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The challenge to coatings in a changing world: Predestination or prophesy?

J. B. Harrison

Surface coatings for the nuclear industry

P. Walker and A. Haighton

Original and maintenance painting systems for North Sea oil and gas platforms
D. Atherton

Solvent loss from paint films

J. Ramsbotham

Priory House, 967 Harrow Road, Wembley, Middlesex, HAO 2SF England

OCCA-32 Exhibition

13–15 May 1980 Cunard International Hotel Hammersmith, London W6

Motif: The motif, designed by Robert Hamblin, uses the compass to symbolize the unique attraction of the OCCA exhibitions which annually draw exhibitors and visitors from numerous countries.

The aim of the Exhibiton is the presentation of commercial and technical information relating to raw materials, plant and equipment used in the paint, polymer, printing ink, colour, adhesive and allied industries, both in their manufacture, processing and application.

The Exhibiton Committee will be particularly pleased to welcome exhibits from companies relating to the new energy efficient. low-polluting technologies, including powder coatings, high solids coatings, radiation curing, water-based coatings and other developments.



The main part of the Exhibition will be in two sections. The entrance to the Exhibition will be on the ground floor in the new Exhibition Hall, in which exhibitors of heavy machinery, plant and equipment or those wishing to have the traditional style of stand will be situated. On the first floor, additional exhibitors, mainly of raw materials, laboratory equipment or other small exhibits, will be accommodated in the Queen Mary Suite. in which the stands will be of a modular design. The Queen Mary Suite is a large pleasant room which is decorated and carpeted as an integral part of the hotel.

In addition, several suites and rooms will be available on the intermediate Mezzanine floor and third floor for those companies who wish to use that type of facility to exhibit, or to entertain their visitors in addition to their stands in the main halls.





The motif for OCCA-30 used the symbol of a moving indicator on a calendar to emphasise the importance of the continuous dialogue year by year between suppliers and manufacturers.



The motif for OCCA-28 emphasised that the target for 1976 was London where all the Exhibitions have been held, regularly attracting both exhibitors and visitors from over fifty countries.

THE ANNUAL FOCAL POINT FOR THE SURFACE COATINGS INDUSTRIES

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Admission to the Exhibition will be free, and visitors will be asked to complete registration cards which will be available in advance from the Association with copies of the *Official Guide*. Copies of the *Official Guide* will be charged at £1.50 each, and both registration cards and copies of the *Official Guide* will also be available at the Exhibition.

The Exhibition provides an ideal opportunity for organisations to display and discuss their products and services to a wide spectrum of visitors from all over the world.

Organisations wishing to receive further details should contact the Director & Secretary, Mr. R. H. Hamblin, Oil & Colour Chemists' Association, Priory House, 967 Harrow Road, Wembley, Middlesex HAO 2SF, England (Tel: 01-908 1086, Telex: 922670 OCCA G).



The motif for OCCA-31 emphasised the inique aspect of the OCCA Exhibitions, which annually provide an international focal point for the surface coatings industries.



In 1977 the motif for OCCA 29 used inward pointing arrows to show the many places from which people come to the Exhibition, and these arrows formed outward pointing arrows to show the subsequent spreading of knowledge.

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W. MacDonald A. McLean, BSc, ARCST, CChem, FRIC, FTSC D. V. Maltman D. J. Morris B. E. Myatt A. J. Newbould, BSc, MRIC	Surface coating	s for the nuclear indus <i>P</i> .	Stry
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T. W. Wilkinson, AMCT, FTSC D. S. Wilson F. B. Windsor, ATSC	Solvent loss fro	m paint films	
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Transactions and Communications-

The challenge to coatings in a changing world: Predestination or prophesy?*

By J. B. Harrison

Consultant, 25 Channel Reach, Burbo Bank Road, Blundellsands, Liverpool L23 6TA

Summary

It is attempted to assess world change on the basis of how it has taken place in the past. The rapidity of change has been remarkable. Some of the failures of change are instanced and the need constantly to reassess its effect is emphasised.

Time and change bring constraints which can add to the difficulties of surface coating development.

Keywords

Specifications, standards and regulations specifications standard procedures test specification Previous demands for change have been largely generated by the user, who will be the mainspring of demand for new products and techniques. The past is analysed in the context of adverse trends that have developed insidiously. In this age of bureacratic interference, there is a marked tendency to over elaboration by specifiers and the providers of Codes of Practice. BS 5493: 1977 is taken as a typical instance.

Miscellaneous terms development

Le défi pour revêtements dans un monde changeant : Prédestination ou prophétie

Résumé

On a tenté de faire une évaluation des changements dans le monde basée sur les événements du passé. La vitesse du processus de changement a été remarquable. On mentionne certains insuccès dans le domaine de changement, et on souligne la nécessité de réévaluer constamment les effets provoqués par ce processus.

L'écoulement de temps et le processus de changement entraînent des contraintes qui augmentent les difficultés associées au développement des revêtements de surface. Jusqu'à présent c'est l'usager qui a suscité les demandes pour changement, et il sera la force motrice de la demande pour de nouveaux produits et techniques. On fait une analyse du passé au point de vue des tendances défavorables qui se sont déroulées à la dérobée. En cet âge de l'intervention bureaucratique, il ya une tendance à surélaboration de la part de ce qui sont chargés de dresser des normes et fournir les Codes de la Pratique. On cite la norme BS 5493: 1977 en tant qu'exemple typique.

Die von einer sich ändernden Welt an Beschichtungsmittel gestellten Anforderungen: Prädestination oder Prophezeiung

Zusammenfassung

Es wird versucht, Veränderungen in der Welt zu beurteilen, wie diese in der Vergangenheit vor sich gingen. Die Geschwindigkeit, mit welcher sie erfolgten, war erstaunlich. Einige der sich als Fehler herausstellenden Änderungen werden erwähnt, und die Notwendigkeit ständig deren Auswirkungen zu bewerten, wird betont.

Zeit und Wechsel bringen Zwangslagen mit sich, welche die Entwicklung von Beschichtungsmitteln noch schwieriger machen.

How will the world change?

It would be a brave man, indeed, who attempted to answer this question. The world has been changing for centuries. It is called evolution, which is a continuous process, inexorable in its progress, and with an increasing rate of change as time progresses. Changes of great moment are usually imperceptible at the time of their inception and pass unnoticed until their portents are realised, when it is too late for mere man to change the course of events. The one retarding effect on change is the inherent conservatism of mankind and it is only when other preoccupations exist that change bounds forward unopposed. Examples of this were World Wars I and II, which produced great leaps forward due to the exigencies that had to be met during wartime conditions. Change is usually costly and today we live in an era when multimillion pound projects are the order of the day. Aerospace development is a case in point. Here, the impetus has come from the rivalry and desire for prestige of the Western and

Bisher ging das Verlangen nach Änderungen grossenteils vom Verbraucher aus, welcher auch die Haupttriebfeder für neue Produkte und Techniken sein wird. Die Vergangenheit wird im Zusammenhang von Gegentrends, die sich heimtückischer Weise entwickelten, analysiert. In diesem Zeitalten bürokratischer Einmischung besteht eine ausgesprochene Tendenz seitens der Ausarbeiter von Lieferungsvorschriften und von Codes of Practice zu sehr ins Einzelne zu gehen. BS5493: 1977 wird als typisches Beispiel herausgegriffen.

Eastern World. On a smaller, but nevertheless still massive expenditure scale, the development of North Sea Oil and Gas resources has its place in the turn of recent events. What should be the time interval by which change is measured and assessed? A lifetime, i.e. 75 years seems reasonable. If so, this takes us back to the early 1900's and when the changes that have taken place since this time are considered, it is clear that it is now an entirely different world from that existing at the start of the century. Now the rate of change is going to be so rapid it will have to be measured in time intervals of a generation at a time to keep pace with events.

But with all these changes, present and portended, the old remains. The family unit is still the basis of living, each man in his house or castle, with urban sprawl the order of the day and with the centre of the cities derelict areas of squalor and neglect and the planners frantically trying to think of ways and means of attracting residents and creating social communities that will have a beautified and enriched living. This is

*Paper presented at the Association's Conference held at Stratford upon Avon from 20-23 June 1979.

one of the failures in the planning scheme. When the slums were cleared they were replaced by high rise blocks of flats, which have proved an abject failure as a social exercise and are now being offered in Liverpool at ludicrously low prices, to encourage developers to demolish and clear the areas to permit the development of more enlightened environments suitable for gracious living by happy, congenial social communities.

Thus, in trying to forecast forward change the possibility that there will be many cases of putting the clock back and reverting to the old ideas and situations cannot be ignored. Change for the sake of change does not mean that the underlying ideas for the change are right and progressive and that it will not present problems in the future needing ruthless reappraisal, for a successful progressive development to result.

It is contended that despite a changing world, much that is old and mundane will remain. New developments there will be, some of a spectacular nature. Man is an inventive animal and the problems of modern life will bring the need for change. Control of pollution and the conservation of energy, two of the current problems, will engender developments in a restrictive sense, particularly from a surface coating point of view.

How will surface coatings contend with the changing world?

The answer here is, as hitherto, by adaption and innovation. There is no doubt that there will still be a positive and growing demand for the present conventional products in the trade and retail fields. With the increasing cost of living and the present trend towards shorter working weeks, it would be expected that the most sensational increase in demand will be in the "Do it yourself" field for the convenience products of the surface coatings field. Demands for special products will, naturally, be large, and the surface coatings industry will, no doubt, meet these demands successfully from the present existing raw material sources.

As with past recent experience, the demand for special products will come from the users to fit their special techniques. Looking back over the past 25 years, the highlights of development have been:

- (a) The development of blast cleaning of steel prior to the painting process.
- (b) Various forms of metal coating are now recommended after blast cleaning, in preference to the previous practice of using blast primers. Galvanising is a long established process, but metal sprayed coats of zinc or aluminium are now also favoured. It is now accepted that these metal sprayed coatings are not as reliable as galvanising, due to their tendency to have minute pores or pinholes after application. It has been found advisable to coat them with sealers, thus overcoming the disadvantages of the pinholed films, and providing a better base for subsequent painting. Even with a metal coating, there has to be protection by means of paint systems to protect the metal coatings from aggressive environments. Zinc is particularly sensitive to acidic, sulfurous environments characteristic of industrial areas. As a consequence, zinc can often require special treatment prior to painting to ensure the removal of corrosion products on the surface.
- (c) Water borne paints for conventional and electrophoretic application. Electrophoretic coating has been subjected to intensive development in recent years. Initially

anodic systems were devised and used and these caused many problems in use. Now that cathodic systems have been devised and are coming forward, the position may greatly improve.

- (d) Powder coating—conventional and thin film types. Powder coating has been predicted as of great potential and usefulness for several years, but it is taking a long time to establish itself as a surface coating process. As so often happens, new application has revealed unforeseen difficulties, and shortcomings.
- (e) High solid paints, including conventional solventless and non-aqueous dispersions.
- (f) Coatings for radiation curing by ultraviolet, electron beam, glow discharge and plasma arc.

The items (c) to (f) have largely arisen out of demands of the user for coatings to fit special techniques and requirements. A considerable proportion are inspired by the needs of the automotive industry. None have achieved the market penetration at one time predicted for them, some falling short by only a little, but others by a wide margin.

It is highly probable that the demand for specialised coatings will proliferate in the changing world of the future. Many will, at best, arise from specialist demands of the user. The objectives set will be difficult to attain, at some times bordering on the impossible. It is a salutary fact that, in retrospect, many recent developments have arisen out of user demand and few have been suggested, conceived and developed by the paint supplier. As a matter of fact, the raw material suppliers to the surface coatings industry are currently more productive of novel ideas and developments than the surface coating industry itself. No doubt, an explanation is the fact that the raw material supplier has the incentive to use creativity and speculative development as a means of creating a demand for his product on offer. However, if this situation continues the surface coatings industry is in danger of developing into a mediocrity with an incapability to meet the challenges of the future. As a result there is a strange uniformity about the many companies in the surface coatings industry. They have the same ranges of products on offer, often in a very similar range of shades. Marketing strategy, rather than product superiority, seems to determine sales success. There is a modern tendency to the proliferation of products. New products are developed, but there is no withdrawal of the products they replace. In the general user and retail fields the only product that has disappeared is the old fashioned water thinned distemper. And what has replaced it? A whole range of emulsion resin formulations e.g. matt finishes, vinyl silk finishes, masonry finishes and even water-based gloss finishes of doubtful utility. The lay public must be thoroughly confused by the paint scene, as presented by the promotional media. Many facets of gimmickry have been used through the years to encourage sales, such as whiteness, washability, cleanability, colour choice, chip resistance, flow and gloss, often presented to the admiring gaze of an Old English Sheep Dog, surrounded by badly brought up children rampaging round their houses. By and large, it is predicted that this situation in the trade and retail field will continue in the changing world.

The same does not hold for the paints demanded by industry i.e. industrial paints, marine paints and automotive finishes and, a comparative newcomer, paint for offshore structures and paints for road bridge schemes, which seem to be developing into another specialised class. Such paints i.e. those for offshore structures, bridges, and large scale developments, are tending to be classed under the heading of "Heavy Industrial Paints" or "High Duty Paints", and they will

probably grow in demand in the future. One thing is certain, the changing world will bring forth large multimillion pound developments of a scale not hitherto experienced. The raising of oil prices by OPEC has produced so much wealth and a desire for modernisation that the third world is just beginning to realise the inadequacies and needs for modernisation and is embarking on lavish schemes of development of basic necessities, such as steel works, port facilities etc. The whole is being financed by the petro-dollars of the Middle East, but great reliance is being placed on the established, first world nations to supply the know-how and plan and manage the developments. There is so much to be done that this situation will continue long into the future. By their nature, these developments require a different treatment and expertise than has been used hitherto. There is a trend towards prefabrication and shop finishing and the shipment to site of the painted steel components, surface prepared, shop primed and part finished, requiring only a final cosmetic coat when they reach their destination for assembly and erection. These developments are bringing problems in their train, such as minimisation of the damage to the part-coated components during transit and the organisation of efficient inspection services to ensure a reliable finished product or structure on site. These new demands and techniques have their cost factors, and they are high, but there is such an accumulation of oil wealth these days that these enhanced cost factors do not seem to have a deterrent effect.

The supplier of surface coatings will have to meet these changing demands. There is such a wealth of knowledge and experience available from the past to draw upon that, largely by trial and error, retaining the good and discarding the inferior, progress will be made and success achieved. Thus, it can be confidently predicted that the surface coating industry will meet its future challenges in a changing world.

Constraints to progress

However, there is one adverse aspect that must be noted. In recent years there has been the development of constraints to progress by the anti-pollutionists and ecologists. Membership of EEC has not eased the situation. In fact, it has made it more difficult. There are now too many cooks spoiling the broth. There are many who may have the best intentions, but the restraints for which they fight and eventually achieve create great difficulties to development in the surface coatings field. This situation adds to the problems of conservation of energy and conservation of resources and raw materials, the impact of the Health and Safety at Work Act, and it is obvious that areas of possible progress will be proscribed. This is an age of bureaucratic interference of which the PSST Scheme is the latest development that will have its irksome repercussions. Rumour has it that, in due course, all the specifying authorities will be under the one umbrella, laying down standards of paint performance that have to be achieved. It has always been somewhat mystifying that the top line branded products, provide automatic "guarantees" implicit in their sale, not meeting the required standards.

Thus, there is one clear lesson to be learned from the past, that time brings its problems of complexity and overelaboration. A typical case in point is the well-known Code of Practice CP2008 for the protection of iron and steel against corrosion. The idea for this laudable document was conceived in the early 1960's and a drafting committee sat under the able chairmanship of Dr J. C. Hudson. Publication took place in 1966. In the years following its publication, a number of developments took place in the protective coatings field, so that in 1972 the British Standards Institution decided to revise the Code and a redrafting committee was set up. It quickly became clear that a simple revision by the addition of new material would not be acceptable or possible, and a complete redrafting was decided upon with a major aim of reducing the size of the Code to half that of the 1966 edition. This reduction in length could have been achieved only by omitting a considerable amount of the original material.

When the addition of new material was taken into account, a new approach to the drafting of the Code was found to be essential. The Code was divided into six main topics:

- 1. Design and principles of corrosion.
- 2. Factors influencing the choice of systems.
- 3. Protective systems.
- 4. Specifications.
- 5. Inspection.
- 6. Maintenance.

Background material was provided in the form of Appendices.

This historical explanation was revealed by the Chairman of the drafting committee CVCP/8 at a Symposium held on 2 December 1975, to consider the "Draft for Comment" of the revised code. This was then a document about 140 pages in length. So much for the original intention of reducing the length of CP2008. As the "Draft for Comment" was considered and discussed, there were urgent pleas, particularly from consulting engineers, for curtailment and simplification with the minimum of elaboration. The revised Code BS.5493: 1977 was eventually published towards the end of 1977 and was then a document 110 pages in length, requiring 2 full pages for the contents and nine for the index.

The drafting committee had obviously tried to condense and curtail some sections as requested. They had simplified the "Tabulation" in such a way that its meaning was obscure and difficult to comprehend. The new topics, Inspection and Maintenance, had had an extended and full write up and the overall result was a document that has caused much concern amongst paint technologists, who described the revised version as representing unattainable protective systems which were beyond the capability of the industry to meet. Having read and re-read the document, it has to be confessed that it is found to be confusing and diffuse and, above all, indecisive. In the case of a consulting engineer, trying to use BS.5493:1977 as a consultative document and an aid to the devising of a specification for a given project, the new redrafted code will be found to be a confusing document. Consulting engineers, as they have done hitherto, will have to depend on that select number of paint suppliers capable and prepared to help in the drafting of specifications and also prepared to provide an inspection and monitoring service to the completion of the contract and able to supply paints of the requisite type and standard.

It used to be jokingly said of CP2008 "Here we have the Bible—where are the Ten Commandments?" BS.5493 is a revised version of the Bible, but still with no Commandments. Maybe Moses was not on the redrafting committee—strange, everyone else seemed to be.

BS.5493:1977 is symptomatic of the times, and the tendency to over elaborate. There are too many "ifs and buts" and "do's and dont's". What is needed is clear concise authoritative directives based on proven facts and experience. Redrafts of Codes should be prepared to be definitive and precise in their recommendations, particularly in the choice of protective systems to give the best results in practice. Such is not the case with BS.5493:1977. Thus it will require greater resolution by the paint suppliers in the future to resist the sometimes unreasonable and unattainable demands of the users or the specifying authorities. Some would argue that such an attitude will delay progress and lose business. However, it will save the generation of unnecessary development costs which are never recouped. It might also serve to temper the conceit of some of the specifying enthusiasts. At all costs, in the future, elaboration of products and techniques must be avoided with a rigid adherence to simple basic factors,

simplicity and comprehensibility of techniques.

Past faults

Refs. 1-6

Before looking towards the future, it should be considered if there have been any cardinal faults in the past in the way developments have been handled. The author has one pet hobby-horse. In the past many new products and development projects have been reported with great euphoria and predictions made claiming outstanding future success. This applies to many facets of paint technology and development, and too often there is good briefing by the progenitors at the outset of the development, but no follow-up, interim or final reporting of the actual outcome after some time. The hazards of new and novel developments are well known. When used in the field, unforeseen factors make their presence felt, often to the extent of vitiating and nullifying the chances of ultimate success. These adverse happenings are seldom reported. Silence reigns and another brave new idea is buried and laid to rest. These unfortunate developments are often picked up by technically interested people piecemeal, and the subject slowly and surely drops out of the scheme of things. Ideally, when development projects start and are reported, there should be some onus on the originator that the progress of the development and tests are continually reported, be they good or bad. No doubt strenuous efforts are made to combat the unfortunate occurances by all concerned. Whatever the results, they are newsworthy and may many times give an entirely different perspective to the merits or demerits of the development in question. The mere fact that the effects of the unforeseen are reported could prevent others falling into the same trap of false prediction with other products and developments. All is not success in life and there is no disgrace in failure. It should strengthen the resolve to continue with the investigation in another way; taking due regard of the hazards of unforeseen developments.

The aversion to the reporting of failure is general and understandable. It not only applies to development products for special industries, but also to many retail products in the surface coating field. If the advertising media are to be believed, all troubles are over and problems solved in the painting field. The paints are cleanable, durable and will stand rampaging youngsters without suffering damage, or so they say.

Reverting to the point about the onus for the progenitors of new and novel developments, who publicise their aims and intentions, to undertake to report progress at suitable intervals, although there is a proliferation of associations, institutes and controlling bodies, there are chinks in the armour. There is a great need for the establishment of a secretariat or panel charged with the monitoring of the progress of new developments, officially reporting progress and giving an opinion on the importance and portent of the results. In the field of protective coatings, the prevention of corrosion of iron and steel is of such economic importance that the idea requires the most serious consideration. Some years ago corrosion was estimated to cost the country £600 million per annum. The figure today, like everthing else, must have radically increased. Think of the millions of capital involved in offshore structures in the North Sea. The importance is such that it should be supported by Government grant, and sponsorship. The organisation envisaged should be responsible for receiving and filing the commencement of newly reported developments in the protective coatings field, and should have the power to ask and receive progress reports and duly report these to all and sundry at suitable intervals.

All that would be required is a panel of experts in the field, preferably retired to avoid any adverse effects of vested interest. It should be a panel and not a committee. Much would hinge on the choice of Chairman and the organisation of the receipt and dissemination of the information. If started and successfully developed the idea could be extended to cover the European Community and, in fact, there is no reason why it should not be world-wide in its concept. At all times the reports should be factual, good or bad, and not adjusted to appease the progenitors of the project.

The author can give these opinions on the need for regular reporting of the progress of novel developments in the protective coatings field with a clear conscience. In his working life in the surface coatings field which started in research, he has had an interest in the development of reliable accelerated tests giving true prediction of performance in actual practice, and in the introduction and development of zinc phosphate as a non-toxic anticorrosive pigment, and has reported progress regularly.

The new ideas about methods of test giving true prediction of ultimate performance were first reported in 1962¹. In 1965 the promise of zinc phosphate was reported² and the commencement of comparative tank tests described. In 1969 there was an interim report³ on the progress of the developments based on a paper that had been presented to the Joint Services Non-Metallic Materials Board Standing Committee on Paints and Varnishes in 1967.

In 1975 the author was invited to deliver a paper to the South African Corrosion Institute⁴. When news of this event leaked out the author was approached by various South African Branches of OCCA to present a paper. This was accepted and the same paper on "The realistic prediction of primer performance—A case history" was read to the Johannesburg Branch on 16 September 1975, the Durban Branch on 23 September 1975, and the Cape Town Branch on 6 October 1975.

Although the script of the paper was available, it was not published at that time, but it has now appeared⁵. It was vital that this publication should take its place as a chronological review of the ideas from their inception to the position in 1975 which covered tank tests 14 years in duration which fully confirmed the prediction of the proposed ammonium sulfate accelerated spray test, the "Goodlass Wall" girder test⁸, and the long term tank tests on wire brushed rusty steel. Now, three years later, it can be reported that the position is unchanged and thus the record is now available of:

- (1) Proposed new accelerated salt spray tests¹.
- (2) Proposed new wire brushed weathered mill scaled girder tests¹.
- (3) The selection of primers and finishing systems based on (1) and (2) for comparative testing on wire brushed tank tests².

335

- (4) Interim reporting of the situation after the tank tests had had 6 years' exposure³.
- (5) Interim reporting after the tank tests had had 14 years' exposure⁴.
- (6) Interim reporting after the tank tests have had 17 years' exposure⁶.

If clarity is desired, the whole situation and philosophy of the author's work and efforts is given in Ref. 6.

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Discussion at Stratford Conference

DR J. RAMSBOTHAM pointed out that during the last ten years, starting in America with the introduction of Rule 66 designed to reduce the amount of solvents contained in coatings, there had been a wave of what might be called "anti-new product" legislation, as a reaction to some of the problems that technology had created. In the light of the scenario sketched in Dr Harrison's paper of increasing shortages of traditional raw materials, and the need for innovation to find alternative sources, would, he asked, in Dr Harrison's opinion, these stringent constraints on the industry be relaxed, or would the situation continue in its present direction?

DR HARRISON stated that in the future some of the problems to be overcome would be very difficult, but he hoped that there would be a decrease in the emotional reaction to technology towards a more rational appraisal of its benefits and drawbacks.

DR F. M. SMITH indicated that most of the legislation, which had been recently introduced in many countries, would have its main effect on the introduction of new chemicals rather than seriously restricting the use of chemicals that were already in common use. The amount of certain solvents which are allowed in coatings had been restricted in an attempt to control emissions into the atmosphere. Dr Smith also stated that he hoped that, in the future, legislation would take into account the diminishing supply of certain raw materials and not make it unfeasible, in terms of time and investment, to develop new alternatives.

DR J. C. WEAVER, from America, mentioned some of the recent trends that were emerging in the anti-pollution legislation in the USA. He pointed out that the California Air Resource Board now had less money to spend, thus restricting its deliberation on rules for the interpretation of the legislation, and resulting in a general relaxation in the standards. In addition, there had been more direct responses from the technical people in the industry who, for example, are able to advise the Environmental Protection Agency, and thus help "educate" their technical people and help in suggesting modifications which are technically and economically possible. Dr Weaver suggested that this was an important interaction, and that efforts should be made in other countries to obtain technical advice from within the industries affected. One example of this co-operation, was the current revision of the analytical method for controlling atmospheric pollutants, to be published later this year in the Federal Register. At present the process is a four-step combustion process which is extremely time consuming. It is hoped that by this co-operation the procedure may be simplified to make it more usable.

