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Goethe's contribution to colour physiology

*J. D. Frazee*

The structure of Prussian blue and analogues *M. F. Dix and A. D. Rae*

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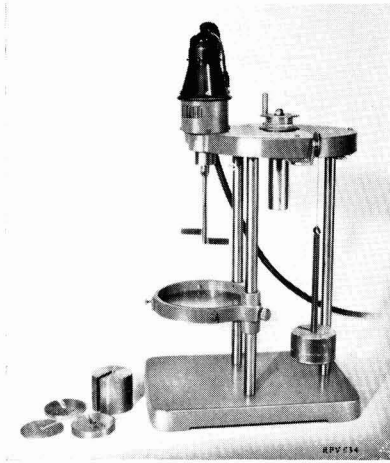
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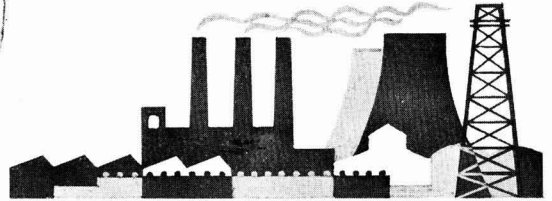
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Contents

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*Transactions and Communications*

<b>Goethe's contribution to colour physiology</b> . . . . .	63
<i>J. D. Frazee</i>	
<b>The structure of prussian blue and analogues</b> . . . . .	69
<i>M. F. Dix and A. D. Rae</i>	
<b>Permeability of epoxy coal tar films</b> . . . . .	75
<i>H. Corti, G. Baro, R. Fernandez-Prini and A. G. J. Maroto</i>	
<b>The ultraviolet screening behaviour of pigments</b> . . . . .	79
<i>P. Marvuglio, R. F. Sharrock and R. J. Kennedy</i>	
<b>Review</b> . . . . .	86
<b>Section Proceedings</b> . . . . .	86
<b>Information Received</b> . . . . .	89
<b>Notes and News</b> . . . . .	90
<b>Forthcoming Events</b> . . . . .	93
<b>Register of Members</b> . . . . .	94

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# Goethe's contribution to colour physiology

By J. D. Frazee

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## Summary

Johann von Goethe made significant contributions to the science of physiological and psychological colour theory. Unfortunately,

his observations are buried in scientific works that are remarkable for their lack of objectivity.

## Keywords

*Properties, characteristics and conditions primarily associated with:*

*materials in general*  
colour

*Miscellaneous terms*  
physiological optics

## La contribution de Goethe à la physiologie de couleur

### Résumé

Johann von Goethe faisait des contributions importantes à la science de la théorie de couleur et physiologique et psychologique.

Malheureusement, ses observations sont enfermées dans les oeuvres scientifiques dont le manque d'objectivité est remarquable.

## Goethes Beiträge zur Physiologie der Farbe

### Zusammenfassung

Johann Wolfgang von Goethe trug in bemerkenswerter Weise zu dem Wissen über die physiologische und psychologische Farbtheorie bei. Unglücklicherweise sind seine Beobachtungen unter

wissenschaftlichen Arbeiten, die für ihren Mangel an Objektivität bemerkenswert sind, begraben.

## Introduction

*Refs. 1-4.*

In 1810, Johann Wolfgang von Goethe published his *Theory of colours (Farbenlehre)*<sup>1</sup>. Goethe (1749-1832), author of *Werther*, *Wilhelm Meister*, and *Faust*, was Germany's greatest literary figure and a man of massive intellect<sup>2</sup>. However, his *Theory of colours* was not well received. The book represented the efforts of twenty years of study, thought, and experimentation, but the scientists of Europe were not impressed: "Everywhere I found incredulity as to my competence in such a matter; everywhere was a sort of repulsion at my efforts; and the more learned and well informed the men were, the more decided was their opposition"<sup>3</sup>.

This is not to say that Goethe was impressed by the views of his contemporaries: "As for what I have done as a poet, I take no pride in it whatever. Excellent poets have lived at the same time with myself; more excellent ones have lived before me, and will come after me. But that in my century I am the only person who knows the truth in the difficult science of colours - of that, I say, I am not a little proud"<sup>3</sup>.

It is not difficult to understand why Goethe's treatise was not well received by the scientific community. In the first place, Goethe did not follow the analytical approach to science brought into service by such specialists as Lavoisier, Cavendish, and Boyle and accepted by such fellow universalists as Franklin and Rumford. It was Goethe's outdated view that the unaided eye should be the final arbiter of truth. He shunned the use of telescopes and other impediments. (A complex personality, Goethe was, nonetheless, an exact and tireless experimenter.)

Goethe's second great folly was his personal and unreasoned attack on Newton (1642-1727). This, alone, was deemed sufficient cause to ignore Goethe's work. The battle over Newton's science had been waged and won a century before, but Germany was late coming into the cold, unromantic world of modern science. A considerable portion of *Farbenlehre* is given over to refuting Newton's *Optics*. Goethe's scientific friends could only marvel in disbelief that a poet should reopen the battle against the enshrined Newton.

The theoretical conclusions that Goethe placed on his experiments further prejudiced his readers. Goethe's view of nature was that of the classical Greek school founded by Socrates and Plato and epitomised by Aristotle and his pupils. This view, which actually goes back to Babylonian times, held that at the base of existence there lies *primal forms* from which specialised forms appear. Goethe called them *Ur* phenomena. For example, the changing variety of plants that one encounters in coming down a mountain side is due to the adaptation of primal plant forms to their environment, rather than the preferential growth of established forms. Such adaptation is possible, according to this view, because nature is in a state of continual flux<sup>4</sup>. Primal matter organised itself into *contraries*: heat and cold, moisture and dryness, positive and negative, revulsion and love, good and evil (and, of course, Goethe and Newton!).

In his own time, Goethe's romantic approach to science, his attempt to overthrow Newton, and the superposition of theory over experiment, blurred his contributions to the physiology of colour and deprived him of the credit he deserved. Recent writers, mindful of his earlier unpopularity, tend to shy away from this flawed genius.

In this paper, the many errors in Goethe's *Theory of colours* have been set aside just as the alchemy of Newton, Boyle, and Priestley have long been forgiven. The interpretation of the prism experiment is discussed, but the main object of this paper is to establish, by quoted illustrations, that Goethe deserves consideration as one of the founders of the science of colour physiology. Furthermore, it is noted that Goethe's published works helped create the great German group of colour physiologists including Schopenhauer, Pukinje, Müller, Helmholtz, and Ostwald.

### Newton's hated spectre

Refs. 2, 5

After having conquered the world of German literature, Goethe turned his mind to science. In 1790, at the age of forty-one, Goethe undertook the study of colour. A Professor Büttner at the University of Jena had lent Goethe some optical equipment. After allowing the optics to lie untouched for several months, he examined one of the glass prisms in a hurried circumstance. He recalled that at one of the physics lectures he had attended at the University of Leipzig a beam of white light had been broken into the colours of the rainbow. Goethe now held the prism up to his eyes and looked at the white wall of his room. Rather than seeing the expected rainbow of colours, only a few edge colours appeared. Goethe was astounded – was the great Newton's theory of light in error?

Goethe consulted with a physicist, Herr Geheimrat, who pointed out that Newton's refraction experiments involved a narrow slit of sunlight and a careful arrangement of the prism in a darkened room<sup>5</sup>. This did not convince Goethe. He obtained a copy of Newton's *Optics*, not for the purpose of trying to reproduce Newton's prism experiments, but rather to see why Newton had been in error. Goethe was offended that the prism experiments must be done in a darkened room. This was a subterfuge on Nature. Likewise, he could not approve of the way the light had to be forced through a small aperture in order to make it cough up its secrets. He noted, ingeniously, that one only had to make the aperture large, "and the beloved spectrum cannot and will not appear"<sup>2</sup>.

Goethe naively thought that he had made a fundamental discovery. He compared himself to Columbus. He decided that all his future efforts would be directed at proving Newton's *Optics* to be in error. Goethe's best colour work, which has nothing to do with Newton and his prism, is only a part of his polemic against Newton.

In his writings, he elected to give Newton's spectrum the earlier and more general name of "spectre" or phantom.

### Contributions to optics

Within a year after undertaking the study of colour, Goethe published his first paper, "Contributions to optics" (*Beiträge Zur Optik*). The title alone was enough to alienate the scientific community. Optics had always been thought of as a part of mathematics. Goethe not only had little formal training in this esoteric field, but was openly critical of reducing natural phenomena to the abstract relations of mathematics. "Its whole certainty is nothing but identity. Twice two is not four but simply twice two, which we call four for short. But four is no new thing"<sup>5</sup>. Goethe would have fit in quite comfortably with the linguistic analysts of today, but his attitude was

hardly appreciated in the world of Laplace, Euler and Lagrange.



Fig. 1. Johann Wolfgang von Goethe, one of the founders of physiological and psychological colour science, at age 42 (after an engraving by Johann Lips). The large, brown eyes that characterise Goethe portraits fit well with his strong visual sense<sup>2,3</sup>



Fig. 2. A woodcut by Goethe showing a rainbow and an eye, superimposed on the sun, triumphing over the prism and mirror<sup>2,3</sup>

For the most part, "Contributions to optics" was simply ignored. Goethe decided, with some justification, that this was because he was not a "priest of the guild". His feelings toward Newton became more bitter. Preparing for a long battle, he undertook a study of the entire history of colour. He obtained the writings of Aristotle, Alhazen, Leonardo, Descartes, Muret, and Boyle. He eventually wrote an excellent history of colour theory. He had glass water prisms made so that he could study refraction phenomena outdoors in his garden. Later, he had a darkroom built in his garden so that he could attempt to prove Newton wrong by refuting his experiments. He became a tireless experimenter and his visual acuity in observing nature became legendary. In 1792 he drew up the six-numbered colour circle (red, orange, yellow, green, blue, and purple) that is still in use today for describing subtractive colour relations. He made an extensive study of how artists can best use colours to produce particular effects. His study of colour even found expression in his literature, particularly *Faust*. He wrote an entire novel (*Chemical affinities*) utilising chemical principles as the shaping force of the action.

