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JOURNAL OF THE
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Relations with the developing countries *A. T. S. Rudram*

The challenge of metal finishing *G. Isserlis*

The role of coatings in corrosion prevention—future trends *V. Ashworth and R. P. M. Procter*

Electrochemical activity of conductive extenders for zinc rich coatings *V. P. Simpson and F. A. Simko*

Priory House, 967 Harrow Road, Wembley, Middlesex, England
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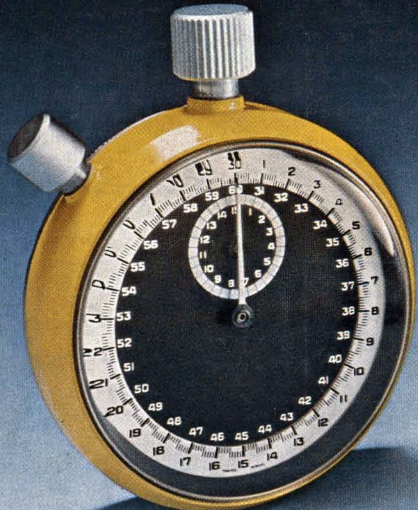

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Transactions and Communications

Relations with the developing countries*

By A. T. S. Rudram

Donald Macpherson Group Ltd, Three Quays, Tower Hill, London EC3R 6EL

Summary

Attitudes are changing daily, but an attempt is made to relate economic and social patterns in the approaching years. The scale of development varies, depending upon the date of independence, location and ethnic factors; but one factor is common to all emergent nations, namely the nationalistic one. There is a desire to control in whole, or in part, their local industries and this desire is marked by a range of interests from expropriation at one end, to some degree of equity participation at the other.

Keywords

Specifications, standards and regulations

government specifications

Rélations avec les pays en voie de développement

Résumé

Bien que les dispositions d'esprit changent chaque jour, on fait une tentative de mettre en rapport les tendances économiques et sociaux des années prochaines. L'échelle est variable, et se dépend de la date de l'indépendance, de la situation géographique et des facteurs ethniques de chaque pays; cependant, une facteur est commune à toutes les nations émergeantes, c'est-à-dire, celle de nationalisme. Il existe le désir de contrôler en tout ou en partie leurs industries, et ce désir se distingue par une gamme d'aspirations entre l'expropriation à un extrême jusqu'à quelque degré de participation d'actions à l'autre.

Dans la mesure que possible, l'auteur offrira une appréciation lors de la Conférence au sujet de l'effet eventuel de ces dispositions d'esprit régionales.

Beziehungen zu den sich Entwickelnden Ländern

Zusammenfassung

Obwohl sich Einstellungen täglich ändern, wird versucht wirtschaftliche und soziale Ideengänge kommender Jahre miteinander in Beziehung zu bringen. Der Grad der Entwicklung ist je nach dem Datum der Selbständigmachung, der örtlichen Lage und der ethnischen Faktoren verschieden; aber einen Faktor haben alle aufstrebenden Nationen gemeinsam, den nationalistischen. Man wünscht die ortsansässige Industrie völlig oder teilweise zu kontrollieren, und dies wird stark durch verschiedenerlei Interessen chatakterisiert; an dem einen Ende will man enteignen, am anderen eine gerechter Weise zustehende Beteiligung erhalten.

Soweit möglich, wird zur Zeit der Konferenz eine Ansicht über die voraussichtliche Auswirkung dieser nationalen Einstellungen zum Ausdruck gebracht werden.

Сношения с развивающимися странами

Резюме

Отношения меняются каждый день, но тем не менее делается попытка согласовать экономические и социальные тенденции в ближайших годах. Масштаб развития изменяется завися от даты присвоения независимости, местоположения и этнических факторов; но один фактор является общим для всех развивающихся стран, а именно национальный фактор. Появляется стремление овладеть контролем, полностью или частично, местной промыленности и это желание характеризуется сферой интересов от экспроприации с одной стороны, до некоторой степени справедливого участия с другой.

По мере возможности будут высказаны мнения в течение конференции относительно веса этих местных соображений.

Introduction

It is difficult, and probably unwise, to be definitive about such a broad subject as the relations with developing countries. The emergence overnight of an Amin-type upheaval, can make nonsense of the most carefully thought out appraisal of yesterday.

It is remarkable how some politicians, or other similar dignitaries, can visit a land, on what is often euphemistically described as a "fact finding" mission and return a few days later as acknowledged experts on the area. Many people are prepared to air their views on Vietnam in, say, Trafalgar Square when they can barely point out the territory on the map. No Vietnamese I have met has any clue where Trafalgar Square is and cares less—he is more interested in the people prepared to come to Vietnam and do something tangible.

These are notes, not prepared by an expert, but merely by one who has visited many of the territories over many years and on several occasions. Between visits, the newspapers of those territories which were printed in English have been read in considerable detail.

---

* Presented at the 1973 Eastbourne Conference.

The so called "emerging nations" vary greatly in their degree of emancipation and adaptability to world conditions. This is not surprising when it is realised that some have been independent for a long time, for example Thailand. Others have only recently, and sometimes precipitately, become independent. Most had three things in common: (a) lack of money but plenty of cheap labour; (b) lack of management and technical skills; and (c) ethnic problems. Many had valuable resources often being exploited, and often at little advantage to the country, by overseas concessionaires.

The economic requirements of the various countries, however, vary enormously due to size, location, population and natural resources.

For example, the size and location of the Caribbean islands means that they need little in the way of defence budgets. The islands are small and fairly widely separated. None could resist military annexation by a major power and each recognises that some form of regionalisation is going to be necessary for economic viability. Federation was tried, but failed largely due to the disinterest of the more prosperous members who were relatively affluent and had little to gain from the small and less well-to-do participants. Since that time, however, the Caribbean Free Trade Area (CARIFTA) has come into being and regionalisation, spearheaded by Forbes Burnham of Guyana, is once again being mooted. The recent Grenada Declaration met with only lukewarm interest from countries such as Trinidad and Tobago, but there is a stirring of interest.

On the other hand, an emerging country in direct physical contact with other nations of a similar type, or with one of the great powers, has to watch its defence interests. In Africa, for example, neighbouring countries may have widely differing tribal attitudes, often sufficiently deep rooted to cause at least border problems and, at worst, direct confrontation. For such countries, defence requirements place additional burdens on already strained economies. This does not, however, prevent apparently senseless activities, in the economic sphere, such as those practised recently by General Amin in Uganda.

Countries in juxtaposition in south east Asia, that are not already at war, run constant risk due mainly to Communist activity. Malaysia and Thailand spend a great deal of time and money attempting to root out the Communist guerillas operating on their borders.

To some extent the extra burden of defence needs, in many of these areas, is met by interested powers outside the territory. For example, the United States' activities in Vietnam are well known, but they also spend a great deal of money to ensure that there will be no more "Cubas" in the Western Hemisphere.

Industrial development

Most of the countries that are grouped under the general heading of "developing countries" were originally colonies and were colonised because of their obvious or potential resources. The colonial power set about the development of these resources using either cheap indigenous labour or imported labour, such as the Afro-slaves and Asian indentured labourers of the Caribbean. Supervision was always by an expatriate from the colonial power.

Even after slavery and exploitation had ended, for very many years there was little change in the overall pattern—labour by indigenous personnel, supervision and management by expatriate personnel—and this situation persisted up to the granting of independence, and continues in some places to the present time. In this situation there was little opportunity for local personnel to acquire technical and managerial skills.

In recent years, however, educational opportunities have enabled more and more of the people of these countries to pursue studies, often in universities outside their own country, that have qualified them in many of the professions and often fitted them for middle-management activities. This has led to a considerable diminution in the numbers of foreigners required and it is often only the top management that is now imported. Work permit systems have been introduced and regulations stiffened appreciably to ensure that senior jobs are progressively "nationalised" and the expatriates withdrawn. The pattern is fairly common and there is a steady decline in the number of workers sent out from a home country to work in an overseas subsidiary and, undoubtedly and understandably, the trend will continue.

Most of the major companies with overseas subsidiaries now have planned training schedules at their main operating centres for overseas personnel who are being groomed for senior posts. The "chief executive" is likely to continue to be a foreigner for a good many years in most of the developing areas but below this level one can look towards a steady increase of nationals at senior level and the withdrawal of the relatively costly foreigner.

With increasing confidence in their ability to run their own industries, it is not unexpected that many of the developing countries are now showing an interest in owning, or partly owning, such enterprises. The attitudes vary from country to country but some degree of participation is being looked for in all of these countries ranging from part ownership or partnership, by the more reasonable, to expropriation, by those more rashly confident of their abilities. The main restraining influence is the need for foreign investment to improve the economics of the countries and few investors are interested in areas where their assets are likely to be seized before the investment has been recovered. Indeed, such is the need for "off-shore" funds that most of the developing countries offer incentives, such as tax holidays, duty free imports and so forth, to attract investors in certain industries.

The Governments of developing countries are much more wary of foreign intervention when it involves their agricultural or extractive activities. Much of the property is owned by the old Trading Companies and these will probably continue to remain part owners, or at least managers, of their enterprises for some time to come, but there is an understandable reluctance to see national resources exported in crude form only to be imported later in finished form but at great expense. It is not long since Mr Forbes Burnham of Guyana, made his speech about the need for countries to have a "meaningful participation" in industries involving their natural resources. It was made fairly clear that he had bauxite in mind and, looked at in retrospect, it might have been wise for Alcan to have offered some of their equity on the local market. They resisted any participation by the Guyanese, with the result that their activities were "nationalised" and the bauxite industry is run by a State Corporation.

There seems little doubt that overseas subsidiaries of foreign companies, will invite increasing local participation in the ownership of the territorial activity. There are probably many advantages in so doing, mainly in terms of the social requirements of areas with which the principal unit at home may be unfamiliar.

Social factors

Almost all the emerging countries are multi-racial or tribal in their make-up which gives rise to a variety of customs between parts of the population, all of which have to be understood and catered for by the would-be foreign investor or his foreign representative on the spot. Experience as a manufacturer in one developing country does not, necessarily, fit a company to enter into the business world of another. Indeed, it can be a handicap in that he may tend to fit the behaviour pattern, learned by experience in one country into that of another and grossly offend local manners and mores.

It is often argued, in this context, that an operation contemplated in a new country should be launched in conjunction with a local partner who is familiar with the "ground rules" and, indeed, some emerging countries require that new investment for industry in their countries shall be made with a local partner. Local customs and superstitions die hard and to defy or break them can be commercial suicide.

There are greater problems where the population is multiracial because each sector has its religious or behaviour pattern. For example, to explain the Chinese attitude, described as "face," is virtually impossible and one has to experience it over a period of time before its precise nuances can be appreciated. A too small or too poorly located factory can lead to company loss of "face" to the detriment of sales. Too harsh or too abrupt dealings with individuals can lead them to think that they have lost "face" and future relations are apt to be strained, for the Chinese do not willingly enter into any form of social or business contact with anyone who has lost face or who makes them lose face.

Attitudes towards the offering of financial or other inducements vary (they are not regarded as venal in some countries) but the manner in which the bribe or inducement is offered can be a matter of serious consequence to the future relationship.

Some of these requirements, the more obvious ones, can be quickly learned, but the more subtle ones are best left to the local partner or the senior indigenous personnel of the company who will go through the ritual with proper courtesy, patience and attitude.

Countries of roughly similar development do not easily accept that expertise in one may be better than in the other and are less likely to import from a developing country than from the USA or UK. This does vary to some extent as is shown by the emergence of CARIFTA and ASEAN (Association of South East Asian Nations), but some remnants of the old prejudices remain.

Racial conflicts erupt from time to time and there is an element of violence and protest present at most times, but is that very different from the developed countries? In some countries, because of the low level of living conditions and the high level of unemployment, crimes of robbery and assault are common. These are unlikely to affect the visitor if he takes the advice of his local colleagues and behaves accordingly.

Commercial relationships with the United Kingdom

Apart from the plantations, mining and similar activities that were the reasons for our presence abroad in the first place, foreign investment for the purposes of manufacture were partly defensive, to replace dying export markets, and partly to take advantage of the inducements offered to attract offshore funds.

A great goodwill exists and British companies are well received in most countries. In some, Britain is well down the league of foreign investors where Japan and West Germany often seem to dominate, with China entering the scene, particularly in Africa and Guyana. Canada and the USA are well to the fore in the Caribbean.

At present, many developing countries have to import most of their raw material, but with increasing investment in infra-structure, particularly power, local conversion of petroleum and mineral products is on the increase and it is likely that significant proportions of raw materials will soon be produced locally by the developing nations.

Membership of the EEC may well have a bearing on our relationships in the years towards 2000. About ninety countries have active relations with the community and about sixty of them have trade agreements. Some will not be unfamiliar trading partners but others may now open their doors to the United Kingdom's activities in their territories where previously this was not possible.

Conclusion

This is a broad outline; if it had been taken country by country it would have taken the space of several large volumes. Geography, politics and tradition are amongst the factors stressed as being most important when considering our relationship with the developing countries.

Acknowledgment

The author takes this opportunity to thank the Chairman and Directors of the Donald Macpherson Group Limited for permission to publish this paper. The views expressed, however, are personal and do not, necessarily, reflect those of his principals and colleagues.

[*Received 6 February 1973*

Discussion at Eastbourne Conference

MR D. E. EDDOWES asked was there much competition in the developing countries, especially the Far East, from paint manufacturers of countries other than the UK, for example Japan, and what was the reaction to these other countries.

MR A. T. S. RUDRAM said that unfortunately there were great competitors. There was a reluctance mainly to be found in South East Asia, to the setting up of foreign industries. There was also a hardening of attitudes by the local countries, particularly Indonesia and Malaysia, against the Japanese incursion, because the people in these countries believed that the hold would become so large to present a real danger to their own independence, politically and otherwise, and in fact they were turning much more towards the west for new industry and for new finance. The Japanese were doing their best to put this right by being rather less aggressive than previously in selling and installation, but they might be a little late in the day because once these people did harden their atitudes, they were not easily changed.

DR J. B. LEY asked Mr Rudram whether he thought that UK paint companies could expect a satisfactory financial return by investing in under-developed countries.

MR RUDRAM thought that was a good question and could only suggest that the answer was "yes," because many of them were there and it had been rewarding up to now. Most potential investors were looking further afield, for there was the attraction of large populations in the East and, for example, in recent years something like 14 paint companies had opened up in Java. These were having to work hard to make a satisfactory profit in so far as it was a low quality market and the margins were small; one had to turn out a lot of paint to get a return, but it was being done and people seemed to be happy. Some of the other countries were flourishing in terms of paint. Malaysia was quite a sophisticated market, and one could run a reasonable operation in such a country even though competition was keen.

DR LEY agreed that existing paint companies were probably obtaining a satisfactory return, but suggested that the threat of nationalisation or "Africanisation" would put off future investment. He believed that one had a moral obligation to help these countries, but obviously required assurances.

MR RUDRAM replied that overseas investment would certainly be looked at carefully certainly so far as Africa was concerned. The African states did tend to act precipitously, so to speak, and expropriate tomorrow when they had only become an independent country today. Some of the other countries had learned lessons from the past and from other countries which had taken financial help when setting up industries. For example, Indonesia had now put paint on the barred list; it was not possible to set up a paint company at this present time in Indonesia. Many countries prohibited an increase in numbers when they felt they were getting to a point where the market would not sustain any more. The mechanism in the more developed countries was one of gradual participation and gradual take-over.

He thought this would happen. Proportions of the equity would be placed on the local market and then further proportions, until by a gradual process they would be ultimately and indubitably owned, and understandably owned, by their own nationals. He agreed in terms of new investment, the return was probably not enough, though one or two countries were still fairly promising. One could argue that looking at the Caribbean, for example, then based upon one island and with CARIFTA, quite appreciable amounts could be exported to other islands in the Caribbean, to the point where one became a significant influence in the paint industry in that new territory. Very often, by export alone one could become number 2 or 3 the market. This suggested that the newer countries, or those to which one exported, could possibly sustain one or two more paint companies. The area would have to be selected very carefully. It was Mr Rudram's personal view that most of the African states were not the kind of place where investment was a good thing at the present time, although the situation might change.

He added that he had been asked at the Conference about corruption in overseas areas. He did not think there was corruption as was known in this country, but he was at a conference recently on Indonesia, and one of the speakers coined the phrase "unofficial taxation," which was something one had to expect and accept. He thought it was a euphemism that was quite useful.

MR G. R. SIDDLE asked what was the general attitude to the environment and its pollution taken by under-developed countries.

MR RUDRAM said that the attitudes varied enormously. Certainly in some countries, they did not worry too much about pollution, or indeed about spoiling of the environment. Once again, this was a question of variation in the state of development. For example, the Malaysian Government had recently instituted quite stringent laws about what could be released into surface water, and were looking seriously at air pollution. They had a lot to do there because, of course, some of the small companies tucked away down back streets in "shop houses" very often had the most elementary notions of pollution, safety and everything else. He had seen lamp fittings being spray painted in a room where people were smoking, where the butane gas cylinders were all close to the actual spraying operation, and the oven merely poked through the wall out of that area. It was a fire trap, because it was upstairs, and up wooden stairs at that. The Authorities were, in fact, taking immediate steps to cut down that sort of thing and introduce health and safety regulations, and indeed pollution regulations.

In some parts of the Caribbean, and the islands varied enormously there, one could release almost anything into the ground and it would probably not worsen its condition; when one had seen some of the debris thrown away there, then paint residue was really rather pleasant stuff by comparison. Most developing countries did have a sense of civic responsibility, and were trying to deal with the situation.

MR A. R. H. TAWN suggested that if capital investment in these countries was considered too risky, then the sale of "know-how" might be a practicable alternative. Even in the event of a take-over of assets, there had to remain a need for continuing know-how, and one might doubt the ability of some of these countries to provide this for themselves, at least in the short-term. He added that licensing arrangements should provide an answer to Dr Ley's fears.

MR RUDRAM replied that this was not only a practical alternative, it was already there. Quite a number were building up fairly sophisticated plants of one kind or another; for example, many of them had quite considerable automotive assembly plants, and in most cases they were licensing the know-how for the finishing and ultimately the refinishing of those automobiles. This was probably the way that our continuing relationship with them would progress, with increasing know-how and increasing licensing of methods and materials. The amount of licensing was quite small, so far as the speaker had been able to determine, but it was already there and might well be the solution to Dr Ley's point.

DR LEY agreed that it was best to sell a "packaged deal" to an undeveloped country but the difficulty had been in obtaining permission for local currency. The alternative was a co-operative venture, but experience had shown that import quota restrictions could be imposed without warning, making co-operation very frustrating.

MR RUDRAM, commenting first on the latter point, said that this was where most of the technological ingenuity, not always by local nationals but often by those expatriated had been displayed to the best advantage, in that they had managed to make a little go a long way. In answering Mr Tawn's question, he was really thinking of the companies who had made the financial investment in a given country. What would happen when the local nationals took over completely was of course, anybody's guess, but if in fact they were going to have a progressive industry, they would probably be amenable in terms of tax concessions and import duties, certainly in those countries quite well developed already. Many of them were very responsible in their attitude towards the future of their industrial development.

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The challenge of metal finishing*

By G. Isserlis

Division of Metal Science, Polytechnic of the South Bank, Borough Road, London, S.E.1

Summary

After a brief review of the progress of metal finishing since the early post-war days, the present scope of this technology and its relation to other technologies will be indicated. The need for specialist education, particularly at the highest level, will be explained.

On the basis of current trends, likely developments over the next decade will be considered and an attempt will be made to predict the role of metal finishing in industry and everyday life at around the year 2000.

Keywords

Types and classes of coating
metal finish

Types and classes of surface
metal

Miscellaneous terms
pollution

Le défi de la finition de métaux

Résumé

Après une brève revue du progrès dans le domaine de la finition de métaux depuis le commencement de l'époque après-guerre, on indiquera la portée de cette technologie et son rapport aux autres technologies. On expliquera la nécessité d'assurer la formation des spécialistes, surtout au niveau le plus élevé.

A base des tendances actuelles, on considérera les développements vraisemblables au cours de la prochaine décennie et on fera une tentative de prédire le rôle de la finition de métaux dans l'industrie et dans la vie quotidienne de l'an 2000 à peu près.

Metallackierung, eine Herausforderung

Zusammenfassung

Nach kurzer Besprechung der seit den frühen Nachkriegstagen gemachten Fortschritte in Metallackierung wird auf die gegenwärtigen Möglichkeiten dieser Technologie sowie deren Beziehungen zu anderen Technologien hingewiesen. Die Notwendigkeit Spezialisten, besonders der höchsten Grade zu erziehen, wird erklärt.

Die voraussichtliche Entwicklung der nächsten Dekade wird auf der Basis der gegenwärtigen Strömungen betrachtet, und ein Versuch gemacht, um die Rolle der Metallbeschichtung in der Industrie und im täglichen Leben um das Jahr 2000 herum vorauszusagen.

Требования в обработке металлов

Резюме

После краткого обзора прогресса в отделке металлов с первых послевоенных лет, анализируется сфера действия этой техники и ее отношение к техническим приемам. Указывается необходимость специализированного образования, в особенности на высшем уровне.

На основе текущих тенденций, обсуждаются направления возможного развития на следующие десять лет и делается попытка прогноза роли обработки металлов в промышленности и в обиходной жизни в 2000-ом году.

Introduction

Metal finishing can be defined broadly as the surface treatment of metals or the application of metallic coatings to non-metals with the object of:

> protecting them against corrosion—and very often simultaneously imparting a pleasing appearance to them—and/or
>
> endowing them with specific surface properties, e.g. hardness, wear resistance, anti-frictional properties, increased resistance to fatigue, and electrical, magnetic, thermal or optical properties.

The following are examples of well-known processes practised by metal finishers:

> cleaning, etching, electrochemical and chemical polishing, mechanical treatments—polishing, abrasive blasting, tumbling—electroplating, chemical (electroless) plating, anodic oxidation, conversion coating, hot dip coating—galvanising, aluminising and hot tinning—diffusion coating—sherardising, calorising, chromising, borodising—surface hardening, vacuum and vapour coating, flame, arc and plasma spraying, organic coating, etc.

This list, although large, is far from complete.

Whereas the main application of metal finishing before the 1939-45 war was in the protection and decoration of metallic articles, such as motor car trim, household articles, etc., an entirely new picture emerged in the post-war era. The vast amount of research work carried out during the war years in all fields of science and engineering became available for peaceful uses, and this resulted in enormous progress in the various aspects of engineering. New industries emerged, instances being the electronics industry, the nuclear engineering industry, the computer industry and space technology. Many of the products had to be made from materials having

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* Presented as a Plenary Lecture at the 1973 Eastbourne Conference.

specific properties not possessed by the conventional materials then available.

Thus, entirely new materials had to be developed having a greatly increased strength, hardness, resistance to wear, to corrosion, to oxidation at high temperatures and to fatigue and creep. Other important requirements which often had to be met were for certain electrical and electromagnetic properties.

Many of these properties are determined not so much by the composition and structure of the bulk of the materials from which the components are made, as by the specific properties of their surfaces. Hence, a large proportion of industrial research was devoted to metal finishing, which is concerned essentially with materials surfaces, in search of solutions to many of the technical problems that arose.

Numerous research and development projects were initiated with this object in view, and the money and efforts invested have paid ample dividends. An ever increasing number of research papers on various aspects of materials' surface treatment have appeared, which is an unmistakable proof of the importance of this aspect of technology to industry.

New applications

The advent of electronics has opened up an entirely new outlet for metal finishing. In this field, metal coatings are used in valve manufacture, for the joining of metals, for imparting high electrical conductivity to low conductivity parts, for trimming and for various other purposes.

In valves, the emission characteristics of a grid depend on the nature of its surface. One of the services offered to the electronic engineer by the metal finisher is the control of the secondary emission qualities of the grids of transmitting valves by controlling the surface of the coating on the grid to give the required properties.

Low primary grid emission in transmission valves with thiorated tungsten cathodes is obtained by using a platinum-coated grid. Techniques have been perfected for electroplating a bright platinum coating, which is stable throughout the life of a valve, on grids in those special cases where a high secondary emission is required. Receiving valves with oxide cathodes require gold plated grids to suppress primary emission. Other metals, such as osmium, are also used for coating cathodes. These are deposited by sputtering.

It is difficult to make reliable welds between two pieces of molybdenum. This is overcome, in the case of large grids for transmission valves, by plating a few microns of platinum on to the grid rods.

In making ceramic seals for vacuum equipment, for instance valves, the molybdenum-metallised ceramic is normally plated with copper or nickel to facilitate "wetting" of the braze metal.

