microdol (micronised dolomite), TiO_2 /Microdol/Microtalc (micronised laminar talc) and TiO_2 /barytes, the latter pigmentation being useful in a chemically resistant system. The systems with these pigments exhibited good anticorrosive properties and excellent resistance to film erosion underwater.

The results of atmospheric exposure are given in Table 9. No checking or pin-holing was observed and no corrosion occurred, due in part to the high film build. In the systems containing red iron oxide pigment, star cracking occurred on exposure at Gladstone, and the available evidence implicates the pigment, as this was found to be an unsatisfactory grade and is no longer available. The loss of gloss was greatest at Widnes during the first twelve months, but thereafter the decline was sharper at the other sites. Among the white paints the Tioxide RCR/Microdol Extra (1/2 pigmentation) gave the best all round gloss results.

Effect of primer variables and variation in surface preparation (series 6)

Experimental details

Previous work carried out on low build chlorinated rubber primers¹⁶ showed that primers based on aluminium, metallic lead, zinc, basic lead silicochromate, and zinc chromate performed well, the latter being surprising in view of its solubility.

As an extension of this work, an investigation was carried out on the performance of a number of chlorinated rubber high build primers, a standard system comprising a low build metallic lead primer overcoated with an inert, high build, chlorinated rubber formulation and also three systems based on other resins, each system having been applied to a variety of surface preparations. This experiment therefore combined an assessment of primer performance with effect of surface preparation on performance, by applying 8 different paint systems to each of 15 different surface preparations.

Table 9
Detailed evaluation of series 8 atmospheric exposure panels after 3 years' 9 months' exposure

Pigments	Volume ratios	Chalking			Cracking			Dirt retention			Initial gloss ranking	Gloss—washed 45°				
		Site*			Site*			Site*				Peckforton	Widnes		Gladstone	
		P	W	G	P	W	G	P	W	G			1968	1970		1968
TiO ₂ /china clay (Supreme)	20:10	8	7	8	10	10	10	8	6	8	12	6	10	9	35	8
TiO ₂ /whiting	15:15	Not exposed														
TiO ₂ /Winnofil S	15:15	8	8	7	10	10	10	8	5	6	1	8	19	14	34	9
TiO ₂ /Microvit 1	15:15	8	7	7	10	10	8	10	8	7	7	33	6	25	7	40
TiO ₂ /slate powder	15:15	8	7	9	10	10	10	8	7	7	4	33	8	17	8	31
TiO ₂ /Barytes RS	15:16	8	M	7	10	M	10	8	M	8		5	11	M	25	5
TiO ₂ /whiting	10:20	8	6	8	10	10	10	8	6	8	3	25	10	17	15	33
TiO ₂ /Microdol Extra	10:20	8	7	8	10	10	10	8	6	7	2	37	11	22	19	34
TiO ₂ /Barytes RS	10:20	8	M	8	10	M	10	8	M	8	6	32	8	11	M	35
TiO ₂ /china clay	7.5:22.5	8	6	7	10	10	10	8	7	5	11	5	1	7	5	30
TiO ₂ /Barytes RS	7.5:22.5	9	8	7	10	10	10	8	5	8	5	23	8	10	11	34
TiO ₂ /china clay/Microtalc	7.5:19.5:3.0	8	M	7	10	M	10	8	M	8	14	13	5	7	M	25
TiO ₂ /china clay/Micro Mica	7.5:19.5:3.0	8	8	7	10	10	10	6	7	8	10	37	11	9	5	26
TiO ₂ /china clay/Dicalite WB	7.5:19.5:3.0	8	7	7	10	10	10	8	6	7	15	8	4	6	4	26
TiO ₂ /Microdol/Microtalc	7.5:17.5:5.0	9	8	8	10	10	10	8	5	7	13	14	7	8	8	29
TiO ₂ /Microdol/Micro Mica	7.5:17.5:5.0	8	8	7	10	10	10	8	5	6	8	21	7	15	10	29
TiO ₂ /Microdol/Dicalite WB	7.5:17.5:5.0	8	8	7	10	10	10	8	4	7	9	27	9	15	15	40
Red oxide/Tioxide A-LF (anatase)	15:15	Not exposed														
Red oxide/china clay (Supreme)	15:15	8	9	8	10	10	8	8	6	8	7	8	3	7	4	29
Red oxide/whiting	15:15	Not exposed														
Red oxide/Microvit 1	15:15	9	8	7	10	10	7	8	6	8	3	25	8	15	5	31
Red oxide/Barytes RS	15:15	Not exposed														
Red oxide/Asbestine 3X	15:15	9	8	7	10	10	7	8	6	8	5	32	9	11	6	31
Red oxide/lithopone	15:15	8	9	8	10	10	7	8	6	7	2	26	6	14	4	32
Red oxide/basic lead carbonate	15:15	8	9	7	10	10	7	8	6	8	1	30	9	14	9	42
Red oxide/basic lead sulphate	15:15	9	8	8	10	10	7	8	6	7	4	32	7	12	5	31
Red oxide/whiting	10:20	8	8	7	10	10	8	8	6	8	6	19	3	15	3	31

*Test site: P = Peckforton, W = Widnes, G = Gladstone Dock.

The panels are assessed for chalking, cracking and dirt retention on the scale: 10 = no change, 0 = complete failure, M = missing

Paint systems

The eight paint systems tested were as follows.

A standard high build system similar to the type tested in series 7, namely: An Alloprenne/metallic lead primer 11A8 (1×25 microns dry) with a high build topcoat, three coats as follows: red paint 11G33/grey paint 11G34/red paint 11G33 (3×75 microns dry) commercial antifouling (1×25 microns dry).

Four different Alloprenne high build primer systems, each system comprising three coats ($3 \times$ approx 80 microns dry) to give a total anticorrosive film of 250 microns plus one coat of commercial antifouling (1×25 microns dry). The high build primers tested contained the following anticorrosive pigments: 21E53 red lead, 21E54 aluminium and basic lead sulphate, 21E55 aluminium, and 21E56 basic lead sulphate.

Two coats of a commercial aluminium/bitumen paint (2×90 microns dry) plus commercial antifouling (1×25 microns dry).

A coal tar/epoxy-amine cured system (60 per cent tar; based on the epoxide resin manufacturer's recommendations), three coats (3×90 microns dry) plus commercial antifouling (1×25 microns dry).

A vinyl chloride/vinyl acetate copolymer system (based on the resin manufacturer's recommendations) as follows: one coat polyvinyl butyral etch primer reference WP1 (1×20 microns dry), three coats high build vinyl resin/red lead paint (3×70 microns dry), anti fouling paint, a vinyl composition (based on the resin manufacturer's recommendations, 2×25 microns dry).

Surface preparation

The various surface preparations of the steel plates were as follows.

Blast cleaned with 16 mesh (1.0mm aperture) grit to Swedish Standards Sa3 and Sa2.

Blast cleaned with 6-8 mesh (2.8-2.0mm aperture) grit to Swedish Standards Sa3 and Sa2.

Blast cleaned with 25 mesh (0.6mm aperture) steel shot to Swedish Standard Sa3.

Plate cut in half along its length, rejoined by welding and either grit blasted with 16mesh (1.0mm aperture) grit to Swedish Standard Sa2 or else wire brush cleaned.

Weathered plate flame cleaned.

Weathered plate cleaned with rotary sand disc.

Blast cleaned with 25 mesh (0.6mm aperture) steel shot to Swedish Standards Sa3 and Sa2, coated with commercial shop primer 'A', and weathered for three months and nine months.

Blast cleaned with 25 mesh (0.6mm aperture) steel shot to Swedish Standard Sa3; coated with commercial shop primer 'B' and weathered for three months and nine months.

Photomicrographs illustrating the surface profiles of a selection of these plates are shown in Fig. 9 (a) to (e).



Fig. 9a. Photomicrograph of profile of steel plate shot blasted with 25 mesh steel shot to Swedish Standard Sa3

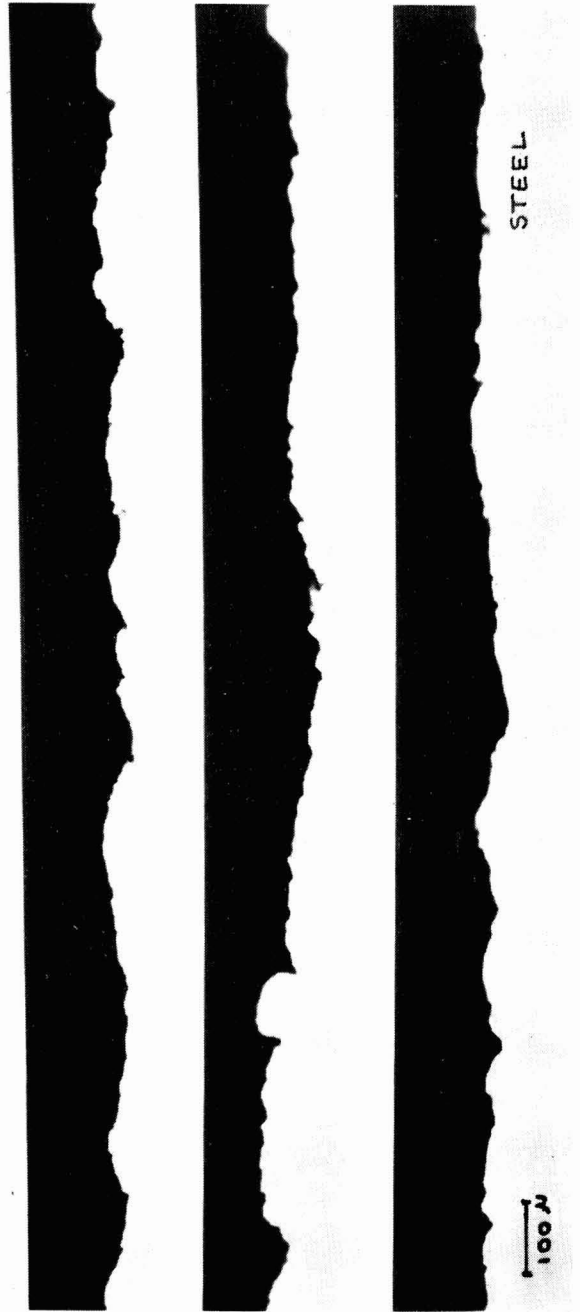


Fig. 9b. Photomicrograph of profile of steel plate grit blasted with 16 mesh grit to Swedish Standard Sa3

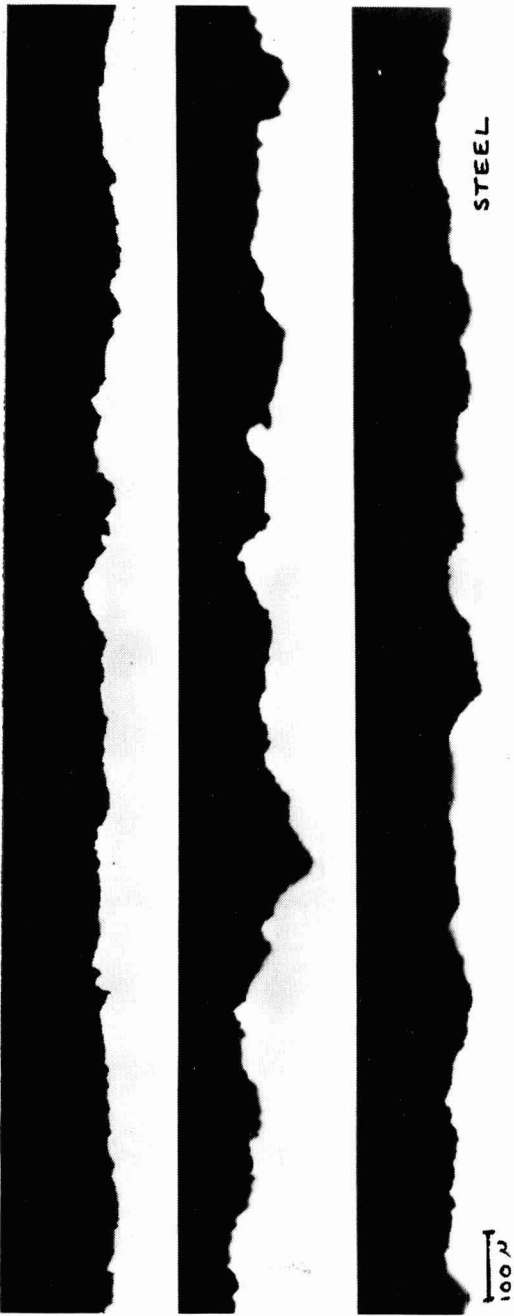


Fig. 9c. Photomicrograph of profile of steel plate grit blasted with 6-8 mesh grit to Swedish Standard Sa3

