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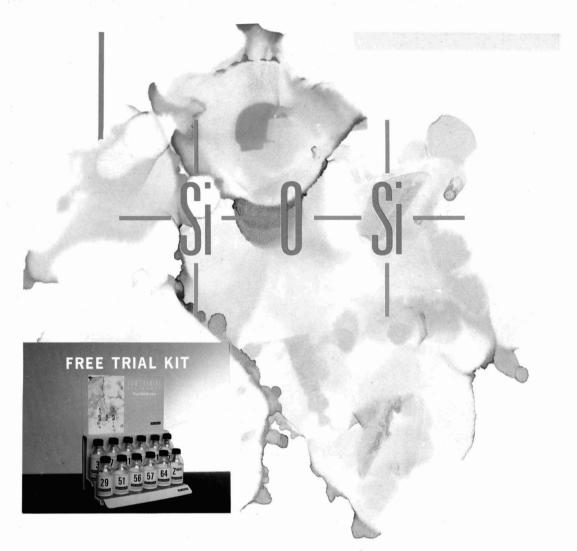
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ALSO IN THIS ISSUE:

- UV curing screen ink resists for PCB's
- Coatings on metals for underwater use: standardisation of electrical insulation testing
 - Corrosion protection properties of various ferrite pigmented paint films
- Advances in environmentally acceptable polyurethanes

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UV curing screen ink resists for PCB's

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Summary

An outline is presented of the application of screen ink resists to printed circuit board production. The history and types of ink and board used are described, culminating with the advantages to be gained by using Ultra-Violet curing as the drying mechanism instead of air or thermal methods. Some future trends for resists and other screen ink applications for PCB's are outlined.

1.0 Introduction

Printed Circuits

For various technical and economic reasons the electric circuits of electronic equipment are nowadays commonly laid down as rigid copper tracks on insulating boards instead of the former practice of using lengths of wire to connect components.

These so-called "printed circuit boards" are prepared from thin sheets of copper foil bonded to one or both sides of flat laminates which themselves are built up from either glassfibre, polyester or paper treated with special insulating varnishes under heat and pressure.

The conducting tracks between components are formed by selectively etching away unwanted copper, leaving only narrow strips which are designed to carry the necessary current in the final circuit. To protect the wanted areas of copper during this etching process it is necessary first to print the board with a pattern which leaves exposed only the unwanted metal. For this purpose a special type of printing ink known as an "etch resist" is applied to the board through a "silk screen" (other materials have replaced the earlier textile) which carries a stencil designed to allow the ink to reach only the areas of copper that are to be protected. The coating is then dried quickly and the whole board treated with a chemical etching solution which dissolves away the unwanted metal. Next, a short application of an organic solvent (or, more usually, a weak alkaline solution) removes the dried ink film, leaving unaffected narrow strips of copper firmly bonded to the insulating board only where required.

Small holes are drilled in the board at predetermined places and the components are placed on the insulated side with their connecting leads projecting through sufficiently to contact the copper tracks on the other side of the board. These connections are then made secure and permanent by soldering. This can be performed by hand, but in a massproduction set-up the boards are treated with flux and passed briefly over a wave of molten solder. In order to make sure that the solder only serves a localised connecting function and does not spread onto adjacent areas where it could cause short circuits, the copper side of the board is pre-coated with a second printing ink-a "solder resist or mask"-leaving exposed only those sites where solder is required. There is no need to remove the solder resist after it has served its purpose and no provision is made for this to be done. It therefore remains as a permanent fixture on the board. Consequently the requirements are more demanding in terms of film integrity and cosmetic characteristics as a protective coating.

In the case of double-sided copper laminates extra operations are needed to copper-plate the holes connecting one side of a board with the other. For this purpose a third ink, known as a plating resist, is applied to both sides, leaving the holes clear. The following operation is one of electroplating which lays down a conductive coating of metal through the holes. Other metals may be used for plating particular areas, such as gold where a high degree of corrosion resistance is called for. The principle is the same, and the plating resist is finally stripped by dissolving it in a suitable organic solvent before further processing takes place.

Boards are identified during production and in service by marking them with special serial numbers printed with "notation", "legend" or "marking" inks. The position of individual components is often marked in the same way.

This depicts a very brief outline of PCB production but there are, of course, many variations and complications that have to be considered by the ink manufacturers. UV curing has revolutionised many aspects of this process. The advantages of UV curing screen inks are summarised at the end of this paper following a general outline of the use of conventional printed circuit board screen printing inks.

2.0 UV Curable resists

Protective coatings that inhibit physical, chemical or electrical attack on an underlying material are called 'resists'¹.

If a photochemical reaction is utilised to change the solubility of the resist, then it is described as a 'photoresist'. An essential feature of the action of a photoresist is that of protecting selected areas of the substrate or support².

The photoresist material can be coated over the complete surface and then selectively exposed to ultra-violet or visible light through a mask such as a negative or positive photographic emulsion. This will insolubilise it (negative working) or solubilise (positive working) it selectively in the regions under exposure. Subsequently an appropriate solvent is used to 'develop' the resist by removing the soluble material.

The above type of photoresist must be distinguished from the kind of system which is the subject of this paper. Screen printing is used to obtain spatial selectivity by printing the image needed onto the PCB substrate employing a negative working resist ink^{3–5}. This screen ink is printed via a negative design on a screen (i.e. the direct photostencil which itself is a 'true' photoresist) and hardening the wet ink deposited by UV light. This coating can then behave as a 'resist' in the normal meaning of the term. So rather than call these types of materials 'photoresists' which are generally obtained via photo-mechanical means it is simpler to view them as 'resists' which are screen printed and happen to be cured by UV light.

3.0 History of printed circuitry⁶ overleaf

The term "printed circuit" is to some extent a misnomer. Not all electronic circuits are "printed". They may be obtained by depositing a resist by some other means than printing on to a copper surfaced laminate.

Necessity is often quoted as being the mother of invention. In this context, the Second World War was the impetus for a continuous expansion of the electronics industry. The printed circuit has been the vital element contributing to automation within that industry. Paul Eisler in 1943 pioneered screen printing for PCB manufacture.

Although the use of printed circuit design in electronic equipment had been advocated during the 1930's, mass production did not occur until some 10 years later, during the war years. This first printed circuit was for a war-time American shell, as a proximity fuse. It was needed because of space inadequacy and also as conditions of shock on firing posed extreme problems for the conventionally wired circuit. An ink based upon silver was printed upon a steatite base and fired at about 1,000°F (538°C) to produce a conductor of essentially pure silver.

The main impetus to the PCB industry in the 1950's arose because of the introduction of the transistor at the expense of the valve. An expansion of PCB manufacture occurred in the next decade owing to the advent of integrated circuits.

Innovation subsequently has led to various alternative methods for circuit production. The subject of this paper is however confined to that of the etched foil method, whereby selective etching of a copper foil is executed on an insulating laminated base.

Three printing methods are commonly used, i.e. screen printing, offset lithography or photomechanical methods. This paper will be concerned with screen printing only, as it tends to be the most widely used for the bulk production of circuits. The main reason for this is perhaps that very thick films may be deposited, yielding superior solvent resistance to that achieved from thin films from the offset litho method, and also its inherent relative cheapness.

4.0 Types of PCB's

Printed circuit boards are essentially of three major kinds⁷. These are in increasing order of complexity:

- 1. Single and double sided
- 2. Plated through the hole
- 3. Multilayer Boards

1. Single and double sided print and etch boards simply have conductive tracks etched upon one or both sides of the board. In the case of a double sided PCB, each individual side is separate. No connection exists between the components on each of them. Manufacture of this type of PCB is simple and conseqently they are employed in relatively non-complex products. These products are for the consumer electronics market. For example in TV, Hi-Fi, etc and so mass production of these boards occurs. This is because they do not require major considerations to size and complexity. They are at the "low end" of the PCB market. Generally, they tend to be made using copper and paper—phenolic laminates, which are cheap. They are mainly screen printed. Production of this type of board is carried out by "captive" PCB producers, for their own use.

2. Plated through the hole boards, which are double sided,

are employed when more sophisticated circuitry is required. Each side of the board has conductive tracks etched upon them. These sides are then inter-connected via plated holes. This type are referred to as "semiprofessional" boards. These find extensive use in communications systems and business machinery. They tend to be produced using copper/epoxy, glass laminates, which are more expensive than paper/phenolics, but which are tougher, and can pass more stringent use tests.

3. Multilayer boards represent the most complex PCB's to design and produce. They comprise several boards bonded together to produce a three dimensional circuit. Consequently, the distance between components is drastically diminished. This saves space and signal time between components. This type of component configuration also reduces interference which might cause corruption in the electronic signals. Industries such as defence (where boards with twenty or more layers may find use), aerospace and information technology, in particular digital telephone exchanges and computer mainframe systems employ these kind of boards. These are often known as "professional" boards. They are at the top end of the PCB market. Fourlayer boards for example are finding use in some consumer electronics. These are especially in home computers, where the relentless drive to miniaturisation has produced the need for smaller areas with increased interconnection capability.

It should be noted however that a technique called surface mounting is rapidly becoming popular. This is because it is reported to reduce the total area used by half, permitting greater compactness with a greater number of circuits mounted on the board. Traditionally, as described previously, components are inserted holes on the boards and then soldered into place. Surface mounting involves a method whereby the components are soldered directly to the board surface, that is not through a hole.

5.0 Types of screen resists used⁸

In the electronics industry, the major kinds of screen process resist inks used are:

1. Solder masks or resists, generally green in colour.

2. Imaging resists such as plating and etch resists (acid or alkali resistant), usually blue in colour.

3. Notation, legend and nomenclature inks which are all synonyms for marking inks. These are predominantly, white, yellow and black in colour although other colours are used.

4. Screen printable flexible covercoats (coverlays). These are generally colourless, although sometimes very pale green.

5.1 Screen printed solder masks or resists

These are protective coatings applied to circuit boards by the screen printing process to mask conductor tracks from the soldering operation. For copper circuitry a temperature of up to 260° C for several seconds is used in the soldering process. The solder mask must withstand this as well as be inert to the flux solution, as must associated legend inks. They must withstand this temperature in the presence of rosin and ethyl or isopropyl alcohol vapour in some cases.

It is important that the copper and board is scrubbed and washed and dried prior to printing for applying any of the inks. This is to obtain good adhesion and is only obtained if

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printing is immediately undertaken after cleaning. It is thought that copper and many of its compounds, in particular when in combination with the atmosphere (air) retards the rate of acrylate radical polymerisation. The consequence of this is incomplete cure of the ink at the ink/copper interface. Polymerisation of the vehicle (binding resin) in the ink competes with this inhibition reaction at that site. To minimise this therefore the polymerisation reaction has to be very rapid, that is much faster than the inhibition rate.

Tin/lead circuitry is subjected to wave soldering or hot air levelling. Separate solder masks are frequently used for copper and on tin/lead. Tin/lead circuitry often presents an adhesion problem. When the solder mask has been cured on the solid tin/lead surface and adhesion developed to the metal, the mechanical bonds thus formed are broken owing to soldering or to the solder being melted by reflow (desoldering). The purpose of a satisfactory solder mask for application over tin/lead is to keep adequate film integrity after the high temperature stress of soldering or reflow. This is in order that a bridge may be kept from points of anchoring to the laminate. The quality of this bridge determines success or failure. Following reflow there is no mechanism to re-establish mechanical adhesion links. As well as this difficulty of re-establishing adhesion after reflow of the tin/lead surface below the cured solder mask the polymers used in the resist must be thermally resistant to the high temperature exposure. In general, all solder resists exhibit wrinkling after wave soldering and is acceptable to a degree.

The enhanced chemical resistance inherent in UV cured surface coating is particularly attractive for their use in PCB materials. They need to withstand alcohols and halogenated solvents. They must not blister, delaminate or change colour. Hydrolytic resistance is also needed whereby ho degradation such as blistering, cracking or tackiness occurs. Again, UV materials possess these properties. Chemically, bad performance in this area is exhibited by polymeric materials possessing a large number of ester links. The ester bond is more readily hydrolysable than those groups found in epoxy or urethane based materials.

The best UV solder masks do not seem as yet to be as satisfactory as that of a high quality conventional two pack epoxy heat cured solder mask. The latter provide excellent adhesion on substrates and solvent and temperature resistance. UV resists are inferior electrically to two pack epoxy based systems. Owing to these types of shortcomings, UV systems are more popularly utilised for lower performance consumer boards. High performance tin/lead plated boards are still mainly coated with two pack epoxy resists which also are not as brittle as UV systems tend to be. There is a tendency towards solder masks having a matt appearance. This arises from production personnel checking the final printed material with small optical magnifying glasses where glaze needs to be kept to a minimum to eliminate eyestrain. Some users still require gloss however for cosmetic purposes.

Normal assembly and soldering procedure

Soldering is generally automatic in most radio and television factories. Prior to soldering, the components are fitted upon the insulation side, that is the non-coppered side of the circuit boards. The leads from them pass through small holes in the board and through to the copper circuit side. The short lead ends are then usually bent over to provide a loose mechanical joint.

With the component uppermost, the assembled board is then placed on a conveyorised soldering machine and passed across the top of a wave of alcohol based rosin flux. The flux removes solder-inhibiting oxide from the surface of the circuit and the component leads. For conventional curing systems, infra-red heaters on the conveyor dry off the circuit slightly and it is then passed across the top of a wave of molten solder at about 240-260°C to effect soldering.

All the circuit configuration and not just the points where component lead ends meet the circuit would be soldered unless steps were taken to prevent this. This is achieved by using the solder mask.

There are many reasons for needing selective soldering of a circuit. An important one is that it prevents "bridging" between narrowly spaced conductor lines. This "bridging" is where during the solder operation, two narrowly spaced conductors are short circuited by an unwanted "bridge" of solder. This would need a time wasting hand soldering operation to remedy the fault.

Solder masks generally need the physical properties of good durability, hardness, abrasion resistance, machinability and flexibility (the latter is often however not too important).

Solder resists are not now normally removed post soldering and generally remain as a permanent fixture of the board in contrast to plating and etch resists. They therefore need greater standards of film integrity and cosmetic appearance and have good electrical properties under a wide range of climatic conditions. In particular, there must be no tendency towards hygroscopicity because this lowers the resistance. The latter may cause circuit breakdown in the form of a low resistance track.

Conventional curing systems have included phenolic, melamine or epoxy/polyamide resins. It has been advantageous however to use systems which require low temperature stoving cycles or which will dry at room temperature to avoid undue laminate distortion or adhesive damage. In the former case, ovens are not particularly efficient however as heat energy is transferred generally across an air environment. It should be borne in mind that oxygen inhibition (from the air) occurs with most acrylate based systems. Ovens may therefore be inert blanketed with nitrogen or argon gas to stop this, but these gases are expensive. The latter problems of course present an ideal case for the use of UV curing.

In summary therefore, the functions of a solder mask include the protection of the tracks from oxidation, moisture and subsequent electrolytic attack, and mechanical damage. It also insulates the tracks electrically and enables wave soldering of components. Originally solder resists were developed to permit mass soldering techniques to be utilised to minimise the amount of solder used. Nowadays the latter function has been superseded with the task of preventing shorts.

5.2 Screen printed etch and plating resists

These protect specific areas on the printed circuit board

from the chemical or electromechanical action of one of these two processes. Owing to chemical similarities in many cases, dual purpose resists are frequently offered.

These resists do not remain as a permanent fixture of the board as the solder resist does. They are formulated to be removed after the etching or plating sequence has been completed. This "stripping" as it is known may be with organic solvent or alkali. Solvent stripping is however becoming less popular owing to the environmental pollution problem.

The use of any screen process etch or plating resist is in direct competition with dry film resists used for imaging. Dry film is used in preference where better resolution is needed and the value of the board warrants the much greater cost.

5.2.1 Screen process etch resists

This is a screen ink which will withstand a variety of acids, or in some cases alkali, such as ammonical etchants. Ferric chloride and ammonium peroxodisulphate (also known as persulphate) are two popular acid etchants. All these type of acid etch resists formulated must be capable of resisting 30-45 Baumé ferric chloride at up to 40°C and ammonium peroxodisulphate solutions at 50°C. The Baumé scale is one of relative density (specific gravity) of liquids named after A. Baumé (1728-1804). It is defined as: Degrees Baumé = 144.3 (relative density -1)/relative density.