## Twenty years of study

*Refs. 3, 5-9*

Shortly after publishing his first paper on "Contributions to optics", Goethe added a second part to this essay. The public remained unconvinced, and Goethe felt his efforts were being "shunted aside with little thanks and hollow dogmatic phrases". One scientist did give Goethe his blessing and, as a result, became his lifelong friend. The anatomist, Samuel Sömmering, congratulated Goethe on his experiments in physiological optics, an aspect of colour that Goethe had examined only occasionally. With this encouragement, Goethe pushed on. "I can almost no longer see the place from where I started. I experiment ceaselessly." He remained convinced that Newton's theory would, in due course, "vanish into thin air . . . as it is only maintained by tricks"<sup>3,5,6</sup>. Nonetheless, Goethe's attention turned more and more to those areas of colour science that are now classified as the physiology and psychology of colour, and are fully accepted as co-equal parts of the several branches of colour science. (His time was not fully spent on colour. Rather, it balanced twenty years of remarkable activity which included the completion of his best literary efforts.) Goethe's eye for colour contrast and colour harmony became his main interest. He spent time in Italy attempting to understand the colour renderings of the artists in that sunny land. He had colour cards constructed with the intention of educating the whole populace on his colour theory. Eventually, he thought he had found his primal *Ur* phenomena in the form of a soap solution which showed one colour in transmitted light and a contrasting colour in reflected light (in the same manner as shown by skimmed milk)<sup>7,8</sup>. He accumulated one of the most outstanding laboratories of light instruments in all of Europe. Friends and literary worshippers presented him with all manner of equipment. Some of these, including the telescope and polarising crystals, he shunned, feeling that they impeded the human eye by complicating the problems of colour theory. Goethe's brilliance allowed much contradiction. His ego was monumental. His dedication to his various projects was staggering.

In 1810, fearing the loss of his papers to advancing armies or an untimely death, Goethe sent to press his unfinished *magnum opus*. He continued to publicise his theories of colour the rest of his life. In fact, he fell victim to the same malady that pursued Newton and other legendary figures: His dying words were "More light!" Soon this translated into a motto of his life quest. In point of fact, he was merely asking his servant to open the window curtains<sup>9</sup>.

## Outline of *Zur Farbenlehre*

*Refs. 1-10*

The *Zur Farbenlehre* is generally translated as *Theory of colours*. It is a massive work, consisting of three main parts: didactic, polemical, and historical. Only the first portion is readily available in English translation<sup>1</sup>. The polemic is a bitter refutation of Newton's colour theory. The historical part has been widely praised for its scholarship.

The didactic part is divided into three main sections: physiological colours, physical colours, and chemical colours. Physical colours derive from light sources: the sun, a candle, etc. Chemical colours are those obtained by pigments, dyes, etc. The treatment of the three sources of colour is followed by sections dealing with such diverse topics as human colour associations and colour harmony.

The scheme of the book is similar to that so skillfully employed by Newton in his *Optics*<sup>10</sup>. Goethe's explanation of prismatic colours makes no sense at all. More generally, Goethe made no contribution to the physical aspects of colour because, having made a useful separation of colours into the physiological, the physical, and the chemical, he was unable to tie the parts together in a logical fashion. His lack of scientific training let him down; mere observation did not suffice to produce a theory.

## Physiological colours

*Refs. 1, 9, 11-4*

Prior to Goethe's time, after images and contrast phenomena were variously thought to be ocular illusions, visual deceptions, or reactions of the fatigued or malfunctioning eye.

Goethe declared that they belong to the eye itself, in a healthy state. "We consider them as the necessary conditions of vision". The alternating quality of these effects with reference to the eye and objects under view tell us a great deal about the nature of human vision. Even those colour phenomena, such as red-green colour blindness, "indicate . . . the existence of organic and physical laws . . . and afford a more complete insight into the nature of the physiological colours".

In today's terminology, Goethe was dealing with what is defined as "colour perception", which includes contrast phenomena. Simultaneous contrast occurs when two colours are placed side by side. Their difference appears exaggerated with the result that the eye is capable of fine discrimination between similar colours. Successive colour contrast occurs when the eye views two different colours in succession. Both effects enhance the contrast between colours of different hue, causing each to move toward the complementary colour<sup>11</sup>.

After images are due to fatigue in the visual system. The more common negative after images occur when the eye gazes at a colour and then views a neutral area. The complementary or negative after image is produced. Positive after images are more fleeting and are most commonly seen when one looks up at an incandescent light while in the process of turning the switch. The positive after image may appear entoptically for five to ten seconds<sup>12</sup>.

Contrast phenomena and after images relate to many visual effects, including coloured shadows, colour harmony, and irradiation phenomena. With this brief review we turn to Goethe's descriptions of perception phenomena in the *Farbenlehre*.

Under the heading of "Physiological colours", Goethe first discusses the eye's adaptation to changes in lighting conditions:

"If we pass from a totally dark place to one illuminated by the sun, we are dazzled. In coming from a lesser degree of darkness to light that is not dazzling, we perceive all objects clearer and better: hence eyes that have been in a state of repose are in all cases better able to perceive moderately distinct appearances".

Next, the phenomena of irradiation is considered:

"A dark object appears smaller than a bright one of the same size. Let a white disk be placed on a black ground, and a black disk on a white ground, both being exactly similar in size; let them be seen together at some

distance, and we shall pronounce the last to be about a fifth part smaller than the other. If the black circle be made larger by so much, they will appear equal"<sup>1</sup>.

Irradiation is defined by Luckiesh as "an apparent increase in size of visual stimulus of relatively high intensity". It is thought to be due to the spreading of excitation to adjacent retinal elements<sup>12</sup>.

Goethe then describes positive after images (and a safe method of observing them—looking at the sun is the poor way):

"If in the morning, on waking, when the eye is very susceptible, we look intently at the bars of a window relieved against the dawning sky, and then shut our eyes or look towards a totally dark place, we shall see a dark cross on a light ground before us for some time. The duration of these visionary impressions varies with the powers or structure of the eye in different individuals, just as the time necessary for the recovery of the tone of the retina varies in passing from brightness to darkness: it can be measured by minutes and seconds, indeed much more exactly than it could formerly have been by causing a lighted linstock to revolve rapidly, so as to appear a circle".

The same conditions can be used to produce an achromatic, negative, after image:

"If, while the image of the window-bars before mentioned lasts, we look upon a light grey surface, the cross will then appear light and the panes dark. In the first case the image was like the original picture, so that the visionary impression also could continue unchanged; but in the present instance our attention is excited by a contrary effect being produced. Various examples have been given by observers of nature".

Goethe's explanation of these effects is quite satisfactory:

"These appearances have been explained as follows: That portion of the retina on which the dark cross was impressed is to be considered in a state of repose and susceptibility. On this portion therefore the moderately light surface acted in a more lively manner than on the rest of the retina, which had just been impressed with the light through the panes, and which, having thus been excited by a much stronger brightness, could only view the grey surface as a dark".

It is explicit in Goethe's argument that after images and contrast phenomena are physiologically interrelated. This is, of course, quite true. Unfortunately, Goethe was not, as we shall see, always so succinct as in the case of after images.

But when Goethe deals with what is now called simultaneous contrast, he is still on firm ground. His first example involves achromatic colours:

"A grey object on a black ground appears much brighter than the same object on a white ground. If both comparisons are seen together the spectator can hardly persuade himself that the two greys are identical. We believe this again to be proof of the great excitability of the retina, and of the silent resistance which every vital principle is forced to exhibit when any definite or immutable state is presented to it. Thus inspiration already presupposes expiration; thus every systole its diastole. It is the universal formula of life which manifests itself in this as in all other cases. When darkness is presented to

the eye it demands brightness, and *vice versa*: it shows its vital energy, its fitness to receive the impression of the object, precisely by spontaneously tending to an opposite state".

Later, he gives a clear explanation of simultaneous contrast involving chromatic colours:

"We have hitherto seen the opposite colours producing each other successively on the retina: it now remains to show by experiment that the same effects can exist simultaneously. If a coloured object impinges on one part of the retina, the remaining portion at the same moment has a tendency to produce the compensatory colour. To pursue a former experiment, if we look on a yellow piece of paper placed on a white surface, the remaining part of the organ has already a tendency to produce a purple hue on the colourless surface: in this case the small portion of yellow is not powerful enough to produce this appearance distinctly, but if a white paper is placed on a yellow wall, we shall see the white tinged with a purple hue. Although this experiment may be made with any colours, yet red and green are particularly recommended for it, because these colours seem powerfully to evoke each other".

Next, dazzling objects are considered. ("If we look at a dazzling, altogether colourless object, it makes a strong lasting impression, and its after-vision is accompanied by an appearance of colour"):

"I happened to be in a forge towards evening at the moment when a glowing mass of iron was placed on the anvil; I had fixed my eyes steadfastly on it, and, turning round, I looked accidentally into an open coal-shed; a large red image now floated before my eyes, and, as I turned them from the dark opening to the light boards of which the shed was constructed, the image appeared half green, half red, according as it had a lighter or darker ground behind it. I did not at that time take notice of the subsequent changes of this appearance."

Halo phenomena have been recently studied by a number of researchers including R. Meyer and N. Minnaert<sup>13,14</sup>. There are numerous types of halos, including those associated with lights in a fog, sun and moon halos, and ground halos on fresh snow;

"A light must shine moderately, not dazzle, in order to produce the impression of a halo in the eye; at all events the halos of dazzling lights cannot be observed. We see a splendour of this kind round the image of the sun reflected from the surface of water.

"Halos appear most vivid when the eye is susceptible from having been in a state of repose. A dark background also heightens their appearance. Both causes account for our seeing them so strong if a light is presented to the eyes on waking at night. These conditions were combined when Descartes after sleeping, as he sat in a ship, remarked about such a vividly-coloured halo round the light".