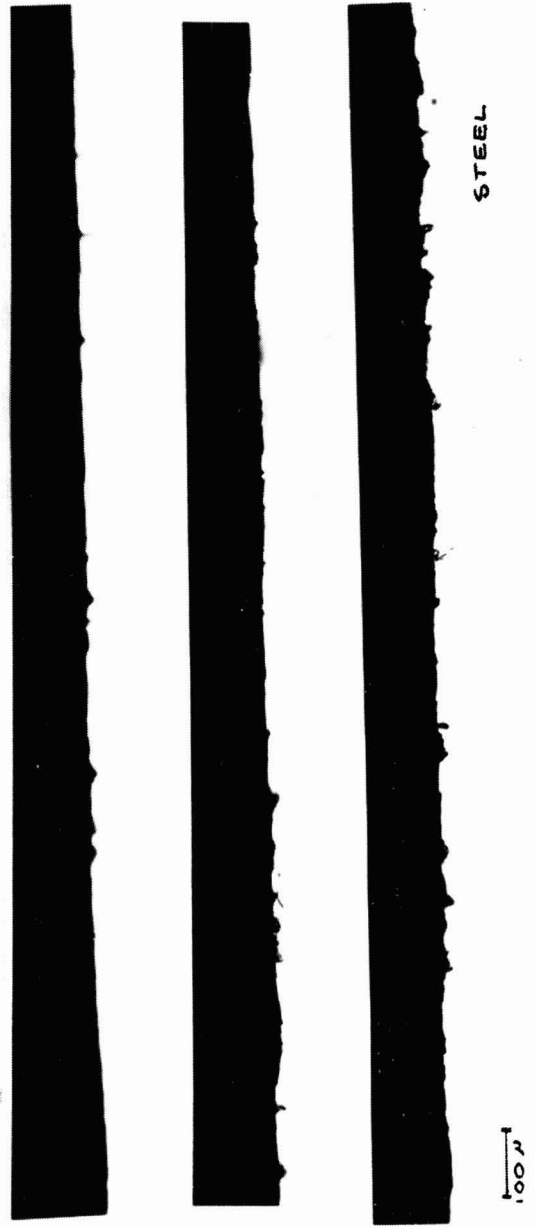


Fig. 9d. Photomicrograph of profile of steel plate abraded by sand disc

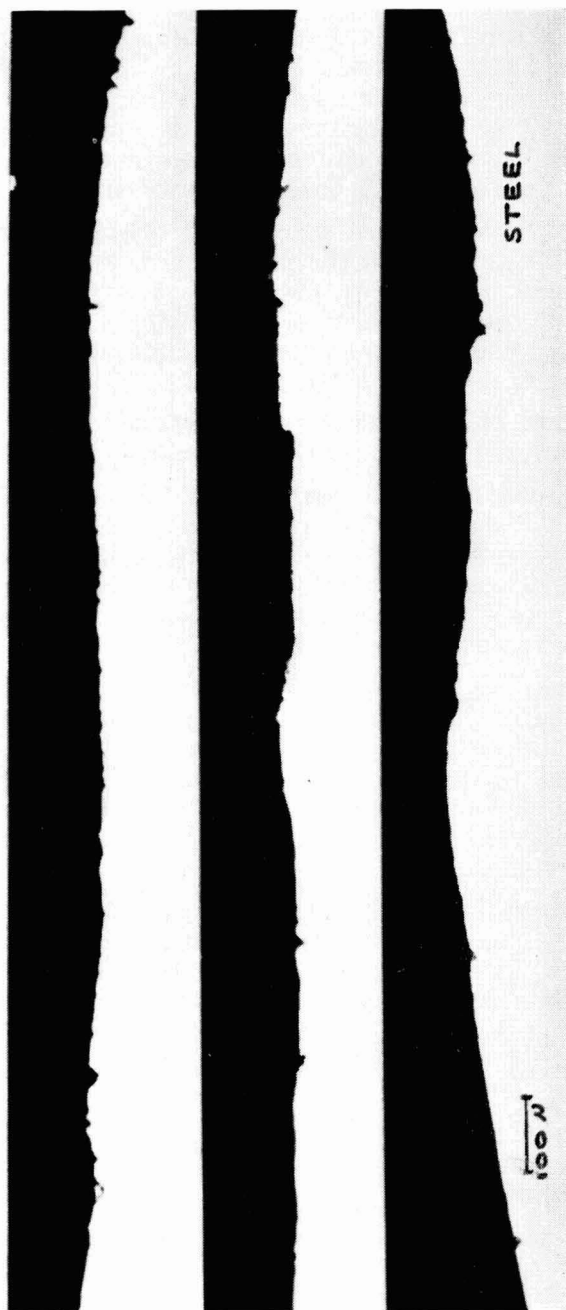


Fig. 9e. Photomicrograph of profile of steel plate wire brushed to Swedish Standard St2

Test results

All the foregoing paint systems on the fifteen different substrates were immersed on the Menai Raft and the same paint systems with a selection of the substrates were also exposed at Poole. The panels were examined periodically and a detailed assessment was carried out on both sites after four years' immersion.

A simplified presentation of these results is given in Table 10, with the performance rated on a non-linear 0-10 scale, as discussed earlier. Examination of the results shows that the chlorinated rubber high build primers containing aluminium or aluminium/basic lead sulphate gave excellent results over all the substrates. The system with the improved low build metallic lead primer followed by an inert high build coating, although not quite as good as the foregoing high build primers, nevertheless gave excellent results.

The coal tar/epoxy and bitumen paints gave reasonable results, but not as good as the above mentioned chlorinated rubber systems. The particular chlorinated rubber/red lead system under test gave poor results, and this has been confirmed by laboratory tests. It is believed that this is not necessarily typical of chlorinated rubber formulations containing this pigment, as there are successful commercial systems based on it.

The vinyl system, which was based on a resin manufacturer's latest formulations and applied as recommended, rather unexpectedly gave poor results.

There was very little difference in performance between the more successful paints on panels prepared using 16 mesh grit and those cleaned with the coarser 6-8 mesh grit, the finer grit having marginally better results. However, with the systems which did not perform so well (namely vinyl and chlorinated rubber pigmented with red lead), their performances were appreciably better on the surfaces blast cleaned with the coarser 6-8 mesh grit.

The results obtained with the shop primed surfaces illustrate the fact that weathered shop primers can be difficult substrates to overcoat, and the variability of these results contrasts markedly with the good results obtained on the grit blasted surfaces. The two systems giving the best overall result on the shop primers were the aluminium pigmented chlorinated rubber high build primer system and the chlorinated rubber metallic lead primer overcoated with chlorinated rubber inert high build.

Examination of the results obtained with the plates shot blasted and primed with shop primer 'A' shows that, in general, better results were obtained with surfaces pretreated to Sa3 than with those given an Sa2 treatment. Comparing these results with the results obtained for unprimed Sa2 and Sa3 grit blasted surfaces indicates that the degree of surface preparation is much more critical with weathered shop primers than with surfaces blast cleaned immediately prior to painting.

On the flame cleaned surface, the performances of all the chlorinated rubber systems—including the red lead pigmented one—were markedly superior to the other three systems.

With the welded plates, either blast or wire brush cleaned, the aluminium or aluminium/basic lead sulphate high build primers gave the best results and they also gave excellent results on the sand disc cleaned surface, the coal tar/epoxy also giving good results on the latter surface. With reference to the coal tar/epoxy system, a high degree of flaking of the antifouling was observed.

The tests on the Poole raft in general confirmed the above findings, in particular the good performance of the aluminium or aluminium/basic lead sulphate high build chlorinated rubber primers.

Table 10
Raft series 6—Effect of surface preparation (4 years' underwater exposure on Menai raft)

Surface preparation Paint systems	Blast cleaned				Other preparations			Blast cleaned and primed					
	Sa3	Sa2	Sa3	Sa2	Flame cleaned	Sand disc	Cut, weld and wire brush	Sa3	Sa2	Sa3	Sa2	Sa3	Sa3
	25 mesh shot	16 mesh grit	6-8 mesh grit	Cut, weld and 16 mesh grit				Shot blast plus shop primer "A" weathered 3 months	Shot blast plus shop primer "A" weathered 9 months	Shot blast plus shop primer "A" weathered 9 months	Shot blast plus shop primer "B" weathered 9 months	3mths	9mths
Alloprene/aluminium high build primer 21E55	10	10	10	10	10	10	10	10	6	10	10	10	9
Alloprene/aluminium/basic lead sulphate high build primer 21E54	10	10	10	9	10	10	10	10	9	10	7		10
Alloprene/basic lead sulphate high build primer 21E56	9	10	10	8	10	6	8	10	10	5	2		7
Alloprene/metallic lead plus inert high build 11G33/34	9	10	9	10	10	8	8	10	10	10	10	10	8
Coal tar/epoxy	9	10	8	8	3	10	10	6	7	9	2	10	8
Commercial bitumen paint	10	10	9	8	3	7	8	9	10	5	8	9	8
Alloprene/red lead high build primer 21E53	7	7	8	9	8	4	3	2	0	5	3	9	7
Vinyl copolymer/red lead	10	1	8	10	2	6	3	7	4	10	3	7	6

0-10 scale, 10 = no failure

Conclusions

Consideration of the main factors involved in the marine paint field reveals that high build coatings based on high performance binders have distinct advantages in marine paint applications. Investigation into performance of chlorinated rubber paints under marine conditions showed that a binder containing a chlorinated rubber/solid chlorinated paraffin wax/liquid chlorinated diphenyl (50/33/17) combination gave best results, but this system cannot now be used because Aroclor chlorinated diphenyls are being withdrawn from use in surface coating applications on ecological grounds. However the chlorinated rubber/solid chlorinated paraffin wax/liquid chlorinated paraffin (50/33/17) blends also gave good results, both below water and on atmospheric exposure, and hence can be considered as a high performance binder.

A more highly plasticised version of this system with a w/w ratio of 40/35/25 also performed well and this system is worthy of further investigation.

For both application properties and performance the 10cP viscosity grade of chlorinated rubber (i.e. Alloprene R10) is the recommended one, and the use of a blend of widely differing viscosity grades gives inferior results to a single grade of the same viscosity. This may be related to the findings of other workers on the effects that mixtures of differing molecular weights can have on the mechanical properties of polymers in general.

The upper limit of pigment volume concentration for good performance is 34 per cent and for good application by airless spray a minimum of 30 per cent is recommended.

Adhesion tests showed that both pigmentation and thixotropic agent can be factors in embrittlement of the film, modified hydrogenated castor oil being the better of the two agents in this respect.

A concentration of titanium dioxide at 50 per cent w/w of the pigment content can be too high, and this can be satisfactorily reduced with the advantage of lower cost, without any reduction in performance.

Extender pigments which gave good results in combination with titanium dioxide in a standard chlorinated rubber binder system, were micronised dolomite ("Microdol"), micronised laminar talc ("Microtalc") and barytes.

High build aluminium/chlorinated rubber primers can give excellent durability and corrosion protection over a range of surface preparations and good results can also be obtained with a suitably formulated chlorinated rubber/metallic lead low build primer overcoated with chlorinated rubber/inert high build paints.

The excellent condition of many of the chlorinated rubber systems after four years' underwater immersion shows that chlorinated rubber can be recommended for use in high performance systems for marine use.

Acknowledgments

The author would like to acknowledge the help of his colleagues in compiling the information for this paper.

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Appendix

Compositions of a selection of paints used in tests

Table 11
Chlorinated rubber anti-corrosive primers

Constituent	Composition by weight (%)				
	High build primer 21E53	High build primer 21E54	High build primer 21E55	High build primer 21E56	Low build metallic lead primer 11A8
Alloprene R20	—	—	—	—	16.2
Alloprene R10	12.1	12.3	12.0	12.0	—
Cereclor 70	7.1	7.2	7.0	7.0	—
Cereclor 42	4.0	4.1	4.0	4.0	7.0
Epoxidised soya bean oil	—	—	—	—	1.0
Thixatrol ST	1.6	1.6	1.6	1.6	0.5
Red lead (non-setting) ..	18.2	—	—	—	—
Red iron oxide	18.2	6.7	1.0	9.6	—
Basic lead sulphate ..	—	13.3	—	18.8	—
Non-leafing aluminium paste (65%)	—	9.2	12.0	—	—
Metallic lead paste (91% in Cereclor 42) ..	—	—	—	—	30.0
Silica graphite	—	—	—	—	13.3
Tioxide R-CR	—	—	6.0	—	—
Barytes	—	6.7	18.0	9.6	—
Magnesium oxide	—	—	0.3	—	—
Xylene	31.0	31.1	30.5	29.9	—
Aromasol H*	7.8	7.8	7.6	7.5	24.0
White spirits	—	—	—	—	8.0

*High boiling aromatic solvent, boiling range 168-200°C; supplied by ICI Ltd.

Table 12
Chlorinated rubber high build paints

Constituent	Composition by weight (%)			
	High build red paint	High build grey paint	High build, high plasticisation (Series 7)	High build TiO ₂ /Microdol (Series 8)
	11G33	11G34/1	11G284	11G286
Alloprene R10	13.6	14.1	10.8	13.4
Cereclor 70	7.9	8.2	9.5	8.9
Cereclor 42	4.5	4.7	6.8	4.6
Epoxidised soya bean oil	—	—	0.4	0.8
Thixatrol ST	2.0	1.9	1.6	1.1
Tioxide R-CR	—	16.4	15.6	11.2
Barytes	15.8	16.4	16.8	—
Red iron oxide	15.8	—	—	—
Microdol extra	—	—	—	15.7
Vegetable black	—	0.2	0.2	—
Xylene	32.4	30.5	30.6	35.5
Cellosolve acetate	8.0	7.6	7.7	8.8

Table 13
Coal tar/epoxy and vinyl paint formulations

Constituent	Composition by weight (%)		
	Vinyl red lead paint	High build coal tar/epoxy (2 pack)	
		Base	Activator
Vynlite resin VAGH* ..	16.6	—	—
Epikote resin 834†	—	24.5	—
Coal tar/pitch	—	36.5	—
Tri-tolyl phosphate	1.7	—	—
Aerosil	—	1.0	—
Asbestine	—	25.0	—
Aluminium stearate	0.1	—	—
Red lead (non-setting)	25.2	—	—
Diethylene triamine	—	—	50.0
Toluene	27.2	—	—
Xylene	—	6.5	—
Secondary butyl alcohol	—	6.5	50.0
Methyl isobutyl ketone	29.2	—	—
		Base to activator ratio = 100 : 6	

*Vynlite VAGH is a vinyl chloride/vinyl acetate resin from BX Plastics Limited.

†Epikote 834 is an epoxide resin from Shell Chemicals Limited.