In the semi-conductor field, evaporated films are commonly thickened up (to 3-5 microns) by plating to permit the thermo-compression bonding of lead wires. High-frequency wave guide equipment with soldered joints has to be plated with silver, copper or gold to provide a continuous high conductivity skin. For very high frequency applications the surface must be smooth or bright. Copper and silver are frequently protected by a thin gold layer to prevent degradation by tarnishing.

The frequency of quartz-crystal shear oscillators is adjusted by plating a controlled thickness of gold on to the electrodes. The thickness of the tantalum metal on thin film microcircuits is trimmed by anodising.

The growth processes in germanium crystals can be studied by electroplating copper on to polished sections. Variations in resistivity, which are reflected in differences in the density of the plating, give information on the evolution of the dendrites. The plating current is supplied in pulses obtained by discharging a capacitor from 500 to 1,000 volts. Similar techniques have given information on the structure of other single crystals.

Electrodeposition of gold is used to provide a surface for mounting silicon crystals, for thermo-compression bonding, and thickening up of patterns of evaporated gold on ceramic slides for the production of microcircuits.

Printed circuitry requires not only the deposition of metal coatings, especially coatings of noble metals, on various substrates, but also specific pre-treatment of these substrates, and special surface preparation techniques have had to be developed. In addition, the properties of the coatings, particularly their porosity, have to be strictly controlled, and as a result of the large volume of research which was devoted to this aspect alone, there is now a much better understanding of the factors responsible for some of the structural characteristics of electrodeposits.

A more recent application of electroplating in the computer industry is the deposition of magnetic alloys on memory bands.

In high temperature engineering, diffusion coatings have been increasingly used for the protection of metallic components against the action of corrosive gases at elevated temperatures. Chromium and other elements are diffused into the surfaces of components to a predetermined depth, thereby alloying with the substrate and forming protective surface films. Numerous methods, some of them electrolytic, have been developed to effect diffusion.

In other engineering applications, specific coatings are often used to provide hard, wear-resistant surfaces, or else to reduce friction between rubbing surfaces. Hard chromium and other coatings have been used for this purpose for a long time, and alloy coatings are becoming increasingly important. Another interesting development is the co-deposition of tiny ceramic particles with metals by electrolysis. Some of these coatings have excellent wear properties, even at elevated temperatures.

Metal finishing provides by far the most important means of protecting metals against corrosion. Early in 1971, Her Majesty's Stationery Office published a report by the Committee of Corrosion and Protection. In it, the cost of corrosion and protection of metallic structures, components and articles is estimated to be in excess of £1,365 million per year, of which some £300 million could be saved by the intelligent application of well-established methods of protection.

The processes used in the protection of metals against corrosion include not only paint application but also the deposition of metal coatings by electroplating, hot dipping, spraying and diffusion. Conversion coatings such as phosphating and chromating are also extensively used for specific protective functions.

Electroplating is also used for the repair of worn parts, and another related aspect of this process, known as electroforming is used as a manufacturing process. Examples of items that can be produced by this process are record stampers, seamless perforated tubes, wave guides, plain and perforated metal foils, razor foils, moulds and dies, diamond cutting tools, aerospace components (e.g. engine intakes, nose cones, fuel tank bulkheads in pockets, wind tunnel nozzles, venturi tubes, erosion shields, etc.) and silverware. It is also interesting to note that electroforming was the technique used in making the crown used at the investiture of HRH the Prince of Wales in 1969.

The advantages of electroforming over other manufacturing techniques are: a better control of the structure, and hence of the properties, of the manufactured products, close dimensional tolerances (hence obviating the need for final machining) and the ability to reproduce accurately mandrel shapes.

It will be appreciated that electroforming is not a metal finishing process, but the principles involved are very similar to those of electroplating, and hence it is not too difficult for a metal finisher to apply himself to this technology.

Although the development of metal finishing processes for industrial purposes has been remarkable, considerable progress has been made in the decorative field. Here, processes such as electrodeposition of nickel and chromium coatings and anodising and dyeing of aluminium, are used not only to protect the underlying metal against corrosion, but also to impart an attractive appearance to a multitude of articles, ranging from household goods to motor cars and machine parts.

Fundamental research on the mechanism of action of organic addition agents has opened the way to the development of a multitude of bright electroplating processes, thereby saving time and labour for the production of attractive finishes. The development of organic levelling agents and their incorporation into plating solutions has obviated the necessity for preliminary high-grade polishing.

Satin nickel, microcracked and microporous chromium coatings, which give enhanced protection to steel and diecast articles, and new anodising techniques, are just a few examples to illustrate the enormous activity that has been taking place in the field of decorative metal finishing. Methods of depositing metals from organic solutions are being experimented with, and the electro-deposition of chromium from solutions in dipolar aprotic solvents has reached the pilot plant stage.

In addition, electrochemical and chemical etching and polishing have been developed to a considerable extent, and great strides have been made in the general field of surface preparation, upon which the quality of the finish largely depends.

The deposition of metals on plastics has now become a very important field. The technical know-how is far in advance of the scientific theory as to the type of bond forces involved between metals and polymers, and a great deal of research is in progress all over the world to elucidate the mechanism of adhesion. Although plated plastics are used in this country essentially for decorative purposes, there are unmistakable signs that in the not too distant future they will be applied to specialised industrial uses. The combination of lightness, ease of fabrication and cheapness make plastics a very attractive proposition for use as substrates for metallic deposits which can confer hardness, wear resistance, electrical conductivity and other properties on them. Deposition of metals on plastics and other non-metallic materials nowadays comes more and more within the purview of everyday metal finishing. The present state of development is only the beginning of the exploitation of the enormous possibilities, since currently only two materials are plated commercially, viz. ABS and polypropylene.

The range of materials that it will be possible to process in this way will widen considerably as the understanding of the mechanism of adhesion increases and materials' surfaces can be pretreated in such a way as to make them accept metal films. Electroless deposition of metals, which is both a process in its own right and an integral intermediate stage in plating on plastics, has specific advantages over electroplating techniques in that coatings of uniform thickness can be deposited on articles of complicated shape, as well as on the inside walls of small-diameter tubes.

Great strides have been made since the commercial introduction of electroless nickel some fifteen years ago, and a far better understanding of the factors controlling the rate of growth of these films, as well as their structures and properties, has been gained. Whereas currently only nickel and copper find widespread use as materials for electroless deposition, the author envisages that other metals will be applied by this technique in the not too distant future and that methods will be developed for producing bright, levelled, ductile coatings.

There has been an increasing tendency to automate most metal finishing processes, from the loading stage to the finished product stage, in order to make them more economical and to ensure uniformity of quality of finish. Machines have recently been developed to handle transfer programmes automatically. They receive orders from a standard telex tape and can run all operations on a plating line. By the mere touch of a button one of several programmes can be set in motion.

It can be assumed that such equipment will be installed over the next few years wherever large numbers of components have to be processed with a variety of different finishes.

Research and education

From this brief account, it can be seen that metal finishing not only covers a whole gamut of processes of the greatest diversity, but is constantly widening its field of application, often by the development of entirely new processes for materials' surface treatment, and hence can be fairly described as one of the most important aspects of the even wider field of materials' surface technology.

Materials' surface technology is a field which is likely to develop at a greater rate than that at which new materials become available, since a considerable proportion of the rapidly emerging new materials require surface treatment, and a whole range of individual and composite treatments have to be worked out in many cases. Hence the application of this technology in engineering is far-reaching and of the greatest importance, and there is tremendous scope for further fundamental and applied research.

Fundamental research is essential, for in spite of the important role played by surfaces in many technologically significant materials problems, there is at present a serious lack of knowledge and understanding of many of the basic mechanisms and parameters involved.

The reason for this gap is partly due to the fact that many of the properties are critically dependent on composition, structure and on mechanisms that occur on an atomic scale, e.g. interface diffusion, presence of impurity atoms at the surface, etc., and the techniques necessary for studying these effects have not been available in the past. More recently, however, new and sophisticated techniques (e.g. field ion microscopy, atomic probe analysis, ultra high vacuum) have been developed, which now make it possible to study the important scientific parameters. It has become possible to formulate the problems more clearly and to define the parameters that should be investigated; and it has become apparent that some of the problems (e.g. surface reactions) should be studied by using an interdisciplinary approach.

A better understanding of surfaces (and interfaces) should lead to the possibility of closer control of their properties, and such control would have far-reaching effects on the development of materials technology as a whole.

Apart from fundamental research, there is obviously enormous scope for applied research and development work, examples being: the development of methods for the electrodeposition of metallic coatings from non-toxic high-speed electrolytes, giving improved control over the uniformity of coating thickness and structure; the deposition of coatings exhibiting a superior resistance to corrosion, particularly at high temperatures; coatings which would improve such properties of metals as fatigue strength; co-deposition of particles having dry lubricating properties with metals on to refractory metals—this would solve a multitude of problems in connection with high-temperature bearings; electrodeposition of ceramic coatings, semiconductor coatings, etc.

Such work would undoubtedly create new outlets and stimulate the development of new industrial processes.

It will be appreciated by now that metal finishing is a technology based on advanced science and engineering, and that future progress will depend on research and advanced development work. In the past, research and development work was carried out by scientists and engineers, often in isolation, so that there was little or no co-ordination between research and its application. This has resulted in considerable waste of effort and resources.

Although it is now realised that an interdisciplinary approach to most metal finishing projects is vital, it is also essential that the efforts should be co-ordinated and directed towards a tangible goal in such a manner as to achieve the desired results quickly and economically.

The role of the co-ordinator must be filled by a metal finishing technologist. This was recognised by the Institute of Metal Finishing some time ago and, by introducing examinations in metal finishing science and technology at various levels up to Honours degree standard, it has encouraged educational institutions to introduce courses preparing students for these examinations. The syllabus leading to the Graduateship of the Institute is interdisciplinary in nature, covering materials' surface science, metallurgy, engineering (including automatic handling and control), corrosion science, metal finishing technology, advanced experimental techniques and management. In addition, the student must carry out extended project work on a metal finishing topic in which he learns the methodology of attacking a problem under the supervision of an experienced research worker, as well as familiarising himself with the manipulation of sophisticated instruments.

These people should be well qualified to initiate and correlate research and development work in metal finishing.

Long-term developments

Before looking at trends which will increasingly make themselves felt in the 1980's, the likely effects of the rapidly increasing world population, the dwindling non-renewable resources in the earth's crust, and the increasing pollution of the atmosphere due to the burning of fossil fuels (i.e. coal, oil and natural gas), on the future pattern of life[1] must be considered.

Population, industrial production and natural resources

The present population of the earth is estimated at some 4,000 million people. Its present rate of growth is about 2.1 per cent per year, corresponding to a doubling time of 33 years. By the year 2000, the figure should approach 7,000 million people if the present rate of growth continues.

The world industrial production, which is a measure of human prosperity, was increasing at a rate of 7 per cent per year during the period 1963-1968. If the production index in 1963 is taken as 100, by the year 2000 it will have surpassed 500. It must, however, be pointed out that the industrial growth of rich nations is much faster than that of poor nations and, therefore, the economic gap between these nations is widening with the passage of time.

The earth's crust contains vast amounts of those raw materials which man has learned to mine and to transform into useful things. However, owing to the ever-increasing rate of their extraction and consumption, and to the fact that their reserves are not inexhaustible, a fixed upper limit will be approached, often very suddenly. Some non-renewable resources will, according to estimates based on proven existing reserves, be exhausted in a measurable time. Despite spectacular recent discoveries, there are only a limited number of places left to search for most minerals. Geologists disagree about the prospects for finding large, new, rich ore deposits. Reliance on such discoveries would be unwise in the long term.

To form an idea of the number of years it will take for some of the more important non-renewable resources to become exhausted if their consumption continues to increase at the present rate:[2]

	Years
Aluminium	31
Chromium	95
Coal	111
Cobalt	60
Copper	21
Gold	9
Iron	93
Lead	21
Manganese	46
Mercury	13
Molybdenum	34
Natural Gas	22
Nickel	53
Petroleum	20
Platinum Group Metals	47
Silver	13
Tin	15
Tungsten	28
Zinc	18

This time-span will be expanded somewhat if new reserves are discovered. However, even being extremely optimistic and assuming that present known reserves of each resource can be expanded fivefold by new discoveries, the time-span for iron, chromium and nickel will only barely double, that for zinc and petroleum will increase two and a half-fold, whilst that for coal will increase by only 25 per cent.

It has been found that, for many resources, the usage rate is growing even faster than the population, indicating both that more people are consuming resources each year and also that the average consumption per person is increasing each year.

It is clear that the present exponentially growing usage rates greatly diminish the length of time that world-scale economic growth can be based on these raw materials.

The prices of those resources in shortest reserve have already begun to rise and are likely to continue to rise at an increasing rate, and it cannot be too long before the prices of even the most abundant resources, viz., iron, chromium and coal, begin to rise steeply.

The simplest conclusions that could be drawn from a consideration of total world reserves of resources are further complicated by the fact that neither resource reserves nor resource consumption are distributed evenly about the globe. Industrialised consuming countries are heavily dependent on a network of international agreements with the producing countries for the supply of raw materials essential to their industrial base. Added to the difficult economic question of the fate of various industries as resource after resource becomes prohibitively expensive is the imponderable political question of the relationship between producer and consumer nations as the remaining resources become concentrated in more limited geographical areas. Recent nationalisation of South American mines and successful Middle East pressures to raise oil prices suggest that the political question may arise long before the ultimate economic one.

Given diminishing resources and increased prices, how are the 7,000 million people expected by the year 2000 to develop economically, so as to ensure a reasonably high standard of living?

Several fundamental steps must be taken by future society, namely:

it must learn to reclaim and recycle discarded materials,

it must develop methods of increasing the durability of products made of scarce resources,

metals will have to be used sparingly and the maximum advantage will have to be taken of their specific properties,

other materials will have to be used and new synthetic and composite materials will have to be developed to take, as far as possible, the place of metals, and

fossil fuel combustion must be replaced by other methods for the generation of energy.

The first three steps, viz reclamation of discarded materials, making products more durable, and using metals economically, are in opposition to current practice and trends.

Reclamation of materials is nowadays practised only in those cases where it is economical so to do.

Most consumer goods are produced with a limited life in view, i.e. with a built-in obsolescence, to ensure a constant turn-over, which is further promoted by the introduction of new designs and fashions.

Metals are at present used wastefully. Many of the metallic characteristics could be imparted to products made of other materials by coating them with metallic films, and it is here that metal finishing will play a dominant role in the future.

Metals should be used as a bulk material only in those special cases where no other materials can possibly take their place. It is only by using metals economically, and mainly in the form of thin surface layers on other materials, that the remaining reserves can be made to last for a long time. The sooner this is generally realised and steps are taken to implement a policy of metal economy and conservation, the better will be the chances for an increasing prosperity for future generations.

Pollution

What happens to the metals and fuels extracted from the earth after they have been used and discarded? In one sense they are never lost. Their constituent atoms are rearranged and eventually dispersed in a diluted and unusable form into the air, the soil and the waters of our planet. The natural ecological systems can absorb many of the waste products of human activity and reprocess them into substances that are usable by, or at least harmless to, other forms of life. When any waste product is released on a large enough scale, however, the natural absorptive mechanisms can become saturated. The wastes of human civilisation can build up in the environment until they become objectionable, and even harmful.

It is little wonder then that another exponentially increasing quantity in the world system is pollution.

Carbon dioxide is one of the by-products of fossil fuel consumption. The concentration of lead particles in the air, released from motor cars, incinerators, industrial processes and agricultural pesticides, is also increasing. At what point will these contaminants become a serious threat to life? Nobody knows at present, since insufficient information is available. It is, however, known from direct evidence that they markedly increase the rate of corrosion of metals. If the cost of corrosion in industrialised countries is extremely high nowadays, it is likely to assume astronomical proportions in the future unless effective measures are taken constantly to increase the effective protection of metals. Since metal finishing is the most widely used method of protecting metals, this problem will increasingly exercise the minds of metal finishers.

The smelting of metals is a large contributor to pollution, and it is highly likely that in future metals will be extracted mainly by "electrowinning," i.e. by electroplating processes.

The present use of gas, coal and petroleum for power generation is not only harmful to health, but is an extremely wasteful application of valuable resources, which should be used entirely as raw materials for the production of chemicals for, amongst other things, the manufacture of synthetic materials.

By the turn of the century it is feasible that atomic energy will have largely taken over from fossil fuels as a source of power generation, but the replacement of the present pollutants by radioactive by-product pollutants may present another problem. However, it is to be hoped that a world society with readily available nuclear power would be able to control industrial pollution generation by technological means.

The generation of power free from harmful by-products from solar energy is a distinct possibility in the future.

The metal finisher of the future

What effects are the world trends likely to have on the future of metal finishing?

From the evidence presented here, it seems likely that metals will be increasingly displaced by other materials from their traditional fields of use as bulk materials. However, no other materials possess the unique combination of properties characteristic of metals. For this reason, coupled with the constantly increasing need of using metals as sparingly as possible, wherever practicable metals will be more and more used as coatings on other materials.

Since the characteristics of surfaces often have a decisive and fundamental influence over many properties of materials, metal coatings will be applied to non-metallic materials not only to impart metallic properties to their surfaces, but also to control many of their bulk properties, and so to suit them for specific applications.

What will be the probable role of the metal finisher of the future? The inevitable conclusion seems to be that he will have to become a materials finisher, i.e. a materials surface scientist and technologist. His task will be to develop methods of treating surfaces of non-metallic, as well as metallic, materials and composites with the object of endowing them with specific physical, chemical and mechanical properties for widespread engineering applications.

His services will be sought by the engineering industry, to which he will act as a consultant at various stages of production, from the planning and design to the finished product stage.

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The role of coatings in corrosion prevention—future trends*

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Summary

Metallic corrosion involves a complex, electrochemical interaction between a metal and its environment. However, in addition to its electrochemical basis, corrosion is affected by chemical engineering factors such as heat and mass transfer, by metallurgical factors such as microstructure and alloy composition, by engineering factors such as tensile stress levels and vibration, and by chemical factors such as adsorption, film growth and environment composition. There are a correspondingly wide variety of approaches to corrosion prevention. In general, however, these may be divided into five categories based on (i) design, (ii) materials selection, (iii) environmental control, (iv) anodic and cathodic protection, (v) protective coatings (which in the widest sense of the term includes paints and other organic coatings, metallic coatings and inorganic coatings). In any particular instance, a combination of methods would normally be adopted and, of course, with very few exceptions, economic factors are of overriding importance.

These and other factors are discussed in rather more detail to put into perspective the present role in corrosion prevention of coatings in general and of paints in particular. The possible future trends in corrosion prevention, and its impact on the role of coatings, is discussed.

Keywords

Types and classes of coatings and allied products
corrosion inhibiting coating

Properties, characteristics and conditions primarily associated with materials in general
electrokinetic effect

Le rôle de revêtements dans le domaine de la prévention de corrosion

Résumé

La corrosion des métaux entraîne une complexe interaction électrochimique du métal et de son environment. Cependent, de même que sa base électrochimique, le degré de corrosion est influence par les facteurs dans le domaine du génie chimique, tels que les niveaux de l'effort de traction, et de la vibration, et par les facteurs chimiques tels que l'absorption, la croissance de la couche des produits de corrosion, et la composition de l'environnement. Par conséquent, il y a une gamme étendue d'abords possibles à la prévention de corrosion. En général, cependant, on peut les repartir sous cinq rubriques, (i) conception, (ii) sélection des composants, (iii) contrôle de l'environnement, (iv) protection anodique ou cathodique, (v) revêtements protecteurs (qui, dans la force la plus étendue du terme, renferment les peintures, les autres revêtements organiques, les revêtements métalliques ou inorganiques). Pour chaque cas individuel, on se servirait generalement d'une combinaison de méthodes, où, naturellement, sauf les cas exceptionnels, les facteurs financiers ont une importance primordiale.

Dans cet article, on discute ces facteurs-ci et d'autres en plus grand détail afin de mettre en perspective, dans le domaine de la prévention de corrosion, le rôle actuel de revêtements en général, et de peintures en particulier. On discute les tendances eventuelles dans le domaine de la prévention de corrosion, et également son influence sur le rôle de revêtements.

Die rolle von Anstrichen im Korrosionsschutz—Künftige Trends

Zusammenfassung

Bei Metallkorrosion finden komplizierte elektrochemische Reaktionen zwischen einem Metall und seiner Umgebung statt. Zusätzlich zu ihrer elektrochemischen Grundlage wird Korrosion beeinflusst durch solche Faktoren wie Verfahrenstechniken, z.B. Hitze und Massenübergang, durch metallurgische, z.B. Mikrostruktur und Zusammensetzung einer Legierung, durch konstrukrive, z.B. Höhe der Zugspannung und Vibration, sowie durch chemische, z.B. Adsorption, Filmwachstum und Zusammensetzung der Umgebung. Dementsprechend gibt es viele Wege zur Korrosionsverhütung. Diese können im allgemeinen jedoch in fünf Kategorien eingeteilt werden, beuhend auf

(i) Anordnung
(ii) Materialauswahl
(iii) Kontrolle der Umgebung
(iv) anodischem und kathodischem Schutz
(v) Schutz durch Beschichtungen (welche im weitesten Sinne des Wortes Anstrichmittel und andere organische Überzüge, metallische und anorganische Beläge einschliesst).

In allen besonderen Fällen würde normaler Weise eine Kombination von Methoden gewählt werden, und natürlich sind dabei, mit sehr wenigen Ausnahmen, wirtschaftliche Faktoren von überragender Wichtigkeit.

Im Vortrage werden diese und andere Faktoren mehr ins einzelne gehend besprochen um die gegenwärtig von Korrosionsschutzmitteln im allgemeinen und von Anstrichfarben im besonderen gespielte Rolle in die richtige Perspektive zu bringen.

Mögliche zukünftige Trends zur Verhütung von Korrosion und deren Einfluss auf die Rolle von Anstrichmitteln werden besprochen.

Роль покрытий в предотвращении коррозии Будущие тенденции

Резюме

Коррозия металлов представляет собой сложное, электрохимическое взаимодействие между металлом и окружающей средой. Но кроме электрохимической характеристики, на коррозию влияют также химические и механические факторы как например теплота и массообмен, металлургические факторы как например микроструктура и состав сплава, инженерные факторы как например растягивающее напряжение и вибрация и химические факторы как например адсорбция, рост пленки и состав окружающей среды.

В связи с этим возможен ряд различных подходов к вопросу предохранения от коррозии. Но вообще говоря, они могут

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* Presented at the 1973 Eastbourne Conference.

быть разделены на пять категорий, на основании (I) расчета, (II) выбора материалов, (III) контроля окружающей среды, (IV) катодной и анодной защиты и (V) предохранительных покрытий (которые в широком смысле включают краски и другие органические покрытия, металлические покрытия и неорганические покрытия). В отдельных случаях обычно применяется комбинация этих методов и, конечно, с очень немногими изключениями, экономические факторы представляют особую важность.

Эти и другие факторы подробно обсуждаются, чтобы дать правильное впечатление современной роли предотвращения коррозии при помощи покрытий вообще и красок в особенности. Обсуждаются возможные будущие направления в предотвращении коррозии и ее отношения к роли покрытий.

Introduction

Current economics of corrosion

The DTI Report of the Committee on Corrosion and Protection estimated[1] that in 1970 the cost of corrosion to the UK was a minimum of £1,365 million. To put this very large sum into perspective, £1,365 million was at that time equivalent to about 3.5 per cent of the gross national product. Furthermore, it was suggested by the Committee that some £310 million of the total cost could be saved merely by the application of existing knowledge and techniques for corrosion prevention and control. Table 1, reproduced from the report, breaks down the estimated cost of corrosion, and the estimated potential savings, into the contributions of the major areas of industry investigated by the Committee. However, although it is extremely expensive today, the overall economic and social importance of corrosion, and more particularly of prevention and protection, seems certain to increase significantly as the year 2000 approaches.

Table 1

National cost of corrosion and protection

Industry or agency	Estimated cost, £ million (1970)	Estimated potential saving £ million (1970)
Building and construction	250	50
Food	40	4
General engineering	110	35
Government departments and agencies	55	20
Marine	280	55
Metal refining and semi-fabrication	15	2
Oil and chemical	180	15
Power	60	25
Transport	350	100
Water	25	4
Total	1,365	310

Future trends in corrosion protection and prevention

Projections such as when, why, and at what level the world's population will stabilise are matters of very heated controversy; as are the questions of when and at what level the world will become seriously over-populated. However, it is a fact that the world's population is at present in the order of 3,600 million, and is increasing at the rate of approximately two per cent per annum; it is almost certain that the population will continue to grow at something like this rate up to at least the year 2000.[2] Similarly, there can be no question that the world's supply of many materials and of conventional energy sources is strictly limited and must eventually be exhausted. The controversy arises when an attempt is made to fit a time scale to the rate of depletion, and to predict the consequences. Again, whether or not the world is already seriously polluted and on the brink of an ecological disaster as a result of the comparatively restricted industrialisation which has already occurred continues to be debated. Yet it seems inconceivable that the majority of the world's population (in Asia, India, Africa and Latin America) will be ultimately satisfied with a standard of living very much lower than that enjoyed by the minority in North America and Western Europe.