The requirements of a screenable acid etch resist include:

1. Clean printing and not readily drying in the screen even at elevated temperatures.

2. Hard drying should be achieved very quickly.

3. Satisfactory acid resistance is vital for acid etchants and alkali resistance for ammoniacal etchants.

4. After etching, it must be readily removable in a cheap solvent system. There is a tendency for UV materials to require stripping in 'powder' form rather than 'flaking'. The latter often causes problems of clogging filters if these are used to recycle the solvent. Conventional materials are not so much at a disadvantage with respect to this. Filtration is an important aspect for all surface coatings⁹.

Inks based upon bituminous resins have been used. Unless modified with the appropriate pigments the print quality is not excellent.

Other resins used having resistance to ammonium peroxodisulphate and ferric chloride include maleics, phenolics and hydrocarbons. This resistance may be diminished however if pigments are used which react with acids.

Removal of the etch resist may be by:

1. Organic solvents such as—trichloroethylene or dichloromethane (methylene dichloride).

2. Aqueous based solvents such as dilute alkali—i.e. sodium hydroxide or sodium carbonate.

The aqueous based systems are now ubiquitous owing to safety and pollution considerations. Dilute alkali solutions of about 1N sodium hydroxide (i.e. 4%) or sodium carbonate (10%) are often used at elevated temperature of about 50°C.

It can thus be seen that the function of a screen printable etch resist is to manufacture circuit boards by printing the image of the circuit required onto copper clad laminates. These resists must print sharply with no pinholes and be resistant to the etchants used.

They should also rapidly dry when in still air at room temperature or under IR heaters for no more than two to three minutes at 90-120°C. Extended stoving tends to distort the circuit board and can severely reduce bond strength between the laminate and the copper foil. UV curing is an obvious remedy here. Alkali etch resists are technically more difficult to produce. Normally pH is about 8.5 but may be as high as 11 in some cases. Alkali UV etch resists tend to be somewhat slower in stripping time compared to their acid resist counterparts.

5.2.2 Screen process plating resists

The necessity for electroplating techniques arise as more sophisticated circuits and their associated better properties such as corrosion resistance, wear resistance and hardness are wanted. The majority of the plating requires to be selective and inks are demanded which possess a high degree of resistance to a variety of plating and pre-cleaning solutions. Plating solutions include gold, tin/lead, bright tin and pyrophosphate of copper. Pre-cleaning solutions for degreasing often contain an alkali such as sodium hydroxide.

Strong acid solutions are often used prior to the final plating bath. The latter may contain a high percentage of alkali metal cyanide such as potassium or sodium. For this process, it is paramount that resists have the required chemical resistance, adhesion and again be easily removable after the completion of plating. Non-conductive inert pigments need to be used.

Plating resists now tend to be superseded by dry film owing to its better definition, although UV curing plating resists still have a marked role. The chemical resistance properties of plating resists are more demanding than etch resists, owing to the fact that the plating resist may be in contact with the plating solution for a time of up to one hour. Etch resists are often required to strip in a time of under one minute.

The avoidance of "mushrooming" of plating over the top of the resist must be prevented. In order to achieve this, plating resists must be capable of printing reversed out lines as low as some ten thou wide along with vertical side walls of minimum thickness equal to that of the plating.

5.2.3 Marking, Legend or Notation Inks

These have no electrical function on the finished board. Their purpose is to designate locations for the insertion of circuit components, dates, serial numbers, and the manufacturer's name or logo. They need good contrast to the solder mask.

Marking inks must also have adhesion both to the laminate and to any solder mask. Also, they must adhere satisfactorily to the different metals which might appear on a board such as copper, tin/lead, nickel and gold. These type of inks can be applied prior to soldering and must therefore be resistant to the soldering process. Generally, they must withstand a 10 second immersion in solder at 260°C without any adhesion loss or colour. For these reasons, UV notation inks are often different colour variations of solder mask formulae.

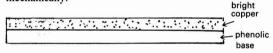
5.2.4 Covercoats (Coverlays)

These are primarily for flexible circuits. Traditionally they have been sprayable air-drying clear coatings. They may be regarded as a flexible solder mask, some of which may have the optional feature of flame retardancy. The circuit film thickness used for screen resists may be of the order of 25 microns whereas covercoats are generally thicker.

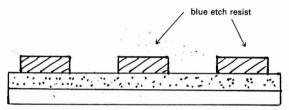
6.0 Principal printing/etching production operations

For a single sided board, the principal printing/etch production operations may simplistically be described by the following outline sequence. It is shown here for UV curing but thermal or air drying systems would be similar although they would involve longer times.

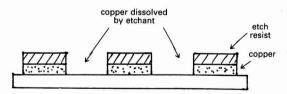
1. Board is cleaned and degreased either chemically or mechanically.



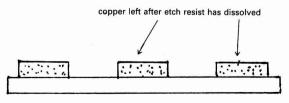
2. The etch resist is then immediately screen printed onto the clean copper through a pre-prepared screen stencil design.



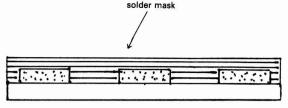
3. The above wet etch resist is then UV cured to give a hard dry etch resistant film. The board is subsequently etched with either acid etchants such as ferric chloride or alternatively with a basic etchant such as those containing ammonia. These both remove the copper by dissolving it. A water rinse is then provided.



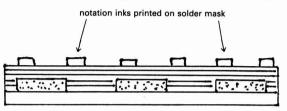
4. The etch resist is then stripped away using a weak caustic alkali solution at elevated temperature or by a solvent. This is followed by a dilute acid rinse and then by water.



5. Solder mask is then screen printed over the copper and UV cured and remains as a permanent fixture.



6. Notation inks are then screen printed to mark the positions of components and UV cured; (these inks may also be applied to the laminate on the reverse side or for that matter on laminate present on the solder mask side).



7. Holes are then punched and soldering operations carried out.

7.0 The UV process for printing circuit boards

UV curing is a process whereby electrically derived light energy causes a wet liquid film to be transformed within a fraction of a second into a hard solid network. This phase change is induced by the incidence of ultra-violet light derived from a lamp source such as a medium pressure mercury arc lamp and has been described in detail by the author¹⁰⁻¹¹.

When circuit boards are printed with inks or resists that "cure" or harden by ultra-violet light, the process has a number of advantages over the use of conventional inks which require heat or a protracted period of time for drying.

1. *Speed:* Only a fraction of a second's exposure to UV is needed for hard drying. Using a conveyor-belt system immediately following the screening operation, the boards can be stacked within a minute of printing. This permits a larger throughput to be achieved.

2. *Space:* Racking is quite unnecessary, and space-wasting conventional hot air ovens are replaced by a compact enclosure housing the UV lamp system.

3. *Distortion:* The boards emerge from the lamps at a much lower temperature than when ovens are employed; this results in very much less distortion.

4. *Pollution:* UV inks do not contain volatile solvents which might pollute the atmosphere or which might constitute a fire risk.

5. 100% Film-forming: The absence of volatile solvents means that the whole of the ink becomes the dried film, with practically no shrinkage. A minute shrinkage will occur owing to a change in density of the binder resin during its phase change from liquid to solid. Lower wet film weights can be used when compared with the normal inks that lose a large proportion of their weight by evaporation.



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The film thickness deposited on printing will become the final film thickness.

6. *Ink mileage:* The finest screen meshes can be used to obtain serviceable film thicknesses. Indeed, within limits, the thinner the coating the better it is cured by UV light. A direct comparison of the cost of wet inks is not valid because in the case of the UV process the inks go so much further to give the same dry film thickness.

7. *Energy saving:* A single UV lamp uses about 200 watts per inch (80 watts per linear cm) of its length. A double-lamp head 24 inches long will use about 10 kilowatts, compared with an infra-red oven consuming say 50 kilowatts.

8. *Open time on screen:* UV inks will stay open in the screen at constant viscosity almost indefinitely, provided they are shielded from direct sunlight and artificial lighting of short wavelengths. This is because they are solventless and have low vapour pressures, preventing drying on the screen and there is no wastage.

9. Cosmetic appearance: Thermal curing ovens often cause the oxidation of the copper surface. UV may also cause this at slow production speeds but faster speeds tend to minimise this effect.

10. *Quality:* Sharp and fine line screen printability is achieved owing to reduced flow out at the printed line edge with UV materials.

11. Reduction of smudging: UV curing inks have no volatile components and do not therefore increase in viscosity on the screen as conventional materials tend to. They do not therefore give the phenomenon of "tail" formation when the screen "snaps off". The ink "tails" flick back onto the screen underside and the problem of smudging occurs with solvent based inks.

There are however some disadvantages¹² which may occur with UV curing resists compared with conventional materials. One such problem is whereby a liquid ingredient may leach out from the ink after printing, especially after high shear conditions. Possibly base resin/diluent incompatibility is the cause of this. For solder resist printing it may be a problem for boards produced for roller tinning. Contamination of the solder pads by the clear leached component can occur and prevent the solder from wetting the copper during the roller tinning. A bright ring or halo may be observed around the pad at the inspection stage. For etch and plating resists, leaching of the component may occur onto the unprinted regions producing a widening of the etch and narrowing of tracks respectively.

Practical hints

1. Commercial UV curing equipment must be well shielded so that direct UV light cannot damage the operator's eyes; interlocking switches will ensure that the lamps are automatically disconnected if the cabinet is opened for any reason.

2. UV inks, although not containing volatile solvents, do have varying degrees of smell. Furthermore, the very small amount of volatile content can be irritating to sensitive membranes in some individuals. For these reasons it is necessary to have a mild system of vapour extraction in the vicinity of the screening machine and at the UV head. Continued or repeated contact with the wet ink has been known (rarely) to upset the skin of some sensitive individuals. Such contact should therefore be prevented by wearing gloves and goggles at the printing stage of the process. The dried film presents no problems generally.

3. All surfaces to be printed should be clean and dry. It may be necessary to use a scrubbing system on boards which are heavily tarnished or contaminated with grease or release agent.

4. Some check should periodically be made on the speed of the conveyor used to take the boards through the UV head. Depending on the type of materials used and the purpose of the coating, speeds of between 20 and 40 feet per minute are common. Too low a conveyor speed will lead to overcuring, with embrittlement of the coating. Fast speeds are sometimes used to slightly undercure (for example the solder mask). This may then permit satisfactory overprinting with notation inks giving adequate intercoat adhesion. The latter is often not satisfactory if the film is too thoroughly cured, leading to embrittlement and 'flaking' of the legend ink. Dual solder resist cure systems employing both a UV 'setting' cure for successful overprinting followed by thermal curing are becoming popular.

5. Inks are usually supplied ready for use and must not have any other materials added.

6. Failure of an ink to harden can usually be traced to a faulty or exhausted lamp. Expected lamp life should be checked with the manufacturers and a spare set always kept in stock. Too high a conveyor speed can also cause undercure when not deliberately done to obtain intercoat adhesion as previously described.

8.0 The future

Apart from general improvements in existing physical/ chemical properties of UV curing solder masks, etch resists and legend inks etc, UV curing will find application in other developing areas of the PCB process.

An example is vapour phase curing (e.g with perflorocarbons) which is the offspring of the vapour solder reflow and surface mounting process utilised for producing hybrid circuits. Vapour phase curing appears to be an alternative to air-thermal curing of solventless conductive inks. Vapour condensation onto the material to be cured yields superb heat transfer. At the same time it blankets the system from air. UV is ideal for rapid vapour phase cure whereby the latter is useful for curing solventless inks on non-flat substrates. Solvent based inks contaminate the vapour phase heating medium unless predried. This time expended for predrying reduces the fast curing benefits of the vapour phase curing process.

The whole of the print-and-etch circuit technique which is somewhat environmentally unsuitable and labour intensive may be gradually replaced by newer emerging technologies. One of these in particular is the solventless, radiation curable, silver filled screen printable conductive ink. Mathias et al¹³ report that these were particularly designed for printing primary electrical circuits and interconnections for rigid and flexible multilayered circuits. They are known as Polymer Thick Films. In cases where they are not able to replace the copper based circuits they can be utilised for obtaining interconnections between copper pads. Thus they can replace many areas where solvent based Polymer Thick Films are now utilised. UV screen printing is useful here owing to the ability to readily produce thin films. Printers of conductive screen inks tend to obtain the thinnest films possible in order to make the expensive silver based inks economically viable. Also, in the case of multilayered circuits thin films are preferable to allow the placing of an increasing number of alternating conductive and dielectric patterns whilst keeping an as flat as feasible surface profile. These types of inks with slight adjustment can also be thermally cured.

Dual cure systems for many electronic ink applications (such as solder masks) are becoming fashionable owing to their versatility to achieve final film properties such as intercoat adhesion with overlying notation inks etc.

Conformal coatings have presented a problem for UV curing owing to the thick films used¹⁴. The may be of the order 3-5 thou compared to other resist materials which are generally less than one thou. There is also a "shadow effect" limiting its use as conformal coatings are usually applied to a three dimensional array of components, leads etc, projecting upwards from the board surface. These tend to prevent parts of the UV radiation from reaching certain areas of the board's surface. Newer UV systems are now emerging, wherein post curing occurs either at ambient or elevated temperatures, eliminating this problem.

Photo-imageable solder and etch/plating resists are entering the PCB market ¹⁵⁻¹⁶. These are applied as a liquid which provides adequate track coverage and a controllable coating thickness. Dry film resists are already available and established but have a high cost and lengthy processing time. Application of the wet photo-imageable resists may be cheaply achieved for small users by screen printing. They may also be laid down by the more expensive roller and curtain coating processes, but give better definition. The liquid film is printed in the former case via an open screen (i.e. with no photostencil present) to produce all over print. After printing, the wet film is generally dried thermally, though not necessarily so, prior to exposure through an appropriate mask and subsequent development in aqueous or halogenated solvents. Rinsing follows with a final drying either thermally or by UV curing. UV tends to produce more precise edges.

The need for this photoimageing technology has arisen owing to increasing demands for smaller conductor tracks and gaps which simple screen printing via a photostencil can not match in terms of accuracy and consistency. Photoimageable solder resists are cheap and versatile in the sense that they may be used over copper, black-oxide and all plated tracks including tin/lead.

As indicated above, recent increases have occurred in the size of PCB's and their associated increase in component density. This has put heavy demands upon conventional screen printing and solder mask application, even though significant improvements have occurred in both these areas. Photo-imageing has considerable accuracy as witnessed by its general acceptance as a dry film resist for plating and etching of PCB's. This in turn led to the dry film solder mask being put onto the market. The latter however has not been too well received owing to some technical inadequacies and high expense.

Photoimageable liquid solder masks however eliminate many of these technical problems. Initially though, special

equipment and large capital investment was needed. Application now of these photo-imageable solder masks by conventional screen printing and exposure equipment already in existence at PCB manufacturers make this technique very attractive. The future will, of course, see great innovation in all these areas.

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Coatings on metals for underwater use: Standardisation of electrical insulation testing*

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Summary

Coatings used for protection of immersed steel rely upon their electrical insulation properties for effective protection. The determination of electrical insulation defects is therefore of major importance in the quality control of coating application. The basic principle of defect detection by a wet sponge electrical method is given. A method of calibration of the sensitivity of the instrument and the development of an improved version of the wet sponge detector are described. Since this method can be used to test one hundred per cent of the surface non-destructively it is considered to be an essential tool in quality control in the application of coatings for underwater use or in very corrosive environments. Since the defects measured by this instrument are very rarely pinholes, i.e. a circular defect through to the substrate, the term electrical insulation defect, or E.I.D., is the preferred term.

1. Introduction

Coatings such as solvent borne and solvent free epoxies, epoxy-tar, thermoplastic and thermoset powders, are applied generally in thin films of less than 500 micrometres thickness. These coatings function by virtue of their electrical resistance, hence continuity of insulation is a vital property of the applied coating, especially when used for underwater applications such as coating of buried and subsea pipelines, underwater surfaces of oil rigs, surfaces of dam and lock gates, and linings of pipes carrying water or aqueous solutions, tanks, valves, etc.

The wet sponge pinhole detector has been known for a long time but lack of standardisation of the parameters controlling its sensitivity has lead to dispute.