Dr Weaver suggested that some figure which had been suggested for the use of water soluble coatings in the future

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were not realistic, and for certain end uses these products might not be comparable with those obtained using different approaches. He cited development work in high solids coatings as one area which could also have many applications in the future.

DR HARRISON agreed that there was a future for technologies, such as high solids, but indicated that the use of such systems would be determined largely by their relative costs, and at the moment, the high solids systems seemed to be more expensive than the water based.

MR D. A. KALWIG referred to the suggested use of oilseeds or other crop seeds as possible raw materials for coatings, many of which had been in use thirty or more years ago. He agreed that, from a technical point of view, it would be possible to return to the use of these high solids oleoresinous products, but he doubted whether such products would be acceptable to the consumer from the point of view of quality. In the last few years the consumer had become used to the high quality ranges of products available, and he doubted if moving back to earlier products would be accepted.

DR HARRISON pointed out that it might not be a matter of free choice, but of necessity, to return to these materials.

MR C. N. FINLAY asked if it would be possible, should a return to these materials become necessary, to grow a large enough amount of the crops to supply the needs of the industry, bearing in mind that the demand for land to produce food was intense.

MR T. R. BULLETT indicated that during the period from 1940 until 1960, there had been three main advances in the industry: the introduction of oil modified alkyds; the development of synthetic latex polymers; and the use of titanium dioxide as the major white pigment. During the period from 1960 onwards, there had been no really major advances, and he suggested that perhaps it was now time for new developments.

The Paint Research Association had been doing some work on renewable raw materials and for example, had been looking at the possibilities offered by the use of sugar. Sugar is a cheap, non-toxic material which is very easily grown giving good yields per acre. It could be produced industrially in large quantities quite readily, but there are still some problems in its use as a polyol for resins. These are not insurmountable and if the prices of other raw materials rise enough, then sugar may well be developed as an alternative. Mr Bullett also expressed interest in the subject to be covered by Mr Turner's paper later in the Conference, concerning the use of oils of low unsaturation. This again opens up another area of renewable vegetable materials. He suggested that because of these possible developments, the petrochemicals shortage would perhaps not have such a drastic effect on coatings as many feared.

MR S. L. DAVIDSON informed delegates that the California Air Resources Board were no longer trying to limit the types of solvents that could be used, but had changed the emphasis to restrict only the amount of solvent, thus necessitating high solids coatings.

Mr Davidson asked if in Britain and the Common Market, as in America, the various agencies believed that the answer to all problems was to be found in the use of water based compositions, regardless of the end use or quality required in the specifications.

MR P. WALKER asked Dr Harrison how he equated his views on the need for the formation of a panel of retired experts with the statement contained in the summary of his paper on "bureacratic interference".

MR E. V. COLLINS returned to the problems of replacing petroleum based raw materials with those based upon crops, with the problems of increasing population and demand for food taken into account. He stated that he doubted whether industry would be allowed to use all the land it would require for this purpose. He asked the lecturer's opinion on the possibility of using coal based products as replacements, as there was a considerably longer expectation of the availability of coal as compared to petroleum oils. DR HARRISON stated that he agreed that this was a possibility and, in fact, there had been considerable interest in obtaining fuel from coal many years ago, but nothing had yet come from this. He hoped that this problem would be looked into closely in future. The main problem in the past had been the cost, but the relative costs of petroleum and coal were now becoming less.

DR F. M. SMITH stated that, in his opinion, the discussions so far had been very relative to the shortages of energy, but that there would probably be no serious problems of raw materials for chemicals themselves. He thought that there was certainly enough coal to supply chemicals for the industry for hundreds of years, and that even though oil for energy was becoming short, there were many oils unsuitable for fuel, which were perfectly adequate as starting materials for the chemical industry.

Many years ago when modern water based coatings were first developed, it had been claimed that within five years all coatings would be of this type; this had obviously not been the case. In certain applications where suitable water based coatings have been developed, they have done very well, but in other applications, such as industrial paints, water based coatings of a suitable standard had not yet been developed, and other types were still in use. When coatings of a high enough standard had been developed, they would be used, but until then, industry would use the coating which gave the required performance.

Surface coatings for the nuclear industry*

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Summary

The painting of nuclear installations and other areas in which radioactive nuclides are handled presents special problems. In addition to the normal decorative and protective properties expected of coatings, the added dimensions of radiation resistance, radioactive contamination and decontamination are of paramount importance. The potentially hazardous nature of radioactivity requires not only that surface coatings absorb the minimum amount of contaminated. Consequently, the coatings need to be resistant to a variety of aggressive reagents.

The accumulative effect of these hostile environments together

Keywords

Processes and methods primarily associated with

drying or curing of coatings

atomic radiation

Revêtements de surface pour l'industrie nucléaire

Résumé

Le peinturage des installations nucléaires et d'autres sites où l'on traite les nuclides radioactifs présente des problèmes exceptionnels. Aussi bien que les propriétés décoratives et protectrices que l'on exige des revêtements, les critères supplémentaires, à savoir la résistance à la radiation, la contamination radioactive, la décontamination ont une importance primordiale. Le danger éventuel présenté par la radioactivité exige que les revêtements absorbent non seulement la quantité minimale de radioactivité, mais aussi qu'ils peuvent être décontaminés avec facilité et rapidité. Par conséquent, les revêtements doivent être résistant à une gamme de réactifs aggressifs.

L'effet cumulatif de ces environnements aggressifs et des exigences normales de l'exposition en service demande que le

Anstrichmittel für die Atomkernindustrie

Zusammenfassung

Der Anstrich von Atomkerninstallationen und anderer Komplexe, in denen radioaktive Spaltprodukte gehandhabt werden, setzt spezielle Probleme. Nicht nur werden die normalen dekorativen und schützenden Eigenschaften von Anstrichmitteln erwartet, sondern die zusätzlichen Dimensionen von Widerstand gegen Bestrahlung, radioaktive Verschmutzung und Decontaminierung sind von überwiegender Bedeutung. Die möglicherweise lebensgefährliche Natur von Radioaktivität verlangt nicht nur, dass Beschichtunsmittel nur ein Minimum an Kontaminant absorbieren, sondern dass sie sich leicht und schnell dekontaminieren lassen. Solche Anstrichmittel müssen folglich gegen eine Vielzahl von aggressiven Reagenzien beständig sein.

Introduction

The nuclear industry, which embraces the nuclear power stations, research reactors, plants for the manufacture and processing of nuclear fuels, isotope production facilities and the associated research and development laboratories, is a customer of the surface coatings industry. The uses to which it puts surface coatings are many and varied, and may be with their normal service exposure, places a great strain on the ingenuity of the paint formulator working in a field where precise data on such factors as the effect of formulation variables and the age of the coating before exposure is both sparse and expensive to obtain.

The information on the mechanisms of radiological contamination, radiation damage, the state of the art in the formulation, testing, assessment and effect of ageing on coatings for nuclear environments is given. Finally, opinions on future demands on surface coatings for the nuclear industry are advanced.

Specifications, standards and regulations specification

Miscellaneous terms radiation protection

spécialiste s'ingénie fortement à mettre au point des formules de peintures dans un domaine où les données précises concernant les facteurs tels que l'effet des différences au point de vue de la composition des peintures et de l'âge du revêtement avant l'exposition se démontrent non seulement peu nombreuses mais aussi coûteuses à obtenir.

On donne de l'information sur les mécanismes de contamination radiologique, des altérations provoquées par la radioactivité, l'état actuel de la mise au point des formules de peintures, l'essayage, l'appréciation, l'effect du vieillissement des peintures destinées pour les environnements nucléaires. Enfin on offre des points de vue sur les exigences à l'avenir auxquelles les revêtements de surface pour l'industrie nucléaire devront répondre.

Die sich anhäufende Wirkung dieser umweltfeindlichen Produkte, zusätzlich der Exponierung während normaler Arbeit, erfordert grossen Scharfsinn vom die Anstrichzusammensetzung ausarbeitenden Lackchemiker, der auf einem Gebiete arbeitet, auf dem präzise Angaben über solche Faktoren, wie Rezepturvarianten und Alter des Anstrichs vor der Exponierung dünn gesäht und nur mit grossen Kosten erhältlich sind. Information über den Mechanismus radiologischer Verschmutzung, Strahlungsschäden, Stand des Wissens bezüglich Rezeptierung, Prüfung, Bewertung und Wirkung der Alterung auf Anstriche für Atomkernanlagen wird gegeben. Schliesslich werden Meinungen geäussert über küftige Anforderungen an Anstrichmittel für die Atomkernindustrie.

divided into the strictly orthodox and those which are peculiar to nuclear industry.

The orthodox uses may be summed up as for decoration, protection and identification, and it therefore follows, that the properties which make paints desirable for use in decoration such as colour and gloss retention, freedom from chalking, checking, cracking and adhesion failure coupled

*Paper presented at the Association's Conference held at Stratford upon Avon from 20-23 June 1979.

with good application properties are required. Equally those necessary for protective purposes; resistance to ultraviolet radiation, water, salt spray chemical resistance and long term general corrosion resistance are also required. Those requirements peculiar to the industry are resistance to radiation, and ease of decontamination, thus coatings are required for (a) areas in which radio-nuclides are handled and a potential or actual contamination problem exists, and (b) areas in which high level radiation sources are used or handled. Therefore, in addition to the already abundant list of properties required of surface coatings for general use must be added resistance to high radiation levels, low pick up of radioactivity, resistance to chemical decontaminants and ease of decontamination. Some, if not all, of these requirements may need to be met in a single area of use. For example, in the case of a metal flask containing irradiated fuel elements which is stored under demineralised water.

Existing and new requirements

Ref. 1

The majority of surface coatings used in nuclear power establishments are normal commercial systems used for corrosion protection or interior decorative purposes in areas where there is no radiation or contamination; most exterior surfaces are brick, concrete or other materials which do not require coating. Specialised coating systems are used in those areas where radioactive contamination is expected to occur frequently, or where it may occur; where high levels of radiation are encountered or where compatable materials are essential.

Safety considerations assume that paint flakes might be carried into a reactor gas circuit and adversely influence the metallurgy of the fuel cladding. Consequently, the coatings used in the fuel handling route must be "metal-free" (Table 1). Such areas include fuel preparation rooms, the fuel charging machine and its associated equipment. In other reactor areas such as the pile cap, circulator rooms, and areas where equipment exposed to reactor gas is maintained or inspected, the "metal-free" restrictions are not applied to primers.

Wherever possible in the selection of coatings for use in radioactive areas, commercial systems are chosen from among those that have been tested to BS 4247 Part 1: "Recommendations for the Assessment of Surface Materials for Use in

Table 1

Metal-free paints and similar coatings for Nuclear Power Stations

- Mercury additions in any form are not permitted and precautions must be taken to prevent accidental mercury contamination by not manufacturing or storing paint in areas where products containing mercury are present.
- (2) No paint containing metals in their elemental form shall be used.
- (3) The lead content shall not exceed the limits laid down by Home Office Regulations for lead-free paints (Factory Acts 1961, Section 132).

Radioactive Areas". A compilation of such systems is held and kept up to date by the United Kingdom Atomic Energy Authority (UKAEA) in Atomic Energy Codes of Practice (AECP) 1002: "The coating of surfaces requiring decontamination". This document also contains guidance on the selection of coatings to meet particular service requirements e.g. radiation resistance, chemical resistance, temperature resistance etc., and is intended for use by designers and maintenance painters. This compilation is also used by the Central Electricity Generating Board (CEGB). Where previously untried coatings are offered for use in radioactive areas they are tested to BS 4247 Part 1 to characterise their performance relative to other materials. A brief tabulation of some areas where specialised coatings are used in CEGB Magnox power stations is given in Table 2.

With the advent of Advanced Gas-Cooled Reactors (AGR's) and the higher radiation doses delivered by the fuel on removal from these reactors, it has been necessary to use stainless steel cladding in fuel dismantling areas where the lifetime radiation dose is anticipated to be in excess of 10¹⁰ Rads; the tendency for higher radiation levels may require more extensive use of stainless steel, unless the radiation resistance of coatings can be improved in the future.

If Light Water Reactors (LWR's) are introduced into the UK in the future, they will bring with them the need for coatings capable of meeting the existing American National Standard Institute (ANSI) requirements. A Manual of Coating Work for Light Water Nuclear Power Plant Primary Containment and other safety-related facilities has now been published in draft form by American Society for the Testing of Materials (ASTM). The manual covers design, quality assurance, surface preparation, application and inspection of

Area of plant	Coating type	Service requirements			
Fuel charging machine	Epoxides, "metal free"	Good wear resistance, occasional de- contamination required.			
Fuel preparation room and associated ventilation ducting	Alkyd, "metal free"	Decorative, dust free.			
Fuel cooling pond walls	Epoxides, possibly with glass fibre re- inforcement. Chlorinated rubber not suitable	High coating integrity essential und immersed conditions. Good chemic resistance required, Must withstand hig radiation levels. Coating must not lead agressive anions, e.g. Cl ⁻ , SO, ²⁻			
Fuel transport flasks	el transport flasks Specially developed epoxy/polyurethane Good system (CEGB System 6) and r contar				
Water treatment plant	Chlorinated rubber	Good chemical resistance. Frequent decontamination. Little radiation exposure.			

Table 2 Uses of coatings in CEGB Magnox power stations

the coating systems. American nuclear grade coatings for use in containment areas of water reactors have to pass a simulated Design Basis Accident (DBA) test in which, briefly, specimens are exposed to steam temperatures up to 170° C and pressures up to 100 psi for 26 days. Full references to the relevant documents are given by Berger¹. At present epoxide systems appear to be the most successful, and a number of US manufacturers have qualified systems available. As yet, it appears that there are no UK manufacturers in a similar position.

Mechanisms of contamination and decontamination of painted surfaces

Refs. 1-6

Radioactive contamination can be defined as the presence of radio-nuclides in quantities above a permissible level, on or at an indefinite depth below the surface of a material. For porous or fissured materials the surface will include those of the pores and fissures. This definition applies to radionuclides which have become associated with a previously uncontaminated surface by some unspecified mechanism; it is not intended to apply to radio-nuclides which have been created in-situ in a material by a process, such as neutron irradiation. In this latter case, radioactivity is said to be "induced" and is normally distributed throughout the bulk of the material concerned. An example of induced radioactivity is the presence of 60Co in structural steel components of nuclear reactor cores. Since decontamination consists of the removal of contamination without damage to the object being decontaminated wherever possible, it does not apply to induced radioactivity.

Most elements have isotopes which are radioactive; consequently surfaces can potentially be contaminated by any of them. Within the nuclear industry the most commonly encountered radioisotopes are those produced by the fission of 235 U or neutron capture by 238 U. The fission products include 137 Cs, 90 Sr, 144 Ce, 106 Rh, 131 I and in the main, they decay by emission of &-rays and β -particles. Neutron irradiation products of 238 U, known as *actinides* include such isotopes as 238 Pu, 239 Pu, 241 Am, and 242 Cm which decay by emission of ∞ -particles.

The SI unit of quantity for radioactivity is the Bequerel (Bq), which is defined as 1 disintegration per second. This unit will replace the Curie ($1Ci = 3.7 \times 10^{10}$ Bq) which is commonly used at present. The maximum permissible level (mpl) of loose contamination of a surface by a radioisotope depends on (i) the classification of the area in which the surface is located, and (ii) the isotope concerned, since isotopes vary in their radio-toxicity, with ∞ emitting isotopes being the most toxic. By way of an example, the mpl for ¹³⁷Cs in a non-radioactive area is 3.7 Bq cm⁻²(10^4 Ci cm⁻²). It is evident, therefore, that minute amounts of material in conventional terms, can give rise to serious contamination problems; similarly for decontamination procedures to be fully effective, they must be considerably more efficient than the normal cleaning processes from which they were developed.

In discussing the contamination mechanisms applicable to surface coatings, two general areas can be defined: contamination by particulates, usually in a dry state, and contamination by ions and other species from aqueous solutions.

Radioactive particulate material behaves in much the same way as its non-radioactive counterpart; its accumulation at a surface is facilitated by electrostatic interactions, which for active particles may be enhanced by self-charging caused by the decay process. Adherence of particles is also enhanced by the presence of an oily film at the surface. Such a film may arise from airborne oil droplets settling on the surface, overgenerously applied lubricants, or the use of excessive amounts of curing agents in two-pack paint systems. Once present on a surface, the particulate material can become embedded by physical pressure, especially if the coating is the softer of the two, as will be the case for metal or oxide particles on painted surfaces. Once embedded in this way the contamination may be difficult, if not impossible, to remove without destroying the whole coating system. The presence of cracks and crevices at the surface of an object also hinders effective decontamination. Consequently, the best surfaces will be those which are clean, smooth, hard and glossy. In the majority of cases, where embedding has not occurred and crevices are absent, particulate contamination should be easily removed by washing with warm water. Wetting agents and detergents improve the contact of the liquid with the surface and also disperse grease films.

Contamination from aqueous solutions can occur in a number of ways, depending on the surface involved, the contaminating isotope and the pH of the solution. These mechanisms include ion-exchange phenomena, solvent extraction, diffusion and chemical reaction. Paint surfaces contain acid groups which undergo ionisation when in contact with solutions of pH greater than 2, e.g. carboxylic groups. The surface can then act a cation exchanger, of admittedly very low capacity, but with sufficient groups to enable significant quantities of radioactive atoms to be exchanged. This is particularly so if the radioactive material is "carrierfree", that is, not diluted with other non-radioactive atoms of the same atomic number, as in chemical terms only minute quantities are involved. In addition to the organic vehicle, oxide pigments e.g. TiO2 may also behave as ion-exchangers should they become exposed to a potentially contaminating solution. When the pH of the solution is greater than the point of zero charge (pzc) of the oxide concerned, hydroxylated groups at the surface lose protons to leave cationic sites which will adsorb positively charged counter ions from the solution. The same mechanism should also apply in reverse, i.e. when the solution pH is below the pzc, protons will be abstracted from solution by hydroxylated oxide groups to give anionic sites which will be capable of adsorbing negatively charged counter ions. Contamination occurring solely by an ion-exchange mechanism alone can be removed simply by a change to solution conditions which reverse the exchange reaction. For cationic contamination, for example, concentrated solutions of acid and polyvalent ions can be used, albeit with the risk of damaging the surface coating. The most commonly used approach at present is to use mild chelating acids; complex formation with the contaminant ions displaced from the surface neutralises or reverses the charge of the ion and thus prevents redeposition.

The most persistent forms of contamination are a result of mechanisms which allow the contamination to penetrate the surface of a coating. This can occur in three ways, the first of which is related to the diffusion of water through the paint film. As described above, most films ionise to form cationic groups which effectively accelerate the diffusion of cations through the film relative to that of water, likewise anions are retarded. Contaminants can also be extracted from solution into the solid organic phase (the coating film) either by formation of a chemical complex with some component of the surface coating e.g. with amine groups under strongly acidic conditions, or by a solvent extraction mechanism. The best well-known example of this latter effect is that of phosphate plasticisers in chlorinated rubber coatings². Once in the coating film, other mechanisms may make a contribution, e.g. pigment particles in the film may hold contaminants by the method described above. Contamination which has penetrated into the body of the film can be very difficult to remove; the only practical method without destroying the coating is repeated washing, either using the aqueous solutions described above where an ion-exchange mechanism is involved, or using a suitable organic solvent if an extraction mechanism is suspected. These methods will necessarily be slow, since the aim is to reverse the concentration gradient within the film; subsequent re-establishment of concentration gradients after treatment may result in the re-appearance of contamination at the surface at some later time.

Some particular ways in which decontamination can be attempted have been pointed out above, but it is important to note the philosophy with which the problem should be approached. Decontamination is the procedure by which contamination is removed from an item. However, since the process merely moves radioactivity from one place to another, it is important to establish at the outset whether any benefit is gained. Factors to be taken into account include the necessity of the operation, and the probability of success, the costs both in terms of plant and of radiation dose to personnel and the treatment of the waste arising. It is only fair to point out, however, that these factors are at their most important when large items of plant are under consideration; surface coatings in the nuclear industry are often selected specifically because of their resistance to contamination pick-up, and consequently decontamination should be a fairly simple process.

The general principle is that of using the least aggressive reagent or method capable of achieving the required degree of decontamination. If the approach chosen does not succeed, the aggressiveness of the method is increased until the contamination is finally removed. This principal applies to both chemical and physical methods of decontamination; it should also be noted that the choice of method may be influenced by the availability of disposal routes for the waste produced.

The choice of methods when dealing with contaminated surface coatings is relatively restricted, since one of the aims must be to leave the surface undamaged at the end of the operation. Of the chemical methods, detergent washing and the use of mild reagents will be acceptable; the use of more aggressive acids or alkalis may or may not be permissible depending on the particular coating. Physical methods of decontamination will necessarily be restricted to swabbing and vacuum cleaning, although ultrasonic radiation can be used on small items. The use of water jetting (with or without abrasives) and the use of abrasives by hand will damage the surface and its subsequent contamination resistance will be low. Where severe contamination is held in a coating the best method may prove to be removal of the entire coating, either by use of a suitable organic solvent or by blasting techniques, prior to recoating. This latter approach, whilst drastic, may save considerable amounts of time and even reduce total waste arising.

The reagents used in the so-called non-aggressive methods vary from water and dilute detergent solutions to concentrated nitric acid.

A partial list of decontaminants, the compositions of which are known, is shown in Table 3. Additionally, a large number of proprietary decontaminants of largely unknown composition are in use together with many organic solvents (aromatic hydrocarbons, ketones and esters).

P. WALKER ETAL. JOCCA

Table 3 Decontaminants for coated surfaces

Reagent	Reference			
Water	Newby & Rohde ³			
Steam	Wilson ⁴			
Detergent solution	Berger ¹			
8–16M Nitric acid	Christenson ⁶ , Newby &			
3M Nitric acid	Rohde ³ , Perigo ⁵			
0.8M Nitric acid				
0.001M Mercuric nitrate >	Newby & Rohde ³			
0.001M Mercurous nitrate				
0.4M Oxalic acid	The second second second second			
0.16M Ammonium citrate >	Newby & Rohde ³			
0.34M Hydrogen peroxide				
0.2M Potassium permanganate				
0.25M Sodium carbonate	Newby & Rohde ³			
0.25M Sodium bicarbonate				
0.5 g/TEDIA	No. 1. P. Dalida			
IM Potassium iodide	Newby & Ronde			
5 W/W EDIA	Newby & Ronde			
32 g/1 Soutum oxalate	Perigo et al ⁵			
15 g/1 Undrogan paroxida)				
1 g/1 Oving	Perigo at als			
5 g/l Peracetic acid	i chgo ci ai			
Citric acid	Wilson ⁴			
Citric acid/detergent	Christenson ⁶			
20% Nitric acid	Cl. i.e. f			
3% Hydrofluoric acid	Christenson			
6-12M Hydrochloric acid	Christenson ⁶			
5% Sodium hydroxide				
1% Sodium tartrate }	Christenson ⁶			
1.5% Hydrogen peroxide)				

The range of chemicals used for decontamination purposes requires a degree of resistance which can be met only by a limited range of coatings which include epoxides, phenolic modified epoxides, polyurethanes and powder coatings. Little is known of the effect of repeated decontamination procedures on the resistance or subsequent ease of decontamination of coatings, but it must be assumed that if the surface is damaged and suffers a loss of the surface polymer rich layer exposing the pigmented matrix, then the ease of decontamination will be adversely effected.

Decontamination testing

Refs. 2, 7-9

The question of assessment of the ease of decontamination is a vexed one, in that a multitude of possible contaminants at a variety of pH's exist. In the initial absence of standard methods of test, a multiplicity of non-standard i.e. incompletely documented methods have arisen, peculiar to particular laboratories or investigators. This has led to a major difficulty in comparing the results obtained by different investigators. At Aldermaston the decontamination test involved the use of cerium-144 and plutonium-239 used in admixture and applied both from 0.1N, pH3 sodium acetate buffer solution and 0.5N nitric acid plus 6.5N sodium nitrate solution in order to evaluate coatings under conditions in which the effects are primarily ion exchange and chemisorption respectively. After counting, the contaminant was removed in a two stage process in which the surfaces were swabbed with a non-ionic detergent, (polyphosphate, EDTA, pH 9.5) solution and an anionic detergent (citrate, EDTA, pH 3.0) solution². At Harwell the contaminant was aged mixed fission products containing a number of nuclides e.g. 137Cs, 144Ce and 106Rs applied at a pH of 5.0. A two stage decontamination procedure was also employed, the decontaminants consisting of a solution of sodium dioctylsulphosuccinate, polyphosphate, sodium salt of

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A typical American test involved the use of mixed fission products in 8M nitric acid solution adjusted to pH 4.0 immediately before use. A three stage decontamination procedure employing water and a solution containing citric acid, sodium fluoride and hydrogen peroxide used at room temperature and 80° C. Samples were immersed in the decontaminant solutions.