Taken together, these trends can be interpreted as indicating that, whatever the short-term, apparent economic advantages, it will not be possible for ever to manufacture and market components or goods which are deliberately designed to be replaced every few years; it will not be possible for ever to substitute a unit quantity of aluminium for a unit quantity of steel, when the former requires many times more energy than the latter to extract; it will not be possible for ever to use sacrificial zinc anodes without taking into consideration total zinc resources and the introduction of more heavy metal ions into the biosphere; nor, for similar reasons, will it be possible to rely on the widespread availability and applicability of lead-rich paints and primers.

In summary, the above trends clearly indicate that corrosion prevention and control will, in the future, assume ever increasing importance, but that some of the corrosion control techniques which are currently well established will have to be critically re-examined.

The electrochemical basis of corrosion and protection: thermodynamics

The application of existing techniques for corrosion prevention and control, and the development of new methods, must inevitably be based on the well-established, electrochemical principles of corrosion. It, therefore, seems appropriate, at this stage, to review briefly, and by way of examples, the basic elements of corrosion science.

Equilibrium thermodynamics can be used to study energy levels and to determine whether or not any particular corrosion reaction is probable. Consider, for example, a divalent metal M exposed to dilute (non-complexing), de-aerated hydrochloric acid. The corrosion reaction is:

$$M + 2HCl \rightarrow H_2 + MCl_2$$

If this reaction is to be thermodynamically possible, the free energy change associated with it must be negative. Assuming that the acid and the metal chloride are both fully ionised, the presence of the chloride ions may be neglected and the corrosion reaction rewritten as the sum of two electrochemical reactions:

$$2H^+ + 2e \rightarrow H_2 \text{ (reduction)}$$

$$M \rightarrow M^{2+} + 2e \text{ (oxidation)}$$

The thermodynamic requirement for the corrosion reaction to be possible can be rewritten, similarly, as:

$$\Delta G_{reduction} + \Delta G_{oxidation} < 0$$

These free energy changes may, in turn, be related to the equilibrium electrode potentials for the particular electrochemical process, as follows:

$$\Delta G_{reduction} = -nFE$$

and

$$\Delta G_{oxidation} = nFE$$

where n is the number of electrons involved in the reaction, F is Faraday's constant, and E is the equilibrium potential. It follows from this that if a corrosion reaction is to be thermodynamically possible, the electrode potential of the oxidation (anodic) reaction must be less positive or more negative than that of the associated reduction (cathodic) reaction.

Under standard conditions of unit activity, the following potentials can be obtained experimentally, or calculated from thermodynamic data:

Reaction	Potential (volts)
$Au \rightarrow Au^{3+} + 3e$	+ 1.50
$2H_2O \rightarrow O_2 + 4H^+ + 4e$	+ 1.23
$Cu \rightarrow Cu^{2+} + 2e$	+ 0.34
$H_2 \rightarrow 2H^+ + 2e$	0.00
$Zn \rightarrow Zn^{2+} + 2e$	− 0.76

Thus, it can be inferred that zinc could corrode with hydrogen evolution, but that copper could not. Of course, if the acid were saturated with oxygen, oxygen reduction would become a possible cathodic reaction, so that both copper and zinc could corrode; gold on the other hand would still not do so.

Under non-standard conditions ($a \neq 1$), the equilibrium potential must be calculated from the Nernst equation:

$$E = E^\circ + RT\ln(a)/nF$$

where E° is the standard equilibrium potential for the reaction (which is related to the standard chemical potentials of the species of reactants and products), and a and n are the activity and charge, respectively, on the participating ions. Otherwise, however, the principles remain the same. In summary, metals can only corrode by an anodic (oxidation) reaction if an associated cathodic (reduction) reaction with a more noble equilibrium potential is available. In natural environments there are two possible cathodic reactions, oxygen reduction and hydrogen evolution; as noble metals, for example gold and platinum, have electrode potentials above those associated with these cathodic reactions, they have excellent corrosion resistance. However, if an alternative cathodic reaction with a very noble electrode potential is available, or if the equilibrium potential of the anodic reaction can be reduced sufficiently by complexing, noble metals can corrode quite readily; an example of these effects would be the corrosion of gold in "aqua regia".

The electrochemical basis of corrosion and protection: kinetics

Equilibrium thermodynamics can be used to determine whether or not a particular corrosion reaction is possible. If the reaction is possible, thermodynamic data give no indication whatsoever of the rate at which the reaction will occur, and a consideration of electrochemical kinetics is required. Thus, although the potential difference $|E_{cathodic} - E_{anodic}|$ is a measure of the thermodynamic driving force for the corrosion reaction, the rate at which the corrosion reaction actually occurs is determined by the current which flows as a result of this potential difference.

The anodic and cathodic potentials calculated from the Nernst equation are thermodynamic equilibrium values, whereas non-equilibrium conditions apply as soon as a current flows. As a result of the current flow, the potential of the cathode becomes less positive or more negative, and the potential of the anode more positive or less negative; in other words, the anodic and cathodic reactions become polarised, as illustrated by the potential versus current (Evans) diagram shown in Fig. 1.

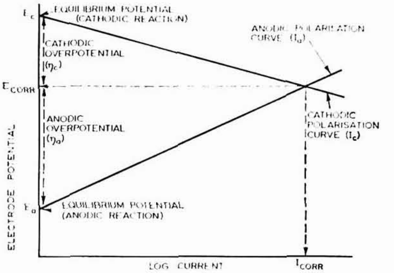

Fig. 1. Simplified Evans' diagram for a freely corroding metal

There are three sources of polarisation which contribute to the total polarisation of the electrode reaction. Activation polarisation is the result of a slow step, with a high activation energy, in the anodic or cathodic reaction sequence. For example, in hydrogen evolution this step is often:

$$H^+ + e \rightarrow H_{ads}$$

Concentration polarisation is caused by the limitation of the reaction rate resulting from the restricted rate of supply at the interface of one of the reacting species, and this is often the case when oxygen reduction is the cathodic reaction. Resistance polarisation is due to a potential ($IR_{interface}$) drop across the metal/electrolyte interface (in many cases as a result of the presence of surface films). It can be shown theoretically, and is observed in practice, that activation polarisation results in a linear relationship between the overpotential η (Fig. 1) and the logarithm of the current ($\log I$); this is referred to as "Tafel behaviour". Resistance and concentration polarisation result in the observed current being less than the value predicted by the Tafel equation.

Clearly, the total anodic and cathodic currents (I_a and I_c respectively) must be equal in magnitude but opposite in sign, otherwise electrical neutrality would not be preserved and charge build-up would occur. These currents, which are an electrical representation of the rate of dissolution and are described alternatively as corrosion currents (I_{corr}), are given by Ohms Law:

$$E_{cathode(polarised)} - E_{anode(polarised)} = \Delta E = I_{corr}R_{cell}$$

In most natural corrosion situations, the internal resistance of the corrosion cell (R_{cell}) is negligible, and the closed-circuit potential difference (ΔE) is therefore negligible. From this, it follows that, to a very good approximation, a freely corroding metal exhibits a single electrode potential designated the corrosion potential E_{corr} in Fig. 1.

In essence, all methods of corrosion prevention and control involve, either directly or indirectly, a reduction of the corrosion current I_{corr} or, more particularly, the anodic current I_a. For example, increasing the electrical resistance between the anodic and cathodic areas results in a large IR drop, a large ΔE, and a greatly reduced corrosion current, as shown in Fig. 2. Similarly, anything which tends to increase the anodic or cathodic polarisation, or preferably both, tends greatly to reduce the corrosion current I_{corr} even though there appears to be no change in E_{corr}; this is shown in Fig. 3. Again, decreasing the potential of the metal from its corrosion potential (by the use of sacrificial anodes or impressed currents) greatly reduces the anodic current by reducing anodic polarisation as shown in Fig. 4. Finally, increasing the potential can, in the case of certain metals, eventually decrease the anodic current as a result of a change in the anodic reaction from active dissolution to protective film formation. In practice, the electrode potential can be raised by means of an impressed current technique, or by the addition of an active cathodic reactant to the environment, the electrochemical reduction of which can proceed at a rate which exceeds the maximum rate of the anodic reaction at the potential of the active-passive transition. A comparison between the two cases of a sluggish and a rapid cathodic reaction (Fig. 5), shows that the former produces rapid corrosion, the latter little corrosion as a result of passivation of the surface.

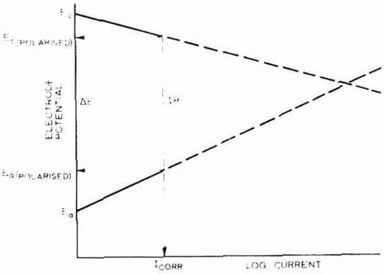

Fig. 2. Corrosion control by increasing the cell resistance

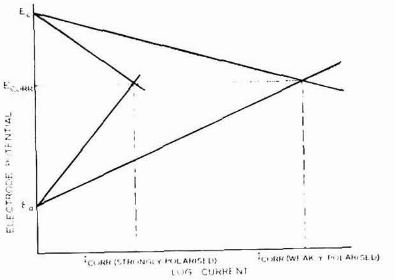

Fig. 3. Corrosion control by intervention in reaction polarisability (in practice only one reaction need be polarised; a movement of Ecorr could well be observed)

Conversely, any effect which tends to increase the anodic current is detrimental in that it also tends to increase the uniform corrosion rate. In practice, the anodic current density is often more important than the total anodic current. For example, a corrosion current I_a distributed evenly over an area A might result in an acceptable rate of uniform corrosion, whereas a reduced corrosion current of $I_a/10$ localised over an area of $A/1000$ would probably result in unacceptable localised corrosion since, locally, the penetration would have increased one hundred fold. In general, any factor which favours the development of discrete anodic and cathodic areas, or which favours localised, high anodic current densities is detrimental, even though the total anodic current might be low, because severe localised corrosion is the probable result.

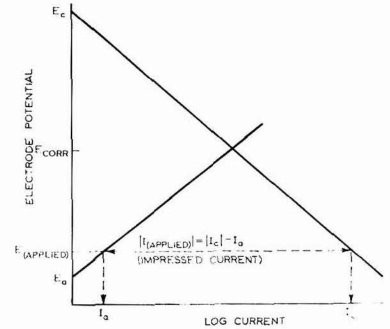

Fig. 4. Corrosion control by cathodic polarisation (cathodic protection)

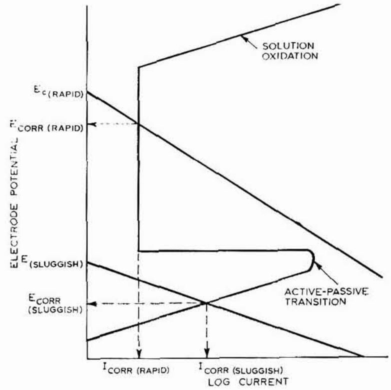

Fig. 5. Corrosion control by anodic polarisation

Figs. 2 to 5 inclusive show the electrochemical basis of the more common methods for corrosion control. In practice, the techniques available for the prevention of corrosion fall into the following five categories:

(a) design

(b) materials selection

(c) environmental control

(d) anodic and cathodic protection

(e) coatings.

The main body of this paper gives a necessarily brief review of the current practices and future trends in the above five approaches to corrosion control.

Coatings

Three essentially different types of coating can be applied to metal surfaces to prevent or control corrosion.

Organic coatings

Organic coatings range from oil-based paints through emulsions, alkyds, polyurethanes and vinyls, to epoxies, zinc-rich paints, bitumenous coatings, rubber and plastic liners. On a tonnage basis, organic coatings protect more metal from corrosion than any other type. The function of the coating is, of course, to separate the metal from its environment, and its principal mode of action is to lower interfacial conductivity by interposing a voltage drop, thus providing corrosion control by the method illustrated in Fig. 2.

Metallic coatings

Metallic coatings can be either less noble than the substrate (for example, zinc coatings on steel) or more noble (for example, chromium and nickel coatings on steel). Whilst these coatings present to the environment a more corrosion resistant material than does the substrate itself, the base metal coatings provide, in addition, temporary sacrificial protection ("Anodic and cathodic protection" section). The more noble coatings, not having this advantage, produce galvanic cells at holidays in the coating, which can give rise to intense local corrosion; their effectiveness, therefore, depends critically on the continuity of the coat. The relative importance of organic and metallic coatings can be judged by the fact that it has been estimated[1] that in 1970 in the UK some £650 million was spent on organic coatings and of the order of £130 million on metal coatings for corrosion prevention. Nevertheless, over half of the world's production of zinc is used for the hot-dip galvanising of steel.

Inorganic coatings

Inorganic coatings range from conversion coatings, such as anodic oxide films on aluminium and phosphate coatings on steel, to vitreous enamels and glass linings. Many of the coatings find specific application and will continue to do so. In view of the more bland electrolytes involved, it is probable that anodic conversion coatings will find increasing use at the expense of electrodeposition coatings, where their performance is comparable, as the problems of waste disposal become more acute.

Design

Ideally, corrosion prevention should be borne in mind whenever any chemical plant, vehicle, structure or component is to be designed. In practice, however, the possibility of in-service corrosion is often completely overlooked; in the case of corrosion failures, it would not be difficult to reach the conclusion that the original designer was in favour of corrosion! Clearly, bad design can completely negate subsequent good materials selection and protective schemes; moreover, good design can permit the use of less expensive materials and systems. Equally clearly, the design stage is the earliest opportunity for the corrosion engineer to improve the overall corrosion resistance of a system, and in many instances the design stage is also the most economic point at which to prevent corrosion.

Uniform corrosive attack is, generally, relatively easy to handle at the design stage. Corrosion rate data (generally expressed as dissolution rates in inches per year) are readily available for a very wide variety of commercial metals and alloys in an even wider variety of service environments and exposure conditions. Furthermore, data not readily available for a particular alloy/environment combination, are often relatively easy and comparatively inexpensive to collate by simulating conditions of use in the laboratory or by in-situ testing. Thus, if a tank of a particular alloy requires a minimum wall thickness of 0.5 inches, a safety factor of 50 per cent, and a life of 25 years in an environment in which the corrosion rate is 0.01 inches per year, the design wall thickness must be 1 inch. On the basis of this rather simple approach, however, and in the narrowest economic terms, it is often more advantageous to make a mild steel tank twice as thick and to let it rust, than to make it rather thinner and to paint it and maintain the paint over a number of years. In practice, even today, the latter, possibly uneconomical approach is adopted because rusty tanks are unsightly and contribute to bad public relations; in addition, there are often tax advantages in a low initial capital investment followed by high maintenance cost. In the future, however, it seems that, increasingly, it will become unacceptable to permit expensive materials to corrode when this could be reasonably prevented; a much more thorough and more long-term social/economic assessment will be advisable and possibly even mandatory.

Many forms of localised corrosion are amenable to control at the design stage, although the approach might be less obvious. It is often overlooked that purely geometrical factors are very important. For example, Fig. 6a represents a good design for the base of a storage tank which requires periodic draining, whilst Fig. 6b represents a very poor design. In particular, the tank shown in Fig. 6b can never be completely drained, and severe corrosion of the base could result; this corrosion might in certain cases be further enhanced by concentration (by evaporation) or dilution (by condensation) of the residual liquid.

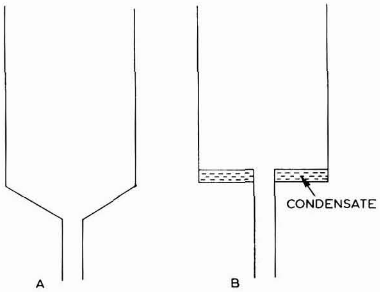

Fig. 6. Examples of (a) good, and (b) bad storage tank design based on the geometry

Very severe local corrosion can often be observed in crevices. This form of corrosion results from the separation of the anodic and cathodic areas in the corrosion cell. The environment at the tip of the crevice becomes depleted of oxygen, highly acidic, and aggressive; the tip of the crevice becomes the anode and suffers very severe corrosion, whilst the mouth of the crevice is the cathode and remains relatively free from attack. Many instances of crevice corrosion can be directly attributed to poor design and can, moreover, be completely eliminated by good design. Examples of good and bad design, in terms of susceptibility to crevice corrosion, are shown in Figs. 7a and 7b respectively. In this context, it cannot be emphasised too strongly that any crevice formed at a metal surface is potentially dangerous; gasket/metal crevices are at least as damaging as metal/metal crevices.

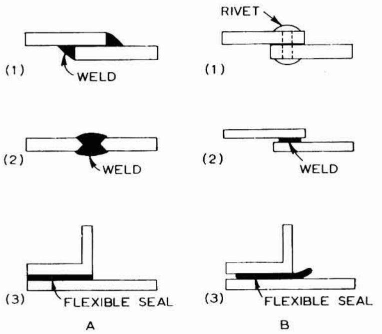

Fig. 7. Examples of (a) good, and (b) bad design to avoid crevice corrosion

When two dissimilar metals with widely differing corrosion potentials are coupled together in service, the familiar problem of galvanic corrosion arises. The more noble metal corrodes less than would normally be expected, whilst the less noble metal suffers accelerated corrosion. Galvanic corrosion can, of course, be eliminated by the selection of other materials. Alternatively, it can be prevented at the design stage, firstly by electrically insulating the two dissimilar metals from each other, and secondly by ensuring that, when contact between dissimilar metals is unavoidable, the area of the less noble metal is as large as possible compared to the area of the more noble alloy; this may often be achieved quite simply by appropriate coating of the noble metal.

Serious localised corrosion is often a result of cavitation; particularly common examples are the tips of propeller and pump impeller blades. To some extent this form of corrosion can be eliminated by changing the design to eliminate the cavitation. Pumps in particular, however, represent extremely severe service conditions and are notoriously prone to failure. The design should, therefore, allow for easy replacement of such components with a minimum of plant shutdown time. Similarly, erosion corrosion is observed when metals are exposed to liquids flowing at high velocities with severe turbulence and continual impingement. This can be greatly reduced or eliminated by the specification, at the design stage, of larger pipes (to reduce flow rate), smooth, streamlined bends (to reduce turbulence) and, if necessary, baffles (to reduce momentum change on impingement).

Finally, high tensile stresses should be avoided if at all possible, because certain alloys exposed to specific environments (for example austenitic stainless steels in chlorides) suffer stress-corrosion cracking. High applied tensile stresses are readily reduced at the design stage by increasing wall thicknesses, by eliminating stress raisers and so forth, whilst residual tensile stresses can often be reduced at the design stage by specifying alternative fabrication, forming and joining procedures. Similarly, alternating tensile stresses tend to cause corrosion-fatigue and can, in certain circumstances, be greatly reduced by careful design.

In summary, good design can eliminate or greatly reduce subsequent uniform or localised corrosion, whereas bad design can often completely negate subsequent attempts to control corrosion. At present, as emphasised by the DTI Report,[1] far too little attention is being paid to corrosion and protection from corrosion at the design stage. It can perhaps be expected that, by the year 2000, better education of undergraduate engineers in the importance of corrosion control, together with inevitable social and economic pressures, will have improved this situation.

Materials selection

Not all materials are equally resistant to corrosion in a given environment, and their corrosion resistance may change with variations in the conditions and circumstances of exposure. For example, changes in the chemical composition, temperature and flow rate of materials in an environment may all have an impact on degradation rates which may or may not be beneficial. Similarly, a hierarchy for the corrosion resistance of various materials in one environment cannot be used with accuracy for another environment. Fig. 8 demonstrates these simple observations for two relatively similar halogen acids. Within a restricted temperature range and above 60 per cent concentration, carbon steel may be used for handling hydrofluoric acid; as the concentration falls below this figure, the corrosion rate of the steel increases rapidly and the material cannot be used. In contrast, plain carbon steels would never be recommended for handling hydrochloric acid; indeed, corrosion inhibitors are added to this acid when it is used as a pickling agent to remove mill scale.

For metals, corrosion rates vary between very wide limits with the result that relatively arbitrary, sometimes unhelpful, classifications are made in order to describe the suitability of a material for a given service application. Typical classifications describe materials with corrosion rates of less than 5 mils per year as "good," those between 5 and 50 as "acceptable," and those greater than 50 as "poor" or "unacceptable." The danger is that the descriptive phrase takes precedence over the corrosion rate, and the fact that a particular environment might be intrinsically aggressive to most materials, and that a corrosion rate of 50 mils per year is, in consequence, particularly good, is overlooked.

Almost without exception, metals are susceptible to one or more of the various forms of localised corrosion, depending on the particular environmental conditions. These forms of corrosion have been discussed briefly above. It is probably worth reiterating, however, that when an alloy experiences serious localised corrosion, the penetration rate may be orders of magnitude greater than the uniform corrosion rate. Tabulations of uniform corrosion rate data should, therefore, give some indication of the possibility of localised corrosion in particular alloys and environments. Conversely, when selecting a material for a particular application, both the uniform corrosion rate and the possibility of some form of localised corrosion must be considered. In this context, it must be emphasised that common contaminants (particularly Cl^- ions) in very low concentrations can often result in severe localised corrosion. A full description of an environment is, therefore, essential when assessing the likely corrosion behaviour of a metal in it. Nevertheless, by careful selection of materials, advantage may be taken from variations in uniform corrosion rates to minimise metal loss.

As outlined above, the differing uniform corrosion rates observed with different alloys and under various environmental conditions can be interpreted in terms of the electrochemistry of the corrosion process, and more specifically in terms of the equilibrium thermodynamics and the kinetics of the process. In this context, Pourbaix[3] has summarised the equilibrium conditions for aqueous systems by plotting

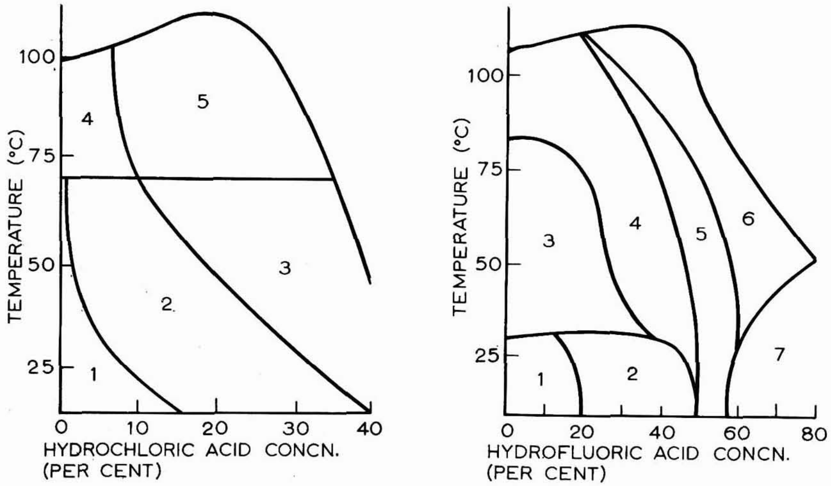

Fig. 8. Corrosion resistance of materials to (a) hydrochloric acid and (b) hydrofluoric acid. Criterion: corrosion rate less than 20 mils per year (G. A. Nelson, Shell Development Co.)