2. Historical

The development of the wet sponge E.I.D. detector in South Africa can be divided into the following stages:

Stage 1 – Simple direct current instruments using the coating as a resistance in the circuit. The probe is a small wet sponge, with an applied voltage of 9, $67\frac{1}{2}$, or 90 depending on the manufacturer. The sensitivity of the instrument, i.e. the minimum current flow to trigger the alarm varied considerably according to the manufacturer's own design.

Stage 2 – More sophisticated instruments having variable voltage and sensitivity controls were then introduced. These could be adjusted by the user to operate the alarm when the probe was set on an artificially made pinhole. In practice these were not satisfactory, due primarily to lack of knowledge in their correct operation. One person would use a large probe area to set the sensitivity whilst another would use a very small contact area, thus giving inconsistent results between operators.

Stage 3 – The next development was a simple method of calibrating the sensitivity of the instrument by the use of a

prescribed voltage and a resistance box of known values. This box was connected between the earth and probe terminals of the instrument. The sensitivity was then adjusted until the alarm sounded at a known resistance value. The calibration box was then removed and testing at a known sensitivity could proceed. This modification gave a considerable improvement in consistency between operators.

Stage 4 – The next development was an instrument containing a built in set of standard resistances, thus requiring no external calibration equipment. This was known as the Mark II instrument.

Stage 5 – Although the threshold value of current flow to operate the alarm could now be accurately set, some further difficulties arose:

1) The trigger mechanism had a significant delay time, hence if the speed of pass was too great, the defect would be passed before the alarm operated.

2) A relatively minor problem in noisy surroundings was that the operator did not hear the alarm, especially when he was chatting—not paying attention to the work in hand!

3) The voltage and sensitivity settings could be accidentally moved, thus upsetting the calibration.

To solve these problems the Mark III instrument was developed and will be described.

3. Principle of the wet sponge detector

The real life causes of defects will be considered later. At this stage we can consider a pinhole through a film of known thickness as a model for development of the principle.

Figure 1 illustrates a paint film on a steel substrate. A "pinhole" of diameter "d" and depth "t" is present in the film. If water is present on the paint film and penetrates to the substrate, then there is a conductive path through the film.

The electrical resistance of this path through the film can be calculated from the cross section area of the pinhole, the length of the pinhole and the specific resistance of the electrolyte:

$$R = \frac{\rho t}{a} = \frac{4 \rho t}{\pi d^2} \qquad (1)$$

Where: R = resistance across the hole in ohms

 ρ = specific resistance in ohm-metres

- t = length in metres
- a = area in square metres
- d = diameter of hole in metres

* Presented at the OCCA South African Division 11th National Symposium held on 21 October, 1986 at Durban

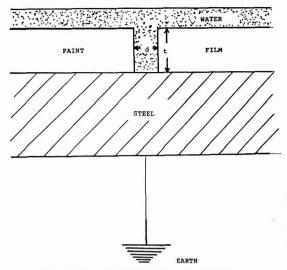


Figure 1. Theoretical pinhole through paint film.

Since the electrical resistance of water is normally expressed in terms of its conductivity, which is the inverse of resistance, equation (1) becomes:

$$R = \frac{4 t}{\sigma \pi d^2}$$
(2)

Where: σ = specific conductivity in Siemens per metre

The value of R can be preset by means of the calibration resistances described earlier.

In a paper by Ward and Logan¹ it is stated:

"in the thin film coating industry, any area with less than 80,000 ohms resistance is defined as a holiday"

The authors refer to the use of an electrolyte consisting of a 3 to 5% solution of salt in water with the addition of 1% detergent.

In this country, the use of specially made electrolytes is not recommended due to:

(a) the high evaporation rate leads to increasing salt concentration,

(b) the residual salt after testing promotes corrosion of the article being tested,

(c) the use of detergent causes wetting of the whole surface under test, hence causes "tracking" from any one defect or area of exposed steel (e.g. the flange of a pipe), thus making isolation of the pinhole impossible.

For these reasons, potable quality water, having a specific conductivity of 20-milli Siemens per metre (or specific resistance of 50 ohm-metre) is preferred.

The salt solution described by Ward and Logan is stated to have a volume resistivity of 0.04 ohm-metres, hence the American calibration standard of 80,000 ohms, detects a theoretical pinhole of 10μ m diameter at a coating thickness of 150 micrometres. To detect the same size pinhole using tap water of 50 ohm-metre resistivity requires a much higher sensitivity setting, as can be calculated from Equation 1, assuming the same film thickness of 150µm.

$$R = \frac{4 \rho t}{\pi d^2} = \frac{4 x 50 x 150 x 10^{-6}}{\pi x 10 x 10 x 10^{-12}}$$

= 95 Megaohms

South African experience is that the quality of coating and lining is generally such that it is difficult to achieve insulation over 100% of the surface even at 2 Megaohm sensitivity. The size of the pinhole detected using an electrolyte of conductivity 20 mS/m at various coating thicknesses is shown for sensitivity settings of 1, 2, 5 and 10 megaohm in Figure 2. In specification SABS 241 – Water for domestic supplies, it is recommended that specific conductivity should not be greater than 70 mS/m. The size of the theoretical pinhole detected when using water of this conductivity at various coating thicknesses, is also shown in Figure 2.

From Figure 2, it can be deduced that:

(a) The lower the sensitivity of the instrument, the greater the variation in pinhole size with change in coating thickness.

(b) The use of a more conductive water reduces the size of pinholes detected at a given sensitivity setting and the variation of pinhole diameter with coating thickness becomes less.

4. Other factors affecting detection

The effect of coating thickness and conductivity of the electrolyte have been considered in Section 3.

Other factors affecting the method are:

(a) specific resistance of the coating material

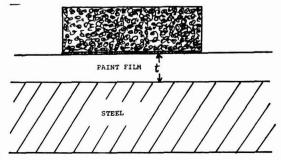
(b) size of the electrode in contact with the surface

(c) speed of pass in relation to reaction time of the instrument

Factors (a) and (b) can be considered together. Figure 3 illustrates a detection probe on a painted surface free from electrical insulation defects.

If the area of the electrode = A

Figure 3. Wet sponge electrode on painted surface.



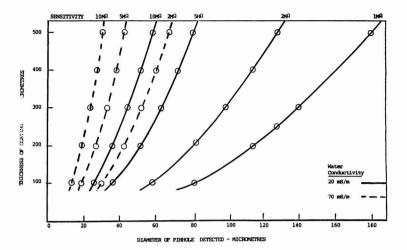


Figure 2. Effect of coating thickness and electrolyte conductivity on diameter of pinhole detected at different sensitivity settings.

S.t

Thickness of coating t S Specific resistance of coating R

Then resistance across coating =

Hence S =
$$\frac{R.A}{t}$$

Using a value of R as 2 Megaohms an electrode area of 250 x 150mm a film thickness of 250 micrometres 106

Then S =
$$\frac{2 \times 10^{\circ} \times 250 \times 150 \times 10^{\circ}}{250 \times 10^{\circ6}}$$

 3×10^8 ohm-metres

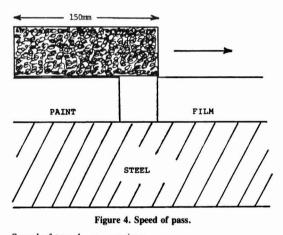
Hence, if the specific resistance of the coating is less than 3×10^8 ohm metres, the alarm of the detector will operate even if there is no insulation defect in a coating of 250 micrometres in thickness. To test for defects in such a coating, either the instrument must be set to a lower sensitivity or an electrode of a small contact area must be used. Fortunately, most coatings used for underwater protection have higher specific resistance. Some results obtained on well aged coatings are given below.

Specific	Resistance	of	some	Aged	Coatings	(Using	an
Elect	rode area =	120	529 mn	n ² , Tes	t Voltage =	= 500V)	

	Specific Resistance in ohm-metres		
Epoxy powder	11,5	x	10 ¹²
Polyester powder		х	10 ¹²
Vinyl coating	0,7	х	10^{12}
Chlorinated rubber coating		х	10^{12}
Epoxy polyamide		х	10^{12}
Epoxy tar		х	10^{12}
Aliphatic polyurethane		х	10 ¹²

Speed of pass of electrode (Figure 4).

If length of electrode in direction of movement = L



Speed of travel = v m/sec L x 10⁻³ Then time to pass over defect secs

Using the general purpose probe of 250 by 150 mm and assuming the traverse is in the direction of the shorter side, then the rate of traverse must be less than 150/t mm per sec. where t is the response time of the instrument. If t = 0.5secs, then the maximum traverse speed is 18 metres per minute. However, if a small electrode is used, of 10 mm length, then the maximum traverse speed becomes 1.2 m per minute.

5. The South African Mark III wet sponge detector

To overcome the problems of: (a) inattention by operator, (b) excessive speed of traverse, (c) noisy surroundings, (d) accidental movement of controls, the Mark III has been developed.

This instrument incorporates a "latch circuit" so that as soon as the preset sensitivity current, as determined by the preset voltage and sensitivity settings level, is exceeded, the latch circuit switches on the alarm, which then remains on until the operator switches it off manually. It is therefore

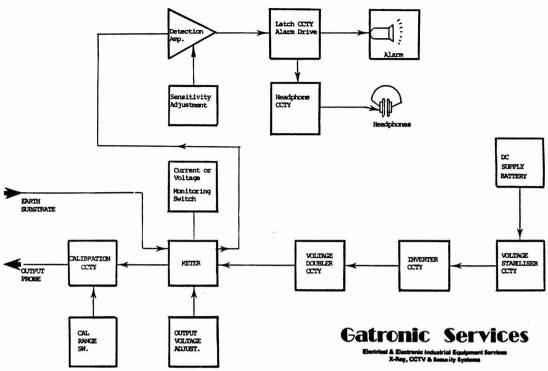


Figure 5. Block Diagram of the Gatronic Pinhole Detector Mk. III.

virtually impossible for him to miss the warning. Being electronic, the latch circuit is instantaneous in its response in relation to delay times previously discussed.

For use in noisy and bright light surroundings, where both audio and visual signals may be missed, an optional headphone set is available. Figure 5 is a block diagram of the instrument incorporating these refinements.

6. Probes used in practice

Standard probe (Figure 6)

The standard probe consists of an insulated handle with a rectangular sponge 150×250 mm clamped between two aluminium plates. The handle may incorporate a warning light to show when a defect is detected and a reset switch to switch off the alarm when the operator has recorded the defect. This probe is used for most easily accessible surfaces such as aerator impellors, small gates, valves and structural steel.

Roller probe (Figure 7)

For very large surfaces a roller probe is used at the end of a long handle. The probe consists of a cylindrical sponge mounted on a roller with conductive carbon brushes, then fixed into an insulating handle, This is used on large dam gates and inside tanks.

Small surface probe (Figure 8)

For use on test panels in the laboratory, a very small probe similar to a tooth brush is used. This is very useful for detecting defects resulting from bend tests and impact testing.

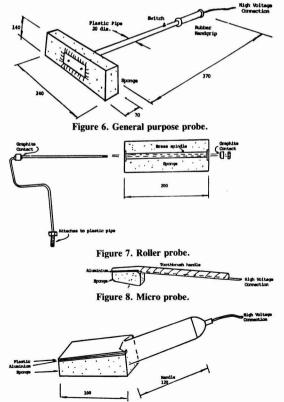
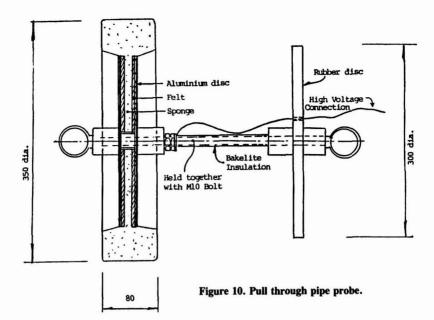


Figure 9. Single face probe.

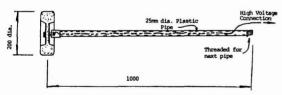


Insulated side probe (Figure 9)

On fitted dam gates, the edges of the gate need to be tested but the clearance between gate and concrete pier is only about 10 mm. For this application a flat probe insulated on one side is used.

Pipes

Circular probes are used for inside pipes. Up to 200 mm diameter and 3 metres in length, a single circular probe is attached to an insulated handle which enables the probe to be pushed, or pulled, down the pipe. (See Figure 11). For larger bore and longer length pipes a pig type of probe is used. This is self supporting and hence may be pulled through the pipe by means of a nylon rope. (See Figure 10).





7. Precautions to be taken

Contact area

For the test to be of value, it is obvious that 100% of the surface must be covered. When testing pipes it is important that the probe is sufficiently larger in diameter than the pipe bore so that it touches the bore along its full length. Alternatively, it must be supported so that the sponge does not sag under the weight of the water sufficiently to lose contact with the crown of the pipe.

Wetness of Sponge

The sponge must be sufficiently wet that it will penetrate defects but not so wet that it leaves a trail of water that will

cause tracking to a previously detected defect or to bare steel such as a bolt hole. The wetness of the sponge must be frequently checked in hot environments where it can dry out fairly quickly. Sponge material needs to be carefully selected with maximum water retention. To assist in holding water, yet retain the conformability of sponge, a backing of felt can be used as shown in Figure 10.

Earth

It is obvious, but frequently forgotten, that a good earth connection to the substrate is essential. In the case of pipes, pipelines and tanks, a very long earth wire of 50 metres or so is required. This must be of multistrand copper construction to minimise voltage drop.

8. Real life causes of E.I.D's

Up to now we have discussed a theoretical pinhole simply to establish meaningful parameters for the various factors involved.

In practice, electrical insulation defects are caused by protrusions or occlusions in the coating. These can arise from three main sources:

(a) in the fabrication of the article, where there may be sharp edges to welds, undercuts, weld spatter, laminations in the steel, burrs on sheared edges and drilled holes. It is imperative that these are removed prior to coating if coating free from electrical defects is required. In the case of pipes, seamless types are preferred unless really efficient scarfing of an electric resistance weld can be carried out,

(b) in the blast cleaning process, where "hackles" can be created if the abrasive is too coarse. Residual debris and abrasive are equally disastrous and should be removed by vacuum cleaning,

(c) during the application and curing of the coating, when wind borne detritus from adjacent blasting operations can settle on and penetrate into the wet coating.

Table 1

"Real Life" causes of pinholes

Causes	Solution	Responsibility
1. Weld spatter	Grind off before coating	Fabricator
2. Projecting or undercut weld	Scarf accurately, grind flush with wall	Fabricator
3. Laminations in steel	Grind out	Fabricator/Steel Supplier
4. Sharp edges	Grind to suitable radius (2 mm or greater)	Fabricator
5. Residual blasting debris	Vacuum clean before coating	Coating Contractor
6. Wind borne dust	Erect wind breaks or work in clean closed shop	Coating Contractor
7. Occlusions in paint film during application	Use clean tools in a clean environment	Coating Contractor
8. Physical damage to partly cured film	Handle with care. Do not move until cured	Coating Contractor
9. Physical damage to fully cured film	Handle with care. Use only broad band slings Use double lift on spacer bar for long pipes	Transport or Erection Contractor

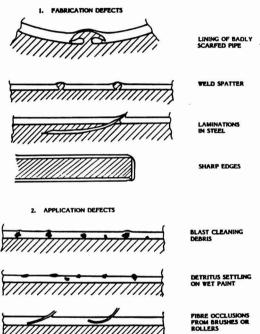


Figure 12. "Real Life" causes of pinholes: electrical insulation defects.

Real life causes of E.I.D's are summarised in Table 1 and illustrated in Figure 12.

Should the precautions listed not be taken, then repair of defective areas can be difficult. Wet sponge testing cannot be carried out until the bulk of solvent has been removed, since solvent lowers the resistivity of the coating (See Section 4). If repairs become necessary, then access to, say the centre of a 9 m long pipe for proper preparation for overcoating is extremely difficult. The result is frequently that an additional coat is applied with subsequent delamination. Hence it is highly desirable to take the precautions to remove sources of defects before coating.

9. Safety

High voltage electrical testing, such as with the holiday (high voltage) spark detector, can be dangerous when carried out in damp surroundings such as a pipe trench bottom.