Thus, in the three tests described, the nature of the contaminant, the decontaminant, the pH's of the contaminant and the decontaminant and the method of application all differed one from another. Many other tests can be cited^{8, 9}.

A major difference also existed in the philosophy of expressing the results of decontamination tests, thus it has been UK practice to classify a surface in terms of activity remaining after decontamination, the US practice is to classify in terms of contamination removed. This is stated in terms of either percentage activity removed or as a decontamination factor (DF). The DF is expressed as a dimensionless number and is the ratio of the original to the residual contamination.

The relationship between percentage removed and the DF is given by:

Percentage removed =
$$100 (1 - \frac{1}{DF})$$

thus a DF of 1000 indicates a removal of 99.9 per cent i.e. a retention of 0.1 per cent activity.

Standards relating to the nuclear industry— Decontamination

Refs. 1, 7, 10

Recognising the difficulties arising from the multiplicity of test methods, standard tests have now been devised, but as will be demonstrated, considerable differences exist between them.

The present UK approach is detailed in BS 4247: Part 1. 1970 in which an area corresponding to a circle of 38 mm drawn on the test substrate is contaminated with 0.1 ml of a contaminant solution 5 millicuries (185 MBq) per litre of caesium-134 (as chloride) of specific activity 0.5 curies (18.5 GBq) per gramme of caesium and 5 millicuries (185 MBq) per litre of cobalt-60 (as cobaltous chloride) of specific activity 5.0 curies (185 GBq) per gramme of cobalt. The pH of the solution is adjusted to 5 by the addition of sodium hydroxide or hydrochloric acid solutions. The contaminated sample is dried under standard conditions before initial counting and subsequent two stage decontamination. The two decontaminant solutions and the processes are carefully detailed. The residual contamination measured in a standard manner is expressed as counts per minute per square centimeter corrected for background, dead time and to a counter efficiency of 100 per cent. The exploratory work related to this method is detailed by Smith7. The classification of surfaces as determined by BS 4247 Part 1 is covered in Part 2:

Class	Residual Contamination after Stage 2 counts/min cm ²	
1	0-1000	Good
2	1001-2000	Acceptable
3	2001–5000	Doubtful but may be acceptable under certain conditions
4	above 5000	Not acceptable

At the present time the assessment of the ease of decontamination after irradiation is not covered by a British Standard, although a specification AESS 6066—Part 2 is in preparation.

The present published British Standard 4247: 1970 Parts 1 and 2 is likely to be subject to revision according to specification AESS 6066 Part 1 in which the concept of DF previously described, has been introduced and the decontamination procedure modified such that immersion and mechanical stirring rather than swabbing are employed. In addition, the specification will allow alternative test methods, method 2

Table 4
Summary of Standard Methods for Ease of Decontamination

Country of origin	Contamin	ation	Decontamination		
Country of origin	Contaminant	Conditions of use	Number of stages	Decontaminant(s)	
United Kingdom	¹³⁴ Cs, ⁶⁰ Co, pH 5	Solution dried at RT	2 (Swabbed)	Sodium polyphosphate/EDTA in water pH 9 Disodium EDTA in water at RT pH 5	
United States	Mixed fission products pH 4	Solution dried at 25°C	3 (Stirred)	Water at 23°C Citric acid/sodium fluoride/ H_2O_2 at 25°C As above at 80°C	
Federal German Republic	¹³⁷ Cs, ⁴⁵ Ca, ¹⁰⁶ Ru, ⁶⁰ Co pH 4	Oven dried at 40 \pm 5°C	3 (Immersed)	Water at 20°C EDTA at 20°C	
Democratic German Republic	Mixed fission products containing ⁶⁵ Zn neutral/ weak acid	Infrared lamp	2 (Immersed)	Alkaline permanganate Acid/detergent solution	
France	Mixed fission products pH 1	Solution dried at 20°C for 24 hours	2 (Rinsed)	Water Acid Detergent solution	
Russia	Mixed fission products ¹³⁴ Cs, ⁹⁰ Sr, ⁹⁰ Y, ¹⁰⁶ Ru	Solution dried at 20°C for 18 hours	2 (Irrigated)	EDTA solution	

being of a more practical nature. The scale of assessment in AESS 6066 is:

Measured DF	Classification	
more than 1000	Excellent	
more than 100-1000	Good	
more than 10-100	Fair	
Up to 10	Poor	

The US approach is detailed in ANSI-N5.9-1967: "Protective Coatings (Paints) for the Nuclear Industry" and calls for the use of a contaminant solution of mixed fission products obtained by the dissolution of spent uranium fuel previously irradiated to about 20,000 MWD/MT (megawatt days per metric ton). The solution in 8M nitric acid having a beta-gamma activity of 5 \times 10⁶ dpm (disintegrations per minute)/0.1 ml. The nuclides present are cerium-144 praseodymium, ruthenium-106 rhodium, zirconium-95 niobium and caesium-137---barium-137. The contaminant is adjusted to a pH of 4.0 with ammonium hydroxide. The three stage decontamination procedure consists of a water wash, a wash in 0.4M citric acid/0.05M sodium fluoride/0.3M hydrogen peroxide solution and a repeat at 80 \pm 2 C. The results are reported as DF's at each stage.

The US standard is comprehensive in that it also covers radiation resistance and chemical resistance tests. The radiation resistance test calls for exposure to a gamma source to be continued to the radiation level at which the paint is damaged sufficiently to limit its further use. After irradiation the painted specimens are observed at a magnification of < 10 and compared with un-irradiated controls. Defects to be examined consist of:

- (a) Fine-line cracking (ASTM D 661-44)
- (b) Checking (ASTM D 660-44)
- (c) Alligatoring
- (d) Mud cracking (ASTM D 661-44)
- (e) Embrittlement
- (f) Bubbling
- (g) Blistering (ASTM D 714-56)
- (h) Orange peeling
- (i) Catalyst migration
- (j) Flaking (ASTM D 772-47)
- (k) Chalking (ASTM D 659-44)
- (1) Discolouration
- (m) Delamination

The presence of any of the above defects or extreme tackiness, softening or loss of adhesion constitutes failure. Further, where retention of the physical properties is important, a change of more than 50 per cent from the original test value also constitutes failure.

There is no provision for the assessment of ease of decontamination after irradiation.

On the continent other national standards apply and all vary in degree from the US and UK approach. Reference to Table 4 shows a comparison of the standards for the determination of the ease of decontamination of the US, UK, France, East and West Germany and Russia. Mixed fission products are the most favoured contaminant.

The authors are aware of only one reference to a work in which the different national test methods are compared using standard paints. Work by Kunze *et al*¹⁰ presents the results of comparative tests in which the UK, US, West German and his establishment's methods were used to measure the ease of decontamination of four different yellow pigmented epoxides at two levels of pigmentation. His results converted to DF's are shown in Table 5. Kunze concludes that the findings of the decontamination tests are in good agreement with each other, whenever these tests are applied to materials with good decontamination properties.

Certainly the four test methods place the different films in the same order of merit with only minor variations, but the DF's are very different. The UK method gives much higher values than any of the other test methods for the glossy surface, but somewhat lower values for the matt surface. Obviously a standard of excellence is required for each method.

Some measure of agreement, therefore, exists in the basic philosophy with regard to performance, in that the US and UK approaches will both call for radiation resistance, ease of decontamination and will define this property in terms of activity removed. However, considerable differences still exist in the test methods for ease of decontamination and these are unlikely to be resolved in the immediate future. Unfortunately, it seems unlikely that paints tested to one specification will be automatically accepted for approval to the other, and it would seem, therefore, that if business is to be sought overseas for paints for nuclear installations, approval to the appropriate National Standard should be sought. As a matter of interest this approval is likely to be 'costly, a figure of \$5000-7000 per system tested was quoted' in 1977 for testing to ANSI- N5.9-1967.

Material	Decontamin	Decontamination factor		¥
Material	UK Standard	USA Standard	FDR Standard	Kunze Method
Epoxide low PVC				
Titanium dioxide	1250	250	101	312
Organic yellow	1110	440	66	526
Cadmium yellow	550	260	63	355
Yellow iron oxide	520	137	71	355
Epoxide high PVC				
Titanium dioxide	29	71	38	66
Organic vellow	11	26	11	47
Cadmium vellow	6	44	8	14
Yellow iron oxide	2	19	5	8

Table 5				
4	comparison of some methods for determination of ease of decontamination			

*Kunze et al. Results recalculated to DF's

1979 (9) SURFACE COATINGS FOR THE NUCLEAR INDUSTRY

Other standards

Refs. 1-3, 8, 9, 11-14

An area in which there is a considerable measure of agreement between the US, UK, and Continental Europe is that of quality assurance for nuclear power plants. This is of great interest to everyone involved in the manufacture, supply, application and inspection of coatings for this purpose.

The US standard ANSI N 101-4-1972. "Quality Assurance for Protective Coatings Applied to Nuclear Facilities" and the UK proposed standard AESS 6066 Part 3 (in draft) are almost identical in philosophy, content and intent, and contain detailed requirements to be met by the paint manufacturer, the paint applicator and the coating inspector.

The manufacturer is called upon to maintain a Quality Assurance Programme and to provide adequate documentation to show that the quality of a given coating system as supplied is reasonably identical to the coating systems previously qualified under ANSI N 5.9. The coating(s) shall be requalified if there are significant changes in formulation or end-product properties. The manufacturer shall also provide application procedures for each coating system on each proposed substrate for each method of application as covered by the project specification. This shall include the maximum and minimum ambient conditions at which application of paint can be made.

The paint applicator is required to furnish a Quality Assurance Programme, detailed methods of application, details of operator experience and skills, paint product identity, surface preparation record for each substrate and an application log.

The Inspection Agency is required to furnish details of coating inspectors qualifications, an inspection plan and to maintain daily records of coating inspection, coating rejection and coating acceptance.

Details of surface preparation requirements and techniques are detailed in ANSI N 5.9 rather than ANSI N 101.4 1972. The proposed ISO Draft Standard ISO/DIS 6215 covers similar requirements, but is not written specifically to cover coating operations. Both the US and the draft UK standards should be compulsory reading matter for anyone in the nuclear coatings field.

A useful document is to be found in AECP 1002, 1972, 5, "The coating of surfaces requiring decontamination" which includes information on related standards, notes for designers, a general assessment of the properties of coatings and suggestions as to the choice of paint for specific environmental conditions.

A guide to selection is reproduced in Table 6.

The fact that the US Nuclear Industry takes a very serious view of the specification of surface coatings for nuclear power plants is indicated by the proposed publication in 1978 of a manual¹ on "Coating Work for Light Water Nuclear Power Plant Primary Containment". Subjects to be covered in the manual include design criteria, quality assurance, coating application, surface preparation, qualification of personnel and inspection. It is intended that one chapter of the manual

	Guide to coating selection						
	Temperature						
Corrosive	Above	ambient	Ambient				
Condition	Moisture condition						
	Wet	Dry	Wet	Dry			
Acid	Chlorinated rubber Catalysed epoxide High-build solventless epoxide Phenolic/epoxide Water miscible epoxide Stainless steel	Chlorinated rubber Catalysed epoxide High-build solventless epoxide Phenolic/epoxide Water miscible epoxide	Chlorinated rubber High-build epoxide Phenolic/epoxide Water miscible epoxide Tiles	Chlorinated rubber High-build solventless epoxide Phenolic/epoxide Water miscible epoxide Glass bead/epoxide Tiles Plastics			
Alkali	Chlorinated rubber Catalysed epoxide High-build solventless epoxide Phenolic/epoxide Water miscible epoxide Stainless steel	Chlorinated rubber Catalysed epoxide High-build solventless epoxide Phenolic/epoxide Water miscible epoxide	Chlorinated rubber High-build solventless epoxide Phenolic/epoxide Water miscible epoxide	Chlorinated rubber High-build solventless epoxide Phenolic/epoxide Water miscible epoxide Glass bead/epoxide Tiles Plastic			
Neutral	Chlorinated rubber Catalysed epoxide High-build solventless epoxide Phenolic/epoxide Water miscible epoxide	Chlorinated rubber Catalysed epoxide High-build solventless epoxide Phenolic/epoxides Water miscible epoxide Polyurethane	Chlorinated rubber High-build solventless epoxide Phenolic/epoxide Water miscible epoxide Tiles Neoprene rubber Aluminium	Chlorinated rubber High-build solventless epoxide Phenolic/epoxide Water miscible epoxide Glass bead/epoxide Tiles High gloss paint Linoleum Plastic sheet Alkyd-tung oil phenolic Plastics Polyurethane			

Table 6

will cover the training of painters and inspectors and will include a practical application test¹. It is also proposed to rewrite ANSI N 101.2 1972. "Protective Coatings for Light Water Nuclear Containment Facilities" and ANSI N. 101.4 1972. "Quality Assurance for Protective Coatings Applied to Nuclear Facilities". Essentially N 101.2 will be used to identify criteria required of surface coatings prior to acceptance and N 101.4 will cover the quality of the finished coating work within the primary containment. All three documents should prove to be interesting and educational documents.

Decontamination properties of surface coatings

Refs. 2, 3, 8, 9, 11-14

Two major problems exist in presenting a clear and definite account of the state of the art in assessing the factors which govern the ease of decontamination of surface coatings. The first, arising from the multiplicity of decontamination tests and the lack of correlation data has already been described. The second, and rather more intractable problem lies in the way that much of the past work has been carried out. Very little of the published work is related to specific and known formulations, and only slightly more to manufacturers designated products. Most of the work describes results on coatings referred to only by their generic names. There are notable exceptions²,^{11,12}.

Obviously much specific information has been gathered in the past and is still being generated, but it is largely in the hands of coating manufacturers who are understandably reluctant to disclose information, the possession of which gives them a commercial edge over competitors.

The difficulty can be readily seen when reference is made to work in which the best and the worst of over 40 finishes tested were both described as being vinyl types⁹. Work in which decontamination factors are given, but formulation details are not, is illustrated by the following US Work using the ANSI method: (1) epoxy, 7 to 125, or 590 for a glass-like surface; (2) vinyl, 14 to 120, or 156 for a glossy surface; (3) chlorinated rubber, 75 to 97; (4) modified phenolic 14 to 34, and acrylic, 20 with ruthenium-rhodium being the most difficult nuclides to remove.

P. WALKER ETAL. JOCCA

This type of approach still persists and in a recent report¹³ Kunze summarises the results of decontamination tests on 595 coatings and flooring compounds of largely undisclosed composition. The products tested cover almost the complete range of chemical types and include nitrocellulose, chlorinated rubber/alkyd compositions, silicones, epoxides, polyurethanes and polyester. Of these 276 were of the epoxide type and approximately 90 per cent were placed in the "good" to "very good" category. Of all the coatings tested 18 per cent were placed in the "poor" to "very poor" category. It is not clear from the original paper if the coatings tested were deliberately formulated to be readily decontaminated or represented normal commercial production.

Work in the author's laboratories in which the standard BS 4247 and the acid contaminant tests were applied to a range of coatings is shown in Table 7. A DF value is quoted together with a subjective assessment. The formulations of most of the paints tested are known.

Reference to Table 7 will show that the reasonably comprehensive range of paints varied from the aromatic isocvanate adduct cured polyester and amine cured epoxide with DF's from 3-8, to the chlorinated rubber paints and the thermosetting acrylics with DF's from 1100-3000. It will also be seen that some of the coatings which would be considered acceptable by the BS test would be rejected as completely unacceptable by the acid contaminant test. It may seem to be a contradiction that some of the coatings rejected by the acid contaminant test are amongst those with the best chemical resistance, but it must be remembered that it is not resistance to the contaminant that is being discussed, but ease of removal from the film. It is also interesting to note that the least decontaminable coatings under acid conditions almost invariably contain nitrogen and it may well be that the nitrogen atoms form complexes with the contaminating ions under acidic conditions and thus resist decontamination.

The coatings detailed in Table 7 were all paints chosen as being the best of the generic types for ease of decontamination and it is interesting to compare the results with those obtained from some proprietory paints of the same basic type. The paints detailed in Table 8 were all obtained from leading manufacturers. With the exception of the amine adduct cured epoxide, all the proprietory paints gave lower DF values than

T	able 7		
Decontamination	properties	of	coatings

Coating type	BS 4247 Test	DF	Aldermaston acid	contaminant Test DF
Alkyds	Fair to Good	80-130	Fair to Good	70-120
Epoxide esters	Good	250-300	Good	120-150
Phenolic modified alkyds	Good	115-130	Good	100-110
Styrenated epoxide esters	Good	105-120	Fair	90-100
Tung oil/phenolic	Excellent	1108-1130	Excellent	1110-1130
Amine cured epoxide	Good	160-840	Poor	3-5
Amine adduct cured epoxide	Good	176-188	Fair	58-75
Polyamide cured epoxide	Fair	60-80	Poor	8-9
Dialkalolamine/isocyanate/epoxides	Good	200-220	Fair	90-100
Aromatic isocyanate adduct/polyester	Poor	3-5	Poor	2-4
Aliphatic isocyanate adduct/polyester	Good	100-160	Fair	70-90
Phenolic epoxides	Good	160-180	Good	105-125
Thermosetting acrylics	Excellent	2700-3000	Poor	5-6
Solvent acrylics	Good	100-115	Fair	60-80
Chlorinated rubber (chlorinated diphenyl)	Excellent	1100-1200	Excellent	1100-1200
Chlorinated rubber (chlorinated paraffin)	Excellent	1200-2000	Excellent	1100-1700
Alkyd/melamine	Fair	50-80	Poor	8-9
Powder coatings (epoxide)	Good	330-380	Fair	15-30
Vinyls	Fair to Good	30-180	Poor to Fair	3-70



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Coating type	BS 4247		Acid Contar	minant Test
presidenti (1997) 🖷 (🐨 🖬 199		DF		DF
Polyamide cured epoxide A	Fair	40	Poor	4
Polyamide cured epoxide B	Fair	45	Poor	5
Polyamide cured epoxide C	Fair	50	Poor	6
Urea formaldehyde/epoxide	Fair	87	Poor	8
Alkyd melamine	Fair	42	Poor	7
Plasticised epoxide/melamine	Poor	9	Poor	5
Epoxide powder coating	Good	250	Fair	15
Chlorinated rubber	Excellent	1240	Good	125
Adduct cured epoxide	Good	245	Fair	50
Aliphatic isocyanate adduct/polyester	Good	120	Fair	65

Table 8
 Decontamination properties of proprietary paints

those specially selected for their ease of decontamination. although the differences were not always large. In general, all the DF values were higher than those reported in the US work. This is in line with the findings of Kunze shown in Table 5. Some work on the formulation of paints for radioactive areas has been reported2'8'11'12'14 and it has been shown that attention to formulation variables is necessary to obtain the optimum ease of decontamination for any given system. The excellent paper by Colclough² details work on "thick build" coatings of chlorinated rubber, epoxide, coal tar epoxide and polyurethane. Precise formulations are given for many of the paints tested. On the basis of long term tests in water and air Colclough concluded that properly formulated "thick build" epoxide resin coatings are suitable for use in radioactive areas. "Thick build" chlorinated rubber paints are useful only as undercoats and care must be taken to ensure that the release of solvent from the coating is sufficient before covering with a fininshing coat. There was insufficient evidence to assess the usefulness of solventless polyurethanes. but on the evidence of four proprietory formulations it appears doubtful if they would be suitable for use in radioactive areas. The most important single variable is the polymeric binder used, and in choosing this plasticisers, curing agents and catalysts must all be considered since their importance has been clearly demonstrated². There are, however, certain basic rules which can be applied to any resin/pigment system; these are to avoid phosphate plasticisers, zinc oxide, barium sulfate, blanc fixe, and high pigment volume concentrations (above 10-15 per cent). As a general rule, any pigmentation will tend to lead to an increase in residual contamination over an unpigmented finish, and in this respect some grades of rutile titanium dioxide are worse than the anatase grades. However, for most practical purposes the difference is small and the compromise between ease of decontamination and chalk resistance is best met by the use of the rutile grades.

Solvent balance is also very important and the use of high boiling solvents which are retained within the film after cure can also lead to excessive retention of radioactivity. Having considered the major components of a paint, i.e. chemical composition of the binder, type and amount of pigmentation, and solvent balance, other minor components of the paint may be of great importance. If, for example, an amine treated clay is used as a suspending agent, then some adverse effect on decontaminability may be expected: similarly the use of amine accelerators in polyurethane based paints will encourage more residual contamination. A recent Soviet patent suggests that the decontaminability of polybutyl methacrylate resin can be improved by the addition of polyphenyl siloxane resin.

Although rapid strides have been made in formulating

coatings having acceptable decontamination properties, it is difficult to see how further improvements are possible unless such work can be carried out within a laboratory having the required radioactive facilities and the necessary formulative expertise.

In this present section it has been demonstrated that the nature of the contaminant is of great importance, particularly with regard to the pH of the contaminant solution. It is, therefore, important to realise that the results of the tests described can only be used as an indication of the suitability of a coating for a specific purpose. Where the ease of decontamination is a critical parameter in the choice of coating, then a method of assessment using the actual contamination process intended should be undertaken. Support for this view is provided by Newby and Rohde who state that the DF's for iodine are less than 10 and from 10-1000 for tellurium, rare earths, caesium and strontium³. The effect of pH has also been clearly demonstrated in this present work.

The effect of ageing on ease of decontamination

Refs. 12, 14, 15

This is a subject on which very little is known and even less has been published^{12*14}. Some attempt has been made to remedy this within the author's laboratories.

In a recently completed study, twelve paints of known composition and covering the complete spectrum of ease of decontamination were applied as two coat systems to mild steel panels and exposed to: natural weathering in a rural environment for two years, accelerated weathering to British Standard 3900 for two thousand hours, water immersion (demineralised) for six months and laboratory storage for three and four and a half years. The paints were:

- (A) Aromatic isocyanate adduct cured polyurethane
- (B) Aliphatic isocyanate adduct cured polyurethane
- (C) Amine cured epoxide
- (D) Polyamide cured epoxide
 (E) Amine adduct cured epoxid
- E) Amine adduct cured epoxideF) Stoving acrylic
- (F) Stoving acrylic(G) Long oil linseed alkyd
- (H) Tung oil/phenolic oleoresinous
- (I) Chlorinated rubber (rutile/chlorinated diphenyl)
- (J) Chlorinated rubber (anatase/chlorinated diphenyl)
- (K) Chlorinated rubber (anatase/chlorinated paraffin)
- (L) Chlorinated rubber (anatase/chlorinated paraffin)

All decontaminated testing was carried out to the dictates of BS 4247, Part I, 1970: "The assessment of Surface Materials for Use in Radio-Active Areas". The panels exposed to accelerated and natural weathering were tested in two conditions: on removal from test, half the panel was washed in a 5 per cent detergent solution using a soft brush and rinsed in running water to remove surface chalking, the other half was untouched. All other panels were tested in the condition in which they were removed from test after drying out for several days before test. The results quoted as percentage residual contamination after two stages of decontamination are shown in Table 9. Natural weathering—chalky There were significant interactions.

A detailed discussion of the possible reasons for the changes in the decontaminability of the paints tested is beyond the scope of this paper and it is hoped to present a fuller account at a later date, but some brief and tentative explanations may be pertinent at this stage.

Table 9
 Percentage residual contamination after Stages 1 and 2 of British Standard 4247, Part 1, 1967

Test Environments	Paint	t A Pa	int B	Pair	nt C	Paint D	Pair	nt E	Paint F	Pair	nt G	Pain	it H	Pair	nt I	Pai	nt J	Pair	t K	Pair	nt L
Controls (Aged 2 weeks at room				N. Salation	3. 41-52	Service is shall															
temperature)	23.09 2	2.13 1.03	0.96	16.72	14.01	6.05 1.82	10.32	10.29	0.03 0.03	0.80	0.80	0.90	0.84	0.18	0.09	0.95	0.37	0.05	0.04	0.92	0.43
British Standard 3900																					
Accelerated weathering (chalky)	2.43	1.52 2.88	1.49	8.21	4.33	2.16 1.62	10.21	5.45	7.91 4.26	2.52	1.51	2.79	1.60	5.57	3.83	17.35	11.29	4.23	2.81	5.21	3.49
British Standard 3900																					
Accelerated weathering (non-																					
chalky)	7.69	6.92 0.79	0.50	4.48	2.79	1.30 1.09	7.14	4.34	2.93 1.92	2.38	1.20	2.94	1.47	3.81	2.51	9.01	6.61	4.69	2.85	3.65	2.76
Natural weathering (chalky)	19.601	5.09 6.08	3.60	17.61	9.69	11.65 8.75	11.81	7.69	13.07 9.31	23.04	18.23	12.42	8.06	15.77	13.42	18.72	12.51	15.47	14.77	16.09	11.90
Natural weathering (non-chalky)	17.031	4.72 5.65	3.48	20.99	12.31	5.32 4.16	7.35	4.91	9.877.66	17.28	14.77	17.43	13.93	5.67	4.77	9.73	7.26	9.75	8.51	10.11	8.83
Water immersion	3.67	2.90 0.25	0.20	0.92	0.59	0.09 0.03	0.32	0.24	0.13 0.07	0.46	0.30	0.96	0.52	1.30	0.85	5.00	3.05	1.77	1.05	2.31	1.16
Laboratory ageing 3 years	12.821	4.40 0.13	0.11	1.31	1.06	0.18 0.13	0.22	0.18	0.93 0.86	9.87	9.47	2.21	1.92	6.61	6.37	4.78	4.24	0.08	0.07	0.07	0.07
Laboratory ageing 4 ¹ / ₂ years	35.08 3	2.51 0.03	0.03	8.98	6.66	0.17 0.15	0.56	0.35	1.49 1.28	5.84	5.84	1.04	0.85	0.37	0.23	7.54	7.54	0.05	0.03	2.73	2.52

The paints tested covered a wide range of decontaminability, ranging from an aromatic isocyanate adduct cured polyurethane (Paint A) which retained almost 25 per cent of the original contamination, to four chlorinated rubber paints (I-L) which retained between 0.04 and 1.0 per cent. The order of merit on initial decontamination was:

1.	Paint F:	Stoving acrylic
2.	Paint K:	Chlorinated rubber
3.	Paint I:	Chlorinated rubber
4.	Paint J:	Chlorinated rubber
5.	Paint L:	Chlorinated rubber
6.	Paint G:	Long oil alkyd
7.	Paint H:	Tung oil/phenolic oleoresinous
8.	Paint B:	Aliphatic polyurethane
9.	Paint D:	Polyamide cured epoxide
10.	Paint E:	Adduct cured epoxide
11.	Paint C:	Amine cured epoxide
12	Paint A ·	Aromatic polyurethane

There were large and obvious differences in the amounts of residual contamination after exposure to the various ageing environments.