Fig. 8A

Zone 1 Ni/Mo/Fe/Si alloy (e.g. Hastelloy B)‡
Mo rich high silicon cast iron†
Ag; Pt; Ta; Zr; W
silicon bronze*
copper*
nickel*
Nu/Cu (e.g. Monel)*
rubber
glass
Zone 2 Ni/Mo/Fe/Si alloy
Mo rich high silicon cast iron†
Ag; Pt; Ta; Zr; Mo
Silicon bronze*
graphite
rubber
glass
Zone 3 Ni/Mo/Fe/Si alloy‡
Mo rich high silicon cast iron†
Ag; Pt; Ta; Mo; Zr
graphite
rubber
glass
Zone 4 Ni/Mo/Fe/Si alloy‡
Mo rich high silicon cast iron†
Ag; Pt; Ta; Zr; W
graphite
glass
Zone 5 Ni/Mo/Fe/Si alloy‡
Ag; Pt; Ta; Zr
glass

Fig. 8B

Zone 1 Ni/Cu alloy*
Cu;* Pb;* Ni;* Pt; Ag; Au
70/30 Cu/Ni*
Fe/Cr/Ni alloy (e.g. Alloy 20)
Ni/Mo/Cr/Fe alloy (e.g. Hastelloy C)
25 Cr/20 Ni steel
graphite
rubber
Zone 2 Ni/Cu*
Cu/Ni*
Cu;* Pb;* Ni;* Pt; Ag; Au
Fe/Cr/Ni
Ni/Mo/Cr/Fe
graphite
rubber
Zone 3 Ni/Cu*
Cu/Ni*
Cu;* Pb;* Pt; Ag; Au
Fe/Cr/Ni
Ni/Mo/Cr/Fe
graphite
rubber
Zone 4 Ni/Cu*
Cu/Ni*
Cu;* Pb;* Pt; Ag; Au
Ni/Mo/Cr/Fe
graphite
Zone 5 Ni/Cu*
Cu/Ni*
Pb;* Pt; Ag; Au
Ni/Mo/Cr/Fe
graphite
Zone 6 Ni/Cu*
Ni/Mo/Cr/Fe
Pt; Ag; Au
Zone 7 carbon steel
Ni/Cu*
Pt; Ag; Au
Ni/Mo/Cr/Fe

electrochemical equilibrium (E/pH) diagrams. Fig. 9a shows such a diagram derived for water itself, the boundary lines arising from calculations based on the Nernst equation for the electrochemical reactions in question. This effectively delineates the regions of stability of water; above line (b) water would be expected to decompose spontaneously to oxygen and protons, below line (a) to decompose to hydrogen gas and hydroxyl ions, whilst between the lines water remains stable. This is not, of course, a novel concept since every schoolboy is familiar with the experiment involving the electrolysis of water; the form of presentation, however, is particularly useful as an aid to materials selection. Essentially similar calculations yield E-pH diagrams for metal/water systems, as shown in Fig. 9b for zinc. This diagram indicates

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*air free conditions. †FeCl$_3$ free. ‡Cl$_2$ free.


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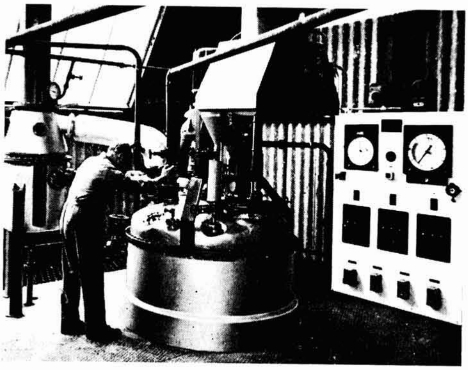

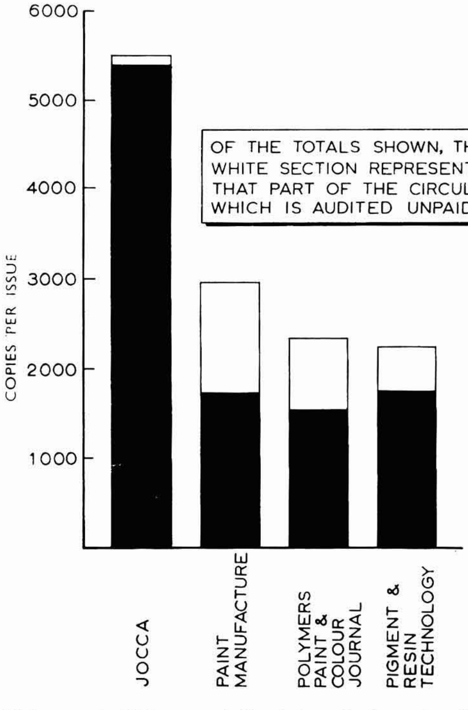
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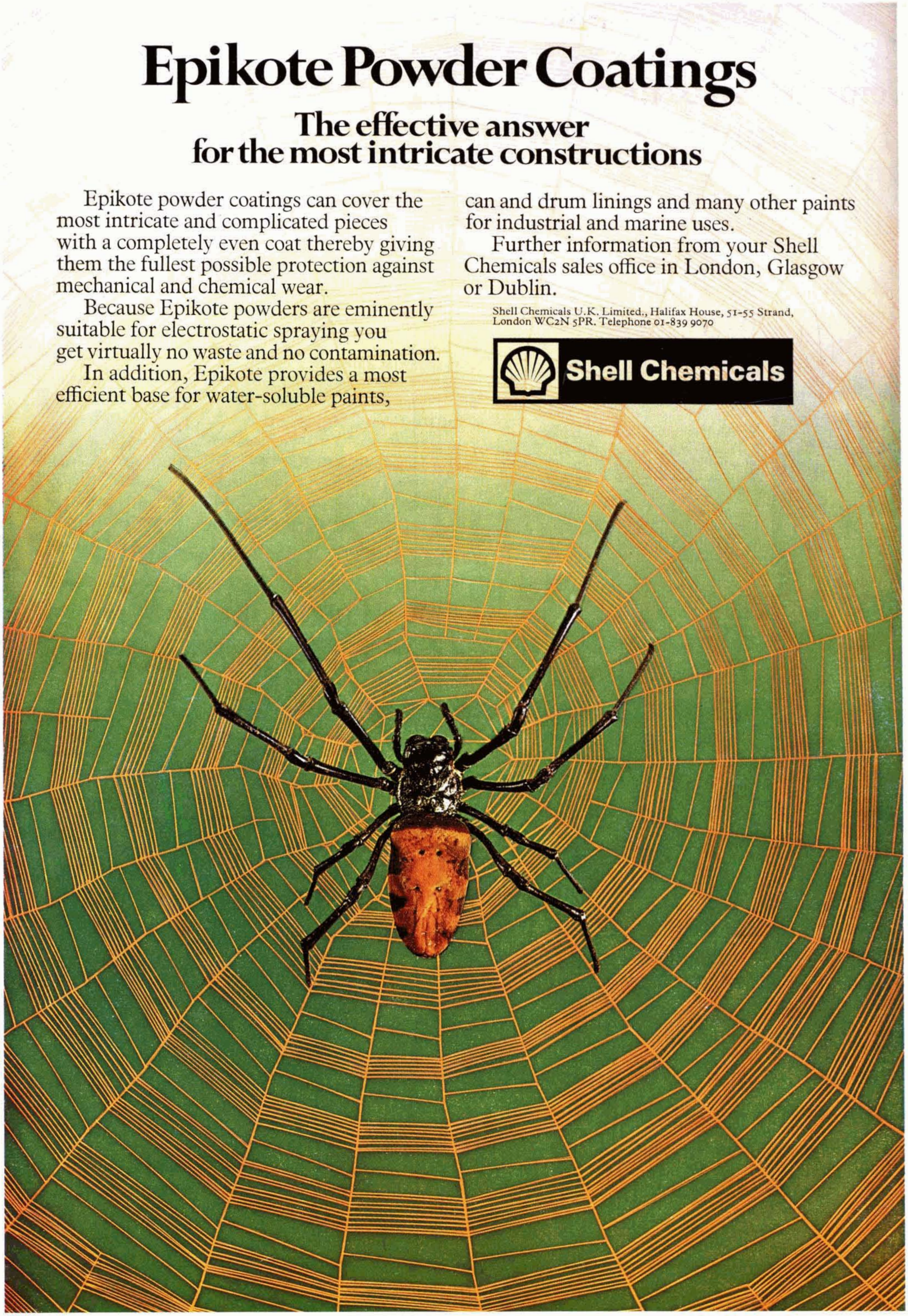

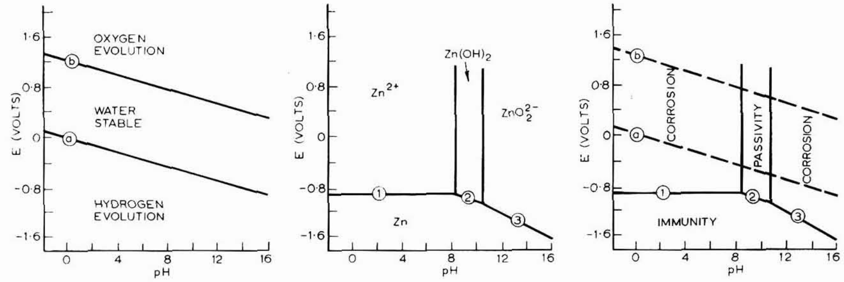

Fig. 9. Electrochemical equilibrium (E/pH) diagrams: (1) water, (2) zinc, (3) zinc/water (simplified)

that if the electrode potential of the metal is raised above lines 1, 2 or 3, the formation at the expense of the metal of soluble zinc cations, insoluble zinc hydroxide and soluble zincate anions become, in turn, thermodynamically possible; conversely, below these lines the unattacked metal will be the stable phase. The potential of a metal can be raised in one of two ways, first by an electrical intervention in the system which abstracts electrons from the metal (for example, by making zinc an anode in an electrochemical cell), and second by exposing the metal to an environment which can provide a cathodic reactant (oxidising agent) with an equilibrium potential above the appropriate line (either 1, 2 or 3) at the particular pH (that is, the cathodic reaction itself would abstract electrons from the metal without the intervention of an external power source). The reduction of the proton is a cathodic process, which will occur in the water system below line (b) in Fig. 9a. Superimposing Figs. 9a and 9b indicates that the hydrogen evolution reaction would be thermodynamically capable of facilitating the oxidation of zinc. The result of this is shown in Fig. 9c, which has been further simplified by adopting the following arbitrary conventions:

1. Any area of the diagram which indicates a stable soluble phase is taken to be an area of corrosion.

2. Any area where the metal is stable is taken to be an area of immunity to corrosion, the boundary being drawn to represent a metal ion concentration of 10^{-6} gm ions per litre.

3. Any stable solid phase is assumed to form adherently, coherently and continuously on the surface, separating the metal from the environment and restraining the corrosion rate; the area is thus defined as a region of passivity.

In the zinc/water system, there are two regions where zinc is able to corrode with hydrogen evolution as the cathodic reaction, and a further region where passivity is possible. If the aqueous environment contains oxygen, at some potential below line (b) the reduction of oxygen to hydroxyl ions is possible. Thus, there are similar, if not larger regions where corrosion or passivity can occur with the reduction of dissolved oxygen as the cathodic reaction. When these equilibrium calculations are made for a variety of metals, very great differences in behaviour are predicted (Fig. 10) which go some way towards explaining the major differences observed in practice.

Potential-pH diagrams have many disadvantages, possibly the most important being that they give no indication of the rate of the corrosion or the passivity. Furthermore, they relate only to the behaviour of pure metals in relatively simple aqueous solutions at room temperature and they take no account of the presence of inhibitors or aggressive species, the possibility of localised attack, or the susceptibility of the material to, for example, stress corrosion. Nevertheless, potential-pH diagrams give a first indication of how a metal might be expected to behave in aqueous environments, and as such they are extremely useful. There is every reason to suppose that their derivation and use for higher temperatures, complex aqueous solutions and non-aqueous solutions will be achieved successfully in due course.

The important role of electrode kinetics for controlling corrosion rates is best demonstrated by appropriate examples. The standard equilibrium potentials of lead and tin are similar (−0.13V and −0.14V respectively); thus their thermodynamic equilibrium driving forces for corrosion in a non-oxidising acid are comparable. However, the hydrogen

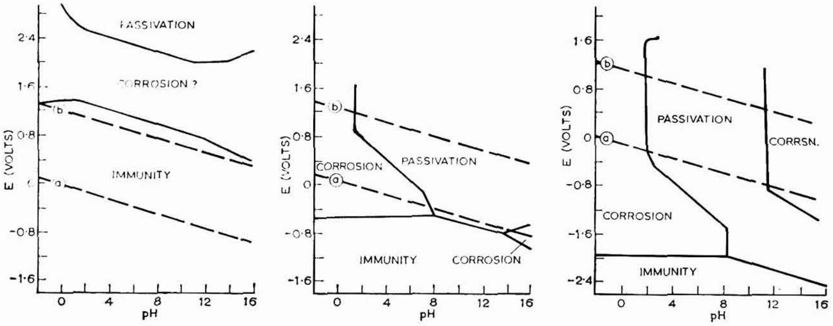

Fig. 10. Electrochemical equilibrium (E/pH) diagrams for metals of differing nobility. (1) gold/water, (2) iron/water, (3) titanium/water

evolution reaction is approximately three orders of magnitude slower on lead than on tin, with the result that the corrosion rate of lead in the acid is significantly lower than that of tin (Fig. 3). Similarly, the hydrogen evolution reaction on pure zinc is slow, whilst on the common impurities in the commercial material (iron and copper) it is very much higher. Thus, the corrosion rate of impure zinc is much higher than that of the pure metal (after an initiation period has allowed the impurities to plate on to the zinc surface and become the sites for hydrogen evolution).

It has been noted that some metals may become passive if the environment can provide a sufficiently rapid cathodic process; Fig. 11 illustrates this situation for iron in nitric acid. The curve *ABCDE* represents the kinetics of the oxidation reactions of iron as the electrode potential of the metal is raised at relatively constant pH. The metal first dissolves to give ferrous ions (*AB*), eventually forms a passive film (*BC*), subsequently maintains and thickens that film (*CD*), and finally sustains the decomposition of the environment (*DE*) without damage to the film. The corrosion potential under any particular conditions will be the potential at which the rate of the anodic and cathodic processes balance. Thus, in dilute nitric acid (with characteristically slow cathodic kinetics given by (i)) the potential is located in the region of active dissolution to ferrous ions and the metal corrodes at the rate given by $I_{corr(i)}$. In concentrated acid, rapid cathodic kinetics can be expected (given by (ii)) and the metal becomes passive immediately. Moderate strength nitric acid (kinetics given by (iii)) apparently offers three possibilities; in practice, however, the possibility of obtaining E_{corr} at *x* can be ruled out because it would represent an unstable state. If untreated iron were exposed to moderate strength acid, the cathodic kinetics would not allow the consumption of electrons at a rate sufficient to allow the iron to surmount the active-passive peak, and the material would dissolve rapidly at the rate given by $I_{corr(iii)}$. If, however, the metal had been previously passified, say by concentrated nitric acid, the cathodic kinetics in the more dilute acid are sufficient to permit retention of passivity, providing the passive film is undamaged. A corrosion rate given by $I'_{corr(iii)}$ would be observed.

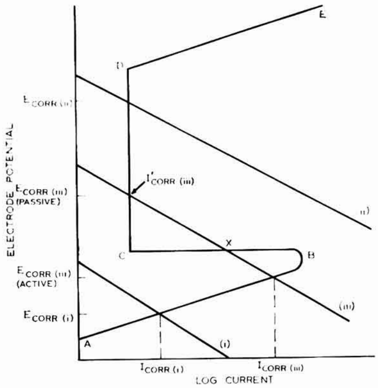

Fig. 11. The corrosion behaviour of iron in nitric acid

At the present time it is technically possible, by careful selection of materials, to produce an article which will totally resist corrosion in service. However, this would normally be a wasteful exercise since the optimum material for any particular application is not necessarily the "best" material from the technological standpoint, whether that judgment is based on an assessment of the mechanical, physical or chemical properties. For example, the object of any industrial installation is to maximise the return on investment within the boundaries defined by the requirements of safety, reliability and legality. Economic factors are of the first importance, therefore, and it is instructive to compare the as-supplied and fabricated costs of a number of common materials (Table 2); clearly there will be strong arguments in favour of mild steel for most applications. Where the chemical resistance of the steel is regarded as inadequate for the service environment, and the cost of a substitute material is unattractive, the possibility arises of a protective coat being applied to the mild steel as an acceptable compromise. Coatings can in practice be both cheap (Table 3) and effective in combating corrosion. Economic factors involve more than the capital cost of the material, and are often conditioned by additional factors arising from the local situation. Local tax regulations might encourage either high capital investment (where investment grants are available), or low capital cost with higher maintenance costs (where the latter are tax deductable). This latter choice will often presume an availability of skilled labour. In developing countries the serious shortage of foreign exchange, or the contractual conditions of foreign aid, often precludes the importing of plant or parts fabricated in the most worthy material, and a less adequate local product must be accepted. Finally, in remote areas the difficulty of transportation may render the supply of spares so difficult as to result in overdesign in terms of materials to ensure reliability.

Table 2

Approximate as-supplied cost of a number of common engineering materials

Material	Bulk (£ per ton)	Fabricated	
		Simple (£ per ton)	Complicated (£ per ton)
Mild steel	66	220	440
Stainless steel (type 316)	330	660	1,320
Monel	330	550	1,980
Nickel	385	1,100	2,420
Incoloy	440	1,320	2,750
Aluminium	385	825	1,760
Copper	495	1,100	2,310
Zinc	129	440	880
Lead	123	385	825
Tin	1,600	2,200	3,300
Pvc	176	440	660
Polyethylene (high density)	143	350	440

Table 3

Coating costs

Coating	Cost (£ ft^{-2})
Paint (one primer, two top coats to 5mil).. ..	0.2–0.3
Paint (primer, undercoat, one top coat to 6mil) ..	0.4–0.5
Air-cured thermosetting resin	0.2–0.5
Stoved thermosetting resin	0.4–0.6
Rubber lining (0.375in)	0.7–0.9
Pvc (0.125–0.25in)	0.3–0.5
Glass enamel	2.0–7.0

Alloys will continue to be developed to meet the increasingly stringent demands of modern technology. However, these developments, where they relate to corrosion resistance, will inevitably mean the use of more expensive materials which are already in short supply. Corrosion and corrosion resistance are both surface phenomena, and it is a matter of conjecture how long attempts based on changing the bulk composition of an alloy with expensive additions in order to change the surface properties of that alloy will be tolerated. There is a clear need for an attack on the problem at the surface rather than in the bulk. Surface alloying techniques are already being used and many corrosion protection systems directed at the surface (painting, conversion, coating, metal cladding, plating) are well established, although there remains room for major developments in this field. Table 4 attempts to express the "room for manoeuvre" as the amount of money which can be spent on protecting a unit area of mild steel, whilst remaining competitive with the use of alternative materials. The figures suggest that it might be possible to use relatively sophisticated techniques and still retain a cost advantage. These figures are somewhat artificial in that they do not take into account the fact that the substitute material might often be used with thinner walls. On the other hand, neither do they consider the social advantages of using more readily available materials (mild steel) in place of materials which will become increasingly in short supply.

Table 4

Justifiable expenditure on protection of mild steel as an alternative to using a substitute material

Thickness (in)	Expenditure (£ ft^{-2})			
	Stainless steel (type 316)	Monel	Incoloy 825	Nickel
0.25	2.5	6.5	7.0	16.1
0.375	3.7	10.0	10.0	24.1
0.50	5.0	13.0	14.0	32.1
0.75	7.5	20.0	21.5	46.2
1	10.0	26.0	28.5	64.2

Anodic and cathodic protection

The electrochemical basis of corrosion permits corrosion control by electrical intervention in the anodic or cathodic process. By supplying electrons to the interface, the metal becomes cathodically polarised and is said to be cathodically protected; withdrawing electrons leads to anodic polarisation which can, in particular circumstances, lead to anodic protection rather than the expected stimulation of the corrosion rate.

The principle of cathodic protection has been described earlier, and is demonstrated in Fig. 4. Briefly, when a surfeit of electrons is provided at the interface, the electrode potential of the metal falls, the cathodic reaction is stimulated, and the anodic reaction slowed down with a consequent decrease in dissolution. As Fig. 4 shows, the net cathodic current required to achieve any particular potential (and, therefore, any predetermined rate of dissolution) is given by the difference between the local cathodic and anodic currents (I_c and I_a respectively). In principle, total protection of a cathodically protected structure can be achieved by polarising to E_A but in practice a lowering of the corrosion rate in order to prolong the service life of a structure is often regarded as sufficient. In thermodynamic terms, the object of cathodic protection is to force the electrode potential of the metal into, or towards, the region of immunity in the *E-pH* diagram. Clearly, if a metal spontaneously adopts a potential in the immunity zone without cathodic polarisation (that is, a noble metal), cathodic protection is superfluous. On the other hand, if the corrosion potential is very much more noble than the immunity/corrosion boundary in the diagram (that is, a base metal), a very large cathodic current would be required to depress the potential sufficiently; in economic terms, cathodic protection would not then be a viable proposition, although it would remain technologically feasible. Between these two extremes falls a group of metals (including iron) which, by moderate cathodic polarisation, particularly in near neutral environments, can be protected very effectively by cathodic protection. Indeed, the protection of mild steel structures, both buried in soil and immersed in sea water, by cathodic protection finds wide applicability.

The necessary polarisation for protection can be obtained using either a sacrificial anode system or an impressed current technique. In the former a galvanic cell is formed between the less noble sacrificial anode (usually magnesium, zinc or aluminium) and the structure to be protected; the accelerated dissolution of the anode material provides the electrons required to polarise the structure cathodically and to protect it. The impressed current method uses a direct current source to produce the same lowering of electrode potential.

Cathodic protection is most commonly applied in conjunction with a secondary protection scheme, either an inhibitor or, more usually, a coating. Whilst the function of the coating is to provide the bulk of the protection, the cathodic current is directed by low resistance paths to "holidays" in the coating, thus reducing or eradicating the damage at unprotected areas. Very adequate protective coatings, which withstand the alkalinity generated by the cathodic reaction, have been developed, and it is unlikely that revolutionary developments will be made or are required in this area of coating technology. The sacrificial anode method of protection, however, is likely to come under increasingly severe scrutiny in the coming decades. According to recent estimates,[4] 1,000 tons of zinc and magnesium alloy anodes were being installed annually to protect drilling rigs then in operation in the North Sea. At that time the Ministry of Agriculture and Fisheries was already expressing anxiety about the effect on the fishing industry of the increasing local concentration in the sea of metal ions from this source. Impressed current techniques are not a major source of pollution since they generate oxygen and hydrogen together with equivalent amounts of hydroxyl and hydrogen ions. It seems inevitable that, within the foreseeable future, the doctrine of "the polluter pays" will be adopted, in which case the impressed current technique may well become the only acceptable method of electrochemical protection, when judged by both social and economic criteria. Meanwhile, the problem of providing compact, rechargeable power sources, which can operate equally effectively in hot or cold climates and which would allow the impressed current method to be used in locations distant from an electrical power line, has yet to be overcome.

Attention has already been drawn to the fact that some metals are able to form stable, protective films when their electrode potential is raised above the active/passive transition in the Evans (*E-i*) diagram. Anodic protection takes advantage of this phenomena by inducing passivity through anodic polarisation of the structure; for this purpose an external power source, rather than a facile cathodic reaction provided by the environment, is used. Thermodynamically, the object is to raise the potential of the metal into the zone of passivity in the Pourbaix (*E-pH*) diagram. Unlike cathodic protection, it is not possible to eliminate corrosion completely by anodic protection; indeed, the efficiency of the process depends entirely on the passive corrosion current flowing in the passive region. Since this passive current tends to increase with an increase in flow rate or temperature, it follows that the rate of dissolution will increase similarly. However, because the unprotected corrosion rate of the metal will often increase with both these parameters, it is probable that the protection efficiency will remain constant or even improve. Once the protected state is achieved, the impressed anodic current required to maintain protection is considerably less than the cathodic current for adequate cathodic protection under similar circumstances. In order to retain a low corrosion rate, the metal must remain in the passive region, whilst to maintain economical operation, the current must not be wasted on unproductive decomposition of the environment (for example, by oxygen evolution from aqueous solutions). It is essential, therefore, that the anodic protection system operates in a very restricted range of electrode potential. A simple constant current circuit is inadequate for this purpose and must be replaced by a system which can deliver the variable current required to maintain a preselected potential in a region where Ohm's Law is not obeyed (the passive region). In the past, this requirement for more expensive control equipment has often made anodic protection somewhat less attractive than other methods for controlling corrosion. However, with the development of more sophisticated, solid state electronic equipment which is both reliable and relatively cheap, there is every reason to suppose that anodic protection will become accepted in many areas where more traditional methods of corrosion control, including coatings, are currently adopted.

Corrosion inhibition

The corrosion damage caused by an environment can often be reduced by the addition of low concentrations of so-called "corrosion inhibitors". These compounds operate by intervening in the electrochemical process, decelerating either one or both of the electrode reactions. There are two distinct approaches to corrosion inhibition; these can broadly be described as negative and positive. The former depends on removal of the aggressive agent from the environment; for example, by vigorous de-aeration of process liquors, or by the addition of chemical deoxidants (for example, sodium sulfite or hydrazine) to boiler waters, with the object of scavenging the oxygen and preventing its cathodic reduction. By contrast the positive approach tolerates the presence of the aggressive agent, but moderates its action by means of an added inhibitor. Both approaches are effective but they usually find application in very different circumstances. Because the negative approach is usually specific to the particular corrosive environment, it will not be considered further; the remainder of this section will be concerned with the positive approach to corrosion inhibition.

Corrosion inhibitors fall conveniently into three main groups: chemical passifying agents, adsorption inhibitors, and filming inhibitors, each group having important specific advantages and disadvantages.