It is natural that Goethe, a great poet with a keen visual sense, should leave us with several quotable observations. The following one on successive contrast is frequently noted:

"I had entered an inn towards evening, and, as a well-favoured girl, with a brilliantly fair complexion, black hair, and a scarlet bodice, came into the room, I looked attentively at her as she stood before me at some distance

in half shadow. As she presently afterwards turned away, I saw on the white wall, which was now before me, a black face surrounded with a bright light, while the dress of the perfectly distinct figure appeared of a beautiful sea-green".

The most important contribution that Goethe made to laying the foundation of modern physiological optics was in his insistence that contrast phenomena was due to opposing forces in the healthy eye:

"Let a small piece of bright-coloured paper or silk stuff be held before a moderately lighted white surface; let the observer look steadfastly on the small coloured object, and let it be taken away after a time while his eyes remain unmoved; the spectrum of another colour will then be visible on the white plane. The coloured paper may be also left in its place while the eye is directed to another part of the white plane; the same spectrum will be visible there too, for it arises from an image which now belongs to the eye.

"As the opposite colour is produced by a constant law in experiments with coloured objects on portions of the retina, so the same effect takes place when the whole retina is impressed with a single colour. We may convince ourselves of this by means of coloured glasses. If we look long through a blue pane of glass, everything will afterwards appear as if in sunshine to the naked eye, even if the sky is grey and the scene colourless.

"We have, hitherto, seen the opposite colours producing each other successively on the retina; it now remains to show by experiment that the same effects can exist simultaneously. If a coloured object impinges on one part of the retina, the remaining portion at the same moment has a tendency to produce the compensatory colour".

A final example of Goethe's work on physiological colours should suffice to establish his line of inquiry. This example, one commonly cited for its prose beauty, involves coloured shadows. As Judd has noted, "Goethe knew all about chromatic contrast"<sup>1</sup>. Although the terminology is missing, Goethe explained as early as 1792 the phenomena of coloured shadows. The effect had long been misinterpreted<sup>9</sup>.

"In travelling over the Harz in winter, I happened to descend from the Brocken towards evening; the wide slopes extending above and below me, the heath, every isolated tree and projecting rock, and all masses of both, were covered with snow or hoar-frost. The sun was sinking towards the Oder ponds. During the day, owing to the yellowish hue of the snow, shadows tending to violet had already been observable; these might now be pronounced to be decidedly blue, as the illumined parts exhibited a yellow deepening to orange.

"But, as the sun at last was about to set, and its rays, greatly mitigated by the thicker vapours, began to diffuse a most beautiful red colour over the whole scene around me, the shadow colour changed to a green, in lightness to be compared to a sea-green, in beauty to the green of the emerald. The appearance became more and more vivid: one might have imagined oneself in a fairy world, for every object had clothed itself in the two vivid and so beautifully harmonising colours, till at last, as the sun went down, the magnificent spectacle was lost in a grey twilight and by degrees in a clear moon-and-starlight night".

## Goethe's colour theory and Newton's prismatic colours

*Refs. 7, 8, 11, 13, 15-22*

Interesting, but less important, is Goethe's *theory* of colour vision. Goethe, who might be called the last Greek, took the classical view that colours result from the intermingling of light and darkness<sup>18</sup>.

Aristotle (or his student, Theophrastus) says, "If light is overspread with much obscurity a red colour appears . . . where the light is deficient, the air is affected by the darkness and appears blue"<sup>17</sup>.

Likewise, Goethe was much affected by that original genius Leonardo da Vinci, "Blue and green are not simple colours in their nature, for blue is composed of light and darkness; such is the azure of the sky, *viz.*, perfect black and perfect white."

To supplant Newton's physical colours, Goethe evolved "the theory of opaques". An example of this theory might be the following: the sun near noon viewed through the atmosphere is a dazzling white; as it approaches the horizon it tends toward yellow; near sunset brilliant reds appear, particularly if obscuring clouds are near the line of vision; finally, the clouds turn blue and darken as the sun dips below the horizon.

Next, consider what happens when light passes through a glass prism. The appearance of the various colours on the adjacent walls had been observed and commented on since antiquity. The classical explanation, the one used by Robert Hooke in 1672 to answer Newton at the outset, was that the spectral colours were not revealed by refraction, but rather created by interaction with the prism<sup>15</sup>.

Goethe derived his position on the spectral colours from his theory of opaques. When it is considered that Goethe had twenty years to develop his attack on the long-departed Newton, his explanation of prismatic colours seems particularly weak. Since Goethe's argument is convoluted by his desire to minimise the importance of the prism, the summary explanation given by Magnus is quoted here. When an image of the sun is projected through a prism on to a white wall, there are really "two images—a main image and a secondary image, just as a poorly made mirror reflects objects double, once from the posterior and once from the anterior surface of the glass, one image seeming to hover in shadowy fashion above the other . . . All these colour phenomena were explained by Goethe on the assumption that the secondary image is a semi-transparent medium through which the main image is seen"<sup>18</sup>.

In other words, the colours produced by the prism result from viewing white light through intervening medium of reflected light. In short, Goethe made no contribution to our understanding of prismatic colours.

Ironically, Newton's own "crucial experiment" did not, in fact, establish the nature of prismatic colours. Sabra has stated the case quite clearly: "Newton's fundamental theory must be understood in relation to the prevailing doctrine of refraction . . . it was the shape of the spectrum, not the colours in it, that formed the basis of his arguments . . . Newton argued that if colours were modifications of light due to the action of the reflecting or refracting bodies, then these bodies should produce the same effects whether the light falling on them has been already disturbed or not. But the

consequence was proved false by the *experimentum crucis*: the rays emerging from the first prism preserved their respective colours and degrees of refrangibility upon their refraction through the second prism. Therefore, Newton concluded, colours must be unalterable properties of the rays and, consequently, white light must be an aggregate of rays that already possess those properties.

"This conclusion, however, does not follow from the experiment. What the experiment does prove is that the light emerging from the first prism behaves differently from light coming directly from the sun. But it does not prove that the properties of the refracted light exist primarily and unaltered in white light. It might well be that those properties are manufactured out of white light by the first prism, but, once generated, they are not alterable by further refractions"<sup>8</sup>.

Newton achieved an internally consistent theory of prismatic colours by assuming that light consisted of particle waves. R. S. Westfall has emphasised that Newton's doctrine cannot be deduced, "without adding his belief in atomism as a necessary premise"<sup>17</sup>.

To Newton, atoms were the bedrock of reality (see *Optics*, Reference 9, Query 31). Newton's belief in atomism finds its correspondence in Goethe's *Ur* phenomena. Historically, Newton's doctrine of colours found eventual acceptance for a number of good reasons: the wave theory of light was only then being developed, while atomism was much in vogue. Newton's optical experiments were absolutely remarkable (particularly the work on the colours of thin films). The publication of his experiments and ideas in *Optics* was one of the greatest scientific presentations of all times—readable, convincing, and yet modest. Newton's reputation awed his friends and overwhelmed his critics<sup>19</sup>. Finally, Newton's atomistic approach to light fitted the available facts as well or better than any competing theory of the time<sup>11, 13</sup>. Scientific historians might find it useful to compare these circumstances to those that surrounded the publication of Goethe's *Farbenlehre*.

Before closing the record on Newton's theory of colours, it is worth pointing out that later findings have been superimposed on his own recorded observations in a way that often favourably distorts Newton's already considerable insights. For example, Newton never measured a wave length. Yet, we have authors saying such things as "modern research has confirmed the relationship between wave length and colour naming given in Newton's original experiments"<sup>20</sup>. This despite the fact that the term "primary colours" is entirely arbitrary in any event.

*Optics* concludes with a series of provocative questions; among them is the perceptive suggestion that light can behave like particles of matter<sup>21</sup>. This statement would be more meaningful if it stated that Newton suggested that light exhibited *wave-like* properties for we know that he was an atomist. Finally, consider the statement that "since Einstein's theory of photons of 1905, many writers have called attention to the similarity between Newton's views and those of the twentieth century."<sup>22</sup>

On the other hand, when the brilliant Thomas Young (1773-1829) proposed the wave theory of light, he was battered from all sides despite his openly acknowledged use of Newton's own precise measurements. Measurements which Young used to calculate wave lengths with high accuracy. A lesser scientist, such as Goethe, should not have expected a favourable reception from the "members of the guild".

## Conclusions

Ref. 23

Goethe deserves his share of credit as one of the founders of physiological and psychological colour science. It can be seen that by failing to follow the rules of the scientific society, Goethe's efforts were ignored. Authority somehow creeps into the halls of science as a necessary arbiter of what is accepted as correct. Still, Goethe was his own worst enemy. His attacks on Newton were intemperate and unsubstantial. The German genius would not have been satisfied with merely making a contribution to colour theory, but the contribution is there. As Deane B. Judd notes in his introduction to the *Theory of colours*, we now freely accept that there is more to colour vision than just wave length<sup>1</sup>.

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# The structure of Prussian blue and analogues

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## Summary

When M(II) is Mn, Co or Cu, preparations of cubic ferricyanide usually result in a single compound M(II) [M(II)Fe(III)(CN)<sub>6</sub>]<sub>2</sub> no matter what other cations are present. Compounds of the type KM(II)Fe(III)(CN)<sub>6</sub> can be made with difficulty and are characterised by a smaller axial length and different infrared and Mössbauer

absorption spectra. Contrary to other ferricyanides, Fe(II) [Fe(III)(CN)<sub>6</sub>]<sub>2</sub> is not formed, compounds of the type KFe(II)Fe(III)(CN)<sub>6</sub> being the preferred product. This anomalous behaviour has resulted in the incorrect formulation of Prussian blue by many authors.

