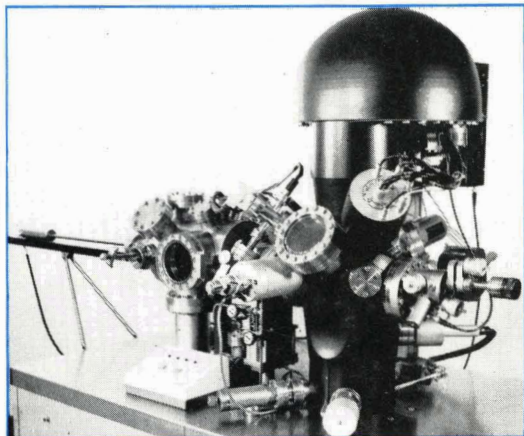


Computers in surface analysis

The roles, benefits and future of computers in surface analysis.



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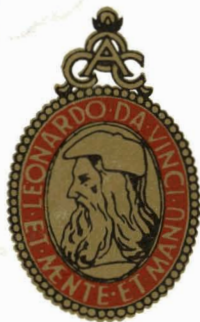
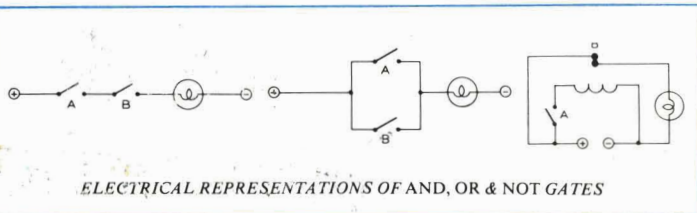
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SURFACE COATINGS

VOL I-RAW MATERIALS AND THEIR USAGE

Prepared by OCCA Australia

As a consequence of the comments and criticisms of the first edition of "Surface Coatings" (1974), it was decided to produce a second edition with a different approach. While it has again been designed to serve as a guide and a reference document for students, it is also intended to provide an up-to-date, in-depth treatment of all relevant areas of paint technology.

The work is presented in two volumes, the first extensively reviewing the raw materials used in surface coatings, and the second the technology of the products that use them. Volume I will also be of considerable benefit to students, technologists and others in related industries such as inks, adhesives, ceramics, textiles and cosmetics, and raw material suppliers. It provides an excellent introduction to polymer science, pigments, solvents and additives. This edition reflects the movement towards aqueous systems: the chapters on alkyds have been reduced in this edition from six to three, and the four solvent chapters combined. Conversely the emulsion chapters have been doubled to six, and three new chapters on aqueous resins added. Volume II, whilst retaining the basic manufacture, application and technology coverage, is based on completely updated contributions. There are additional chapters on lacquers, powder coatings, UV-cured coatings and decorative paint selection. Reflecting the increasing impact of computers, there are new chapters on automated colour matching and applications in resin and coating formulation.

Volume I is to be published in the UK on 1 September 1983. Copies will be available by placing orders (prepayment only) through the Oil & Colour Chemists' Association at £27.50 (inc. p&p in the UK).

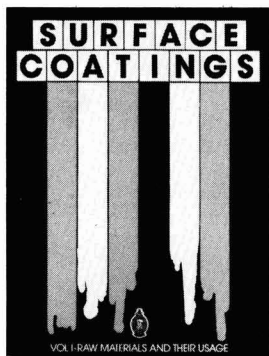
Volume I - Hardback - 408 pp.

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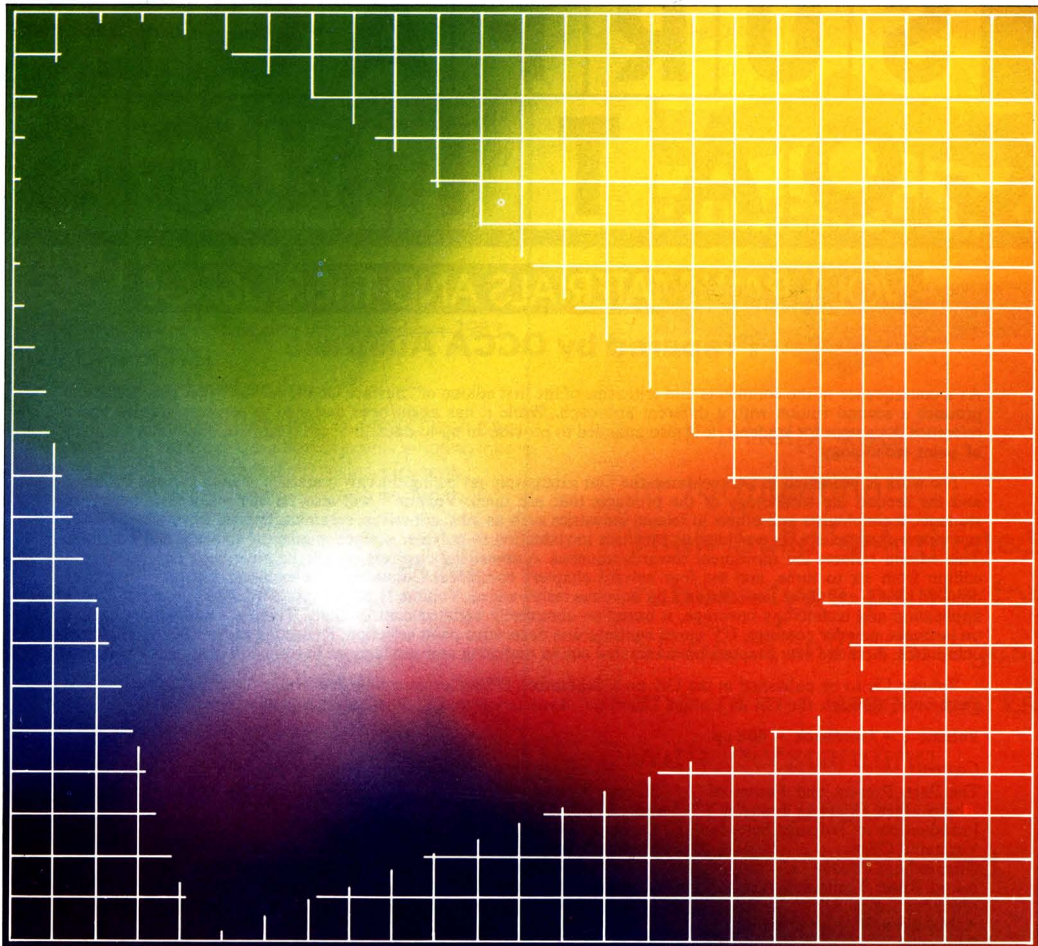
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Computer aided analysis of surfaces and surface coatings*

A. Carrick

Kratos Analytical Instruments, Barton Dock Road, Urmston, Manchester M31 2LD, UK

Summary

An overview of surface analysis techniques is presented, concentrating on the basics of the photoelectron and particle spectroscopies – XPS, AES/SAM, SIMS and ISS. General principles of how computers are employed in surface analytical instrumentation which uses these techniques, the balance of power between instrument and computer, and the benefits of such computer-based instrumentation are discussed. Speculations on the nature and capabilities of future instrumentation are advanced.

1. Preamble

The opening words of Digital Equipment Corporation's *Microcomputer Handbook* are "Today is the advent of the microcomputer age". A recent editorial in *Analytical Chemistry*, "Software and Analytical Instrumentation" alerts editors (and their readers) to "a developing problem – in which – instrument vendors will not share software with purchasers. Some will not even share the algorithm that describes what the software does." There could scarcely be two more contrasting pictures of life in a computer aided laboratory. On the one hand the broad vistas of the promised land: on the other, the menacing clouds of the inscrutable system – unknowing and unknowable – rolling across the plains, blindly sweeping all before it.

In the world of real analytical problems where epic superlatives fade into routine determinations, what role do computers play in an analytical method, how are they helpful and what should we expect in the future? This paper briefly examines these questions in the context of surface analysis.

2. Introduction – surface analysis techniques

Solids contain two kinds of atoms – those which make up its surface and those which are contained within its bulk. For a 1 mm diameter sphere, the ratio of surface atoms to bulk atoms is about $1:10^6$, and so for most purposes in solid state physics and solid state chemistry where overall properties are studied, the surface atoms can be ignored.

Chemical interactions of materials, together with emission and adsorption of particles all take place – at least initially – at the surface. The composition and structure of the outermost atomic layers, then, dominate the properties of the material and thus determine much of its final usefulness in many practical applications, whether for decoration or protection, separation or joining. Surface properties are unarguably of great economic significance and a knowledge and understanding of these properties is crucial to future developments in fields such as catalysis, corrosion, thick and thin film coating (including paints), energy conversion devices and the like.

Methods for studying composition and structure of surfaces must fulfil four main criteria. Their information

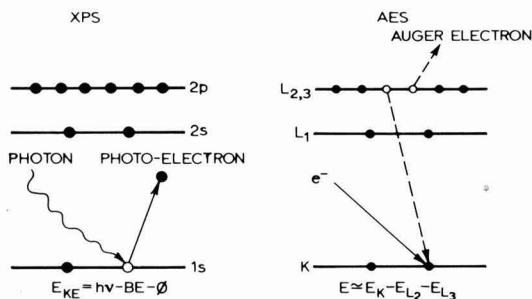


Figure 1. Energy level diagrams showing the energetics of the photo-electron and Auger electron emission process

sampling depth must be of the order of a few atomic layers, they must identify the elements present, and if possible their chemical state, they should be essentially non-destructive, and they must be applicable to any solid surface irrespective of topography. All presently available methods of surface analysis utilise some type of emission – photons, electrons, atoms, molecules or ions – caused by the excitation of the internal and external energy levels of the atoms of a surface. The most important methods, in historical order of application, are X-ray photoelectron spectroscopy (XPS or ESCA), Auger electron spectroscopy (AES) and its derivative scanning Auger microscopy (SAM), and secondary ion mass spectrometry (SIMS). Over the last few years, instrumentation to enable ion scattering spectroscopy (ISS) has emerged and this technique has also become important for some specialised analyses. Each technique has its strengths and weaknesses, and often considerable skill must be exercised in deciding which technique to use for a particular problem. To some extent, however, the situation has been improved by the recent availability of multi-technique instrumentation, in which more than one analytical method may be applied to the same sample in the same environment without moving it and without compromising the performance of any single technique.

The basic principles of the four techniques are straightforward:

(a) X-ray photoelectron spectroscopy (ESCA – electron spectroscopy for chemical analysis)

A solid under analysis is flooded with low energy X-rays which excite photoelectrons from the surface. The major advantage of the technique is that the photoelectron energy is dependent on the precise configuration – that is the chemical state – of the surface atoms. Pronounced "chemical shifts" are generated for peaks in the ESCA spectrum by changes in the chemistry of the observed atoms. Thus XPS is of greatest utility where *chemical*

*Paper presented at the Association's York Conference, 15-18 June 1983. An edited transcript of the discussion that followed this paper can be found on page 277.

characterisation of a uniform surface is required. Incident X-ray flux is low and so surface damage is minimised. Frequent applications of XPS include analysis of delicate powder materials or thin polymeric coatings.

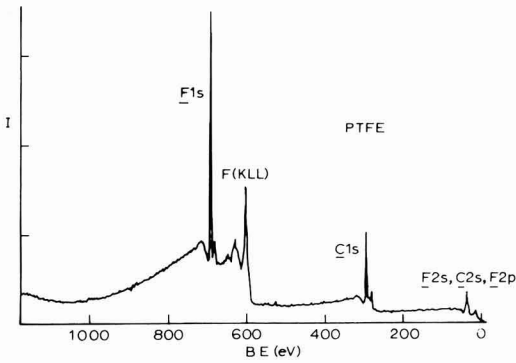


Figure 2. XPS spectrum of the polymer PTFE, showing discrete peaks assigned to carbon and fluorine

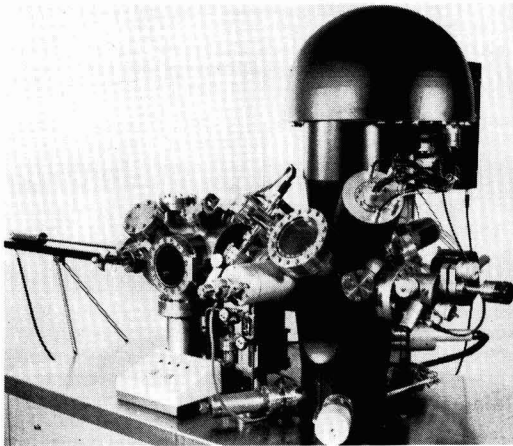


Figure 3. A photograph of an XSAM 800 Spectrometer showing the vacuum console with its preparation and analysis chambers

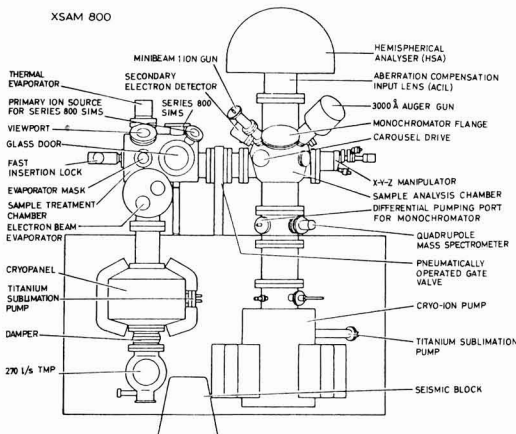


Figure 4. A schematic diagram of a dual-chambered XSAM 800 configuration with specially constructed sample treatment chamber

(b) Auger electron spectroscopy (AES)

A finely focussed beam of electrons can excite Auger electrons – inner atomic shell electrons – in surface atoms. Sub-micron beam diameters, typically 3,000 – 300 Å, mean that scanning electron microscope techniques can be used to obtain both physical (topographic) and elemental (analytical) images of a surface. Thus the technique is ideal for determinations of, for example, the origin of small areas of contamination or physical defects which cause failure in microelectronic components. The technique is also well suited to composition depth profiling and hence the analysis of thin films and surface coatings. Although hitherto AES has been considered as yielding only elemental analyses, high performance instrumentation can provide some chemical shift information.

(c) Secondary ion mass spectroscopy

Whilst both the electron spectroscopies are based on determination of energies of emitted electrons and deduction of the nature of the emitting material, secondary ion

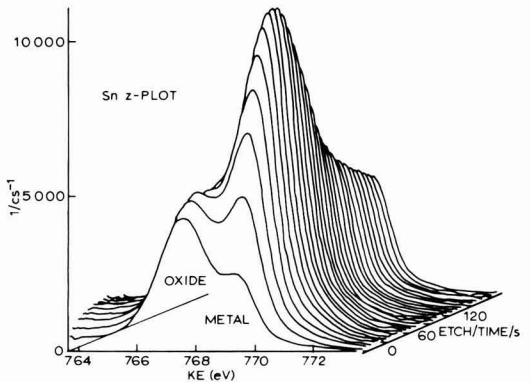


Figure 5. High resolution computer graphics gives the variation of the tin spectrum with depth for a depth profiling analysis in an easily assimilated form

mass spectroscopy (SIMS) employs direct determination of the mass of ejected (sputtered) surface particles – ionized atoms, molecules and molecular fragments. This destructive nature is balanced by an extremely high sensitivity for the technique, so that in practice under controlled operating conditions SIMS removes so little material that it may be regarded as non-destructive. In this circumstance the technique is termed “static SIMS”. A low current density ion beam, usually of noble gas, confines analysis to outermost surface layers. A quadrupole mass spectrometer is used to detect sputtered fragments and these provide details of the precise chemical state of the surface. Secondary ion yields – sputter yields – are notoriously variable: energy, angle and matrix dependence are all significant and so quantification is difficult.