In an analysis of variance for both decontamination stages the Tukey critical difference¹⁵ for the paints showed the order of merit to be:

Best	1	Paint B
	2	Paint D
		Paint K
		Paint F
	3	Paint I
		Paint L
		Paint H
		Paint E
	4	Paint G
		Paint C
	5	Paint J
Worst	6	Paint A

The groupings indicate that statistically the paints within a group are not distinguishable because of the scatter of results, so the order within a group is simply that of the averages. For the ageing environments the Tukey critical difference showed the order of merit to be:

Best Water immersion

Laboratory ageing for 3 and 4¹/₂ years and unaged control. Accelerated weathering---non-chalky Accelerated weathering---chalky Natural weathering---non--chalky

In their initial unaged state a large number of reactive chemical entities will be present, either within the film or at the surface. Amongst these will be amines, ureas, biuets: hydroxyl and isocyanate groups in the polyurethane paints; amines in the epoxide paints; aldehydes, ketones, short chain acids (formic, acetic butyric, etc.) and peroxides in the oil containing coatings. Many of these will be reactive, volatile and water soluble and therefore readily available for reaction. Thus, initially, the possibility for contamination by chemical adsorption, ion exchange and diffusion exists. The coatings after exposure to the various ageing regimes, with the exception of water immersion, contain the same chemical groups but to lesser or greater extent depending on the solubility and/or volatility of the entities. Additionally, the surface of the paints exposed to both natural and accelerated weathering will have been considerably modified, in most cases exposing highly pigmented matrix material. Water immersion would certainly remove many of the low molecular weight materials. Thus when the many possible interactions are considered, it is hardly surprising that profound changes in the ease of decontamination were discovered.

The obvious conclusion from the work reported is that the ease of decontamination of surface coatings will change considerably with age. This change may represent an improvement or deterioration depending on the coating and the ageing environment.

Some of the findings in this investigation appear to contradict those of Colclough¹² who found that all the coatings tested in his investigation become more difficult to decontaminate as they aged, the rate of change being more marked for some coatings than others. However, the work reported was on high-build epoxide, polyurethanes and chlorinated rubber coatings only.

Mechanisms of radiation attack

Ref. 16

When placed in a radiation field, all materials absorb energy. The dissipation of the absorbed energy results in a sequence of chemical reactions, which may result in changes to the physical properties of the material concerned. In comparison with metals and many inorganic materials, organic polymers, and hence coating systems, are relatively sensitive to radiation and, consequently, they are not used in areas where doses are very high, e.g. in the interior of cactors. The radiation environment to which coating systems are subjected consists of:

- (a) charged particles e.g. β^- , ∞^- particles, and
- (b) electromagnetic radiation e.g. γ , X-rays.
- The mechanisms of energy loss by these types of radiation, and the resulting chemical effects, are discussed below.

Charged particles, unlike electromagnetic radiations, lose energy through a series of events each of which reduces the remaining particle energy. Energy loss mainly takes place through electric interactions with electrons in the absorbing material; the electrons concerned are increased in energy with the result that the absorbing atom is either raised into an electronically excited state or becomes ionised. Energy transfer from ∞ -particles to the absorber depends on the velocity of the particle and its closest approach distance to the absorber electron involved. The Coulombic force is proportional to the product of the interacting charges/ (closest approach distance)² and the impulse imparted is the product of the Coulombic force and the length of time of the interaction. Hence an *c*-particle loses more energy as it is slowed down; it finally acquires two electrons to become a helium atom. B-particles lose energy either by a series of inelastic collisions with the electrons of the absorber or by interactions with the electromagnetic field of the nucleus of an absorbing atom. This latter process produces X-rays, known as bremsstrahlung (braking radiation). Since 3-particles are much lower in mass than ∞ -particles, they change direction more frequently in the absorption process.

Electromagnetic radiation is indirectly ionising, and three types of interaction are very important in describing the absorption process. These are (a) the photo-electron effect, where an incident photon ejects a bound electron from an absorber atom, (b) Compton scattering, where a photon undergoes an elastic collision with an electron causing it to recoil while simultaneously changing the path of the photon, and (c) pair production, where photons of energy greater than 1.02 MeV interact with the nucleus of the absorbing atom to produce a positron—electron pair. Photoelectric absorption dominates for low energy photons, e.g. 0.1 MeV, whilst the Compton effect is responsible¹⁶ for most effects in the energy range 0.1-2 MeV.

The net result of all the processes outlined above is the deposition of energy into absorber atoms. There are two primary processes: electronic excitation and ionisation, e.g.:

$$M \xrightarrow{M^+ e^-} M^+ = M^+$$
 ionisation
excitation

Multiple ionised species can be formed, but such molecules are difficult to observe because of the rapid dissociation which follows:

Excited molecules are also able to dissociate into radicals, that is, atoms or molecular fragments containing odd or unpaired electrons; the excess energy is converted into kinetic energy:

$$M^* \longrightarrow A^{\cdot} + B^{\cdot}$$

In hydrocarbon molecules, carbon-hydrogen bonds are most frequently ruptured but carbon-carbon bonds can also be broken if sufficient energy is available and hence a variety of reactive radicals and hydrogen atoms is produced. Furthermore, charged species resulting from ionisation may also be present, and as a result a wide range of ion-molecule, ionradical, radical-molecule and radical-radical reactions may take place to produce a complex mixture of products. The major types of radical reaction are:

(1) Recombination:

$$CH_3CH_2^{\bullet} + (CH_3)_2CH^{\bullet} \rightarrow (CH_3)_2 CH.CH_2 CH_3$$

(2) Abstraction:

$$CH_3CH_2CH_3 + H \rightarrow H_2 + CH_3CH_2CH_2$$
.

- (3) Disproportionation: $2CH_3CH_2 \rightarrow C_2H_6 + C_2H_4$
- (4) Addition: $CH_{a} + C_{a}H_{1} \rightarrow CH_{a}CH_{2}CH_{2}$ $CH_{a}CH_{2}CH_{2}CH_{2} + C_{2}H_{1} \rightarrow CH_{a}CH_{2}CH_{2}CH_{2}CH_{2}c$

The range of reactions can be divided broadly into two categories; those causing cross-linking (combination of molecules into a network) and those causing scission (degradation into smaller molecules). Cross-linking leads to an increase in molecular weight of the material concerned, the threedimensional structure causes an increase in tensile strength and softening temperature, whilst solubility and elasticity are decreased. Scission leads to the reverse, molecular weight is decreased, tensile strength and softening temperature are reduced; solubility and elasticity are increased. The evolution of gas cannot by itself be taken as evidence for either of these limiting processes. Since competing reactions take place, the net effect of absorbtion of radiation will depend on the competition between scission and cross-linking mechanisms, the material involved and the conditions under which it was irradiated. A number of general tendencies can however be outlined. Molecules containing halogenated carbon atoms on the main polymer chain tend towards scission, with the release of low molecular weight halogen compounds, e.g. polyvinyl chloride, chlorinated rubbers. Molecules containing adjacent methylene (-CH₂) groups tend to cross-link with the release of hydrogen, e.g. polyethylene, phenolic resins. Polymers containing aromatic groups tend to be more radiation resistant than those with aliphatic groups, as the resonance stabilised benzene ring is capable of absorbing and dissipating energy without molecular disruption. Consequently, the use of aromatic curing agents for epoxy resins, for example, improves the radiation resistance of the product. The effects on coating systems can also be modified by pigments and plasticisers (see later). Failure of a coating system after exposure to irradiation must be arbitrarily defined in terms of changes which take place in the physical appearance of the film. Such changes include blistering, caused by separation of gases or liquids from within the polymer; cracking caused by shrinkage of the polymer; discolouration and peeling due to failure of adhesion.

The radiation resistance of coatings

Refs. 12, 17-20

Obviously, the radiation resistance requirements for surface coatings will depend to a great extent on the facilities to be coated and not all paints used will be required to have maximum radiation resistance. To a lesser extent the requirements may be different for ceilings, walls and floor. Some indication of the requirements is given in Table 10: the values quoted are for an expected life of 40 years for the facility and it is not intended that coatings will last without the appropriate maintenance or recoating. Reference to Table 10 will show that generally the floor area requires the maximum radiation resistance.

	Essiliar or ores	Ge	neral level of exposure	e* (rad)
	Nuclear reactor sites	Floors	Walls	Ceilings
(a	Canals for fuel storage and handling	$7 \times 10^9 - 1 \times 10^{10}$ (2 x 10 ⁹ - 7 x 10 ⁹)	$7 \times 10^9 - 1 \times 10^{10}$ (2 x 10 ⁹)	
(b) Fuel disassembly and examination areas	2×10^9	2×10^9	2×10^9
(c	Off-gas ductwork and filtration	$5 \times 10^8 - 1 \times 10^9$ (0.5 x 10 ⁹ - 1 x 10 ⁹)	5×10^8 (0.5 x 10 ⁹)	5×10^8 (0.5 × 10 ⁹)
(d) Contaminant structure	1×10^{2}	1×10^{2}	1×10^{2}
(e)	Laboratories	1×10^{3}	1×10^{2}	1×10^{2}
N	uclear fuel processing plants			
(a)	Canals for fuel storage and handling	$5 \times 10^9 - 1 \times 10^{10}$	1 x 10 ¹⁰	
(b) Spent fuel carriers	$5 \times 10^8 - 1 \times 10^9$	$5 \times 10^8 - 1 \times 10^9$	$5 \times 10^8 - 1 \times 10^9$
(c)	High level laboratories	$1 \times 10^9 - 5 \times 10^9$	1×10^{9}	$5 \times 10^8 - 1 \times 10^9$
(d	Decontamination and waste disposal	1×10^{4}	1×10^{3}	1×10^{3}
(e'	Research and analytical laboratories	$1 \times 10^3 - 1 \times 10^3$	1×10^{3}	1×10^{3}

Table 10Fadiation exposure guide (ANSI—N 5-9-1976)

*Values in brackets according to Berger1

A Rad is the unit of specific absorbed close and is equal to the imparting of 0.01 J/kg

Having established the degree of radiation resistance required for a coating, it is necessary to know the resistance of the proposed polymer binder. Approximate deterioration doses are shown in Table 11. The deterioration resistance is usually defined as the level of radiation below which breakdown of the coating would not be due to the radiation alone.

 Table 11

 Deterioration dose of some film forming polymers

Polymer	Approximate deterioration dose (rad)				
Aliphatic polyurethanes	5 x 10*				
Aromatic polyurethanes	2×10^{9}				
Alkyds (short oil)	5 - 7 x 10 ^s				
Alkyds (long oil)	1×10^{9}				
Chlorinated rubber	5 x 10 ⁷				
Cellulose esters	1 x 10 ⁶				
Diphenyl silicones	2.5 x 10 ⁹				
Epoxides	$5 \times 10^8 - 2 \times 10^9$				
Epoxide phenolics	$3 - 6 \times 10^9$				
Methacrylate resins	5 x 10 ⁶				
Neoprene	5 x 107				
Phenolics	$1 - 5 \times 10^9$				
Polyesters	$5 \times 10^8 - 1 \times 10^9$				
Urea and melamine formaldehyde	$1 - 5 \times 10^9$				
Vinyl resins	4 x 10 ⁸				

The values in Table 11 are largely based on work carried out on unmodified films of polymer, generally in sections thicker than those obtained by the use of paint. However, these doses are no more than a general guide to paint performance as the normal modification of a polymer to produce viable surface coatings can significantly alter the radiation resistance of the formulated coating. Inert inorganic fillers, such as pigments and extenders, can materially upgrade the radiation resistance of a polymer, but titanium dioxide appears to accelerate radiation damage. Carbon black inhibits radiation damage and the toluidine reds appear to have little effect¹⁷. In general, coatings having a high pigment volume concentration (PVC) are more resistant than glossy coatings containing the same pigment at a lower PVC.

The radiation resistance of chlorinated rubber paints is very dependent on the type and amount of plasticiser used and chlorinated diphenyl plasticisers can upgrade the resistance to $1 - 2 \times 10^8$ rad. Aromatic curing agents for both

polyurethanes and epoxides will increase the resistance over aliphatic cured systems.

In general then, the radiation resistance of correctly formulated paints is likely to be considerably greater than the resistance of the bulk polymer. Almost without exception, coatings will darken on exposure and may approach dark brown on maximum exposure. Fortunately, this discolouration in no way effects their other properties and cannot be taken as a visual indication of failure. Unfortunately, the whole of the work on paint radiation resistance is hindered, as is the work on decontaminable coatings, by the fact that almost all the work reported has been carried out on formulations of largely undisclosed composition, usually of proprietary manufacture, and described either by a generic title or a trade name. Despite this, it is possible to place formulated coatings in some merit order and indicate the level of radiation resistance provided.

Inorganic zinc rich primers are known to have a resistance in excess of 5×10^{10} rads, but unfortunately their intrinsic poor chemical resistance militates against their use unless correctly overcoated. Phenolic modified epoxide coatings are resistant to levels in excess of 1×10^{10} and have been used in 80 per cent of the US nuclear power plants on those areas where maximum radiation resistance is required. Polyamide cured epoxides and polyurethanes are also capable of surviving exposures of a similar magnitude, although the notably poor colour retention of the aromatic cured polyurethanes has been a bar to their general use. It is likely that epoxide powder coatings will also have a high radiation resistance.

The remaining types of coating, alkyds, chlorinated rubber, vinyl, etc. do not have the required radiation resistance for those areas in which maximum resistance is required (see Table 10), but are sufficiently resistant for use in the remaining areas. Watson *et al*¹⁷ investigated fifty seven coatings supplied by twelve manufacturers and reported that although the epoxides and phenolic modified epoxides had the greatest irradiation resistance, vinyl paints were surprisingly resistant to gamma radiation, their tolerances ranging in air from 2.2-6.6 \times 10⁹ rads and, in deionised water, from 1–9 \times 10⁸ rads. They concluded that vinyls can be used for moderate exposures, and in many instances, for severe exposures for short periods of time.

It should be emphasised that the effect of radiation on coatings in general is greater in water than in air. The resistances quoted above can be reduced considerably for water exposure. A very useful account of radiation studies on high build epoxides, polyurethanes and chlorinated rubber under immersion conditions has previously been noted12. At a total integrated dose of 5 \times 10⁸ rad, the chlorinated rubber paints had reached the end of their useful life and at 1×10^9 several of the high build epoxide systems had also started to deteriorate. The complete failure of a proprietary high-build epoxide and a glass reinforced epoxide are reminders of the potential dangers which may arise from formulating coatings for general applicability and using them for specific working environments. Watson¹⁸ makes the general point that glass reinforcement in the form of fabric materially helps radiation resistance under immersion conditions but does not appear to extend the useful life of a coating irradiated in air. Chopped glass fibres do not appear to improve a coating's resistance to gamma radiation in either air or water.

It has been suggested19 that the high radiation resistance of some polymers appears to be primarily due to the presence of a large proportion of aromatic rings in the molecule. Little²⁰ has pointed out that conjugated double bonds and ionic linkages are other stabilising factors.

The past, present and future

Ref. 21

In assessing the role, properties and performance of surface coatings in nuclear industry in the past, present and future, both hindsight and crystal ball gazing are necessary.

Prior to the mid 1950's, the coatings then available based on oleoresinous, bitumen, alkyd, chlorinated rubber compositions and vinyl resins were largely unsatisfactory due to a combination of less than optimum properties and a lack of understanding of the principles of formulation for nuclear applications. After this period the possibility of using coatings as engineering materials having a useful contribution to make as barriers to radio-nuclides was recognised and an additional impetus was given by the advent of epoxides and polyurethane based coatings. With a greater understanding of the principles of formulation coupled with the availability of resin systems of optimum performance, great strides were made in meeting the level of performance required.

At the present time the epoxide, polyurethane, modified phenolic, chlorinated rubber and vinyl coatings are adequate to meet the requirements of the industry. It is only fair to say that the few troubles which have been experienced have been due to conventional reasons and have arisen due to either neglect of surface preparation or failure on the part of the contractor to provide adequate supervision and control of labour. Hopefully, the proposed standards and quality assurance documents together with the degree of control that they imply will further improve the situation. For the future, the requirements will be for coatings having higher temperature resistance, improved resistance under immersion conditions, improved radiation resistance and improved application properties, particularly under adverse climatic conditions. The aim will be to meet the definition of the ideal surface contained²¹ in AECP 1002:

"The ideal surface would be permanent, smooth, impermeable, chemically inert, fire resistant, radiation resistant, mechanically hard and strong, easily cleaned and cheap Contamination would easily be removed from it".

More specifically, it is suggested that the following developments would provide useful additions to the range of coatings available to the nuclear industry. Duplex systems in which a readily soluble topcoat is applied to a permanent base coat. The topcoat being removable without damage to the base coat.

A completely inorganic based finishing system which could be expected to have extremely good radiation resistance for use in hot cells. A useful start has been made with the inorganic zinc-rich paints already available.

Improved flooring materials having good wear and point impact resistance which could be readily decontaminated, although heavily filled.

Single pack systems having the same ease of decontamination properties and radiation resistance as the two pack systems which could be applied from pressurised containers and be applied by remote handling techniques.

A strippable coating which can be readily stripped after long ageing periods after high radiation exposure.

In conclusion it may be said that although there are gaps in the knowledge of how and why surface coatings behave in a nuclear environment, the authors are confident that the surface coatings industry will respond to the continued challenge posed by nuclear industry.

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Discussion at Stratford Conference

MR E. L. FRENCH stated his interest in seeing one of the slides which had shown the Wylfa Power Station where plastic coated cladding had been used. He was interested to see that the steelwork, which had been coated with a red lead oil based paint, had stood up well over the years of operation.

On the question of fuel cooling pond walls, Mr French pointed out that there were still problems being experienced, where the same materials had been applied to different ponds under strict supervision, but adhesive failure was still experienced in some cases and, as yet, no explanation could be given. Mr French agreed that the epoxide systems had proved most successful, and suggested that the reason why no British manufacturer had a qualified system available was purely commercial, due to the large amount of development that has to go into a coating for these applications, so that no UK manufacturer can afford to develop a commercially viable product to rival the proven US systems. However, he pointed out that although the American material had been approved, there were still a number of problems in its use, not with its ease of decontaminability, but with the other effects of radiation upon the coating. He suggested that the test methods being used which were on coatings separated from the concrete substrate, were not satisfactory from the point of view of the contractor.

DR HAIGHTON agreed that the market for these specialised coatings was not very large and might not justify the large investments required by British firms to develop an approved system. He added that where an approved coating had been used, there would be a reluctance to change to a relatively untried system on which full data might not yet be available. Dr Haighton agreed that pond walls were a problem and pointed out that in some cases, where particularly high radiation was encountered, stainless steel might have to be used. He suggested that glass reinforced epoxy materials might find some uses, although again there were certain foreseeable problems. Regarding problems of application, the Atomic Energy Authority and CEGB are preparing a document on quality assurance in nuclear areas for paint and it is hoped that this might improve matters.

Whilst agreeing that the potential market for these specialised coatings was small, MR WALKER pointed out that it was important to have qualified coatings, and suggested that the price charged could be commensurate with the work involved, and that, at the moment, many of the coatings being used by the UK AEA and CEGB had to be developed within their own laboratories.

The American manufacturers seem to be moving towards the use of epoxy/novolac systems, which have shown up particularly well for long periods, and they are moving into the British market to pick up what business there is, appointing agents, which might indicate that the rewards are more substantial than had been suggested. On the question of the problems of coating pond walls, Mr Walker suggested that the problem might not only be the radiation doses, but also the type of substrate involved.

MR A. SAARNAK stated that in Scandinavia there had been a number of failures of coatings due to blister formation on concrete structures, such as on the interior of reactor domes. He suggested that this might be due to the thickness of the concrete used, up to 0.5 metre thick, which would take years to dry out completely, and coating such a surface with an impermeable coating would entrap water in the structure, which would lead to the failures observed. This problem would be aggravated if the structures were also subjected to high temperatures.

MR WALKER had also heard of these porblems and expressed surprise that on an engineering material as well established as concrete, such problems still occured. However, adhesion failures had the attribute that they are easy to recognise, but the reasons why they should occur are complicated, factors such as the age of the concrete, the type of concrete, the amount of supervision and the Code by which it was applied, all having an influence. Mr Walker suggested that perhaps the answer might lie with another system, or by the use of adhesion promoters.

DR HAIGHTON added that when the concrete of reactor domes was coated, only one side was covered, which allowed some of the entrapped water to escape. If both sides had been coated, then more serious problems would be encountered.

DR D. ATHERTON suggested that a major problem with coating concrete was the large number of pores, which are either bridged by coatings or produce holes in the coating. This problem has been overcome in sewage installations, even those below the water table, by blasting the surface to expose aggregate and break off all pinholes and voids. The surface is then spray coated with an epoxy/sand composition and trowelled to fill the surface. This epoxy/sand surface is substantially void free, and can then be coated with chemically resistant epoxy coatings. The results obtained by using this system had been particularly good, with substantial reductions in the number of failures due to the loss of adhesion.

DR HAIGHTON agreed that removing the concrete surface and replacing it with an epoxy/sand composition solves some of the difficulties, but the problem was that this method took a long time, and in high capital cost projects, such as nuclear installations, any delay in the schedules was very expensive.

MR WALKER said that the American approach was to grind the surface at joints, which were then filled with an epoxy/sand composition, to achieve the same result by removing surface porosity.

Original and maintenance painting systems for North Sea oil and gas platforms*

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Summary

The various types of floating and fixed offshore structures are described. Sea bed structures and pipelines are also discussed. Painting systems are outlined with reference to composition and the performance in service; the reasons for inadequate performance

Keywords

Types and classes of coatings and allied products

structural steel coating corrosion resistant coating are discussed in some detail. The remedies suggested are either improved formulation of a particular class of coating or by a change to a more suitable type.

Types and classes of structures or surfaces to be coated oil rig steel

Les systèmes de peinture premiers et de manutention pour les installations de pétrole et de gaz dans la Mer du Nord

Résumé

On décrit les divers types de structures soit flottantes soit fixes et situées en pleine mer. On discute d'ailleurs les pipelines et les structures posées sur le lit de la mer. On donne un aperçu des systèmes de peinture à l'égard de leur composition et leur rendement en service. On discute en quelque détail les raisons pour tout rendement insuffisant. On suggère que les remèdes sont soit l'amélioration d'un certain genre de revêtement ou l'utilisation d'un autre genre plus convenable.

Erstmalige und Reparaturanstrichsysteme für Off-shore - Konstructionen bei der Öl- und Gas-foederung in der Nordsee

Zusammenfassung

Die verschiedenen schwimmenden und verankerten Konstruktionen werden beschrieben, einschliesslich solcher für den Meeresboden und Rohrleitungen. Anstrichsysteme werden aufgeführt mit Bezug auf Zusammensetzung und Verhalten im Gebrauch.

Introduction

Ref. 1

It is necessary before discussing corrosion conditions on offshore structures to outline briefly oil and gas exploration and production procedures and to describe the service conditions of the very varied types of equipment.

Exploration drilling, and sometimes drilling of production wells, is carried out from mobile drilling rigs. These vary from quite small jack-up rigs working close inshore, or in equatorial swamplands, to large anchored semi-submersible drilling platforms and, in very deep waters, to dynamically positioned drilling platforms or ships.

Installation of sea bed wellhead structures, valves, etc., sea bed cellars or manifolds, and installation of static platforms, is carried out by a variety of heavy lift barges and diver support vessels, some of which are now of the semi-submersible type. Sea bed pipelines are laid from very large lay barges, again, some are of semi-submersible type, and in the near future relatively narrow bore (about 150 mm) flow lines (these will carry oil from sub-sea completion wellheads to underwater manifolds or to platforms) will be laid in long lengths from large diameter reels installed on a laying ship or barge. These barges, platforms, or ships, may be very large and may be positioned by anchors or self propelled. Die Ursachen für unbefriedigendes Verhalten werden eingehend besprochen. Die vorgeschlagenen Abhilfemassnahmen bestehen entweder in besserer Rezeptierung einer besonderen Anstrichmittelart oder Wechsel zu einem geeigneterem Typ.