## Keywords

Raw materials for coatings

prime pigments and dyes

Prussian blue  
iron blue pigment

Equipment primarily associated with

analysis, measurement or testing

colour

Processes and methods primarily associated with

analysis, measurement or testing

infrared spectroscopy  
X-ray spectroscopy

Properties, characteristics and conditions primarily associated with

materials in general

crystal structure  
electronic spectra

## La structure du bleu de Prusse

### Résumé

Quand M(II) est Mn, Co ou Cu, la préparation du ferricyanure cubique aboutit en général à un simple composé, M(II)[M(II)Fe(III)(CN)<sub>6</sub>]<sub>2</sub>, quel que soit les autres cations qui sont présents. On ne saurait préparer les composés du type KM(II)Fe(III)(CN)<sub>6</sub> qu'avec difficulté et ils se caractérisent par une longueur axiale réduite et aussi par les spectres d'absorption à l'infra rouge et

Mössbauer différents. Contrairement à d'autres ferricyanures, Fe(II)[Fe(III)(CN)<sub>6</sub>]<sub>2</sub> n'est pas produit, les composés du type KFe(II)Fe(III)(CN)<sub>6</sub> sont les produits favorisés. A cause de ce comportement exceptionnel, plusieurs auteurs ont accordé une formule fautive au bleu de Prusse.

## Die Struktur von Preussischblau und Analogen

### Zusammenfassung

Wenn M(II) aus Mn, Co oder Cu besteht, erhält man gewöhnlich Präparate von kubischem Ferrizyanid als eine einzige Verbindung M(II)[M(II)Fe(III)(CN)<sub>6</sub>]<sub>2</sub>, unabhängig von der Anwesenheit anderer Kationen. Verbindungen des Typs KM(II)Fe(III)(CN)<sub>6</sub> sind schwierig herzustellen und durch kleinere axiale Länge und

verschiedene infrarote und Mössbauer Absorptionsspektren charakterisiert. Im Gegensatz zu anderen Ferrizyaniden wird Fe(II)[Fe(III)(CN)<sub>6</sub>]<sub>2</sub> nicht gebildet, vorzugsweise dagegen Verbindungen des Typs KFe(II)Fe(III)(CN)<sub>6</sub>, Wegen dieses abnormen Verhaltens benutzten viele Autoren falsche Formeln für Preussischblau.

## Introduction

Refs. 1-10

Many statements have been made in the scientific literature concerning Prussian blue and its analogues, but perhaps the most significant is that of Keggin and Miles<sup>1</sup>: "The whole subject is surprisingly confused in spite of the large volume of work which has been published". More recently Wilde, Ghosh and Marshall<sup>2</sup> state "In spite of a large number of powerful physical methods such as x-ray analysis, visible-ultraviolet transmission and reflectance spectroscopy, magnetic susceptibility studies and Mössbauer spectroscopy having been brought to bear on the structural problem of Prussian blue, there is still uncertainty as to the actual constitution of Prussian blue and the large number of Prussian blue analogues". In fact, the literature is full of what perhaps is best described as attempts by authors to rid themselves of a somewhat intractable problem by publication.

The situation has not been helped by the erroneous addition to the list of Prussian blue analogues of a few compounds

which are definitely not cubic, e.g. Ag<sub>3</sub>Fe(CN)<sub>6</sub><sup>3,4</sup>, Tl<sub>3</sub>Fe(CN)<sub>6</sub><sup>3</sup> and even K<sub>3</sub>Fe(CN)<sub>6</sub><sup>4</sup> to name perhaps but a few.

Particle size investigation immediately reveals the cause of many of the problems encountered, *viz.* the meaninglessness of chemical analyses because of the effects of surface absorbed ions. The compounds are structurally ordered and the widths of the x-ray diffraction powder lines gives an average particle size by the Scherrer formula<sup>5</sup>

$$\beta = \lambda / (L \cos \theta_0)$$

Here  $\beta$ , measured in radians, is the integral breadth (integrated intensity/maximum intensity).  $\lambda$  is the x-ray wavelength,  $\theta_0$  is the Bragg angle and  $L$  is the average particle dimension.  $L$  is found to be about 150 Å for many preparations. A 5 Å adsorbed layer on a cubic particle of 150 Å edge constitutes 18 per cent of the total volume. Another important factor is the adsorption of water by the precipitates. The authors have found it impossible to distinguish between surface water and interstitial water, thermogrammetric

analysis giving regular dehydration to the point of decomposition. Water has not been included in the structural formulations used in this paper. The particle size is such that the precipitates have colloidal properties. The presence of excess highly charged negative ions such as  $\text{SO}_4^{2-}$  and  $\text{Fe}(\text{CN})_6^{3-}$  causes dispersion of the precipitate, whilst the presence of excess highly charged positive ions such as  $\text{Co}(\text{NH}_3)_6^{3+}$  causes flocculation. Such considerations have been used successfully in attempts to produce larger particles and thus obtain better x-ray diffraction data.

The confusion of the picture has been increased by the assertion by many authors, and summarised by Hansen, Litchman and Daub<sup>6</sup>, that Prussian blue has the formulation  $\text{KFe}(\text{III})\text{Fe}(\text{II})(\text{CN})_6$  despite the fact that electrode potentials indicate that  $\text{Fe}^{2+}$  and  $\text{Fe}(\text{CN})_6^{3-}$  are the stable species in aqueous solution. The acceptance of this formulation has probably come about from the Mössbauer study of Duncan and Wigly<sup>7</sup>, for which the presence of only two Mössbauer absorbers precludes formulations of  $\text{Fe}(\text{III})_4[\text{Fe}(\text{II})(\text{CN})_6]_3$  or  $\text{Fe}(\text{II})_2[\text{Fe}(\text{III})(\text{CN})_6]_2$  despite the fact that van Bever<sup>8</sup> and Weiser Milligan and Bates<sup>9</sup> expounded a model for the Prussian blue analogues incorporating a transition metal ion rather than a potassium ion in their structures to make up the charge balance. Keggin and Miles<sup>1</sup>, however, when postulating the basic  $\text{M}(\text{II})\text{Fe}(\text{III})(\text{CN})_6$  framework of the Prussian blue analogues, proposed that either an alkali metal ion or a transition metal ion could make up the charge.

The authors attempted to make and identify a range of Prussian blue analogues:  $\text{M}(\text{II})[\text{M}(\text{II})\text{Fe}(\text{III})(\text{CN})_6]_2$ ,  $\text{N}(\text{I})\text{M}(\text{II})\text{Fe}(\text{III})(\text{CN})_6$  and  $\text{N}(\text{II})[\text{M}(\text{II})\text{Fe}(\text{III})(\text{CN})_6]_2$  where  $\text{M}(\text{II}) = \text{Mn}, \text{Co}, \text{Ni}, \text{Cu}, \text{Cd}, \text{Zn}, \text{Pb}, \text{Hg}$ ;  $\text{N}(\text{I}) = \text{Li}, \text{Na}, \text{K}, \text{NH}_4, \text{H}_3\text{O}, \text{Cs}$ ; and  $\text{N}(\text{II}) = \text{Mg}, \text{Ca}, \text{Ba}$ .

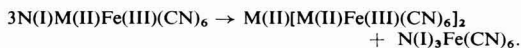
Axial length, x-ray intensity and infrared measurements have permitted the classification of the preparations into two discrete classes; those unsuccessful and those wholly or partly successful<sup>10</sup>. This latter class is quite small and the measurements enable it to be stated that Prussian blue is the same as Turnbull's blue and has the formula  $\text{KFe}(\text{II})\text{Fe}(\text{III})(\text{CN})_6$  in agreement with the result expected from electrode potentials of the aqueous ions.

## Preparative methods

Refs. 4, 8, 11-13, 29

A casual perusal of the literature would suggest that the ion incorporated into the cubic  $\text{M}(\text{II})\text{Fe}(\text{III})(\text{CN})_6^-$  lattice to neutralise the charge simply depends on which cation is present in excess. This is definitely not so. The initial attempts to prepare  $\text{KCo}(\text{II})\text{Fe}(\text{III})(\text{CN})_6$  gave an identifiable two component mixture, the proportions of which could be altered by the preparative method. Only then was it realised that for other preparations using a different  $\text{M}(\text{II})$  there was a tendency to make the same compound every time, the only difference being the surface adsorbed ions which can be a large percentage of the total precipitate.

It was found that  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  do not form Prussian blue analogues, in agreement with van Bever<sup>8</sup>. However, in disagreement it was found that Prussian blue analogue using  $\text{Zn}^{2+}$  could not be formed. For  $\text{Cd}^{2+}$ , a Prussian blue analogue, viz.  $\text{Cd}(\text{II})[\text{Cd}(\text{II})\text{Fe}(\text{III})(\text{CN})_6]_2$ , was formed only when  $\text{Cd}^{2+}$  was in excess. An explanation of the frequent failure of attempts to prepare compounds of the types  $\text{N}(\text{I})\text{M}(\text{II})\text{Fe}(\text{III})(\text{CN})_6$  and  $\text{N}(\text{II})[\text{M}(\text{II})\text{Fe}(\text{III})(\text{CN})_6]_2$  is the possibility of reactions of the type.



The most success with this range of compounds was obtained by keeping the reactant solution saturated with respect to the highly soluble salts,  $\text{N}(\text{I})_3\text{Fe}(\text{CN})_6$  (or  $\text{N}(\text{II})_3[\text{Fe}(\text{CN})_6]_2$ ).

Contrary to the general pattern, whereby  $\text{M}(\text{II})[\text{M}(\text{II})\text{Fe}(\text{III})(\text{CN})_6]_2$  compounds are readily formed, no evidence could be produced for the formation of  $\text{Fe}(\text{II})\text{Fe}(\text{II})\text{Fe}(\text{III})(\text{CN})_6]_2$  in any preparation. Thus, purposely,  $\text{M}(\text{II}) = \text{Fe}$  is omitted from the discussions at this stage.

## Preparation of $\text{M}(\text{II})[\text{M}(\text{II})\text{Fe}(\text{III})(\text{CN})_6]_2$

A simple method of preparation is the dropwise addition of dilute  $\text{K}_3\text{Fe}(\text{CN})_6$  to a strong solution of excess  $\text{M}(\text{II})\text{Cl}_2$ . Particle sizes of 200-250Å were generally obtained in this manner. Larger particles, 400-660Å could be obtained by following a method, analogous to an attempt to produce  $\text{Mg}[\text{M}(\text{II})\text{Fe}(\text{III})(\text{CN})_6]_2$  (see Figure 1).