Discussion at the Midlands Section

MR H. SCHIERBAUM asked if there were special problems with regard to the adhesion of chlorinated rubber to polyvinyl butyral primers.

MR K. S. FORD answered that adhesion was quite satisfactory in his experience, which largely covered two-pack polyvinyl butyral primers, though he could not speak for one-pack.

MR H. J. CLARKE asked if there were special considerations regarding the choice of plasticiser and its effect on anti-fouling.

MR FORD replied that the systems investigated showed no problems with the anti-fouling.

MR SCHIERBAUM inquired if weld lines required special treatment.

MR FORD replied that the Scandinavian recommendations required re-blasting of all weld lines, as there was a problem with residual flux.

MR D. PENRICE asked about pretreatment before re-painting.

MR FORD said that chipping, wire brushing or portable sand blasting were commonly used, depending on the size of the job. He also mentioned that one large marine paint company had a training scheme for deck-hands.

MR R. J. KING questioned the influence of extender type on honeycomb formation in airless spraying.

MR FORD replied that crystalline mineral extenders appeared to give a better result than laminar ones and that the thixotrope was important in this respect, less honeycombing occurring if the modified hydrogenated castor oil was dispersed correctly before gelling, in order to prevent "seeding."

MR H. DREW questioned the importance of total film thickness.

MR FORD emphasised that this was most important, and that 300 micron dry thickness was recommended and was readily achievable with three coats applied by airless spray.

Next month's issue

The Honorary Editor has accepted the following papers for publication, and they are expected to appear in the August issue of the *Journal*.

"Factors which affect the efficiency of ball milling," by *W. Carr*

"Kubelka-Munk theory and colour matching," by *D. F. Tunstall*

"The role of research on paint technology in the Australian building industry,"
by *E. Hoffmann*

Review

POLYMER NETWORKS—STRUCTURE AND MECHANICAL PROPERTIES

BY A. J. CHOMPPF AND S. NEWMAN (Editors). New York: Plenum Press. 1971. pp. xiv + 493. Price £12.85

This is a collection of 22 papers, most (*sic*) of which were presented at the ACS Symposium on highly cross-linked polymer networks held in Chicago in 1970. Their commendably rapid appearance in book form has been facilitated by photolithography of the original typescript, a technique increasingly used by publishers as much to contain costs as to save time. In view of this, the price must be considered high. Again, whilst most authors had access to typewriters (and typists) able to cope with Greek symbols and mathematical formulae, some did not, and one or two of these were untidy penmen. The facsimiles of their scrawls do not enhance the appearance of a work of such erudition.

It is, perhaps, invidious to select individual authors for mention, but such well known names as Gordon, Bikerman, Landel, Dusek and Prins may serve to indicate the generally high level of these presentations. As the editors remark in their preface, most studies of structure property relationships in the forties and fifties were on polymers in the rubbery state and, of necessity, were based essentially on the continuum approach. Now the more difficult problems of the glassy state and network inhomogeneity are being tackled. Roughly half the papers are concerned with continua, the rest with inhomogeneous networks. Naturally, there is no shortage of statistical mechanics and other mathematical theory, but it is significant that most if not all contributors emphasise the nature of the experimental evidence and the shortcomings of the techniques currently available.

Of particular interest to readers of this *Journal* will be the papers on the stages of polymer network formation (Gordon *et al.*), intermolecular forces in polymers and liquids (Cuthrell), glass points of polymer networks (Chomppf), inhomogeneities induced by crosslinking (Dusek), and swelling (Rigbi). Polymer scientists for many years have intuitively recognised the significance of network interpenetration: the papers of Sperling *et al.* and of Frisch *et al.*, though short, do at least show that detailed treatment of these difficult systems is at last within reach. Bikerman's review of the rupture work of cross-linked polymers raises some fascinating questions and strongly opposes the long postulated identification of rupture work with surface energy. Cogent arguments are presented in support of the view that, in reality, work is done on the deformation leading to rupture rather than on the break itself, a concept which is in better accord with observation and permits the rupture of solids and liquids to be treated in the same way.

A. R. H. TAWN

Student Review

Paint Technology Manuals. Part Seven: Works practice

Chapter IV. Paint manufacture

(Part II)

Paint milling machinery

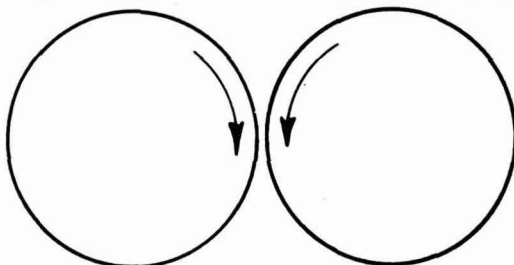
Machines used for dispersing premixed bases

Machines which are used to disperse premixed bases include multi-roll mills, single-roll or bar mills, rotating surface mills—colloid mills, sand and bead mills, and sealed sand mills.

Multi-roll mills

The principle upon which these machines operate may be envisaged by considering two parallel rollers rotating in opposite directions with a small gap between them.

If the two rollers are of equal diameter and rotate at the same number of revolutions per minute or if the peripheral speeds of two rolls of unequal diameter are the same, then there is no relative motion between the two rollers at their points of closest approach.



Therefore there would be no substantial shear forces in a layer of a fluid filling the gap between the rolls*, so that the only force operating on the fluid is a crushing action on any solid particles present which are too large to pass through the gap. However, if the two rolls are rotating at unequal peripheral speeds, for instance one travels 1.5–2 times faster than the other, then there will be shear forces in the fluid within the gap. Since, at a given rate of shear, the shear forces will increase proportionally with the viscosity of the fluid, roll mills are most effective when used with highly viscous mixes.

In agreement with theoretical reasoning, it is found in practice that, after passage through the gap, the fluid will adhere to the faster roll as a thicker layer than it does to the slower roll. Multi-roll mills have been constructed with two, three, four or even five rolls, but all except the triple-roll mill have virtually disappeared from the paint industry. The use of the triple-roll mill has markedly decreased during the last twenty years, largely because of the high cost of using it. It is undoubtedly capable of making small batches of paint cheaply, but as only a small batch can be made at a time it is unsuitable for making larger volumes and the labour costs are high because they require almost constant attention. Triple-roll mills give, however, perhaps the most effective means of obtaining a very high degree of dispersion.

*This is true only if the amount of fluid brought into the gap by the rolls does not exceed the amount which can pass through them without causing flow in the fluid. When, as is usual, the fluid is brought to the gap at a greater rate than it can pass through, flow will occur and minor shear and compressive forces are present.

Interest in the behaviour of fluids on rolls is not limited to paint manufacture; it is important in some printing processes and in the application of paint by rollers, e.g. tin-plate. Papers relevant to this general behaviour, which are suggested for further reading, are: Mill, C. C., *JOCCA*, 1961, **44**, 596; Mill, C. C., and South, G. B., *JOCCA*, 1963, **46**, 487; and Cropper, M., *JOCCA*, 1972, **55**, 128.

Triple-roll machines

The triple-roll machine, the most widely used form of multi-roll mill, consists of three parallel rolls running at different speeds (see Fig. 18); each rotates in the opposite direction to that of the roll which it nearly touches. Material is fed between the "nip" of the slowest pair of rolls, transfers mainly to the faster of the pair, is carried into the second nip of the machine and again transfers mainly to the faster of the pair of rolls; it is finally removed by a scraper blade on to an apron in front of the machine from which it passes to a container. The pressures at each nip are variable, but the relative rotational speeds of the rolls are not. The rolls are made of either chilled steel or granite; the latter is unusual in modern machinery, except for making special products. Some of the causes of this change are the greater accuracy to which steel rolls can be machined, the homogeneity of the surface and the ease with which water cooling of the rolls can be included; recently there has been some reversion to granite rolls. Other changes in the development of these machines include greater rigidity of the frames and the shafts on which the rolls rotate and, with the introduction of roller or ball bearings in place of plain bearings, greater

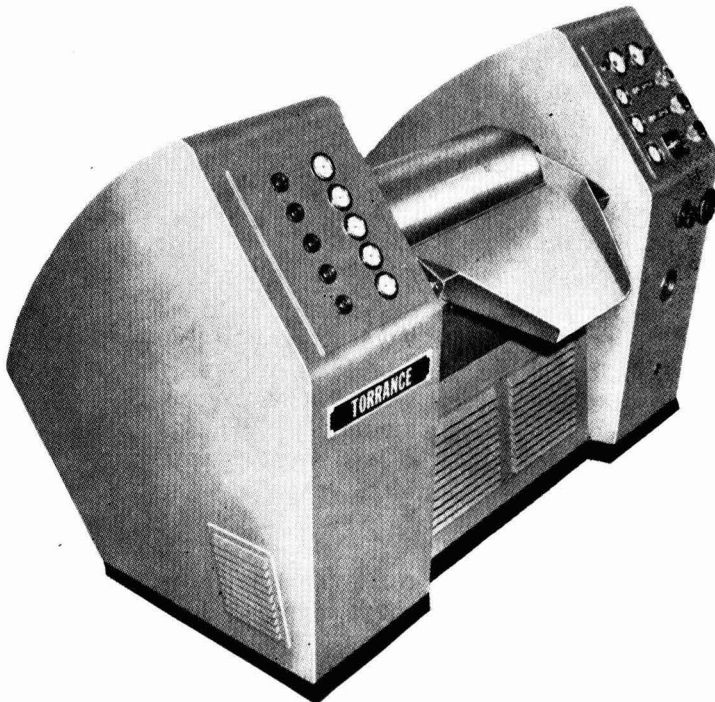


Fig. 18. Triple-roll mill (courtesy of Torrance & Sons Ltd.)

accuracy of alignment of the rolls. In addition, the means of varying the gap and pressure between the rolls has developed to a high degree of accuracy with the introduction of micrometer settings on the handwheels, and the old difficulty in the gearing (which was due to variation in the depth of engagement of the teeth as the rolls were moved) has disappeared with indirect methods of driving. There is little uniformity in the ratio of the rates of rotation of the rolls; 1:2:3 is probably the lowest used for general purposes and 1:3:9 is the highest in general use. Parallel with other developments which have taken place, overall speeds of rotation have increased, but no uniformity seems to exist and a mill should be tested with the material to be produced before deciding on either the speed ratios or the overall speeds. Three-roll mills commonly have the centre roll supported so that it will oscillate slowly with a lateral displacement of about $\frac{1}{2}$ in along the axis of rotation.

Two other factors require consideration, viz., the method of limiting the spread of the feed in the first nip, and the scraper for removing the product. Originally, the feed was constrained by two wooden "cheeks", which were carried by a bar supported by the main frame. These were adjustable laterally so as to allow a spread along the whole surface of the front roll when the machine was in use, but the tendency nowadays seems to be for the use of a hopper similarly supported from the frame. This may be satisfactory when similar materials are being produced regularly, but when the machine has to deal with a large number of products, each of which has different milling properties, then adjustable cheeks provide the best solution. The base of the hopper and cheek is made of phosphor-bronze which, being softer than the chilled steel roll, results in sacrificial wear and so ensures good seating on the rollers.

The scraper is supported by the apron and consists of a thin flexible steel strip. This is adjusted against the front roll in an approximately tangential position, the angle between the blade and the radius of the roll at the point of contact being slightly more than 90° . If the angle of contact or the thickness of the blade is increased, quite a large proportion of the more finely divided product will be found to pass between the scraper and the roll; the scraper then behaves similarly to the bar in a single-roll mill, inasmuch as the coarser particles are retained and removed by the scraper. Scraper maintenance is an important factor in determining the output and the operator should keep a close watch on this vital part.

In production, the machine is fed with premixed material, usually as a heavy paste, but sometimes in a semi-liquid condition. Initially, the front and back rolls are set at a very slight clearance; some paste is fed on to the back roll and the machine started. The back roll is adjusted, making use of the micrometer settings, so that a uniform feed at the desired rate is obtained along the whole of the operating length of the roll; the pattern made by the paste on the back roll should be uniform throughout its length. The front roll adjustment is made, again making use of the settings, so that the paste is taken evenly off the middle roll and uniformly covers the front roll over almost its full length. The scraper is so adjusted that a perfectly uniform ribbon of paint is taken off the front roll and passes down the apron.

When the machine is operating satisfactorily and the desired degree of dispersion is obtained at the delivery point, the initial delivery of paint is removed from the apron and returned to the back roll, and the run continued.

Once the correct pressures are set on the front and back rollers, balanced on each side, the triple-roll mill is suitable for long runs; the mixer or mixers performing the premixing operation are arranged to feed continuously into the hopper and the operator removes containers of once-through material from the front.

Attention must, however, be given to the following points. It will be noticed that the material delivered from the end parts of the rollers is not so well dispersed as the bulk from the centre of the delivery apron. The edges should be scraped from the apron and returned to the back roll, or separated from the main product by means of guides, collected and returned to the feed. A falling off of dispersion may also be noted towards the end of a run, owing to some refining action in the first nip of the rolls, and this is usually most noticeable with high ratio mills and the more liquid feeds. The product should, therefore, be watched closely towards the end of the run, returned for re-grinding if necessary, and the final residue discarded. During a run, paint may tend to dry on the ends of the rollers; this is controlled by a drip feed of linseed oil or appropriate medium to keep the ends moist. Formulation of the premix paste is important; pigment/medium ratios will vary for different pigments as well as for different media, and the consistency should generally be as high as possible.

The triple-roll mill is probably the most dangerous paint machine to clean, particularly at the first nip. A guard that removes most of the danger can be constructed by supporting a piece of flat steel sheet, say 1½ in wide, from a structure similar to that used for the cheeks or hopper; the bar with the guard is substituted for the bar which supports the cheeks. The flat steel sheet is so adjusted that, when in position, it just clears the surface of the rolls. The machine can then be cleaned while it is running with very little chance of the operator's fingers and hand being pulled into the nip. When cleaning, particular attention should be paid to the hopper seating edges, roller ends and sides, scraper and apron edges and sides. It should always be remembered that the scraper edge is razor sharp.