By contrast, “dynamic SIMS”, with higher current density beams, often of reactive species such as oxygen or, for fine focus imaging, heavy metal ions, provides well characterised quantitative depth profile information for dilute systems such as dopant levels in semiconductors. With detection limits of the order of 10^{13} atoms/cm³ and dynamic range of six orders of magnitude, dynamic SIMS ranks as perhaps the most powerful of surface analytical methods.

(d) Ion scattering spectroscopy (ISS)

Elastic scattering of ions from a surface, as in all ballistic

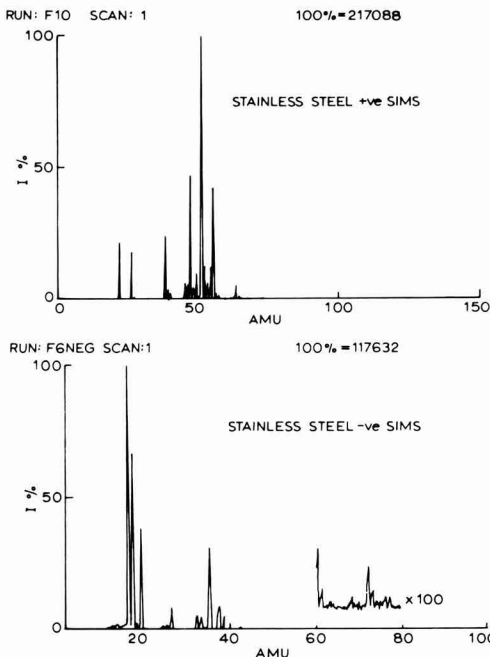


Figure 6. Negative and positive SIMS spectra of a stainless steel sample

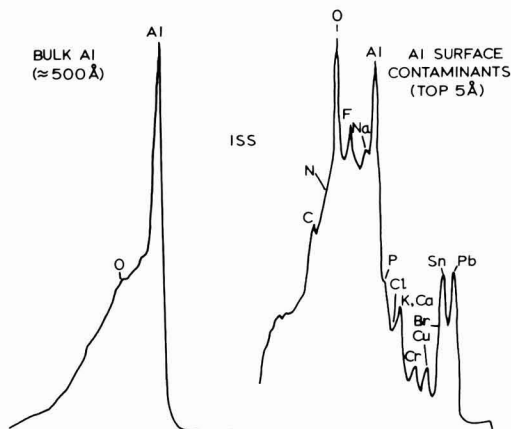


Figure 7. In this ISS spectra, the top monolayer contaminants of an aluminium sample are identified

collisions, yields information on the mass (atomic mass and so element type) of the scattering particle. Determination of the kinetic energy spectrum of ions of a known primary energy scattered through a known cone angle thus provides elemental identification of surface atoms. ISS is an extremely sensitive technique involving only the outermost atomic layers, and by virtue of its sensitivity and low current density requirements can provide depth profile information at finely graduated depths involving fractions of a monolayer. Newer techniques also give hope of yielding chemical information.



All these analytical techniques require an ultra high vacuum environment for their operation to enable detec-

tion of emitted particles and to minimise surface contamination. Each has surface depth sensitivity of the order of nanometers, but is not limited to that because of depth profiling methods. All the techniques produce considerable quantities of data at a respectable rate and can yield useful information on difficult problems: the computer thus has a role in data acquisition, instrument control and information handling for all these techniques.

3. The computer and surface analytical instrumentation

(a) Data acquisition

The action of recording a spectrum benefits greatly from the use of a computer in the process. Even the simple act of ensuring that an instrument communicates directly with a computer has benefits of accuracy and flexibility. There is little room for ambiguity in a digital value digitally transmitted and stored as a numerical representation. Numerical versions of spectra are immediately accessible to a wide range of mathematical treatment methods which are most appropriately performed by a digital computer and whose electrical analogue is either difficult to perform in real time (for example resolution enhancement) or whose application could result in irrecoverable loss of information (smoothing processes for instance).

In electron spectrometers the nature of the spectroscopic process ensures that the absolute data rate of the spectrum signal is modest, well within the capacity for data handling of widely available mini- and micro-computer systems. A typical system has the capability to acquire and store spectra directly and leave ample processing power for dealing with already acquired data at a high rate. This is a so-called "foreground-background" capability. Collection of spectra occurs essentially automatically once set up, unattended by the spectroscopist in the foreground – a high priority but fast activity; in the background partition, data are numerically treated, plotted, displayed and evaluated on a more leisurely time scale but one still fast in comparison with the human interaction through keyboard and visual display. This apparent ability to perform two independent tasks at once clearly considerably enhances the usefulness of the total system to the analyst. Sensible systems also build in synchronising functions and deferred command sequences so that a complete analysis including evaluation, calculation and reporting of figures can take place automatically over extended periods, overnight or over weekends. More will be said of this when we consider instrument control.

In the case of the particle spectroscopies both data rates and data volumes increase because of the indirect nature of the technique in the case of SIMS and because of the high speed and high resolution capabilities in the case of ISS. Demands on storage thus increase and special purpose hardware becomes appropriate at the data collection point. Special purpose hardware is best generated these days by adding special purpose software to general purpose hardware and so interfaces from the instrument computer to the signals from the mass spectrometer used for the SIMS experiment are typically constructed from another microprocessor system complete with memory, peripheral controllers and support circuits.

(b) Data processing

Quite simple numerical methods often prove extremely powerful when they can be applied easily and act quickly. Smoothing routines, background subtraction, spectrum subtraction, comparison and addition, integration and

differentiation are all straightforward mathematical operations which, when made available in a fast, easy to use display orientated system, positively aid inference making in research applications and can lead immediately to desired results in routine determinations.

One prerequisite, however, is that such a package should have a capability for preserving original data integrity no matter how far the working copy of that data is processed and reprocessed.

Spectroscopists have a natural tendency to seek reassurance that a "peak" in a spectrum represents a single component. Deconvolution procedures, whilst perhaps scientifically hazardous, prove no problem to a well-behaved computer system. Fitting a number of elemental gaussian, lorentzian, or "experimental" peak shapes to a suspected multiplet can yield invaluable analytical information, both qualitative and quantitative, from complex spectra, often removing the necessity for elaborate instrument set up or long experiment times because the program can sort out poorly resolved signals. For the procedure to be most useful, however, an immediacy of action is required which in turn requires careful and cunning programming of the system by its designer. The spectroscopist presented with the results of his hypothesis quickly is more likely to persevere to a satisfactory solution to a problem rather than stop short because the program takes too long. It is in such simple practical points that some otherwise adequate systems completely fall down. There has to be enough processing power in an instrument computer system to cope with all requirements. Curve fitting procedures for say a six component multiplet should operate on a time scale of a few tens of seconds, and this is easily within the compass of most worthwhile central processors' arithmetic units these days.

A numerical technique related to the same instrumental problem – resolution – involves domain changes using the Fourier transform. Passing from time-based to frequency-based representations and applying suitable filter functions can provide some measure of resolution enhancement without significant degradation of spectrum integrity – a procedure which is quite impracticable without a moderately powerful computer (even fast Fourier transforms can be remarkably slow when you are actually waiting for the answer!).

The full power of an instrument computer system is developed only when spectroscopic data becomes analytical information. Again careful system design is the key, especially where the data lie at more than one remove from the final result as, for example, in SIMS. The system must provide easy set up of appropriate experiments, be able to identify and implement specific analytical requirements though use of table look-up routines, have well designed calibration and calculation procedures and a flexible reporting structure. One surprising specific of this many faceted problem is that the real information content of a screen is seldom significantly improved by a colour display, especially if the programs driving it operate quickly. Readability can be improved by colour and there is much to be said for the production of presentation hard copy which includes discrete use of colour.

(e) Instrument control

Repeatability and reliability are the key aspects here: both should significantly benefit in an instrument under computer control. This relates to an unvarying operating regime, constant checks on suitability of settings and

operating conditions and the precision of numerical drive for scanning systems and detectors. At a less fundamental but equally important level, the ability to operate on several samples unattended – that is to interact with sample changing mechanisms and automatically set analysis conditions – is a crucial one, especially in a cost-benefit analysis of the operation of a sizeable capital investment. In the particular case of surface analytical instrumentation, computer control of specimen carriages and manipulators when these must operate in ultra-high vacuum is by no means trivial. Equally the benefits to the analyst, once this is achieved, are not trivial – the ability to perform complete unattended analyses on ten or a dozen samples by running the instrument overnight or over a weekend, thus leaving it free for more research orientated problems which must include human supervision, can be an extremely significant factor in the operation of an analytical facility.

Instrument control extends to instrument accessories, and there are clear advantages to implementing a unified policy of standardisation across an instrument range. Well specified standards for digital communication interfaces exist internationally and these should be used when appropriate.

(d) Newer computer techniques and computer aided systems

Digital control of analysers and excitation sources allied to digital signal detection brings the ability to a suitable computer system of storing images generated by fine focus beams. Once the appearance of a sample is held in store then conceptually it is a simple matter to define points or areas for analysis on the sample by use of the stored image. Automatic multipoint analysis is thus a further level of analysis within multispecimen handling procedures, although this further depth is seldom useful in practice because of the requirement for human decision on what is or is not significant. Images generated by microprobe style analysers can be strictly physical (topographic) where merely secondary electrons (uniformly emitted regardless of the character of the sample) are detected. Equally the image can consist of direct analytical information as in scanning Auger microscopy and SIMS imaging.

Recent advances in the application of image enhancement techniques of the sort used to refine pictures from satellites, space vehicles and surveillance systems have yielded outstanding results when applied to ion scattering images. A variety of image restoration and image enhancement methods based on convolution of the detected signal with known instrument smearing functions can remove blurring effects imposed on the image by the finite diameter of the analysing beam. The methods provide improved special resolution and the capability to provide finer detail than is available directly.

Computer control of source and analyser parameters has resulted in the ability of so-called linked scanning – where parameters which to a first order approximation are independent do provide characteristic variations in output signal when varied in concert. Oscillatory ion scattering – a charge exchange resonance phenomenon – becomes an easily accessible analytical technique rather than an academic curiosity when a computer controlled instrument is available.

Computer control of an excitation source can be limited to simpler but no less effective concepts than steering a fine focussed beam. For broad beam sources, X-ray guns

for example, the ability to switch automatically between a number of photon energies provides a powerful facility for optimising analysis or non-destructive depth profiling. The ultimate extension of this is a fully tunable synchrotron-like source – Kratos instrumentation overcomes the size (and other!) limitations of the synchrotron by providing a four anode, eight target source which operates totally under computer control.

Detectors also play their part in increasing analytical performance. Focal plane detectors, in contrast to the slit defined single channel devices, require quite complex "house-keeping" actions during the full position-sensitive recording of a static spectrum region, and even more complex arrangements to cope with the case of a scanning system. Initial readout rates for photodiode array detectors are typically in the MHz range and so fast, dedicated logic (derived from a high performance "bit slice" microprocessor) is required. Such a signal pre-processor represents the furthest extent of the complexity of the computer-instrument interaction. The need for at least two computers in the system (even if one is special purpose) impacts on the design of what might be termed the "normal" instrument control systems, changing the detailed functioning and external shape of the instrument. In its operation new modes are revealed: very high speed scanning resulting from the "parallel" determination of a whole section of spectrum at one instant makes study of transient species a possibility. The sensitivity increase, again resulting from parallel detection, enables use of lower incident flux, which in turn means possibilities of analysis of materials prone to radiation damage and so on.

4. Future computer aided instrumentation

Within the analytical instrument there are well-developed trends in the use of new techniques, deriving from both high precision manufacturing of sources, analysers and detectors, and also from a better understanding of the nature of the analytical method and the physics of the instrument itself.

Independently, computers exhibit strong trends in the

development of communication methods in both machine to machine links and man to machine interfaces, trends towards increasing use of natural language in dealings both with computers as computers and computers as parts of other devices, trends towards use of deductive processes in programs, and finally inexorable trends in miniaturisation – cramming more and more computational power, whether memory or arithmetic, into small and smaller chips. Taken together, an exciting scenario unfolds. Talking cars are with us now. There is undoubted capability for control of instrumentation by voice rather than by buttons, keyboards, knobs or similar inelegant apparatus. Enunciated indication of sequences complete, alarms, status changes and so on can either be a blessing or an annoyance, depending on circumstance; add to that the ability of the machine to schedule an analysis using automatic sample handling to make most effective use of instrument resources, to write a coherent report on the whole analysis, neatly, in plain English on paper, by using conclusions drawn from a series of experiments, and perhaps analysts do have serious worries to address.

But, you might add, at least the photoelectron effect and the study of surfaces requires some recognisable instrumentation at the source-analyser-detector end. Who is to say that principles such as those adopted in a recently developed (by IBM) new form of microscope utilising a quantum mechanical tunnelling effect of electrons in high fields over small distances cannot provide much the same information that say AES/SAM does today? One might conceive of a paperback size complete instrument including computer, readout screen, and analytical transducer conveniently situated so that it could be placed in contact with the surface under test and provide both physical and chemical images of the surface *in situ* at speed, communicating (by short range radio link) to host computers making analysis inferences and recommendations without the intervention of the analyst except to carry it to the analysis site. Fortunately, however, analytical scientists are not yet totally dispensable – and this kind of device exists only in science fiction doesn't it?

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Linear polymonosulphide and polysulphide polymers – general survey, recent developments and applications*

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1. Introduction

Research into sulphur-containing polymers has increased considerably due to the existence of many different sulphur reactions which can produce many possible chemical and physical properties such as radiation resistance, high adhesion, good dielectric properties and resistance to oxidation. The presence of polysulphide linkages in a polymer generally confers a marked degree of resistance to solvent attack or swelling. This is due to the

fact that the solubility parameter of a polymer is greatly increased by the presence of these linkages. A high value of solubility parameter tends to produce a high glass transition temperature. However, this is counter-balanced by the ease of internal rotation of the polysulphide linkage. Polysulphide polymers, therefore, combine resistance to solvent attack with good flexibility at low temperatures.

Another interesting point is the very low price of sulphur S_8 .

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2. General survey

The methods of preparation of polymonosulphides¹, $\{R-S\}_n$, are as follows:

(a) Ring opening polymerization

It is known that episulphides² or the thiiranes³ are able to polymerize or to copolymerize with α -methylstyrene⁴, styrene⁵ and butadiene⁶ under the influence of anionic initiators. Thiiranes and thietanes are also polymerized by cationic initiators such as strong acids, Lewis acids⁷ or strong alkylating agents. A common feature of the cationic polymerization of nearly all thiiranes is the formation of cyclic oligomers during and after the polymerization.

Coordinated ionic polymerization can be carried out on methylthiirane, and stereospecific reactions take place with metal alkyls and diethylzinc⁸.