As the name implies, chemical passivators are oxidising agents (for example, ferric ions, chromates and nitrites) which promote passivity by providing sufficiently rapid cathodic reactions for the metal to undergo a spontaneous active-passive transition. The corrosion potential thus falls in the passive region, and because it is the anodic reaction which is stifled, chemical passivators are often described as anodic inhibitors. Whilst these compounds are extremely effective and find widespread use, there is always the danger that if the oxidising agent is locally depleted, for example by dilution, it may be unable to sustain passivity. When this occurs the corrosion potential falls below the potential of the active-passive transition but remains above the value expected of an uninhibited system; stimulation rather than inhibition of corrosion inevitably occurs.

The common adsorption inhibitors are organic compounds, notably amines, aldehydes and thio-compounds, which effectively mask the metal surface by becoming adsorbed. Often, these inhibitors are specific for a metal or group of metals because of the relative values of zero charge and corrosion potentials for each metal. When the zero charge potential is below the corrosion potential, it might be expected that only negatively charged species would absorb from the corrosive on immersion. For this reason, only negatively charged species could conceivably inhibit the corrosion reaction in this instance. Conversely, a compound of positive charge should be effective as a corrosion inhibitor if the zero charge potential is above the corrosion potential. Since a relatively uniform interfacial potential exists on a corroding metal, it is probable that the inhibitors are absorbed generally and act, therefore, upon both the anodic and cathodic reactions. The effectiveness of adsorption inhibitors depends critically on the tenacity with which they are adsorbed and the masking they confer; that is, on the charge distribution in the molecule and upon its size and shape. Under-inhibition, often leading to localised corrosion, can occur with the use of organic adsorption inhibitors, particularly in a system where the corrosive's flow varies markedly through the system due to changes in operating circumstances or constrictions introduced by the design.

There is evidence that certain inorganic inhibitors (for example, benzoates) should be classified too as adsorption inhibitors. These compounds retard the anodic reaction by increasing its polarisability without conferring passivity and are distinct in action, therefore, from the chemical passifiers. Effective inhibition will occur only if the corrosion potential on immersion is either above or below a critical value (which again can be clearly related to the potential of zero charge). An increase in flow rate is not necessarily deleterious to the performance of the inorganic inhibitors, particularly if it raises the corrosion potential of the system above the zero charge potential in the presence of a negatively charged inhibitor.

The common cathodic reactions of corrosion raise the interfacial pH of the system by consuming hydrogen ions or by releasing hydroxyl ions. This pH change can be used, particularly in the presence of dissolved carbon dioxide, to precipitate insoluble compounds, for example, carbonates and hydroxides, at the metal surface where they can act as barriers to the cathodic reaction in particular, and to the corrosion reaction in general. Filming inhibitors, for example the soluble salts of zinc and calcium, when added to the corrodent encourage the formation of these protective compounds. The advantage of cathodic inhibitors for corrosion control is that they are "safe"; local loss of inhibition only marginally increases the general corrosion rate of the metal, in contrast to local loss of anodic inhibition which directs the corrosion to the isolated, uninhibited site and promotes intense local penetration. On the other hand, a major defect of filming inhibitors is that in forming the film they decrease the efficiency of heat transfer, which is often an important consideration.

Corrosion inhibitors represent a cheap and effective method of corrosion control, but a reserve of inhibitor must be retained at the surface in order to maintain efficiency. This is a clear disadvantage when the corrosive is part of a "once-through" system because a continual dosage becomes necessary, or when the purity of the process fluid is an important consideration. The ideal corrosion inhibitor would be applied to the metal by a "single dip" process which would confer almost permanent corrosion resistance. If this could be achieved by the formation of a temperature-stable surface compound of restricted thickness (say, a few tens of Ångström units) then the metal could be inhibited equally effectively in isothermal and in heat transfer situations because the efficiency of the heat transfer process would not be affected. In recent years, the understanding of adsorption, and of interfacial reactions generally, has increased significantly, and so has the appreciation of molecular geometry and molecular charge distribution. It now seems likely that not only more effective conventional inhibitors but also compounds which have the attractive properties described above will be designed in the future. Undoubtedly, if the chemist can see the social and economic importance of corrosion inhibition and its relevance to the surface effects which he is already investigating, there is no reason to suppose that the methods of inhibition described here should not be commonplace by the year 2000. It is a matter of semantics whether the surface compounds could then be described as inhibitors or coatings. What is certain is that with their development the relative importance of the conventional coatings would diminish significantly.

Conclusion

There is little doubt that economic growth cannot continue into the next century without considerable advances in the economical use and recycling of the world's non-renewable resources. In this context, the application of the techniques for corrosion prevention and control will assume increasing importance, although it must be recognised that it will not be justifiable to expend on corrosion prevention more resources than would be consumed by allowing corrosion to take its natural course. Neither will it be acceptable to employ techniques which pollute the biosphere whilst preventing corrosion. Although coatings find widespread use in corrosion prevention at present, and are likely to continue to do so well into the next century, it is probable that the relative emphasis on the various coatings will change markedly. In the authors' view, the metallic coatings will be replaced partially by organic and conversion coatings as the problems of waste disposal become more severe. Similarly, some of the conventional organic coatings will be surpassed by "designed coatings" with markedly better adherence and coherence and which will permit efficient heat transfer in industrial installations.

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Acknowledgments

The authors are indebted to Professor T. K. Ross for providing the cost data incorporated in Tables 2 and 3.

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Discussion at Eastbourne Conference

DR J. E. O. MAYNE said that benzoates inhibited down to pH 6, and at pH 7 the air-formed oxide film was thickened by 40 per cent and weak spots in the film were reinforced by the deposition of ferric benzoate, or a basic salt. He asked what then was the evidence that inhibition was by adsorption.

DR R. P. M. PROCTER agreed that benzoates were basically filming inhibitors, but it was the authors' opinion that there was adequate evidence to show film formation to be preceded by an adsorption step.

MR J. S. BOROKY said that he would like to ask Dr Procter about modern trends (developments) in the corrosion protection of steel in extremely saline environments. This problem was encountered in most states of Australia. Where there was ground water with high levels of salt content, they had to pump salty subterranean water from artesian wells, and worked with desalination plants. Anodic protection was impractical and caused pollution, whilst design was very restricted in a limited drilling space, and turbulence limited the effectiveness of coatings.

DR PROCTER suggested that until more effective coatings were provided, one answer might be cathodic protection.

MR BOROKY pointed out that turbulence in a plant system would after a while eliminate the coating.

DR PROCTER said he recognised that there were cavitational effects. At present, this problem could only be solved by materials selection; selecting a material that was resistant to cavitation corrosion. These were all present day solutions, however; they would not, in the authors' opinion, be acceptable in 50 or 100 years time, when greater efforts would have to be made to eliminate the cavitation.

MR D. S. NEWTON asked whether the lecturer had any comment to make on the "cost effectiveness" of materials now, as against say in 100 years time. It might be that steel could literally become a rare metal.

There was going to be a second cost effectiveness from the point of view of how much it would cost the country in terms of the loss or drop in total resources.

DR PROCTER replied that he did not regard these as cross-over points. He preferred to see them as additions to the simple economic cost; it would be necessary to add on to that the cost, the real cost of the energy required to extract the metal as it became more and more expensive, the real cost of the metal which would become increasingly expensive as the resources dwindled, and so on.

MR NEWTON asked Dr Procter whether, as a follow up to that, he could see any marked change in the relative costs of raw materials.

DR PROCTER assured Mr Newton that he would be in the commodites market if he could. Presumably, one could extrapolate from the figures that Prof. Isserlis had quoted, although all these things would obviously be affected by the discovery of new deposits.

DR J. B. LEY asked Mr Newton if he had been looking at Table 2 in the paper. Dr Ley had been studying those figures very carefully in relation to the cost of metal after its fabrication; mild steel was the cheapest, but super-imposed on mild steel would be the cost of preventing it from corroding.

MR NEWTON said that he was more concerned here about what could best be called the "future scarcity value." One could see in perhaps 100 years time, steel being more expensive than some of the materials at present known as "rare metals."

DR LEY agreed; this was not only confined to these materials. In the paint industry, they were having to look again at the basic intrinsic values of the materials used.

MR M. HESS commented that design being one of the main means to prevent corrosion, many people including himself had called for this since the 'thirties without sufficient effect. It seemed to be necessary to exert some pressure, through Government Departments for example, to have all-round more attention paid to this aspect.

DR PROCTER thought that the pressures which could be exerted were on the one hand from the top downwards, by people like the British Standards Institution, the Department of Trade and Industry, and so forth and, on the other hand, pressures from the bottom upwards. To take a classic case, people no longer wanted to put up with their exhausts falling off every eighteen months. Pressures could be exerted on the manufacturers from both sides.

DR M. ELLINGER pointed out that, in her experience, efforts on the part of the paint industry, to persuade the mass production industries to improve design, had so far failed. It would be welcomed if, in view of the desired higher efficiency of organic coatings, the design could be improved and contribute to prolonged durability of the metal substrates.

DR LEY added that many present were on the technical side of the paint industry and, of course, many had a commercial responsibility as well. He referred to Table 1 in the paper, which showed that a high percentage saving in corrosion could be made if those in industry went out and sold protective coatings, or tried to get such industries as the car industry to implement this potential saving. The Hall Report stated that almost 42 per cent of corrosion could be saved in the power industry, or the Government itself could reduce its corrosion costs by 36 per cent and general engineering by 32 per cent. Dr Ley wondered what pressure was being put on these industries to implement a campaign for corrosion prevention. This would, no doubt, consume quite a considerable amount of organic coatings, which was, of course, to the commercial benefit of those present.

DR PROCTER thought that, in the case of the power industry, it was difficult for pressure to be applied other than by the Government, as the nationalised industries had a monopoly. Certainly, in the power industry, it was not easy to apply pressure. Although Dr Procter had mentioned ways whereby pressure could be applied, he believed that relatively little was being applied. Of course, this did not make the Hall Report a hypocritical one because, although it detailed the cost of protection and what should be done about it, it was not in the least responsible for implementation. It was a fine report, and Dr Procter was not criticising it.

DR E. E. LONGHURST wished to point out the dangers in attempting to summarise the whole of corrosion science in one short paper. The simple description of corrosion in terms of "anodic" and "cathodic" reactions tended to overlook the vital part played by the corrosion anions in the polarisation processes; the inter-position of a resistance in a corrosion mechanism might induce heavier corrosion current densities at anodic areas (a point already made by the author but not sufficiently emphasised in Dr Longhurst's opinion). To state that austenitic steels might be susceptible to stress corrosion cracking suggested that martensitic stainless steels might not suffer in like manner. It needed to be stated too that not only could inhibitors be specific for one metal, but also they could, in fact, seriously increase the rate of corrosion of other metals for which they were not intended.

He then moved on to the effect of the environment and particularly the effect of trace amounts of materials which could act as very considerable catalysts for corrosion reactions (for example, the effect of the evolution of traces of vapours of organic materials). The paint industry ought to be aware that paints could be one of the greatest sources of trouble in this respect; trace amounts of organic acids given off from the paint coatings themselves could seriously effect the corrosion of unprotected metals in other areas.

This having been said, however, it had to be acknowledged that the authors had produced a most useful paper. Particularly, he supported their contention that much more attention needed to be paid at the design stage, and suggested that painters would do industry a service if they refused to try to cover up bad design by applying paint as a preservative. Perhaps the best thing the paint industry could do was to refuse to allow the painting of equipment which was badly designed. Dr Longhurst considered that, at the moment, the hidden sections of the modern motor car were a first class example of this type.

DR LEY (Chairman) thanked Dr Longhurst for his contribution, which had certainly raised other points for a discussion on another occasion.

DR C. G. BELL said that several speakers had referred to poor design as a factor in the corrosion of structural steel. He recalled the excellent photographs prepared by BISRA some 20 years ago, which showed good and bad design. He saw about him examples of bad design in recent construction, and asked why the message had failed to get across to engineers and architects.

DR PROCTER agreed. It was a matter of continually reminding the designers that it is possible to prevent a lot of corrosion by good design.

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Electrochemical activity of conductive extenders for zinc rich coatings*

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Summary

The work to assess the corrosion controlling properties of zinc rich primers, both with and without extenders, is summarised. The investigation included salt fog exposure tests, topographical studies, and a study of the electrochemical phenomena involved. The difficulties of welding zinc coatings are mentioned.

Results indicated that a high percentage of zinc can be replaced often with negligible effect on the corrosion resistant properties of the coating. Di-iron phosphide is a particularly suitable replacement for zinc, and especially so because it improves the weldability of the primer. Electrochemical studies have shown that availability of the metallic zinc in the coating varies considerably during exposure to corrosive materials.

Keywords

Types and classes of coatings and allied products

rust inhibitive primer
zinc rich coating

Properties, characteristics and conditions primarily associated with materials in general

electrical conductivity

Le comportement électrochimique des extenders conducteurs pour les primaires à poudre de zinc

Résumé

On donne un résumé des études sur l'appréciation des propriétés anti-corrosives des primaires fort en poudre de zinc, avec ou sans extenders. L'investigation comprennait les essais d'exposition au brouillard salin, les études topographiques, et une étude des phénomènes électrochimiques mises en jeu. On mentionne les difficultés recontrées lors du soudage des primaires à base de poudre de zinc.

Les resultats indiquent que l'on saura remplacer un fort pourcentage de zinc, souvent en l'absence d'un effet important sur les caractéristiques anti-corrosives du primaire. Le phosphure diferreux (Fe_2P) se montre en tant qu'un remplacement fortement efficace pour le zinc, surtout parcequ-il améliore la facilité de faire le soudage du primaire. Les études électrochimiques ont indique que la teneur en zinc métallique en état disponible se varie fortement au cours de l'exposition aux agents anti-corrosifs.

Elektrochemische Aktivität Leitender Extender für Zinkreiche Anstriche

Zusammenfassung

Eine Zusammenfassung der Arbeiten, die zur Bewertung der die Korrosion kontrollierenden Eigenschaften zinkreicher Primer mit und ohne Extendern durchgeführt wurden. Die Untersuchung schloss Prüfungen durch Salzsprühnebelexponierung, topographische Studien und Beobachtung der auftretenden elektrochemischen Phänomene ein. Erwähnt werden auch die beim Schweissen von Zinkanstrichen auftretenden Schwierigkeiten.

Die Ergebnisse zeigen an, dass ein hoher Prozentsatz von Zink, oft mit unbedeutendem Einfluss auf den Korrosionswiderstand des Anstriches, ersetzt werden kann. Besonders geeignet ist der Austausch von Dieisenphosphid für Zink, vor allem weildies die Schweissfähigkeit des Primers verbessert. Elektrochemisches Studium zeigte, dass sich die Verfügbarkeit des metallischen Zinks im Anstrich, während es korrosiven Stoffen ausgesetzt ist, wesentlich ändert.

Электрохимическая активность проводящих наполнителей для покрытий богатых цинком

Резюме

Рассматривается работа по оценке противокоррозийных свойств грунтовок богатых цинком, как с наполнителями так и без наполнителей. Исследования включали испытания на стойкость против соли и тумана, топографические исследования и исследования присущих электрохимических явлений. Упоминаются трудности связанные со сваркой цинковых покрытий.

Результаты показали что значительный процент цинка может быть заменен, часто с ничтожным эффектом на антикоррозийные свойства покрытия. Дифосфид железа является весьма подходящим заместителем для цинка, в особенности потому что он улучшает свариваемость грунтовки. Электрохимические исследования показали что наличие металлического цинка в покрытии изменяется значительно при подвержении влиянию коррозийных материалов.

Introduction

Both metallic zinc and zinc compounds have played a prominent role in the coatings industry for a considerable period of time. The electrochemical and inhibitive properties of this metal have been the subject of many studies dating back to the nineteenth century[1–3]. The use of finely divided zinc dust with a binder to protect a steel substrate is a comparatively recent innovation, probably stemming from the work of Evans and Mayne[4–6] in the 1940s. Their studies demonstrated the role of high loadings of zinc dust in a paint vehicle, resulting in exceptional corrosion controlling properties. The interesting factor of nearly all of the recent zinc rich primers is that they are truly interactive with the environment. That is, they play a dynamic role in offering protection (electrons) to the steel substrate by anodically

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* Presented at the 1973 Eastbourne Conference.

dissolving into it. Consequently, the normal barrier action of primers is not so evident in these systems. This is especially true of silicate bound zinc rich primers. In the early stages, when the zinc-rich primed steel surface is exposed to an electrolyte, the zinc dissolves anodically offering cathodic protection to the substrate. This protective mechanism is clearly limited due to the formation of zinc compounds which react with hydroxyl ions, produced on the cathodic sites, and with other environmental anions. These compounds precipitate both at the paint/metal substrate interface and throughout the coating, being identified, usually, as white corrosion products, and acting as cathodic inhibitors to the steel substrate.

Whilst these coatings do offer a very high degree of corrosion protection, they are amongst the most costly primers on the market, and have some other shortcomings; these include low adhesion over unprepared surfaces (especially with a silicate binder), poor weldability in the range 1.0 to 4.0mm thickness, and they often have low intercoat adhesion. Zinc rich coatings are often applied to steel substrates which are then fabricated by welding. The zinc rich paint protects the substrate from corrosion in the pre-construction stage. It is desirable that the zinc coatings should not interfere with the subsequent fabrication by welding. Very often the zinc volatilises during welding causing porosity in the weld and giving off fumes which affect the work of the welder.

As a family of primers, zinc rich coatings do not possess exceptional physical properties, due to their high pigment loading (often in excess of 70 per cent pigment volume concentration (PVC) or 92 per cent by weight). Below PVCs of approximately 60 per cent, corrosion resistance and sacrificial activity begin to be seriously decreased, due, in part, to the poor electrical conductivity between zinc particles and the substrate.

More recently, several studies have been initiated in an attempt to overcome some of these problems. Work by Evans and Taylor[7] was centred on the use of conductive, anodically active extenders, such as cadmium, aluminium and iron, together with various inhibitive pigments. This showed that mixtures of cadmium and zinc, together with inhibitors, gave similar performance to the normal zinc rich coatings. The use of aluminium or iron powders as extenders (or co-pigments), however, proved inferior. In the former case, this was probably due to the high resistivity of the surface film on the aluminium particles, and in the latter case it was probably due to dissolution of iron and accelerated activity of the zinc dust. Other studies by ILZRO[8] have shown that relatively small amounts of non-conductive extenders (such as silicon dioxide, aluminium oxide, etc) can be introduced into zinc rich primers without affecting corrosion resistance. However, the authors' studies have indicated that similar compositions degrade welding severely.

The work performed at Hooker Chemical Research Center was directed towards the study of various extenders in zinc rich coatings. From studies by Evans[7] and others, it was decided to concentrate on increasing the conductivity of the film whilst maintaining good physical properties and favourable economics. Any extender in this class, by virtue of its high electronic conductivity, may be electrochemically active either anodically (protecting the steel substrate) or cathodically (fostering oxygen reduction, and therefore galvanic activity). Thus, it was decided that the electrochemical activity of a variety of conductive extenders should be studied. Those chosen included carbon, aluminium, and the refractory ferro-alloys. Corrosion, conductivity and welding tests were also performed. The class of materials found to be most effective in this role were the refractory ferro-alloys, specifically di-iron phosphide (Fe_2P).

Experimental

In order to assess the corrosion controlling properties of zinc rich primers both with and without extenders, it was felt that a combination of experimental techniques would be necessary. These included salt fog exposure, topographical studies (scanning with electron microscope), and those necessary for an understanding of the electrochemical phenomena.

Polarisation of bulk metals and extenders

The polarisation studies were carried out using a potentiostatic technique in a two-compartment H cell (PAR model 173 potentiostat). Bulk specimens were prepared by encapsulation of the specimen in epoxy resin, followed by polishing in aqueous media. Both anodic and cathodic polarisation curves were determined in aerated 3 per cent sodium chloride solution. 1020M steel, zinc and ferrophosphorous (Fe_2P) were studied. Scans were made, changing the potential in steps of 100mV every thirty seconds. Figs. 1 and 2 are plots of log i/A against E, where i/A is the corrosion current per unit area and E is the potential.

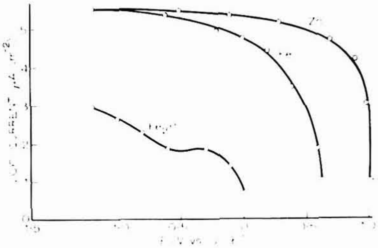


Fig. 1. Anodic polarisation: 3 per cent NaCl solution; 25°C; aerated

The low anodic activity of Fe_2P in comparison with iron and zinc is evident in Fig. 1. Fig. 2 shows the similarity in cathodic activity between Fe_2P and 1020M steel. Thus, it is to be expected that oxygen reduction will have relatively low over-potentials on both of these surfaces. By the introduction of 20gm l^{-1} of zinc chloride into the electrolyte, the cathodic activity of both Fe_2P and steel were reduced by factors of five.

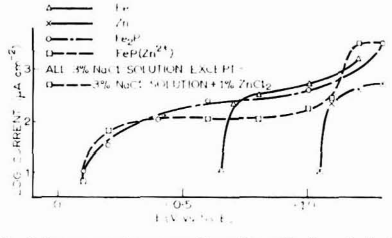


Fig. 2. Log current versus voltage for cathodic polarisation

Mixed corrosion potentials and linear polarisation studies of zinc coated steel

Whilst the mixed corrosion potential of a system being studied can often indicate the nature of the processes occurring, it rarely describes the kinetics of the process. These data can only be obtained from analytical procedures or from linear polarisation data. Both techniques were used in order to find the rate of zinc dissolution and the potential lifetime of a system in aqueous environments.

Both laboratory made and commercially available primers were used in the testing scheme. Table 1 shows typical formulations which were spray applied to 3in × 5in cold rolled steel panels (silicate vehicles). Electrical contact to the specimens was via an insulated welded steel strip. After immersion in 3 per cent sodium chloride solution, the panels were electronically connected via the potentiostat and high impedance voltmeter to a counter electrode and a saturated calomel reference electrode which was connected to the specimen by a Lugin-Haber capillary (Fig. 3).

Table 1

Typical formulations used in the testing scheme

Formulation	Composition	Weight ratio
Epoxy-polyamide	Epon 1001 (50% solution)	45.4
	Versamid 115	17.5
	Solvent	34.3
	Federated III zinc dust	465.0
		562.2
Chlorinated rubber	Parlon 520	20.9
	Aroclor 5460	5.6
	Aroclor 1254	9.1
	Dioctyl sebacate	2.2
	Solvent	62.2
	Zinc dust	471.0
		571.0
Lithium polysilicate	Polysilicate 48	200.0
	Ben-a-gel EW	0.8
	Potassium dichromate	0.1
	Federated III zinc dust	580.0
		780.9

Note—All extenders were introduced as a weight per cent of the zinc dust.

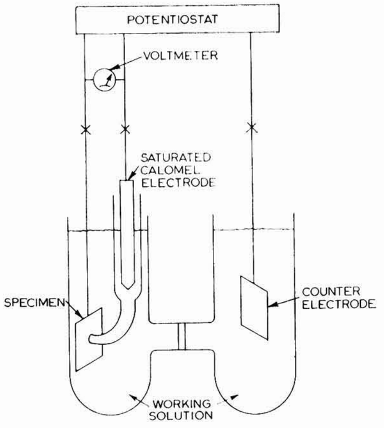


Fig. 3. Schematic diagram of potentiostatic cells

Stern and Geary have previously shown that a reasonably accurate determination of the corrosion current can be obtained using the equation

$$i_{(corrosion)} = 2.3 \frac{\Delta I}{\Delta E} \frac{\beta_C \beta_A}{\beta_C + \beta_A}$$

where $\Delta I/\Delta E$ is the rate of change of current with voltage close to the rest potential (10mV), and β_C and β_A are the Tafel slopes for the cathodic and anodic polarisation respectively.

At the start of the experiments, β_A and β_C were measured by polarising duplicate specimens both anodically and cathodically (Fig. 4). The slope of the Tafel portion was thus determined for each panel. Following this, the potential and linear polarisation rate $\Delta I/\Delta E$ were measured, initially every few hours and later every day. From a knowledge of the apparent surface area of the specimen and the weight of zinc in the specimen, an estimate of the percentage of zinc dissolved could be calculated. This method was further refined by the use of a computer to estimate the potential lifetime of metallic zinc based on an extrapolation technique. Table 2 shows a typical computer print out. Figs. 5 and 6 are plots of rest potential versus time. Fig. 7 is a graphical plot of total zinc dissolved versus time. Chemical analyses of the remaining metallic zinc were determined by stripping the coating and measuring the ratio of total zinc present to metallic zinc. This was accomplished by means of a leaching technique and determination by atomic absorption. The following results were obtained at 8.3 and 21.5 day intervals.