Low voltage testing is intrinsically quite safe because of

both low voltage and low current consumption. In fact, to determine the exact spot of a defect, it is common practice to hold the wet sponge in one hand and use a wetted finger to feel over the suspect area to find the spot. Body resistance is sufficiently low to make negligible difference to the sensitivity as shown in Table 2 (ref 3).

Table 2

Human resistance to electrical current*

0.0 SIN/3	a Second provide the provide and the
Dry skin	1,000,000 to 5,000,000 ohms
Wet skin	1,000 ohms
Standing or lying in water	150 ohms
Internal body – hand to foot	400 to 500 ohms
Internal body – ear to ear	(about) 100 ohms

*Accident Prevention Manual for Industrial Operations – National Safety Council and Frank A. Jenkins, "Hazards of Low Voltage Electricity" U.S. Department of Labor Pamphlet MP-8-0, (June, 1962).

The effect of A.C. current on the human body is shown in Table 3 (ref 3). Since the wet sponge detector described earlier has a built in 1 Megaohm resistor, the maximum current flow at 100 volts (its maximum voltage setting) is 100 microamperes, which is one tenth of the minumum current required to give any sensation of shock.

Conclusions

1. Wet sponge E.I.D. detection is the only method of testing the quality of a coating over 100 per cent of its surface.

2. By calibrating the detector, parameters can be specified to ensure minimum variation between operators.

3. The Mark III instrument has built in controls to eliminate errors by inattention of the operator and accidental alteration of settings. It is electrically safe.

4. Probes have been designed to cover a wide range of applications from laboratory panel testing to lining of pipes from 100 to 400 mm, large tank surfaces and dam gates 10 m wide by 8 m high.

5. Most electrical insulation defects emanate from mechanical deficiencies in the surface being coated and lack of cleanliness in the application of the coating.

Precoating inspection and good housekeeping in coating application are necessary to ensure freedom from E.I.D's.

Table 3

60Hz Alternating current values affecting human beingst

Current	Effects
1 mA or less	No sensation – Not felt
1 to 8 mA	Sensation of shock – Not painful; individual can let go at will; muscular control not lost.
8 to 15 mA	Painful shock – Individual can let go at will; muscular control not lost
15 to 20 mA	Painful shock – Muscular control lost; cannot let go
20 to 50 mA	Painful shock – Severe muscular contractions; breathing difficult
50 to 100 mA (possible)	Ventricular fibrillation – Death will result if prompt cardiac massage not administered
100 to 200 mA (certain)	Defibrillator shock must be applied to restore normal heartbeat. Breathing probably stopped
200 mA and over	Severe burns – Sever muscular contractions; chest muscles clamp heart and stop it during shock (ventricular fibrillation is prevented). Breathing stopped – Heart may start following shock, or cardiac massage may be required.

†Accident Prevention Manual for Industrial Operations – National Safety Council. W. B. Kouwenhoven, Ph.D., "Treatment of Electric Shock" in low voltage shock hazards, The John Hopkins University, (June, 1962).

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Corrosion protection properties of various ferrite pigmented paint films

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Summary

The corrosion protective properties of the paint films prepared from the various ferrites (MO·Fe₂O₃; M=Mg, Ca, Sr, Ba, Fe, Zn) and epoxy resin have been determined by various electrochemical measurements. The weight loss of mild steel in extracted aqueous solution of pigments and paints, and the transport number of C1⁻ anions were measured. From these results, there was a direct relationship between the pigment concentration, the corrosion protection properties, and the transport number in Mg ferrite paint, Sr ferrite paint and Fe ferrite paint. The Fe ferrite paint of the six types of ferrite paints showed comparatively good corrosion protection properties in combination with the epoxy resin.

Introduction

The investigation of non-toxic ferrite pigments has been reported by Kresse¹ for Ca ferrite and Zn ferrite, and these pigments showed their corrosion protective effects by intensifying their combination with vehicles by reaction with the fatty acids to form soaps and by reinforcing the paint film by the flocculation of the pigment.

Accordingly, in this work, paints were prepared by mixing the various Mg, Sr, Ba, Fe ferrites in addition to above mentioned Ca and Zn ferrites, and an epoxy resin. Their corrosion protective properties were investigated by measuring the natural electrode potential (NEP), the tan δ and the impedance with time on the coated steel plate. These results were correlated with the results of the transport number of C1⁻ ion calculated from the membrane potential and of the weight loss measurement of mild steel in the extracted aqueous solution of pigments, and paints.

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Experimental

Preparation of paints

The paints were prepared by mixing in the weight ratio of epoxy resin: pigment = 4:1, 4:2, and 4:3 and by adding the curing agent and accelerator. The mean particle size of various ferrites was about $1\mu m$.

Specimen and solution

Cold rolled steel plate (JIS G3141), 7 x 15 x 0.08 cm, which was used for specimens was polished with emery paper to No. 1200 after soldering of the connecting wire and cleaned successively by immersion in perchloroethylene and ethanol. The paint was coated by an applicator about 100 μ m and dried for a week. The back and edges of the specimen were thickly masked in paraffin wax so that a surface area of 50cm² was exposed. The solution for immersion was 3% NaCl aqueous solution used at 30 ± 0.5°C.

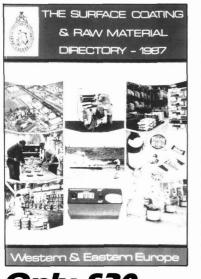
NEP measurement

NEP was measured by a electrometer. A saturated calomel electrode (SCE) was used as a reference electrode.

tan δ measurement

The tan δ value was calculated from the film capacitance C_p and the film resistance R_p which were measured by a phase sensitive detector as the parallel circuit at 500 Hz (tan $\delta = 1/2\pi f C_{p} R_{p}$). A Type 304 stainless steel plate, 7 x 15 x 0.05 cm, was used as a counter electrode. The reference signal voltage of sinusoidal wave was 9mV (RMS).

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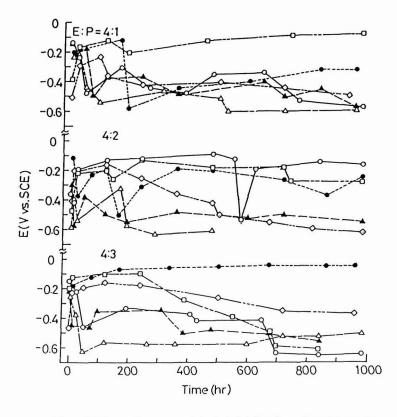


Figure 1 NEP vs. time curves of ferrite paint films in various mixture ratios. $\circ = Mg, \Delta = Ca, \Box = Sr, \diamondsuit = Ba, \bullet = Fe, \blacktriangle = Zn.$

Impedance measurement

The measurement of impedance was carried out at NEP using a lock-in amplifier in the frequency range 8 KHz to 1 Hz, and using the Lissajous method in the frequency range 1 Hz to 0.01 Hz. The counter electrode and the reference signal voltage were the same as those for tan δ measurement.

Weight loss measurement

The weight loss measurement of mild steel in extracted aqueous solution of pigment and paint was determined^{2,3}. The extracted aqueous solutions of pigment and paint were obtained from 25g of pigment + 500ml of distilled water, and 25g of pigment + 97g of vehicle + 500ml of distilled water, respectively. These extracted aqueous solutions were allowed to stand for eight days with periodic shaking. The blank solution was the distilled water after standing for eight days. The mild steel plate (JIS SS41), $2 \times 5 \times 0.02$ cm, which was used for specimen, was polished with emery paper to No. 1500, and then degreased with methanol and acetone. Specimens were immersed in these solutions for seven days and then the weight loss was measured.

Membrane potential measurement

The vessel which was divided by the free film, was filled by 0.1N KCl and 0.01 N KCl, respectively. Electromotive force $E_{\rm M}$ of Hg/Hg₂Cl/sat.KCl/KCl (0.1N)//Membrane//KCl

(0.01N)/sat. KCl/Hg₂Cl₂/Hg cell was measured. A saturated calomel electrode was used as a reference electrode.

The transport number t of the anion was obtained by inserting the measured $E_{\rm m}$ into the following equation. $E_{\rm m} = (t_{-} - 1) \text{ RT/F} \text{ 1n } a_1/a_2$

Results and discussion

Figure 1 shows the NEP against immersion time for various ferrite paints. The NEP value of each specimen was dependent on the ratio of pigment to vehicle. All of the potentials shifted to less noble potential with immersion time. However, the NEP values for 4:1 ratio of Sr ferrite, 4:2 of Mg ferrite and 4:3 of Fe ferrite paints showed more noble potential than about -0.2 V during the test period. In the case of 4:2 of Mg ferrite paint, the NEP shifted rapidly at about 550 hours after immersion. It is thought that the NEP shifted to less noble potential by permeation of water into the interface of the paint film and metal, and then shifted to noble potential again due to passivity.

As for Sr ferrite and Fe ferrite paints, there was a direct relationship between the pigment concentration and the NEP value with the passage of time. In Sr Ferrite paint, the value of the NEP became less noble and in Fe ferrite paint, the NEP value became more noble as the pigment concentration increased. However, in the cases of Ca ferrite and Zn ferrite paints, the NEP gave a value of about -0.6 V in all pigment concentrations.



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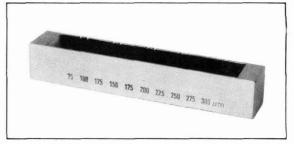
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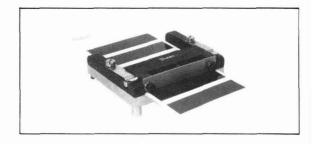
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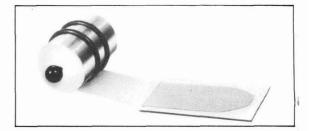
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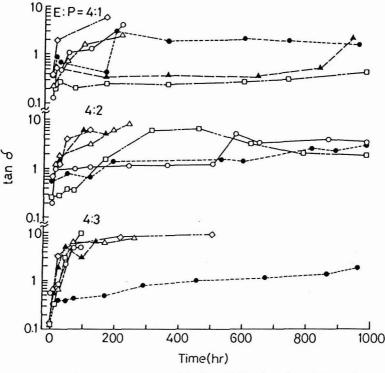


Figure 2 tan δ vs. time curves of ferrite paint films in various mixture ratios. $\circ = Mg, \Delta = Ca, \Box = Sr, \diamondsuit = Ba, \bullet = Fe, \blacktriangle = Zn.$

It is thought that the paint, which held a noble potential and did not shift in NEP to a less noble potential for a long test period, has good corrosion protection^{4,5,6}. Consequently, the mixture ratios such as 4:1 of Sr ferrite, 4:2 of Mg ferrite and 4:3 of Fe ferrite paints are seen to possess good corrosion protection properties.

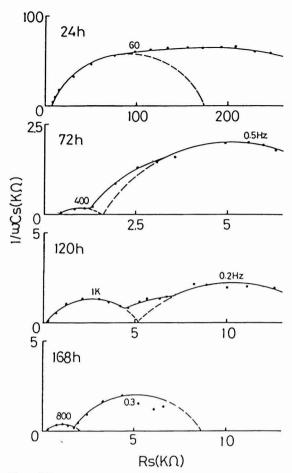
Figure 2 shows the tan δ against immersion time for various ferrite paints. It is evident from the figure that the tan δ of most of the paints increased for short period, and the paint films deteriorated. In general, the tan δ showed an increasing tendency for a short period as the pigment concentration was high. As for Sr ferrite paint, its tendency was clear, and the tan δ increased with increasing concentration of pigment. There was the mutual relationship between the tan δ and NEP.

In the cases of 4:1 of Sr ferrite paint and Zn ferrite paint, these indicated a small tan δ . The NEP of Sr ferrite paint shifted to noble potential, but that of Zn ferrite paint did not do so. The tan δ of Fe ferrite paint gave a steady value from 1 to 2, but the value of NEP varied with the concentration of pigment. In general, the paint, which showed a small tan δ value for a long period, had good corrosion protective properties^{4,7,8}. Consequently, the paints such as 4:1 of Sr ferrite and Zn ferrite paint would be considered to have good corrosion protective properties. However, tan δ is related to the paint film, and its relation with the corrosion under the paint film is small⁹. It is thought therefore that the paint showing the more noble potential and a small tan δ value, should possess excellent corrosion protective properties. The 4:1 of Sr ferrite paint gave the highest corrosion protective property. Figure 3 shows the complex impedance plane plot against immersion time of the steel plate coated with the 4:3 Ca ferrite paint. 24 hours after immersion, the plots indicated a part of the semi-circle in the high frequency range and a flat loop in the low frequency range. At 72 hours, the circular arc in the high frequency range became very small, and in the low frequency range the semi-circle appeared. At 120 and 168 hour, each circular arc in the high and low frequency ranges became small.

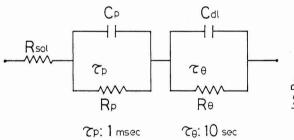
Figure 4 shows the equivalent circuit of the coated steel plate which corresponds to such a result¹⁰. The semi-circle in high frequency range was based on the paint film resistance R_{ρ} and capacitance C_{ρ} , and the semi-circle in the low frequency range was based on the charge transfer resistance or corrosion reaction resistance R_{θ} and the double layer capacity C_{d} at the interface of paint film and metal substrate¹¹. Thus, the values of R_{ρ} and R_{θ} can be obtained from the diameter of each semi-circle.

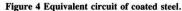
Figure 5 shows the log R against the immersion time for various ferrite paints. The R for most of paints decreased with the lapse of time. These results showed the mutual relationship of the variation of tan δ with time. Consequently, evaluating the corrosion protective properties on the basis of the variation of log R and tan δ with time, the paints such as 4:1 of Sr, Fe and Zn ferrite paints, 4:2 of Mg, Sr and Fe ferrite paints, and 4:3 of Fe ferrite paint were found to be excellent in the corrosion protective property, because they gave larger log R than 5.

Figure 6 shows log R_{θ} against immersion time for various ferrite paints. In this figure, the paint without a plot did not









show a semi-circle in the low frequency range, and the number of the plots increased with increasing concentration of the pigment. As seen from the variation of tan δ and log \mathbf{R}_{p} with time, it is thought that the paint film of high pigment concentration deteriorates quickly and the penetration of water into the interface of paint film and metal substrate occurs easily.

Consequently, the corrosion protective property of the paint film is considered to be improved when either the semi-circle in the low frequency range does not appear in the long term, or when the R_{θ} value was large. However, since the impedance was not measured over the long term,

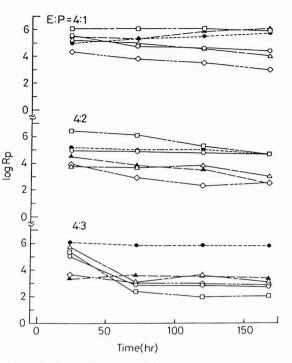
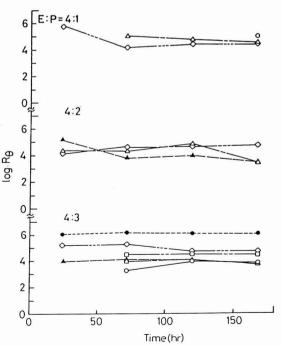


Figure 5 log \mathbf{R}_{p} vs. time curves of ferrite paint films in various mixture ratios.

• : Mg, △ : Ca, □ : Sr, ◇ : Ba, • : Fe, ▲ : Zn.



6. log \mathbf{R}_{o} vs. time curves of ferrite paint films in various mixture ratios.

 $\circ: Mg, \bigtriangleup : Ca, \Box : Sr, \diamondsuit : Ba, \bullet : Fe, \blacktriangle : Zn.$

it was impossible to evaluate the corrosion protective property based on the impedance measurement alone. In general, the R_{θ} value has a mutual relationship with the NEP except in the first stage of immersion^{11,12,13} and the R_{θ} tends to decrease as the NEP shifts to less noble potential.

Consequently, evaluating the corrosion protective property on the basis of the variation of the log R_0 and the NEP with time, the paints such as 4:1 Sr ferrite, 4:2 Mg ferrite and 4:3 Fe ferrite paints were considered to possess good corrosion protective properties.