(b) Polycondensation

The addition of a thiol to an olefin in the presence of radical generating groups is a well-known reaction in organic chemistry. It was extensively investigated by Marvel and co-workers⁹ and a large number of poly-alkylene polysulphides were synthesised in this way – in bulk, in solution or in emulsion. The latter method gives the highest yields and the polymers have high molecular weights.

The polycondensation of thiolates with polymethylene dihalides yields polymers with molecular weights¹⁰ between 1,500 and 3,000.

Other polycondensation reactions can be quoted – such as production of polyarylenesulphide – but very often they are carried out at very high temperatures, e.g. *p*-dichlorobenzene with sulphur and sodium carbonate¹¹, and *p*-dichlorobenzene with sodium sulphide (20 hours at 300°C) in a polar medium¹². The polymer obtained in this way is commercially available under the trade name of Ryton.

2.1 Synthesis of polysulphide polymers $\{R-S_x\}_n$

The average number of sulphur atoms, x , in polysulphide units is referred to as the "rank" of the polysulphide polymer and varies from approximately 1 to 4.5. Patrick¹³ produced the first commercial polysulphide polymer when he treated 1,2-dichloroethane with sodium polysulphide. The product was a rubbery mass and appeared on the market under the name Thiokol A. A great improvement was the substitution of 1,2-dichloroethane by bis(2-chloroethyl)ether and by bis(2-chloroethyl)formal.

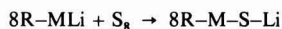
Two other methods of preparing polysulphide polymers are the polycondensation of bis(2-hydroxyethyl)disulphide with formaldehyde¹⁴, or the polycondensation of bis(2-chloroethyl)formal with disodium disulphide (Thiokol WD 2).

S. Penczek later copolymerized isobutylene sulphide with S_8 at 60°C using an anionic initiator¹⁵.

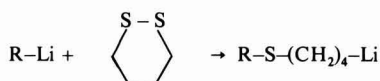
In our work we have extended the scope of polysulphide synthesis to include a large range of vinylic monomers using anionic reactions in the presence of elemental sulphur.

3. Polysulphide oligomer synthesis by anionic reactions with elemental sulphur

Our research has shown the possibility of using anionic reactions to produce polymers in which the sulphide group is part of the polymer. Few reactions with nucleophilic reagents on elemental sulphur have been studied. Schuman and Schmidt have added organometallic compounds in excess to sulphur and have obtained thiolate¹⁶:



Eller¹⁷ has reacted 2,3,4,5-tetrafluorophenyllithium with sulphur below the stoichiometric amount and has obtained thiolates. Using the same nucleophilic attack, Hallensleben¹⁸ has added some carbanions onto cycloalkyldisulphides, which causes the sulphur bridge to open:



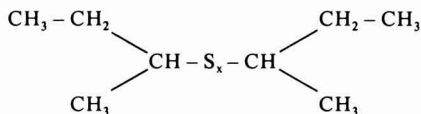
To characterise the reaction between carbanion and sulphur, we prepared different monocarbanionic oligomers and analysed the different compounds obtained after reacting them with S_8 .

3.1 Study on model molecules

3.1.1 Influence of the K parameter: $K = (\text{anion})/(S_8)$

We have studied, at room temperature in benzene solution, the reaction of S_8 elemental sulphur with different organolithium compounds¹⁹: secondary butyllithium, 1,1-diphenylhexyllithium, oligomeric styryllithium, oligomeric α -methylstyryllithium, oligomeric isoprenyllithium, and all oligomeric chains initiated by *sec*-butyllithium.

The first parameter studied was the influence of the K ratio ($K = (\text{anion})/(S_8)$) on the resulting compounds. All the oligomers described gave very similar results to those obtained with *sec*-butyllithium (Table 1):



For K below 2, the analytical results show that only the dialkylpolysulphides, $R-S_x-R$, were obtained.

The average number of sulphur atoms per coupled compound varied from 3 to 4 according to the structures of the carbanions used (Table 2).

In Table 1 it can be seen that besides the coupled compounds, for low values of K ($K \leq 1/2$) a large part of the sulphur is left unreacted, but the average number of sulphur atoms per dialkylpolysulphide remains constant. When the anion concentration is increased ($K = 4$), the coupled compounds are always obtained, but the number of sulphur atoms in the bridge is lower: $x = 1, 2$ or 3. Besides these compounds, the presence of thiolate was noted (Table 1) and no sulphur remained.

For the high values of K ($K = 8$) only one coupled compound type was obtained: $R-S-R$ and thiolate compound (60 per cent).

Table 1
Proportion of different polysulphides for
different values of $K = (A^-)/(S_8)$

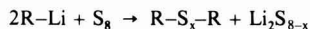
K	R-S _x -R (% molarity)					R-SH/R-SH + R-S _x -R (% weight)	S ₈ unrected
	\bar{x}	1	2	3	4		
8	1	100				60	no
4	2.3	21	31	48		30	no
2	3.6	5	11	36	46	0	traces
1	3.6	5	11	36	46	0	yes
0.5	3.6	5	11	36	46	0	yes

Table 2
Molecular weights of oligomers after reaction of carbanions
with elemental sulphur

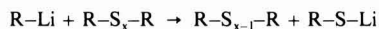
R-Li compound	\bar{M}_n :R (H)	Analysis (%S)	\bar{M}_n found (a)	Yield (%)	R-S _x -R \bar{x}	R-S _x -R theoretical value for \bar{M}_n
A	214	22.2	520	79	3.6	541
B	176	21.9	420	77	2.9	441
	194	19.8	450	82	2.8	474
C	178		250	86	3.5	250
D	238	21.3	571	85	3.8	595

(a) determined by cryometry, $K = 2$, solvent = benzene

It is suggested that the first step of the reaction, the nucleophilic attack of the elemental sulphur, is as follows:



When the elemental sulphur has been completely consumed, the carbanions react with the sulphur bridge of the dialkylpolysulphides present in the solution. This reaction explains the decrease in the number of sulphur atoms in the bridge, and the appearance of thiolate.



However, other reactions giving coupled compounds

and thiolates have been observed during the study of the solubility parameter and the mode of deactivation.

3.1.2 Influence of the solvent

In a non-polar solvent the carbanions are associated, but in a polar solvent the classical scheme theory applies:

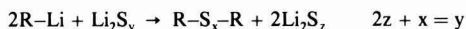


Table 3 indicates the proportions of the products obtained with the 1,1-diphenylethylene anion/S₈ reaction in benzene and in THF.

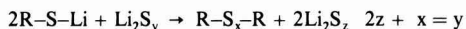
Table 3
Description of the different compounds obtained
from $J = \text{sec-Bu-CH}_2\text{-C-O}_2$ with S_8 for different K values
and for different solvents

K	S_8 in excess		J - S_x - J		\bar{x}		J - S - H	
	THF	C_6H_6	THF	C_6H_6	THF	C_6H_6	THF	C_6H_6
2	yes	<u>traces</u>	95	<u>95</u>	3.9	<u>3.8</u>	5	<u>5</u>
4:1	none	<u>none</u>	73	<u>75</u>	2.4	<u>2.5</u>	27	<u>25</u>
8:1	none	<u>none</u>	56	<u>37</u>	1.2	<u>1.0</u>	44	<u>63</u>

For $K = 2$, similar products in the same proportions were obtained, but elemental sulphur remained unreacted. This fact showed that in a polar solvent, mineral polysulphides are soluble and the carbanions can react with them to form coupled compounds:



For $K = 8$, the thiol ratio in THF is lower than in C_6H_6 and the thiolate can react with the soluble mineral polysulphide to give coupled compounds:

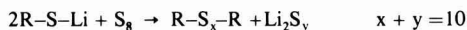


To confirm this reaction we used a benzene solution containing $\text{sec-Bu-S}_x\text{-sec-Bu}$ and sec-Bu-S-Li ; Li_2S_y precipitated. By the addition of THF to this benzenic solution, the mineral polysulphides became soluble and it was observed using GPC that the amount of coupled compounds with high values of sulphur atoms in the bridge increased considerably.

3.1.3 Influence of the deactivation mode

If sec-BuLi was poured onto S_8 , or S_8 solution into sec-BuLi solution, for the same values of K up to two, the same products were obtained in the same proportions.

This reaction can occur only if the thiolate reacts with elemental sulphur to give coupled compounds:



3.1.4 Influence of the reaction time

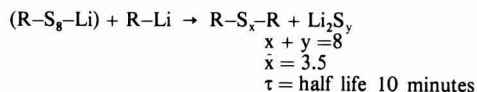
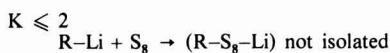
Attempts were made to determine the rate constant of the reaction of carbanion with S_8 by using the stopflow system with UV analysis. For K below two, $(A^-) = 5 \times 10^{-3}M$, and $(S_8) = 4 \times 10^{-2}M$, the disappearance of the carbanion UV absorption was instantaneous.

3.1.5 Temperature and concentration effects

The temperature and active end groups concentration did not influence the results previously described.

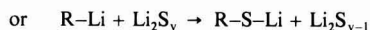
3.1.6 Conclusions from the model molecule studies

For different values of K , the overall reactions between the carbanionic model molecule and sulphur can be represented as follows:



$$2 < K < 8$$

Above $K \approx 2$, polyalkylsulphide and thiolate formation was noted:



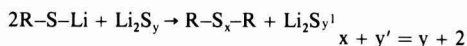
The last reaction is not promoted in benzene solution since alkaline sulphides are not soluble.

$$K = 8$$

In this case:



The stoichiometric reaction yielded 75 per cent thiolate. Indeed for all the oligomers the yield was about 60 per cent. This result shows that the reaction between thiolate and alkaline polysulphide became important in increasing the alkylpolysulphide yield:



4. Application to monocarbanionic polymers

4.1 Definitions

After the addition of sulphur S_8 to monocarbanionic polymers a coupling reaction on the GPC chromatogram was noted.

We have defined the coupling yield (C) as the ratio of the number of active end groups, $2N_2$, which have participated in the coupling reactions divided by the total number of initial active chains ($N_1 + 2N_2$).

N_1 = number of non-coupled macromolecules

N_2 = number of coupled macromolecules

\bar{M}_{n_0} = average molecular weight of non-coupled chains

\bar{M}_n = average molecular weight of the final polymer

$$C = \frac{2N_2}{N_1 + 2N_2} = 2 \left(1 - \frac{\bar{M}_{n_0}}{\bar{M}_n} \right)$$

Table 6

Poly- α -methylstyrene polysulphide obtained from the reaction of α -methylstyrene dicarbanionic tetramer with sulphur. Influence of the K ratio on the length of the polysulphide chains

K	S ₈	\bar{M}_{n_0}	\bar{M}_{n_1}	S %	C	\bar{x}
1:1	yes	472	7 000	16.8	12	3.2
2:1	yes	472	73 000	17.3	13	3.2
4:1	none	472	5 100	12.0	9.5	2
8:1	none	472	2 800	6.8	5.5	1

Table 7

Molecular weight and degree of coupling of dicarbanionic polystyrene after reaction with S₈.
T = 20°C, K = 2:1

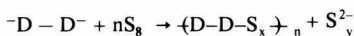
(S ₈)	(LiPSLi) × 10 ² M	\bar{M}_{n_0}	\bar{M}_{n_1}	C	\bar{x}
262	2	0.5	12 000	53 000	4.4 3.8
272	1	1	6 700	42 700	6.3 4.3
292	2	1	13 000	70 000	5.4 4

Table 8

Results obtained from single batch reaction between styrene, sodium and S₈

Monomer		K	S ₈	M	T(°C)	\bar{M}_{n_0}	S %	Yield (%)
Styrene	S ₈ homogeneous	1:1	2 × 10 ⁻²	2 × 10 ⁻²	+25	2 600	34	57
Styrene	S ₈ homogeneous	2:1	2 × 10 ⁻²	4 × 10 ⁻²	+25	2 500	33	68
Styrene	S ₈ homogeneous	4:1	2 × 10 ⁻²	8 × 10 ⁻²	+25	13 000	23	76
Styrene	S ₈ homogeneous	2:1	0.34	0.68	+25	40 000	34	77
Styrene	S ₈ homogeneous	2:1	0.34	0.68	-60	60 000	23	98
Styrene	S ₈ homogeneous	2:1	0.27	0.54	+25	55 000	32	76
α -methyl styrene	S ₈ soluble	2:1	0.34	0.68	+25	18 000	36	92

The polycondensation reaction takes place currently:



5.2 α -methylstyrene dimer

The second dimer used to study this reaction was the α -methylstyrene dimer. With this carbanion no monomer formation was observed and consequently there was no electron transfer reaction. With this carbanion a large amount of mono- and disulphide cyclic dimer was recorded, also a low yield in the condensation reaction. The Dreiding model of the molecules of this dimer showed that the two carbanionic ends are in the best position to give cyclic compounds during the reaction of the carbanion with elemental sulphur. This proximity explains the large amount of cyclic oligomers.

5.3 α -methylstyrene tetramer

This dicarbanionic oligomer was prepared by the Szwarc method. In this case, the anionic sites were separated by six carbon atoms. The Dreiding models indicate that there is steric hindrance preventing the carbanions from getting very close as in the case of the dimer. This conformation prevents cyclic sulphide molecule formation, and the GPC chromatogram showed that the primary reaction is that of polycondensation.

The number of condensations, C, and the number of sulphur atoms, x, in the bridges of the polyalkylpolysulphanes are given in Table 6.

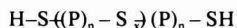
In conclusion, it seems that it is necessary to prevent secondary reactions such as cyclic molecule formation. This can be done using dicarbanionic chains where the carbanionic ends are separated from each other by six carbon atoms.

5.4 Dicarbanionic polystyrene

Biphenyllithium was used as an initiator (or naphthalene lithium) dissolved in THF to initiate the formation of polystyrene. The initiated solution was poured into a solution of THF containing soluble sulphur.

With these polymers the condensation yield was less than with the oligomer condensation, but the number of sulphur atoms in the bridge was similar.

The former reaction indicates the possibility of preparing mercaptoditelechelic polymer polysulphanes:



5.5 "One pot reaction"

To extend this reaction for industrial requirements we carried out one pot reaction. In this single batch type reaction, we simultaneously added lithium or sodium pellets, monomer and sulphur to THF. There was an exothermic reaction and polymers with high sulphur content were obtained.

We think that:

- (i) In the first step there was an anionic initiation of styrene, a coupling reaction of the anion radicals and formation of dianions.
- (ii) In the second step there was competition between the propagation step and the reaction of carbanions with sulphur S₈ as previously described.

The results are shown in Table 8. A high ratio of sulphur in the polymers of up to 35 per cent was noted, and polymers having a molecular weight of between 2,000 and 300,000 were obtained.

6. Conclusions

The reaction between carbanion and sulphur has been investigated. We conclude that there are two principal reactions:

- (a) An attack on sulphur S_8 by the carbanion to give dialkylpolysulphide,
- (b) and functionalisation of the end chains with thiol function.

We hope to simplify these anionic reactions with single batch systems to obtain a wide variety of polymers or copolymers.