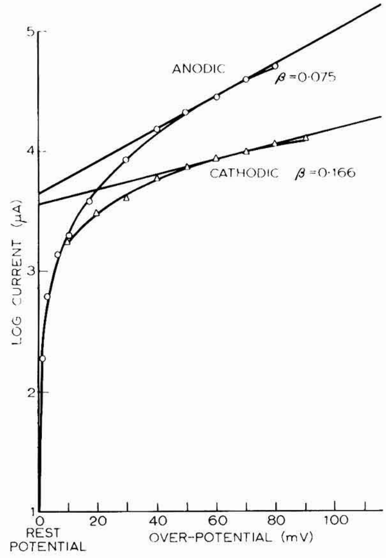


Fig. 4. Anodic and cathodic polarisation diagram
Rest potential 1080 mV (SCE)

Pigment	Exposure time	Dissolved zinc
Zn	8.3 days	18.7%
Zn	21.5 days	25.3%
Zn/Fe_2P (3 : 1) ..	8.3 days	25.2%
Zn/Fe_2P (3 : 1) ..	21.5 days	32.0%

Table 2
Computer print out

DATE 08/06/70	PANEL NO. 2585-16-16	SURFACE PREP SAND BLAST	
AMNT ZINC 2.8600 G.	HOLIDAY — NONE	ENVIRONMENT 3% NaCl	
AREA OF ZN EXPOSED 193.60 CM**2	RATIO		

PRIMER	COMPONENTS	GMS.
METH OF APPL — SPRAYING	ETHYLSILICATE VEHICLE	160.0
THICKNESS 3-4	ZINC DUST	279.0
PCT ZN IN DRY FILM 71.250	FERROPHOSPHORUS	93.0

HRS	DAYS	POT. IN (—) MV	CURR IN MICRO A	ZN/DAY DISSLV	CUMM ZN DIS GM.	CUMM PCT ZN DIS.	PROJ ADDT LIFE IN DAYS	PROJ TOTL LIFE IN DAYS
0	0.0	1064	2050.0	0.1644	0.0000	0.00	17.3	17.3
6	0.2	1089	2300.0	0.1844	0.0402	1.40	15.2	15.5
12	0.5	1084	1900.0	0.1523	0.0823	2.88	18.2	18.7
24	1.0	1086	1250.0	0.1002	0.1455	5.08	27.0	28.0
48	2.0	1080	1350.0	0.1082	0.2626	9.18	23.9	25.9
72	3.0	1059	1200.0	0.0962	0.3666	12.82	25.9	28.9
96	4.0	1050	850.0	0.0681	0.4461	15.60	35.4	39.4
144	6.0	1020	103.0	0.0082	0.5226	18.27	282.9	288.9
200	8.3	996	80.0	0.0064	0.5523	19.31	359.6	367.9
240	10.0	1000	130.0	0.0104	0.5640	19.72	220.1	230.1
367	15.2	1017	180.0	0.0144	0.6367	22.26	153.9	169.2
518	21.5	926	25.0	0.0020	0.6799	23.77	1087.2	1108.8
830	34.5	900	17.0	0.0013	0.6957	24.32	1587.2	1621.8
1176	49.0	1036	6.0	0.0004	0.7101	24.83	4467.3	4516.3
1704	71.0	869	14.0	0.0011	0.7277	25.44	1898.8	1969.8
2424	101.0	830	17.0	0.0013	0.7650	26.75	1536.4	1637.4
3624	151.0	961	14.0	0.0011	0.8313	29.37	1423.2	1574.2

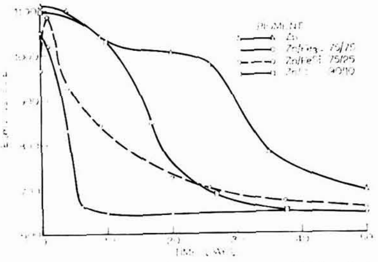


Fig. 5. Rest potential versus time: 3 per cent NaCl solution; ethyl silicate vehicle

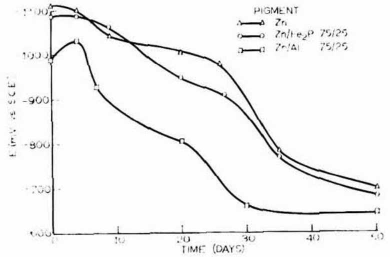


Fig. 6. Rest potential versus time: 3 per cent NaCl solution; ethyl silicate vehicle

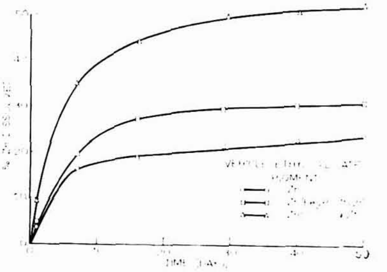


Fig. 7. Cumulative percentage zinc dissolved versus time

The error between the computed and experimental percentage of zinc dissolved is significant due to several anomalies in the data used. Both the large, diffuse nature of the surface under study and the presence of two or more significantly different electrode surfaces contributed to the error. Also, β_A and β_C (Tafel slopes) changed during the course of the experiment. Nevertheless, the data is in general agreement with those of other workers, showing that a study of electrode potentials bears little correlation with the metallic zinc remaining in the coating. It is interesting to note that the anodic activity of these systems is reduced significantly during the initial 10 to 20 day period, attaining a finite low rate. Although this rate can be extrapolated to yield the lifetime of the zinc, it only describes partially the corrosion resistance of the total system. Electronic conductivity from particle to substrate, the nature of the film on the zinc particle, and the overall inhibiting properties tend to be the controlling factors.

Salt fog exposure

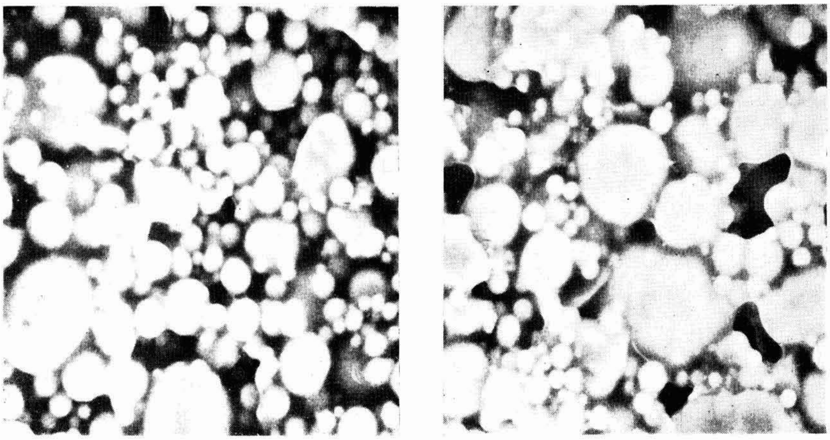
Panels were placed in a standard 5 per cent salt fog cabinet on plastic racks so that they were held 3in apart and at 30° to the vertical. Both panel ratings and operation of the cabinet complied with ASTM recommended practice (ASTM B117). Blister and rust formation on both the scoreline and panel surface was rated on a 0 to 10 scale with 10 corresponding to zero rusting and 0 to 100 per cent rusting.

Table 3

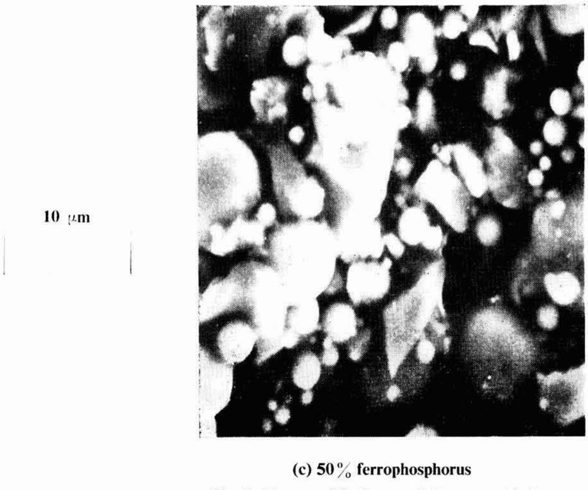
Salt fog exposure—ASTM B 117

Rating: 10 = 0% rusting; 0 = 100% rusting

Binder	Pigment	Extender in pigment	Rust on scoreline	Rust on surface	Blisters on scoreline	Blisters on surface
Lithium polysilicate	Zinc dust	0	10	10	10	10
	Zn/Carbon	10%	0	10	0	8
	Zn/Al	10%	8	10	10	10
	Zn/Al	20%	5	10	9	10
	Zn/Cd	10%	10	10	10	10
	Zn/Cd	20%	8	10	10	10
	Zn/Fe_2P	25%	10	10	10	10
	Zn/Fe_2P	50%	10	10	10	10
	Zn/FeSi	25%	9	10	10	10
	Zn/FeCr	25%	9	10	9	10
Epoxy-ester	Zinc	0	9.7	10	10	10
	Zn/Carbon	10%	0	8.2	10	8
	Zn/Al	10%	7	9.5	10	10
	Zn/Fe_2P	25%	8.5	10	10	10
	Zn/Fe_2P	50%	3	9.7	10	10



(a) 0% ferrophosphorus (b) 25% ferrophosphorus



(c) 50% ferrophosphorus

Fig. 8. Topographical scan of the epoxy binder
3,000× magnification

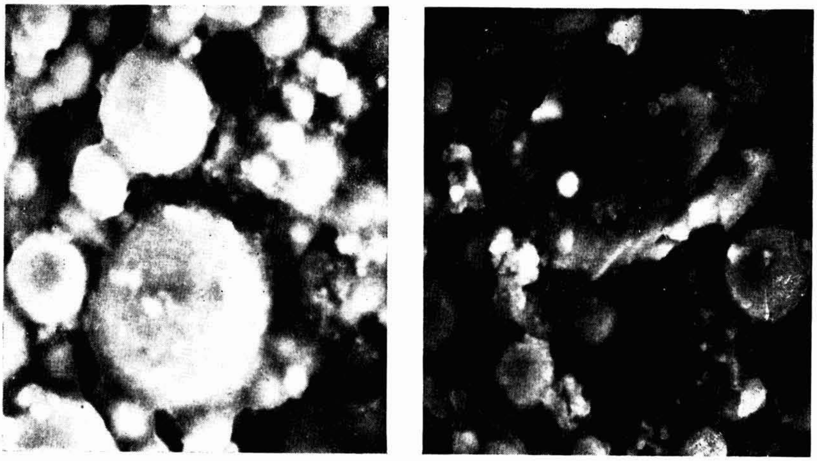
The chief results, necessarily summarised, are grouped in Table 3. The salient features of these are:

1. The inorganic bound primers tended to give better corrosion resistance and scoreline protection than the organic vehicles.
2. Of the extenders studied, cadmium and Fe_2P gave similar results to those of the non-extended primers when an inorganic silicate binder was used.
3. When an epoxy ester binder was used, the corrosion resistance of Fe_2P extended systems appeared to be satisfactory when 25 per cent (by weight) of zinc is replaced. However, at 50 per cent substitution, corrosion of the scoreline was less than satisfactory.
4. Carbon appeared to activate the anodic dissolution of zinc, yielding heavy white corrosion deposits.
5. In other studies the performance of the extender seemed to be very dependent upon the binder system and the PVC.

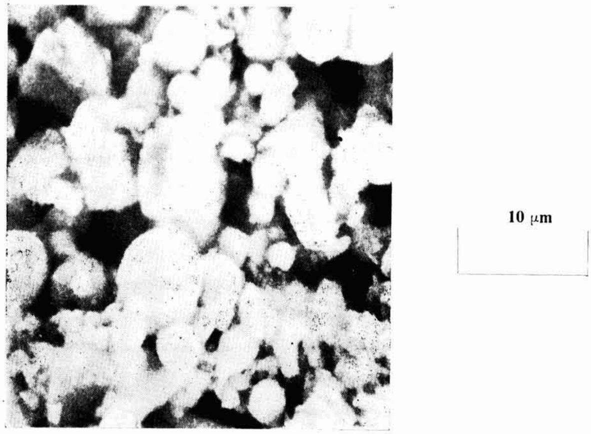
Topographical studies

Scanning electron micrographic studies of both the extender and zinc rich primers were made. Figs. 8 and 9 show epoxy and silicate bound primers at various levels of extender. These plates are direct topographical scans on the outer surface of the zinc rich coating. The difference between organic and silicate matrices is clearly evident. Although the void areas are visible, packing of the zinc and ferrophosphorus is random, with no obvious interpacking of the small particles between the large ones.

Fig. 10 shows a sectioned view of the coating on the steel substrate.

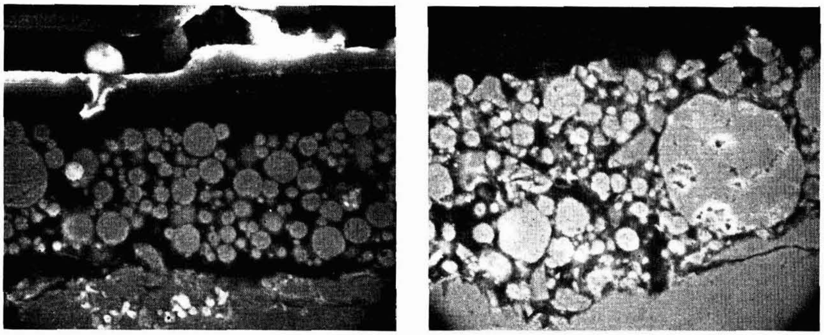


(a) 0% ferrophosphorus (b) 25% ferrophosphorus



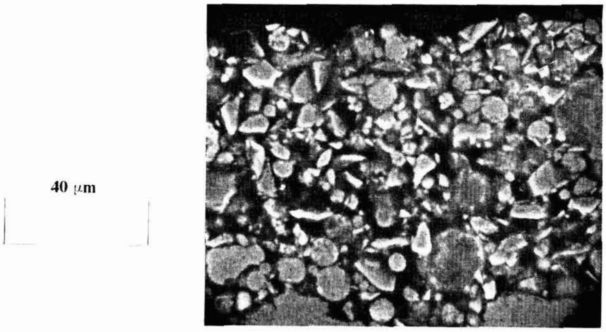
(c) 50% ferrophosphorus

Fig. 9. Topographical scan of the silicate binder
3,000× magnification



(a) 0% ferrophosphorus

(b) 25% ferrophosphorus



(c) 50% ferrophosphorus

Fig. 10. Zinc rich polysilicate
1,000× magnification

Welding studies

Whilst cadmium has been shown to be an acceptable partial replacement for zinc in zinc rich coatings, the problems of toxic fumes during welding precludes its use[7]. Thus, it was felt, a critical appraisal of zinc coated steel (with and without extender) during typical welding practices was mandatory. It was well known that standard zinc rich coatings tend to interfere with the welding processes. This normally takes the form of increased porosity in the weld, volatilisation of the zinc, and often difficulty in striking the weld.

Both resistance and arc welding were studied extensively. The results of this work indicate that the welding process is generally improved by the incorporation of di-iron phosphide. For resistance welding, this improvement takes the form of high shear strength and nugget size after 2,000 continuous welds, together with almost negligible electrode wear. For submerged arc welding, significant reduction of both porosity and zinc smoke is obtained.

Discussion

Anodically active metals (aluminium, cadmium, magnesium) and inert non-conductive extenders (silica, barytes) have been introduced in the past into zinc rich coatings but with limited success. The use of an inert conductive and cathodically active extender (Fe_2P) has been shown to be of greater interest. In zinc rich systems containing these alloys, the zinc corrosion products tend to adsorb on to the extender, zinc and substrate. Thus, on weathering, the film still contains a conductive skeleton by which anodic and cathodic processes are greatly reduced. Electrochemical studies have indicated that the availability of metallic zinc is grossly reduced during the corrosion processes. This availability, however, reaches a low, fixed, finite level, which is somewhat independent of the extender employed. The differences in the corrosion resistance of various extenders are not solely a function of electrochemical activity, but also of the interaction between Zn^{2+} ions and the surface of the extender, the overall conductivity of the film, and the types of anion present. The linear polarisation studies and extrapolation techniques describe some of the electrochemical phenomena occurring on the surface, but only in a semi-quantitative manner.

Conclusions

Corrosion testing of extended zinc rich primers indicates that a high percentage of replacement of zinc can be achieved with slight or no diminution in corrosion resistance. This is true for the refractory ferro alloys, especially di-iron phosphide.

Electrochemical studies have shown that the availability of metallic zinc changes substantially during exposure to a corrosive environment. The anodic dissolution of the zinc reaches a finite, fixed, low value which is determined by the environment and concentration of zinc compounds in the coating.

Linear polarisation studies of this system have proved useful, but limited due to the heterogeneous nature of the surface being studied.

The weldability of primers is improved by the incorporation of di-iron phosphide.

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Discussion at Eastbourne Conference

MR D. S. NEWTON asked the authors whether there was any risk of phosphine evolution from ferrophosphorous during the weathering of an extended zinc rich primer containing this product.

DR V. P. SIMPSON said that they had been confronted by the same question themselves at the beginning of this work and had taken some initial steps to answer it. The most immediate steps had been, in fact, simple things like oral toxicity of the material itself. They had had studies run by Hazleton laboratories and these proved that ferrophosphorous was not toxic in the acid environment of the stomach. The laboratories ran dermal toxicity of that particular material and again found it to be non-toxic. He did not have the actual figures with him, but the LD 50's were available. The material had been handled for thirty years at Hooker Chemical Co. Ltd., without incident. Moreover, in the patents in this particular area, there was a tendency to purify the material overnight in the initial stages with high concentrations of sulfuric and hydrochloric acid. Under these conditions, there was no reaction with the ferrophosphorous.

After these initial studies, the authors had used phosphine detectors, and also a mass spectrometer to determine any toxic gas which might be given off. Again, they had not been able to find anything at all in their studies relating to the generation of phosphine.

Conceivably, phosphine could be given off during welding processes. They had enclosed a welding machine in a high density polyethylene bag, welded a very large number of samples and used two methods of analysis for detecting phosphine. One was using a mass spectrometer; a standard sample was injected into the spectrometer and molecular weights of the order of phosphine were searched for but could not be found. A standard laboratory phosphine detector, that measures in parts per million for standard laboratory purposes, was used too, but again nothing was found.

MR D. S. NEWTON asked whether it was possible to incorporate ferrophosphorous in zinc to be applied to steel strip in the "hot dip" process with the object of producing a more readily weldable zinc coating which would tend to reduce electrode contamination ("brassing") and to obviate the necessity for phosphate pretreatment, as in the iron/zinc alloy coating now being produced by steel companies in the USA.

DR SIMPSON said that to answer the first portion of this question with regard to "hot dip" galvanizing, they had never looked at this. He did not know whether or not there would be dissolution of some phases of ferrophosphorus in zinc. He thought that if the ferrophosphorous were introduced in very small particle sizes, particularly 3μm size, there might be some enhancement of welding, but this was basically, only a guess based on little work. He asked whether the second part of Mr Newton's question was to do with having ferrophosphorous there to improve weldability, with the possibility of using the phosphate coatings with it.

MR NEWTON replied that the point he really wanted to make was the comparison with iron/zinc alloy hot-dipped coating. With this type of coating system, one could obtain very good adhesion, and good results from paint coatings in corrosion testing without the use of a conventional type of zinc phosphate pretreatment. He wondered whether there was a possibility that this could also be extended to the type of system the authors had described.

DR SIMPSON agreed that there might be some applicability there. He had not really considered that point before. One of the interesting factors in the whole conductivity/weldability improvement was that it might be possible, in fact, to put a zinc rich coating over a phosphate coating, and achieve good conductivity and weldability. This was not unlike a system called "Zincrometal," sold in the States by Diamond Shamrock. Of course, the particles were very hard indeed, very brittle, and very angular, and remained so during the weathering process. Consequently, in spot welding, where there was something like 500lb pressure on the electrodes, the particles of ferrophosphorous were, in fact, pushed through the zinc to the surface of the metal so maintaining conductivity. If only zinc particles were present, the zinc would coin or squash and would not penetrate through the phosphate or chromate type of coating.

MR J. R. TAYLOR asked whether the particle size distribution of the conductive extenders as seen in the electron micrographs was the optimum and what effect a change in surface area had on the adhesion of the system described.

DR SIMPSON said that they had looked at various particle sizes. In the States, they used, typically, the 5 or 6μm zinc dust with a "cut-off" of 30μm. It was evident that here in Europe a 3μm product (2 or 3μm) with a cut-off of 15 microns was used. Therefore, they had manufactured those two types, as well as an intermediate grade. They had not found in their limited studies in this particular area, very great differences due to different particle sizes (or surface areas), although with the linear polarisation method there was initially a greater activity because of the greater surface area. This was soon blocked off by zinc corrosion products acting as cathodic inhibitors. So over all, they had not noticed great differences due to different particle sizes. Dr Simpson emphasised that they had not been a paint company over the last four years and did not have the expertise which most of the audience possessed.

DR J. E. O. MAYNE remarked that zinc dust paints could be divided into two classes: those high in zinc dust which protected at a scratch line, or break in the coating, and those containing less zinc dust, which conferred good protection, but only under the paint film. He asked how much iron phosphide could be added to a paint without loss of protection at gaps in the coating.

DR SIMPSON confirmed that they had studied this, and had also contracted the Ontario Research Foundation in Canada to look at the phenomenon. They had used the standard techniques of having holidays (gaps) produced artifically in the film using, typically, a V at the bottom of the panel which was 2.5in high × 0.5in across increasing to zero at the top. They found that up to 30 or 40 per cent substitution could be made (the figure was very much dependent on the binder) and good gap protection would still be maintained. This was, basically, freedom from corrosion over that whole triangle. The tests were based on chlorinated rubber systems. Silicate would be somewhat better in this respect, but the authors thought that gap protection (holiday protection) was afforded up to levels of substitution of 30 and a maximum of 40 per cent. This was a weight ratio but it was close to the volume ratio as well, because the densities were so close. When working at the 50 per cent level, the experimental technique had to be studied seriously, because gap protection experiments could be run replacing the solution every day, every hour or every week, thus allowing the zinc ions into the solution, and consequently inhibiting the gap. Results at 50 per cent substitution were very anomalous. The authors felt that this was due to the experimental techniques used rather than the reality of the situation. The conductivities of the zinc were substantially improved in almost every system looked at.

MR P. M. PROUDLEY asked whether there was any effect on the rate of settlement of zinc rich primer when ferrophosphorous was included as an extender in, for example, a typical organic binder.

Secondly, he asked whether any work had been carried out on the use of zinc rich/ferrophosphorous primers under high speed cutting or welding conditions such as those pertaining to shipyards. He wished to know whether the rate of welding or cutting increased or decreased.

MR F. A. SIMKO answered that they had not observed a profound effect or difference between the settling rate of zinc and ferrophosphorous. Sometimes, they had found a softer cake, probably because of the irregular surface characteristic of the ferrophosphorous. The re-suspension was easier after the material had settled out, but the settling rate would probably be about the same.

As far as the second question was concerned, more recently they had found a very profound effect on the torch cutting of zinc coated steel when the coating contained ferrophosphorous in that there was a major improvement in the maximum cutting rate, more so for natural gas torches than acetylene ones, but even with acetylene, major improvements in the maximum cutting rate were noted. In addition, the cleanliness of the cut was better when ferrophosphorous was present. It seemed that for some reason the zinc interfered with the cutting process due to volatilisation through the flame, causing a ragged steel cut and slowing down the rate quite substantially. This result was from work in a shipyard, as was the weldability information.

DR R. P. M. PROCTER said that the authors stated that Fe_2P extenders improved weldability, and he thought that they would also increase the phosphorous content of the metal in the fusion zone. This might be expected to result in brittleness and poor fracture toughness, of the weld metal, and he asked whether the authors had any data in this connection.

MR SIMKO replied that, to answer briefly, they had looked at the effect of the ferrophosphorous on the strength of weld involved, and there was essentially no effect (no beneficial effect and no negative effect). This was the result of a concerted series of experiments run in the General Electric welding laboratories in the US.

DR SIMPSON added that they had, in fact, measured the phosphorous pick-up level in the weld as well. The typical phosphorous level was of the order of 0.015 per cent for the "virgin" steel used. With 25 to 30 per cent ferrophosphorous included, the figure would be increased, but only to the order of .025 per cent. Most of the welding firms consulted said that these were the normal limits of phosphorous in most steels. Ferrophosphorous contained only 21 per cent phosphorous and if it were in a coating at a level of 25 per cent there was only, say, 6 per cent phosphorous in the actual coating, and most of that would be oxidised to ferric phosphate and γ-ferric oxide. They had carried out high temperature oxidation studies on ferrophosphorous to show what the products were; the end-products were ferric phosphate and ferric oxide.

MR NEWNAM remarked that the authors' initial objective was to improve the conductivity of the film. He wondered whether Dr Simpson was able to give any data on the conductivity of the ferrophosphorous itself, or of the films containing ferrophosphorous at the time of first painting, or during the weathering life.