As mentioned above, from these results, the Sr ferrite paint and the Fe ferrite paint showed the direct relationship between the concentration of pigment and the corrosion protective property. The Sr ferrite paint with the low concentration of pigment, and the Fe ferrite paint with the high concentration of pigment showed good corrosion protective properties, the paints such as 4:1 Sr ferrite, 4:2 Mg ferrite, and 4:3 Fe ferrite showed especially good corrosion protection protection.

These results were further investigated from the viewpoint of the corrosion protective effects of pigments and paints themselves.

The pH of extracted aqueous solution of pigments and paints, and the corrosion rate of mild steel in this solution were measured, and their results compared with the previous results.

Tables 1 and 2 show the pH of extracted aqueous solutions of pigments and paints, and the corrosion rate of mild steel. Each aqueous solution of the pigments and paints indicated a higher pH than that of the blank. These results proved that all the ferrite pigments are basic. As for the extracted solutions of Mg and Ca ferrites, they were seen to have a high pH and their corrosion protective properties could be expected. But from the results of electrochemical measurements of coated steel, Mg and Ca ferrite paints did not show the excellent corrosion protective properties except for the 4:2 Mg ferrite paint. This could be ascribed to the fact that the particles of Mg and Ca ferrite pigments were coarser than those of other four types, and that the dispersion of the Ca ferrite in the epoxy resin was poor. In the other four types of ferrites, the Fe ferrite paint showed the best corrosion protective property, because the pH of its solution was comparatively high and the corrosion rate indicated the lowest value. This result was consistent with that of the electrochemical measurements previously described

The corrosion rate in extracted aqueous solutions of the paints was lower than that of the pigments. It is considered that the soluble components of the paint acts as a corrosion inhibitor.

As for the relationship between the transport number t of anion and the corrosion protective properties, Table 3 shows the transport number of CI^- ion in free ferrite paint films in various pigment ratios. In the case of the Mg ferrite paint film, the value of t maximised at a mixture ratio of 4:2. The t value of Sr ferrite paint film was high as the concentration of pigment was low, and the t value of the Fe ferrite paint film was high as the concentration of pigment is high. Comparing these results with those of the electrochemical measurements of coated steel, the corrosion protective property of paint improved as the t value increased.

Table 1

Corrosion rate of mild steel in extracted aqueous solution of pigments

Pigment	pH	Corrosion rate (mdd)
Mg-ferrite	8.82	12.75
Ca-ferrite	12.35	0.26
Sr-ferrite	7.85	16.71
Ba-ferrite	8.20	18.00
Fe-ferrite	8.40	14.95
Zn-ferrite	7.31	14.71
Red iron oxide	3.35	20.35
Blank	6.15	15.82

Table 2

Corrosion rate of mild steel in extracted aqueous solution of paints

Paint	pH	Corrosion rate (mdd)
Mg-ferrite	9.3	1.00
Ca-ferrite	12.2	0.07
Sr-ferrite	8.7	5.66
Ba-ferrite	8.4	8.21
Fe-ferrite	8.4	3.58
Zn-ferrite	7.4	15.00

Table 3

Transport number of chlorine anions in membrane of ferrite paint films in various mixture ratios

	Mixture	e ratio (E.P)	
Paint	4:1	4:2	4:3
film		t _	
Mg-ferrite	0.42	0.47	0.40
Ca-ferrite	0.49	0.50	0.48
Sr-ferrite	0.54	0.52	0.28
Ba-ferrite	0.53	0.60	0.55
Fe-ferrite	0.49	0.52	0.62
Zn-ferrite	0.49	0.50	0.46

 $E_{m} = (2t_{-1})RT/F \ln a_{1}/a_{2}$

As for the paints pigmented with Mg, Sr and Fe, there was a direct relationship between the concentration of the pigment, the corrosion protective properties and the transport number of Cl^- ion.

Conclusion

- From the results of electrochemical measurement of coated steel, the paints such as 4:1 of Sr ferrite paint, 4:2 of Mg ferrite paint, and 4:3 of Fe ferrite paint were found to show excellent corrosion protective properties.
- Sr ferrite paint at a low pigment concentration, and Fe ferrite paint at a high pigment concentration showed excellent corrosion protective properties.
- The corrosion protective properties of Fe ferrite paint was excellent in all mixture ratios, and this result showed a direct relationship with that of the aqueous extracts of the pigment and paint.
- In the ferrite paints made from Mg, Sr and Fe, there was a direct relationship between the concentration of pigment, the corrosion protective properties, and the transport number of the Cl⁻ ion. References p267

Advances in environmentally acceptable polyurethanes

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Abstract

The versatility of urethane chemistry allows for the synthesis of a variety of polymer compositions useful for the manufacture of surface coatings. Environmental considerations have influenced the direction of research and development of urethane resins and led to the development of new products with reduced solvent and lower VOC levels.

A review of basic urethane chemistry and the property/structure relationships of common compositions is presented. The evolution of the more environmentally acceptable waterborne, higher solids and single package high performance versions of various urethane types is discussed and contrasted to older technology. Coating formulations and performance of old and new technology systems are compared and associated end use discussed.

Introduction

Polyurethanes grew rapidly during the last few decades until they became a well established class of coating resins. Because of the versatility of urethane chemistry, and largely because of the fact that diisocyanates, the building blocks of polyurethanes, are reactive at normal ambient temperatures, a large number of different types of urethane resins have become available.

Most urethane papers start off with a basic explanation of urethane chemistry to assist in the understanding of the different types, however this discussion will try to avoid as much of that as possible and concentrate on discussing the various classes of urethanes, differentiating between them on the basis of the end uses in which they are used, and then identifying the types which are capable of being modified by producing higher solids or water reducible versions, thereby improving them in the area of environmental acceptance.

The American Society for Testing and Materials (ASTM) has made this differentiation easier for us by establishing definitions for the various types of urethane resins. ASTM has broadly defined six different categories which are given in Table 1.

Table 1

ASTM Urethane Classification

Type I	Oil Modified
Type II	Moisture Curing
Type III	Blocked
Type IV	Catalyst Curing
Type V	Polyol Curing
Type VI	Lacquer

Each of the six types may also be subdivided into aromatic and aliphatic, depending on whether the diisocyanate is an aromatic one or an aliphatic one. In general aromatic diisocyanates are considerably less expensive than aliphatic ones, and are used wherever possible, especially in interior coatings. The higher price of the aliphatics is justified for exterior coatings or where their superior color is required. In practice, aliphatic diisocyanates do not contribute enough performance improvement to the oil modified urethanes (Type I) to justify their use.

Table 2 depicts that fact, and also introduces the areas where environmental improvements are being sought, namely in water reducible and high or higher solids versions.

Table 2

Urethane Resin Types

Туре	Description	ARO	ALI	WD	HS
I	Oil Modified	X		X	X
II	Moisture Cured	Х	Х	-	X
III	Blocked	Х	X	?	X
IV	Catalyst Cured	х	Х	-	X
V	Polyol Cured	х	X	-	X
VI	Lacquer	X	X	x	X

ARO = Aromatic, ALI = Aliphatic, WD = Water Dispersible, HS = High Solids

Note that there is not much in the way of commercial aliphatic oil modified urethanes available for reasons just mentioned. Also note the lack of activity under the WD column. The primary reason is that Types II, IV and V are prepolymers and these cannot be made in water because of their reactivity with active hydrogen containing materials. It is theoretically possible that WD versions of the blocked urethanes could be made since the isocyanate groups are blocked with materials which would prevent their reaction with water, but the author is not aware of much activity in this area. All of the six types, however, are adaptable to improvements in solids levels to at least some degree. The lacquers will never likely be raised to solids levels much above 40% however.

In the water thinned work, especially in the lacquers, effort is being made to reduce the ratio of coupler solvent to water as well as simply to make better performing polymers.

Each of the urethane categories will now be discussed in turn to see what areas of activity are involved in reducing solvent levels.

Oil modified urethanes (ASTM Type I)

This class of urethanes is the one-package type often referred to as urethane alkyds or uralkyds. While the pure oil modified urethane contains no phthalic anhydride, they can be blended with alkyds or even be prepared with both toluene diisocyanate and phthalic anhydride to form an insitu blend of alkyd and urethane. They are almost always based on TDI (Toluene Diisocyanate) and are therefore aromatic in nature. They can be made from aliphatic diisocyanates as well but any small advantage from the aliphatic diisocyanate is usually overshadowed by the oil component, usually linseed, soya, safflower or TOFA (Tall Oil Fatty Acids), depending on the end use.

A) High solids versions

These resins are usually supplied at 50-60% solids in mineral spirits for the DIY trade or in aromatic solvents for industrial use, such as in prefinishing applications. Higher solids versions are possible and in fact they can even be supplied at 100% solids, making them true high solids resins just as alkyds often are. House paints and printing inks are two of the applications where high solids oil modified urethanes have been used.

Their most important uses, however, are in floor finishes and clear interior varnishes. In these applications, dry time and abrasion resistance are important and those are two of the properties sacrificed when higher oil level products are developed. The reason for this is that urethanes derive their unique properties from the diisocyanate content in the resin, and as its level is reduced, as is necessary in higher solids products, some properties suffer. Pure oil modified urethanes usually have about 20% TDI on a solids basis when they are supplied at the normal 50-60% solids and have to contain lower levels in higher solids resins because of its effect on molecular weight and viscosity.

Table 3 presents a comparison of standard and high solids oil modified urethanes.

	Standard	High Solids
Percent Solids	60	100
Viscosity, Stokes	17-28	46-98
Solids @ 1 Stoke (D)	52	78
Tack Free, Hrs.	3.5	9
Sward Hardness, 1 day	12	6
Sward Hardness, 7 days	45	15
Wgt Solids, White Enamel	63	82.8
VOC, grams/liter	488	216

B) Water dispersed oil modified urethanes

The synthesis of waterborne oil-modified urethanes begins similarly to their solvent counterparts, however in order to impart water solubility to the resin, again as is common in alkyd technology, the polymer is chemically modified with a solubilizing agent containing pendant acid groups. The synthesis is carried out in appropriate solvents which will eventually act as couplers for solution stability as well as coalescing aids for final film formation.

The formulation of the actual water dispersed urethane varnish first requires neutralization of the acid functionality followed by letdown with water and addition of the driers. The final film forming mechanism is identical to that of their solvent counterparts and relies on crosslinking through the unsaturation present in the drying oil portion of the resin.

	Solvent	Water
Percent Solids	60	70
Viscosity, Stokes	20	400
Acid Value, Solids	1.7	50
Solvent	MS†	Coupler

†MS = Mineral Spirits

In this table, the water reducible resin on the right and the solvent product on the left are typical commercial resins. The viscosity difference is primarily related to the solids levels. The higher acid value of the WD resin is the primary evidence of the difference in composition required to obtain water reducibility. Both resins are based on TDI and linseed oil.

The differences in finished varnish formulations can be seen in Table 5. Note that to obtain an acceptable application viscosity the WD system requires a greater solids reduction. Also note, however, that the VOC level of the WD version is below 350 grams/liter (less water) while the solvent product is over 500 grams/liter.

Table 5

Clear wood varnish formulations

	Solvent	Water
Percent Solids	50	27.8
Viscosity, GH [†]	D	н
pH	—	8.5
VOC (less water), g/l	500	345

†GH = Gardner-Holdt

In general, the typical dry film properties of the two resins, as given in Table 6, are comparable. Dry hard times are quite similar but the hardness development of the WD version is more rapid. Recoat time depends on coupler solvent selection but is more critical for the WD resin, and while abrasion resistance is good it is not as good as for the solvent system. As might be expected from previous discussions, this is probably related to the lower level of TDI on solids. Stability (about two years) has been found to be adequate but further improvement would be helpful since the primary uses are in the DIY sector.

Table 6

Dry film properties

	Solvent	Water
Dry Time, Hrs		
Set	0.25	0.50
Through	2.0	2.0
Hard	3.0	3.0
Sward Hardness		
1 day	7	28
7 days	22	42
Critical Recoat Time	4-12 hrs	8-40 hrs
Abrasion Resistance (Mg. loss)	90	135

Moisture curing urethanes (ASTM Type II)

Moisture curing urethances are prepolymers based on either aromatic or aliphatic urethanes which have enough flexibility built into the molecule so that when they cure by atmospheric moisture they are able to provide very tough, flexible, abrasion resistant films. While designed to be cured by moisture, they may also be cured with other short chain active-hydrogen containing crosslinkers. The largest use of these resins is coatings for wood and concrete floors.

Since moisture curing urethanes are reactive with moisture, they cannot of course be made into water reducible versions. They are usually made to be applied at about 40 to 45% solids by brush, spray or lambs wool applicator and therefore must not be above a viscosity of about one stroke or poise at that solids level.

However there is another reason why they have usually been produced in the 40 to 45% solids range. When moisture curing urethanes begin to react with moisture, carbon dioxide is given off as a by-product of the reaction. Being a gas, it must be dissipated from the film or it will form bubbles. The degree of bubble formation is influenced by several factors. The first is the rate of cure. Urethane prepolymers react relatively slowly with moisture, so in order to obtain reasonable cure rates urethane prepolymers which are designed to be used as moisture curing resins have catalyst added and therefore are more sensitive to bubbling than uncatalyzed prepolymers would be. For this reason some moisture cures are supplied uncatalyzed and catalyst addition can be made on the job site at varying levels depending on the temperature and humidity, the two most important factors influencing their rate of cure. While this essentially makes them into two-package systems it gives the user control over the rate of cure and correspondingly the sensitivity toward bubble formation.

The second factor influencing the degree of bubbling is film thickness. Control of film thickness during application is determined to a great extent by both the viscosity and the solids level of the resin. Low viscosity allows for adequate spreading rates and the solids level determines the amount of dry film thickness remaining after evaporation of the solvent. Generally it has been found that keeping film thickness below about 2 mils dry film per coat will minimize bubble formation to an acceptable level with standard catalyzed moisture cures. Film thicknesse higher than that can be obtained with lower than normal catalyst levels.

A third factor influencing bubbling is the degree to which air bubbles are entrapped in the film during application. It has been shown that air bubbles can act as nuclei for the development of larger bubbles as the carbon dioxide is given off. Degassing a film under vacuum to remove the air bubbles allows the curing of thicker, bubble free films by dissipation of the carbon dioxide. Degassing is of course not practical during application, but any steps taken to reduce the amount of air entrapment during application are beneficical. Air entrapment can be minimized by low viscosity, low film thickness, and slower evaporating solvents which are able to keep the film "open" longer, thereby allowing the escape of air and carbon dioxide.

The above discussion of some of the practical considerations of the application of moisture curing urethanes relates to the development of higher solids versions, of which both aromatic and aliphatic products are available. When applying the higher solids products, more care must be taken during application to avoid excessive film thickness and air entrapment which could cause bubbling. The benefit of this additional care is the reduction of VOC from over 600 grams/liter to about 420 grams/liter or 3.5 pounds/gallon.

Table 7 is a comparison of typical normal (40% solids) and higher solids (64% solids) aromatic moisture curing urethanes:

Table 7

Aromatic	moisture	cures

	Standard	High Solids
Percent Solids, Wgt.	40	64
Vol.	35	58
Viscosity, Stokes	0.7-1.3	0.5-2.0
GH†	B-E	A-H
Color, max.	1	2
Percent NCO [‡] , min.	2.2	4.7
Solvent	Xylene	Xylene

A similar comparison of aliphatic products is presented in Table 8.

Table 8

Aliphatic moisture cures

	Standard	High Solids
Percent Solids, Wgt.	40	62
Vol.	35	56
Viscosity, Stokes	0.5-1.1	0.5-2.0
GH†	A-D	A-H
Color, max.	1	2
Percent NCO [‡] , min.	2.8	4.0
Solvent	Xylene	Xylene

†GH = Gardner-Holdt, ‡NCO = Isocyanate

Blocked urethanes (ASTM Type III)

Blocked urethanes are storage stable prepolymers in which the isocyanate functionality is reacted with a blocking agent which can be driven off with heat to regenerate the isocyanate. The isocyanate is then free to react with other hydroxyl containing components in the formulation. Originally they were used primarily in thermosetting wire coatings but lately they are surfacing in a variety of other applications such as crosslinkers for powder coatings, speciality coil coatings, automotive primers for flexible plastics and on chip-resistant metal coatings. The primary reason for their growth is their ability to be used in higher solids coating systems meeting reduced VOC requirements where heat curing is possible.