When the number of sulphur atoms in the sulphur bridge is around 3 or 4, the polymers seem to be thermodynamically stable at room temperature. Work is continuing on other monomers and on the physical properties of sulphur-containing organic polymers, to compare them with the properties of organic polysulphide polymers having uniform repeating units as described by Fitch²¹.

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Solving paint problems with the aid of a computer*

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Summary

In a well-known base coat/clear coat system for car refinishing unexplained complaints about adhesion occurred from time to time. The complaints were about the stripping of the clear coat from the base coat. This caused our customers great annoyance, therefore an investigation was started to solve this adhesion problem. The investigation was hindered by the fact that the results were unpredictable; the same experiment led to different results when performed by different sprayers. During this investigation more than 800 panels were sprayed and about 20,000 results were processed with the aid of a computer. Factorial designs were used and the results were analysed with a P-stat program. With these designs it was possible to find the significant factors and interactions. So in a number of series the cause of the adhesion problem was unravelled and was traced to two application factors; the first was the time between spraying base coat and clear coat, and the second was a way of spraying that was too dry. When the cause of the adhesion problems became clear, several actions were taken: the customers were warned of the danger of too long a time between spraying base coat and clear coat, and the formulation was changed to reduce the danger of spraying too dry.

Introduction

The composite nature of paint makes it a product liable to all kind of problems. A well-established paint generally consists of about 20 different raw materials, each contributing to the product's properties, usually chosen on the basis of practical experience rather than on theoretical considerations. All raw materials, mainly delivered by independent raw material suppliers, vary in their properties. Additional complications can arise because the parameters of the paint production process can also influence the end properties, and last, but not least, the application stage is sometimes, as is the case in the car refinishing market, beyond the control of the paint supplier.

From this compilation of potential difficulties it will be clear that paint is indeed a product prone to all kinds of problems. And when a problem suddenly arises, it is often difficult to pinpoint the cause of the problem. This paper describes the history of a complicated case of an adhesion

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Figure 1. Paint film compositions of conventional metallic (a) and base coat/clear coat (b) systems showing the different aluminium flake distribution

problem in a base coat/clear coat system for car refinishing, but the problem solving technique discussed is also useful for attacking other paint problems such as optimising formulations.

Base coat/clear coat systems are of great commercial value because the automobile manufacturers are supplying an increasing part of their production with base coat/clear coat paint systems.

Introduced in the early seventies and having a high aesthetic value, these base coat/clear coat systems are increasing to a 50 per cent market share in the eighties. The differences between a conventional metallic system and a base coat/clear coat system is shown in Figure 1. The essence of the latter system is that the same quantity of aluminium flake may be used in it as in a conventional system, but that it is concentrated in about a quarter to a third of the thickness of a typical paint layer. A clear film is then applied to make up the rest of the paint film. The introduction of this new type of paint film technology was accompanied by all kinds of problems, such as cracking, yellowing, loss of adhesion, blistering from primer coat and fading. Most problems have now been overcome. These problems did not only occur in the base coat/clear coat systems on newly assembled cars (on so called OEM systems: original equipment materials), but also in the base coat/clear coat systems developed by the suppliers of car refinishing paints, because fundamentally both products are based on the same principle.

This paper discusses an example of one of these problems, where in an established base coat/clear coat system for car refinishing unexplainable complaints about adhesion were received from time to time. The complaints were about stripping of the clear coat from the base coat ("peeling"). Because this phenomenon caused a great deal of annoyance to our customers (a repeated repair was necessary) it was decided to start an investigation.

Experimental methods

Application

All laboratory experiments and equipment, unless stated otherwise, were carried out as in general practice (spray gun, pressure, nozzle, etc). A typical base coat/clear coat refinishing operation consists of the following: first a single layer of base coat is applied, and after 2-5 minutes flash-off a cross coat is sprayed. After 3-10 minutes a mist coat is used to eliminate unwanted cloudiness and colour and flow differences. To complete the repair the clear coat is applied after 10-20 minutes in two cross coats or three single layers with 5-10 minutes flash-off.

Adhesion

There are many methods of testing adhesion but most of them were not suited to this investigation. Considering the large numbers of panels to be tested, it was decided to use a fast method. The test chosen was to mark a cross in the paint film with a sharp knife; the cross being marked in such a way that the steel substrate was reached. Sticky cellulose tape was pressed onto this cross and lifted off.

Table 1
Influence of application factors on adhesion (standard deviation 1.0)

Factor	Fixed level	Adhesion
1 Thinner in base coat	80% 120%	2.9 3.2
2 Thickness of base coat	1 cross coat 2 cross coats 3 cross coats 4 cross coats	4.7 4.7 5.0 4.9
3 Mist coat	applied not applied	2.5 3.6*
4 Time between spraying base coat and clear coat	10 mins 1 h 5 h 24 h	3.4 2.6 3.4 2.9
5 Thickness of clear coat	1 cross coat 2 cross coats 3 cross coats 4 cross coats	3.8 2.9 2.7* 2.6
6 Cure	room temperature 20 mins at 60°C 45 mins at 60°C 90 mins at 60°C	2.7 3.0 2.9 3.3

*Significant factors influencing adhesion.

The measure of adhesion was given by the amount of clear coat that was peeled off (1 = strong peeling, 5 = no peeling).

Factorial designs

Because a large number of variables were to be investigated, it was decided to base the investigation on statistical principles. The so-called factorial designs were used, which can show which variables are influencing a property such as adhesion and how large the influences on the property are.

In a factorial design a variable is called a factor. Each factor is fixed at two or more levels. For example, if we want to know whether the film thickness of the clear coat influences the adhesion, the clear coat is sprayed in two and four cross coats. We then have the factor "film thickness" with the fixed levels "two or four cross coats". The results are obtained from tables with numerical values. The number of experiments necessary increases exponentially with the number of factors, therefore often only a part of a factorial design is actually investigated, a so-called fractional factorial design. By neglecting three factor and four factor interactions, such a fractional design can still give results with the same accuracy as a complete factorial design.

The numerical results are suitable for processing by computer to determine their significance and scatter. In this case the investigation was split and started with a fractional design of 128 test panels (an 1/8 fraction of a 2¹⁰ factorial design).

Results

In three different fractional designs of 128 test panels, the influences of formulation and application factors were investigated. An example of the type of results obtained is given in Table 1, where the influence of application on adhesion is shown. After these three designs were carried out, the following conclusions could be reached.

– Formulation factors did not have any influence on

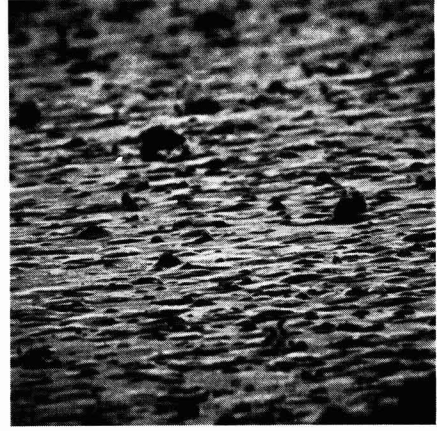
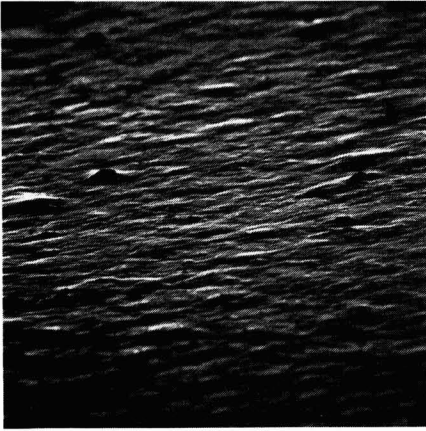


Figure 2. Surface of base coat with a "wet" applied (left) or a "dry" applied (right) mist coat



Figure 3. Base coat surface with a dry mist coat without silicone oil (left) and with silicone oil (right)

adhesion; only the formulation factors that were of practical value were investigated.

- Two factors were found to increase the peeling of the clear coat, these were film thickness of the clear coat and the application of a mist coat (see Table 1). Of these two factors only the last is of importance, because only thin layers of clear coat guaranteed good adhesion.
- The experimental error was still high (standard deviation was ± 1.0) which meant that the most important influence had not yet been found.

Because of these results the application of the mist coat was further investigated. It was found that the peeling of the clear coat was strongly affected by the way the mist coat was applied ("wet" or "dry"), and the timing of its application. It became clear that when a dry mist coat was applied onto a dry base coat, the mist coat did not flow out satisfactorily and the surface became very rough. The result was a loss in adhesion of the clear coat (see Figure 2).

When the most important influence on the adhesion of

Table 2
Influence of application of mist coat on adhesion of clear coat
(standard deviation 0.3)

Factor	Fixed level	Adhesion
Colour of base coat	colour A	4.1
	colour B	4.3
Paint sprayer	sprayer A	4.2
	sprayer B	4.4
Silicone oil	not present	3.6
	present	4.9
Mist coat application	wet base coat/wet mist coat	4.8
	dry base coat/wet mist coat	4.5
	dry base coat/dry mist coat	1.4
	dry base coat/wet mist coat	5.0

the clear coat was identified, and also a physical model proposed to explain the adhesion loss, it became possible to work out a solution for this problem.

It is the common practice of paint formulators to improve wetting behaviour by adding silicone oils. Silicone oils lower the surface tension and enhance the spreading of liquid paint systems. A number of silicone oils were screened and indeed it was found that in this way a smooth base coat surface could be obtained after applying a "dry" mist coat (see Figure 3).

Confirming this, the adhesion of the clear coat on the base coat was drastically improved with no negative side effects. It was therefore decided to add this silicone oil to the base coat. As a check a final fractional design was carried out and the results are given in Table 2. The standard deviation was now reduced to 0.3 compared with 1.0 for the earlier results shown in Table 1.

Besides the formulation change a warning went out to our customers in which the dangers of over long times between spraying of base coat and clear coat were pointed out.

Conclusion

The statistical designs were very helpful in understanding and in achieving a solution to the problem of clear coat stripping from base coat. This method of investigation would not have been possible without the aid of a computer as about 20,000 adhesion results were processed.

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An introduction to computers*

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Introduction

The rapid spread of computers from a narrow scientific field into the everyday life of a public who's school-days passed in blissful ignorance of such machines, has had a most unfortunate effect. Instead of being hailed with enthusiasm as the next in a long line of labour saving devices, they are regarded with suspicion and sometimes downright hostility. Whatever their initial reaction, most come to look upon them as some form of superhuman brain. Thus on being informed that the one and only thing they can do is to add together zeros and ones, their response varies from incredulity to speculation on the exact nature of the institution from which one escaped.

In simple terms, however, it is true that all a computer does is to add (not subtract, nor multiply, nor divide) zeros and ones. The clever part, if that it be, is the speed with which it does it – a speed which approaches that of light. The basic concept therefore is not hard to grasp. It is the elaboration of this concept which has added the mystery to computers.

It is the aim of this paper to attempt to dispel some of that mystery by breaking the computer down into its component parts and by briefly explaining how each works. We will also cover basic computer parlance during the course of the paper.

Firstly lets deal with the terms software and hardware. As with most computer terms the definitions are not hard and fast. Changes in computer technology mean that original definitions can no longer be strictly applied. Essentially the term hardware applies to all the machinery of a computer, the parts you can see and touch. Software applies to the parts you cannot see or touch such as the programs.

Another area where there is often confusion is over the terms mainframe, mini and micro computers. These terms are largely historical and are best understood in that context as the divisions between them are now well and truly blurred. The first electronic computer filled a room 36 ft x 18 ft, used 18,000 valves and 150 kW of electricity yet could only deal with 20 numbers up to 10 digits long. As time passed, computers became smaller and more

powerful, particularly with the advent of the transistor to replace the valve. The transistor, however, was still 2,500 times larger than the silicon chip it contained. In the sixties the new technology of integrated circuits (ICs) grew up whereby complete circuits were assembled on the surface of small chips of silicon. With this, the size of computers took a dramatic downward step. The power of these new minicomputers was, however, not as great as the previous generation of transistorised machines and thus they were often used as satellites or logical terminals to the larger mainframe. As time passed, the chips became smaller and minis became more powerful until in many companies the mini replaced the old mainframe. The term mainframe, however, stuck so that now mainframe can be defined as referring to any computer which stands on the floor. Modern mainframe computers are, in fact, minis. The continued development of ICs – the complexity of which is currently only restricted by the wavelength of light (the production process is photographic) – led to a new generation of small desk-top computers called micros. These are usually distinguished by the fact that they only do one job at a time as opposed to the mainframe mini, which appears to do many jobs simultaneously. Recently, however, even this distinction has become blurred.

So what actually is a computer? What most think of as a computer consists of two basic components:

1. Central processor unit (CPU)
2. Peripheral units

In its turn each basic component can be further divided

CPU

1. Main memory

Holds data being processed and the processing instructions (program).

2. Control unit

Controls and monitors the computer's actions.

3. Arithmetic and "logic unit"

Performs all "logic unit" calculations.

*Paper presented at the Association's York Conference, 15-18 June 1983.

Peripherals

1. Input units

Keyboards, light pens, OCR units etc.

2. Output units

Printers, screens (VDUs), microfilm, telex, telephone etc.

3. Backup storage

Magnetic tape, drums, disks, floppies etc.

4. Console

A specially designated VDU and keyboard for giving additional instructions to the computer during operations.

CPU

Main memory

Historically the basis of computer memory was a tiny doughnut-shaped piece of ferrite material about the size of a full stop. These doughnuts were called cores and the memory of a computer is still often referred to as its core or core space. These cores were threaded on very fine wires along which was passed a pulse of electricity which permanently magnetised them in one direction. By reversing the direction of the current the direction of magnetism could be reversed. Each core could therefore exist in two states depending on the direction of magnetism. These core memories have now been replaced by ICs, which use transistor technology – one transistor replacing each core. The transistor, being an electronic switch, can exist in two states (like the magnetic core) either on or off.

Computer memory therefore relies on discrete components which can exist in two states – on or off. When in the open or off state this is known as the “0” (zero) state; when in the closed or on state it is represented by a “1”. A computer thus only deals in 0s and 1s and therefore cannot undertake calculations based on the ten part decimal system which we use. Instead it uses the two part binary system of mathematics. In computer parlance the basic unit is called a bit – short for BInary uniT – and is physically represented in memory by one switch (transistor).

It is worth briefly digressing at this stage to see how numbers are represented by collections of transistors or bits. If we look at one bit, as we discussed earlier, it can be in one of two conditions, either 0 or 1 (i.e. off or on), and can thus be used to represent these figures in decimal notation. If we now add a further bit there are now four possible combinations of 0 and 1 and the numbers 0-3 can thus be represented as shown below.

Bit 2	Bit 1	
0	0	= 0
0	1	= 1
1	0	= 2
1	1	= 3

This can conveniently be thought of along the following lines. The presence of a “1” in Bit 1 contributes 1 to the decimal number. The presence of a “1” in Bit 2 contributes 2 to the decimal number.