Other points to be noted in triple-roll mill maintenance are:

if the mill is not to be used for some days, the cooling water supply must be turned off and the rollers covered with a thin layer of a non-drying oil, such as castor oil (not mineral oil) to protect from condensation and rusting;

drip feeds to roller ends and lubricating oil feeds to the roller bearings should be kept clean and operational;

occasionally a mild abrasive and linseed oil may be run through the machine to maintain "tooth" on the roller surfaces.

The modern high speed roller mill provides the most satisfactory means available for the production of high viscosity, well ground pastes. Labour costs, however, are high, particularly when considered in conjunction with premix and thinning time, and it is advisable to keep runs as long as possible.

Whilst remaining the mainstay of printing ink manufacture, the triple-roll mill has been largely outmoded for the manufacture of most types of paint.

Single-roll mills

These comprise a single water-cooled roll mounted on bearings and driven in such a way that it both rotates and oscillates on its axis. A close fitting hopper is supported by the frame of the machine (Fig. 19); the front of the hopper is

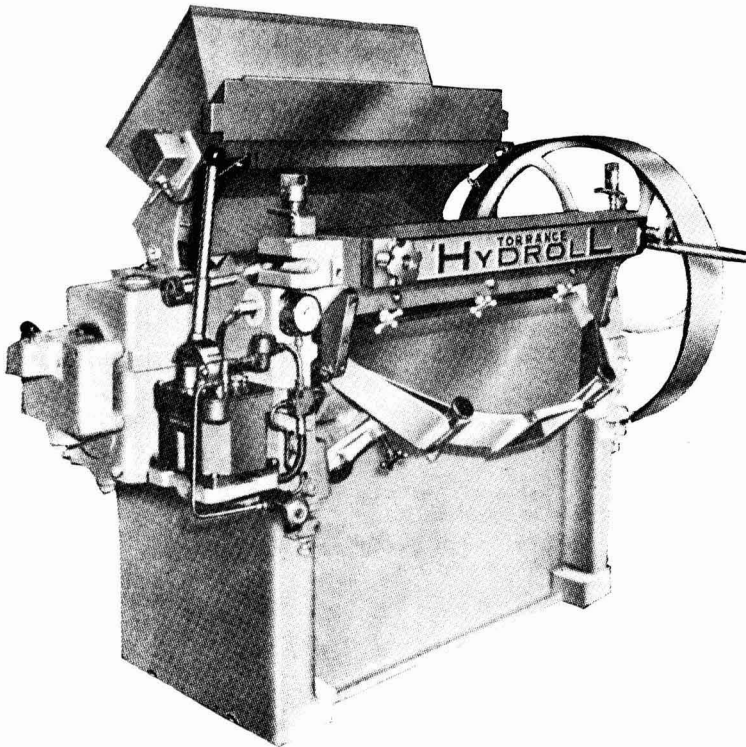


Fig. 19. Single-roll mill (courtesy of Torrance & Sons Ltd.)

fitted with a soft iron bar which is pressed on to the chilled iron roll by means of three or five screws manually or hydraulically operated and spaced over the length of the bar. The material in the hopper is drawn by the revolving roll into the gap between the bar and the surface of the roll; it is here that the shearing action takes place. The material passing under the bar is carried on the surface of the roll until it is removed by a scraper. The shearing and dispersion action of the single-roll mill is limited; coarse particles are, however, retained behind the bar so that the mill is often used for refining and reconditioning purposes.

Development of the original design of the single-roll mill followed very closely the development of the triple-roll mill.

Hydraulic methods are now used to exert pressure on the bar, which is made extremely rigid, and a number of hydraulic rams in cylinders are spaced

along it. These in turn are supported by a very rigid frame which is independent of the hopper. The result is that pressure is exerted evenly over the whole length of the bar.

The sealing of the ends of the hopper where it is in contact with the roll is important; one method is to line this portion of the hopper with brass. This avoids undue wear on the roll because the softer brass wears away more readily than the surface of the chilled iron roll. Adjustment may be effected by lowering the hopper by means of adjustment screws with a fine pitch thread.

The bars used are of plain rectangular section either with a slight chamfer or an inclined vane on the hopper side. The use of low angled vanes increases the pressure that can be applied to the bar without breaking the paint film, thus increasing efficiency and output. The grinding efficiency is further increased by recessing the grinding bar, so that the film gets two positions of shear pressure, interspersed with violent agitation in the recessed section of the bar (Fig. 20).

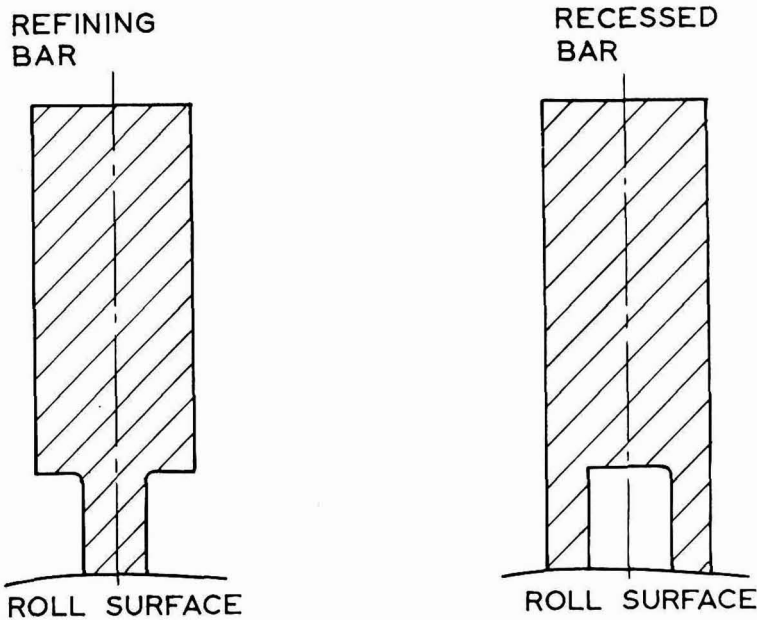


Fig. 20. Normal and recessed grinding bars for single roll mill

The general design and adjustment of the scraper are similar to those described for the triple-roll mill, but since wear of the scraper is usually considerably more than in the case of the triple-roll, some means of continuously adjusting it is most valuable. It is usual to arrange for the product coming from the outer edge of the roll to be removed from the main output. This is achieved by adjustable dividing strips which are clamped to the sides of the apron and divert the product on the outer sides of these strips through separate exits from the apron. Material collected in this manner is returned to the hopper for further treatment.

The single-roll mill is used for milling and for refining material already milled. For refining, the simple bar is used and this holds back coarse material until the end of the run. The mill should never be allowed to run to the dry point, as the coarse material remaining would be carried through and score the bar. For a similar reason, when cleaning the mill the bar should always be raised. On fairly long runs coarse particles are apt to become trapped behind the bar, thereby reducing the output and these should be removed by stopping the roll for a moment and pulling it round in the reverse direction. From time to time the bar should be reground in contact with the roll by removing the scraper and running the mill with a little very fine carborundum and oil for a short time, when the bar should attain an even matt surface.

For use as a dispersion mill, the recessed or vane bar is used. The premix is prepared at a semi-paste consistency with adequate vehicle solids and the minimum of thinners. Efficient premixing is essential for the best results. A double compartment, horizontal shaft mixer, mounted above the single-roll, is typical. In this, one batch is premixed while the contents of the other compartment, previously premixed, is discharged to the hopper of the mill. After charging the hopper, the mill is started with only slight hydraulic pressure, and this is then increased to the minimum capable of giving the required degree of dispersion. The ends are separated from the main delivery, as mentioned above, and remilled. With pigments that are difficult to disperse, a second pass may be necessary. The dispersed paste is usually collected in a changeable pan of a vertical mixer, where the remainder of the vehicle, thinners, etc., is slowly added.

When cleaning the mill, particular attention should be given to the removal of any paint from the hopper seating, from the bar housing and from the scraper.

These mills are not suitable for handling coarse and abrasive pigments and extenders. It should also be noted that the very intense shear force operating between the bar and the roll generates considerable heat and, even with water cooling, difficulties may arise with some sensitive media.

Colloid mills

These mills, also known as high speed stone mills, are the modern version of the stone mill, which was one of the earliest used in the industry.

The machines are comparatively small in size (floor space 4 sq ft), the grinding stones are up to 10in in diameter and usually contain carborundum. The top stone is stationary and the bottom rotates in close proximity at speeds in the region of 3,600 revolutions per minute (Fig. 21).

The paint base flows by gravity from a conical hopper on to the eye of the stator stone and is thrown by centrifugal force, with or without the aid of an impeller, into the gap between the working surfaces, where it is subjected to a short period of intense shear and turbulence. A fairly free flowing mill base is necessary, and attention to mill base composition essential, for optimum yields.

Colloid mills are extremely versatile and will handle a very wide range of products in aqueous or solvent based media. The mills are easily cleaned and

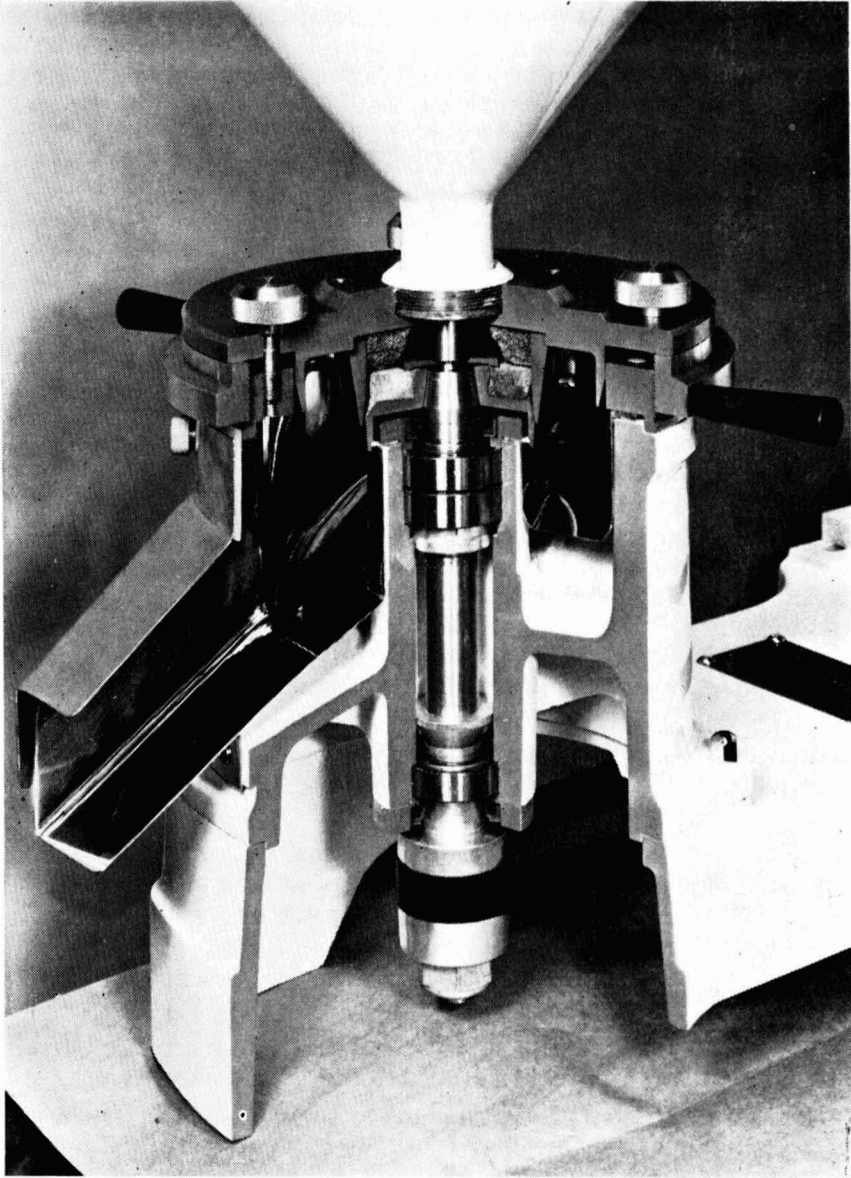


Fig. 21. Colloid mill (courtesy of Premier Colloid Mills Ltd.)

are of particular use in the “smalls” department. One typical use is for finishing an emulsion paint premixed in a high speed mixer; outputs as high as 1,000 litres per hour from a 6in mill are claimed.

Sand mills

The sand mill, developed by E. I. du Pont de Nemours, is a pump-fed machine which can be adapted to continuous or batch production; its advent has transformed paint production methods over the last decade.

The machine consists of a water jacketed grinding chamber or shell in which there is a central agitator shaft, carrying a series of discs spaced along its length and driven by means of an electric motor at fairly high speeds, e.g. peripheral speeds of 2,000ft per minute (Fig. 22). In this chamber is a charge of grinding media (Ottawa sand of 20-40 mesh, ballotini, steel balls or zirconium oxide pellets). The premixed mill base is pumped into the bottom of the grinding chamber through a one-way valve and then through the grinding media, which are kept in motion by the agitator (Fig. 23) and finally flows out of the machine through a screen at the top which retains the grinding media. The degree of grinding is controlled by the length of time that it takes the base to pass through the grinding chamber (dwell time) and this is in turn controlled by the pumping rate. The principle of action is that the individual grinding media are rapidly accelerated by the agitator, which produces high pressures at the points of contact of the sand or beads; the mill base passing through is subject to shear at these points, thus effecting pigment dispersion. Because of the small diameter of the sand or beads (normally less than 2mm) there are an enormously greater number of points of contact per unit volume of grinding media than with larger diameter media, which results in high throughput rates from relatively small machines.