The blocking agent used determines the unblocking temperature required for cure. Some examples of the more common blocking agents are phenol which unblocks at 320F, methyl ethyl ketoxime at 250F, caprolactam at 325F and diethyl malonate at 195F. Since both the blocked urethane and the curing agent are of relatively low molecular weight, products made using this technology can be supplied at high solids, low viscosity and in a stable onepackage coating.

A typical analysis of an aromatic blocked urethane prepolymer given in Table 9.

Table 9

Blocked aromatic coating system

Percent Solids	80
Viscosity, Stokes	10
Color, Gardner	<1
Specific Gravity	1.047
Solvent:	Cellosolve Acetate

This product represents a typial MEKO (methyl ethyl ketoxime) blocked urethane coating resin. It contains both prepolymer and crosslinking component, and is designed for use on elastomeric substrates.

It has an excellent solids viscosity relationship compared to the elastomeric ASTM Type VI urethane lacquers that it is designed to replace. Being blocked with MEKO, it cures at about 250F. Formulated into a primer for use on elastomeric substrates like TPU (Thermoplastic urethane), microcellular foam or RIM (Reaction Injection Moulding), the formulation would have the following characteristics as shown in Table 10 compared to a urethane lacquer made for the same purpose.

Table 10 Elastomeric primers

	Blocked	Lacquer
% Solids, Weight	71.9	42.3
% Solids, Volume	54.3	26.5
% PVC	30.0	30.0
Pigment/Binder	1.5	1.3
Viscosity, KU [†]	76	72
VOC, Grams/Liter	396	672
Pounds/Gallon	3.3	5.6

Note the advantage in solids and VOC for the blocked system. The lacquer coating is based on a very high molecular weight resin which even at a lower pigment to binder ratio produces a high viscosity coating with a much higher VOC.

Performance for the two systems is essentially equivalent, the main criteria being low temperature flexibility and impact resistance when topcoated with the proper flexible automotive topcoat.

Polyol cured urethanes (ASTM Type V)

The Type IV (Catalyst Curing) urethanes will not be discussed as a separate class because most of what will be discussed for the polyol cured type is the same and the polyol cured class is the much more important of the two. These consist of a high NCO (isocyanate) urethane prepolymer and a hydroxyl terminated polyol. When mixed together they react to form a crosslinked polymer network with the typical urethane properties of toughness, abrasion resistance and low temperature cure. The degree of crosslinking and the composition of the polyol component can be varied over a wide range to produce coatings offering a wide variety of properties. Those based on aromatic prepolymers are used in interior product finishing like office equipment and computer housings, telephone refinishing, industrial machinery, roof coatings and waterproofing coatings. The aliphatic based coatings are used for transportation finishes for aircraft and marine, automotive refinishing, chemical storage tanks and other exterior maintenance applications.

Since the choice of polyol is so wide, many of the required film properties are dependent upon it rather than upon the urethane component. The number of available prepolymers is fairly limited in number and they are kept as high in NCO content, as high in solids and as low in viscosity as possible in order to allow a wider selection of materials used for the second components, which are usually based on polyesters, polyethers, modified castor oils and acrylics.

Improvements in both the prepolymer and the polyol components have been made during the last few years for the purpose primarily of reducing the VOC level of these coatings.

Table 11 shows a comparison of four commercial aromatic urethane prepolymers and how they have evolved for use in higher solids coatings.

 Table 11

 Evolution of aromatic urethane prepolymers

	A	В	С	D
Percent Solids	60	75	75	75
Viscosity (Stokes)	3	30	30	30
Color	4	4	4	4
NCO (Solids)	16	16	16	16.7
Solvent†	CA	CA	PMA	MAK

†CA = Cellosolve Acetate, PMA = Methoxypropylacetate, MAK = Methyl Amyl Ketone

Note that while the solids level is higher, the viscosity is higher also, so the intrinsic viscosity has not changed much. Neither has the %NCO as it was optimized years ago to make the prepolymer as versatile as possible. The principal change was first to go to the PMA for toxicity reasons, and then to MAK since it is stronger and will give a lower viscosity when the polyol is added.

Now the polyol side of the formulation shall be considered. Table 12 compares two proprietary polyols designed for use in product finishing.

7	Table 12
Polyols for	product finishing

	Α	В
Percent Solids	50	80
Viscosity, Stokes	6.3-10.7	30-50
Hydroxyl Value (NV)	90-110	150-172
Solvent [†]	MEK	n-BuAc

Here the solids/viscosity relationship is improved quite dramatically without greatly affecting film performance.

Though at a higher viscosity as supplied, polyol B has a much lower intrinsic viscosity which shows up as a 28% higher solids in a white gloss formulation for product finishing. Table 13 shows the effect of replacing the prepolymer and polyol with their lower VOC replacements. Although the dry hard time is somewhat longer, the fast set time and hardness development still qualify this low VOC coating for fast production line finishes.

Two coat	urethane	enamels
----------	----------	---------

	Conventional	Lower VOC
Weight Solids, %	45	73.6
Volume Solids, %	35	62.2
Viscosity, #2 Zahn	81	60
% PVC	18	20
VOC (lbs/gal)	6.23	2.87
(gms/lit)	747	345
Dry time		
Set, Min.	10	15
Tackfree, Hrs.	1	2
Hard, Hrs.	2.25	9
Sward Hardness		
1 day	40	36
7 days	50	50

High quality polyesters have been developed which have even lower intrinsic viscosities than the product finishing polyols described above and these can be formulated into gloss and texture coatings having VOC levels below 2.5 pounds/gallon. Compared to the product finishing polyols, their disadvantage is slower dry time, as might be expected due to their lower molecular weight, but they have the higher hardness and better chemical resistance which is generally true of polyester cured urethanes. Table 14 shows a comparison between a conventional polyester (A) and two newer versions (B and C).

Table 14 Polyester polyo، comparison			
	Α	В	С
Percent Solids	100	100	100
Viscosity, Stokes	300-600	6-10	8-12
Hydroxyl Value	275-300	255-285	245-275

-		15
- 1	able	15

	Gray Texture	Gloss Yellow
Percent Solids, Wgt.	83.93	83.34
Vol.	72.38	72.07
Pigment/Binder Ratio	1.90	1.33
Percent PVC	41.0	25.03
NCO/OH Ratio	1.1	1.1
Viscosity, Sec. #2 Zahn Cup	70	60
VOC, lbs/gal	2.16	2.30
gms/lit	259	276

Aliphatic urethane prepolymers have also been improved from a VOC point of view, and a high performance polyester cured system is now available which will give a VOC of less than 3 lbs/gal in a high gloss white enamel formulation at 72.6% weight solids, even using the conventional polyester A above. With the lower viscosity polyesters above, it is possible to raise the weight solids above 80% (over 70% volume solids) at application viscosity. For example, Table 15 shows the analysis of twocomponent aromatic gray texture and gloss yellow finishes.

Urethane elastomers (ASTM Type VI)

The last category to discuss is the fully reacted, single package elastomer, or lacquer type, designated as ASTM type VI, which dry to tough, flexible films by evaporation of the solvent alone. These are very linear polymers so that they will be soluble in fairly common strong solvents, but since their molecular weight is quite high, they are generally supplied at solids levels no higher than about 40%. Prior to application they must be reduced to solids levels below 20%.

Coatings made from these products are used in applications requiring great toughness and flexibility such as in textile coatings, magnetic tape binders, and leather and plastic coatings. Typical applications are in coatings for automotive weatherstripping and because of their excellent adhesion to many types of plastics, as primers for plastic automotive parts. While low application solids is an advantage in some end uses such as where low film build is desirable like primers and coatings over patterned surfaces, the large amount of volatile organic solvent in these applications made the urethane lacquers prime targets for the development of higher solids and water reducible versions. In practice only modest increases in solids are possible, but a great deal more has been accomplished in water reducibility.

Table 16 compares a solvent and a water reducible resin which were designed to give similar dry film properties. The physical form of the water version is a colloidal dispersion, which is true of all the WD urethane elastomers.

	Solvent	Water
	20	
Percent Solids, Wgt.	30	30
Viscosity, Stokes	100	0.5
Solvent [†]	Tol/IPA	Water/NMP
Appearance	Clear	Colloid
Flash Point, F	38	None
Film Properties		
Tensile Strength, psi‡	5000	5600
Elongation, %	500	410
100% Modulus	1300	1100
300% Modulus	3000	3000
Tear Strength, pli‡	500	390
Hardness, Shore D/Sward	40/14	40/14

†Tol = Toluene, IPA = Isopropyl Alcohol, NMP = N-Methyl-2-Pyrrolidone

‡ psi = pounds per square inch, pli = pounds per lineal inch

This comparison emphasizes the differences in solids/viscosity relationship of the resins as supplied. At equivalent solids and relatively equivalent molecular weights, the water thinned resins have much lower viscosity. This is explained by the non-Newtonian viscosity/molecular weight relationship exhibited generally by colloids. A normal relationship is exhibited by the solvent product.

This difference is important because it ultimately allows for the application of the water based materials at higher solids and lower VOC. As an example, it was found that with proper formulating, a pigmented waterborne system could be sprayed at 31.8% solids versus 18.7% solids for the solvent system. An added benefit of course is the wide variation in flash points allowing safer handling and application.

An additional advantage of the collodial dispersions is that they can be crosslinked with amino resins in baking applications and with aziridine resins in air dry and force dry applications. Crosslinking gives the films added

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chemical resistance, hardness and toughness and opens them up for other applications such as floor finishes and more demanding plastic coatings.

Conclusion

From the above discussion it should be clear that the importance of urethanes as versatile coating resins will not be diminished as environmental pressures increase. Rather, the versatility of urethane chemistry will allow them to continue to evolve to meet these challenges.

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next month's issue

The Honorary Editor has accepted the following papers for publication in the October Issue:

Alkyd emulsions, properties and applications by T. Fjeldberg, Dyno Industrier AS, Lillestrøm, Norway.

Membrane separation for the production of nitrogen enriched inert gas by N. G. Henwood, Dow Chemical UK and R. T. Krueger, Dow Chemical GmbH.

Production of zinc and zinc alloyed dusts by fine atomisation by M. Leclercq, Vieille-Montagne, Angleur, Belgium.

Novel polyamide type epoxy curing agents by R. H. E. Munn, Cray Valley Products Ltd, Farnborough, UK.

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Fifty years of the London Section – The early history – 1937 to 1950

There is an old saying "flattery will get you nowhere"! However when Ken Arbuckle approached the author to write the 50 years' history of the London Section he obviously thought it was worth trying, and in view of the praise lavished it was impossible to refuse his request. Apart from researching old journals etc, it was felt that talking to ex officers and committee members would provide interesting information and indeed it did so. I must apologise in advance if I have missed out names or events, this is inadvertant and unintentional.

One of the earlier discussions gave me something of a surprise as I had been informed that the 50th anniversary was in September '87 but I was then told by David Roe that we had the dates wrong and that the time of the inaugural meeting of members was held on the 3 February 1937 (The notice calling the meeting is reproduced below).

The foundation of the section was inaugurated at the Council Meeting held under the Presidency of Dr G. F. New on 7 April 1937 when the Manchester Section suggested the formation of local sections with members attached to the one nearest their home. A meeting to prepare for the formation of the Section was held in September 1937 with an interim committee of Mr A. J. Gibson in the chair, Hon. Sec. Cecil W. A. Mundy, Treasurer Mr H. L. Howard, Hon. Publications Sec. Mr G. C. Attfield. This led to a petition to council signed by 30 members asking that a London Section be formed.

A meeting was duly called for on 3 February 1938 with the President Dr G. F. New in the Chair who proposed that a small interim committee be formed and officers appointed with Mr A. J. Gibson as Chairman. This was seconded by Dr F. W. Stoyle. Cecil Mundy was asked to serve as Hon. Secretary a position he had to relinguish shortly afterwards on being made Hon. Secretary of the Association. The London Hon. Secretaryship being taken over by Harry Gosling. The committee consisted of Mr G. C. Attfield, Dr T. Hedley-Barry, Dr J. O. Cutter, Dr H. B. Footner and Mr Harry Gosling. There were 60 members present.

It is interesting to note the future careers in OCCA and in the industries of some of the members mentioned already. Dr Frank Stoyle and Dr J. O. Cutter became London Chairmen whilst Mr A. J. Gibson, Mr Cecil Mundy and Mr Harry Gosling all became Presidents. Mr A. J. Gibson was London Section Chairman for only a short time before being elevated to the Presidency. His place as London Chairman being taken by Dr J. O. Cutter noted for his work on colloid chemistry.

The first paper to be read to the newly formed section was given by Leslie Kekwick and Alfred Pass on "Acicular Zinc Oxide" and took place during May of 1938. Yet another illustrious name Leslie Kekwick joined us, later to be Treasurer of the Section, Chairman and finally President of the Association at the same time as Mr R. H. Hamblin in 1951.

OIL AND COLOUR CHEMISTS' ASSOCIATION President: G. F. NEW, Ph.D., F.Inst.P.

LONDON SECTION

Interim Chairman: A. J. GIBSON, F.C.H., F.L.S.

An inaugural meeting will be held on

THURSDAY, FEBRUARY 3, 1938, at 7.30 p.m.

in the India Room of the Royal Empire Society,

Northumberland Avenue, London, W.C.2

AGENDA:

- To elect a small interim Committee and Officers to carry on the formation work of the Section until the opening of the next Session, i.e., at the beginning of October, 1938.
- 2. To hear informal accounts of the recent visits to America by:

The President, Dr. G. F. New.D. E. Roe, Esq.Dr. H. B. Footner.T. Cornelius, Esq.

The talks will be illustrated.

(The Association was searching for its own premises, not without difficulty but due to Leslie Kekwick's good offices the premises in the Memorial Hall, Farringdon Street were leased). From this time it can be concluded that the Section moved forward on an organised basis. The first committee meeting took place on 20 June 1938. Present were Mr A. J. Gibson (President of the Association and interim Chairman). His place as Chairman being taken by Dr J. O. Cutter. Whilst Harry Gosling was made Hon. Secretary of the Section to replace Cecil Mundy who had by now been made Hon. Secretary of the Association (another section officer of the early days who became President of the Association). Mr G. Attfield was appointed Treasurer. An announcement of the committee was made in the August 1938 issue of the Journal that a programme for 1938/39 was in course of preparation.

The next reference in JOCCA to the Section's activities is the report of a committee meeting held on the 8 September 1938, when what appears to be a full committee is first mentioned although its legal constitution is not outlined.

The Chairman continued to be Dr J. O. Cutter, the Hon. Secretary Harry Gosling and the Treasurer G. C. Attfield. For the first time David Roe is mentioned as an officer of the new section being given as Hon. Publication Secretary.

The Committee consisted of David Annand, Dr T. H. Barrs, Dr R. F. Bowles, Harold G. Gorer, Hubert Idle, H. C. F. Randall. Many of these committee members moved on to other offices in the Section of the Association including Reg Bowles who for many years was Editor of the Journal. Records seem to be confused in JOCCA at this stage—the first AGM was held on 20 April 1939 when N. A. Bennett (later to become Chairman, Treasurer of the Association and finally President) and Dr R. F. Bowles were "elected to fill the vacancies"!

In July of 1939 the committee announced that it was arranging for an informal dance to be held on 27 October 1939. (Little did they know that the sands of time were running out and that war was less than two months away). The war had an immediate effect on the Section and in October 1939 an emergency committee was formed at which it was envisaged that the Section may have to be split into small groups should air raids occur! The effect of war time conditions began to be felt when a committee meeting was held at the Russell Hotel and when Harry Gosling resigned as Hon, Secretary as his company had moved him to Manchester. This is really the time when a long period of distinguished service started for David Roe, for at this same meeting he was appointed Hon. Secretary,



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Berger Britain, Petherton Road, Hengrove, Bristol BS99 7JA. Telephone: (0272) 836110. Telex: 449006. Fax: 0272 891762. a position he held until he became Chairman in the mid 40's.

Surprisingly, the Section held a dance at the Criterion on 23 February 1940—perhaps they were lucky in having this function early in 1940—certainly later on in the year it would have been impossible! It is an interesting point that the charge of the tickets was 5/-(25p to ouryounger members). The author remembers some years ago, a wine list for that function and recollects port and sherry 5d (under $2^{1/2}p!$) and wine 3-6d $(17^{1/2}p)$ a bottle. Also in 1940 a joint meeting was held in Birmingham with the Birmingham Paint Varnish & Lacquer Club which is not recorded.