It will be appreciated that offshore oil technology changes very quickly indeed and these mobile ships, barges and platforms, work in very arduous conditions. They can, however, be brought into dock or at least into a sheltered anchorage for modification or repair of structure and replacement of protective coatings. Normal high performance ship painting systems can be used and in general give adequate performance for the relatively short useful working life of this class of equipment.

The fixed installations on the sea bed, whether these are well-head structures, sub-sea manifolds, pipelines, or support structures for platforms, cannot readily be removed for repair and are very difficult and costly to replace if they should fail due to corrosion. They may be expected to give a service life of 25 years or more and for these components, a totally new approach to corrosion control has been necessary.

The upper parts of a fixed offshore structure may be supported on a steel underwater structure (called a jacket) or on concrete pillars which, in turn, may rest on concrete oil storage tanks.

Underwater steel in these support structures must, like steel on the sea bed, be protected from corrosion for from twenty-five to perhaps fifty years and again new procedures have had to be developed.

*Paper presented at the Association's Conference held at Stratford upon Avon from 20-23 June 1979.

The superstructure of the platform invariably is of steel. It usually consists of braced tubular steel support structures supporting a heavily stiffened steel deck. Box girder deck support structures have also been used on some platforms. The machinery spaces, accommodation spaces, drilling equipment, helicopter platforms, etc., are now almost invariably built in module form and lifted on to the support deck either at sea or, in the case of gravity concrete structures, in very deep water sheltered anchorage after flooding the concrete support structures to reduce lifting height.

Protection of steel in the tidal and splash zones presents some problems because coating renewal at sea is expensive and difficult. Protection of steel in support deck structures and machinery or drilling modules presents new problems since the areas involved are very large; damage to paint during installation, hook-up and later modification, and due to impact in service, is frequent and widespread. Repair is always difficult to organise and reblasting is sometimes impossible for hazard or other reasons. Any system which cannot be patch repaired without blasting or lapped over with the repair system after only superficial cleaning becomes troublesome in service.

In addition to these relatively normal service conditions, there are a number of components with guite unusual and very troublesome corrosion problems. These include hot gas and oil risers passing through the atmospheric and splash zones and through the tidal zone to the sea bed; steel inserts in concrete exposed to the sea; rebars in the concrete which may be in contact with external steel components which are exposed to the sea and protected by, for example, sacrificial anodes or impressed current systems; very hot surfaces on flare booms; surfaces which become soiled by hydrocarbons including liquid components of flare gas blown back with cooling water spray on to the structure; surfaces subjected to crude oil spills, spills of alkaline drilling muds and cement slurries, and even the strong mineral acids which are used for well treatment. Almost every class of lubricating oil will at times be spilled on decks or paintwork, either from containers or from the equipment itself. Spills of aviation fuel, diesel oil and hydraulic fluid, are daily occurrences. All these spills will be constantly washed down with strong detergent and sea water in order to maintain a clean, safe surface and all deck surfaces are subjected to heavy foot and machine traffic and much impact damage.

All of these exposure conditions can, in theory, be met by correct design and correct choice of the protective system; the real problem which becomes apparent during construction and service is that expediency during construction and erection will demand that paint application takes a late place in the order of priorities. The enormous cost of bringing an oil field into operation creates huge cash flow problems, so that any avoidable delay in initial production or interruption to flow of gas or oil after the start-up becomes quite unacceptable. Initial and maintenance painting systems must be designed to fit in with these hectic construction and operation schedules. If they do not, then the specified but perhaps unsuitable paint system will just be slapped on regardless of the consequences and recrimination will follow when it falls off again. In the following review, the main types of exposure conditions are discussed together with the properties, both good and bad, of paint systems favoured by oil companies, their consultants, and sometimes by their suppliers. Bayliss and Dunkley1 have reviewed initial painting and repair procedures and have drawn particular attention to control of surface preparation and inspection. The following review is confined largely to the properties of the paint systems.

Paint systems for underwater surfaces

Ref. 2

It is usually argued that concrete structures do not require to be painted, and evidence of the long durability of the Mulberry Harbour and Estuary gun platform structures is used to support this argument. At the same time, there is growing concern² about corrosion of steel inserts at or near the point of contact with the concrete and also suggestions that rebars in electrical contact with steel inserts which may be protected by a cathodic protection (CP) system can corrode sacrificially in the depth of the concrete and result in spalling. Steel inserts can be coated and in certain cases rebars have been galvanised but there is still some doubt about the durability of the embedded and attached steel in the submerged concrete structures. Underwater steel support structures for platforms. underwater steel wellhead valves, wellhead structures. underwater cellars, underwater manifolds, etc., and in fact, any steel which is cold and exposed only to the sea can, in theory, be entirely protected by sacrificial or impressed current cathodic protection. Anode consumption or current requirement can be reduced and, in some cases, performance improved, by coating all or at least part of such underwater structures. The coating must have good water and alkali resistance, very good adhesion to the steel and good resistance to cathodic disbonding. It is quite impractical to assume that any painted underwater structure will be constructed, transported, installed or linked up, without substantial damage to any coating applied and it is, therefore, essential that the principal line of defence against corrosion must lie with the CP system. Any coating system used is a supplementary aid to this CP system.

Good results in service have been obtained in these underwater areas with coal tar epoxy coatings, usually applied in at least 400μ dry film thickness (dft). Single coat high build systems are feasible, but are likely to suffer from excessive or inadequate thickness from place to place on the structure. Multi-coat (e.g. 2 or 3 layer) systems are probably best. The coatings must be applied to clean blasted steel and any holding primer must be totally alkali resistant and resistant to cathodic disbonding. Epoxy primers pigmented with essentially insoluble and inert pigments (e.g. iron oxide) are best. Vinylbutyral based primers are not suitable since they promote cathodic disbonding and metallic zinc primers must be carefully sealed before overcoating.

Sub-sea flow lines and pipelines present quite different problems. Pipelines are usually large diameter (about 600 to 900 mm), thick-wall pipes and must be laid after welding lengths together on a lay barge. Sections may also be welded together on the sea bed by divers using a "habitat". The pipe must be weight coated (with concrete) to give it negative buoyancy both during laying and service and this is applied over a 5 mm thick hot applied tar coating reinforced with glass fibre tissue. It is absolutely essential that this coating system is complete and unbroken and nowhere detached from the pipe, since anode bracelets which are welded on at intervals cannot protect steel at any crevice between the tar/ concrete coating and the pipe. Severe corrosion can occur in such crevices. Lay barge welds may be coated after welding during the laying process, but anode bracelets are also applied at junctions. Flow lines are relatively narrow (about 150 mm) diameter, thick wall pipes and have negative buoyancy without a concrete weight coating. At present, they are usually welded together and laid by a normal lay barge technique but laying of long lengths from a reel or coil is imminent. An epoxy coating is normally used and due to the need for very fast cure and early resistance to handling damage, together with water resistance and cathodic disbonding properties, epoxy powder coating techniques are coming into favour.

The problem of corrosion of riser pipes has received much publicity due to rupture and fire of a concrete coated riser at Ekofisk and localised severe corrosion of two epoxy coated risers at BP Forties Field. Riser pipes are usually of about 600 mm diameter and carry oil or gas at pressures of up to 500 KPa and temperatures of up to 100°C from the sea bed upwards through the sea, through the tidal, splash, and atmospheric zones, to or from the production or manifold area on the platform.

There is sometimes confusion caused by the name "riser". Oil from a well immediately below a platform ascends via a "conductor". After processing to separate gas, oil, and water, the oil and/or gas usually descends to the sea bed and so to a tank, to a loading buoy or to a sub-sea pipeline, for export ashore, via "risers". It may ascend again via another riser at another platform which may be a pressure booster, or a collecting centre from a number of production platforms; in such a case it will descend to the sea bed again by yet another "riser" and pass on, on its journey to the shore or perhaps to a loading buoy.

The temperature gradient through the pipe wall and its protective coating, the expansion and contraction of circumference of the pipe itself at say 5°C during water pressure testing during installation and later expansion and contraction during service at 50° C- 100° C obviously imposes very severe strains on any organic coating, particularly when immersed in cold sea water. Service experience and laboratory investigation has shown that the following types are unsatisfactory:

- Highly pigmented high build solvent borne epoxy compositions of the tank coating types (these have inadequate water resistance at higher temperatures).
- (2) Sand or quartz filled, so-called solvent-free epoxy compositions (these invariably contain reactive diluents which may volatilise on heating and may even be slightly soluble in warm water).
- (3) "solvent-free" tar epoxy compositions (again these contain reactive diluent and very low viscosity tars contain volatile components).

Traditional amine or polyamide cured coal tar epoxy compositions of low pigmentation type have given variable results in service, some good, some poor. One type of isocyanate cured epoxy pitch composition pigmented largely with graphite gave very good results in laboratory trials and to date is giving good results in service.

The present opinion of corrosion technologists in the offshore oil industry on protection of risers can perhaps be summarised by stating that Monel Metal sheathing is preferred in the tidal zone and in the turbulence areas below this level and that cathodic protection should provide the main protection below that level. Any coating on the underwater part of the riser must be of a type which will not disbond under CP conditions and for this reason fairly thin coatings are preferred at present. Neoprene sheet wrap is also being used on some new riser installations and results are reported to be good. There are less problems in coating splash zone and atmospheric exposure areas of risers and some types of coal tar epoxy and pure epoxy compositions have given satisfactory service.

The repair of risers in service and showing corrosion

presents great difficulty. Existing coatings must be removed to allow inspection and it is usual then to rely entirely on CP in immersed parts. Tidal and splash zone repairs are sometimes carried out by application of heavy epoxy mastic compositions applied by hand at low water after blasting. This type of repair is successful only if it can be done during quiet weather, since otherwise the coating tends to be washed off by wave surge. Glass cloth reinforcement of paste epoxy compositions is not favoured due to danger of concealed disbonding at the steel surface and consequent risk of severe corrosion in the crevice formed.

Past difficulties with the corrosion of risers in North Sea oil fields were due, perhaps, to reliance on techniques developed in the Gulf of Texas and Arabian Gulf where oil from wells has a temperature around 50° C. Gas in the southern North Sea has similar temperature and after processing before passing through a riser, such products usually have temperature between 30° C and 50° C. The much hotter oil from northern North Sea wells may only be reduced to 75° C to 85° C after processing and corrosion hazard of risers is, therefore, considerably greater and repair or replacement is also much more difficult due to the prevailing severe weather in this part of the North Sea. Oil producers have now become very aware of the difficulties and much effort is still being expended to find improved protection systems for these very critical components.

Above water support structures and superstructures of fixed platforms

Most structures are supported on braced tubular steel columns which are welded on to the steel jacket. Part of this steel may be wetted by waves in heavy weather, and all areas up to and including the underside of the support deck will be wetted by salt and also subjected to condensation, particularly at night. Steel box girders and stiffened deck structures on concrete platforms are exposed to similar conditions.

Tidal and splash zones

Steel in the tidal and lower splash zone will usually be coated with at least 400 μ of coal tar epoxy, sometimes applied over a holding primer. In some cases sand reinforced solvent free epoxy coatings with a high impact resistance have been used These parts should be very carefully painted during construction but, almost invariably, the coatings are damaged during installation and link-up by impact with crane barges. pile driving barges and even supply ships. It is not unusual to find that wire ropes have been passed round tubular columns and allowed to chafe off the epoxy coal tar coatings. It is commonplace to carry out total overhaul of this part of the structure after erection (or towards the end of initial drilling operation if the platform duplicates as a support for drilling equipment). Mechanical damage to coatings may total as much as 25 per cent of the surface coated and in such cases it is usual to reblast completely and re-apply the protective systems. Coal tar epoxy systems can be applied (over a zinc epoxy or iron oxide epoxy holding primer) down to the tidal zone, but below this level solvent free epoxy coatings which can displace water and which will cure underwater must be used; these can be either tar modified or tar free.

Support structure and deck support structures

Refs. 3-6

Above the tidal and lower splash zone it is common to use

bright coloured "high visibility" coatings (usually white, yellow or red) and there has been much debate on the properties of primers, build coats and top coats, and the relative merits of epoxy, vinyl and chlorinated rubber systems. The following is a brief review of the relative properties and observed performance in service.

Primers

It is usual to apply a zinc primer after blasting to SA 21 or 3 standard. Most operators prefer zinc silicate primers (about 75μ dft) but some use zinc epoxy primers (about 35μ dft); both are satiafactory in service. Self cure zinc silicate types rely on hydrolysis of the alkyl silicate to effect cure and may be troublesome in an arid climate or even in very cold low humidity conditions of the type that can develop on the Scandinavian coasts in anticyclonic winter conditions, when cold easterly winds are dehydrated during passage over the frozen interior land mass of Europe. In arid desert conditions cure can be effected by water spray, but this is not practical in dry freezing conditions. Coatings superimposed before effective cure has taken place can fail by rupture within the weak undercured zinc silicate and, in such cases, there is advantage in the substitution by zinc epoxy primers. Single pack zinc rich primers based on high molecular weight epoxy binders are effective when applied to ice free steel down to -20°C and can be overcoated within 24 to 48 hours.

Zinc silicate primers suffer to some degree from the inherent defect of low film strength. It is normal to use levels of pigmentation above critical pigment volume concentration (94 to 95 per cent by weight of zinc in zinc silicate, and 90 to 92 per cent by weight of zinc in zinc epoxy primers). They develop increased film strength during weathering when voids in the primer fill with zinc corrosion products, but these corrosion products when formed on the surface can detract from adhesion of superimposed coatings. Zinc primers are also troublesome in that they are rapidly contaminated by industrial atmospheres and when soiled with oil or grease, this soaks into the porous surface and cannot readily be removed. For these reasons, it is not good practice to use zinc primers as holding primers during prolonged construction periods. They should be of a type which will cure rapidly in the prevailing conditions and should be overcoated or "sealed" as soon as possible after they have cured. The sealing operation must also be approached with caution. Freshly applied zinc silicate primers, in particular, but also zinc primers to a lesser extent, contain entrained air in the voids and this is displaced in part by liquid components of the first coat of the system. If a high build, low solids coating is used as first coat then inevitably this must be of thixotropic nature in order to facilitate application of thick wet films without sagging. Air displaced by binder will pass through the thixotropic coating and if, in the meantime, this has "set" then the void or pinhole formed by passage of the air bubble will not close up again. It is essential, therefore, when overcoating fresh zinc silicate primers that the superimposed first coat or sealer should be fluid in consistency and should be applied in a fairly thin layer (25 μ to 35 μ). This is sometimes attempted by extra thinning of the first high build coat and applying a mist coat. This may perhaps provide a solution to the problem, but the correct remedy lies in formulation of a sealer coat of suitable consistency.

The problem is not so acute with zinc epoxy primers, but direct application of thick layers of very thixotropic, low solids coatings (such as vinyl or chlorinated rubber types) can give pinhole defects and should be avoided.

High build protective coating systems

Zinc rich primers will give excellent protection for steel provided that they are covered with a sufficient thickness of water resistant coating to prevent penetration of water to the sinc/iron interface. If water does penetrate, it can initiate sacrificial corrosion of the zinc and in due course the zinc corrosion products can cause detachment of the system but, in any event, eventually the steel will rust. The high build system must have sufficient thickness to protect high spots in the surface profile of the blasted steel (up to about 100μ), must have adequate thixotropy to prevent sagging on vertical surfaces at the specified wet film thickness, even when applied in double or perhaps triple the specified thickness in a corner or overlaps between spray passes. Three principal classes are used, these are briefly reviewed below:

High build vinyl systems: The early vinyl coating systems were based on plasticised vinyl acetate-vinyl chloride copolymers, maleic acid modified versions being used in primers to improve adhesion to steel, also extender resins, including petroleum resins and chlorinated paraffins.

Acrylic and methacrylic ester polymers, also fall within this class as do copolymers of styrene and vinyltoluene copolymers with butadiene and acrylic monomers. More recently vinyl ethers and vinyl acrylic copolymers have also been widely adopted. It will be appreciated, therefore, that the term "vinyl" covers much too wide a group of compositions to allow definition or specification of a paint system, but despite this users and their consultants frequently refer to for example, "a high build vinyl coating to give 200μ in two or three coats", without any definition of the type of material to be used.

Such lack of definition allows the competitive paint industry more than enough rope to hang itself. Within the group termed "vinyl" it is, of course, possible to make very useful and durable systems, particularly if multicoat, relatively low build (e.g. 3 coats each 75μ) products are used. Vinyl chlorideacetate copolymers properly plasticised give good water resistance and good durability but these properties can easily be dissipated by use of unsuitable migratory or volatile plasticisers, the excessive use of, e.g. petroleum resin extenders, by overpigmentation, or by use of unsuitable thixotropes.

Choice of solvent can also influence performance. High proportions of true ketone solvents give higher non-volatile coatings, but tend to be retained in thick films and can impair water resistance, or at least, resistance to condensation, e.g. 6 to 12 hours after application. High boiling solvents (e.g. cellosolve and butylacetate) improve spraying properties but tend to be retained in the film.

In offshore practice, vinyl systems have great attraction in that they are single pack, they can be used (in absence of condensation) at low temperatures and set rapidly to a tackfree condition. They can be overcoated without difficulty after long exposure periods. They have good chemical and mineral oil resistances, and develop very good water resistance after all polar solvent has evaporated. In practice, they do not always give the expected results and this is probably due to improper formulation or incorrect application.

Pila³ gives a useful review of technology of high build vinyl systems and he draws particular attention to the need for precise formulation detail if high durability is to be obtained. A careful reading of this typical paper will support the writer's view that this degree of detail is unlikely to be capable of definition in users' specifications and indeed may not be followed closely by the highly competitive world-wide offshore paint making fraternity.

The reason for the need for very close attention to detail of formulation is, of course, the use of rather low molecular weight polymers and copolymers which are needed to obtain even the relatively low solids (about 20 per cent by volume) compositions. Higher molecular weight (and more durable) copolymers give even lower solids and cannot be made into high build coatings without use of excessive pigmentation and/or excessive thixotropy which in turn are deleterious In brief, it is unreasonable to expect to use a low molecular weight preformed polymer and at the same time expect to make a high solids high build coating with good exterior durability. Sykes⁴ recently made the most valid observation that the paint industry, in its attempt to meet the somewhat unreasonable demands of its customers for high build coatings, has developed systems which are so critical that they must be used under the most precise control of application if they are to succeed. Such control is particularly difficult on the huge lattice type structures built for offshore work and it is for this reason that vinyl systems have given, and are likely to continue to give, lower performance than could be expected.

High build chlorinated rubber systems: Many of the comments made on effect of formulation on performance of high build vinyl systems apply equally to high build chlorinated rubber systems.

The solids content of chlorinated rubber resin solutions is governed primarily by molecular weight and demand for higher build products has led to adoption of ever lower molecular weight (and therefore lower solution viscosity) chlorinated natural and synthetic rubbers.

The author in his youth was taught by his senior and very experienced paint technical management that chlorinated rubber with lower solution viscosity than e.g. Alloprene 40 did not have good exterior weathering properties and even Alloprene 40 should be modified with a proportion of a drying oil alkyd if it was expected to give prolonged durability outdoors.

Demand for high build chlorinated rubber paints has led to widespread adoption of R10 grades and recently Caldwell and Fergusson⁵ published work on the durability of a wide range of coatings based on this low viscosity grade of chlorinated rubber. This work showed that in high actinic light (South Africa), some improvement in resistance to weather checking could be obtained by use of an ethylene/vinylacetate copolymer as plasticiser and/or use of a proportion of higher molecular weight chlorinated rubber or acrylic polymer as part of the binder. It was indicated, however, that at higher pigmentation, water resistance of such blends was reduced.

Again it must be said that owners', consultants', and applicators' specifications which merely define "a high build chlorinated rubber system" together with a film thickness, allow more than enough scope for improper formulation. Offshore exposure demands a high degree of water resistance, but it must never be forgotten that it also involves exposure to clear skies and sunlight. Any coating which degrades rapidly in sunlight will soon lose water resistance and will then fail to protect the zinc primer underneath and rusting will soon follow.

This type of failure of chlorinated rubber systems has been

seen on offshore structures and it must be concluded at this stage that without very precise and defined formulation chlorinated rubber high build systems are not well suited to protection of offshore support decks and superstructures. It may be significant to note that a UK investigation by the Department of the Environment of bridge painting systems has shown that coatings based on chlorinated rubber modified by major proportions of DCO alkyd give much improved weathering properties. It seems that the author's old teachers perhaps knew their job better than many of those who have followed them.

High build epoxy systems: The use of epoxy coatings on steelwork in underwater and tidal zones has already been described. In this section, the properties of epoxy coatings in splash zone and superstructure areas will be discussed; coatings for working decks will be described separately.

Coal tar epoxy coatings have been used in superstructure or machinery spaces for special reasons, but usually light coloured finishes are required and pure epoxy coatings are used. There have been attempts to overcoat coal tar epoxy coatings with light coloured cosmetic coatings (e.g. chlorinated rubber), but tar bleed is difficult to overcome completely and they are now rarely used.

Epoxy coatings have some definite advantages over chlorinated rubber and vinyl systems. They have, at least, equal water resistance, equal or better weather resistance, and much better solvent resistance. Chemical resistance is of the same order, in so far as the range of chemicals encountered on a platform is concerned. They have one major disadvantage. however, as traditional epoxy coatings derived from early work on chemical resistant systems (such as tank coatings) very rapidly develop such high resistance to strong solvents that they do not provide a good surface for overcoating. This defect may be capable of control (by limiting the intercoat interval) during some stages of construction or repair, but inevitably some areas will ultimately require late touch up repair both during erection, link up, machinery installation, and even later on due to mechanical damage in service. If such touch up repairs fail by lack of adhesion at overlaps, then the system can become quite impractical in service.

Earlier types of epoxy compositions also tended to require close control of the temperature and humidity conditions during application. Polyamide cured epoxy coatings do not cure well below 13°C to 15°C. Amine or amine adduct cured coatings tended to give "amine blush" or carbamate formation on the surface if applied at high humidities (e.g. RH over 75 per cent to 80 per cent). This surface defect is not always easily detected and can cause loss of adhesion of following epoxy coats.

For these reasons, it has become quite common to allow use of chlorinated rubber or vinyl systems as "cold weather alternatives" to specified epoxy systems. This in part has been due to Houston derived epoxy painting specifications defining polyamide cured systems, which although excellent in the Gulf of Texas, tropical South America, Pacific Islands and the Arabian Gulf, are virtually unusable in winter in the North Sea and even in summer in offshore conditions. A constructor or applicator faced with such alternatives will invariably choose the vinyl or chlorinated rubber cold weather systems, since when tendering he can rarely even guess the weather conditions which may prevail during the whole extent of the construction, erection or repair process. It must be said that many structures coated with vinyl systems, and some with chlorinated rubber systems, have given acceptable performances in service, but most have required major overhaul at sea before a good result was achieved.

Epoxy systems, when properly applied, have in general given better initial performance, probably due to lower risk of failure due to blistering in condensation conditions, but also due to much improved impact and abrasion resistance and not least to much better solvent and oil resistance.

During the last five years, determined efforts have been made to produce epoxy systems designed for North Sea conditions and capable of application in low temperature, high humidity conditions and capable of repair and overlap or overall recoating after prolonged curing intervals.

Accelerated polyamide adduct and amine adduct epoxy coatings have been developed which will cure at temperatures down to 5° C (there is promise in current work that even lower temperature cure can be achieved). Aromatic amine curing agents will give reasonable cure down to 0° C, but these products are not always acceptable for health reasons. Amine bloom and carbamate formation has been controlled by correct use of accelerators and elimination of free amine in adducts.

Isocyanate cure of high molecular weight (i.e. high hydroxyl content) epoxy resins allows the formulation of coatings (tar free and tar modified) which will cure at temperatures down to even -20° C, and diisopropanolamine modification of lower molecular weight epoxy resins to increase hydroxyl content has been more widely adopted. These modified epoxy resins can be cross-linked with isocyanate curing agents.

These classes of epoxy compositions have been used in sub-zero winter conditions during construction of several offshore deck structures, including Shell Brent B and Shell Dunlin A, which the author inspected closely during the summer of 1978 (two to three years after construction) and found no significant evidence of any delamination or loss of adhesion to the underlying zinc epoxy coating. During construction coatings were applied at temperatures down to about -20° C and during later construction and rection at temperatures up to about $\pm 15^{\circ}$ C. It was particularly significant that the general condition was much better than those of platforms inspected by the author which had been coated with combination epoxy/chlorinated rubber or epoxy/vinyl systems.

Isocyanate cured epoxy systems, however, are not ideal for all forms of offshore work. Pot life after mixing is short and they can blister or even become detached if applied over condensation. It is very easy to specify that the painting inspector must establish temperature and humidity conditions and calculate that steel is, for example, 3 to 5 °C above dew point before permitting painting. In practice life is much more difficult than that. He may check the weather forecast and check the air temperature, humidity and steel temperature and decide to allow blasting and coating to proceed.