When a third bit is added the number of combinations increases to eight so that the decimal numbers which can now be covered are 0-7. The presence of a “1” in Bit 3 now contributes 4 to the decimal result.

e.g. Binary 1 1 1 = 7

Decimal 4 + 2 + 1 = 7

The pattern which emerges is that as each new bit is added the presence of a “1” in it adds the next power of two to the decimal representation.

e.g. Binary 1 1 1 1 1 = 31

Decimal 16 + 8 + 4 + 2 + 1 = 31

Power 2 $2^4 + 2^3 + 2^2 + 2^1 + 2^0 = 31$

In this way any decimal number can be represented in binary code.

e.g. 1 0 1 0 1 1 1 0 1

$8 + 0 + 2 + 0 = 10$ $16 + 8 + 4 + 0 + 1 = 28$

The core of a computer is in fact organised into eight bit units called bytes (pronounced bites). One bit of the eight is used to signify the sign (+ or -) of the number represented by the other seven bits. Each byte can therefore hold a number in the range -128 to +127 (only +127 as 0 is held as +0). Larger numbers can be held by continuing the binary coding into a second byte giving the range -32768 to +32767 and so on. Within a computer system, however, there is usually a specified maximum number of bytes which can be allocated to one number, and here we introduce the terms magnitude and precision. Precision describes the detail with which the number is held and magnitude describes its size. Thus 4296 and 0.4296 have the same precision of four digits but are of very different magnitudes. A two byte eight bit system would therefore have a precision of five digits and a magnitude of -32768 to +32767.

Large numbers such as 1,000,000 can be represented as IE6, where 6 is the exponent of the mantissa 1, i.e. 1×10^6 .

Similarly, fractions can be represented as integers with negative exponents. However, though magnitude can be increased in this way, it is at the expense of precision, as some bits must be used to store the exponent and thus less are available for the mantissa.

One of the reasons for organising the core space into eight bit bytes as opposed to any other number of bits is the need not only to deal with figures but also with letters. If you consider the need for 26 lower case and 26 upper case letters, together with 10 numbers, around 12 punctuation marks and 20 mathematical and other symbols you can see that there is a need for 94+ combinations. The smallest number of bits which will accommodate this number of combinations is eight. The system of representation adopted as an industry standard is called ASCII (pronounced askey) standing for American Standard Code for Information Interchange. Simply, each letter, number or symbol is represented by a decimal number up to 128, which can thus be translated into a one byte binary code. In this sense the terms byte and character become synonymous terms used to describe eight bits of information.

We now come across the term word. As the name implies it is a collection of characters (or bytes) and it represents the size of the package of information with which the computer works. In smaller micros (e.g. Apple, PET) the word size (length) is eight bits so that the terms word, byte and character all mean the same thing. However, in larger computers the word length may go up to 40 bits; more usually, as on IBM, the length is 32 bits (4 bytes).

We have seen how using ASCII we can store letters etc. in binary form. If, however, we only need to handle numbers it is a waste using 8 bits for each digit when 4 would suffice. Some computers, therefore, when dealing purely with numbers, store two digits in each byte. This is known as packed mode or simply as packed.

To return to our consideration of CPU memory, we have seen that the memory is organised into 8 bit units called bytes and that the unit of information with which a computer works is a word, which in turn is made up of one or more bytes. Within the memory each word can be addressed individually and is often referred to as a storage location. It is, however, the number of bytes of memory which is quoted by the manufacturer when specifying the core size of his hardware, not storage locations (unless the word length = 1 byte). A 64K machine means that there are 64 thousand bytes of memory space – but beware, they are not all available to you. Some space is used to hold the operating program and some is used to hold the interpreter (software which translates from the program language, e.g. basic, into binary which the machine can understand, i.e. machine code).

We have thus far seen that the CPU contains a memory inside which information can be held and accessed by reference to its location. What happens now?

Control unit

In the original breakdown of the CPU into its component parts, we identified a part called the control unit. This is the part of the CPU which monitors and controls the operation of the computer and acts as an interface (link) between main memory, peripheral units and the arithmetic unit by way of links called buses. There are three buses, the address bus, the control bus and the data bus.

The address bus carries information about which storage location to access. The data bus carries the information to and from that location. The control bus carries the instruction to either read or write the information to or from location. The data bus can only carry the contents of one storage location at a time and you may see manufacturers referring to data transfer as being 16 bit etc. This merely means that each storage location/word length is 16 bits or 2 bytes wide. Generally the larger the computer the greater the word size therefore the faster the data transfer rate.

This, then, is how a CPU interfaces with its memory, but it must also interface with the outside world, i.e. its peripherals. Data moves in and out of the CPU by way of input/output (I/O) ports. Simply, the control unit regards these ports merely as additional memory locations and can thus reference (address) them for either reading (input) or writing (output) in the same way as for memory. These portions of memory are usually referred to as buffers.

Having mentioned I/O it is probably an appropriate point to explain the terms RAM, ROM, PROM, EPROM (pronounced phonetically). The term random access

memory (RAM) is used to refer to the type of memory we have so far discussed, where data can be stored, read and overwritten at random. The term is a little of a misnomer as strictly speaking all memory can be randomly accessed, the distinction is whether stored information can be randomly overwritten or not.

The term read only memory (ROM), however, correctly implies that the information stored there can only be read and not overwritten. This type of memory is usually set by the manufacturer and contains information to set the hardware in operation, power up. The important point about ROM is that, as opposed to most RAMs, the stored information is not lost when the power is turned off. Most ROMs are of the masked type, where the programs they contain are manufactured-in during the production of the chip. In some cases, however, using special equipment, a ROM can be programmed. This type of programmable ROM is known as a PROM. Even with a PROM, though, once a program is fed in it is stuck there for good. If there is a likelihood of needing to change the program, a reprogrammable PROM or eraseable PROM (EPROM) is used.

Also within the control unit of the CPU are a number of registers, such as the program counter, the accumulator and the datum register. These hold the immediate information with which the computer is working and directly link with the human interface i.e. the program. It is impossible to consider programs and how they control the operation of the computer in any detail within the context of this paper. In essence, in whatever language a program is written, it is reduced to a set of binary coded instructions.

Each instruction will contain a two figure function code defining a particular type of arithmetic, input or output action to be undertaken. The instruction will also contain the memory location of the data to be processed and may, as appropriate, contain a memory location in which the outcome will be stored. A program will consist of a series of such instructions and during its operation the various CPU registers will come into play. The accumulator will be used as a temporary store for the outcome of calculations. The program counter is used to hold the memory location of the next instruction in the program. The datum register will hold the location of the next piece of information to be retrieved from memory.

With all these storage locations (both for data and program) to be accessed and with numerous registers, input and output devices, buses, arithmetic units etc. to be coordinated, it is very important that the control unit handles things in an organised and well orchestrated fashion. The analogy with music is a valid one as this important coordination function is achieved on the basis of a rhythmic beat. Everything a computer does follows a two beat fetch/execute cycle. For example, a program instruction will be fetched and executed. In order to facilitate this execution a data item will be fetched and a calculation executed on it. The result will then be sent (negative fetch) and a "write into a storage location" will be executed. In order to assure that this happens in a controlled manner and in correct sequence, it occurs in time with a strict beat set up by a quartz crystal clock, like that used in watches, located in the CPU.

Arithmetic and logic unit

At its simplest a computer moves data from memory to register, from register to register (often via an arithmetic operation) and from register back again to memory. All this is under the control of the control unit, but the arithmetic operation is performed by the last part of the

CPU we will consider, the arithmetic and logic unit (ALU).

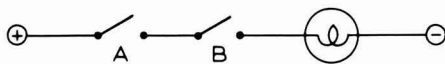
It is the ALU part of the CPU which many have been led into fearing. This is the part that actually does the reasoning and performs the calculations. However, if this is "Big Brother" – 1984 and all that – then we really have nothing at all to fear. All the ALU can do is to add together one and one.

This entire paper could be taken up with considerations of the ALU but suffice it to say that reasoning, as far as a computer is concerned, is a matter of comparison – is A larger than B, is $C \times D$ larger than E etc. Computer reasoning, therefore, is a result of the application of the four basic arithmetic functions of addition, subtraction, multiplication and division. One of the beauties of binary maths is that all these functions can be achieved by addition in various ways.

Remember, in a computer numbers are represented by electrical circuits (interconnected switches). When two (or more) numbers are brought together for calculation in our world they can be written on a piece of paper and remain separate entities even during the calculation. In electrical terms (in a computer), however, for two numbers to come together the circuits must be connected, thus the effect can only be additive. How fortunate therefore that all four arithmetic functions can be accomplished in binary by additive means and can thus be done electrically.

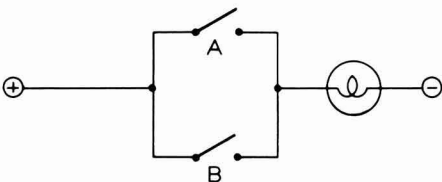
The electrical connections within an ALU are based on three logic building blocks called AND, OR and NOT gates. This is known as Boolean logic as it is based on a paper written in 1847 by George Boole, an English mathematician, and later applied to electrical circuits by Shannon in 1938. Boole dealt with truths and falsehoods in his logic and considered there to be three basic possible logic statements.

1. If my father is dead AND my mother is dead then I have no living parents. The AND gate can be expressed as two truths resulting in a truth. If one is false then the result is a falsehood. Electrically this is represented by two switches in series.



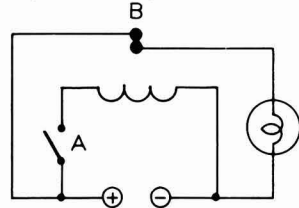
Only if both switches A and B are closed will the bulb light.

2. If the sun shone this morning OR the sun shone this afternoon then the sun shone today. The OR gate can be expressed as an either/or situation where if either one or the other or both of the statements are true the result is a truth. It requires both statements to be false before the result is a falsehood. Electrically this is represented by two switches in parallel.



If either switch A or B or both were closed the bulb would light.

3. It is hard to find an analogy for the last logic statement but it perhaps can be illustrated if one considers the two following statements: "I have my finger over the end of the tap" and "Water flows from the tap". Whilst like the other statements each can be true in its own right, if one is true then clearly the other is NOT. It can best be summed up by saying that if there is an input there is no output, and conversely, if there is no input then there is an output. This can again be represented electrically by two switches but in this case one switch is a normally closed relay.



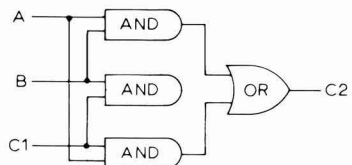
With the relay contacts B normally closed and no input to the relay being provided (switch A open) the bulb will be alight. As soon as switch A is closed an input is provided to the relay and the contacts B open extinguishing the bulb.

The AND, OR and NOT logic elements are called gates because each can be represented by a collection of transistors configured in such a way as to apply the test. If the input passes the test the gate is said to be opened and current flows. We will now go on to see how these elements are combined to form a binary adder.

Binary addition is much like decimal addition, where the digits are summed up to ten and then one is carried and the sum digit returns to zero. In binary addition, however, the one is carried when the sum reaches two as in the example below.

$$\begin{array}{r} 101 = 5 \\ + 001 = 1 \\ \hline 110 = 6 \end{array}$$

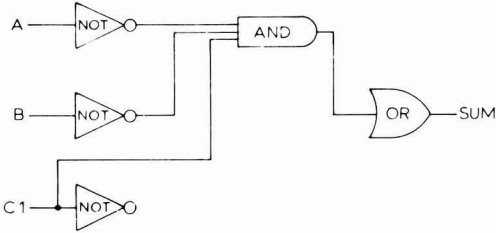
Thus, as in decimal maths, in adding two digits together we are in fact adding three as we must include the carried digit, albeit a zero. If we consider the connections in the following diagram where A and B are the digits to be added and C1 is the carried digit:



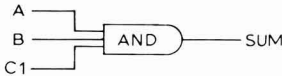
the top AND gate, connected to A and B, will only open if both A and B are set at 1. Similarly the second AND gate deals with B and C and the third with A and C. Thus if the sum of any two of the three digits equals two a signal will be passed to the OR gate and this will thus be passed on to C2. Thus C2 is set at one and becomes the carried digit (C1) of the next column of digits to be added. In this way the carry digit resulting from the addition has been ascertained.

However, we still need to ascertain the sum digit. This

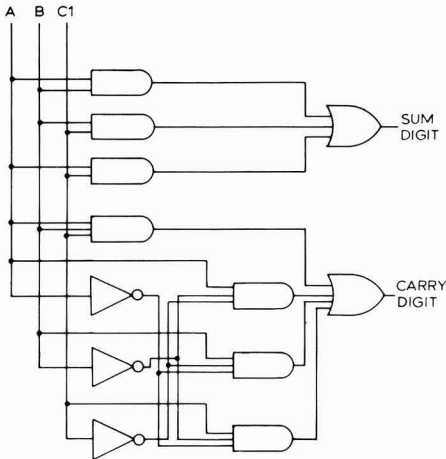
time we need to detect whether the sum is 1 or 3, in which case a 1 must be set as the sum digit, or if it is 0 or 2, in which case a 0 must be set.



In this case only if A and B do NOT equal 1 and C1 does will all three connections carry current to the AND gate, which thus opens. This in turn passes current to the OR gate which sets the sum at 1. The circuit is repeated for the other possible combinations of A, B and C1. In this way the sum digit can be correctly set at 1 or 0 when the actual sum is 0, 1 or 2. It does not, however, detect the condition where the sum is 3, i.e. $A=B=C1=1$. This is simply dealt with as shown below.



Thus for the binary addition of two single digits we have calculated the sum and carry digits using the following circuit.



Peripherals

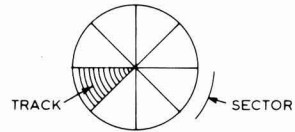
Disks

We have dwelt at some length on the CPU as this is essentially the heart of a computer and indeed is what many think of as the computer. A computer, however, would be useless without being able to communicate with the rest of the world through its peripheral units. One of the most important of these peripheral units is the disk.

As we have seen the core of a computer can be used to store information. However, even with the biggest computers this would very quickly become full if we tried to store all the data required for the company accounts, payroll etc. What is required is a facility for the mass

storage of data which is not currently being worked on. Historically this problem was solved by storing the data on magnetic tape, identical in principle to reel to reel audio tape. However, just as with audio tapes they suffered from the problem that to find the piece of information which you want, you have to start at one end of the tape and search through until you find it. Because speed of access to information is vitally important to a computer, tapes have now very largely been replaced by disks. A disk is very like a gramophone record but with each side covered with magnetic oxide (like a recording tape) instead of grooves. The disk spins at high speed (up to 2,500 rpm) and information is accessed by a read/write head, rather like a gramophone stylus but which never actually makes contact with the disk. There is one head for each side of the disk.

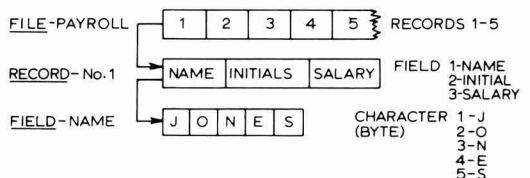
Each disk is organised into concentric rings called tracks and into pie segments called sectors, as illustrated below.



In this way a form of grid reference can be built up for any piece of information so that the read/write head can be quickly and accurately homed in. These grid references are all that is usually held in the core memory. As the demand for even greater storage capacity increases, the disks come in packs of half a dozen or so mounted 15 mm apart rather like records in a juke box.