Secondly, Dr Simpson had commented that the normal silicate primers were not completely satisfactory in terms of adhesion to the substrate or in respect of inter-film adhesion. If this were a matter of pigment concentration, then the ferrophosphorous mixtures might give somewhat better adhesion. He asked, finally, whether the ferrophosphorous was regarded as being an inert extender, or whether it participated in the reactive mechanism.

DR SIMPSON said that they had very explicit data on the conductivity, but which was not listed in the paper, and it was obtained using the United States Air Force (USAF) specification. He had a booklet which described that particular test for measuring dry film conductivity as a standard method used by the USAF. Using this method for, for example, epoxy polyamide films baked on and cured (that is with 100 per cent zinc) the resistances were of the order of 10,000 ohms per in. When 25 per cent ferrophosphorous was introduced, this would drop to the order of 10 ohms per in. When the ferrophosphorous was increased to 50 per cent, it would drop to 0.5 ohms per in. The conducivity was very substantially increased.

As regards intercoat adhesion, Dr Simpson had two comments. Firstly, the critical pigment volume concentration of ferrophosphorous was substantially lower than that for zinc and, therefore, the point Mr Newnam made was well taken. It was possible in fact, to put more binder in and still maintain very good conductivity, which should improve adhesion properties and general film properties. The second point was that after the zinc had been sprayed on to the substrate and it had been placed in a corrosive environment, for example out-of-doors (in the shipyard), it ultimately needed a top coat, and good intercoat adhesion had to be ensured. Again, they had noted major improvements in that area. There were less white corrosion products on the surface.

With regard to the question on inertness, the ferrophosphorous was inert in the normal sense of the word; however, it was electrochemically active, cathodically. In other words, it did foster oxygen reduction, therefore, it did act as a couple to zinc. However, this couple had reduced significance with time due to the adsorption of zinc, iron—namely inhibitors—on to the surface.

Next month's issue

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

"Chloride ion transport in epoxy polyamide films and the substrate effect," *by J. D. Murray*

"Environmental problems of the chemical industry," *by H. Gysin*

"Standardisation and the paint industry. One hundred years of standards—a personal view," *by C. Meredith*

"The future for colour measurement in paint manufacture," *by K. McLaren*

"Tomorrow's packaging," *by G. Scott*

Correspondence

Solvent retention in high build vinyl coatings

SIR—In the recent article "Factors involved in the formulation of anti-corrosive high build vinyl coatings" (*JOCCA*, 1973, **56**, 195-209), some general observations were made concerning the factors governing solvent retention by such films. I feel that these observations are not justified by the quoted results and, presented as general conclusions, could be misleading in other contexts. Furthermore, our experimental evidence suggests that they are incorrect.

The statements are:

vinyl films retain ketone solvents for much longer than they do ester solvents, so that it is possible to minimise solvent retention by using esters as solvents instead of ketones

This conclusion is reached from results on four solvents, namely n-butyl acetate, "Cellosolve" acetate, MIBK and cyclohexanone (Fig. 4 p. 198). While not disputing these particular results, our own findings on the retention of single solvents by a vinyl copolymer ("Vinylite" VYHH) support those of Hansen[1] that molecular size and shape, rather than chemical type, controls the rate of solvent loss at this stage. The quoted example compares straight-chain esters with branched and cyclic ketones, and differences are to be expected on this basis. We have compared MEK with ethyl acetate and MIBK with isobutyl acetate and in both cases a comparable level of retention is shown between ketone and ester (if anything, the ester is perhaps retained to a greater degree!).

Normally, a resin will retain the solvent in which it is soluble and the non-solvents will tend to evaporate faster than the solvent.

This statement is illustrated by the retention of MIBK/toluene by a vinyl film laid down from a solution containing equal parts of each solvent (Fig. 3 p. 198). However, the dominant factor in this situation is the difference in volatility between MIBK and toluene, the latter having the higher evaporation rate. This can be demonstrated by substituting a slower evaporating diluent, such as xylene, in place of toluene. Xylene, the non-solvent, now becomes the major component retained if examined at the levels shown in Table 3.

We hope that these and other findings on solvent retention will be included in a technical paper to be presented during the coming year.

Yours faithfully,

C. J. NUNN

for Shell Research Limited

PO Box 11,
Whitehall Lane,
Egham, Surrey TW20 9NJ.
26 July 1973.

Reference

1. Hansen, C. M., *Off. Dig.*, 1965, **37**, 57-77.

Section Proceedings

Scottish

Eastern Branch

Treasure hunt

The annual car Treasure Hunt was held on 2 June 1973. Mr J. Brunton had arranged a most interesting and exacting route covering much of Mid- and East Lothian. The winners were Mr and Mrs R. Webster, with Mr D. Sharp and Mr A. McKendrick taking second and third prizes respectively. The treasure hunt was followed by a barbecue, after which the chairman, Mr J. Stewart, presented the prizes.

P.S.N.

Information Received

CIBA-GEIGY (UK) sales increase

CIBA-GEIGY (UK) Limited has announced that consolidated sales for 1972 were £85.77 million, an increase of 17 per cent over the 1971 results. Exports were up by £5.77 million to a record £23.89 million, and capital expenditure was again at a level of £5.4 million.

At the Annual General Meeting the Chairman, Mr A. A. S. Rae, CBE, said that the results showed very encouraging progress during the concluding stages of a two-year period of intensive organisational restructuring, which was now largely completed. The rising sales trend had continued strongly into 1973, with an increase in the first six months of 16 per cent over the corresponding period last year.

Garrick Ltd sole UK distributors for SAPICI

Garrick Chemical and Equipment Company Ltd. has been appointed sole UK distributor by SAPICI, Italy, for its range of polyurethane surface coating materials. The "Polurene" range consists of different isocyanate polymers in solution ready for blending into polyurethane surface coatings. "Rexins" are alkyd resins suitable for blending with Polurenes, and "Ucopol M3" is an isocyanate prepolymer for single component varnishes catalysed by moisture in the air.

Hoechst UK Limited to distribute SKW products

Hoechst UK Limited and Süddeutsche Kalstickstoff-Werke, Aktiengesellschaft (SKW) have reached an agreement whereby Hoechst will be handling in the UK the products Melment® and Melpers®.

Melment has been specially developed by SKW as a new concept for the building industry. It is used as admixture for concrete, mortar and gypsum, greatly improving the properties of these products. Of special interest is the labour saving "flowing concrete" made with Melment which involves a new concrete technology.

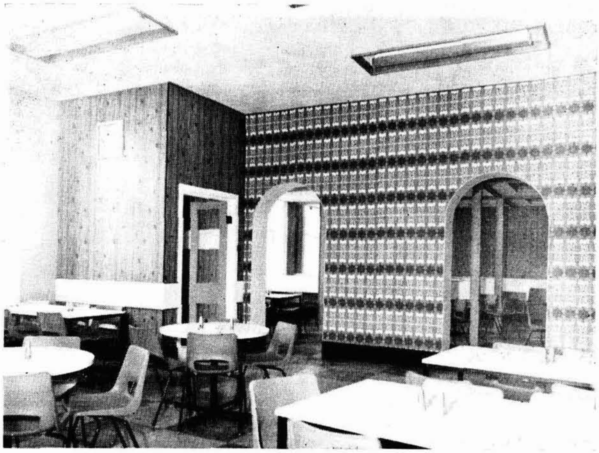
Melpers is the trade name for a group of products used in the production of decorative laminates, particularly melamine-faced chipboard. The range includes plasticisers, catalysts, and a release agent.

SKW is jointly owned by Farbwerke Hoechst Aktiengesellschaft, Frankfurt and VIAG (Vereinigte Industrie-Unternehmungen Aktiengesellschaft).

SPL Group preparing to climb the league table

A Management Seminar was held recently by Silver Paint and Lacquer Group, one of the largest independent paint manufacturers. The purpose of the seminar was to give everyone involved in management-making decisions for the company an opportunity to examine the overall future requirements of the Silver Paint and Lacquer Group and to ensure that the organisational structure would enable the company to continue to grow at its present rate. The seminar was organised in consultation with the Huddersfield College of Education (Technical).

Mr A. Odams, a principal lecturer in industrial training and education at the Huddersfield College of Education (Technical), presenting a paper to the executives of the SPL Group



The recently converted canteen at SPL's Batley works is now one of the most modern in the country

In 1963, the company's total sales were £82,600; in 1973 sales were anticipated of over £2,500,000. All these sales were achieved by indigenous growth. By paint trade standards, the company is sixteenth in a league of some 150 paint manufacturing firms. Mr Silver, Chairman and Managing Director and currently President of *OCCA*, said that the company wanted to climb this "league table" by training its own people to play in the top class. This was the first step towards overcoming some of the problems likely to be met in the continuation of growth.

Science Reference Library

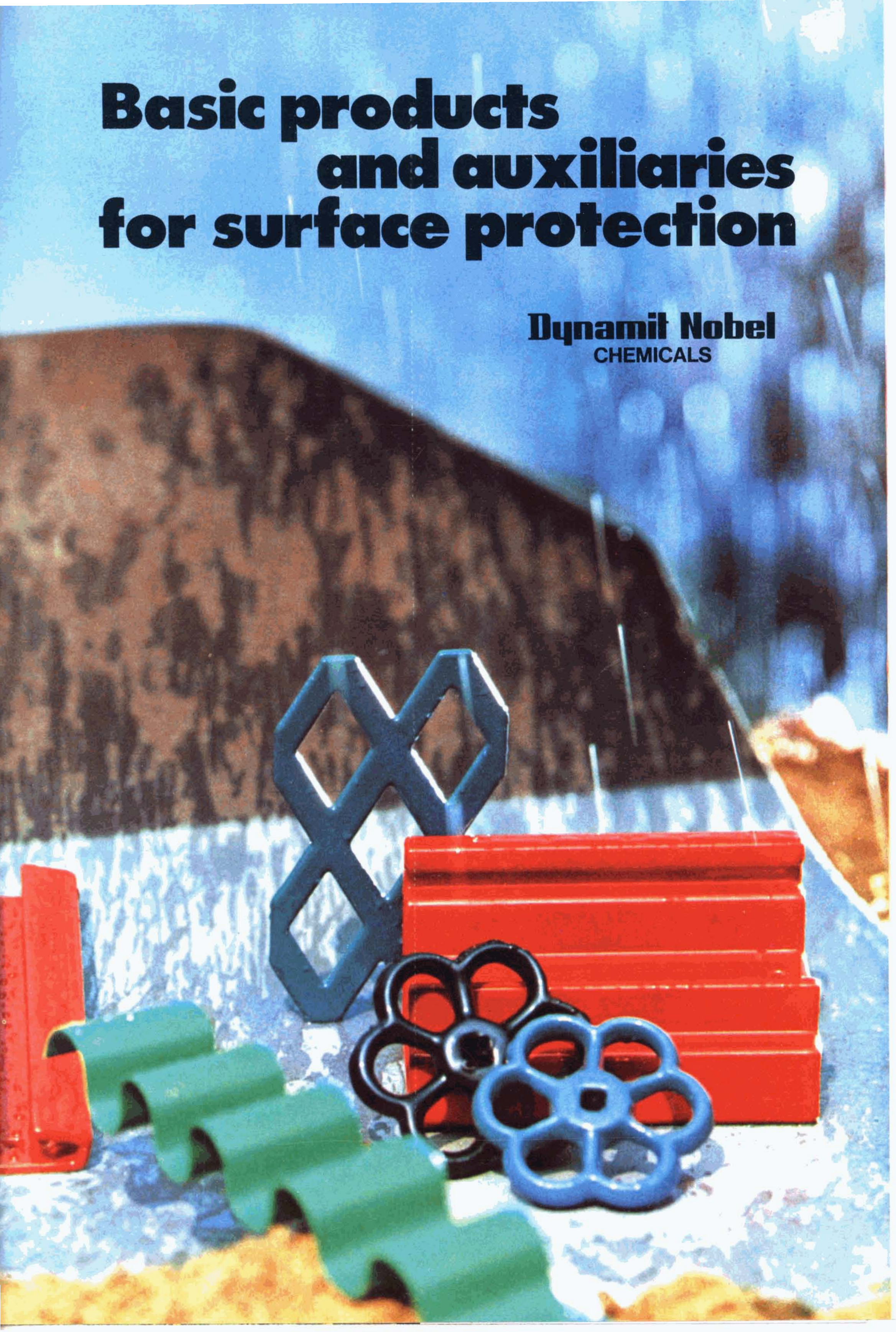
The National Reference Library for Science and Invention has been renamed the Science Reference Library and responsibility for it, as for the other library departments of the British Museum, has been transferred from the Museum to the newly formed British Library. The appellations "Holborn Division" and "Bayswater Division" are still used.

Tioxide christening?

In 1791, the Reverend William Gregor, whose interests included mineralogy and chemistry, was sent a sample of a black

Basic products and auxiliaries for surface protection

Dynamit Nobel
CHEMICALS



For Coil Coating:

DYNAPOL® L

provides coatings eminently suitable for stamping and deep-drawing.

High-molecular, linear, saturated polyesters containing terephthalic acid.

DYNAPOL L types are suitable for the production of coatings having high stamping, deep-drawing and weather-resistant properties and which, in addition to having good adhesive strength, are scratch and impact resistant, and neither yellow nor chalk. DYNAPOL L types are best used for coil-coating. Coating surfaces can have a finish ranging from high gloss to matt as desired. Pigmentations of all shades are possible.

Main fields of use:

- Packaging,
- Packaging for foodstuffs (including sterilizable packaging),
- Fascia sections,
- Appliances

DYNAPOL L types are also suitable for single or double coat roller application on aluminium, steel or galvanized iron.

Technical data:

Sheen (Gardner)	max. 95 — 100 % approx.
Pencil hardness	max. H
Impact test	180 in. lbs.
T bend	max. depending on type up to T = O
Salt spray test	depending on type 400 — 1000 hours, unaffected
Kesternich test	Unaffected after 15 — 20 cycles

These details conform to the test standards of the ECCA (European Coil-Coating Association, Brussels).

PVF Polyvinylfluoride

for long-life coatings

Wherever particularly long-life and outstanding weather resistance at both high and low temperatu are called for, PVF coatings are ideal. For they are corrosion proof, are resistant to chemicals and ha excellent shaping properties.

PVF is, among other things, particularly suitable fo coil-coating. Surface finishes may range from a si gloss to matt as desired; they discourage dirt and neither yellow nor chalk. Many shades are possibl

PVF should be used where the usual coatings affor insufficient protection against corrosion.

Main fields of use:

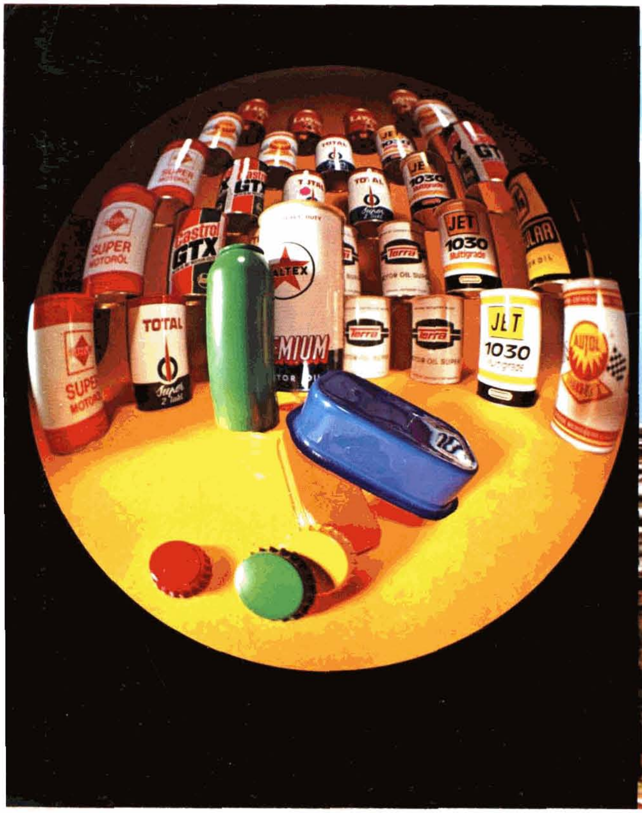
- Building units where industrial pollution is seve
- Facings for industrial plant,
- Prefabricated building sections.

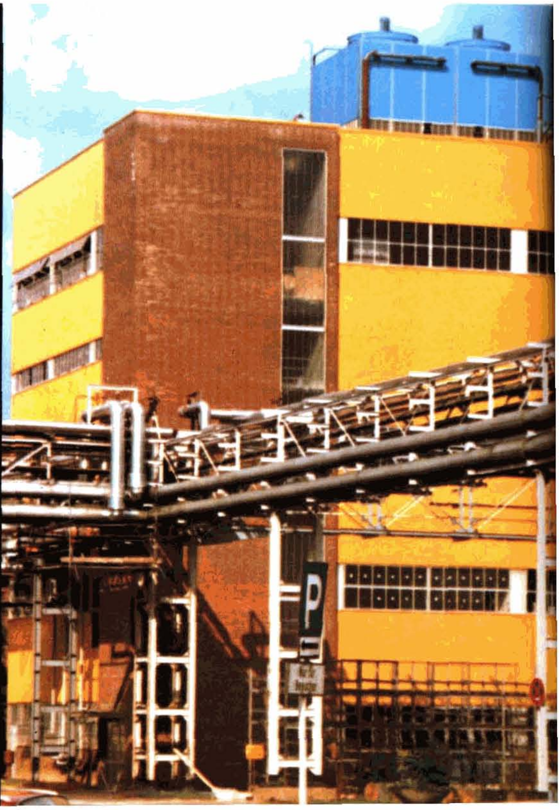
PVF is suitable for single or double coat roller application on aluminium, steel or galvanized iron.

Technical data:

Sheen (Gardner)	max. 80 % approx.
Pencil hardness	F — H
Impact test	180 in. lbs.
T bend	OT
Salt spray test	Unaffected after more than 1000
Kesternich test	Unaffected after 30 cycles
Friction constant	0.136

These details conform to the test standards of the E





For electrostatic powder-coating and whirl-sintering:

DYNAPOL® P

Saturated polyesters containing terephthalic acid for the production of powders both for electrostatic powder-coating and for whirl-sintering.

Powders with a DYNAPOL P base are suitable for coating all metals.
By virtue of their special properties (e. g. high resistance to weathering, yellowing and chalking) such coatings are equally suitable for external use.

Main fields of use:

- Metal furniture,
- Metal window frames,
- Garden furniture,
- Apparatus,
- Metal facings,
- Tubing,
- Household appliances.

Technical data:

Thickness of single coating 50 — 70 µ
Erichsen test 8 — 10 mm approx.
Pendulum test (depending on type) 175 — 185 sec. as per DIN 53 157
Indentation hardness 75 — 120 approx. (depending on type)
Sheen as per Lange. Angle of incidence 45°
80 — 115 (depending on type)
Adhesive strength: very good
Kesternich test up to 30 cycles (depending on type)

HARD PVC COATING POWDER

A plasticizer-free polyvinyl chloride compound in powder form for whirl-sintering and powder-coating.

Advantages:

- Surface toughness
- Weather resistance
- Enduring gloss
- Chemical resistance
- No tendency to brittleness

Advantages when processing:

- Pleasant to work with: no offensive odours due to plasticizer vapours,
- High sheen surfaces within seconds,
- No post-treatment necessary.

Can be used:

- In the streets: Sign boards, posts for traffic signs, street lighting,
- In industry: Housings, mountings, sectional units, tubing,
- In the building world: Profiles, fittings, fascias,
- In the household: Appliances.

Technical data:

Coating thickness depending on method of application
80 — 400 µ
Erichsen test 8 — 11 mm approx.
Pendulum test 170 — 185 sec. approx.
Sheen as per Lange. Angle of incidence 45°
120 — 140 %
Kesternich test. Unaffected after 40 cycles
Adhesive strength: with bonding agent, very good

For protection against corrosion even at high temperatures:

DYNASIL® H 500

A binder having a silicic acid ester base for inorganic zinc dust coatings. When it is a question of protecting iron and steel from corrosion, even at temperatures up to 400° C, zinc dust paints having DYNASIL as a binder serve the purpose admirably.

Zinc dust paints with a DYNASIL base are particularly suitable for industrial processing. They can be welded over; they can be applied either by air or airless spraying, brush or roller, and can be used alone as a one-coat process or serve as a foundation for covering with any of the usual colouring methods.

Main fields of use:

- Shipbuilding,
- Industrial plant construction,
- Power plant construction,
- Bridge building,
- Large steel structures,
- Mass produced building units.

Test results of DYNASIL based zinc dust coatings:
Salt spray test (DIN 50 021) Unaffected after 1000 hours.
Adhesive strength, grating as per DIN 53 151
Grating value 0.
Temperature loading resistance: Permanent load, maximum 400° C. Short term load, maximum 600° C

DYNAPOL L

PVF

DYNAPOL P

HARD PVC
COATING POWDER

DYNASIL H 500

Other tried and tested products for use in surface protection:

Paint and varnish resins
HYDROXYESTER RESINS
Thermo-setting, branched polyester resins containing hydroxyl groups for coil-coating and conventional painting techniques and having excellent stamping and deep-drawing properties.

ICDAL®
Alkyd resins for making high-grade commercial and artists' paints, stove enamels and nitro cellulose combination lacquers.

Electrically insulating paint resins
ICDAL® TE/TI
Ester and esterimide resins, wire lacquer resins for producing insulated leads resistant to permanent temperature loads, resins for insulating impregnating lacquers.

Titanic acid esters
Reactive cross-linking agents for paint and lacquer resins, binders for high temperature lacquers.

Nitrocellulose
COLLODION COTTON
PLASTICIZED NITROCELLULOSE

Vanadyl alcoholates
Catalysts for polyurethane coatings with variable adjustment of setting times.

Plasticizers
WITAMOL®
for use with various lacquers. Special plasticizer for heat-sealing and non-toxic aluminium coatings.

Chlorinated paraffins
WITACLOR®
For making lacquers flame resistant.
For producing fascia paints.

Chlorophenoles
WITOPHEN®
Oil and dispersion paint additive for preventing fungus formation and decomposition during storage.
For the production of fungus-resistant wall paints.

Chlorinated hydrocarbons
DYNATRI® LQ, trichlorethylene. Solvents for paint and varnish resins for hot or cold dip coating processes.

For the de-greasing of metals:
DYNAPER® perchloroethylene
DYNATRI® trichlorethylene
MECLORAN® 1.1.1. tri-ethane chloride
MECLORAN® D 1.1.1. tri-ethane chloride (vapour type)
For the de-greasing of light metals:
DYNATRI® LM trichlorethylene.

Special hard aggregates
TROCOR®
Electro-corundum as an aggregate for high-stress concrete pavings and for abrasive coatings having a synthetic resin base.

Blast mediums not conducive to silicosis:
REWAGIT®
Standard corundum, economical in use, low in dust, rustproof. For the cleaning or roughening of material surfaces.

DYNAMULLIT® — balls
for the matting and densifying of material surfaces.

Please contact us if you have problems or require further information. We shall be pleased to give you the benefit of our experience.

Dynamit Nobel Aktiengesellschaft
Vertrieb Chemikalien M5
D-5210 Troisdorf-Oberlar, Haberstraße 2,
Telephone (02241) 180-1, Telex 889401

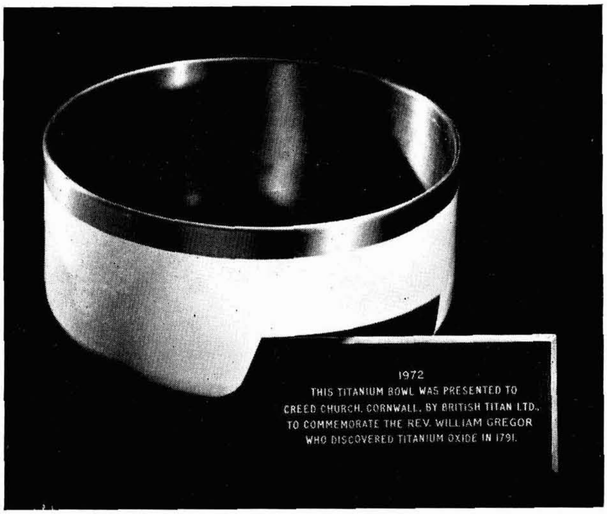
® = Registered trade mark

Dynamit Nobel
CHEMICALS

sand and, as a result of his studies of it concluded that it contained besides iron, the oxide of a hitherto unknown element. The sand, known today as ilmenite, is the source of the white pigment titanium dioxide, which Gregor had prepared in a hydrated form.