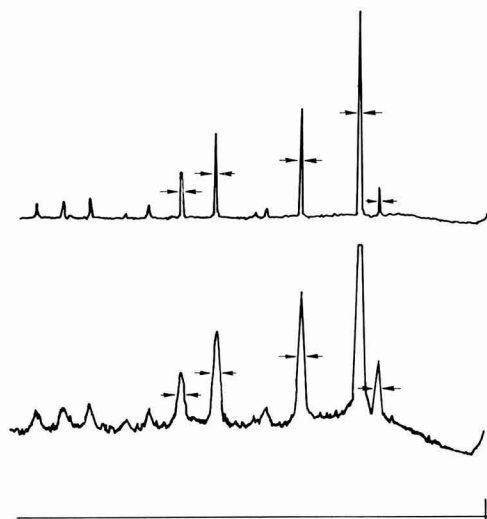


Fig. 1. Powder x-ray diffraction traces of  $\text{Ni}[\text{NiFe}(\text{CN})_6]_2$  using different preparative methods. The narrower lines correspond to the larger particle size

$\text{Co}(\text{NH}_3)_6\text{Fe}(\text{CN})_6$  is usually rather insoluble<sup>11</sup> but solutions of this compound can be made using heated (60-70°) saturated  $\text{MgCl}_2$  solution as solvent. A solution of dilute  $\text{M}(\text{II})\text{Cl}_2$  in saturated  $\text{MgCl}_2$  solution is dropwise added. Neither  $\text{Co}(\text{NH}_3)_6^{3+}$ , nor  $\text{Mg}^{2+}$  is incorporated in the structure, but the presence of excess highly positive ions aids particle growth by neutralising the surface charge of the precipitate. As might be expected, a preparation by mixing  $\text{NiCO}_3$  and  $\text{H}_3\text{Fe}(\text{CN})_6$  resulted<sup>12</sup> in very small particles 100-150Å.

## Preparation of $\text{KM}(\text{II})\text{Fe}(\text{III})(\text{CN})_6$

A dilute solution of  $\text{M}(\text{II})\text{Cl}_2$  in saturated  $\text{KCl}$  is added dropwise to saturated  $\text{K}_3\text{Fe}(\text{CN})_6$  solution. Even with a  $\text{K}:\text{M}(\text{II})$  ratio of 100:1, pure  $\text{KM}(\text{II})\text{Fe}(\text{III})(\text{CN})_6$  could not be made except for  $\text{M} = \text{Co}$ . Particle sizes of about 150Å are obtained by this method, the excess  $\text{Fe}(\text{CN})_6^{3-}$  preventing large particle growth.



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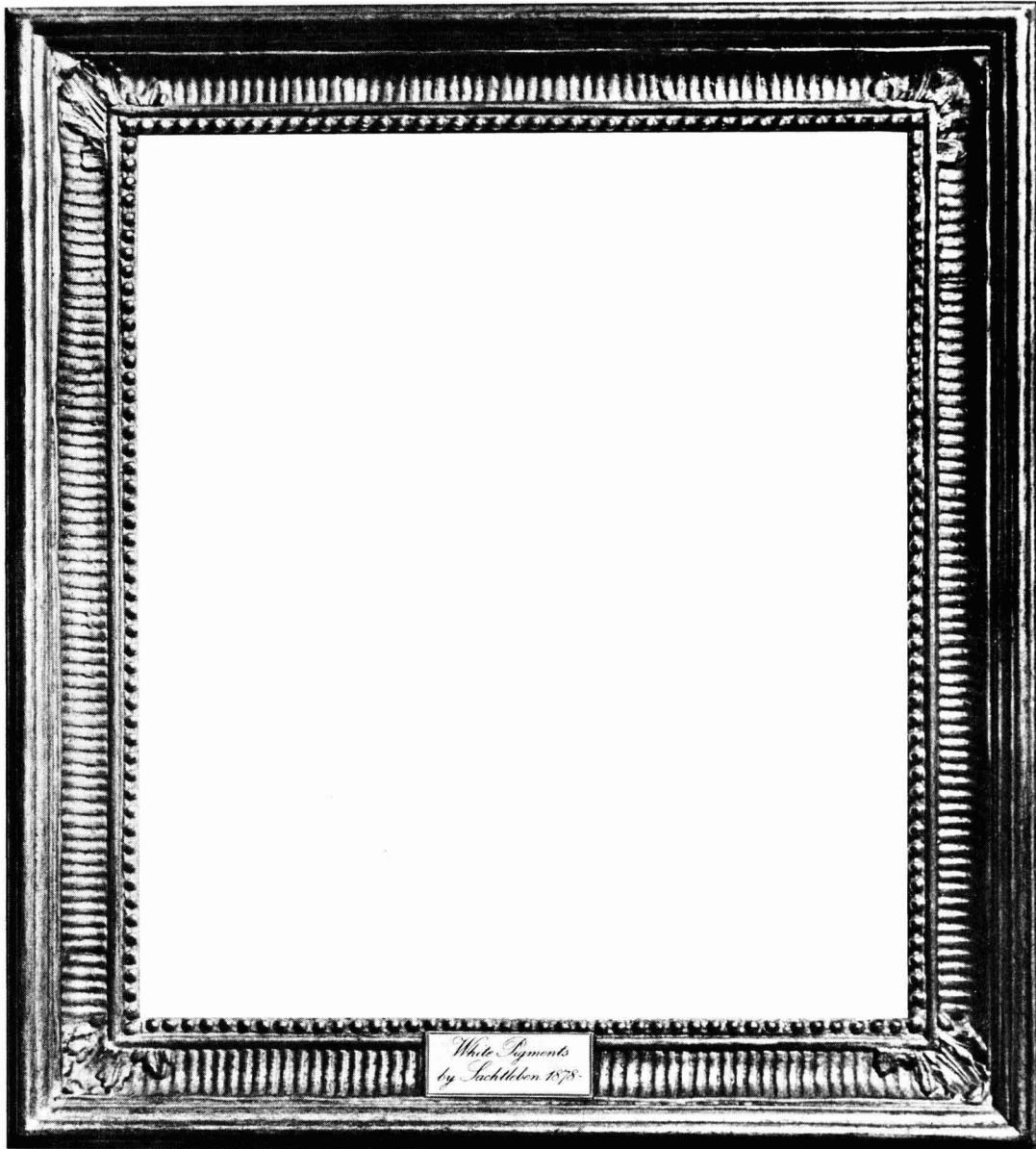
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### Attempts at preparations of $N(I)M(II)Fe(III)(CN)_6$ and $N(II)[M(II)Fe(III)(CN)_6]_2$ .

$NH_4CoFe(CN)_6$  was prepared by the dropwise addition of  $CoCl_2$  in strong  $NH_4Cl$  solution to  $Co(NH_3)_6Fe(CN)_6$  in strong  $NH_4Cl$  solution. No success was obtained when trying to make other compounds in this group by this method. Modifications of the previous method, using different soluble salts of  $Fe(CN)_6^{3-}$  were also attempted with varying success. Preparations of these soluble salts by the addition of the relevant carbonate to  $H_3Fe(CN)_6$  gave<sup>12</sup> a certain amount of decomposition product which had to be filtered out of the solution. A simpler preparation is by the action of a solution of the relevant chloride on  $Ag_3Fe(CN)_6$ , giving  $AgCl$  and the soluble salt in solution<sup>4</sup>. It is difficult to make this reaction proceed sufficiently to be useful. Possibly this is because the  $Ag_3Fe(CN)_6$  was prepared from  $Co(NH_3)_6Fe(CN)_6$  and  $AgNO_3$  rather<sup>13</sup> than from  $K_3Fe(CN)_6$  and  $AgNO_3$  in order<sup>4</sup> to keep  $K^+$  ions from the preparations. Infrared analysis of the preparation in the CN stretching region indicates a single CN stretch at  $2160cm^{-1}$ , whereas a preparation using  $AgNO_3$  in excess with  $K_3Fe(CN)_6$  yields two equally strong absorptions at  $2100cm^{-1}$  and  $2170cm^{-1}$ . A preparation using strong  $KNO_3$  solution as solvent for a dilute  $AgNO_3$  solution gave a product exhibiting four strong absorptions at 2100, 2120, 2140,  $2160cm^{-1}$ . In all cases these absorption bands are much sharper than for cubic ferricyanides and the frequencies quoted are completely resolved and quoted to  $\pm 5cm^{-1}$ . Chemical analyses<sup>13</sup> justify the assumption that  $Ag_3Fe(CN)_6$  is not the product of the reaction using  $K_3Fe(CN)_6$ .

A paper by Prout, Russell and Groh<sup>29</sup> on ion exchange absorption of Cs on to the Prussian blue analogue made from  $Co^{2+}$  and  $Fe(CN)_6^{4-}$  suggests that  $Rb^+$  and  $Cs^+$  should be readily incorporated into the cubic lattice and displace both  $Co^{2+}$  and  $K^+$  irreversibly from interstitial sites in the  $CoFe(CN)_6^{2-}$  lattice. It would appear from their paper that there is again competition between  $K^+$  and  $Co^{2+}$  for these sites.

Preparations of  $CsM(II)Fe(III)(CN)_6$  were made by adding  $K_3Fe(CN)_6$  dropwise to a solution of  $M(II)Cl_2$  with a two fold excess of  $CsCl$ . These conditions would not produce  $KM(II)Fe(III)(CN)_6$ . Pure  $CsCo(II)Fe(III)(CN)_6$  is prepared by this method as shown by both the infrared spectrum and

x-ray diffraction but mixtures of  $CsM(II)Fe(CN)_6$  and  $M(II)[M(II)Fe(CN)_6]_2$  are formed for  $M(II) = Cu, Ni, Mn$ .

Particles sizes were  $\sim 100\text{\AA}$  for these preparations.