Smaller computers use floppy disks or diskettes, which differ from the larger coated metal disks in that they are based on a flexible plastic material. They are contained in a dry lubricated cardboard sleeve inside which they are rotated and basically work in the same way as hard disks. They have the advantage that they are cheap and can be easily swapped so that different programs can be run (important on small computers), but the disadvantages are less storage capacity and the seek time (speed at which information is retrieved) is 5-10 times greater.

Three terms which you will often come across with peripheral storage are file, record and field. We have seen how a disk is organised by the hardware into tracks and sectors in order to locate information. Equally it needs to be organised so that information can be located by the software. A good analogy is a filing cabinet - this is organised into drawers by the manufacturer who represents the hardware, but it is up to us, the user, representing the software, to organise our files and place them in the drawers. From the software point of view the disk consists of a number of files (set by the software), which would cover a general topic such as payroll, customer accounts etc. Taking the payroll file as an example, this would be divided into records, one for each person on the payroll. Each record would then be further divided into fields such as surname, initials, salary etc.



The tie up between the software and hardware organisational systems is handled automatically by the DOS (disk operating system) in the CPU.

Printer

Another important piece of peripheral equipment is the printer. This is a pure output device to produce hard copy printouts of the results of the program's operation. There is a vast array of operating principles for printers but mainly they fall into two categories, line printers or character/serial printers (not to be confused with serial communication). Line printers are high speed devices printing 150 characters a line at up to 2,500 lines per minute. They are categorised by having in effect 150 separate print heads arranged in a line so that a complete line is printed at each impression. The character printer on the other hand prints one character at a time at speeds of up to around 200-250 characters a second. It is in effect a very fast typewriter and by using a daisy wheel printer, typewriter quality printing with interchangeable type faces can be produced as is the case with word processors.

The most common type of printer these days is a dot matrix printer, which can be either a line or character type machine. The print head is commonly made up of 35 "needles" arranged in a 5 x 7 matrix. Each needle has the capacity to be fired independently against the ribbon and paper. Each character is formed from a pattern of dots created by the selective firing of the needles.

Printers, like all input and output peripherals, can be worked in series or parallel communication with the CPU. In parallel communication all eight bits of a byte are sent simultaneously down eight separate parallel wires. In serial communication they are all sent one after another down a single wire. Obviously parallel communication is faster, but one can see the advantages of serial communication where long distances are involved (especially along telephone lines).

VDUs

The modern computer would hardly be recognisable without a television screen and keyboard. This set up is described as a visual display unit (VDU), although strictly this term only applies to the screen and also legitimately to LCD and LED readouts. For convenience in operation the screen is divided into a matrix of columns and lines and

often you will hear a VDU referred to as a "so many column display". The commonly used configurations are 40 or 80 columns and 24 lines. Just as on a television screen the picture is made up of dots. Usually only separate locations of the 80 (40) x 24 matrix are individually addressable and one character is displayed in each. In some cases, though, each dot is addressable and this is termed high resolution graphics and is used for graphical and drafting work.

No VDU would be complete without its associated keyboard. As we have said, strictly a VDU is the screen which is an output device, whereas a keyboard is an input device and as such is probably, these days, the most common form of input device. Usually it resembles a typewriter keyboard but often has a duplicate set of number keys grouped together to form a numeric pad. This is because one tends to deal more with numbers on a computer than on a typewriter. A keyboard operates like a typewriter in that you can type information on it. Usually this information appears on the screen and forms input to the computer. A further difference from a typewriter is that an enter key is always present. Pressing this will commit you to entering what you have typed to the CPU.

There are of course many more input and output devices for computers, some highly specialised and others of vital importance for the future. Currently coming into widespread use, for example, is bar coding, which are the series of black lines, like iron railings, you see on the side of most items you buy from the supermarket. This is merely part of a computer input device. Probably the most exciting areas for the future are OCR (optical character recognition) and voice simulation, which will allow us to write and talk to computers. However exciting or daunting these prospects seem (depending on your point of view), they are only input and output devices for the heart of a computer, the CPU. However clever it all appears, remember the CPU can only add 1 and 1 together. What makes it seem so clever is merely the speed at which it does it.

I hope that in this short paper I have been able to dispel some of the mysteries surrounding computers. I apologise to the specialists, who will without doubt find statements to be erroneous in detail because of their generality, but ask them to bear with the rest of us in our struggle to keep up with the ever changing face of this important technology.

[Received 8 March 1983]

conference discussion

Discussion is encouraged at OCCA Conferences following the presentation of papers. Those who put questions were asked to fill in discussion slips with the details of their questions. The answers given by the lecturers/authors were recorded on tape. Edited versions of the discussions that followed the papers published in this issue appear below: questions in ordinary roman type, answers in italic. Only those questions for which discussion slips were received are published.

Computer aided analysis of surfaces and surface coatings

A. Carrick

R. R. BLAKEY: In view of the expense of the instrumentation presented, isn't it likely that not many companies will be able to afford them? Most of us have to hire time on other people's equipment, so is a breed of new testing companies arising?

A. CARRICK: I think your comments are quite correct. Although the larger industrial organisations can and do

afford their own instruments, a number of contract laboratories do exist which can supply SIMS, ESCA and Auger analyses. Also, most of the universities have that kind of capability.

In the future the cost of instrumentation is going to come down because in this case its applications are very broad and more people will want it: we as manufacturers

are always under pressure to supply instrumentation at lower cost. The inclusion of computers helps in that much of the push button electronics can be done away with, reducing production costs.

Speculating for a moment, as I stated in my paper years

from now we will probably have small throw away instruments. In the more immediate future and even today, multi-analytical techniques will and are becoming important: the ability to carry out different spectroscopies – ESCA, SIMS, Auger – on the same sample without moving it. That is the direction in which we are moving.

Linear polymonosulphide and polysulphide polymers – general survey, recent developments and applications

J. Brossas and J. M. Catala

It is hoped to be able to publish the discussion that followed this paper in next month's issue.

Solving paint problems with the aid of a computer

H. J. van der Stoep

H. FOSTER: In Table 1 of your paper you quote a standard deviation of 1.0 relating to adhesion tests between base and clear coats, assessed on a 1-5 scale. Is this an average standard deviation obtained from all the adhesion tests quoted in the table? If so, how did this standard deviation influence conclusions on the use of mist coats?

H. J. VAN DER STOEP: The answer to your first question is yes, in Table 1 it is the average deviation obtained from the adhesion tests. This relatively high standard deviation indicated that an important factor had not yet been found and that it was not under complete control. This stimulated us to further investigate the influence of the mist coat.

The standard deviation was partly caused by the experimental error of the adhesive tape test, which is fairly high. Therefore, the figures given were not based on one experimental determination of adhesion, but at least two incisions were made on each panel and the tests were repeated after three days and after a week. These averaged figures are the ones used in this paper.

R. B. TENNANT: What method of spray application was used in these experiments?

H. J. VAN DER STOEP: The method used was by hand

spray. Variations due to application were only really important with regard to adhesion in the application of the mist coat.

K. J. SMITH: Did you have a ready made computer program for processing the results of the tests or did you write your own program?

H. J. VAN DER STOEP: We used a ready made program for statistical calculations called the P-Stat Program, the Princeton Statistical Program. This software is available throughout the world; we only used part of it.

A. A. GAMBLE: The results of the statistical analysis show that a smooth mist coat is important to produce good adhesion of the clear coat. Do you have a molecular explanation for this result?

H. J. VAN DER STOEP: No, unfortunately I do not have a molecular explanation. One might have expected, theoretically, rougher surfaces to produce better adhesion.

But it is a big step, of course, between surface roughness as discussed here and the molecular level. The pictures of surface roughness shown in my paper, for instance, were done at an enlargement of about $\times 500$ and are in no way related to molecular phenomena.

next month's issue

The Honorary Editor has accepted the following papers for publication. They are expected to appear in the October issue:

NMR analysis of paint media* by M. Marshall

Efficiency and change in metal decoration* by A. A. Gamble

Quality Control and standardisation in the titanium pigment industry* by R. R. Blakey

Prediction of performance of exterior wood coatings* by E. R. Miller

*Paper presented at the OCCA Conference, York, 15-18 June 1983. The relevant discussions that took place will also be published in this issue.

Letters to the Hon. Editor should be sent to the Association's offices, see contents page for address.

New methods of performance testing – prediction of durability

Sir – It is four years since you published my paper on “Prohesion” (*JOCCA*, 1979, 62, 131) and it is now reasonably accepted as a viable addition to existing methods of test.

The test simply involves frequent cycling of a simulated industrial atmosphere representing extreme condensation/drying conditions.

In conjunction with the ageing test (POP test) it forms the only realistic means of predicting the durability of the modern polymer/elastomer coatings, which are tending to replace the older type oxidising paints.

Further information from the publishers of the titles reviewed can be obtained by completing the *Reader Enquiry Service* form at the back of the *Journal*.

Colour Vision in the Nineteenth Century

P. D. Sherman
Adam Hilger Ltd, Bristol
ISBN 0-85374-376-9, 1981
pp. xiv + 233, £35

This fascinating book describes the period when colour science was being transformed from the notions of the seventeenth and eighteenth centuries to those of today.

The difficult asses' bridge lay between the objective and subjective worlds. Light and its important property of colour were (since Newton), obviously based on physical entities. It was hard at that time to conceive how fundamental were the contributions of the human eye and brain in various observed phenomena. Since Newton had demonstrated the elemental nature of the many spectral colours, how could Young (and the earlier mysterious Palmer) ascribe all colour to only three types of retinal receptor?

Another large red herring was thrown up by the authoritative Brewster, who had already achieved great distinction as an optical physicist, but who obstinately regarded his colour theory as a masterpiece to be defended bitterly. He sadly misinterpreted the faint white light he could see as a background to the spectral lines. It is now explained as stray light too faint to be distinguished as coloured. From his accurate observations, Brewster con-

Information regarding membership of OCCA is obtainable from the Association's offices, see contents page for address.

Newcastle Section

The fall of OCCA; depression ends 1994

The final lecture of the 1982-83 session was held on Thursday 3 March 1983 at 6.30 p.m. at the normal St. Mary's College venue in Durham City. The lecture entitled “Business cycles” was presented by a past President of OCCA, Dr F. M. Smith, and was based on his work when employed in Ciba Geigy's New Venture Group. It was also an update of his paper, “The outlook for the eighties”,

1983(9)

letters

Prohesion lectures have involved approximately 3,000 people in six countries with no adverse criticism.

Since performance tests are vitally needed, can the philosophy of “Prohesion” be considered for the basis of a BS method of test?

7 St. Mary's Road
Dunsville
Doncaster DN7 4DQ

Yours faithfully,
F. D. Timmins, CChem, FRSC
19 July 1983

The Hon. Editor would be interested to hear the views of readers on this topic, not necessarily for publication.

reviews

which he had discovered a special kind of white light which was an ingredient in forming all the other colours.

The subsequent controversy was hard to resolve because Brewster's facts could not be faulted, though some critics tried unsuccessfully to attack him on that ground. Finally another genius, Helmholtz, sorted things out.

The last part of the book recounts the dénouement by Maxwell, who is the true father of modern colour science. One of his great achievements was to show how to represent colours lying outside his triangle. He introduced the concept of negative coefficients in his colour equations, and so opened up a path which ultimately led to a method of estimating Young's basic spectral response curves, necessarily without negative lobes. It is not true to claim that Maxwell himself produced such curves and on this point Sherman falls into fallacy. One wonders how many errors the present century still entertains.

In spite of a few such scientific lapses, Sherman has succeeded in writing a brilliant historical study.

Reader Enquiry Service No. 21

D. A. Palmer

OCCA meetings

presented as the keynote address of the 8th National Symposium of OCCA, Durban, South Africa in November 1980, and published in *JOCCA*, 1981, vol. 64, pages 144-155.

The disappointing attendance of 20 (18 members and 2

279

occa meetings

guests) was proof that the lecture title had probably frightened off all but the faithful occaholics. Nevertheless, Dr Smith turned the evening into the essence of OCCA by enthraling his audience so much that at the end the Newcastle Chairman had to halt the questions to prevent the formal meeting extending much longer than usual. Although Dr Smith was not the best of speakers, he was so steeped in his subject and brought it so much to life that most of those present will long remember the context of his talk.

Dr Smith reported how S. T. Lunt (when a member of ICI Plastics Division) had shown in 1971 that the UK industry and economy as a whole, experiences a series of ups and downs, and that the consistency of the time intervals between successive peaks and troughs is 5 to 4.5 years. This basic concept was demonstrated from graphs over the years 1955 to 1975 of:

- UK Consumption of PVC
- UK Consumption of polythene
- UK production of steel ingots
- Fixed capital investment in the chemical and allied industries
- Index of industrial production
- Financial Times index of industrial share prices
- UK bank rate
- Cyclical introduction of new products

At times of growth, i.e. during the mid-sixties, the 5-4.5 year cycle tended to be hidden, but could be seen as oscillations in the overall upward growth curve. Indeed the 4.5 year cycle was then shown to be oscillations on a 55 year cycle, known as the Kondratieff cycle, because it was first observed by this Russian economist.

The Kondratieff Cycle is recognised as a period of prosperity, followed by recession, depression, and finally revival with each of the four stages taking approximately 14 years, and the whole cycle about 55 years. Commencing from 1785, four cycles were illustrated, the final one being the one in which we are currently in the depression stage of. It was interesting to note that from Kondratieff Cycle predictions, revival will not genuinely take place

news

Paintmakers support Government on lead

The UK Government's initiatives on lead announced in Parliament on 29 July by Patrick Jenkin, Secretary of State for the Environment, were welcomed by the Paintmakers Association, the paint manufacturers' representative trade body, as being constructive and positive.

Further information on any items mentioned below is obtainable by completing the Reader Enquiry Service form at the back of the Journal.

Commenting on the minister's announcement, Michael Levete of the Paintmakers Association said: "We welcome the Government's initiatives. We have for a long time had close relationships with the Departments of Environment and Trade and the Health and Safety Executive over the lead in paint issue. We have recently set up a new working party to investigate those specific recommendations put forward in the report by the Royal Commission on Environmental Pollution."

He continued: "We are most anxious to supplement the Government's work on

publicising ways of dealing safely with the dangers of old leaded paint. The Commission emphasised however that emulsion paint, which is most commonly used in the home, for practical purposes contains no lead at all. A survey has been commissioned jointly by us and the Government to establish the quantities of lead involved in paint making."

Mr Levete added: "The paint industry, through the Paintmakers Association, has taken an early lead in responding to the Royal Commission's report and to most of the indications of Government policy." *Reader Enquiry Service No. 31*

until 1994, the end of the revival occurring around 2008. Any uplift in the economy before 1994 will merely be the minor oscillations of the 4.5 year Lunt Cycle.

Dr Smith clinically went through each stage of the Kondratieff Cycle explaining how each stage develops, and how particularly in the recession and depression stages "the monetarist policies aimed at controlling the money supply in an attempt to control inflation, merely aggravate a condition of stagnation". The way out of depression is a result of innovation and the upsurge of new industries and technologies. A swarm of basic innovations to take us out of the current depression is predicted between 1983 and 1995, with the peak year being 1989.