Blasting offshore must be done in daylight and coating of blasted areas (or indeed on any areas after cleaning) tends to be done towards the end of a working day. Sudden change of temperature or humidity can and does occur and on occasion the inspector can be wrong in his assumption that condensation will be absent. There is still a need, therefore, for coatings which will allow offshore work to proceed with reasonable assurance of a good result, even when they are applied in less than perfect conditions. In brief, there must be a built-in safety margin, otherwise failure on some occasions is inevitable. It is difficult to build such a safety margin into high build vinyl or chlorinated rubber systems, but it is feasible with amine or polyamide cured epoxy coatings. These products are remarkably tolerant to both traces of water on the substrate and also to early condensation after application. A search was mounted, therefore, for coatings of this class which would cure down to $5^{\circ}C$ even at high humidity and which would allow overcoating or touch up after short or long intervals.

There was experience of similar problems and their solution with polyurethane decorative coatings used during construction and maintenance of ships' superstructure. The remedy was found to be by incorporation of a water resistant, but strong solvent sensitive extender resin in the polyurethane composition. A degree of success was achieved and a range of coatings produced which have continued to give good service during 10 to 15 years. The superstructure of "Queen Elizabeth 11" was coated, and still is maintained, with such a polyurethane system and shows excellent intercoat adhesion even when overcoated gloss on gloss for cosmetic purposes.

Similar expedients were examined in epoxy systems and a method developed for introducing long chain aliphatic groups into the epoxy molecule. This method allowed the production of epoxy coatings which retain the characteristic water and aliphatic solvent (i.e. oil) resistance, but reduced strong solvent resistance sufficiently to promote the key of following coats applied after long intervals. Primers, build coats and finishing paints can be produced and all can be used at temperatures down to 5°C and overcoated after intervals between 24 hours to months or even years of exposure. An added, and perhaps unexpected, bonus property was that the finish paints had much improved colour and gloss retention compared with the unmodified epoxy coating.

This class of coating has been adopted for repair coating of offshore platforms and also for onshore refinery and oil storage tank exterior coating. It has also found a substantial outlet in Holland for coating road bridges over waterways or estuaries.

It is indeed a typical example of the need to reassess the ultimate use of a coating composition and where necessary to modify or totally reformulate, rather than to supply the nearest product in the existing range.

Extension of the selling range is, of course, disliked by commercial and particularly by the manufacturing and financial management, but in the offshore field it is inevitable if the problem of application in hostile conditions is to be solved.

Conventional systems: Before leaving the subject of coatings for support structures and superstructures of offshore platforms, it is necessary to say that traditional oxidising coatings still find some uses. They may have inferior oil and water resistance to epoxy, vinyl and chlorinated rubber systems, but they are easy to use and they can be remarkably tolerant to adverse weather conditions and imperfect surface preparation. Epoxy ester and urethane/alkyd primers (e.g. red lead or zinc phosphate pigmented primers) have been used with success and it is interesting to note that Bailey *et al*⁶ found that a system comprising a urethane/alkyd primer and an old fashioned tung phenolic micaceous iron oxide finish outperformed a wide variety of sophisticated coatings on test pieces in the laboratory and on an offshore gas platform. This test is of interest because it shows that such materials can be used for repair under difficult conditions and the author has, from time to time, used such materials for this type of work. It would be unwise, however, to extrapolate this result to the assumption that such systems could be used for general protection of offshore structures. This would inevitably lead to increased failure by reduced resistance to water, solvents, oils and chemicals, and also due to reduced abrasion resistance.

Working decks

It is perhaps confusing to refer both to "deck structures" and to "working decks" and an explanation of the difference is perhaps required.

A "deck structure" includes all the structural steel support steelwork carrying modules, etc., and may, in fact, be a box girder with internal stiffeners. A "working deck" as it implies, is a horizontal surface perhaps inside a module or enclosure, or in the open exposed to weather and usually will be subjected to traffic ranging from heavy foot traffic to mobile cranes or fork lift trucks, drill pipes, containers, drums of all sorts and, of course, helicopters on the flight decks.

The factor in common with most offshore working decks is that they are quite small in relation to the number of men and the scale of work and it is very difficult indeed to find a suitable time for surface preparation and painting. Blasting is sometimes possible, particularly in the earlier type of structure which was fairly open to the weather. The new deep water structures in the northern North Sea have very few open decks and most decks are in enclosures; most of these are classed as hazard areas and are maintained at slight positive air pressure to prevent ingress of any gas from outside.

Epoxy coatings are almost invariably used on the decks, sometimes over zinc silicate and sometimes over zinc epoxy primers. If applied in good conditions they perform well, but tend to become smooth and slippery in service. Grit (sand or quartz) is often incorporated and some very heavily loaded sand/epoxy paste compositions applied in thick layers by mortar gun have proved very effective.

Repair at sea is always difficult and blasting may be very difficult and perhaps impossible. There is still a need for a rust tolerant composition, which can be applied on a damp surface and which will cure in high humidity conditions. The oil companies will welcome the chemist who can provide the complete answer or answers to those particularly intractible problems of offshore maintenance.

Conclusions

The paint industry may not always have reacted quickly to the

Discussion at Stratford Conference

MR T. R. BULLETT was interested in the examples of inadequate film protection from high build vinyl and chlorinated rubber coatings, which Dr Atherton had attributed to inadequate film thicknesses. Work on this subject had been carried out by the Paint Research Association for a number of years, specifically on failures in high build airless spray applied coatings, including epoxies, in tank and pipe linings. On microscopic examination, it was found that the coatings were honeycombed with ellipsoidal airsacs, which had been

challenge of the offshore oil industry and, in particular, to the special problems imposed by prevailing severe weather in the North Sea oilfields.

The oil companies and their consultants were perhaps partly to blame, since they were no doubt lulled into a sense of false security by the early success of fairly simple painting systems on structures built and operated in good weather areas. They have, however, contributed to the problems experienced in the North Sea by a tendency towards lax generic resin type specifications of coatings which have allowed unwary paint manufacturers to supply materials unsuitable for use in North Sea conditions.

The severely competitive nature of construction and repair work in offshore operations, together with the overpowering urgency of all offshore construction and repair procedures has tended to promote the use of the least complicated systems and, of course, the lowest cost systems within the approved descriptive specification are always chosen. Such situations have on occasions led to use of protective systems which have not performed well in service and which have required very expensive repair.

The situation is, however, rapidly correcting itself. Platform owners and paint manufacturers specialising in this work are now much more aware of the problems presented by North Sea conditions and real progress is being made in their solution.

It is easy to criticise the industries and their customers, but it is useful to remember that it is only about eight years since the results of the first mistakes on the Dogger Bank gas platforms were seen and only about three years since the outcome of the first efforts on oil platforms in operation in the British sector of northern North Sea were seen. The lead time from platform specification and order to start up of production is usually about three to five years and any unforeseen paint defects may not be apparent for one or two years after that.

Perhaps the industry has not been so dilatory in its efforts to correct the mistakes or misconceptions, but it is still useful to review where and why it went wrong.

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named vacuoles, often occupying half to two-thirds of the film thickness. Thus, the measured film thickness gives no true indication of the protective film thickness. Mr Bullett mentioned that the PRA was about to start a major programme designed to eliminate the source of this problem.

DR ATHERTON stated that the majority of the materials in which this effect had been noted were highly pigmented better results in practice.

MR E. L. FRENCH asked about the concrete semisubmersible structures which were attached to the sea bed by means of plastic-coated cables, and the problems of

this combined with much higher volume solids gives much

providing long-term protection to the steel. There were two problems, one being the prevention of fouling, and the other being the long-term protection of the reinforcing steel.

DR ATHERTON stated that the antifouling problem had not been covered by the paper as it is a controversial subject. It was now possible to provide protection against fouling for periods of up to twenty years with the new tin copolymer hydrolysable coatings.

Solvent loss from paint films*

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Summary

The manner in which solvents are lost from paints has a very important bearing on the surface appearance and mechanical properties of the films formed. Consequently, it is important for a formulator to be able to predict how a given solvent blend will

Keywords

Raw materials for coatings solvent solvent Processes and methods primarily associated with

drying or curing of coatings solvent evaporation manufacturing or synthesis azeotrope behave once the film-forming process commences and to what extent solvents will be retained in the film. This paper introduces simple, practical techniques which allow this to be achieved.

Properties, characteristics and conditions primarily associated with materials in general solubility parameter solvent parameter evaporation rate compatibility raw materials for coatings and allied products solvent volatility dried or cured films solvent retention

Le degagement de solvant à partir des films de peinture

Résumé

La manière par laquelle les solvants se dégagent des peintures exerce une influence importante à la fois sur l'aspect superficiel et sur les caractéristiques mécaniques de leurs films. Ainsi il est important que le formulateur sache prédire comment un melange

Losungsmittelverdunstung aus Anstrichfilmen

Zusammenfassung

Die Art, in welcher Lösungsmittel die Anstriche verlassen, beeinflusst die Ausbildung der Oberfläche und mechanischen Eigenschaften des gebildeten Films stark. Folglich ist es für den Formulierenden wichtig, vorauszusehen, wie sich eine gegebene

Introduction

Refs. 1-4

Formulators are being faced increasingly with the threat of environmental and legislational constraints on the free use of solvents. This, coupled with increasing labour and material costs, makes it more important than ever before that a series of simple, practical techniques should be available which allow "trial and error" methods in the formulation of costoptimised solvent blends to be avoided. This paper describes part of such a series of techniques which are being used successfully at several Shell establishments throughout the world.

A solvent for a paint should meet three main technical requirements, namely:

- It should dissolve the polymer or resin binder system present (solvent "power").
- (2) Give appropriate "solution" properties, e.g. viscosity, flash-point.
- (3) Have appropriate evaporation and retention characteristics.

The first and last requirements are very much inter-related and cannot be considered in isolation from each other, donné de solvants se comportera dès le commencement du processus de formation du film et à quel point les solvants seront retenus dans le film. Cet exposé présente des techniques faciles et pratiques pour atteindre ce but.

Lösungsmittelmischung verhalten wird, wenn der Filmbildungsprozess beginnt, und in welchem Masse Lösunsmittel im Film zurückbehalten werden. Diese Arbeit beschreibt einfache, praktische Techniken, die dies ermöglichen.

particularly from a practical viewpoint. Generally speaking, candidate solvents for a formulation are chosen on the basis of their cost, availability and with a volatility suited to the desired application technique. They are then combined to form a solvent blend which must retain sufficient solvent power as its components are lost from the film so as to avoid precipitation of the binder. This aspect of solvent blend design is commonly called "solvent balance" and is the topic with which this paper is mainly concerned.

Whilst solvent cost and availability are self-evident properties, a practical quantification of "volatility" is less straight forward. Several yardsticks can be adopted ranging from vapour pressures to one of the several evaporation rate measurement methods. The practical question which must be answered is "Which (if any) one of these measurements gives sufficiently reliable information on solvent balance and how this could be applied in a practical situation?".

The topic of solvent loss from polymer films has, not surprisingly, received considerable attention in the literature¹. It is generally accepted that the loss occurs in at least two stages: a "wet" stage and a "dry" stage. During the wet stage, solvent loss is fairly rapid and many workers have assumed that similarities to "pure" solvent blends can be made with a

^{*}Paper presented at the Association's Conference held at Stratford upon Avon from 20-23 June 1979.

fair measure of safety. This naturally facilitates any theoretical treatment, but still leaves a question regarding the applicability of these findings to paint systems. Any similarities between "pure" solvents and paint formulations vanish once a paint film enters the "dry" stage of formation. As Hansen² has pointed out in an elegant mathematical treatment, the rate determining step for solvent loss from a polymer during the dry stage is the rate at which solvent diffuses within the polymer. Moreover, Hansen³ has recently indicated that much of the data on diffusion coefficients must be viewed with some suspicion. Fortunately, Newman and Nunn⁴ in a review of published literature have shown that quite empirical rules can be made for selecting solvents with high diffusion coefficients. The same review demonstrates quite clearly that solvent loss in the dry stage of film formation is unrelated to the solvent volatility. In this paper, it is proposed to deal largely with the "wet stage" of film formation.

Solvent volatility measurement

Refs. 5, 6

Solvent volatility measurements fall into two types. The first of these bases its criteria of volatility on the properties of bulk solvent in the sense that an equilibrium property of the solvent is used. Examples are the boiling point and the vapour pressure and these require little further explanation. The second type of volatility data involves measurement of the rate at which a given weight or volume of solvent evaporates under defined conditions. Results are generally reported relative to some particular standard solvent such as n-butyl acetate or diethyl ether; absolute evaporation rates are less widely used.

Recently, a method of measuring evaporation rates using the "Shell Automatic Thin Film Evaporometer" has been adopted by the ASTM under standard number D.3539.76. This apparatus is shown in Figure I and consists of a humidity controlled double cabinet fitted with a thermostat and containing a sensitive balance connected to an external recorder. (Details of the operating conditions and commercial availability are contained in the ASTM method.) A relative evaporation rate of a solvent, R², is defined as:

 $\mathbf{R}^{\circ} = \frac{\text{Time taken for 90\%}}{\text{Time taken for 90\%}} \text{ wof n-butyl acetate to evaporate}$

(Equal volumes of solvent are used at 25 C, 0-5 per cent relative humidity, with an air flow of 21 1.min-1.). A filter paper substrate supported on a light metal framework is employed in order to obtain a reproducible spreading of the solvent. In Europe, similar work in Shell laboratories using the same definition for relative evaporation rate has been founded on the philosophy that one should seek to immitate a simple paint system. Accordingly, solvent evaporation rates are measured from a shallow dish containing the solvent in which 10 per cent tritolyl phosphate plasticiser is dissolved to simulate a binder system. In Figure 1, the small aluminium dish used to perform this so-called "liquid film" measurement can be seen to the lower left hand side of the filter paper. Rocklin⁵ has recently published details of a third type of measurement using the evaporometer where rates are determined from solvents distributed on an aluminium disc rather than a dish or filter paper. This type of measurement from a so-called "smooth surface" represents an attempt to reduce "the effects of instrument peculiarities and variations in standardisation". In addition, Rocklin's paper provides an excellent account of the technique of performing evaporation measurements.

In Germany, DIN procedure 53170 is widely used. This



Figure 1. Shell Automatic Thin Film Evaporator

again employs a filter paper and defines a relative evaporation speed (S) as:

- s evaporation time of test solvent
- evaporation time of diethyl ether

(Equal volumes of solvent are used at 20°C, 65 per cent relative humidity in a turbulent air flow.) An obvious point of difference between the evaporometer and DIN type of measurements is the definition of the evaporation rate. Besides using a different standard solvent, the evaporometer measurements (i.e. filter paper, smooth surface and liquid film) are based on the behaviour of the first 90 per cent of the solvent to evaporate, whilst the DIN method considers the total quantity of solvent.

Comprehensive lists of solvent evaporation rates are published elsewhere⁶; Table 1 illustrates comparative data for a number of hydrocarbons and alcohols. In view of the definitions, the reciprocal of the DIN evaporation speed must be used in any direct comparisons with evaporation rates obtained from either the evaporometer or vapour pressure data.

Pseudo-azeotrope formation

Refs. 7 11

It would be very convenient if solvents evaporated from blends in a way which was directly allied to their relative evaporation rates. Unfortunately this is not so. For example, if blends of xylene with n-butanol are considered, the evapora-

		Solvent volut	iniy uuru			
Solvent		Auto (n-	matic Evaporo butyl acetate=	Vapour pressure	DIN 53170	
Solvent		Liquid Film	ASTM D3539.76	Smooth Surface*	(kPa, 25°C)	(diethyl ether $= 1.0$)
Toluene		2.3	2.0	2.14	3.796	5.7
Shellsol A	al)	0.75	0.76	(0.63)	1.000	15.1
(aromatic hydroca	rbon fraction)	0.25	0.20	(0.26)	0.400	46
Isopropanol	(IPA)	2.2	1.5	2.36	5.913	11.0
n-Propanol	(NPÁ)	0.94	0.94	1.22	2.730	16.0
sec-Butanol	(SBA)	1.1	0.89	1.15	2.357	20
Isobutanol	(IBA)	0.85	0.64	0.775	1.545	25
n-Butanol	(NBÁ)	0.46	0.47	0.477	0.864	33
Methylisobutylcarl	binol (MIBĆ)	0.3	0.28	0.285	0.800	66

Table 1 Solvent volatility data

*Data in brackets are extrapolated from vapour pressures using relationship given in reference 5.

tion rate data in Table 1 indicate that xylene is more volatile than n-butanol. If the blends behaved ideally, it would be expected that the residual solvent would become richer in butanol throughout the course of evaporation. In practice, blends can grow richer in either butanol or xylene or neither, depending on the composition of the solvent. Snowden and Tysall demonstrated this for solvents containing plasticiser⁷. Ellis and Goff⁸ have published an interesting article which examines this phenomenon in detail using GLC measurements on solutions of both alkyd resin and linseed oil. In addition, they put forward the idea of formulating solvent blends having a composition which corresponds to an azeotrope so as to avoid problems of solvent balance. (The author has adopted a similar strategy in this work, but has chosen to use the term "pseudo-azeotrope" to emphasise the importance of the dry stage of film formation).

Walsham and Edwards⁹ developed a model which satisfactorily describes the evaporation behaviour of solvent blends not containing any dissolved resin; they based their work on that of Sletmoe¹⁰, who found that the solvent evaporation was rate limited by boundary layer diffusion into the vapour phase. On this basis, the rate of evaporation is proportional to the vapour pressure of the solvent. This line of reasoning was continued by assuming that deviations in evaporation behaviour from ideality were directly analogous to deviations from Raoult's law of vapour pressures and could be corrected accordingly using activity coefficients. Since for most solvent molecules, activity coefficients are determined largely by the chemical functional group and only to a minor extent by the nature and size of the hydrocarbon part of the molecule, it is possible to prepare graphs of activity coefficients for "classes" of solvents.

Solvents used in the paint industry can be divided for the present purposes into three classes: hydrocarbons, alcohols and glycol ethers (hydroxyl group), and ketones and esters (carbonyl group).

This classification, in conjunction with data published by Deal and Derr¹¹, has been used to construct graphs of solvent activities which can be used in a way similar to that lescribed by Walsham and Edwards. Figure 2 shows the activities of alcohols and hydrocarbons relevant to this publication. These activities (γ) may be used to define a corrected solvent evaporation rate (R) as being equal to $R^{\circ}\gamma$. Solvents from each of the three classes just referred to show positive deviations from Raoult's law when blended. However, the deviations from ideality are most marked in the case of alcohol/hydrocarbon blends and consequently have been chosen to test the practicality of the various volatility measurements coupled with the activity correction.



Figure 2. Solvent activity data

A working hypothesis for solvent behaviour in the wet stage of film formation is that the *relative* rates of solvent loss are adequately described by $R^{\circ}\gamma$. This expression can then be used to define a pseudo-azeotrope in the case of a hydrocarbon/alcohol combination as:

$$R_A^{O}$$
. $y_A = R_{H/C}^{O}$. $y_{H/C}$

This relationship can be rearranged to:

$$R_A^{\rm o} / R_{H/C}^{\rm o} = y_{H/C} / y_A \ldots (1)$$

The total volume fraction of solvent is equal to 1.0 and therefore, for each chosen alcohol content, the amount of hydrocarbon is automatically defined in a binary blend. Figure 2 allows the determination of $\gamma_{H/C}$ and γ_A and hence the value of $\gamma_{H/C}/\gamma_A$ as a function of solvent composition at the pseudo-azeotrope point. This relationship using expression (1) in turn allows the volatility of the (*pure*) hydrocarbon and alcohol solvents to be related to the composition at the pseudo-azeotropic point as shown in Figure 3. The various solvent volatility data in Table 1 may now be used in conjunction with Figure 3 to predict solvent compositions at the pseudo-azeotrope. These predicted compositions are summarised in Table 2.



Figure 3. Solvent composition at pseudo-azeotropic point

these resins, therefore, provide an excellent system for testing the predictions in Table 2. Moreover, epoxy resin formulations are also systems where alcohol/hydrocarbon blends play a key role in the cost optimisation process.

Solubility prediction and solvent balance

Ref. 12

The use of solubility parameters to quantify solvent power is now well-established. These parameters can also be used to describe the solubility of resins and polymers when maps are generally used; Ramsbotham¹² has recently published details of such maps, which deal quite explicitly with the solubility characteristics of epoxy resins. These maps allow quantitative information to be obtained on the range of compositions of various alcohol/hydrocarbon blends, which are solvents for various solid grades of Shell epoxy resin (Epikote). For convenience, these compositions for two Epikote grades, 1001 and 1004, are summarised in Table 3; these data are valid for all formulations containing ≥ 10 per cent w dissolved resin

Armed with a solubility map and having selected an alcohol/ hydrocarbon combination with a volatility suited to the particular application technique, it is necessary only to find out if the pseudo-azeotrope is a solvent for the resin. As Table 3 shows, there is usually a range of alcohol/hydrocarbon compositions which dissolve the resin. If the composition of the residual solvent in the wet stage of the film

	Predicted pseu	do-azeotropic co	mpositions	
Percentage	volume of alcoh	ol in hydrocarbo	n at pseudo-aze	otrope*
		alco	hol	
IPA	NPA	SBA	IBA	NBA
 45	24	27.5	22	12.

Table 2

hydrocarbon IPA NPA SBA IBA NBA MIBC (a) 45 24 27.5 22 12.5 7.5 Foluene (c) 49 31 30 22 14 8 (d) 63 37 33 24 15 13 (e) 29 22 18 15 11 ~4 (a) >90 54 60.5 50.5 33 24 (b) 14 53.5 52 41 33 22 (d) ≥90 73 72 53.5 38 26 (d) ≥90 90 >90 84 63 42 40 (e) 57.5 44.5 38.5 32.5 26 15 (a) ≥90 ≥90 ≥90 >90 71 53 shellsol A (c) ≥90 ≥90 ≥90 >90 79 75						alcoh	ol						
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	ydrocar	bon	IPA	NPA	SBA		IB	A	N	IBA		MIBC	:
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		(a)	45	24	27.5		22	2		12.5		7.5	5
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Foluene	(c)	49	31	30		20	,		14		8	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		(d)	63	37	33		24			15		13	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		(c) (a)	> 00	22	10		1.	, 				~4	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	(a (t) (ylene (c) (c) (e	(b)	> 90	53.5	52		41	0.5		33		24	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		(c) (d)	≥90 ≥90	73 90	72 84		53	5.5 1		38 42		26 40	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		(e)	57.5	44.5	38.5		32	2.5		26		15	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		(a) (b)	≥ 90 ≥ 90	≥ 90 ≥ 90	≥90 ≥90		≥90 ~95)		71		53 58	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	ihellsol A	(c) (d)	≥ 90 ≥ 90	≥ 90 ≥ 90	≥90 ≥90		~ 95	5		71		50	
Data are reported as follows: ASTM D3539.76		(e)	≥ 90	~92	82		71			58		36	
ASI M D3539.76	Data are	e reported	as follows:	Liquid films	.:	34/4							(a)
Vapour Pressures				ASTM D3539.76		••	••	• •	• •	••		••	(b)
DIN 53170 (reciprocated))	Vapour Pressures	••	•••	••	19.12		•20•2	• •	• •	(c) (d)
			l	DIN 53170 (reciprocat	ed)	••			•••				(e)

It has already been stated that a formulator bases his choice of solvents on their availability and price coupled with their volatility and solvent power. Viewed in a practical light, a formulator will generally seek to maximise the hydrocarbon content of his solvent blends so as to minimise costs. Oxygenated solvents such as alcohols, ketones and glycol ethers will increase the cost and, therefore, since the alcohols are usually the cheapest of these solvents, the commercial importance of alcohol/hydrocarbon blends becomes apparent.

3

S

Since neither alcohols nor hydrocarbons are solvents for most of the solid grade epoxy resins, but blends of them are,

remains within these limits, a balanced formulation has been obtained. Thus, if a pseudo-azeotrope is initially a solvent for the resin, this working hypothesis states that it will also be a balanced blend

At this juncture, it is necessary to examine what happens on departing from the pseudo-azeotropic composition, Reference to the activity data in Figure 2 indicates that activities increase in value as the amount of solvent decreases in a blend and vice versa. In the case of a pseudo-azeotrope of hydrocarbon/alcohol, increasing the alcohol content would lower its activity and raise that of the hydrocarbon. This

		Sorrent of	enus for Epikore	restris		
Epik	ote 1001: Permissi	ble percentage ve	olume of alcoho	l in hydrocarbor	n to form a solv	ent*
			alcohol			
Hydrocarbon	IPA	NPA	SBA	IBA	NBA	MIBC
Toluene	7-63 (3) (15.5)	6-69 (2.5) (13.5)	7–69 (3.5) (13.5)	8-63.5 (3.5) (15.5)	9–76 (4) (13)	12-62 (5.5) (16)
Xylene	11-60 (5.2) (16.5)	10–68 (4.5) (14)	14.5–65.5 (7) (14.5)	13–59 (6) (16.5)	12.5–70 (6) (13)	21–54.5 (9.5) (18.5)
Shellsol A	15–55 (6.5) (18)	14–65 (6.25) (14.5)	16.5–62 (7.5) (16)	17–54.5 (8) (18.5)	19–68 (8) (13.5)	t
Epik	tote 1004: Permiss	ible percentage v	olume of alcoho	l in hydrocarbo	n to form a solv	ent*
				alcohol		
Hydrocarbon	IPA	NPA	SBA	IBA	NBA	MIBC
Toluene	11–56 (5) (18)	11–62 (5) (16)	13–61 (6) (16.5)	13–55 (6) (18)	11–65 (5) (15)	19–50 (8.7) (20)
Xylene	18–52 (8) (19)	17-67 (7.5) (14)	21–57 (9.3) (17.7)	22–51 (10) (19.5)	19-63 (8.5) (15.5)	50 (20)
Shellsol A	50 (20)	24-57 (10.7) (17.5)	31–51 (13.3) (19.5)	50 (20)	27–59 (12) (17)	-

	Table 3					
Solvent	blends for	Epikote	resins			

*These compositions were determined by titrating solutions containing 20% resin dissolved in 50/50 blends of alcohol/hydrocarbon with both the hydrocarbon and the alcohol to a turbid end point. Figures in parentheses refer to the approximate resin content (%w) of the solution at the end point. The similarity in relative densities of the hydrocarbons and alcohols is such that the above data are applicable to

The similarity in relative densities of the hydrocarbons and alcohols is such that the above data are applicable to %w calculations without significant loss of accuracy.