### Identification and classification of compounds

Refs. 1, 14-21

X-ray diffraction data was collected on a Phillips automatic powder diffractometer fitted with a Geiger counter tube and a chart recorder. A high intensity Co x-ray tube was used giving  $CoK_{\alpha} = 1.7900\text{\AA}$ . Infrared spectra over the range  $250-4000cm^{-1}$  were recorded on a Perkin Elmer 521 recording spectrometer using capillary films of mulls between KBr and CsBr plates. Instrument calibration is accurate to  $1cm^{-1}$ . The bands examined were all broad, half widths varying between  $20cm^{-1}$  and  $80cm^{-1}$ . The Mössbauer spectrometer used was built to a design described by Ruegg and Spjörkerman<sup>14</sup>. The source used was  $10mc\ Co^{57}$  in Pd foil. Measurements were obtained at liquid nitrogen temperature ( $77K$ ) and room temperature. Calibration of the instrument was with a standard soft iron foil using the positions of the six line spectrum and with sodium nitro-prusside for which  $\Delta E_Q = 1.726mms^{-1}$ . Isomer shifts were measured with respect to the midpoint of the sodium nitroprusside spectrum<sup>15</sup>.

Axial lengths of the various cubic ferricyanides are given in Table 1. The salient feature of these measurements is that the axial lengths of  $KM(II)Fe(III)(CN)_6$  compounds are appreciably smaller than the axial lengths of the  $M(II)[M(II)Fe(III)(CN)_6]_2$  compounds, even though the latter compounds are preferably formed;  $M(II)$  is a smaller ion than  $K$  and there are fewer  $M(II)$  ions required. The observation of Keggin and Miles<sup>1</sup> that the blues having no alkali metal present have an unusually high water content can be interpreted by suggesting that the interstitial  $M(II)$  is hydrated and this hydration causes the lattice expansion of 2-4 per cent. This difference in axial length is readily determined, see Figure 2.

The infrared spectra are discussed in detail elsewhere<sup>16</sup>. Band assignment can be made by comparison to  $K_3Fe(CN)_6$ . Using the notation recommended by Mulliken<sup>17</sup> and adapted

Table 1  
Axial lengths ( $\text{\AA}$ ) of cubic ferricyanides

(i) Compounds of type $M(II)[M(II)Fe(III)(CN)_6]_2$							
M(II)	Mn	Co	Ni	Cu	Cd		
Axial length ( $\sigma$ )	10.51(2) $\text{\AA}$	10.29(2)	10.25(2)	10.20(2)	10.63(3)		
(ii) Compounds of type $N(I)M(II)Fe(III)(CN)_6$ and $N(II)[M(II)Fe(III)(CN)_6]_2$							
M(II)	Co	Co	Co	Co	Co	Mn	Mn
N(I)	K	Cs	$NH_4$	$H_3O$	—	K	Cs
N(II)	—	—	—	—	Ba	—	—
Axial length	9.94(4)	10.03(8)	9.95(4)	10.02(4)	10.02(4)	10.11(8)	10.57(10)
M(II)	Ni	Ni	Cu	Cu	Fe	Fe	Fe
N(I)	K	Cs	K	Cs	Li	K	Cs
N(II)	—	—	—	—	—	—	—
Axial length	10.06(8)	10.20(10)	10.10(8)	10.10(10)	10.18(4)	10.18(4)	10.21(1)
M(II)	Fe	Fe	Fe				
N(I)	$H_3O$	—	—				
N(II)	—	Mg	Ba				
Axial length	10.1(1)	10.2(1)	10.2(1)				

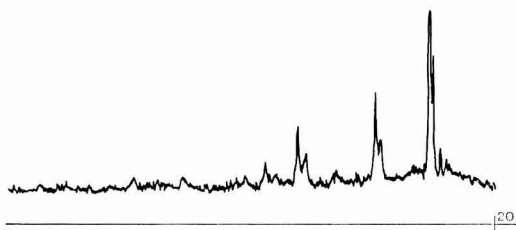


Fig. 2. A powder diffractometer trace of a preparative mixture of  $\text{Co}[\text{CoFe}(\text{CN})_6]_2$  and  $\text{KCoFe}(\text{CN})_6$ . The K compound has the shorter axial length and appears to be the major component

by James and Nolan<sup>18</sup> infrared active  $T_{1u}$  modes are assigned  $\nu_6$  CN stretch,  $\nu_7$  FeC stretch, and  $\nu_8$  FeCN bend. The higher frequency band in the  $500\text{cm}^{-1}$  region was assigned to metal ligand stretch at variance with Jones<sup>19</sup>, but in agreement with Nakagawa and Shimanouchi<sup>20</sup>. Results are given in Table 2.

Table 2

Frequencies ( $\text{cm}^{-1}$ ) of spectral features of  $M(\text{II})[\text{M}(\text{II})\text{Fe}(\text{III})(\text{CN})_6]_2$

M(II)	$\nu_6$ CN stretch*	$\nu_7$ FeC stretch	$\nu_8$ FeCN bend
Mn	2146 2068	527	425,413
Co	2146 2091	527	425
Ni	2161 2091	530	427
Cu	2166 2091	539	439
Cd	2135 2070	525	410
$\text{K}_3\text{Fe}(\text{CN})_6$	2113	510	390

\*The higher frequency CN mode is the more strongly absorbing by a factor of about 3.

Frequencies of spectral features of  $N(\text{I})\text{M}(\text{II})\text{Fe}(\text{III})(\text{CN})_6$  and  $N(\text{II})[\text{M}(\text{II})\text{Fe}(\text{III})(\text{CN})_6]_2$

N(I)	N(III)	M(II)	$\nu_6$	$\nu_7$	$\nu_8$
K	—	Co	2116	587	537
Cs	—	Co	2108	584	534
$\text{NH}_4$	—	Co	2108	586	530
$\text{H}_3\text{O}$	—	Co	2125	578	532
—	Ba	Co	2085	586	535
K	—	Mn	2065	—	590
Cs	—	Mn	2077	—	586
K	—	Ni	2095	—	584
Cs	—	Ni	2093	—	587
K	—	Cu	2097	—	581
Cs	—	Cu	2092	—	585
Li	—	Fe	2080	600	501
K	—	Fe	2073	591	489
Cs	—	Fe	2070	595	492
$\text{H}_3\text{O}$	—	Fe	2076	597	500
—	Mg	Fe	2078	594	492
—	Ba	Fe	2076	596	495

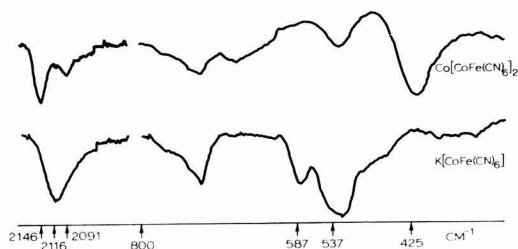


Fig. 3. The infrared spectra of  $\text{Co}[\text{CoFe}(\text{CN})_6]_2$  and  $\text{KCoFe}(\text{CN})_6$  showing the regions of the  $\nu_6$ ,  $\nu_7$  and  $\nu_8$  frequencies

The spectra of pure  $\text{KCoFe}(\text{CN})_6$  and pure  $\text{Co}[\text{CoFe}(\text{CN})_6]_2$  are shown in Figure 3 and the spectra of various mixtures of  $\text{KNiFe}(\text{CN})_6$  and  $\text{Ni}[\text{NiFe}(\text{CN})_6]_2$  are shown in Figure 4.

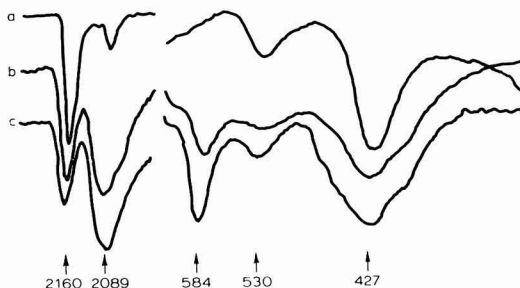


Fig. 4. The infrared spectra of (a) pure  $\text{Ni}[\text{NiFe}(\text{CN})_6]_2$  and (b) and (c) mixtures of  $\text{Ni}[\text{NiFe}(\text{CN})_6]_2$  and  $\text{KNiFe}(\text{CN})_6$ . Pure  $\text{KNiFe}(\text{CN})_6$  could not be made. The regions of the  $\nu_6$ ,  $\nu_7$  and  $\nu_8$  frequencies are shown

The evidence for the non-manufacture of other compounds is by comparison of x-ray powder photographs using both intensities and axial lengths, and by comparison of infrared spectra. It should be noted that all the preparations used  $\text{Cl}^-$  ions rather than  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , etc. This simplifies the infrared spectra. Preparation using sulfate ions do show effects of the surface activity of these ions in the infrared spectra.

Mössbauer Spectral results are given in Table 3.

Table 3

Mössbauer Spectral results in  $\text{mm s}^{-1}$  ( $\pm 0.05\text{mm s}^{-1}$ )

Compound	$\Delta E_q$ at 295K	$\delta$	$\Delta E_q$ at 77K	$\delta$
$\text{Mn}(\text{MnFe}(\text{CN})_6)_2$	0.24	0.11	0.70	0.18
$\text{Co}(\text{CoFe}(\text{CN})_6)_2$	0.36	0.12	0.90	0.15
$\text{Ni}(\text{NiFe}(\text{CN})_6)_2$	0.41	0.16	0.72	0.22
$\text{Cu}(\text{CuFe}(\text{CN})_6)_2$	0.55	0.19	0.82	0.12
$\text{Cd}(\text{CdFe}(\text{CN})_6)_2$	0.39	0.19	0.84	0.23
$\text{KCoFe}(\text{CN})_6$	0	0.14	0	0.21
$\text{NH}_4\text{CoFe}(\text{CN})_6$	0	0.18	0	0.30
* $\text{KFeFe}(\text{CN})_6$	0	0.16(0.77)	0	0.27(0.93)
* $\text{LiFeFe}(\text{CN})_6$	0	0.20(0.90)	0	0.27(1.03)
* $\text{H}_3\text{OFeFe}(\text{CN})_6$	0	0.15(0.91)	0	0.26(1.04)
* $\text{Mg}(\text{FeFe}(\text{CN})_6)_2$			0	0.20(1.07)

\*A broad peak showing no apparent quadrupole splitting gives a shoulder on the  $\text{KFeFe}(\text{CN})_6$  spectra, but a resolved peak for the other starred compounds.