By reviewing the previous three cycles, Dr Smith showed the relationship between invention and innovation. He predicted that the inventions that would take us out of the current depression had already been made, but it was the innovative development of these inventions that was needed before revival begins around 1994.

In the paint and printing industries, except for the non-aqueous dispersion concept, all the innovations in recent years have been concerned with new methods of application and more attention to surface preparation. There is unlikely to be any significant growth or major new developments until major technological changes occur. The introduction of long-life inorganic coatings as a commercial basic innovation after 1989 was predicted. Dr Smith forecast that the "Oil and Colour Chemists' Association will continue to decline in numbers in the industrialised countries, and to grow in the developing countries." Certainly a check on the "new members" page of *JOCCA* each month confirms the latter, while the growing concern within the sections, though less apparent at the top of the Association, at the falling membership and attendances is proof of the former.

During question time the theme was developed that just as the Lunt 4.5 year cycle was an oscillation on the Kondratieff cycle, was this in turn not just an oscillation on some greater cycle? If this were so, and knowing the despair of the current depression, the predictions for a trough on the greater cycle would be unthinkable.

Dr Smith was warmly applauded at the end of the lecture, and the enjoyable evening was rounded off with the customary delicious free buffet supplied by the staff of St. Mary's College.

I. Mim

Conductive polymers and plastics compositions

The above title will be the subject of a comprehensive multi-client study by Skeist Laboratories, Inc., consultants to the polymer industries. The study is being undertaken because of strong interest expressed by many companies worldwide.

Two areas of rapid growth are involved. Carbon- and metal-filled compositions, already at the hundred million dollar mark in the US, are expected to burgeon at 25 per cent per year as the result of government (FCC) pressure to shield electronic devices against electromagnetic interference. A side benefit will be the control of static electricity. Meanwhile, R & D is proceeding at a frenetic pace on polymers that are themselves conductive. High dollar value markets are foreseen in light weight batteries and electrical devices for space and military applications.

The technology and markets for more than 50 conductive compositions will be thoroughly studied for plastics, coatings, adhesives and elastomers. Conductive polymers whose commercial potential will be assessed include quaternary polymers, polyacetylenes, polyphephenylenes, poly(sulphur nitride), poly(phthalocyanines), poly(vinylcarbazole) and 15 others.

Information will be obtained through about 250-300 interviews with end-users, formulators and raw material suppliers, fabricators, as well as industrial and academic research teams.

Reader Enquiry Service No. 32

Biocide plant ahead of schedule

The Rohm and Haas Company's major new European biocide plant initiated in 1982 at an estimated cost of \$20m is on stream one month ahead of schedule. Making the announcement that the new facility, built in the UK at Jarrow on Tyne, was on stream Mr Brian Yeats, Rohm and Haas' European production director, was also pleased to report that construction was completed within budget.

The new highly automated plant will produce most of the products in the Kathon™ biocide range, which is based on the company's patented isothiazolone technology. The UK plant will be the supply source for Europe and a number of export markets.

Reader Enquiry Service No. 33

Paint testing equipment

Impex Trading Ltd has recently concluded a representation agreement with G. Zehntner Electronic of Switzerland to distribute its range of mains/battery glossmeters, retroreflectometers and Helmen chalking testers throughout the UK and Ireland.

Reader Enquiry Service No. 34

Surface coatings certificate course

The TEC Certificate in Science with Specialisation in Surface Coatings was first offered at the Polytechnic of the South Bank in 1977 and has now run its allotted course. The Technician Education Council require a regular updating of all its courses every five years. And so, starting in September this year, the Polytechnic will be offering a newly approved Certificate course.

While it does not differ substantially from the former course, there are some significant differences as will be seen from the following account. All the science units (chemistry, physics and mathematics) have been replaced by more recently devised standard units, while the four standard technology units have been retained until such a time as they also shall be revised.

The real innovation lies in the introduction of some options that were not available under the old scheme. As well as the standard option there is now a science rich option that contains more practical chemistry. This, it is felt, will appeal to the student who wishes to extend his manipulative skills and who sees his future more in R & D or the analytical section rather than the production side of the surface coatings industry.

Further details of the new programme are available from Mr P. J. Barnes, Dept. of Sciences & Technology, Polytechnic of the South Bank, London SE1 0AA.

Reader Enquiry Service No. 35

Isocyanates monitoring

Dutom Meditech plc has extended its range of occupational hygiene and analysis services to include isocyanates monitoring.

The monitoring and analytical methods used conform to the latest UK Health and Safety Executive requirement which came into force on 1 February 1983.

Reader Enquiry Service No. 36

products

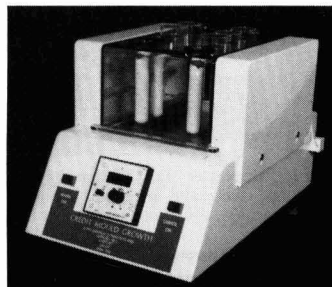
New micronised white extender

Capricorn Chemicals Ltd has introduced Mikal 00180, a white phlogopite mica with a maximum particle size of 20 microns.

It is recommended for use in anticorrosive paints and exterior coatings. The closely controlled particle size distribution of Mikal 00180 makes it, Capricorn says, ideally suited for use in primers, putties, dipping varnishes, electrophoretic paints as well as floor paints.

Reader Enquiry Service No. 37

news



Credit Mould Growth Cabinet from John Godrich

Mould/algal growth cabinet

The Credit Mould Growth Cabinet has just been introduced into the range of machines available from John Godrich. Based on the Paint Research Association's ideas, the cabinet has been developed to maintain constant temperature with the option of artificial light.

The basic cabinet allows for the testing of products against mould and algal growth and is supplied with temperature controller, lighting system, samples holder and ten etched test tubes. Accessories include special sample holders for individual testing and a cyclic timer to allow for a heat/cool cycle.

Reader Enquiry Service No. 38

Resin removing cream

Amoa Chemical Co. Ltd has developed Amoa Resinoff resin removing cream for the effective removal of such materials as paints, resins, bitumen, sealants, adhesives and printing inks. The cream is sufficiently tough to deal with heavy deposits even when they have dried on the skin.

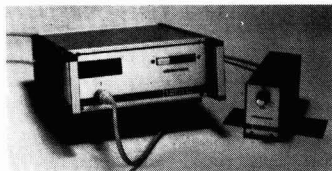
Reader Enquiry Service No. 39

New differential refractometer

ChemLab Instruments Ltd now has available the Atago Model DD-5 Differential Refractometer, which has been specially developed to measure solution concentrations of 1 per cent or less.

Typical applications include the measurement of total solute concentrations in industrial waste and the diluted concentrations of substances such as detergents and surface active reagents.

Reader Enquiry Service No. 40



The Reflektometer 517 – high quality optics and electronics are used to achieve high accuracy, consistency and linearity

Brightness measuring instrument

Pearson Panke Equipment Ltd has announced the introduction of the Erichsen brightness measuring instrument, the Reflektometer 517.

The instrument is a reflection photometer with a 45/0° geometry. The measurements correspond to the Y values as measured with colour measuring instruments. As in the case of the colour measuring instruments, the specimen is lit using light type C and the sensitivity characteristics of the light receiver have been arranged to match the human eye.

Reader Enquiry Service No. 41

Indoor UV durability testing

A new fluorescent UV-A lamp for evaluating the lightfastness of plastics, textiles, paints and inks in all ASTM G-53 type weathering testers has been developed by the Q-Panel Company. The light output is concentrated in the UV-A range (320 nm – 380 nm).

Sunlight, when filtered by window glass, is the most common cause of UV-A damage. Indoor products are also exposed to minor amounts of UV-A energy from cool white fluorescent lamps.

Products exposed to sunlight under



New UV-A lamps are a new alternative to UV-B lamps, probably the most widely used light source for testing materials. UV-A lamps are claimed to provide a more accurate prediction of indoor durability

glass are generally subjected to UV-A exposure at relatively high temperatures. Car interiors and shop display windows are typical examples. This type of exposure can be simulated by using the UV-A fluorescent lamps in the ASTM G-53 weathering apparatus at temperature of 70°C to 90°C.

The acceleration produced by the new lamps has been demonstrated by tests using the AATCC Blue Wool Standards. Twenty fading units on these standards will require approximately 10 hours exposure to fluorescent UV-B lamps, 15 hours exposure to the new UV-A lamps and about 20 hours exposure with xenon lamps.

Reader Enquiry Service No. 42

New EMI, RFI shield coating

A new nickel-filled conductive coating, researched and developed by International Paint, for plastic mouldings used in the information technology and consumer electronics industries, overcomes the problems of dissipation of electrostatic build-up and shielding from electromagnetic interference (EMI) and radio frequency interference (RFI).

The coating, named Interscreen 2000, can be applied with conventional spray equipment at low atomising pressures, avoiding waste through overspray particularly on complicated mouldings.

At present, various methods such as foil laminating, zinc metal spraying by plasma arc and vacuum metallising are used to overcome problems associated with EMI and RFI. But the most economic process is said to be the application of a conductive coating.

Reader Enquiry Service No. 43

Safer solvents from BP Chemicals

BP Chemicals has added three new solvents to its range of propylene glycol ethers and esters: ethoxypropanol (EP), methoxypropyl acetate (MPA) and ethoxypropyl acetate (EPA).

BP Chemicals now claims to offer the widest range of propylene glycol ethers and esters in Europe. These products are less hazardous than their ethylene glycol analogues and can be used as alternative solvents.

Propylene glycol ethers can be used as solvents for surface coating resins and printing inks, coalescing aids in emulsion paints, grease dissolvers in hard surface cleaners and metal degreasing agents. They cover a wide range of evaporation rates. For example, methoxypropanol (evaporation rate 70, n-butyl acetate 100) is useful in some paint and ink applications where a fast evaporating solvent is needed, whereas methoxypropoxypropanol (evaporation rate 3) can be used as a solvent in stamp pad ink, ball-point pen ink and textile dye applications. Ethoxypropanol falls in the middle of this range (evaporation rate 40) and can be

used as a straight substitute for ethyl glycol ether. In this role it has found applications in marine and automobile refinishing paints, as a retarder in printing ink formulations and as the major solvent in screen printing inks.

Methoxypropyl acetate and ethoxypropyl acetate are of use where good solvents of low volatility are required. Their physical properties closely match those of the corresponding ethylene glycol ether acetates. As such, according to BP, they are likely to become an essential component of many future surface coating formulations, particularly those based on polyurethanes.

Reader Enquiry Service No. 44



The Sheen Positector 3000 version for non-ferrous metals

Pocket size thickness meter

Sheen Instruments Ltd has added the Positector digital gauge to its range of thickness measurement instruments. There are two versions available, the Positector 2000 for measuring non-magnetic coatings such as paint, plating or galvanising, on steel; and the Positector 3000 for measuring anodic or organic coatings on aluminium or copper, without the need to calibrate. Both versions weigh only 90 grams and measure 114 mm × 54 mm × 25 mm. The Positector has a range of 0-1500 microns and an accuracy of ±3 per cent in any position.

Both versions have a ruby tipped probe and utilise a newly patented, self-balancing magnetic principle (an eddy current simulation in the case of the Positector 3000) which is unaffected by shock, ageing or exposure to other magnetic fields.

Reader Enquiry Service No. 45

literature

The work of the Paintmakers Association

The Paintmakers Association of Great Britain has produced an informative leaflet entitled: "The Paintmakers Association – Serving a Vital Industry". The leaflet provides a brief description of

the modern UK paint industry together with a concise account of the role of the PA, its membership structure and activities. A summary of its recent achievements is also included.

Copies of the leaflet are available from Michael Leveté, Paintmakers Association, Alembic House, 93 Albert Embankment, London, SE1 7TY; Tel: 01 582 1185 (work) or 01 638 9058 (home).
Reader Enquiry Service No. 46

people

Silver Paint & Lacquer Company has announced the appointment of **Barry Burwell** as technical development manager.

He was previously chief chemist with

the Trade and Retail Decorative Paint Division of Donald Mepherston & Co. Ltd, for whom he worked for the past 26 years. Mr Burwell is currently a member of the Manchester Section of OCCA.



Vinyl Products Ltd has appointed **Dr Tudor E. Thomas** as technical director from 1 August 1983, with responsibility for manufacturing, research and development.



Following the purchase by the Ault & Wiborg Group plc of Sherwood Parsons Ltd, manufacturers of vehicle finishes, the board of directors were pleased to announce the appointment of **Dr Graham Collingham** as managing director of the new subsidiary.

news



The paint industry lost one of its best-known characters on 30 June with the retirement, after 49 years service with Goodlass Wall & Co. Ltd, of national sales manager **Mr A. P. Kerr**.



Brian Carter has been appointed general manager of Ransburg UK Ltd. He joined the company in May 1983 as company secretary.

exhibition news



- **OCCA-35 Exhibition**
- **1-3 May 1984**
- **Cunard International Hotel**

Free standing space

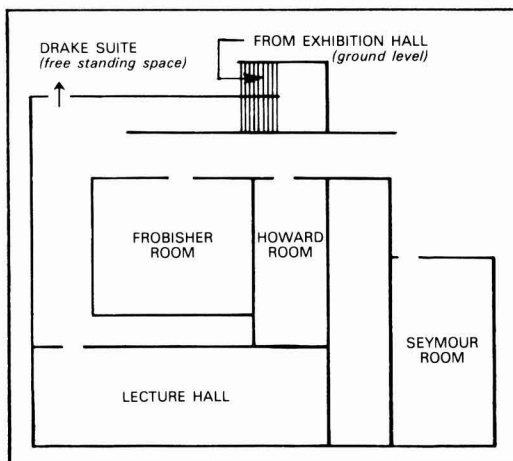
A new feature at OCCA-35 will be the opportunity for exhibitors to use free standing space in the Drake Suite. The areas are 3 m and 4.5 m deep and exhibitors can state the length required. Like the other suites on the mezzanine floor, the Drake Suite is carpeted and is close to the lecture hall. The charge for free standing space is £50 m² so that, for example, an exhibitor whose requirements are for an area 3 m x 3 m would be charged only £450 and he would enjoy the same privileges as other exhibitors in respect of all items such as free editorial entry in the April 1984 Preview issue of *JOCCA* (circulated to 80 countries with an average estimated readership of over 22,000 per issue); the special advertising rates applicable to exhibitors in that issue, badges, direction sign etc., but no stand would be provided.

The innovation introduced at OCCA-34 of a series of lectures by exhibitors on commercial and technical themes of their own choosing received considerable support from exhibitors and visitors alike. This is *not* an attempt to organise a conference on a specific topic but is an extension of exhibition facilities which enables exhibitors to highlight various aspects of their products or activities to an audience for further discussion and demonstration on their stands.

It is stressed that the number of rooms on the mezzanine floor and the amount of space available in the Drake Suite for free standing displays is **limited** and will be allocated on receipt of applications.

Space has already been reserved for OCCA-35 and organisations wishing to participate in this prestigious event should send in their applications without delay.

Invitations to Exhibit together with a "question and answer" feature and application forms were despatched in mid-July but any organisation wishing to have further copies or copies of the ABC's Exhibition Data Form should contact the Director & Secretary of the Association at Priory House, 967 Harrow Road, Wembley, Middlesex HA0 2SF, England (telex 922670, telephone (01) 908 1086).