The first mentioned formal AGM appears to be that held at the Federation of British Industries on 25 April 1940. When the Annual Report was presented by the Chairman, Dr Cutter, who reported, amongst other things, that 43 London members had attended the 1939 Harrogate conference. The adoption of the report was proposed by Douglas Waite one of the pioneers of Titanium Dioxide in the UK. Dr H. G. Rains proposed the adoption of the finanacial report.

The new committee once again had names in it which since then have become well-known in OCCA and indeed within the industry. The names I have in front of me include Dr Harry Keenan (Chairman)-later to become President and later as Chairman of the involved committee being responsible for the introduction of the OCCA qualifications. (This only came about because of Harry's tenacity as he had to deal with some unreasonable opposition). At this same meeting Hubert Idle became Publications Secretary-a position he held for some years, David Roe became Hon. Secretary (officially) with G. F. Jones (who in later years gave yeoman service to the ink industry) and R. J. (Jimmy) Ledwith later to become Chairman. Another name to appear was T. Drummond Kerr well known as a Borough Polytechnic lecturer on pigments.

By September 1940 it was only too clear that normal life in the South of England was no longer possible and the Chairman, Harry Keenan decided the Regional Plan should operate. This is covered in JOCCA September 1940 which stated "when it is realised that at the moment communications are difficult within the London area". On reading the list of "regions" the author is forced to the conclusion that fragmentation was the order of the day as 17 regions appeared to be in the London Section. In the same issue of JOCCA is a report from Norman Bennett detailing a meeting at the home of Mr W. V. Lee in which the technical discussion on "The respective merits of Linoleum or Wood as substitutes for Glass" was followed by a practical demonstration.

I think at this stage a few words of tribute to Harry Keenan are not out of place. I first met him as a young man and was a little diffident about meeting such a well-known character. I need not have worried I was soon put at ease by his most kindly manner.

An interesting piece of information is in the January 1941 issue of JOCCA when it was mentioned that John Hawkey had joined OCCA, later he became Publications Secretary and eventually Chairman of the Section. The AGM in 1941 was held on the 8 May—possibly the most peaceful London Section Meeting for some months as the nightly 'blitz' had almost ceased.

Dr Harry Keenan continued as Chairman, David Roe as Hon. Secretary and Mr Attfield as Treasurer. It was announced that the membership had reached 385 by the end of 1940 and that 35 had been recruited during the year.

In May 1942 the Post Graduate Lectures commenced (a brainchild of David Roe and Harry Keenan) with Dr H. B. Watson, University of Cardiff lecturing on "Modern Views of some reaction of organic compounds". The fee for the two lectures 10/- (50p). Another event took place in December of the same year (1942) which I feel sure was David Roe's brainchild - a Members' Evening when various problems were discussed. Amongst those present were Mr W. E. Wornum (President) Alan Fillingham from Hull, Dr T. Hedlev-Barry, Dr Harry Keenan summed up. In spite of war time conditions a social gathering took place in the form of a lunch at Oddeninos on 10 April 1943 at which 75 members and guests were present.

The venue for the AGM on 17 April 1943 was the Charing Cross Hotel at which Norman Bennett was elected Chairman. David Roe, Hon. Secretary, George Read-Baker as Treasurer and Hubert Idle as Hon. Publications Officer. Four committee members elected were Philip Gay (later to become a President), Leslie Kekwick (to become section Treasurer, Chairman and finally President), Mr W. G. Wade and Mr E. R. Wells who, a few years later emigrated to the USA. The AGM was followed by a Brains Trust. It appears that a precedent was started at the first meeting of the session on 17 September when the new Chairman Norman Bennett gave the lecture entitled "Some thoughts on the Post War pattern of the Paint Industry". This event, the first lecture of the new session, has become known as the Chairman's evening.

Until February 1943 no Hull Section existed as it was a region of London. At that time David Roe travelled to Hull and inaugurated the Section.

It is interesting to read the London Section programme in JOCCA. The papers covered a wide and very well balanced range which would not be out of place in 1987 and included Management, Emulsions, Exports and Fuel Efficiency. No-one will be surprised to read that Technical Education was discussed by the Committee on 18 June 1943. Perhaps it would be unkind to say they are still discussing it.

The 1944 AGM was held during the early summer of 1944. No date is given in JOCCA but David Roe can place it as after May 12 of that year as his son was born on that date. Norman Bennett was elected for a second year of office, David Roe continued as Hon. Sec., George Read-Baker as Treasurer and Hubert Idle continued as Publications Sec. Two committee members, Mr D. H. Hewitt and Mr J. D. Morgan were elected to the committee. It is worthy of note that one of the items discussed at the meeting was the need to find a larger meeting room due to increased attendances!

The 1945 AGM was held on Friday April 20 (no venue is given in JOCCA!). The new Chairman was R. J. Ledwith (Jimmy). the Hon, Sec. David Roe, Hon, Treasurer Leslie Kekwick, Publications Sec. Hubert Idle. Three new members were elected to the committee, Mr A. G. Collings, Mr J. A. L. Hawkey (in later years he became Chairman), and Mr C. Montague-Smith. This appears to be the first time a meeting had been held at the Royal Society of Tropical Medicine and Hygiene in Portland Place - a venue which was used for some years. In the opinion of the author a sad loss when we were forced to leave because of the need for extensive repairs. A note appears in JOCCA of October 1945 stating that Mr R. J. Kekwick had given the Chairman's address on 21 September. thus establishing another precedent.

In February 1946, D. H. Hewitt and Frank Armitage gave a paper on "Styrene Copolymers in Surface Coatings" – a new subject at the time. It was early in 1946 that the London Section started its Refresher Courses, largely for members and others who had been serving in H.M. Forces. The courses were given at both East Ham and the Borough Polytechnic (now the South Bank). Over 100 attended.

The AGM for 1946 was held at the Royal Society for Tropical Medicine in Portland Place, the formal meeting being followed by a talk on "Post-War Germany", by Dr L. A. Jordan (later became President). The following were elected: Chairman R. J. Ledwith, Hon. Secretary D. E. Roe, Hon. Treasurer L. O. Kekwick. A report was given by Mr G. A. Garvie on "The co-operative investigation of the melting point of resins" and members took part. The author was one of the participants and well remembers the wide variations in results. (Perhaps with hindsight it would have been better to keep quiet about the results as they could do OCCA little credit.) A number of announcements of note were made at this AGM, a victory party was to be held on May 17 and further post graduate lectures to be held on 3, 10, 17 October were read by Prof H. W. Melville FRS on "The chemistry of high polymers". Once again the modest fee of 10/- (50p) was charged. (Does the London Section *always* undercharge?) Another member of the Section, (and a future President), Dr J. E. Arnold, lectured on "Some rheological properties of carbon black suspensions".

Having normalised the activities of the section in the post war world other problems arose which many of us well remember. On February 19, 1947, W. Esmond Wornum was booked to lecture us on "The difference between paint and ink" and the journey by train from Wolverhampton took no less than 36 hours due to snow. As obviously he was too late (much too late) to lecture, a Brains Trust (does this mean anything to the younger members?) was hurriedly formed – the volunteers (?) being Messrs R. F. Baker, N. R. Fisk, R. S. Law, H. A. Newnham (later chairman) and Dr R. F. Bowles.

By the time the AGM came round (23 April '47) the Arctic Winter had finished and the meeting was held at Manson House under rather more pleasant conditions than for some time. David Roe was elected Chairman, L. O. Kekwick Treasurer and Herbert Worsdall Hon. Secretary (later to become Chairman). Committee members elected were Mr R. F. Baker and Dr A. C. Healey. Mr A. H. Soane was appointed auditor, a position he held for many years. It was announced that the post graduate lectures would be held on 2, 9, 16 October and that Sir W. Lawrence Bragg would lecture on "A review of recent advances in x-ray analysis". The new Chairman, David Roe, announced that in future section meetings would be held at 7.0 p.m. and that his subject for Chairman's evening would be "The way ahead".

A special meeting was held on 26 September at which Mr Rahin B. Kahn lectured on "The fresco paintings of Ajanta". The lecture was illustrated with colour slides and later the paper was published in JOCCA, the slides being reproduced in colour, the first time colour had been used in the Journal. In January '48 the committee introduced another innovation, that of serving refreshments at 6.30 p.m. at the price of 2/- (10p). At the same committee meeting Neil Fisk was appointed publicity officer to the section. In January 1948, Col Urwick gave a talk on Management problems - Manson House was filled to capacity and members were standing. This means well over 200! Alas how times change. Works' visits seemed to be a feature of 1947/8 and included Vauxhall Motors (with an overflow visit), Bergers at Homerton and Waterlows at Park Royal.

The '48 AGM was held on 20 April again at Manson House when David Roe was

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Jotun-Henry Clark, manufacturers of high quality paints and protective coatings congratulate the London section of the Oil and Colour Chemists Association on their first 50 years.

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elected Chairman for his second year, Leslie Kekwick Treasurer, Herbert Worsdall Hon. Secretary, whilst Reg Holness as Publications Officer (later he became Chairman) and Philip Gay as Chairman of the Programmes Committee. Elected to the committee were Mr E. J. Coker, Mr J. T. Richmond and Dr J. J. Sleightholme.

Midsummer 1948 saw a reintroduction of petrol rationing, so the committee decided to arrange an outing for wives and families, to Whipsnade Zoo. An amusing incident occurred-the section had two coaches starting on the Embankment, a third coach was also parked near and it appeared had been hired by a party visiting Cambridge. When 6.30 p.m. arrived and our party were seated in the coaches ready to return the author counted heads and found one was missing. We waited for some time and eventually deduced the missing person had not been eaten by a lion but in the first place had got into the wrong coach at the Embankment! In May a visit was made to the EMI works at Hayes, radio and television manufacture as well as records (78 rpm!) were seen.

The first lecture of the session was a members' evening in which new tools and gadgets developed by them were demonstrated. The title was "New ideas in test tools and methods". The post graduate lectures continued. The 1948 lectures being given by Prof H. J. Emeleus, the title being "The impact of radio-activity on inorganic chemistry". The session also saw the first of a series of Ladies' Nights to be held at the Criterion on February 15, 1949, at which some 200-plus attended and at which guests from other sections attended. The price of the tickets was $\pounds 1.1.0d$ ($\pounds 1.05$).

At this time the germ of the idea for the exhibition came forth from the Treasurer, Leslie Kekwick. The exhibition and the AGM were combined and David Roe relinquished his Chairmanship to Leslie Kekwick who had served five years as Treasurer. In recognition of his services a cigarette case was presented to David Roe. The exhibition was organised by the Hon. Secretary and proved to be well attended, there being well over 20 exhibitors. Other appointments at this AGM were Alan Newnham as Treasurer (later he became Chairman), Herbert Wordsall to continue as Hon. Secretary. Arthur Soane was elected to the committee, so could no longer serve as auditor, his place being taken by John Hawkey. Rupert Law and Dr Chatfield were elected to the committee whilst C. R. Pye was co-opted to replace Dr J. J. Sleightholme who had resigned due to moving north.

During this session of 49/50 two works' visits took place to Howards of Ilford and to B. Winstone at Harefield and to Shellhaven. The post graduate lectures were given by Prof M. G. Evans and were titled "The design of experiments". Due to the

good offices of Dr F. W. Stoyle an Ink Symposium was arranged and held on 5 January, 1950. Many who remember that evening will agree that it was one of the best of its kind ever run by OCCA. Three lecturers were involved - Dr Julius Grant who talked about paper, Dr R. F. Bowles who covered ink, and Mr R. B. Fishenden who dealt with printing. Manson House was overcrowded, if my memory does not fail there were over 250 present. A feature of the London Section has always been the backing the ink industry gave – quite out of proportion to its members. The second Technical Exhibition was held on 4 April. 1950 and in spite of the fact that it was a one-day event over 1,000 attended.

The 1950 AGM was held at the New Inn, Westminster Bridge Road, the proceedings being enlivened by the presence of an Australian OCCA member, Mr Langabeer, who told a series of jokes suitable only for a completely male meeting.

The officers were re-elected, Leslie Kekwick as Chairman, Alan Newnham as Treasurer and Herbert Worsdall as Hon. Secretary. Elected to the Committee were Dr Frank Stoyle, Norman Bennett and Hubert Idle with Reg Holness continuing to do publications.

H. C. Worsdall

The concluding instalment of this fascinating history of the London Section (1950-1987) will be published in a future issue of JOCCA.

PUBLICATIONS AVAILABLE THROUGH THE ASSOCIATION

Introduction to Paint Technology, illustrated with index, over 30,000 copies of this book have been sold. A 4th edition is available, which revises and updates the book and includes for the first time a glossary of terms. Published 1976. Priced £10.00 (US \$24.00). Registered students of the Association half-price.

Journal of the Oil and Colour Chemists' Association. Published monthly. Subscription rate to non-members, post free, including yearly index: £70.00 (US \$130.00).

The Monograph Series:

Monograph 1 - Marine Finishes by Dr. T. A. Banfield. Price £2.00 each (US \$5.00).

Monograph 2 - Water-borne Coatings by Dr. J. W. Nicholson. Price £7.50 each (US \$18.00).

Monograph 3 - Painting on Zinc Surfaces and Zinc Containing Anti-Corrosive Primers by E. V. Schmid. Price £7.50 each (US \$18.00).

Ultraviolet Curing Papers from a Symposium of the Newcastle Section. Published 1976. Price £5.00 (US \$12.00).

Ultraviolet Curing 2 Papers from the second Newcastle Section Symposium. Published 1978. Price £7.50 (US \$18.00).



DECJOCADA

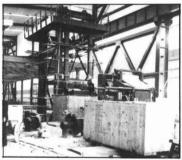
new/

BP Chemicals announces new strategic arm

Following the acquisition by BP of the minority interests in Standard Oil, the Standard chemicals business will become part of BP Chemicals International (BPCI) and be renamed The Sohio Division. This division will remain headquartered in Cleveland and will assume responsibility for the BPCI acrylonitrile (AN) business worldwide. This in effect will provide a fourth strategic arm for BP Chemicals, alongside the olefins wedge, acetyls and speciality chemicals. The Division's responsibilities will include the licensing of Sohio technology, used in over 90% of the world's AN production.

ICI coil coatings to China

ICI Paints has won an export order to supply coil coatings (165,000 litres) to China from the China Metallurgical Import and Export Corporation. The paint will be used by the Wuhan Iron & Steel Company (WISCO) in the start-up period on the first coil coating line ever built in China, which is scheduled to begin operations at the end of August. Under the terms of the agreement the order has been formulated and manufactured over an eight-week period, using existing technology at ICI Paint Division's headquarters at Slough, and will be exported to ICI China. From there it will be forwarded to the giant steel works in Wuhan, Chian's fourth largest city.



China's first coil coating line.

NOVA paint club passes billion dollar mark

The aggregate annual turnover of member companies of the Nova Paint Club will this year exceed the billion US dollar mark. This was announced during the Club's fifth annual conference held at the end of June at Wichita and Buffalo, locations of the United States member Pratt & Lambert. During the conference a new company was elected to the Club, bringing the membership to eight. The latest recruit is Tambour Ltd, an Israeli company that supplies 80% of that country's paint. Other members of the Club are CIN (Portugal), Jenson & Nicholson (India), Kalon (UK), Nan Pao (Taiwan), Societe Francaise Duco (France) and Sico (Canada).

The Nova Paint Club, formed in 1983, is now a major force in the world's paint industry. It is a 'community of technology and co-operation' whose members are companies with strong positions in their own paint markets but which are not multinational in organisation. At this year's conference, Leslie Silver, chairman of Kalon, handed over the presidency of the Club to Raymond D. Stevens Jr, chairman of Pratt & Lambert. Among the decisions reached by the conference were the setting up of a data base for the interchange of technology and the setting up of a raw materials price index.

UCB acrylates take over

Union Chimique Belge (UCB), Brussels, has acquired from Degussa AG of Frankfurt am Main (FRG) its range of UV and electron-beam hardened multifunctional acrylates and Degacure prepolymer acrylate-based resins.