120 % w in 50:50 MIBC/Shellsol A gives a very turbid solution.

would, therefore, result in a blend which would become increasingly rich in alcohol as evaporation progressed. An analogous state of affairs would also apply to hydrocarbonrich blends.

This line of reasoning in the context of epoxy resins implies that if a solution is made in an alcohol/hydrocarbon blend, such that the solvent composition departs significantly from that of the pseudo-azeotrope, the blend will be out of balance. Since neither hydrocarbons nor alcohols alone are solvents for the resins, a film of an out-of-balance resin solution applied to a clean glass plate would be expected to become turbid as resin precipitated from solution during the wet stage of film formation. This does indeed happen and experiments with solutions containing 20 per cent w of dissolved *Epikote* 1004 allow a determination of the extent of the compositions of balanced alcohol-hydrocarbon blends for the resin. These are recorded in Table 4.

Balance is achieved over a range of compositions for two

reasons, namely:

- Resin solubility is achieved over a range of compositions such that there is scope for some change in solvent composition during evaporation. (On a solubility map this would be constructed as solubility parameters moving within the area of solubility).
- (2) The power of solvents required to dissolve an epoxy resin *decreases* as the concentration of resin increases during the wet stage of film formation¹². (For this reason, *Epikote* 1001 was not chosen for balance trials since it does not always give completely unambiguous information. It dissolves at high concentrations (> ca 60 per cent w) in aromatic hydrocarbons).

Bearing these points in mind, the experimental information described in Table 4 can now be compared with the various predictions in Table 2 to assess the applicability of theory to practice.

		Solvent ba	Table 4 lance for Epikoto	e 1004				
	Percentage volum	ne alcohol in hy	drocarbon to acl	nieve good prac	tical balance*			
	alcohol							
Hydrocarbon	IPA	NPA	SBA	IBA	NBA	MIBC		
Toluene Xylene Shellsol A	35-50 no balance no balance	20-35 50-67 no balance	20-30 50-57 no balance	13-25 40-51 no balance	1115 25-40 59 (borderline)	no balance no balance no solution		

*Balance was judged by making solutions containing 20% Epikote 1004 and using them to draw films (150 μ , wet) on degreased glass plates. A solution was judged to be in balance when the film dried to a clear, smooth finish; light orange peel was taken as a sign of borderline balance.

Solvent balance—Theory and practice

Ref. 5

If the results in Tables 2 and 3 are compared, many of the predicted pseudo-azeotropes lie outside the range of compositions corresponding to solvents for the resin. Reference to Table 4 confirms that these are indeed combinations for which "no balance" is observed. There is one possible exception, that of Shellsol A/n-butanol blends. All data, except the DIN evaporation speeds, fail to predict a solvent balance where it is indeed observed. However, this is in line with most DIN predictions, which predict lower alcohol contents than other volatility data and must be considered an exception rather than a rule.

If the results generally in Tables 2 and 4 are considered. predictions using measurements on the Shell Automatic Evaporometer are far better than those based on either vapour pressures or DIN evaporation speeds. DIN evaporation speeds predict blends which are too low in alcohol content; vapour pressures tend to predict blends which are too high in alcohol content. The Shell Evaporometer measurement predictions, using smooth surface evaporation rates, tend to yield blends which are rich in alcohol. There is little to choose between predictions based on ASTM D3539 measurements (filter paper) or liquid film data; both give predictions which are acceptable in practice. (All evaporometer predictions were acceptable for Epikote 1001, although blends which tended to become rich in hydrocarbon during evaporation yielded results which did not satisfactorily distinguish between the various predictions).

Rocklin's work⁵ provides valuable insight into the reason for the generally poor predictions obtained with DIN evaporation data. He showed that there is quite a strong interaction between the cellulose fibres of filter paper, used as a substrate in the method, and hydroxylic solvents such as the alcohols. Moreover, this interaction is particularly noticeable during the evaporation of the last 10 to 20 per cent of the solvent from the paper, where the weight loss on a recording balance deviates guite markedly from linearity as a function of time. By calculating evaporation speeds based on the time taken for 100 per cent of the solvent to evaporate, the DIN method clearly leads to evaporation rates which are too low for the alcohols. ASTM D3539, also a filter paper method, by contrast gives good balance predictions for the practical tests described here. The indication is, therefore, that evaporation data calculated on the time taken for the first 90 per cent of the solvent to evaporate avoid most, if not all, of the artefacts introduced by filter paper-solvent interactions.

At the other extreme, data based on solvent vapour pressures predict blends which are too rich in alcohol. Again, reference to Rocklin's work on evaporation from smooth surfaces⁵ reveals that although the relationship between relative evaporation rate and vapour pressure is linear in the case of hydrocarbon solvents, this is not the case for alcohols. Indeed, if a linear relationship existed, it would be expected to find much higher evaporation rates than are measured. In this light it is not surprising that vapour pressures predict blends which prove in practice to be too rich in alcohol.

Predictions using data obtained from the automatic evaporometer proved to be reliable when judged using the practical test of a film drawn on a glass plate. This has also proved to be the case in all applied solvent formulation work. However, there is no escaping from the fact that the various methods of volatility measurement do sometimes give quite

widely differing predictions for a pseudo-azeotropic composition. There is no doubt that the very simple theoretical treatment used to correct for solvent evaporation from a blend could be improved, but it is open to debate whether this would improve the quality of predictions from a practical point of view. Although this requires some further experimental work continuing that initiated by Rocklin⁵, it is more probable, in the author's opinion, that the differences are simply inherent in the methods used for measuring solvent evaporation rates. In mitigation, it must be stated that alcohol/ hydrocarbon blends are among the most non-ideal used by paint formulators. If the artificiality is considered, of determining all evaporation data at a stipulated temperature, air flow and relative humidity, for subsequent application under widely differing applied conditions, it is perhaps remarkable that predictions are as good as they are !

Solvent formulation

Ref. 4, 6

The establishment of a technique for predicting solvent balance using pseudo-azeotropes, together with solubility data, permits the setting up of a procedure for the formulation of a solvent blend. In the case of the epoxy resins which have been used in this study, a typical procedure is as follows:

- (a) Select the resin/curing agent system suitable for the end use and establish the way in which the formulation will be applied.
- (b) On the basis of the technique of application, select candidate solvents for the solvent blend primarily on the basis of their volatility. For example, a typical requirement of a spray-applied formulation is a rapid initial film build (volatile solvents) with sufficient "wet-edge" (less volatile component) to give a smooth, even finish.
- (c) Take the solubility map of the resin (the resin is invariably more difficult to dissolve than the curing agent) and note down the candidate solvents and their prices.
- (d) In end uses, particularly those with ambient temperature cures, where rotained solvent could be a problem (dry stage of film formation) try to restrict the choice of solvents in accordance with the guidelines published by Newman and Nunn^{4,6}. (This is not always possible and the technique then is to design the solvent behaviour in the wet stage of film formation, so that the most involatile solvents do indeed have high diffusion coefficients as defined by Newman and Nunn^{4,6}. This is a way of keeping the film "open" longer).
- (e) Select suitable pseudo-azeotropic pairs of alcohol/ hydrocarbon solvents (usually one pair is sufficient) and note their position on the solubility map.
- (f) Maintain the solvent ratio of the pseudo-azeotrope and add a third (true) solvent bearing in mind points (b) and (d). As a general rule, this will improve balance. It is at this stage that the skill of the solvent formulator plays a great part. Solvents are added with an eye to achieving the required viscosity, flashpoint and other constraints; techniques exist for predicting these properties, but are outside the scope of this paper. Calculation of corrected evaporation rates in the solubility map may now reveal that the blend may be cheapened by, for example, raising the hydrocarbon content.
- (g) Having decided upon a trial solvent blend, the formulator decides how this can be best distributed between



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his epoxy-resin and curing agent (solubility maps) and a small-scale test is conducted.

These guidelines, with suitable modification, are generally applicable to many paint formulation problems. As the complexity of the formulation increases, a computer can be a useful aid to the formulator, but it can never be a substitute for knowledge of the basic principles governing the way in which solvents interact in blends and coatings.

Conclusions

During the wet stage of film formation, the relative rates of loss of solvents from films can be predicted with an acceptable degree of accuracy by combining simplified solvent activity data with relative evaporation rates measured using a commercial Automatic Evaporometer constructed to Shell designs. Evaporation data based on bulk solvent properties, such as vapour pressure, or data which do not compensate for any possible substrate-solvent interactions are unreliable.

These concepts can be applied to solvent formulation by using them to predict pseudo-azeotropes and in turn using these together with solubility maps as a basis for solvent blend design.

Discussion at Stratford Conference

DR J. C. WEAVER asked Dr Ramsbotham if he considered that the next generation of evaporation measurements could be performed using gas chromatography with temperature programming to give better data on solvent evaporation versus retention.

DR RAMSBOTHAM pointed out that what was actually being measured in the Evaporometer was the evaporation rates of pure solvents relative to the standard, which were fixed quantities. The results were tabulated and were available, so that it was not necessary for them to be measured by other workers. The paper had been intended to indicate in which ways these figures could be utilised.

On gas chromatographs, Dr Ramsbotham referred to work carried out in America by Ellis and Goff which used this approach, and also in combination with pseudoazeotropes. However, he expressed the opinion that unless it was intended to follow the changes quantitatively with extreme accuracies at every step of the way, there seemed to be little point in using the complicated GC technique. The GC technique has far more relevance when examining the solvent retained in the film during the dry stage of film formation, but this had not been covered in the paper.

DR W. FUNKE thought that there was good reason to measure the composition of the solvents in the drying film as in some cases phase separation takes place in the late stages of film formation, and it is of interest to know at what stage this takes place. Dr Funke had used a head space gas chromatograph to study the retardation of evaporation of residual solvent, left as an imbalanced phase, with both two and three component solvent mixtures. Dr Funke asked if it were possible to combine such gas chromatography with the Shell Evaporometer.

DR RAMSBOTHAM stated that it was indeed possible to couple the exhaust gases from the Evaporometer to a GC. He emphasised that a major point of the paper had been the application of the volatility data, in conjunction with

Acknowledgements

The author extends his sincere thanks to many colleagues within the Shell Group whose work has been drawn upon in this publication and especially to Mr J. W. van der Klauw who performed the solubility and balance measurements. He is also grateful to the directors of Shell Research BV for permission to publish these findings.

Received 18 December 1978

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solubility maps, to design a solvent blend for the binder system which would remain a solvent during the drying process and not change in composition during drying which might cause binder precipitation.

DR FUNKE pointed out that in the case where chemical reactions were taking place, the parameters involved were changing continuously, and it was not possible to predict a solvent blend as in the paper.

MR S. L. DAVIDSON informed delegates that work on a form of evaporometer had been carried out in America as early as 1953.

DR RAMSBOTHAM stressed that whilst the . Evaporometer was basically a simple device, it had been refined and the important point here was the combination of the data obtained with the solubility maps as an aid to formulation of true solvent blends.

MR T. R. BULLETT congratulated Dr Ramsbotham on a useful technique, but queried whether the effect of interactions with the resin component on the activity coefficients of the various components in the solvent blend could be neglected for the whole of the wet stage, bearing in mind that this might extend up to say 80 per cent resin content.

DR RAMSBOTHAM stated that as far as they had found, to a very good approximation the answer to the question was yes. In terms of solvent balance, if a system is taken which is out of balance in the initial stages of evaporation, starting with say 30 per cent alcohol, then because of the form of the activity curve, the system will become deficient in alcohol resulting in the activity coefficient of the alcohol becoming larger, and relatively more alcohol being lost. Thus, it is the initial stages of evaporation which are the most important in determining whether a solvent balance is maintained. It is possible for a solvent blend on the

borderline of balance to move slightly out of balance and then due to entropic interactions move back into balance again, but this is a very complicated subject and outside the scope of the paper.

MR A. SAARNAK asked if the relative humidity had an influence on the relative evaporation rates and also about the influence of the polymer.

DR RAMSBOTHAM stated that the humidity did have an influence on the relative evaporation rates. For conventional solvent based systems, the effects of humidity are not large enough significantly to effect the predictions for solvent balance. For systems where solvent is used in combination with water, then the effect becomes significant. The higher the relative humidity of the surroundings, the slower is the evaporation of the water content of the blend.

Next month's issue

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

Water borne industrial thermosetting systems by H. J. Luthardt and W. Burckhardt

The influence of light intensity on photoactivity in TiO₂ pigmented systems by T. A. Egerton and C. J. King

Aqueous coil coatings by E. J. Percy and F. Nouwens

Dispersion of pigments: What is the ultimate? by D. M. Varley and H. H. Bower



On 23 June 1979, a meeting was held in Paris to discuss the formation of an international co-ordinating committee for societies covering the surface coatings industries to be known as ICCATCI. Those present were:

Standing (l-r); K. Meguro (JSCM), D. Pagani (FATIPEC) Mr Blake (translator), J. McCormick (FSCT), F. M. Smith (OCCA), Ms A. Chauvel (hostess).

Seated (l-r); C. Bourgery (FATIPEC), B. Andersson (SLF), Mme Bourgery, M. F. Kooistra (FATIPEC), J. Roire (FATIPEC).



Shown at the Annual Ladies' Night of the Bristol Section (see page 372) held on Friday 23 March are:

Standing (l-r); Mrs Bayliss, Mr F. Hellens (Chairman, Newcastle Section), Mr Harper, Mr D. Bayliss (Chairman London Section), Mr D. Heath (President, Birmingham Paint Varnish and Lacquer Club), Mr A. J. Hughes (President, Paintmakers Association), Mr A. McLean (President, OCCA), Mr R. H. Hamblin (Director & Secretary), and Mrs Hellens.

Seated (l-r); Mrs E. Harper (Chairman, Bristol Section), Mrs Heath and Mrs Hughes.

Section Proceedings

Natal

The causes and prevention of fire in paint manufacture

A meeting of the Natal Section was held on Wednesday 27 June 1979 in the Science Lecture Theatre S1, University of Natal, Durban, when 24 members and guests were present to hear a lecture by Mr S. J. Smith, Deputy Chief Officer of the Durban Fire Department, entitled "The causes and prevention of fire in paint manufacture and spray application".

Having shown an excellent film on the hazards of flammable liquids, Mr Smith divided into five groups the precautions which should be taken in industrial situations:

- Buildings Must have fireproof walls (9½ inch brick); must be compartmented, separating storage from production areas; self-closing fire doors activated by a fusible link must not be obstructed, e.g. by drums.
- Plant Wiring and electric motors must be regularly maintained; drums used to carry or measure flamm-

Information Received

PM accepts Honorary Fellowship

The Prime Minister, the Rt. Hon. Mrs Margaret Thatcher, PC, MP, has accepted invitations of the Chemical Society and the Royal Institute of Chemistry to become an Honorary Fellow of both organisations and has been so elected.

Mrs Thatcher has strong associations with chemistry, having studied chemistry at Somerville College, Oxford, and then worked as a research chemist for British Industrial Plastics Ltd and J. Lyons. In 1971, when she was Secretary of State for Education & Science, she was the guest of honour at the OCCA-23 Exhibition Luncheon.

Chemical writers award

BASF is offering an award of £1000 for the journalist who has contributed most to the awareness and understanding of the chemical industry and its benefits to society. Judges for the award will be the Baroness Phillips, JP, HM Lord Lieutenant of Greater London, Michael Hyde, *Chemical Insight*, and Martin Trowbridge, Director General of the Chemical Industries Association.

To be considered for the award, articles must have been published in a British journal between 1 October 1978 and 30 September 1979.

UK agency

Fireliant Equipment Co. Ltd and Paramount Metal Works Ltd have signed an agreement under which Fireliant will now market all flammable liquid safety containers manufactured by Paramount in the UK.



The new safety waste solvent disposal unit available from Fireliant.

Previously, both Fireliant and Paramount have been marketing Paramount-made products, a range of safety containers for storing, dispensing and applying flammable liquids, and the new deal makes Fireliant the biggest UK supplier of British-made flammable liquid safety equipment.

Filter press installation

The first production model of a completely new 125 cu ft capacity filter press has been installed at the Stockport factory of

able solvents must be self-closing; bowsers should be of the "dead-man's-finger" type.

- (iii) Flammability of materials stored, used and produced must be known.
- (iv) Employees must be trained to recognise fire risks, and to fight fires; also must be alert to urban terrorism – to form an effective team to fight fires in case all fire services are fully committed elsewhere.
- (v) Fire Protection Equipment must be clearly marked, accessible, and serviced at least annually. Alarms must be regularly tested, escape routes kept clear, and not padlocked.

Mr Smith stressed that each company should give the Fire Department contact phone numbers (e.g. the Chief Chemist) who could advise on the dangers, toxicity, flammability etc., of drums or chemicals stored on their premises.

Following a large number of questions, the vote of thanks to Mr Smith was proposed by Mr J. R. Gush.

> Burrell Colours Ltd. Makers of the press, P & S Filtration Ltd, have installed the equipment under a novel "trial before purchase" agreement. P & S will have access to the machine during pigment production to assess and improve its performance.

> Among the features of the P & S press is the self-compensating hydraulic closing system which makes allowances for the expansion and contraction of the filter plates containing the slurry during filtration.

New products

Cationic surfactant

Alkaril Chemicals Ltd, specialists in imidazoline chemistry, have available Alkazine O, oleic hydroxyethyl imidazoline with an imidazoline content in excess of 85 per cent.

Imidazolines are prepared by reacting a fatty acid with an n-substituted ethylene diamine. The initial product is a fatty amido amine, which on continuing the reaction and altering the conditions, cyclises to form the five-membered imidazoline ring.

During the cyclisation, conditions are such that the newly formed ring may be ruptured leading to undesirable byproducts, a poor conversion rate and a low yield of imidazoline in the finished product. For this reason, imidazolines are commonly sold on an activity basis rather than on their imidazoline content.

Alkazine O, a cationic surfactant, is absorbed on to negatively charged surfaces such as glass, plastics, textile fibres,

INFORMATION RECEIVED JOCCA

papers, siliceous materials and oxidised metals. It is used as a wetting agent, a foaming agent, an acid inhibitor, an emulsifier and a flocculating and dispersing agent.

Pressure vessel coatings

A new process described as a breakthrough in coating technology has been announced by Plastic Coatings Ltd. The process gives an all-over coating of enclosed pressure vessels with Vylastic RS60 PVC1 which is used in the water treatment and chemical industries. Vylastic RS60 PVC1 plastisol coating is applied in thicknesses up to 6 mm and provides a tough, seam-free corrosion resistant finish.

New sealer

A new grey acrylic lacquer sealer, PS-19, formulated for superior adhesion on aluminium substrates, has been introduced by Inmont Corporation as the latest addition to its Rinshed-Mason line of automotive refinishing products.

The new undercoat, intended for use with Inmont's Alpha Cryl acrylic lacquer topcoats, does not require sanding after it is applied, but can be lightly scuffed if required to remove dirt particles.

New precision refractometer

ChemLab Instruments Ltd, UK agents for Atago, have announced the introduction of a new high accuracy precision Abbe Refractometer. The new Abbe Model 309 replaces Model 308, and gives improved measuring accuracy and ease of use. The refractive index range is nD 1.30000 - 1.7100.

New DC motors

Two new metric frame size DC motors, designed for variable-speed control from single phase AC supplies, have been introduced by Normand Electrical Co. Ltd. The new D90 and D112 frames are an extension of the company's established range of DC machines and can be supplied as a packaged variable-speed drive complete with full-wave thyrister controller. The motors have applications such as for conveyors, pumps, feeder mechanisms etc.



The new metric frame motors from Normand Electrical Co. Ltd.



Two enclosed pressure vessels which have been coated in Vylastic RS60 for corrosion protection by Plastic Coatings Ltd.

New polymer dispersion

BASF has introduced Acronyl S 305 D ca. 50 per cent, a polymer dispersion used as binder for paper coating colours. Due to its high film hardness, the product is claimed to impart excellent stiffness to the coated paper, and is characterised by good stability even when subjected to strong mechanical shear forces, excellent hiding power and water resistance.

Acronyl SO 309 D ca. 46 per cent is a new BASF all-synthetic binder for coating colours for offset paper. The product can be thickened with alkali and can be processed in pigment coating colours without incorporating co-binders.

Food packaging inks

A new ink series called Minarome which possesses a very low odour and taint level has been formulated by Lorilleux & Bolton, specifically for the food packaging area of printing, where there is a demand for inks of this nature.

Waterproof pH meter

A completely waterproof battery operated pH meter is now available from

F.T.Scientific Instruments Ltd. Manufactured by Knick, the instrument features a bright LED display and is housed in a pressure sealed cylindrical casing which is resistant to chemicals and shock.

Polypropylene finishing system

Sonneborn & Rieck Ltd have announced a new finishing system for moulded polypropylene products, which has met hitherto unattainable specifications set by major motor manufacturers. The new Jaxa finish, is supplied as a two coat system comprising a primer and a twopack urethane based top coat, and is available in all degrees of gloss ranging from a "wet look" to a textured surface.

Propellor mixers

Lightnin Mixers Ltd have introduced the new VL and VH range of variable speed mixers to their range of propellor mixers. These mixers give the operator the flexibility needed for applications involving changes in viscosity, varying liquid levels, aeration control, pilot plant studies and multiple step operations. The variable speed range is available in sizes from 0.25 kW to 2.2 kW.

1979 (9) INFORMATION RECEIVED

Fail-safe piping

A new fail-safe development by the Chemical Pipe & Vessel Co. Ltd can be incorporated in plastics pipework systems conveying hazardous chemicals to ensure the exacting standards demanded by the Health & Safety at Work Act in areas such as chemical plants. It is what is termed a dual containment system, and has a simple but effective design. It is meant to be installed in those parts of the pipework system which are adjacent to pedestrian or vehicular traffic areas, where the risk of spillage is unacceptable.

The type of chemicals conveyed would be, for instance, full-strength acids or alkalis, and for such liquids, CPV make pipework in polypropylene or polyvinylidene fluoride. The dual containment system merely entails the provision of a second, slightly larger diameter pipe, equi-spaced around the main pipe system, either by utilising spacer discs at intervals, or ribs, to act as a containment in the event of the main pipe being fractured by extremes of temperature or pressure.

Non-metallic pump

A new non-metallic self-priming chemical process pump designed for long service life with severe corrosives is being marketed by Durco Europe. The casing, impellor and rear cover of the Mark II FRP pump are all moulded from proven glass fibre/resin composite specially formulated by Durco to provide high strength and durability in addition to corrosion resistance.

The new composite materials, Durcon 700 (glass fibre/epoxy resin) and Durcon 710 (glass fibre/phenolic resin) are nonsparking and immune to stray current or galvanic corrosion.



The non-metallic chemical process pump from Durco Europe.

New burner system

Wellman Selas Ltd is to market the British Gas Midland Research's new design of vat and tank heating burner. The unit is called the Vatpak, and typical installations include degreasing and pickle tanks and phosphating tanks.



A cut away view of the new fail-safe pipework systems.

The Vatpak burner system has been specifically designed for the heating of solutions in vats and tanks by the direct gas firing of small bore immersion tubes. The burner design is such that it combines the efficiency of gas firing with the compactness of steam heating.

Conferences, courses etc.

Organic coatings

The 6th annual conference in organic coatings science and technology will be held in Athens, Greece from 14–18 July 1980.

Switches booklet

A new leaflet is available from Techmation Ltd which describes the Giannini range of Enviro-Switches, switches whose contacts are enclosed within a welded chamber and are operated externally by magnetic action, to avoid failure due to agressive environments.

Tank cooling brochure

A new brochure has been produced by the Engineering Division of Porter-Láncastrian, giving information on the aluminium flat plate cooling coils produced by the company for tank cooling systems.

Manufacturing programme

Baker Perkins Chemical Machinery Ltd has published a leaflet entitled "Manufacturing programme" which describes the ranges of machinery which they market.