Mezzanine floor

Diagrammatic representation only to show the relative position of the suites on the mezzanine, the lecture hall, and the new facility for free standing space (only) in the Drake Suite

Manchester Section

Northern Sections Golf Tournament

Thursday 9 June 1983 was the date for another successful event in the OCCA golf calendar. A record number of 36 entrants played golf dictated by the Single Stableford scoring system. Personal ability on an excellent Pannal Golf Course was accompanied by fine weather.

The hat trick was complete when the winning team was once again from the Manchester Section. It consisted of Brian Carroll, Brian Lamb, John Roberts, Alan Booth, Jack Godson and, last but not least, Ron Ashton. Highest scores were attributable to Brian Carroll as an OCCA member, 34 points, and David Armstrong as a visitor, also with 34 points.

In addition to the allocation of the Tony McWilliam Trophy and six individual plaques, prizes were received by all present. A special reward was given to Brian Lamb for his ability to strike his tee shot only four yards from the 141-yard tenth hole. The prize-giving ceremony followed the evening meal and for the record it is planned to hold the 1984 event at Pannal on 31 May, although this date is provisional.

F. B. Windsor



The captain of the victorious Manchester Section, Brian Carroll, receives his prize from Norman Seymour, Section Treasurer

OCCA International

In the report of the July Council meeting, which appeared in the August issue, it was recorded that Council had accepted the report of the OCCA International Working Group which had met at the York Conference, on the implementation of this scheme. For the initial three years the secretariat of OCCA International

will be provided by OCCA Australia and the office of International Coordinator for OCCA International will be filled by Mr Tom Backous, a former President of the Australian Federal Committee.

Jordan Award

The Jordan Award Committee now invites applications for the eighth award of £100. The rules of the Award are:

1. The Award will be made for the best contribution to the science or technology of surface coatings by a member of the Association of any nationality working in either the academic or industrial fields who is under the age of 35 at the date of application.

2. The final date for submission of applications will on this occasion be 31 December 1984 and it is hoped to present the award at the Association's Conference in the following year.

3. The selection of the recipient of the Award will be made by the Jordan Award Committee under the chairmanship of the Association's Hon. Research and Development Officer.

4. There will be two methods of application. First, by the submission of a paper describing original work by the candidate which is offered for publication in the *Journal* or has been so published during application. The alternative method will be by recommendation by a superior for work which for reasons of commercial secrecy cannot be published; in this case the candidate will be expected to submit a dissertation on a topic relating to his work and demonstrating his superior knowledge of the principles thereof. The Award is for individual merit and clear evidence of the candidate's own contribution will be required if a paper is offered under joint authorship.

5. Applications should be addressed to the Director & Secretary at the Association's offices.

Natal Section

Titanium dioxide in alkyd media

Mr Robin Archer of SA Tioxide (Pty.) Ltd, in a lecture entitled "Titanium dioxide in alkyd media", reviewed the parameters affecting the efficient utilisation of titanium dioxide pigments in alkyd gloss paints. The lecture was supported by a short film and slides which highlighted optimum mill base formulations using the Daniel Flow Point technique. Examples of fineness of grind and flocculation gradients in ideal conditions were shown and compared to commercially available alkyd gloss paints in the UK and RSA. Whereas the UK products had an average FOG of 10 microns and a flocculation gradient of

0.41 the average figures for seven commercially available products in SA gave readings of 16 microns and 0.76 respectively. Indications are that insufficient attention is being paid to optimum dispersion levels and ideal stabilisation of mill bases in SA paint factories resulting in products with a high degree of flocculation.

These statements and the supporting evidence Robin Archer produced evoked a lively question time and a vote of thanks was given by Mr Ron Gough, who also thanked SA Tioxide for sponsoring the evening.

R. Philbrick

Obituary

Rupert Marcus Walter William Wilson

Marc Wilson, who died suddenly at his home in Harlow on 9 July 1983 at the age of 72 years, was widely known to OCCA members in the UK and overseas.

An OCCA member for many years, he served on the London Section Committee from 1968 to 1971, and represented the Association on the East Ham Technical College Consultative Committee for the Science Department for a number of years.

A graduate of Imperial College, he joined Jenson & Nicholson as a pigment chemist in 1934. He became works manager during the war when the factory became known as W. Symonds Ltd, and served on the board of that company until it went out of business. In 1960 he joined Burrell & Co, serving in various capacities until his retirement in 1977. He was very interested in technical education and lectured for a number of years immediately after the war at the then Borough Polytechnic and at East Ham Technical College.

Following retirement, he continued his contact with the pigment industry as a consultant which involved travelling in the UK and on the continent, his fluency in French, Spanish and Italian being a great asset.

A man for all seasons, he played rugby for several years for Upper Clapton and until quite late in life played for Roydon Cricket Club, and was their President when he died. A story teller of renown, one of his claims to fame was that he opened the bowling for Imperial College with "Bill" Penny. With a view to spending some time afloat, he took a course in offshore navigation at the age of 70.

Marc leaves a widow and family, to whom his very many friends extend their deepest sympathy.

P. H. Joel

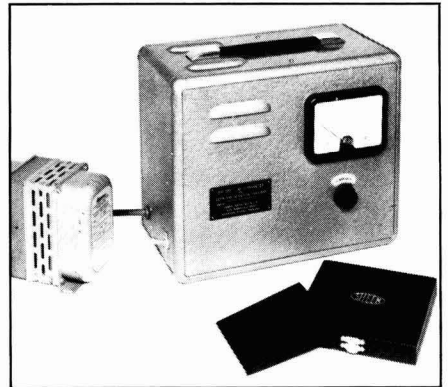


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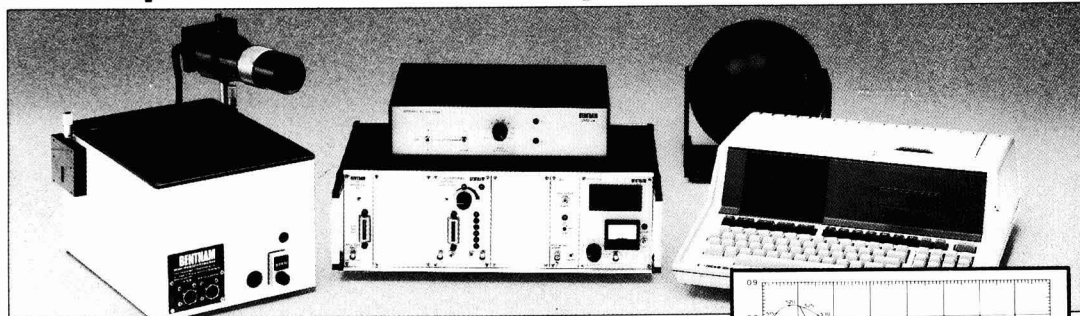
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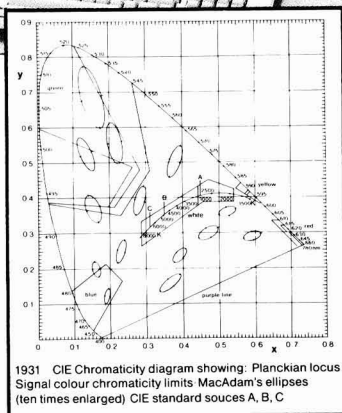
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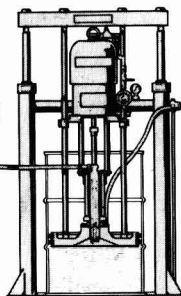
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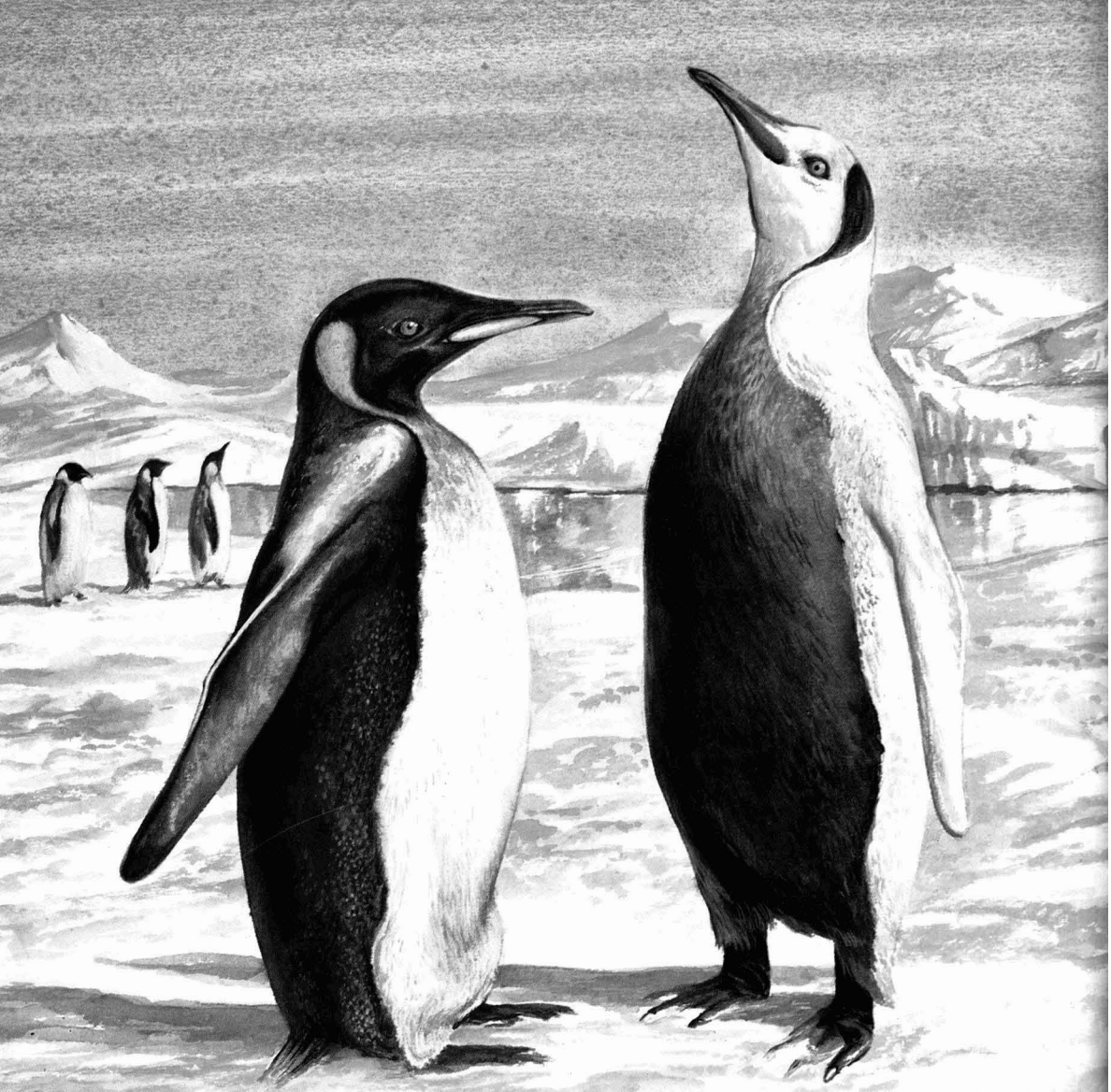


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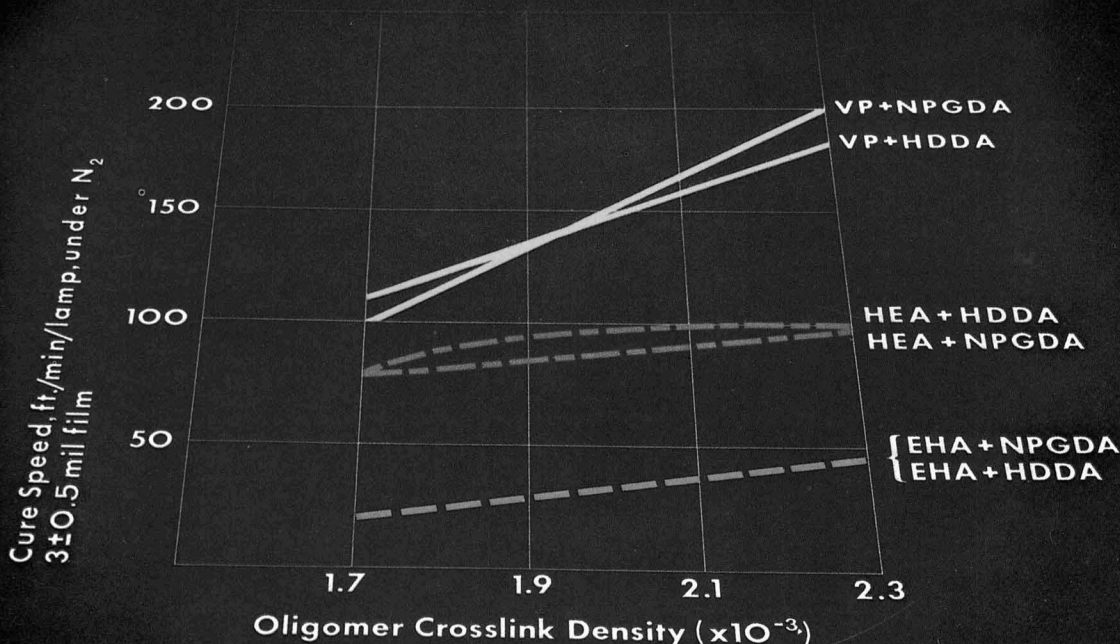
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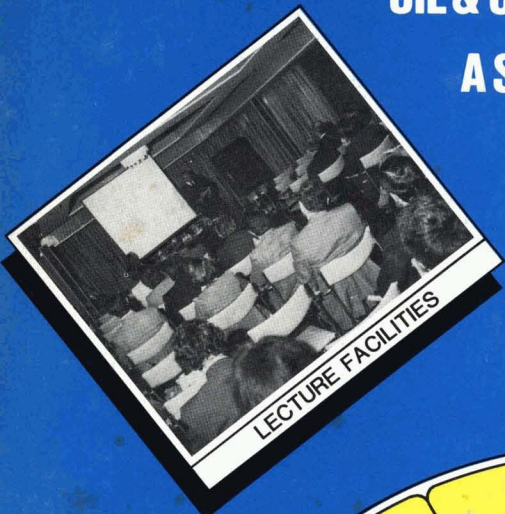
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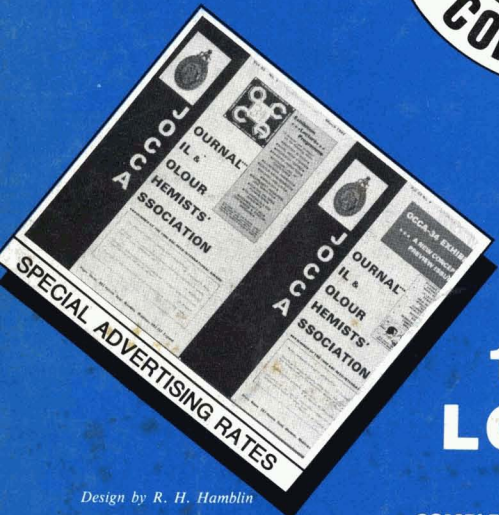
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