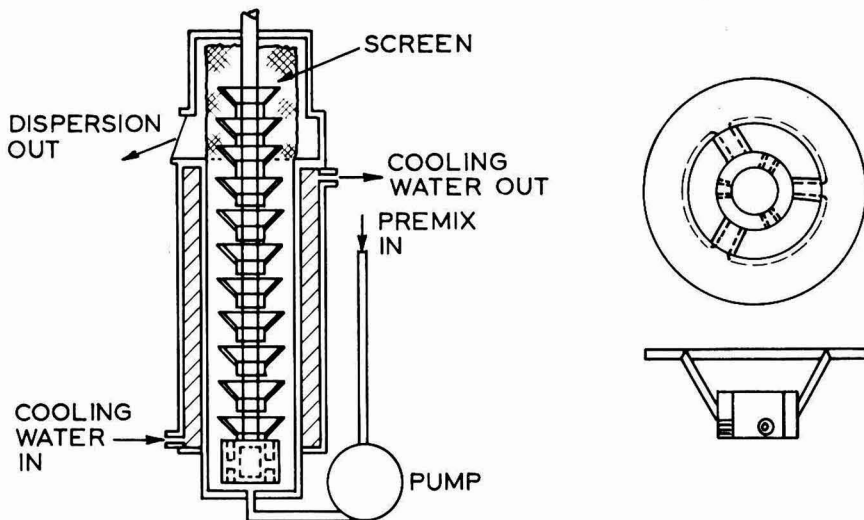


Fig. 22. Sand mill production unit, showing impeller design and detail of disc (courtesy of Du Pont)

The mill can accommodate very wide variations of batch size and this fact, coupled with the excellent quality of the final dispersion, has resulted in the growing popularity of the equipment. A further feature is that it does not need highly skilled operators and, since little attention is required during running, one operator can look after several machines, thus leading to high productivity per man hour. However, it must be stressed that, in order to obtain good results, the mill base must be carefully formulated and it is essential that good premixing is carried out, preferably with a high speed disperser.

When formulating the mill base the points shown below must be kept in mind.

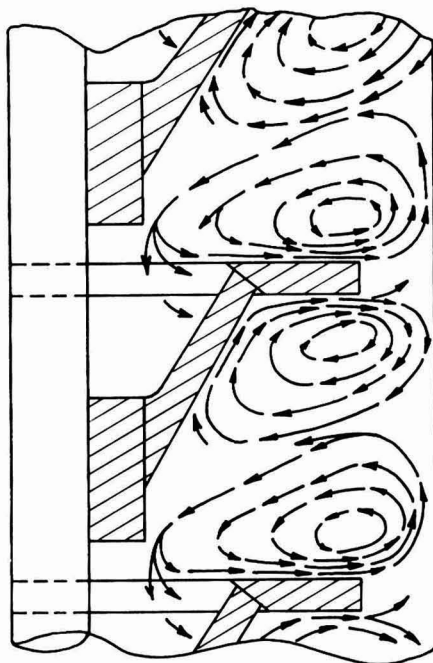


Fig. 23. Flow pattern around discs (courtesy of Du Pont)

The pigment/vehicle solids ratio must be such that the mill base is stable and not susceptible to colloidal shock on dilution. With pigments of low oil absorption, a medium of 25 per cent resin solids is generally suitable; for pigments of high oil absorption a medium containing 35 per cent resin solids should be used.

The mill base must be sufficiently free-flowing to be pumped easily. A range of 65–105 Kreb units is recommended, with best results at 80–90 KU. When using organic pigments that develop substantial structure when fully dispersed, the mill base should be of lower consistency, otherwise the dispersed material will not flow from the mill.

Du Pont suggest the following pigment concentrations:

Titanium dioxide	57%	Red iron oxide	33%
Scarlet chrome	71%	Toluidene red	23%
Middle chrome	63%	Phthalocyanine blue	9%
Ferrite yellow	57%		

Small scale tests with the pigment and medium should be carried out before bulk production is attempted with a new formulation. A small beaker attachment is often supplied with production mills to enable such trials to be carried out.

Equal volumes of sand, or other medium, and mill base is considered to be the optimum.

The operating temperature of the mill is about 50°–60°C. Heat sensitive media and fast evaporating solvents, therefore, should not be used.

Pigments containing hard or oversized aggregates and hard extenders will not disperse satisfactorily on a sand mill.

The following factors should be borne in mind when operating these mills.

Grinding media. In Du Pont's original patent on the sand grinder, Ottawa sand of 20-40 mesh (approximately 0.18mm) was specified as grinding medium, and this is still used widely. The sand contains a small amount of finer particles which are removed before use for pigment dispersion. This is achieved by running the charge of sand in the mill together with an unpigmented composition for about one hour, when the fines pass through the screen and are so eliminated. Glass beads (ballotini) of 1mm diameter are also used, and whilst from the point of view of size they may appear less effective as grinding media, it is generally accepted that their use does not lead to loss of grinding efficiency. Zirconium oxide beads, having the advantage of higher specific gravity and hardness, will disperse a given mill base at a much faster rate than sand or glass beads. They can also be used with more viscous mixtures and will disperse some pigments which sand cannot do; they are, however, expensive, and can accelerate wear of the discs.

Cleaning the mill. At the end of a run, cleaning is carried out by pumping solvent through while the mill is still operating. This will remove most of the mill base, and the solvent can be used in the final let-down. When there is to be a substantial colour change and contamination cannot be tolerated, the charge of grinding media is removed and the pump and lines thoroughly cleaned. As grinding shells are readily changed, it is usual to have a number of shells for each mill and to reserve the different shells and their charge for a particular pigment or resin. The shells and their charge may be kept immersed in solvent.

During a temporary shut down, it is necessary to clean the screen by brushing down with solvent, and to pour a little solvent on top of the mill to prevent skinning over.

Sealed sand mills

The sand mills described in the last section are subject to the disadvantages in that:

if when starting up, the premixed paint is pumped into the dry sand too fast, the air in the interstices of the sand can be expelled so rapidly that some of the latter may be expelled from the mill; when the sand is partially wetted with paint, this can involve a considerable cleaning up operation;

when the premixed paint is pumped into the mill faster than the finished paint is able to pass through the screen, an overflow can occur;

when volatile solvents are present in the grind charge, considerable loss by evaporation may occur;

the evaporation of the solvent mentioned above may give rise to unpleasant odours in the machine shop, and a fire hazard may arise if low flash solvents are present; this danger is enhanced because of the considerable temperature rise during the operation of the mill.

A sealed unit has been developed (see Fig. 24) which overcomes these difficulties. It is designed to operate at slightly above atmospheric pressure under the influence of the input pump. This increased pressure forces the finished paint more rapidly through the screen or alternatively the mill may operate with a higher viscosity charge. The machines are capable of processing products of any viscosity provided that they can be handled by positive displacement pumps. A higher output can thus be achieved by using a more highly pigmented mill base followed by dilution with additional medium after dispersion. Highly pigmented mill bases may be dilatant and it is claimed in British Patent 1,021,592 that this difficulty can be overcome by metered injection of medium at one or more levels in the grinding shell.

A pressure switch is fitted to the product input pump which cuts out the motor if the pressure becomes too high, for instance owing to a blocked screen.

A certain amount of difficulty has arisen with sealed mills, owing mainly to the use of increased pressure. If the pumping rate is too high, the pressure

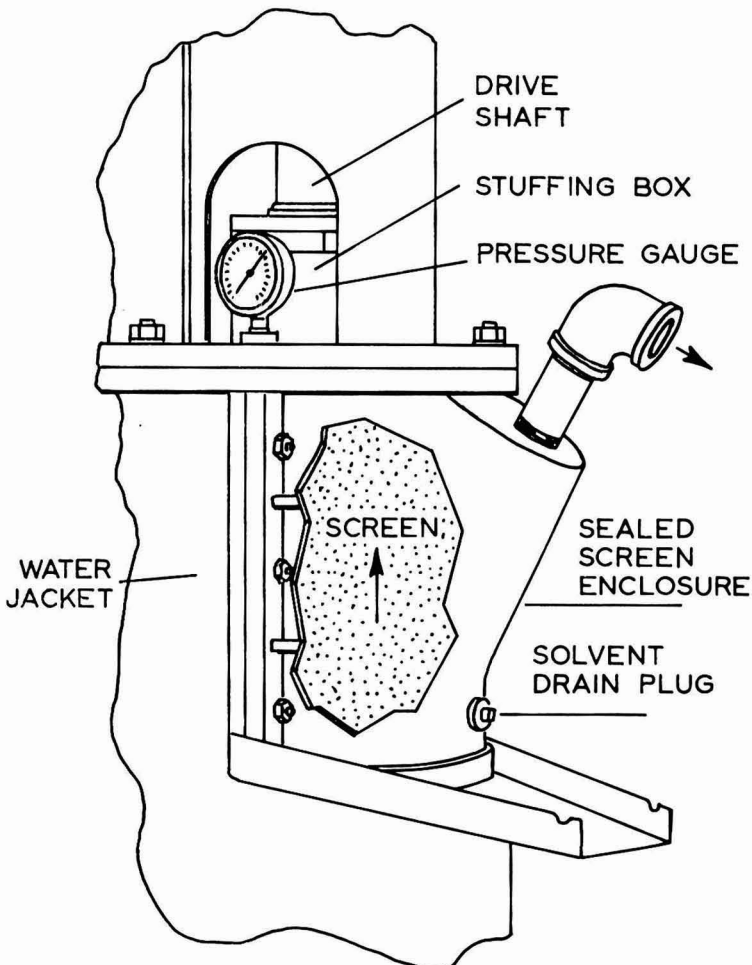


Fig. 24. Detail of a sealed sand mill (courtesy of Morehouse Cowles International SA)

may rise to such an extent that leakage through the gland sealing the drive shaft occurs, and this may result in paint escaping through the gland and flowing over the external parts of the machine. Improved designs are becoming available which avoid this difficulty by pressurising the seal with compressed air or inert gas. The seal is connected to a pressure switch which prevents the machine from being started without the necessary pressure, and also cuts out the motor driving the pump if the pressure rises above a predetermined limit.

Other advantages claimed for the sealed mill are that no drying occurs if the mill is left overnight and, under these circumstances, cleaning is facilitated. No air is injected into the mill during operation, so that oxidation is reduced to a minimum.

The grinding media used in sealed mills are usually ballotini, ceramic beads or sintered beads of zirconium oxide. These may have a higher density than some of the media used in open sand mills. To avoid machine and bead wear, the higher the density of the media the greater should be the viscosity of the grind charge in order to ensure an even distribution of the beads throughout the grinding shell.

A fairly extensive literature exists on sand grinding; interesting papers for further reading are: Callahan, W. B., and Manz, W., *JOCCA*, 1964, **47**, 737; Mathews, A. C. B., *JOCCA*, 1967, **50**, 407; Carr, W., *JOCCA*, 1970, **53**, 884; (the last named paper is a comparison of sand grinding with ball milling).

No text has been printed on this page in order that reprints of the extracts from Part Seven of the Paint Technology Manuals may be run-on at the time of printing this issue of the Journal. It is intended at the end of the year to collate and bind these extracts and to offer them for sale. Registered students of the Association will be able to purchase one copy each at a considerably reduced rate.

Manchester Section

Modern applications of polyurethanes

On Wednesday 29 March, some 50 members attended at the Manchester Literary and Philosophical Society to hear Mr A. C. Jolly of Synthetic Resins Ltd. present a paper entitled "Modern applications of polyurethanes".

The lecture consisted of a brief outline of the wide variety of applications in which polyurethanes were involved to date. A quick review of the major properties of this family of polymers was also made together with the elementary chemistry. The lecture continued with comments on current trends in the use of polyurethanes in the paint and varnish industry, with reference especially to intumescent polyurethane products—in particular of the moisture curing type. Some considerable time was spent in discussing the application of elastomeric polyurethanes in the coating of flexible substrates, in particular textiles. The importance of these saturated lacquers was also stressed in the context of over-print varnishes and in particular the coating of pvc. Finally, the development of urethanes in flooring was discussed with particular reference to aggregate-filled systems. The talk closed with some comments about the future, especially in respect of urethane emulsions and polyurethane powder coatings. Mr Jolly pointed out that his object was to present polyurethanes in proper perspective and dispel the two incorrect theories of "universal panacea" on the one hand and "gimmick" on the other.

Mr Roy Wilkinson assisted with slide presentation and joined Mr Jolly during the lively discussion time that followed.

Mr Norman Piper proposed the vote of thanks which was received with enthusiasm.

A.MCW.

Correspondence

SIR—I read with interest the papers in the April 1972 issue of *JOCCA* presented by Hoffmann *et al* and Hoffmann concerning the hiding power of paints. The object of the exercise is defined in the introduction as being to determine the “number of units of surface area that can be obliterated by a given weight or volume unit of paint”.

The method proposed “needs a great deal of calculation and a simplified quick procedure which obviates this would therefore be of advantage”—Hoffmann. His further suggestion of measurements relative to a “standard coating” seems rather dubious, especially when different laboratories are involved.

You will be aware that in *JOCCA* 1968, **51**, 191-197, I described an opacity gauge for this purpose. This instrument is comparable with the fineness-of-grind gauge, but has a black and white channel. The paint to be examined is drawn down the gauge in the same manner as a fineness-of-grind gauge and is allowed to dry. Normally evaporation of solvents is sufficient as the opacity changes little during oxidation or stoving. The wet thickness giving dry opacity can be read directly from the gauge and the covering power of the paint is simply 1,000 divided by the dry opacity thickness, the result being given in m^2l^{-1} as the gauge is calibrated in microns. Several hundreds of these instruments have been sold, which are I trust proving useful to the various laboratories and factories who have purchased them. Possibly the best way of reading the opacity gauge would be to use a mask with a 5mm slit placed across the channel and to note the two positions where the black and white halves are just distinguishable and just indistinguishable and to average the two readings.