Appointments

Mr F. L. Ward of McLaren Ward & Partners has been elected as Chairman of the Association of Consulting Scientists. The Association is made up of 77 independent practices, able to advise on almost any scientific subject.

Mr D. Williams has been appointed Sales Manager for D. H. Industries Ltd, suppliers of equipment for the paint, chemical and allied industries, including mixing, dispersing, grinding and filling equipment.



Mr D. Williams

His appointment is part of a restructuring programme currently being undertaken by D. H. Industries, prior to the introduction of a new range of products to be announced shortly.

Notes and News-



Within the first week of the Invitation to Exhibit at the OCCA-32 Exhibition being despatched, applications to take space had been received from many companies for each of the various types of facilities available, in the most enthusiastic response to the Exhibition yet experienced.

Amongst these companies, including multi-national organisations, from which applications for space have been received, are a number that have not shown at an OCCA Exhibition for several years, as well as more regular participants.

The new venue for the 1980 Exhibition will be the Cunard International Hotel, Hammersmith, London W6, and the main part of the Exhibition will be in two sections: on the ground floor, forming the entrance to the Exhibition, traditional style stands will be accommodated in the New Exhibition Hall where exhibitors of heavy machinery, plant and equipment will be located; on the first floor of the hotel, in the Queen Mary Suite, the stands will be of a simplified nature with the objective of allowing exhibitors to use modular display systems. These stands will have no platform, being erected directly on to the carpeted Suite floor, and so it will not be possible for heavy equipment to be displayed in this section.

Access between these two areas will be through the intermediate Mezzanine floor, where there are a number of rooms for companies to display free standing exhibits. These rooms were amongst the first to be requested, and have been

OCCA-32 Exhibition

13-15 May 1980 Cunard International Hotel Hammersmith, London W6

Many applications received from UK and overseas in enthusiastic response to new arrangements

Closing date for applications 30 November 1979

allocated to companies, the deposits already having been received.

In addition, there will be several suites and syndicate rooms on the third floor of the hotel, either for companies who wish to use this type of facility to exhibit, or for those who wish to have somewhere convenient to entertain their visitors in addition to their main stands elsewhere in the Exhibition. Already, several organisations have taken advantage of this opportunity to have a main stand for general enquiries, and the more private room for detailed discussions.

Dates and times

The thirty-second annual OCCA Exhibition, a three day event, will be open as follows:

Tuesday 13 May 1980 09.30 to 17.30 Wednesday 14 May 1980 . 09.30 to 17.30 Thursday 15 May 1980 ... 09.30 to 17.30

Theme for the Exhibition

Motif: The motif, designed by Robert Hamblin, uses the compass to symbolize the unique attraction of the OCCA exhibitions which annually draw exhibitors and visitors from numerous countries.

The aim of the Exhibition is the presentation of technical and commercial information relating to raw materials, plant and equipment used in the paint,



A view of the Information Centre at the OCCA-31 Exhibition, showing the throngs of visitors to this unique annual event

polymer, printing ink, colour, adhesive and allied industries, both in manufacture, processing and application.

The Exhibition Committee will be particularly pleased to welcome exhibits relating to the new energy efficient, low polluting technologies, including powder coatings, high solids coatings, radiation curing, water-based coatings and other developments.

Applications Received

The response to the Invitation to Exhibit has already been very favourable and applications for space to be allocated in all sections of the Exhibition have been received from many companies within the first month.

These applications are to show products as varied as resins, pigments, equipment, solvents and additives, and have come from some companies returning to the Exhibition after an absence of several years, as well as from more regular exhibitors.

Companies intending to apply for exhibition space are reminded that the closing date for applications is 30 November 1979, and shortly after this date the Committee will meet to make the first allocation. Preference for stand shapes, etc. will naturally be given to early applicants.

The Cunard International Hotel

The Exhibition Committee has decided to move the venue of the 1980 Exhibition to the Cunard International Hotel, as it is felt that the more central site and greater range of types of exhibiting facilities it offers will be welcomed both by exhibitors and visitors to the Exhibition.

The Hotel has a selection of restaurants. shopping facilities and bars. There is a coffee shop immediately adjacent to the Queen Mary Suite (which itself contains a bar), an Exhibitors' Lounge on the Mezzanine floor, and there are plans for a coffee bar to be erected in the New Exhibition Hall for the Exhibition.



The Hotel is situated near Hammersmith Station on the Piccadilly Underground Line between Heathrow Airport and the centre of London. Visitors from overseas may board the Piccadilly Line in the Airport complex, which will take them direct to Hammersmith Station or to central London where they may be staying. Hammersmith Station is also served by the Metropolitan and District Underground Lines (the latter of which connects to Victoria Station for those arriving at Gatwick Airport). The Hotel is adjacent to the Hammersmith flyover on the M4 Motorway which links Heathrow Airport by road. Car parking at the Hotel is limited, but there is a large NCP car park close by in King's Mall off King Street.

Admission to the Exhibition will be free, and visitors will be asked to complete registration cards which will be available from the Association with copies of the *Official Guide* in advance. Copies of the *Official Guide* will be charged at £1.50 each, and both registration cards and copies of the *Official Guide* will also be available at the entrance to the Exhibition.

The Annual Exhibition

The OCCA Exhibition is recognised as the world's most important international exhibition for the surface coatings and related industries, and annually provides companies with the opportunity to display their products and services and discuss them with visitors from many parts of the world.

"... we obtained countless inquiries from representatives from nearly 30 different countries"

In recent years, the Exhibition has regularly attracted visitors from over 50 countries, with a remarkably high proportion of top personnel from both the UK and overseas attending. The value of exhibiting need hardly be stressed when it is considered that it is possible, at this one annual event, to contact and maintain contacts with companies involved in the surface coatings industries from all over the world. "... the accomplishments of the first day alone were enough to justify our participation in the Exhibit, and I should also point out that the subsequent days were even better ..."

"Anyone visiting this exhibition (OCCA-31) could not have failed to be impressed by the spacious and comfortable layout and the ease with which one could identify individual stands. For those whose range of interests includes all of the varied displays, to be able to see at a glance individual stands and the personnel available for discussion and yet at the same time, while promenading, enjoy the many re-unions is recognised as another of the unique characteristics of this annual event. The atmosphere in this exhibition has never been bettered ... the deserved claim to be the international forum for the surface coatings industries.'

"The exhibition was well attended and seemed to need all of the vast space in the crowded middle periods when so many overseas visitors dominated."

The British Ink Maker, May 1979

Invitations to Exhibit

Invitations to Exhibit, giving details of the various types of exhibition facilities available at OCCA-32 have been despatched, together with application forms, to those companies who have exhibited at previous OCCA Exhibitions, or have requested information for the first time for OCCA-32. Any organisation which has not yet received a copy of the Invitation to Exhibit and wishes to do so, should write to the Director & Secretary at the address on the Contents page.

Completed application forms should be returned to the Director & Secretary of the Association by **30 November 1979**, as the initial allocation of space in the New Exhibition Hall and Queen Mary Suite will then take place. As mentioned earlier, all the rooms on the Mezzanine floor have already been allocated, and those remaining on the third floor will be allocated on a first come, first served basis. Early application is advised.

Official Guide

It is intended, as in previous years, to publish the *Official Guide* to the Exhibition several weeks in advance so that it may be sent to visitors to enable them to plan the itinerary for their visits. The *Official Guide* will contain descriptions of all the exhibits together with much other useful information for visitors, such as maps of the exhibition areas, details of facilities, travel information and an analysis of the exhibits.

Many thousand copies of the Official Guide will be printed and distributed on a world-wide basis. Advertising space will be available in this publication, and details of availability, rates, special positions etc., may be obtained from the Assistant Editor at the address on the Contents page.

QUEEN MARY SUITE

STANDARD SHELL SCHEME SHOWING SINGLE UNIT ONLY



A diagram showing the simplified shell scheme which will be used in the Queen Mary suite

Bristol Section

Ladies' Night

On Friday 23 March, the Mayfair Suite of the new Bristol Centre opened its doors to a record attendance of over 220 for the Annual Ladies' Night of the Bristol Section. The Section was honoured to include amongst its guests the President, Mr A. McLean, the President of the Birmingham Paint Varnish and Lacquer Club, Mr D. Heath and Mrs Heath, the President of the Paintmakers Association, Mr A. Hughes and Mrs Hughes, the Chairman of the Newcastle Section, Mr F. Hellens and Mrs Hellens, the Chairman of the London Section, Mr D. Bayliss and Mrs Bayliss, and the Director & Secretary, Mr R. H. Hamblin.

In her speech of welcome, the Chairman, Mrs E. Harper, paid tribute to the companies which by their support had helped to make the highlight of the season so successful once again.

After 25 years of continuous service to OCCA and to the Section, including two terms of office as Chairman, the Association had honoured Mr L. Brooke with a

Report of Council Meeting

A meeting of the Council of the Association was held on 11 July 1979 at the Great Northern Hotel, King's Cross, London N.1 at 2 p.m. with the President, Dr F. M. Smith, in the Chair. There were 27 members present.

The President extended a welcome to all members serving on Council for the first time, both at home and abroad, and to those returning to Council after an absence.

It was noted that Mr J. Rackham would be presenting a paper on behalf of the Association, written jointly by himself and Mr T. Entwistle, a member of Council, entitled "Dispersion of TiO₂ in water-borne industrial finishes" at the Convention of the Federation of Societies for Coatings Technology at St. Louis, USA on 3–5 October 1979.

Mr J. McAllister was appointed as the Association's representative on the British Standards Institution's Committee PVC/1/12 – Organic Pigments.

The dates of the Council Meetings for the forthcoming session were agreed.

Consideration was given to the appointment of Council and representation of the Association on other organisations and these were agreed.

The arrangements for the Reunion Dinner for present and past members of Commendation Award. Mrs Harper's pleasure in presenting the award was warmly echoed by Mr Brooke's many friends present.

The friendly atmosphere of the gathering was reflected in the entertaining response on behalf of the guests by the President.

Thanks to the organisational efforts of Mr A. Lageu, Social Secretary, and the excellent fare and facilities of the Mayfair, this was a most enjoyable and happy evening.

J. R. T.

Scottish Section

Annual golf outing

The Scottish Section held their annual golf outing at Aberdour Golf Club on Friday 11 May, 1979. Of those attending there were 10 members, 10 visitors and 4 nonplayers. Despite an early morning downpour, members and visitors were able to enjoy a warm and sunny day which undoubtedly lent itself to the spirit of the occasion.

The winners on this occasion were W. Donaldson with a gross score of 86 (nett 62), who won the Whittaker Trophy and F. T. McIntosh with a gross 79 (nett 62) who won the Newton Cup Visitor's Trophy.

Perhaps as an indication of the standard of the golf played on this occasion it was suggested that a special trophy should be awarded for the most improved OCCA member over the next twelve month period. Needless to say the winner of such a trophy may have to spend a considerable time on the golf course between now and then.

W.L.M.

News of Members

Mr M. F. Worsdall, a Registered Student attached to the London Section, has been awarded a degree in biology with second class honours at Queen Mary College, University of London.

Council to take place at the Great Northern Hotel, King's Cross, London N.1 on 24 October were noted. A report was given on the Stratford Conference which had attracted an attendance of 212, drawn from the United Kingdom and fifteen overseas countries. It was agreed that the Conference had been extremely successful; all the technical sessions were well supported as was the social programme arranged for delegates' ladies.

Discussion took place on the format and venue for the 1981 Conference.

It was agreed to hold the Association's Biennial Dinner Dance at the Savoy Hotel, London WC.2 on Friday, 11 April 1980.

A report on the 1979 Exhibition was received, it being recorded that the event attracted visitors from more than 40 overseas countries. Members of Council were given copies of the Invitation to Exhibit for OCCA-32 (13-15 May 1980 at the Cunard International Hotel, Hammersmith, London W.6) which were being despatched to potential exhibitors at home and overseas and it was noted that, in response to requests received from many companies, a wide choice of methods of exhibiting had been arranged, including opportunity for hospitality suites. All Members of Council and Section Committees were urged to make the information known as widely as possible and to encourage companies to participate.

A report was received on the number of members whose 1979 subscriptions had not yet been received and despite the special difficulty encountered by the prolonged postal strike in Ireland, the total compared favourably with those at the same time in 1978 and 1977.

The Director & Secretary reported that he had had the pleasure of meeting Mr D. Pienaar (a former Vice President from South Africa) and Mr T. W. Slinn (a former Vice President from New Zealand) and discussed Association matters in those countries. Mr D. J. Morris (Hon. Secretary) had recently paid a visit to South Africa and had also held discussions with Association members.

The Hon. Editor (Mr S. R. Finn) reported on the position of papers for the Journal and explained the reason why there had been very considerable difficulty in printing the Journal during the last three months. In April, the company which had printed the Journal since 1950 went into liquidation and it was necessary to find another printer at short notice to take over and complete both the May issue and the Conference preprints. This printer, although willing to help through long association on other printing work, was unable to undertake the printing of the Journal on a regular basis and a third printer had to be found for the June and subsequent issues. This necessitated a change from letterpress to sheet-fed offset

1979 (9) NOTES AND NEWS

litho which it was hoped would prove more economical in due course. At the same time, the despatchers for the *Journal* had been unable to continue so that another firm had to be engaged. Naturally, these problems, together with the postal delays of recent months, had led to late despatch of the *Journal*, but it was envisaged that the August and subsequent issues would be appearing during the early part of the relevant months.

The Hon. Research & Development Officer (Mr C. N. Finlay) reported on the technical sessions at the Stratford Conference and asked Council for suggestions for topics and lectures for the 1981 Conference. A call for papers would be published in the January 1980 issue of the *Journal*.

The Director & Secretary reported that, at a meeting of the Professional Grade Committee held earlier in the day, three Fellows and two Associates had been admitted, and one Associate transferred to the Fellowship grade.

A report on the Association's Liaison Committee held at the Stratford Conference, to which the Presidents of FATIPEC and SLF and the representatives of FSCT and OCCAA had been invited, was given and the President reported on the meeting which he had attended on 23 June in Paris to discuss a proposal for an International Coordinating Committee.

The Sections reported on their activities and various points of interest to Council were raised in respect of symposias and discourses being organised, the content of the *Journal*, educational courses being held overseas and arrangements for Section programmes.

There being no other business, the President thanked Members for their attendance and declared the meeting closed at 4 p.m.

Register of Members-

The following elections to membership have been approved by Council. The Section to which each new Member is attached is given in italics.

Ordinary Members

- ASHMORE, TERENCE WILLIAM, Advanced Coatings Pty. Ltd, PO Box 1305, Vereeniging 1930, South Africa (Transvaal)
- BUNDY, COLIN THOMAS, BSc, Box 3645, Salisbury, Rhodesia. (Transvaal)
- CASAL, OTILIO MANUEL DE ARAUJO, 2 Greentrees Southey Road, Hillside, Salisbury, Rhodesia. (Transvaal)
- DUGGAN, TIMOTHY ART, 4 Laurel Close, Elland, West Yorkshire HX5 0QD. (West Riding)
- HOLLAND, NEVILLE HARRY, 24 St. Ledger Road, Claremont 7700, South Africa. (Cape)
- MCKEOWN, JOHN FRANCIS, 45 Ullswater Road, Congleton, Cheshire, CW124JE. (Manchester)
- RYAN, LESLIE OWEN, Valmore Paints, 15 Douglas Road, Workington, Salisbury, Rhodesia. (Transvaal)

- SCHUTTE, MEINOLF, PO Box 2953, Cape Town 8000, South Africa. (Cape)
- SULLIVAN, CHRISTOPHER JOHN, PO Box 2091, Wellington, New Zealand. (Wellington)
- TAYLOR, DAVID EDWARD, 27 Winchester Avenue, Walderslade, Chatham, Kent. (London)

Associate Members

- CALASSE, JOSEPH CLAUD, PO Box ST 92, Southerton, Salisbury, Rhodesia. (Transvaal)
- JONES, PHILIP HOWARD, 8 Whinmoor Crescent, Leeds LS14 1AG. (West Riding)
- LOWRIE, PETER CHRISTOPHER, PO Box 344, Salisbury, Rhodesia. (Transvaal)

Forthcoming Events-

Details are given of Association meetings in the United Kingdom and Ireland up to the end of the second month following publication and in other parts of the world up to the end of the third following publication.

September

Tuesday 4 September

West Riding Section: "Extender slurries for emulsion paints" by D. J. Huxtable and Mr McGuffog of EEC International, at the Mansion Hotel, Roundhay Park, Leeds 8, commencing at 7.30 p.m.

Wednesday 12 September

Manchester Section: Golf Tournament, to be held at Stockport Golf Club.

Thursday 13 September

Manchester Section: Technical Discourse, "The whys and wherefores of corrosion", to be held at UMIST, University of Manchester.

Friday 14 September

Irish Section: "Fire prevention in the factory" by G. Bell of Dublin Fire Department, at the Clarence Hotel, Dublin, commencing at 8.00 p.m.

Thursday 27 September

London Section: Chairman's Evening,

"Painting ships" by T. A. Banfield, at the Princess Alice, Romford Road, Forest Gate, E7, commencing at 6.15 p.m. To be followed by a buffet supper.

Midlands Section and Trent Valley Branch: Joint meeting, "OCCA – Where do we go from here?" by R. H. Hamblin, Director & Secretary, at the Calthorpe Suite, County Cricket Ground, Edgbaston, Birmingham, commencing at 6.30 p.m.

Friday 28 September

Bristol Section: "Latest developments in driers" by J. H. W. Turner of Manchem Ltd, at the Royal Hotel, Bristol, commencing at 7.15 p.m.

Midlands Section: Ladies' Night, Dinner Dance at the Botanical Gardens, Edgbaston. Details to be announced.

October

Monday 1 October

Hull Section: "Plant and machinery for the processing of oil seed and vegetable oils" by N. Lithgoe of John L. Seaton & Co., at the Humber Bridge Hotel, Barton, South Humberside, commencing at 6.45 p.m.

Tuesday 2 October

West Riding Section: "The use of titanium dioxide in air drying paints" by J. Clark of BTP Tioxide Ltd, at the Mansion Hotel, Roundhay Park, Leeds 8, commencing at 7.30 p.m.

Friday 5 October

Hull Section: Annual Dinner Dance, at the Willerby Manor Hotel, Willerby, near Hull. Details to be announced.

Thursday 11 October

Midlands Section – Trent Valley Branch: "Pigment dispersions for solvent based decorative paints" by H. H. Bower and A. Kelly of Ciba-Geigy Ltd, at the Derby Crest Motel, Pastures Hill, Littleover, Derby, commencing at 7.15 p.m.

Newcastle Section: "Leather finishing" by G. J. Ward of Rohm & Haas Ltd, in the Students Common Room, St. Mary's College, Elvet Hill Road, Durham, commencing at 6.30 p.m.

Scottish Section: "Corrosion" by C. U. Chisholm of Paisley College of Technology, at the Albany Hotel, Glasgow, commencing at 6.15 p.m.

Thames Valley Section: Works visit, to Pyrene Chemical Services Ltd, Iver, Bucks, commencing at 6.30 p.m.

Friday 12 October

Manchester Section: "European versus UK test methods for emulsion paints" by J. Legg of Vinyl Products Ltd, at the Manchester Polytechnic, New Administration Building, All Saints, commencing at 6.30 p.m.

Wednesday 17 October

London Section: "The maintenance and protection against corrosion of North Sea structures" by M. Small of Berger (UK) Ltd. Joint meeting with the London Branch of the Institute of Petroleum, at 61 New Cavendish Street, London W1, commencing at 6.00 p.m.

Thursday 18 October

Midlands Section: "In-line coatings – Another approach to accelerated drying in print" by G. Gooding of Mander Kidd Ltd, at the Calthorpe Suite, County Cricket Ground, Edgbaston, Birmingham, commencing at 6.30 p.m.

Friday 19 October

Irish Section: "Printing ink lecture" at the Clarence Hotel, Dublin, commencing at 8.00 p.m. Details to be announced.

London Section: Ladies' Night, to be held at the Selsdon Park Hotel, Sanderstead, Surrey, commencing at 7.00 for 7.30 p.m.

Manchester Section: Annual Dinner Dance, at the Piccadilly Hotel, Manchester. Details to be announced.

Scottish Section – Eastern Branch: Annual Skittles Match for the Newton Cup, in the Telecom Club, Chesser Avenue, Georgie Road, Edinburgh, commencing at 7.30 p.m.

Thursday 25 October

London Section: "Preservation, priming, putty and paint" by J. J. Froggatt, at the Rubens Hotel, Buckingham Palace Road, SW1, commencing at 7.00 p.m.

Friday 26 October

Bristol Section: "Problems of painting at tropical and sub-zero temperatures" by J. R. Taylor, at the Royal Hotel, Bristol, commencing at 7.15 p.m.

Midlands Section – Trent Valley Branch: Halloween Buffet & Dance, at the Cross Keys Inn, Turnditch. Details to be announced.

November

Thursday 1 November

Newcastle Section: "Antifoulings" by J. D. Symonds of International Marine Coatings, in the Students Common Room, St. Mary's College, Elvet Hill Rooad, Durham, commencing at 6.30 p.m.

Monday 5 November

Hull Section: "Instrumental colour control in the paint industry" by Miss S. Williams, Director (Applications Department), Instrumental Colour Systems, at the George Hotel, Land of Green Ginger, Hull, commencing at 6.30 p.m.

Tuesday 6 November

Scottish Section: "The effect of instrumentation on management" by J. M. Scadlock of J & P Coats UK Ltd. Joint meeting with the Society of Dyers & Colourists, at the North British Hotel, Glasgow, commencing at 7.30 p.m.

West Riding Section: "The biology of paint and paint films" by E. Allsop of the University of Aston, at the Mansion Hotel, Roundhay Park, Leeds 8, commencing at 7.30 p.m.

Thursday 8 November

Thames Valley Section: "The pigmentation of non-polluting coatings" by T. Entwistle of British Titan Products Ltd, at the Beaconsfield Crest Motel (White Hart), Aylesbury End, Beaconsfield, Bucks, commencing at 6.30 p.m.

Friday 9 November

Irish Section: Annual Dinner Dance, at the Clarence Hotel, Dublin, commencing at 8.30 p.m.

Monday 12 November

Manchester Section: "Photography-Do you need help?" by N. Webster of Nicholas Webster Photography Ltd, at the Woodcourt Hotel, Sale, commencing at 6.30 p.m.

Wednesday 14 November

Scottish Section – Eastern Branch: "The language of colour" by J. Hunter of the Design Department, Scottish College of Textiles, at the Maybury Road House, Maybury Road, Edinburgh, commencing at 7.30 p.m.

Thursday 15 November

Midlands Section: "Solvent system design" by R. L. Mawer of Shell Chemicals Ltd, at the Calthorpe Suite, County Cricket Ground, Edgbaston, Birmingham, commencing at 6.30 p.m.

Wednesday 21 November

London Section: "Pigments". Day meeting at the Thames Polytechnic, Woolwich, SE18, commencing at 10.00 a.m. Details to be announced.

Manchester Section: Students' Lecture, "Weatherability of surface coatings" by E. Oakley of BTP Ltd, at the Manchester Polytechnic, New Administration Building, All Saints, commencing at 4.30 p.m.

Friday 30 November

Bristol Section: Ladies' Evening. "Furs" by D. Bauers of F. K. Bauers of Bristol, at the Royal Hotel, Bristol, commencing at 7.15 p.m.



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West Riding Section Chairman's Golf Competition

The Chairman's Golf Competition of the West Riding Section will be held at the Knaresborough Golf Course on 4 October. Any member of the Association wishing to participate should contact the Hon. Social Secretary, Mr N. Cochrane, The Coach House, Red Holt, Hainsworth Wood Road, Ingrow, Keighley, West Yorks BD21 5BJ.

Hull Section

Annual Dinner Dance

The Annual Dinner Dance of the Hull Section will be held at the Willerby Manor Hotel, Willerby, near Hull on Friday 5 October at 7.15 p.m. for Dinner at 8.00 p.m.

Tickets are priced at £10.50 (inc. Vat) each, and some overnight accommodation will be available at the Hotel (Tel: Hull 652616). Other nearby hotels which may be used for accommodation are the Crest Motel (Tel: Hull 645212) and the Grange Park Motel (Tel: Hull 653382).

Further information and tickets are available from the Hon. Social Secretary, Mr A. R. Van Spall, "Jusrite", 5 Middle Garth Drive, South Cave, North Humberside (Tel: 04302 2410).

JOCCA

Change of production method

From the June 1979 issue of *JOCCA*, the production method has been changed from letterpress to **sheet fed offset litho**.

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INDEX TO ADVERTISERS

Ashby, Morris, Ltd	vi
B Banner, Samuel, & Co. Ltd	ii
C Ciba-Geigy Plastics & Additives Co., Paint Resins Crosfield, Joseph, & Sons Ltd	vii Inserts
D Dow Chemicals – Methocel	x
G Glen Creston Machinery Ltd Co	over, xiii

Highgate & Job Ltd	xiii
Johns-Manville International	ix
O OBS Machines Ltd	i
S	
Sachtleben Chemie GmbH	xi
Sanyo-Kokusaku Pulp Co. Ltd	ii
Servo BV	viii
Sheen Instruments (Sales) Ltd	i
Sub-Tropical Testing Service Inc	iv

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