Values of  $\delta$  for this extra Fe atom are given in brackets.

These results roughly agree with those of Hryniewicz, Sawicka and Wawicki<sup>21</sup> for the  $\text{M}(\text{II})[\text{M}(\text{II})\text{Fe}(\text{III})(\text{CN})_6]_2$  complexes. The quadrupole splitting gives almost completely resolved peaks of the single Mössbauer absorber at 77K. There is no quadrupole splitting for  $\text{KCoFe}(\text{CN})_6$  and  $\text{NH}_4\text{CoFe}(\text{CN})_6$ , nor for the Prussian Blue.

## Discussion

Refs. 2, 7, 16, 22–28

A detailed interpretation of the infrared spectra is published in another paper<sup>16</sup> and a discussion of structural models is expounded along with x-ray structural analyses in a further paper<sup>22</sup>.

The splitting of the  $\nu_6$  frequency for  $M(II)[M(II)Fe(III)(CN)_6]_2$  complexes can only be interpreted by having two chemically distinct CN groups in these structures<sup>16</sup>.

The expansion of the  $M(II)Fe(III)(CN)_6$  lattice for the  $M(II)[M(II)Fe(III)(CN)_6]_2$  compounds reduces the size of the modification to the  $K_3Fe(CN)_6$  vibration frequencies compared with the  $N(II)M(II)Fe(III)(CN)_6$  compounds.

Prussian blue fits into the pattern for its formula to be  $KFe(II)Fe(III)(CN)_6$ .

The single CN vibration frequency is in no way anomalous despite assertions to the contrary<sup>26,23,24,27,28</sup>. The lack of quadrupole splitting in the Mössbauer supports this formulation. The isomer shifts of the two absorbers only indicates that there is a high spin and low spin ion present and that there is not a third type of Fe in the spectrum. Duncan and Wigley's<sup>7</sup> interpretation is dependent on the insistence that Fe atoms in certain electron configurations must show a quadrupole splitting, even though an environment of exact cubic symmetry precludes this. Thus, an ill-defined shoulder in the  $KFeFe(CN)_6$  spectrum is interpreted as a quadrupole split  $Fe^{3+}$  ion, instead of a broad unsplit band of an  $Fe^{2+}$  ion, and for the freshly prepared  $Fe(II)/Fe^{2+}$  compound, one half of a supposedly quadrupole split  $Fe^{2+}$  is conveniently hidden under an unsplit band for  $Fe(II)$ . The authors consider that the quadrupole splitting of the  $M(II)[M(II)Fe(III)(CN)_6]_2$  compounds is associated with the idea that there are two chemically distinct CN groups in these compounds, whilst only one CN group in compounds of the type  $KM(II)Fe(III)(CN)_6$  as shown<sup>16, 22</sup> in the observed CN stretching frequencies. The absence of detectable splitting of either the high spin  $Fe(II)$  or low spin  $Fe(III)$  for  $N(II)[FeFe(CN)_6]_2$ ,  $N(II) = Mg, Ba$  implies the point charge distribution of these  $N(II)$  ions does not greatly effect the Fe atom environments. The  $N(II)$  ions cannot be distributed to maintain a purely cubic symmetry of the Fe sites.

The only remaining arguments for the formulation of  $KFe(III)Fe(II)(CN)_6$  is the paper by Robin<sup>25</sup> on the electronic spectrum of Prussian blue and magnetic susceptibility measurements<sup>25</sup>. These latter measurements depend on chemical analysis, including identification of impurities and, since Prussian blue particles are less than 100 Å in dimension, such measurements are of dubious merit. Robin's paper is highly empirical, interpreting the spectrum by shifting an electron from a low spin  $Fe(II)$  in a C hole to a high spin  $Fe(III)$  in a N hole. He is motivated by the apparently corroborative evidence mentioned above. There thus seems small reason to disagree with the result predicted from electrode potentials.

The infrared vibration  $\nu_8$  varies more in value than  $\nu_7$  and this supports the proposition that  $\nu_7$  is the metal ligand vibration frequency<sup>16</sup>. The ionic radii of  $K^+$ ,  $NH_4^+$ ,  $H_3O^+$  and  $Ba^{2+}$  are all very similar ( $\sim 1.3 \text{ \AA}$ ) and this seems to be the lower limit of ionic radii for which alkali metals and alkali earths can compete with  $M(II)$  species other than  $Fe(II)$  for incorporation into the lattice. The ability to prepare  $KM(II)Fe(III)(CN)_6$  would appear to be correlated to the  $\nu_8$  ( $FeCN$  bending) frequency. Prussian blue ( $\nu_8 = 489 \text{ cm}^{-1}$ ) is easily made. For  $M = Co$  ( $\nu_8 = 537 \text{ cm}^{-1}$ ) the compound can be made pure with difficulty, whilst for  $M = Ni$  ( $\nu_8 = 584 \text{ cm}^{-1}$ ),  $M = Cu$  ( $\nu_8 = 581 \text{ cm}^{-1}$ ) and  $M = Mn$  ( $\nu_8 = 590 \text{ cm}^{-1}$ ), pure compounds cannot be made. Only one strongly absorbing band (see figure 4) was found in the  $500 \text{ cm}^{-1}$  region for each of these final compounds. Investigation shows that  $Fe(II)[Fe(III)(CN)_6]_2$  is very difficult to make and all attempts have failed.

The uncertainty in both spectral frequencies and axial lengths makes it difficult to distinguish effects associated with the choice of  $N(I)$  and  $N(II)$  species apart from the observations that Cs complexes have longer axial lengths than K complexes and the Mössbauer spectrum of the high spin  $Fe(II)$  in Prussian blue may be resolved by appropriate choice of  $N(I)$  and  $N(II)$  species.

To the paint and ink technologist colour is an important feature of these compounds, but like so many important properties it is difficult to discuss quantitatively starting from the atomic structure. Robin<sup>30</sup> has given a theoretical basis for the colour of Prussian blue and his reasoning may be extended to the analogues discussed in this paper. The transition responsible for the blue colour in  $KFe(III)Fe(II)(CN)_6$  occurs at  $14700 \text{ cm}^{-1}$  and is an electronic transition from an  $Fe(III)$  atom to an adjacent  $Fe(II)$  atom. Since the authors' crystal structure studies show that both of these atoms are in an octahedral environment, the valence electron levels will be split in the same manner for each oxidation state and the transition will be between  $t_{2g}$  levels. This transition is quite common in compounds having both  $Fe(II)$  and  $Fe(III)$  ions present. For example, the compounds formed between  $[Fe(II)(CN)_5X]^{2-}$  ions and  $Fe(III)$  ions where  $X$  is  $H_2O$ ,  $NH_3$ ,  $AsO_2^-$ ,  $SO_3^{2-}$ ,  $NH_2NH_2$  or  $CO$  are all deep blue and exhibit electronic spectra similar to that of Prussian blue.

It is possible to extend this qualitative approach to include other types of compounds, but results must be treated with caution. Certainly, the fact that the compound  $Fe(II)_2Fe(III)(CN)_6$ , a reduced form of Prussian blue, is colourless, is entirely consistent with the above explanation, but that the oxidised form  $Fe(III)Fe(III)(CN)_6$  is green instead of the expected orange-brown colour of the  $[Fe(III)(CN)_6]^{3-}$  ion, is unexpected. By consideration of the electric spectrum of  $Fe(III)Fe(III)(CN)_6$  the extraneous band at  $20,000 \text{ cm}^{-1}$  is clearly seen. However, it has been demonstrated that  $Fe(III)Fe(III)(CN)_6$  is very readily reduced by water to a Prussian blue-type compound which will give rise to the  $20,000 \text{ cm}^{-1}$  band corresponding to the characteristic  $Fe(III)$  to  $Fe(II)$  transition.

Further and more detailed discussions do not form part of this work, but will be the subject of subsequent publications.

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# Permeability of epoxy coal tar films

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## Summary

The permeabilities of NaCl and THO through unattached epoxy coal tar films have been determined, as well as the electrical resistances of some films. The heterogeneous nature of epoxy coal tar films, in particular with reference to the non-uniform cross-linking, influences the transport properties of the films. Two types of transport behaviour were found: regions that behave as

membranes bearing weak positive charges, and regions of D-type where transport occurs mainly through micropores flooded by electrolyte solution. These lower resistance areas may be the site of initial film deterioration in immersed structures protected by epoxy coal tar coatings.

## Keywords

*Types and classes of coatings and allied products*

coal tar epoxy coating

*Types and classes of structures or surfaces to be coated*

steel

*Raw materials for coatings binders (resins, etc.)*

coal tar epoxy resin

*Properties, characteristics and conditions primarily associated with*

*materials in general*

permeability

*dried or cured films*

permeability

## La perméabilité des films époxyde/goudron de houille

### Résumé

On a déterminé les perméabilités à NaCl et à THO des films détachés à base des résines époxydes et du goudron de houille, et d'ailleurs dans le cas de certains films, on a déterminé leur résistance électrique. Le caractère hétérogène des films époxyde/goudron de houille, surtout en ce qui concerne la présence des liaisons transversales désordonnées, exerce une influence sur leurs caractéristiques de transport. A l'égard du phénomène de transport on a trouvé deux

types de comportement: des zones qui se comportent comme membranes dont la charge est légèrement positive, et d'autres zones du type D, où le transport se produit largement par des micropores pleins de solution de l'électrolyte. Dans le cas des constructions immergées et protégées par les revêtements à base des résines époxydes et du goudron de houille, ces zones de résistance électrique plus faible peuvent être les sites de l'altération initiale du film.