We did attempt to carry out a survey of opacity measuring techniques in which we compared results obtained from the opacity gauge, the cryptometer, inspection of different film thicknesses over hiding power charts and contrast ratio determination, but found this to be too time consuming for a small laboratory concerned mainly with other products.

It would be interesting to learn whether other organisations have carried out tests of this nature and would be prepared to publish them.

Yours faithfully,

I. H. DAY

*Polymark Limited,
Jeddo Road, Shepherds Bush,
London W12 9EE
21 April 1972*

Information Received

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

D. G. Bennett Chemicals Limited has announced its appointment as sole UK distributors of the polyethylene, polypropylene and ethyl vinyl acetate moulding powders produced by **L'Air Liquide** of Paris.

A new PTFE low friction, anti-stick additive has been introduced by **Du Pont**. The new product, *Vydax 78U*, is an extension of Du Pont's range of fluorocarbon telomers for home and industrial use, and in its powder form can be added to paints, waxes, polishes, greases and industrial processing soaps. It is also available dispersed in *Freon TF* for use as a spray-on coating.

Allied Colloids Manufacturing Co. Ltd. has received the Queen's Award for Industry for export achievement. Following a decision to promote exports particularly, the company's overseas sales have increased from a figure of £129,000 in 1966 to £1,432,000 in 1971.

Allied Colloids has also introduced a new patented acrylic-based dispersant designed for high and semi-gloss emulsion paints. For use with inorganic pigments, *Dispex G40* is claimed to give improved dispersion and opacity without causing a reduction in gloss. Supplied as an aqueous solution with 40 per cent active content, *Dispex G40* is also soluble in glycols and can be employed in anhydrous mill bases. Also from this company is *Aleolec 532*, a new carboxylated vinyl polymer for flexographic inks and lacquers.

It has recently been announced that **Bayer AG** is now the company style of **Farbenfabriken Bayer AG**. This change took effect from the company's general meeting in June.

F. Copley & Sons has announced the availability of a new booklet entitled "Rheological measuring instruments". After a brief general discussion of the principles of viscosity measurement of Newtonian and non-Newtonian substances, the booklet describes the range of instruments manufactured by **Kombinatbetrieb Prüfgerate-Werk** of Dresden, whose instruments are supplied by Copley in the UK.

The third edition of the review "Patents on UV paint curing" has been published by **R. H. Chandler Ltd.** The steady stream of patents published on this topic have necessitated the production of an expanded third edition, which contains abstracts of over 90 patents.

Rex Campbell & Company Limited has recently been appointed distributor of *Stay/Steel* stainless steel flake pigment. This product was first produced in the US by Pfizer Inc., and marketed in the UK by Pfizer Ltd. Production was taken over by **US Bronze** in 1971, and it is this company's UK subsidiary, **Canbro (UK) Ltd.**, that has made the appointment of Rex Campbell.

A weekly bulletin containing up-to-the-minute abstracts of paint industry information, individually tailored to the recipient's requirements, is to be offered by the **Paint Research Association** to its members and to subscribers to the quarterly "World Surface Coatings Abstracts". The system is to be based on an IBM 360 computer,

into which abstracts of all important papers from the large range of journals and patent literature that the PRA scans will be fed. The bulk of the information will then be scanned weekly to extract all the abstracts in a given subscriber's "profile" or subject range. The subscriber is then supplied with abstracts of about 100 words typed in an easy-to-read format. The cost of this service would be £30 per profile, additional profiles being £20 per subscriber. The PRA will advise on the drawing up of each profile as part of the service.

Another of the PRA's developments, prefabricated paint films, has recently been featured on the BBC-TV programme "Tomorrow's World". These films are laid down on polymer foils in the factory, and when dry are peeled off and applied to the substrate using a suitable adhesive. Although not intended to replace conventionally applied paint for normal uses, prefabricated films offer advantages for porous substrates, rough surfaces such as concrete and steel, and damp or semi-immersed structures. Another interesting suggestion is to lay the coating on a textured surface previously coated with a release agent; the dried film is then reversed to give a textured coating.

On 30 June, **Albro Fillers & Engineering Company Limited** celebrated 50 years' service to the packing and bottling industries. Albro supplies several types of filling equipment for the paint industry.

Two new vinyl acetate-ethylene copolymer emulsions are now available from **Vinyl Products Ltd.**, which claims to be the first company to manufacture this type of product in the UK. Full details of the emulsions, *Vinamuls 3240* and *3250* are given in Vinyl's "New development note G106"; they are the first in a series of high-pressure emulsions incorporating ethylene and other gaseous monomers, and are expected to find application in adhesives and binders, surface coatings, and textile and paper finishes.

A new tank level system that is particularly well suited for storage bins containing pelletised carbon black and other such pigments is announced by **Metritape Inc.** The system consists of DBS-CH sensing elements with a tensile strength in excess of 3 tons suspended within each of the tanks to be monitored. Leads run to a central control unit, at which the levels in each tank can be monitored instantly after operation of a selection switch; all full tanks show an illuminated high-level light indication. A remote operational display can also be provided at the loading dock, indicating tank level conditions and giving audible warning when the tank is nearly full.

Section Proceedings

Bristol

A meeting of the Bristol Section was held on 7 April 1972 at the Royal Hotel, Bristol, when the speaker for the evening was Mr J. L. Thomas of the University of Bristol. The subject of Mr Thomas's talk was "The implications of the Industrial Relations Act at factory level".

Because of the intense interest shown by members in this subject, the meeting took the form of a discussion, during which Mr Thomas outlined various aspects of the new Act which were then discussed. Some of the topics covered included the rights of individuals to join or refrain from joining trade unions, the benefits to trade unions from registering under the new Act, conditions under which union shops could operate, and the conditions under which employers could dismiss employees. The meeting was eventually curtailed through lack of time and a vote of thanks for an excellent presentation of the subject was proposed by Mrs E. Harper and warmly supported by all members present.

T.I.P.

Irish

Some new approaches to solvent formulation

Mr C. J. Nunn of Shell Research Ltd. gave a talk entitled "Some new approaches to solvent formulation" to the Irish Section on Friday 24 March.

He began by stating that the solvent mixture in a paint or lacquer could have a marked effect on its application, characteristics, appearance and performance. Many solvent mixtures contained three or more components, and their selection presented problems owing to the lack of data for anything but the simplest blends. The actual choice would probably depend upon a combination of available data, the formulator's general experience, and the results of a few laboratory trials with the aim of achieving a satisfactory performance at minimum cost.

With the availability of computers, Mr Nunn stated that more systematic approaches to solvent selection were possible, and he detailed two of them.

A planned statistical approach was carried out on a coating containing a multi-component solvent blend. The composition of the blend was varied so that the relevant formulating area was covered with a minimum number of experiments. In programmes completed, quantitative measurements were made on the viscosity of test lacquers and the flow of the applied film. The resulting data was processed by computer and could then be used in a variety of ways, such as finding the cheapest solvent mixture to meet a specific performance requirement.

A more fundamental approach involved the use of the basic properties of a solvent mixture. These are taken to be "solvency" (as indicated by three parameters), viscosity (which related to solution viscosity), and volatility (as indicated by the time taken to reach 90 per cent weight loss on a standard evaporometer). Since these properties could all be expressed numerically, blends with specific properties could be optimised for cost by means of a suitable computer programme.

Mr Nunn emphasised that these techniques were still in their development stages, but eventually they should be of great assistance to the formulator.

He illustrated many points in his excellent talk with slides, and a very appreciative vote of thanks on behalf of the 35 members present was given by Mr D. Power.

A.R.

Midlands

Trent Valley Branch

The design and printing of bank notes

On Thursday 6 April 1972, 17 members and guests, under the chairmanship of Mr E. Hare, attended the British Rail School of Transport, Derby, to hear a lecture on the above subject given by Mr D. R. Lowther of Thomas de la Rue & Co. Ltd.

Mr Lowther's talk was in fact preceded by the Annual General Meeting of the Branch, full details of which will be published at a later date.

Mr Lowther commenced by giving a brief history of the bank note and then went on to describe the printing of currency on a world wide basis, with particular reference to the contribution made by Thomas de la Rue & Co. Ltd., which currently provided notes for almost 70 central banks and issuing authorities.

He then dealt with the special printing processes involved and the way in which their characteristics were exploited, and outlined briefly the utilisation of craft skills and technical expertise. Finally, some indication was given of the tremendous amount of work that was required and also the sequence of events that lead up to the production of a new currency.

Mr Lowther illustrated his lecture with a fine series of slides.

A vote of thanks for this very interesting talk was proposed by Mr J. R. Bourne and heartily endorsed by all present.

D.F.G.

West Riding



At the West Riding Section Luncheon Lecture (left to right) Mr D. Morris (Vice-Chairman), Mr D. H. Du Rieu (Hon. Secretary), Mrs K. Driver (Chairman), Mr S. Coppins (Lecturer), Mr L. H. Silver (OCCA President Designate)

Luncheon Lecture: The paint industry and the Common Market

The Seventh Annual Luncheon Lecture of the Section was held on Friday 28 April 1972, at the Astoria Ballroom Restaurant, Leeds. The guest speaker was Mr S. Coppins, Deputy Chairman of ICI Ltd., Paints Division, who gave an excellent talk concerning the European paint industry and the possible effects of UK entry into the European Economic Community.

Within the EEC, paint consumption was approximately 4.5 times that of the UK and had a growth rate during the period 1963-69 of about 8 per cent per annum, compared with about 2 per cent per annum for the UK. Western Germany produced about 30 per cent, France about 20 per cent and the UK about 15 per cent of the paint consumed in Western Europe. Within any country, less than 5 per cent of consumption was accounted for by imports. During 1963-69, the Gross National Product (GNP) of France, Germany and Italy had grown by 5 per cent per annum, and paint consumption by somewhat more. In the UK the GNP had grown by $2\frac{1}{2}$ per cent per annum and paint consumption by 2 per cent, whilst in the USA the GNP had grown by $4\frac{1}{2}$ per cent per annum, and paint consumption by 4 per cent. During the period 1970-75, France, West Germany and Italy were predicting 20 per cent growth in both GNP and paint production, while the USA predicted 25 per cent growth in GNP and 20 per cent growth in paint production. In the UK, however, the forecast was for a 12 per cent rise in GNP and 10 per cent in paint production over the same period.

Entry into the EEC would lead to a lowering of tariff barriers from the current level of about 10-12 per cent to zero in 1977. These were modest tariff levels and Mr Coppins felt that this aspect alone was unlikely to have much impact on either the UK or EEC paint industry in terms of competition.

Turning to profitability, there were differences between the UK and Western Europe. In the UK, decorative paints were the most profitable, whilst on the Continent the industrial market held this position, provided the right sectors were selected. In both areas automotive finishes showed medium profitability but, in contrast to the UK, decorative paints in Western Europe showed very poor profitability, particularly the West German emulsion paint market.

Mr Coppins inferred from his wealth of data that there would be no revolutionary changes within the paint industry as a result of the UK entering the EEC.

International trade in paint was very small. The UK exported about 10 per cent of production and imported about 1 per cent. UK prices were on about the same level as those of France and Germany, below those of Switzerland and greater than those in Spain. The effect of UK entry on the decorative market would be minimal, owing to the logistics of distribution. He did not anticipate the West Europeans entering the UK market in any big way. The UK industrial paint market was less profitable than that of Europe and was unlikely to prove attractive to Continental producers. Marine paints had very poor profitability, and in any event this was already a world-wide business. Mr Coppins considered that the greatest changes might be seen in the automotive market, owing to its concentration in a few outlets and the international character of the business.

The speaker considered that, within Europe, there would be a continuation of the rationalisation which had already occurred as a result of the involvement of the German chemical industry in paint manufacture. Nevertheless there would be a good future for the small manufacturer who was able to supply a local market. Mr Coppins foresaw further sophistication of the product range by the addition of paints that were more convenient to use, and this would tend to favour the bigger company.

He felt that the UK would maintain its lead in convenience paints, as the DIY market was more highly developed than in Europe, and thought that the UK companies were better equipped to promote and sell products. Nevertheless, UK companies would be well advised to keep in touch with European markets.

A lively discussion followed, opened by Mr Silver, who asked the speaker whether he foresaw a movement of UK companies into Europe by acquisition, thus reversing the recent trend of overseas companies establishing themselves in the UK. Mr

Coppins thought that this was possible but felt that the barrier was profitability; better use could be made of the money available for investment.

In response to a question from Mr Gray, the speaker said he was not gloomy about the prospects upon entry. He believed that there would become a more cohesive West European industry in which the UK would take a part. He considered our promotional and distribution arrangements better than those on the Continent and felt that we should be able to exploit this expertise.

Referring to the annual growth rates, Dr Hargreaves wondered if the slower UK performance was due to being ahead in the first place. Mr Coppins agreed that we had a more mature economy than, for example, Italy and Spain, and it was unrealistic to expect growth rates as high as in these countries. The German, Belgian, Netherlands and Scandinavian economies were similar to ours but they maintained a better rate of improvement in GNP than the UK.

Mr Gray asked whether there was much difference between the types of paint required in the UK and in Europe. Mr Coppins said that there was no simple answer, although there were many different sub-markets, for example Germany and Austria were big users of clear varnish. However, the major markets were broadly comparable with the UK and the outstanding rate of growth was in emulsion paint.