Almost immediately after he had made his discovery, Gregor became Vicar of the Parish of Creed, near Grampound in Cornwall. The mineral development manager of British Titan Products Ltd., Dr F. R. Williams, visited Creed Church, and noticed that there was no reference in the church to the important discovery made by Gregor, which ultimately led, more than a century later, to the founding of a new section of the chemical industry, the manufacture of titanium pigments. British Titan, which manufactures "Tioxide" pigments, decided, therefore, to present to the church a titanium metal christening bowl, suitably inscribed, and having most of the outer surface coated with a titanium dioxide paint. This was used for the first christening in May 1973.

There have been no reports, so far, of improved whiteness and purity over the titanium dioxide pigments put to more secular uses!



The titanium christening bowl presented to Creed Church by BTP in memory of the Rev. William Gregor

New Products

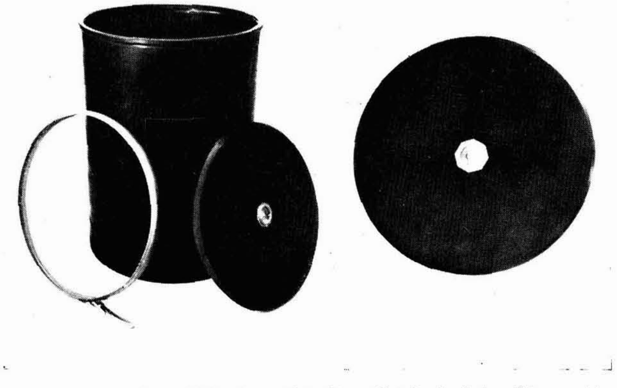
High standard of fire retardance from new water-based multicolour finish

Britain's first fully water-based fleck paint, Brolac Vinyl Multicolour Finish from Berger Paints, has been shown by independent fire retardance tests to give results well within a Class "O" performance when tested to British Standard 476. Class "O" is the highest standard of performance encountered within the Department of the Environment's Building Regulations 1972, and indicates a finish suitable for the circulation spaces and protected shafts of all large residential, industrial and institutional buildings.

The fire tests, for ignitability and propagation characteristics according to Parts 5 and 6 of BS 476, were carried out by the Warrington Research Centre, and were based on a normal system of Brolac Vinyl Multicolour applied over a base coat of Brolac pep emulsion to a non-combustible surface.

Laminated drum from PD (Technical Mouldings) Ltd

The "Rigidrum", a 45 gallon plastic drum designed to provide improved stacking performance and durability for in-plant handling and storage, has been launched by PD (Technical Mouldings) Ltd., a member of the Associated Packaging Group. The drum is rotationally moulded as a laminate of high and low density polyethylene to provide extra rigidity around the rim, and is compounded black to resist degradation by ultraviolet light when stored out-of-doors. The manufacturing process ensures complete fusion, so there is no danger of delamination.



The "Rigidrum" from PD Ltd is supplied with a skirted polyethylene lid secured by a heavy-duty steel toggle clamp

Coates offers improved Co-Sol

Further improvements have been made to Co-Sol ultra-thin film screen inks. Of particular interest to the progressive screen printer, and of course the operator who wishes to improve workshop conditions, is the reduction in odour level of the ink in the screen.

Additionally, the new inks are free from control under the 1972 Regulations governing Highly Flammable Liquids, and this has been achieved without the use of nitrocellulose as a binder.

Conference, courses, symposia

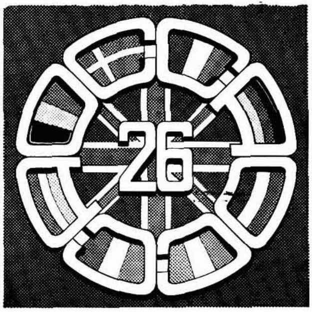
Corrosion in the marine environment

A two-day conference on corrosion in the marine environment, arranged jointly by the Institute of Marine Engineers, the Institution of Corrosion Technology and the Chamber of Shipping of the UK, will be held at the Memorial Building, 76 Mark Lane, London, on 8 and 9 November 1973.

Adhesives and rubber technology

The IRI Adhesives Group will be holding a symposium on "Adhesives and rubber technology" at the Hotel Russell, London, on 10 October.

Topics include the compounding of EPDM rubbers for improved adhesion. the use of solvent adhesives in bonding rubber to plastics, anaerobic and cyanoacrylate adhesives, the behaviour of hot melt adhesives, the use of aqueous polymer dispersions in pressure sensitive coatings,



World-wide interest in OCCA 26—the European Economic Community's forum for technical display and discussion in the surface coatings industries

The motif adopted for the Association's 26th Technical Exhibition, showing the flags of the enlarged EEC, has aroused world-wide interest, and amongst the enquiries from new sources which are being received at the Association's offices are many from Eastern Europe. Already applications have been received from organisations which have not shown previously at the Association's Exhibition, as well as from previous exhibitors.

Venue

As already announced in the August issue of the *Journal*, OCCA 26 will take place at the Empire Hall, Olympia, London, from 23 to 26 April 1974.

Invitation to Exhibit

Invitations to Exhibit were despatched in July to those organisations in UK and abroad who have exhibited at previous Exhibitions or have requested information on the 1974 Exhibition. Any organisation which has not received an Invitation to Exhibit, but wishes to do so, should apply at once to the Director & Secretary of the Association at the Association's offices. *The closing date for applications to exhibit is 1 November 1973.*

International character

The Exhibition, which has long been known as the forum for technical display and discussion for the surface coatings industries, in 1973 attracted visitors from more than 50 overseas countries, and there was direct contribution by exhibitors from 14 overseas countries. The motif chosen for this year's Exhibition shows the flags of the enlarged European Economic Community and, by converging on the flag of the UK, symbolises the welcome extended for many years to exhibitors and visitors not only from these countries but from farther afield to the OCCA Exhibitions in London, one of the capital cities of the European Economic Community. To further the aim of a truly international character, the Exhibition is widely advertised in technical journals both at home and in 18 technical journals overseas. Furthermore, it has been the practice for many years to issue information cards in six languages (English, French, German, Italian, Spanish and Russian) and these are widely distributed to firms and individuals in many countries. Interpreters are available at the Exhibition without charge to help both exhibitors and visitors alike.

Hours of opening

On this occasion the Exhibition Committee has decided to dispense with the Monday opening and to concentrate on four full days as follows:

Tuesday 23 April	.. 09.30 to 18.00hrs
Wednesday 24 April	.. 09.30 to 18.00hrs
Thursday 25 April	.. 09.30 to 18.00hrs
Friday 26 April	.. 09.30 to 16.00hrs

Exhibition Dinner

Following the success of the Exhibition Dinner on the opening day in 1973, the Committee has decided to hold a Dinner at the Savoy Hotel, London WC2 on Tuesday 23 April at 19.00 for 19.30hrs. At the request of some exhibitors a cash bar will be made available after the function for those visitors wishing to use this facility. Full details of the Dinner will be announced in this *Journal* from time to time and an application form for tickets will be enclosed in each copy of the *Official Guide*.

Official Guide

The *Official Guide* will be prepared well in advance of the dates of the Exhibition so that copies can be circulated widely, both to members and non-members, thus allowing visitors an opportunity to plan their itineraries. As well as maintaining the Exhibition's unique position as a purely technical display, manned by technical personnel, the Exhibition Committee has for many years followed the successful policy of encouraging visitors in this way, and by making no charge for admission so that the maximum, flow of communication between exhibitors and visitors can take place.

Aims of the Exhibition

The Exhibition Committee wishes the aims of the Exhibition as stated in the Invitation to Exhibit, to be as well known as possible and accordingly these are reproduced below.

The aim of the Exhibition is the presentation of technical advances in those industries supplying the paint, varnish, printing ink, colour, linoleum and other allied industries. The technical advances may relate to: new products, new knowledge relating to existing products and their uses, or in suitable cases, existing knowledge which is not generally available in the consuming industries.

The Committee stipulates that exhibitors present a technical theme—that is display in a technical manner the technical developments in raw materials, plant or apparatus illustrated by experimental evidence. It is essential that a technically or scientifically trained person, who has full knowledge of the products displayed, be available on the stand throughout the official hours of opening.

Whilst the Committee naturally encourages the showing of new products, it does not stipulate that a new product has to be shown each year, since it fully appreciates that there are occasions when this is not possible. Accordingly, the Committee draws attention to the fact that new technical data on existing products are regarded as acceptable subject matter.

Charge to Exhibitors

The OCCA Exhibitions have for many years been planned to keep costs as low as possible for exhibitors. The charge (which includes stand space, floor, walls, muslin ceiling, fascia with coloured felts and pine trims, and painted name plaque), will be £110 (plus Value Added Tax) per unit of 4.32m^2, and exhibitors receive a free supply of *Official Guides*, six language cards, badges, folders, and so forth. Since there is no charge made for admission to the Exhibition, no "special facility" tickets are issued for distribution by exhibitors. Each visitor is given a copy of the *Official Guide*, together with a folder for technical literature, showing the location of the stands, upon arrival at the hall.

Travel Agents

The Wayfarers Travel Agency Ltd., Cranfield House, 97/107 Southampton Row, London WC1B 4BQ., will be allocated a stand adjacent to the OCCA Information Centre at the Exhibition and will be prepared to advise on, and arrange, hotel accommodation and travel facilities to the Exhibition. They will also be able to make theatre ticket reservations for the evenings of the Exhibition.

Please address all enquiries to The Wayfarers Travel Agency AT THE ADDRESS SHOWN ABOVE, and not to the Association.

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

ASHER, MASUREIK, BSc, T. & C. Chemicals, PO Box 2953 Cape Town, South Africa. *(South Africa)*

BARDEN, BRIAN, Crown Cork Co. Ltd., Scotts Road, Southall, Middx. *(London)*

BATCHELOR, WILLIAM ANTHONY, AIST, 32 Gold Drive, Whitestone Nuneaton, Warwickshire. *(Midlands)*

BETTS, PETER CHARLES, BSc, Consolidated Chemicals Ltd., Box 15-104 New Lynn, New Zealand. *(Auckland)*

BONGI, SERGIO, BSc, British and Continental China Clays, 15 Rue Blanche B1050, Brussels, Belgium. *(General Overseas)*

CHAPMAN, COLIN BRUCE, BSc, GOLLIN (NZ) Ltd., 302 Great North Road, Grey Lynn, Auckland, N. Zealand. *(Auckland)*

CLACHER, NOEL IRWIN, 57 Wall Road, Penrose, Auckland, New Zealand. *(Auckland)*

CUTLER, ARTHUR ANTHONY, BSc, PhD, Revertex Industries (NZ) Ltd., PO Box 12180, Penrose, Auckland, New Zealand. *(Auckland)*

DERWIN, DENIS, Staperm Limited, Wollaston, Wellingborough NN9 7RL. *(Midlands)*

GUNN, JOHN EDWARD STUART, BSc, c/o Gollin (NZ) Ltd., PO Box 3740 Auckland, New Zealand. *(Auckland)*

HAYDEN, PHILIP ROSS, BSc, A. C. Hatrick (NZ) Ltd., PO Box 2359, Auckland, New Zealand. *(Auckland)*

HUMPHREYS, BRIAN, 16 Ventnor Avenue, Bury, Lancs. *(Manchester)*

JONANZI, BILLY, Valmore Paints (Malawi) Pvt. Ltd., Box 555, Blantyre, Malawi. *(General Overseas)*

JONES, ROBERT JOHN, BSc, 10 Brett Avenue, Takapuna, Auckland, New Zealand. *(Auckland)*

LINDSAY, DOUGLAS MICHAEL, LIRI, PO Box 1366, Johannesburg, South Africa. *(South Africa)*

LLOYD-JONES, OWEN ANTHONY, LRIC, 9 Rosewood Drive, Higher Walton, Preston, Lancs. *(Manchester)*

MACHIN, MAURICE WILLIAM, 54 St. Barnabas Road, Woodford Green, Essex. *(London)*

MARTIN, KINGSLEY ROGAN, BSc, 14 Selous Road, Highlands Salisbury, Rhodesia. *(South Africa)*

MEHTA, KAMAL KISHORE, BSc, MSc, 110 Stuart Avenue, South Harrow, Middx HA2 9AZ. *(London)*

MENDEZ, DAVID WILLIAM, 65 Elliston House, Wellington Street Woolwich, London, SE18. *(London)*

MERRITT, WILLIAM THOMAS, The Peerless Gold Leaf Co. Ltd., Fairfield Works, Fairfield Road, Bow, London, E3. *(London)*

MORRIS, JOHN ARTHUR, Newmor (Plastics) Ltd., Henfaes Lane, Welshpool, Mont. *(Midlands)*

MURDOCH, NEIL WALLACE, c/o Lusterloid Paints Ltd., PO Box 22, 122 Otahuhu, Auckland 6, New Zealand. *(Auckland)*

OLDRING, PETER KENNETH THOMAS, BA (Chem), ARIC, 29 Sunfield Avenue, Moorside, Oldham, Lancs. *(Hull)*

TABBERNOR, GEORGE ALAN, BSc, 17 Paviors Road, Chasetown, Walsall, Staffs. *(Midlands)*

UMFREVILLE, JOHN HERBERT, PhD, ARIC, 4 Manland Way, Harpenden, Herts. *(Thames Valley)*

WOUTERS, JOHANNES ALOYSIUS ANTONIUS MARIA, Valmore Paints *(Malawi)* Pvt. Ltd. PO Box 555, Blantyre, Malawi. *(General Overseas)*

Associate Members

BALKE, HERMANN PETER WOLFGANG, PO Box 11337, Johannesburg, South Africa. *(South Africa)*

BARALE, FRANK, PO Box 2953, T. and C. Chemicals (Pty) Ltd., Cape Town, South Africa. *(South Africa)*

Registered Students

BUSH, STEPHEN CHRISTOPHER, 11 Normans Close, Hillingdon, Uxbridge, Middx. UB8 3RR. *(Thames Valley)*

JONES, GARY SIDNEY, 120 Hodge Hill Road, Hodge Hill, Birmingham, B34 6EA. *(Midlands)*

PHILLIPS, MICHAEL OWEN, 38 Barrington Road, Sutton, Surrey. *(London)*

Forthcoming Events

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

Monday 1 October

Hull Section: "Polyacrylates in emulsion paints" by a speaker from Allied Colloids, to be held at the Dorchester Hotel, Beverley Road, Hull at 7.00 p.m.

Thursday 4 October

Newcastle Section: "Painting of wooden joinery" by Mr A. F. Sherwood of Paint Research Station, to be held at the Royal Turks Head Hotel, Grey Street, Newcastle at 6.30 p.m.

Thames Valley Section—Student Group: "Aerosols" by Mr Southby, Aerosols International Limited, Downmill Road, Bracknell, Berks at Main Lecture Theatre, Slough College at 4.00 p.m.

Friday 5 October

Hull Section: Annual Dinner Dance to be held at Cave Castle, South Cave, Hull.

Saturday 6 October

Scottish Section—Student Group and Eastern Branch: "Dispersions of titanium dioxide in modern paint making" by Mr D. Craig of Tioxide International Ltd., at Lady Nairn Hotel, Willowbrae Road, Edinburgh at 10.30 a.m., followed by lunch and the annual skittles match at the Abercorn Inn.

Tuesday 9 October

Manchester Section: Joint Meeting with the North-Western Branch of the Institute of Printing. "Change in printing ink technology and the influence of Europe" by Mr G. Whitfield, Mander Kidd (UK) Ltd., at Cottons Hotel, Manchester Road, Knutsford at 7.00 p.m.

West Riding Section: "The performance of wood primers" by Mr P. Whitely, of the Building Research Station, at Griffin Hotel, Leeds at 7.30 p.m.

Thursday 11 October

Scottish Section: Visit to Planetarium of Glasgow College of Nautical Sciences.

Midlands Section—Trent Valley Branch: "Paint manufacturing techniques" by Mr B. L. Lucas, Joseph Mason & Co., Derby, to be held at the Birmingham Chamber of Commerce and Industry, PO Box 30, 75 Harbourne Road, Birmingham at 6.30 p.m.

Tuesday 16 October

London Section: "Some aspects of technical training" by Mr G. P. Birtles, of Selection and Industrial Training Administration Ltd., to be held at the Great Northern Hotel, Kings Cross, London N1 9AN at 7.00 p.m.

Wednesday 17 October

Manchester Section—Student Group: "Instrumental colour measurement" by Mr Bravey, of Berger Paints Ltd., to be held at the Manchester Literary and Philosophical Society at 4.30 p.m.

Scottish Section—Eastern Branch: "Advances in polymers" by Dr I. Soutar, of Heriot Watt University, Edinburgh, to be held at the Carlton Hotel North Bridge, Edinburgh at 7.30 p.m.

Thursday 18 October

London Section—Southern Branch: "Problems in painting of yachts" by a speaker

Forthcoming Events—*continued*

from Camper and Nicholsons Ltd., to be held at the Pendragon Hotel, Southsea at 7.00 p.m.

Friday 19 October

Irish Section: "The use of extenders in titanium dioxide" by Mr M. Hart, of Croxton & Garry Ltd., to be held at the Clarence Hotel, Dublin at 8.00 p.m.

Manchester Section: Annual Dinner Dance at the Piccadilly Hotel, Piccadilly Plaza, Manchester.

Midlands Section: "The current status and role of amino resins in surface coatings" by Mr R. McD. Barrett, BIP Chemicals Ltd., to be held at the Birmingham Chamber of Commerce and Industry, 75 Harborne Road, Birmingham B15 3DH at 6.30 p.m.

Thursday 25 October

Thames Valley Section: "Printing inks in the '70s" by Mr G. H. Hutchinson, of Croda Polymers Ltd., to be held at the Beech Tree Hotel, Maxwell Road, Beaconsfield, Bucks at 7.00 p.m.

Friday 26 October

Bristol Section: "The testing and performance of flame-retardant paints" by Mr F. C. Adams, to be held at the Royal Hotel at 7.15 p.m.

Thursday 1 November

Bristol Section: "Future trends and requirements for automotive finishes" by Mr W. Dodds, of Pressed Steel Fisher Ltd. Joint Meeting with the Birmingham Paint Varnish & Lacquer Club, at the Imperial Hotel, Birmingham.

Newcastle Section: "Acrylic emulsions in maintenance paints" by Dr R. N. Washburne, Rohm & Haas Ltd., to be held at the Royal Turks Hotel, Grey Street, Newcastle at 6.30 p.m.

Thames Valley—Student Group: "Printing and printing inks" by Mr B. Ellison, Winstones Limited, Hereford, to be held at the Main Lecture Theatre, Slough College at 4.00 p.m.

Tuesday 6 November

Hull Section: "Some aspects of personnel management" by Mr K. Yates, of Laporte Industries Limited, to be held at the Haven Inn, Barrow, Haven, Lincs at 6.30 p.m.

Wednesday 7 November

London Section: "Newer analytical techniques and their application to the surface coating industries." One day joint meeting with the Society for Analytical Chemistry, Analytical Division, Chemical Society, to be held at the Thames Polytechnic, Woolwich at 9.30 a.m.

Scottish Section—Eastern Branch: "Marketing" by Mr G. Mandel, of Thomas & Green Ltd., to be held at the Carlton Hotel, North Bridge, Edinburgh at 7.15 p.m.

Thursday 8 November

Midlands Section—Trent Valley Branch: "Solvents and safety" by Mr K. W. Smith, HM District Inspector of Factories, Derby, to be held at the Birmingham Chamber of Commerce and Industry, 75 Harborne Road, Birmingham, B15 3DH at 6.30 p.m.

Friday 9 November

Manchester Section: "Industrial relations and communications" by Mr W. Davies, Manchester Business School, to be held at the Manchester Literary and Philosophical Society, 36 George Street, Manchester, at 6.30 p.m.

Scottish Section—Students Group: "Powder coatings" by Mr M. P. Stanley, Shell Chemicals UK Ltd., to be held at St. Enochs Hotel, Glasgow at 10.15 a.m.

Saturday 10 November

Scottish Section—Student Group: "Powder coatings" by Mr M. P. Stanley of Shell Chemicals UK Ltd.

Monday 12 November

London Section: "Optical methods in colloid and surface chemistry". Joint Meeting with Society of Chemical Industry, Colloid and Surface Chemistry Group, to be held at 14 Belgrave Square, London, SW1X 8PS at 11.30 a.m.

Tuesday 13 November

West Riding Section: "Water-based metal primers" by Mr K. A. Safe, Vinyl Products Limited, to be held at Griffin Hotel, Leeds at 7.30 p.m.

Thursday 15 November

Irish Section: Annual Dinner Dance at Clarence Hotel, Dublin.

Friday 16 November

Midlands Section: "Recent progress in organic pigments" by Mr E. R. Inman, of CIBA-GEIGY (UK) Ltd., to be held at the Birmingham Chamber of Commerce and Industry, 75 Harborne Road, Birmingham B15 3DH at 6.30 p.m.

Tuesday 20 November

Scottish Section: "Colour difference—the measure of the future" by Mr M. McLaren, ICI Organics Division. Joint Meeting with the Society of Dyers and Colourists, Scottish Region, to be held at the Whitehall Restaurant, West George Street, Glasgow at 7.30 p.m.

Thursday 22 November

London Section—Southern Branch: "Webb offset printing" with a film, by Mr J. D. Freeman, the News Centre, Portsmouth, to be held at the Pendragon Hotel, Southsea at 7.00 p.m.

Thames Valley Section: "Newer modified hydrocarbon resins for paint and printing inks" by Mr K. Gilkes, of Berger Chemicals Resin Division, to be held at the Beech Tree Hotel, Maxwell Road, Beaconsfield, Bucks at 7.00 p.m.

Friday 23 November

West Riding Section: Annual Dinner Dance at the Crown Hotel, Harrogate.

Friday 30 November

Bristol Section: "Water pollution—legislation, case study and one answer" by Mr B. Cryer and Mr Shepherd, of Berger Paints, Mr Hunt of Bristol City Engineers Department, and Mr R. Evans, of Pollution Technical Services, to be held at the Royal Hotel, Bristol at 7.15 p.m.

London Section: Ladies' Night.

News of Members

Mr G. Rossa, an Ordinary Member attached to the London Section, has taken up an appointment as co-ordinator, Resins, for Scandinavia with Shell Norden NV. Mr Rossa was previously Senior Scientist in the Surface Coatings Laboratory of Shell Research Limited.

Mr H. B. Smith, an Ordinary Member attached to the Scottish Section and Section Hon. Secretary, has taken on additional sales responsibilities for Synthetic Resins Ltd. (SRL), a sister company of Vinyl Products Ltd. Mr Smith is now responsible for the sales of SRL's resins for surface coatings in Scotland and Ireland, two countries where the company has previously been without direct representation. He will continue to operate from the Glasgow office of Vinyl Products Ltd.

Mr H. B. Smith

Mr I. Moll, an Ordinary Member on the Committee of the Manchester Section and a Fellow in the Professional Grade, has left ICI to act as an independent consultant-tutor. For the past three years, he has been Head of the Application Research and Technical Service Dept., ICI Organics Division where he worked for over 31 years.

Mr Moll is now offering a line-management approach to improve effectiveness of meetings, practical teamwork and creative productivity, as well as individual coaching in human relation skills, based on self-understanding.

CLASSIFIED ADVERTISEMENTS

Classified Advertisements are charged at the rate of 60p per line. Advertisements for Situations Wanted are charged at 15p per line. A box number is charged at 10p. They should be sent to the Director & Secretary, Oil & Colour Chemists' Association, Priory House, 967 Harrow Road, Wembley, Middlesex HA0 2SF

SITUATIONS VACANT

Assistant required for small plastics/rubber colour service and product control laboratory in north-west area. At least three years experience in colour matching and use of laboratory machinery necessary. Chemical education up to HNC standard with some general knowledge of polymers. The position has possibilities of further development to applicants with initiative and a responsible outlook. Best age group 21-25 but older men not excluded. Salary to be negotiated according to experience and qualifications. Reply in confidence to Managing Director. Box No. 378.

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MISCELLANEOUS

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introduction to paint technology

The sales of this Association publication now exceed 16,000, and now includes an eleventh chapter entitled "Recent Development." The book contains 204 pages including 11 line diagrams, 8 photographs of common paint defects, and comprehensive index.

To keep the price of this book at its present low level, it is essential to reduce book keeping to a minimum. Copies of this book will only be supplied if remittance is sent with the order. **Accredited** Booksellers'. discount: **25%**

Copies are available, at £1.00 (post free in UK), from the Association's offices.

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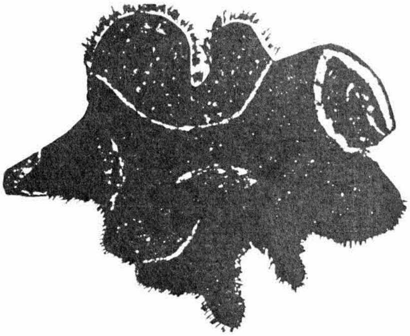

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