Goodyear UK office move

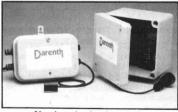
Goodyear France have moved their UK office to Greenfield House, 69-73 Manor Road, Wallington, Surrey SM6 0DE.



Non-invasive level controls

Darenth Ltd of Belvedere, UK, has available a new range of switches to monitor pre-set liquid levels using a through-wall technique. These units can be fitted without piercing the tank wall, ensuring no problems of re-positioning. The ultrasonic sensor, which is attached externally to the vessel or pipe, is an epoxy resin-sealed component and functions well on most types of homogeneous materials, e.g. glass, plastics, steel etc.

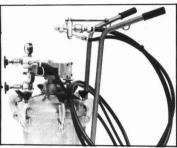
Reader Enquiry Service 20



Non-invasive level controls.

High output spray unit

Kremlin Spray Painting Equipment Ltd of Slough, UK, has introduced a new high fluid output unit for spray application of heavy coatings, including very abrasive materials. The special trolley mounted application system is based on a 25 litre air agitated pressure pot for internal atomisation of the coating material, with



Kremlin's heavy coating spray unit.

special fluid hoses and a spray lance. It has no electrical components and operates off the customer's compressed air supply.

Reader Enquiry Service 21

New coating kills off super bugs

Liquid Plastics Ltd of Preston, UK, has developed a coating called Steridex to eradicate a super strain of bacteria (known as Methicillin resistant staphylococcus aureus (MRSA)) which has been causing concern to Health Authorities. MRSA can be dangerous to patients in hospitals and clinics. Steridex is a water based copolymer wall coating applied by brush or spray equipment. It forms a tough hardwearing elastomeric finish that expands and contracts with temperature variation and substrate movement to prevent the cracking associated with conventional wall coatings.

Reader Enquiry Service 22



Water soluble polymers – a growth market

A wide-ranging symposium on the use of water soluble polymers in a variety of industries throughout Western Europe is being organised by the Functional Chemicals Group of the Industrial Marketing Research Association (IMRA) on Thursday, 19 November 1987 from 9.30 am to 5.00 pm at the Cafe Royal, Regent Street, London W1. The cost for this symposium is £109.25. For further information contact: IMRA Office, 11 Bird Street, Lichfield, Staffordshire WS13 6PW, UK.

Additives and UV Curing

The Centre for Professional Advancement will be holding two separate in-depth courses. Both will be held at the Crest Hotel, Amsterdam, on 2-4 November 1987. The titles of the two courses are "Additives for Coatings" and "Radiation Curing – Ultraviolet Light and Electron Beam Technology". The fee for each

new/

course is \$1,000. For further information on these courses contact: The Centre for Professional Advancement, Palestrinastraat 1, 1071 LC Amsterdam, The Netherlands.



This is the first of a series of pieces to appear in each edition of JOCCA up to the conference in 1989. The hope is that as the readers will be following the build-up it will have the effect of creating an increased interest and hence attendance.

The technical side has still to be settled and will be at John Taylor's Technical Committee Meeting in late September. So far the one thought is that we will focus on the ultimate financial reward from research and development. This will involve not only technical papers but also a few giving the marketing and financial view of R & D. Naturally the technical papers would, if this subject was chosen, include some potentially profitable indications.

The administration side is more or less completed. A varied range of hotels will be put forward for delegates with the centre of activities being the Chester Grosvenor. The innovation will be that delegates will be encouraged to book for bed and breakfast at conference rates since ALL delegates will be issued with luncheon to have this particular meal each day at the Chester Grosvenor to obviate some having to return to their hotels in the middle of the day and return again for the afternoon sessions.

The social programme is virtually completed. The Friday night dinner and dance has been fixed and the band and toast-master booked as has a trip up the River Dee through the Duke of Westminster's Estate in the Lady Diana with drinks, set meal and an unamplified jazz band. Also proposed is a trip in the mountains of Wales (including Llangollen), a tour of the Chester pubs, organised to give a fascinating historical (not hysterical) background. Similarly a city tour and one around the continuous Roman walls is in prospect.

The next 'column' will deal mainly with the technical aspects.



Ellis & Everard plc

Ellis & Everard plc, the UK's leading industrial chemical distributor, announced record pre-tax profits and significant growth. Pre-tax profits "imped by 77% to £6.61m and sales were up by 47% to £91.89m. In 1986/7 Ellis & Everard acquired Cargo Fleet Chemicals, in the USA, Apperson Chemicals, and in Ireland, Euro Chem.



Paul Hermon has been appointed Manager of the Plastics Coating Division at Sonneborn & Rieck Ltd.

Ian Watson has been appointed Director of UK Coating Sales for Cray Valley Products.

Roy Crawford has been appointed Director of Export Sales for Cray Valley Products.



BSI publications are obtainable from: BSI Sales Department, Linford Wood, Milton Keynes MK14 6LE (orders by post only).

British Standards

The following publications are available: BS 6857: Specification for cadmium pigments for paints.

.

BS 391: Specification for tung oil for paints and varnishes.

literature

Sealants

Sealants, V, a multi-client, technoeconomic study, has recently been completed by Skeist Incorporated of New Jersey, USA, consultants to the polymer industries. The demand for sealants depends on two industries: construction and automotive. In the next five years, construction-related sealants applications, which include insulating glass, highways, and bridges, are expected to grow at twice the GNP rate while in the automotive outlets, little growth is forseen. Consumption of sealants was 640 MM lbs. valued at \$875 MM in 1986 and is projected to increase to 760 MM lbs. by 1991. Polyurethane sealants are expected to have superior growth, about four times the overall rate. These sealants are used widely: in construction, they have made significant inroads in high-performance joints; in motor vehicles, polyurethane is the material of choice as a glazing compound; in insulating glass, they exhibit good physical properties. This publication consists of an investigation of markets, applications, raw materials, prices, suppliers, marketing shifts, and technological trends. The subscription fee is \$6,500.00. A free brochure with Table of Contents is available from Skeist Incorporated, 375 Route 10, Whippany, New Jersey 07981, USA.

Anti-corrosives roadshow

Buckman Laboratories will be hosting an anti-corrosive roadshow at Newcastle, Manchester, Birmingham (28, 29, 30 Sept respectively), Bristol, London (1, 2 Oct). For further information call 061-226-1227.

occa new/

Report of Council Meeting

A meeting of Council took place at 1.30 pm on Wednesday 15 July 1987 at the Great Northern Hotel, King's Cross, London N1 9AN. The President (Mr J. R. Bourne) was in the Chair and there were 24 members present.

The President thanked the Director & Secretary for postponing his holiday until after the Council meeting and extended a welcome to Mr C. Pacey-Day whose official appointment as General Secretary Designate would commence in September.

The President stated that only two nominations, that of Mr J. Coates and Mr G. Fielding, had been received for the three elective places on Council. Accordingly the first act of the Council would be to fill the one vacant place. One nomination had been received from Council members and accordingly Mr Cyril Williams of 26 Oakfield Close, Horwich, Bolton BL6 6JR, was declared elected.

Council stood in silent tribute to the memory of the late Norman Bennett (President 1957/59) who died on 30 May whilst staying at his son's home in the UK.

The President extended a welcome to new members, both at home and overseas, who were serving for the first time on Council or returning after a break from former service.

A report was made on the AGM which had been held during the Eastbourne Conference on 19 June.

The dates for Council meetings, the appointment of Council committees and the Association's representation on other organisations for the forthcoming session were agreed.

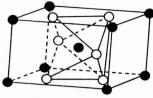
Discussion took place on the proposed arrangements for the 1988 AGM on 15 June, during the SURFEX Exhibition at Harrogate, and the Council Reunion which would be held at the Dinner thereafter.

Paint and Surface Coatings



Theory and Practice

Edited by R. LAMBOURNE, Technical Manager, INDCOLLAG (Industrial Colloid Advisory Group), Department of Physical Chemistry, University of Bristol.



696 pages; Published April 1987; £79.50/\$152.75 (incl. of p+p, overseas orders are sent surface mail)

PAINT AND SURFACE COATINGS comprehensively reviews the polymer chemistry of all common paint binders, bringing together technical information on pigments, enabling the beginner to understand pigment selection. The authors, all acknowledged experts in their field, critically review particle size and its relevance to paints, as well as the colloid chemistry of dispersions, and the rheology of paints and their optical properties. The book offers a totally new approach to building and house paints, looking at the requirements of substrates; and introduces the theory not generally found in paint technology texts.

CONTENTS: Paint Composition and Applications—A General Introduction; Organic Film Formers; Pigments for Paints; Solvents, Thinners and Diluents; Additives for Paint; The Physical Chemistry of Dispersions; Particle Size and Size Measurement; The Industrial Paint Making Process; Coatings for Buildings; Automotive Paints; Automotive Refinish Paints; General Industrial Paints; An Introduction to Rheology; The Rheology of Paints; Mechanical Properties of Paints and Coatings; Appearance Qualities of Paint—Basic Concepts; Specification and Control of Appearance; Durability Testing.

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Cheques must be made payable to OCCA—Post with remmitance to the above address

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occa new/

A list showing the number of members in arrears with their 1987 subscription was tabled and Council was pleased to note that this was lower than in 1986.

A report was made on the sale of publications, including the preparation of two new monographs and the sale of a new book by the publishers John Wiley.

The Honorary Research & Development Officer reported on the technical sessions at the Eastbourne Conference, which had been well attended, and suggested ideas for a possible topic at the Chester Conference 21/24 June 1989.

The Honorary Conference Officer reported on the general response to the Eastbourne Conference and thanked the Director & Secretary for running yet another well organised event. Thanks were recorded to the London Section for the splendid entertainment which they provided on the first evening as the start of their 50th Anniversary celebrations.

An up to date report was given on the arrangements for Chester and Council were asked to consider the venue for the Association's Conference in 1991.

Council were pleased to be notified that the Nigerian Branch had restarted its operations, elected new officers to its committee and had a series of activities planned for the year.

The President reported that following his visits to the FSCT and JSCM Conventions he would be visiting members in Singapore together with the Honorary Overseas Secretary, Mr W. Borrell.

The Honorary Exhibition Officer reported on the excellent response to SURFEX 88 with all but 10 stands allocated. He further reported that at the request of exhibitors he had made a preliminary booking to hold SURFEX 90 on 14/18 May at Harrogate subject to confirmation.

On behalf of the Council the President would present a commemorative scroll and an item of Wedgwood to the retiring Executive Vice President of the FSCT, Mr Frank Borrelle. He would also present a commemorative scroll to the JSCM in recognition of their 60th Anniversary.

It was reported that the Professional Grade Committee had admitted two Licentiates and two Associates.

At the request of the Ontario Section, Council agreed unanimously to award the Commendation Award to Mr Peter Birrell.

Council were pleased to learn that the "Chairman's Chair" donated by DSET in memory of the late Dr Marianne Ellinger had arrived and was in the Committee room at Priory House. A photograph had been taken and appears on page 277.

There being no further business, the President thanked members for their attendance and in particular the Director & Secretary for his efforts on behalf of the Association over the last 36 years and declared the meeting closed at 3.20 pm.

Technical Committee Amendment (August JOCCA)

Mr E. L. Farrow is no longer serving on the Technical Committee and Mr B. A. Canterford has been elected to this committee.

General Overseas Section Zimbabwe

Tenth anniversary celebrations

This grand occasion was celebrated by holding a Golf Tournament and a Dinner/Dance on Friday 26 June 1987.

The Golf Tournament was well supported and the ICI Paint Manufacturers' Golf Trophy for the best team was won by Berger. Alka, Astra and Dulux also put forward teams for the competition. The ICI Individual Stableford Trophy was won by M. Harris of Berger with 40 points.

The dinner/dance following the golf tournament was a resounding success with 55 members and guests attending. This function was held at the Jameson Hotel, Harare, in a French ethnic atmosphere with a cabaret including the inevitable "Les Filles" doing the Can Can which was received with much enthusiasm. Dinner was followed by dancing to a quartet. An enjoyable evening was had by all participating.

M. A. Johnson

Nigeria

Appointments

Mr F. B. Adefarati, Chairman of OCCA Nigeria has been re-elected for another two years as the Secretary of Paints Manufacturers' Association (PMAN) a body similar to PMA UK. He is currently a council member of the Chemical Society of Nigeria, a body similar in objective and function to the Royal Society of Chemistry in UK. Mr Adefarati is the Technical Manager of Berger Paints Nigeria Limited. Mr A. Adekoya, OCCA Nigeria new Assistant Secretary has been appointed to serve on the Nigerian Standards Organisation Committee on Paints as PMA representative alongside Mr F. B. Adefarati. Mr Adekoya is also currently involved with the Review of Curriculum for Painting and Decoration at the Technical Colleges. Mr Adekoya is the Works Manager of ICI (CAPL) Nigeria.

Newcastle Section

Annual golf tournament

The annual golf tournament of the Newcastle Section OCCA once again sponsored by The Tioxide Group was played on Friday 3 July at Bishop Auckland Golf Club. Twenty-two players took part in excellent weather and the outcome was a win for Ian Walton with Dave Thomas taking the visitors' trophy.

L. Morpeth



Mr G. Carr (Immediate Past Chairman, Newcastle Section) presenting Mr I. Walton with the Annual Golf Tournament Trophy.



Mr G. Carr (Immediate Past Chairman, Newcastle Section) presenting Mr D. Thomas with the visitors' trophy.

Gift in memory of Dr M. Ellinger

In memory of Dr Marianne Ellinger's association with their organisation, DSET Laboratories Inc of Pheonix Arizona have donated a chairman's chair for the Committee Room at Priory House. The CLASSIFIED ADVERTISEMENTS



1987(9)

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Applicants, who should be aged 21-35, should either have a number of years formulating experience in one of the above areas or should have extensive knowledge of the use of epoxy, polyurethane, SBR or acrylic resins in surface and/or high-build coatings.

Reporting to the Technical Director, the successful candidate will be expected to work as part of a team rapidly and effectively progressing projects through to marketable products. This key position will be rewarded by an attractive salary and benefits package coupled with the opportunity to work for one of the fastest growing and most technologically advanced companies in the world.

Please write, giving full personal and career details, to: Dr. P. K. Battey, Technical Director, Belzona Molecular Metalife Ltd., Claro Road, Harrogate, North Yorkshire HG1 4AY.



As the major UK Consultancy which specialises in appointments within the Surface Coating Industry, we have ben retained to advise on the following appointments:

1. Liquid Inks Development, for a young graduate/HNC, (24-27), experienced in the development of solvent inks for packaging. This is a progressive appointment within the small R&D team of a major ink makers. SOUTH

2. Liquid inks QC Manager, to be responsible for QA/QC team with a substantial and expanding international company. SOUTH

3. Development Technologist for growing central R&D team for liquid inks serving three operating divisions of major ink company.

4. Laboratory Manager, (23-27), for liquid inks to control team of three in short term development, formulation and QC work. SOUTH WEST

5. Liquid inks Graduate, (25-30), to lead development team for packaging inks for top UK ink manufacturer.

SOUTH WEST

6. **Oil Inks Technologist**, (25-35), for specialised Litho Ink Development and production. This is a new venture for a well established and major supplier. **NORTH**



7. Oil Inks Laboratory Manager to lead team covering development, formulation, trials and service for well established ink ranges, produced by major manufacturer. SOUTH

8. **Oll Inks Graduate**, (25-30), to become independently responsible for Litho inks development and service for long established, growing, specialised ink maker. **SOUTH**

9. Graduate OII Inks Chemist for advanced heat set development, trials and service for major American ink manufacterer. NEW JERSEY

10. **Technical Manager** for coatings for plastic, to lead development projects, particularly for coatings for automotive applications for Strickingly successful company established in this field. **SOUTH**

11. Colour Matcher to major automotive standards for coatings for plastic developed through advanced International technology by leading company in this growing field. SOUTH 12. VR Technologist, (25-30), for development of new VR systems for a profitable and expanding organisation new to this technology. MIDLANDS

13. Polyester Chemist, (25-30), to work under chief chemist and through team of five, in development. Trials and service for unsaturated polyesters. SOUTH

Candidates for these appointments are invited to write in absolute confidence or to phone: G. P. Birtles, SITA Selection, 203 Gardiner House, Broomhill Road, London SW18 4JQ. Telephone: 01-871-5011/2.

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