Other questions were from Messrs Phillips, Burley, Morris and Du Rieu. The vote of thanks was proposed by Mr L. Silver.

R.A.C.

Association Dinner and Dance 1972



The President, Mr A. W. Blenkinsop, and Mrs Blenkinsop (right) with the Association's Guest of Honour, Mr A. S. Hooper (President of the Paintmakers' Association) and Mrs Hooper

The Association's biennial Dinner and Dance took place at the Savoy Hotel, London, WC2 on Friday 12 May 1972 when 280 members and guests were received by the President, Mr A. W. Blenkinsop, and Mrs Blenkinsop.

In his address of welcome to the guests and ladies the President stated that the form of the proceedings varied on this occasion in that there would be only two speeches and no cabaret, but a gift was made to each lady.

It was clear that the company approved the new arrangement as was shown by the fact that the dance floor was crowded until the end of the evening.

The Association's guests were:

Mr J. B. Cotton, President of the Institution of Corrosion Technology, and Mrs Cotton.

Mr A. S. Hooper, President of the Paintmakers' Association, and Mrs Hooper.

Mr G. Norman, President of the Society of British Printing Ink Manufacturers, and Mrs Norman.

Dr E. S. Paice, President of the Research Association of British Paint, Colour and Varnish Manufacturers, and Mrs Paice.

Mr W. Penn, Past President of the Society of Dyers and Colourists, and Mrs Penn.

Mr F. C. Porter, President of the Institute of Metal Finishing, and Mrs Porter.

Dr F. A. Robinson, President of the Royal Institute of Chemistry, and Mrs Robinson.

Replying to the President's address of

welcome Mr A. S. Hooper paid tribute to the work of the Association and its value to the industries which it serves, mentioning in particular the new professional grade for Ordinary Members introduced in 1971. The Paintmakers'

Association were delighted to welcome this innovation and had pledged their full support to the scheme. Mr Hooper's speech continued in a humorous vein which was much appreciated by the company.



New arrangements at OCCA 25 Exhibition

The Silver Jubilee Exhibition

The Exhibition Committee has announced the preliminary plans for the Twenty-Fifth (Silver Jubilee) Technical Exhibition, at which certain new arrangements are being introduced which, it is felt, will have the support of both exhibitors and visitors.

New hours of opening

As already announced, this unique annual exhibition of raw materials, plant and equipment used in the paint, printing ink, colour and allied industries will take place at the Empire Hall, Olympia, London, and the Committee wishes the following times of opening to be as widely known as possible:

Monday 21 May	12.00 hrs.—18.00 hrs.
Tuesday 22 May	} 09.30 hrs.— 18.00 hrs. each day
Wednesday 23 May	
Thursday 24 May	

It has been thought for some time that an earlier opening on the Monday would be welcomed, and the new arrangement affords six hours on the opening day.

Exhibition Dinner

At the same time, it has been suggested that many exhibitors and overseas visitors

would welcome an Exhibition Dinner in place of the Exhibition Luncheon on the opening day. Accordingly, on the occasion of the Silver Jubilee Exhibition, a Dinner will be held at the Savoy Hotel, London WC2, on the opening day, the reception being at 19.00 hrs. for dinner at 19.30 hrs. Informal dress will be worn. Following the custom of many years, the Association will invite as its guests to this function principal officers from other scientific societies and kindred organisations, who will be invited to visit the Exhibition in the afternoon. Full details of the Exhibition Dinner will be announced in the *Official Guide* to the Exhibition, each copy of which will contain an application form for tickets.

Invitation to Exhibit

Copies of the Invitation to Exhibit—which naturally incorporates silver in the colour scheme—have now been despatched to those companies and organisations, in the United Kingdom and overseas, which have shown at past exhibitions or have already requested information on the 1973 exhibition. Completed application forms for stand space must be returned to the Director & Secretary of the Association **not later than 1 October 1972**. In view of the intention

that on 1 January 1973 the United Kingdom will become a member of the European Economic Community, it is expected that even more Continental firms will participate in this exhibition; any organisation from any part of the world wishing to exhibit should write immediately for details from the Director & Secretary of the Association. At the Twenty-Fourth Exhibition, in April 1972, there were direct overseas exhibitors from 12 countries, besides many overseas companies who showed through British associates. Representatives from 33 overseas countries signed the Visitors' Book at the Information Centre on that occasion and the importance of this event to the surface coatings industries can be demonstrated by the way in which as many as 14 new exhibitors were attracted to show. The Exhibition affords a splendid opportunity for the technical display of information and a forum for the interchange of technical advice and experience between those employed in the supplying and manufacturing industries.

Technical Education Stand

In continuance of its interest in the educational field, the Association will

once more provide a stand devoted to technical education, at which details of courses at technical colleges will be available as well as information on the optional Professional Grade for Ordinary Members, introduced in September 1971, which has attracted widespread interest and support.

Information in Foreign Languages

The practice of distributing abroad a specially designed information leaflet in six languages (English, French, German, Italian, Russian and Spanish), will be continued and interpreters (French, German, Italian and Spanish) will be available without charge at the Exhibition for the convenience of visitors and exhibitors.

Admission

As at all previous exhibitions organised by the Association, there will be no charge for admission, and free copies of the "Official Guide" will be available to those intending to visit the Exhibition several weeks before the event so as to enable them to plan their itineraries to the maximum benefit.

Optional Professional Grade for Ordinary Members

As a result of *viva voce* examinations held on 22 May at Wax Chandlers' Hall, the following Ordinary Members have been admitted to the Licentiate and Associate grades.

Licentiates

Canterford, Barry Albert (London)
Moss, Noel Sydney (London)

Associates

Flood, Geoffrey Terence (Manchester)

Johnstone, James William (Manchester)
Khan, John Mohammed (London)
Parry, Martin Gerald (London)
Sutton, Michael Peter (London)

A meeting of the Professional Grade Committee was held at Wax Chandlers' Hall on 7 June at which 12 Ordinary Members were admitted to the Fellowship grade and 23 to Associateship. A complete list will appear in the August issue.

Foundation Lecture 1972

Sir James Tait to present 1972 Lecture

The Council is honoured to announce that the 1972 Foundation Lecture will be

given by the Vice-Chancellor of the City University, Sir James Tait, LL.D., Ph.D., B.Sc., C.Eng., F.I.E.E., F.I.Mech.E., who has

chosen for his subject "The city—a technological university. Are tradition and technology compatible?".

The Lecture will be given at Painters' Hall, Little Trinity Lane, London EC4, on Tuesday 3 October 1972 at 7.15 p.m. and will be preceded by a short service at St Vedast-alias-Foster, Foster Lane, London EC2, at 6.15 p.m. This is the church at which the commemorative

service took place on the occasion of the Association's fiftieth anniversary celebrations in 1968.

Following the Association's usual custom, the Foundation Lecture will be followed by an informal dinner at the Painters' Hall.

Full details and forms of application for tickets will be sent to members in due course.

Jordan Award

This award was instituted by the late Mrs M. R. Jordan in memory of her husband Dr L. A. Jordan, who was President of the Association 1947-49 and an Honorary Member, and who died in December 1964.

The Committee invites applications for the third award of £100.

The rules of the Award are:

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 **29 December 1972** and it is hoped to present the award at the Eastbourne Conference in the following June.

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 Association's offices.

The two previous awards were made in 1969 and 1971. In 1969 it was made jointly to Mr M. J. B. Franklin, for his paper "The effect of zeta potential on the optical properties of paints" (*JOCCA* 1968, **51**, 499), and Mr R. J. King, by recommendation of a superior for work which could not be published for reasons of commercial secrecy; in 1971 the recipient was Mr J. R. Groom, for his paper "Milling—a printing ink variable" (*JOCCA* 1971, **54**, 266).

Manchester Section Symposium

Paint performance and the microbiological environment

Full details of the symposium "Paint performance and the microbiological environment", to be organised by the Manchester Section at the University of Manchester Institute of Science and

Technology on Tuesday 19 and Wednesday 20 September 1972, are now available, and programmes, together with application forms, are included in all copies of this *Journal* sent to the UK.

There is an increasing awareness in the surface coatings industry of the problems

associated with microbiological attack, and the symposium aims to cover the fundamentals of microbiology as well as its practical aspects in the coatings field. Emphasis will be given to the areas of preservation, stabilisation, anti-fouling and corrosion. In addition, architectural and environmental aspects will be considered. A full programme of 16 papers has been arranged, commencing at 10.30 a.m. on the Tuesday, when Professor D. E. Hughes of University College, Cardiff, will open the first session, subtitled "Microbiology—fundamental aspects". The afternoon session will have the theme "Preservation and stabilisation", and the two sessions on the Wednesday will be "Anti-fouling and corrosion resistant coatings" and "Architectural and environmental aspects". An informal symposium dinner will be held on Tuesday evening, at a cost of £1.80; registration fees, including lunch on both days, are £7.50 for Members, £2.00 for

registered Students of the Association and £12.50 for non-members; Students attached to the Manchester Section will be admitted free of charge. All lectures will take place in the main lecture theatre of the Renold Building at UMIST, and some accommodation is available in the nearby Wright-Robinson hall of residence; early application is advisable as the number of rooms is strictly limited. The timing of the symposium has been chosen with the intention that it will qualify for grant from the Chemical and Allied Products Industry Training Board, but this will depend on individual circumstances; application should be made direct to the CAPITB.

Registration forms should be returned as soon as possible, and by 1 September at the latest to ensure the receipt of preprints. All enquiries should be addressed to Dr F. Dalton, CIBA-GEIGY (UK) Ltd., Roundthorne Estate, Wythen-shawe, Manchester M23 9ND.

London Section

Annual General Meeting

The 34th Annual General Meeting of London Section was held on 14 April 1972 at the Polytechnic of the South Bank, London SE1. In presenting the Annual Report, Mr R. H. E. Munn referred to the innovation this year of including a lecture to which the ladies were invited. Half-day symposia had been very successful with a high attendance and two had been scheduled for the coming session.

Mr J. Tooke-Kirby spoke of the activities of Southern Branch. Four technical meetings had been held, together with a joint meeting with the Institute of Metal Finishing.

The following Officers were elected or re-elected. Chairman: Mr D. E. Eddowes; Hon. Secretary: Mr R. H. E. Munn; Hon. Treasurer; Dr H. R. Hamburg; Hon. Publications Officer: Dr V. T. Crowl; Hon. Programmes Officer: Mr J. K. B. Burke; Hon. Auditor: Mr A. H. Soane. The three new members elected to the committee were: Mr G. E. Westwood, Mr A. G. Hudson and Mr F. Morrow.

Following the AGM, a buffet meal was served, after which Mr H. R. Cornwell of the English Country Cheese Council gave a very interesting talk on cheeses, which was followed by a wine and cheese tasting session.

V.T.C.

South African Section

Annual General Meeting

During the Annual General Meeting of the South African Section, held at the Ocean Terminal, Durban, on 12 April 1972, the following Officers were elected for the 1972-73 period:

Chairman: Mr K. R. McDonald; Hon. Treasurer: Mr K. M. Engelbert; Hon. Secretary: Mr T. Entwistle; Hon. Publications Officer: Mr R. A. Eglington; Committee: Mr L. Saunders, Mr A. J. Dowds, Mr P. B. Smith.



Mr T. Howard (left) receives his scroll of Honorary Membership from the Chairman of the South African Section, Mr L. F. Saunders (right) watched by Mr K. R. McDonald (incoming Chairman)

After the meeting, the Members rejoined their wives, who had been entertained by Mr P. Warby, conjurer extraordinary!

The main guest (and speaker) for the evening was Mr T. Howard, well known to all sectors of industry, and in particular to the paint industry. When introducing the speaker, Mr Saunders, the outgoing Chairman, mentioned that Mr Howard came to South Africa in 1935 to join Lewis Berger & Son in Durban. During his stay in South Africa, he remained with this company (or subsequent companies as various mergers took place) rising rapidly through the years to become "the most important person." He did not only look after his company, but also became vitally interested in the paint industry as a whole. During his career Mr Howard had become (at various times): chairman of the South African Paint Manufacturers Association, chairman of the Natal Chamber of Industries, and chairman of the Industrial Representatives of the South African Paint Research Institute.

Not least of Mr Howard's activities were those directed at OCCA. He was the

driving force which caused the South African Section to be formed. As a fitting reward, he had been elected the first Chairman of the Section, and now became the first South African member to be awarded Honorary Membership.

Mr Saunders then presented Mr Howard with the illustrated scroll sent by OCCA from London, the text of which read as follows:

HONORARY MEMBERSHIP

was this day conferred upon

THOMAS HARRISON HOWARD
*Ordinary Member of the Association,
Founder Chairman of its South African
Section 1949-51 and a Vice-President
1950-52*

In appreciation of his outstanding service to the Association and to industry in South Africa and to express the thanks of the Council of the Association for his continued interest in the welfare of the South African Section since its inception.

Signed A. W. Blenkinsop, President

D. S. Newton, Honorary Secretary

R. H. Hamblin, Director & Secretary

12 April 1972

In his reply Mr Howard stated how completely overwhelmed he was in receiving Honorary Membership. He pointed out that he initially started negotiations to form the Section around 1947, and during his frequent trips to England was able to have direct discussions with members of Council before the final inception.

He then made mention of a few of the original members; amongst those present at the dinner were Mr K. Engelbert and Mr R. Everitt and also Dr K. Hart who joined a few years later. Mr Howard said, however, that the man who most deserved

this honour was the late Dr Lawrence Whitby who was Director of the South African Paint Research Institute at the time of the formation of the Section. During the early years, they had relied almost entirely on him for their lectures.

Mr Howard ended his speech by saying how conscious he was of this tremendous honour which he would cherish, and thanked the Section for nominating him. He said he also felt that it was a great honour for the South African Section that OCCA held him in such high esteem that they were prepared to accede to this request.

K.R.M.

Newcastle Section

Annual General Meeting

At the Annual General Meeting of the Newcastle Section, held at the Lambton Worm, Birtley, on Thursday 6 April, the following officials were elected:

Chairman: Mr A. A. Duell; Vice-Chairman: Mr C. N. Finlay; Hon. Secretary: Mr A. Laws; Hon. Treasurer: Mr J. Clark; Hon. Publications Officer: Mr F. Hellens; Hon. Research Liaison Officer: Mr K. F. Baxter; Hon. Co-ordinating Officer for Technical Education: Mr W. J. P. Buchanan.

The Chairman thanked the various

retiring Officers for their work during their period of office and in particular thanked the retiring Secretary, Mr B. Ridley.

After the main business and an excellent buffet supper, an illustrated talk on "Wine production in Europe" was given by Mr Goschalk, in which he principally discussed the production of champagne. As the lecture also included several bottles of samples, the meeting ended on a cheery note with the Chairman, Mr Duell, thanking Mr Goschalk for an excellent talk.

A.L.

West Riding Section

1972 Golf Tournament

The West Riding Section is to hold its golf tournament at the Wetherby Golf Club on Friday 4 August at 2.15 p.m. Two trophies will be played for, the OCCA Trophy, entry for which is open to all Members of the Association, and the West Riding Chairman's Trophy, entry for which is restricted to Members attached to the West Riding Section. Both trophies will be decided over 18 holes under Stapleford rules.

A buffet will be available prior to the tournament, and there will be an evening meal afterwards; ladies are welcome to attend. The entry fee for the tournament is £1.40 per player, and will include green fees, and a charge of 50p and £1.00 per person will be made for lunch and the evening meal respectively. Those wishing to participate should contact the Hon. Social Secretary of the West Riding Section, Mr M. J. Cochrane, 49 Almsford Drive, Harrogate, Yorks, HG2 8ED, as soon as possible.

Obituary

Mr J. L. Mandeno

It is with regret that we record the death of Mr J. L. Mandeno, who made an outstanding contribution to the establishment of OCCA in New Zealand. He began his career at Dominion Laboratory, DSIR, in 1929 and concurrently studied at Victoria College of the University of New Zealand, graduating as MSc in 1934. Following overseas study in 1945, he headed a paint and building materials group until entering the paint industry in 1949, first as technical superintendent with Pinchin Johnson NZ Ltd and later as

chief chemist with Giant Paints Ltd. Mr Mandeno's association with OCCA began as a member of the steering committee that brought into being the New Zealand Section, of which he served as first Chairman in 1952. Indicative of his wide scientific interest was long-term active membership of the New Zealand Institute of Chemistry and the Royal Society of New Zealand. These services were matched with an equal contribution to the social and cultural affairs of the community. His genial personality will be missed among a wide circle of his friends and colleagues.

News of Members

Dr T. A. Banfield, an Ordinary Member attached to the Newcastle Section, has now left the Newcastle area to take up a new appointment with Berger Paints Ltd in London. Dr Banfield has been a member of the Newcastle Section for 21 years and during that time has served as Section Representative on Council, Elective Member of Council, and Section Research Liaison Officer and Treasurer.

Miss D. Tilleard, an Ordinary Member attached to the London Section, was appointed MBE in the birthday honours list. Miss Tilleard, who was at the Paint Research Association for 40 years until her retirement from full-time employment in 1970, represented OCCA on a number of BSI committees.

Mr E. J. Ross, an Ordinary Member attached to the London Section, and a director of Berger Paints, is now responsible for specific products for Berger Paints and for the Berger, Jenson and Nicholson Group. Mr Ross was previously director of the company's automotive division.

Mr N. Jeffrey, an Ordinary Member attached to the London Section, has been appointed manager of the automotive and agricultural division of Berger Paints.

Mr K. McLaren, an Ordinary Member attached to the Manchester Section, was re-elected a vice-president of the Society of Dyers and Colourists at its AGM in April.

Association of Professional Scientists and Technologists

The Association of Professional Scientists and Technologists has now informed this Association that under its Rule 3.3 Members of OCCA who are desirous of joining the APST may be considered individually, and that they should complete Sections 2 or 3 and 4 of the application form which can be obtained from the APST, 30 Russell Square, London WC1B 5DT.

Symposium on liquid polymers

There is increasing interest in the application of liquid polymers in many branches of industry—in surface coatings, adhesives, mastics, textile coatings and laminates among others. In common with non-solvent based materials generally, liquid polymers are likely to find increasing use in many applications in view of current thinking and likely legislation relating to the environment.

An important feature of liquid polymers is the fact that they can be processed on types of equipment currently used for

making coatings, adhesives, mastics, and so on, as distinct for example from powder coatings based on solid polymers which require more specialised plant.

With these facts in mind, *Polymers Paint and Colour Journal*, in association with Mr A. K. Unsworth, a well known consultant in the surface coatings field, is sponsoring a two-day symposium under the title "Liquid polymers". It will be held at the University of Surrey, Guildford, on Tuesday 26 September and Wednesday 27 September 1972. Residential accommodation will be available at the University for the night of the first day.

This symposium, which aims to review the types of polymers used in a variety of applications covering chemical, technological and economic aspects, is aimed at the stimulation of interest in a wide range of industries. The programme comprises 16 papers given by technical personnel from well known companies in the UK and overseas. Subjects to be covered include: cis-polybutadienes; liquid polymers based on diphenylolpropane; polyurethanes, both liquid and rigid cast types; epoxy resins; polysulphides; the curing of unsaturated polyesters; and liquid elastomers. End-use applications will include surface coatings, laminates, sealants, mastics and adhesives.

Preprints of the papers will be available before the symposium, allowing the fullest possible opportunity for discussion.

Details and registration forms can be obtained from D. E. Eddowes, Editor, *Polymers Paint and Colour Journal*, 17/19 John Adam Street, London WC2N 6JH (Telephone 01-839 6171).

GDC Paint and Pigment Group Conference

Full details of the conference to be organised by the Paint and Pigment Group of the German Chemical Society are now available. The conference is to be held at Bad Pyrmont, near Hanover, from 26-29 September 1972. Programmes and application forms can be obtained from Dr H. Rechmann, i.Fa. Kronos

Titan-GmbH, 509 Leverkusen, Postfach 80/90, West Germany.

FSPT 50th Anniversary Luncheon

The Federation of Societies for Paint Technology has announced that the speaker at its 50th Anniversary Luncheon, to be held at Chalfonte-Haddon Hall, Atlantic City, on 24 October 1972, will be Eddie Albert, star of many stage and screen plays and musicals. As well as his career as a show business personality, Mr Albert has for many years been active in humanitarian causes, in particular ecology, and holds many awards gained through this facet of his life.

ZDA/ZPDA Seminar

"Protecting steel with zinc dust paints" was the title of a seminar organised jointly by the Zinc Development Association and Zinc Pigment Development Association, and held at the Cafe Royal, London, on 16 May. Papers were presented by authors from Britain, Germany, Holland, Japan and the USA, all demonstrating the impressive reduction of corrosion on steel structures in aggressive environments obtained by the use of zinc dust paints; inorganic zinc silicate formulations were preferred in the USA and on the Continent, while organic types were more popular in Britain and Japan. The main point emerging from the papers and the ensuing discussions was the importance of surface preparation. Shot or grit blasting to white metal seemed essential; performance of the paints over even slightly rusted steel was much reduced. Although zinc pigments do not present the ecological difficulties of lead anti-corrosive pigments in service, health hazards have been noted when zinc-primed steel has to be welded. Solutions to this problem were proposed.

Corrigendum

In the technical review of OCCA 24 published in the June issue, the product numbers of the three new acrylic resins from Cray Valley Products Co. Ltd. were given incorrectly (pages 546 and 547). The correct names are Synocures 867S, 868S and 869S.

Register of Members

The following elections to Membership have been approved by Council. The Section to which new Members are attached is given in italics.

Ordinary Members

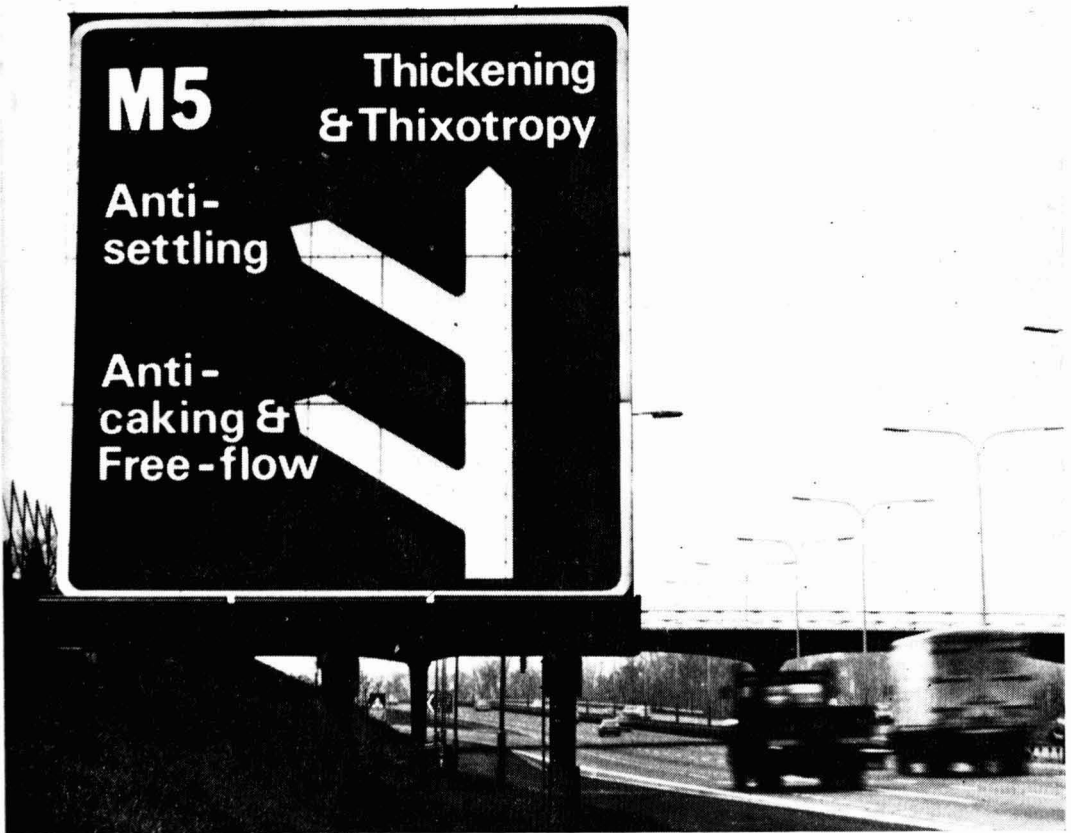
- ANDERSON, RICHARD, BSc, 5 Valley Gardens, Darlington Lane, Stockton-on-Tees, Teesside. *(Newcastle)*
- ARRIECHE, GILBERTO, Sherwin Williams Venezuela, Apartado 94, Valencia Carabobo, Venezuela. *(Overseas)*
- BENITEZ DE LA GARZA, CARLOS, Centeotl 223, Mexico, Mexico 16, DF. *(Overseas)*
- BROWN, MATTHEW, 6 Ethel Street, Dudley, Cramlington, Northumberland. *(Newcastle)*
- DOOLEY, DAVID BRIAN, BTech, 2 Woodville Road, Ealing, London W5 5JR *(London)*
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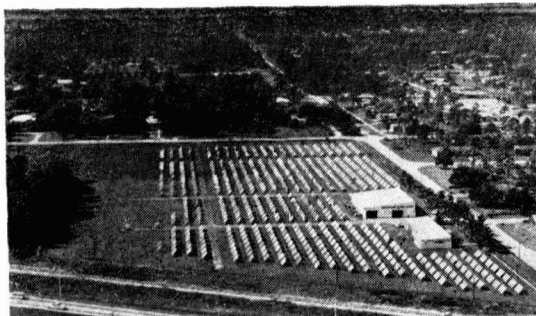
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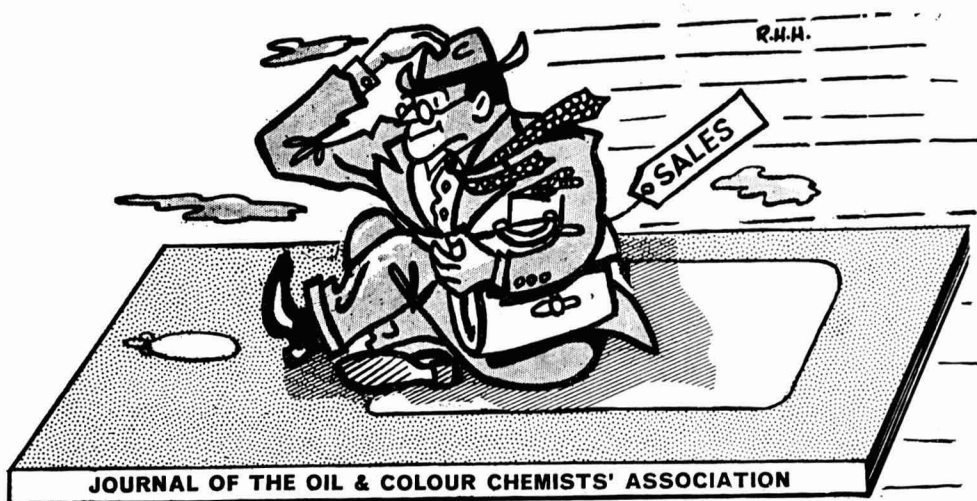
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