## Durchlässigkeit von Epoxy-Kohlenteerfilmen

### Zusammenfassung

Die NaCl- und THO- Durchlässigkeit abgelöster Epoxykohlenteerfilme wurde bestimmt; ebenso bei manchen der Filme der elektrische Widerstand. Die heterogene Beschaffenheit von Epoxy-Kohlenteer-filmen insbesondere bezüglich ungleichmässiger Vernetzung beeinflusst die Transporteigenschaften der Filme. Es wurden zwei Typs des Transportverhaltens festgestellt: Stellen, die sich wie Membranen verhalten, welche schwache positive Ladung besitzen,

und Stellen vom D-Typ, wo der Transport hauptsächlich durch Mikroporen, die von Elektrolytlösungen gespült werden, stattfindet. Diese niedrigen Widerstand besitzenden Stellen könnten die Ausgangspunkte für den Beginn der Filmzerstörung auf unter Wasser stehenden, mit Epoxy-Kohlenteeranstrichen geschützten Konstruktionen sein.

## Introduction

*Refs. 1, 2*

Epoxy coal tar paint is currently employed as a topcoat to protect immersed steel structures. Its high mechanical strength and its reputed hydrophobicity, are important properties which guarantee a prolonged service-life under adverse conditions. The mechanism by which epoxy coal tar protects steel from corrosion is considered to depend on its high electrical resistance, thus acting as an effective ohmic barrier in decreasing the rate of corrosion of the metal.

In spite of its widespread use, the physico-chemical information on epoxy coal tar films is rather scanty. It has been shown recently<sup>1</sup>, that these films act as membranes having fixed charges. The films prove to be heterogeneous in regard to their electrochemical properties and their water

uptake capacity. It was shown that the deterioration of epoxy coal tar paint is strongly influenced by the existence of regions in the film having a lower electrical resistance; the curing temperature appeared to be an important factor in determining the membrane characteristics of the films. A property of the paint membranes directly related to its function as an ionic barrier is the permeability of ions and various small solutes through the paint film; measurements may be carried out employing a radioactive tracer ion or by measuring directly the flow of salt through the film. Recently Murray<sup>2</sup> has shown that the permeability of Cl<sup>-</sup> ion through unattached films is different from that of the coating on a substrate. This difference is, however, not large and valid conclusions regarding the magnitude of the permeability may be obtained from studies in free films. This contention is supported by the fact that electrical resistance measurements of unattached and applied epoxy coal tar films lead to the same general conclusions about the film behaviour<sup>1</sup>.

The permeability through polymeric films of various solutes is known to depend on structural and compositional factors, e.g. degree of cross-linking, presence of plasticisers, glass transition temperature, state of hydration, etc. The bearing of some of these factors on the observed permeability of H<sub>2</sub>O and NaCl through epoxy coal tar free film will be discussed.

**Experimental**

Refs. 1, 3

**Materials and film preparation**

A commercial two-component epoxy coal tar paint (S. A. Alba), has been used for the preparation of the free films studied in this work. The dry paint film contained 36 per cent coal tar, 42 per cent epoxy resin cured with an amine-epoxy adduct, and 22 per cent inorganic filler.

The films were applied to glass plates with a doctor blade and allowed to cure for two weeks at 20° C. They were then peeled off and left at the same temperature for periods of from two to six weeks before being used for the measurements. The films had a thickness that was in the range of 120 to 200µm.

**Electrical resistance measurements**

The cell employed and the method of measurement have been described elsewhere<sup>1</sup>.

**Permeability measurements**

The paint film membranes were held between the two compartments of acrylic cells; these compartments could be pressed against each other causing the paint membrane to act as a diaphragm separating the two halves of the cell. The cells were kept at 20 ± 1°C during the measurements.

The determination of the permeability coefficient of epoxy coal tar film requires a very sensitive technique for detecting the amount of solute which has passed through the paint membrane, due to the low permeability of epoxy coal tar films; otherwise, the experiment requires an inconveniently long time in order to estimate the amount of solute that has diffused.

The permeability of NaCl was determined by filling one of the cell compartments with 0.5 molar NaCl solution. The other compartment was filled with deionised water having a conductance less than 10<sup>-6</sup> S.cm<sup>-1</sup>. The amount of NaCl diffusing through the membrane was established by conductivity measurements on the compartment having originally no NaCl. The conductivity cell used consisted of two lightly platinised platinum electrodes closely spaced and introduced into the water compartment. The cell constant was about 0.1cm<sup>-1</sup>. In this way it was possible to detect when amounts less than 0.01 per cent of NaCl had diffused. A measurement of NaCl permeability coefficient took 7 to 15 days to be completed.

Tracer diffusion measurements were carried out filling both compartments of the cell with 0.09 molar NaCl. In order to have sufficient sensitivity, the <sup>22</sup>NaCl and the THO solutions had a large specific activity (corresponding to 10<sup>8</sup>-10<sup>7</sup> counts min<sup>-1</sup>). In this way it was possible to detect fractions smaller than 0.01 per cent which had diffused through the paint membrane.

Aliquots were withdrawn from the inactive compartment when required, the volume of this compartment being replenished with inactive NaCl solution. The aliquot was diluted if necessary and its activity measured with a solid scintillation crystal for <sup>22</sup>Na<sup>+</sup>, or a liquid scintillator for tritium. Figure 1 shows the fraction of THO passing through the paint membrane as a function of time. It is observed that after 20 days, less than 0.4 per cent of the original THO has passed through the paint film. The first part of the plot is curved because the membrane is reaching an equilibrium concentration of THO. The plot becomes linear for times larger than five days.

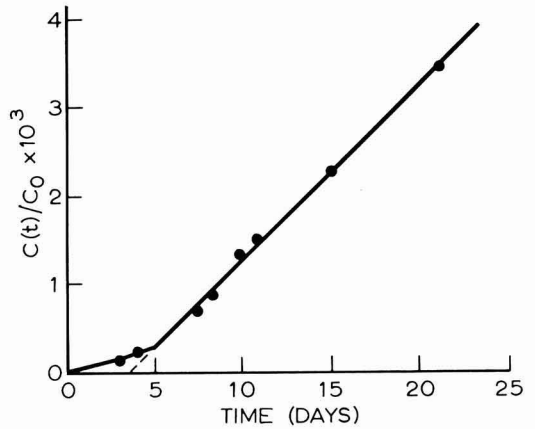


Fig. 1. Fraction of THO passing through an epoxy coal tar membrane against time

The permeability coefficient for the experimental conditions employed, may be calculated with the expression<sup>2</sup>:

$$P = \frac{V.l}{2A.t} \ln \frac{C}{C-2\Delta} \dots\dots\dots (1)$$

where *V* is the volume of the cell compartments, *A* and *l* the area and the thickness respectively of the film, *t* the time, *C* the concentration of active species and  $\Delta$  the concentration of radioisotope in the inactive compartment. When the fraction of solute that has permeated ( $\Delta/C$ ), is small, eqn. (1) becomes,

$$P = \frac{V.l.\Delta}{A.t.C} \dots\dots\dots (2)$$

so that the fraction which has diffused is linearly related to the time. This was always the case in the present work. In order to calculate the diffusion coefficients *D*, of the solutes inside the films, it would be necessary to know the distribution constant *Q*, of the solute between the paint film and the solution because,  $P=Q.D$ . In the present work the distribution constants have not been measured, hence the data are reported as permeability coefficients on the solutes.

All the membranes employed in this work were examined with a high voltage porosity detector. Only those membranes having no pores were used.

**Results**

The permeability coefficients of NaCl, <sup>22</sup>Na<sup>+</sup> and THO are reported in Table I for various epoxy coal tar membranes.



Table 1  
Permeability coefficients

Diffusing species	Medium	Membrane thickness (μm)	10 <sup>10</sup> × P (cm <sup>2</sup> s <sup>-1</sup> )
NaCl	NaCl 0.5 molar → 0.0 molar	200	0.37
		150	0.15(a)
		200	0.43
		160	0.86(b)
THO	0.09 molar NaCl	200	0.64
<sup>22</sup> Na <sup>+</sup>	0.09 molar NaCl	200	0.0009
		200	0.60
	0.09 molar NaCl (pH=10)	120	2.60
		0.09 molar NaCl (pH=3)	170

(a) membrane A of Fig. 2.  
(b) membrane B of Fig. 2.

It may be observed that the value of the coefficient varies somewhat from one film portion to another. In particular, one membrane appeared to offer an unusually large barrier to <sup>22</sup>Na<sup>+</sup> diffusion. These variations are due to the heterogeneity of epoxy coal tar films which has been already observed in the study of other properties of these films<sup>1</sup>. For instance, the electrical resistance of various parts of the same paint film differed by as much as two orders of magnitude, furthermore the electrical resistances also showed different types of behaviour from one piece of film to another when the salt concentration changed. It was decided to measure the permeability of NaCl through two epoxy coal tar membranes which presented different curves for the variation of electrical resistance with the concentration of the external NaCl solution. Figure 2 illustrates the curves of R against C<sub>NaCl</sub> for two such epoxy coal tar membranes;

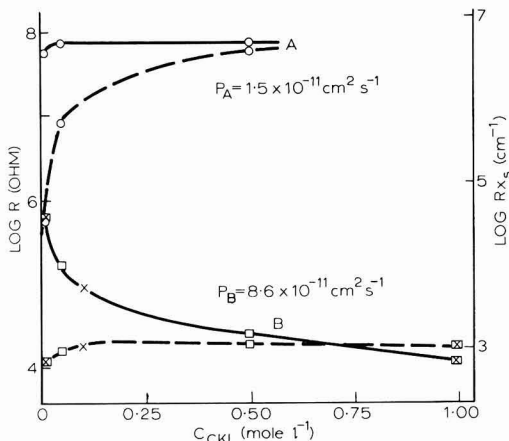


Fig. 2. Resistance (R) of epoxy coal tar membranes against the concentration of KCl (full lines)  
Product (R<sub>Zs</sub>) of epoxy coal tar membranes against the concentration of KCl (dashed line)

the values of P for NaCl (included in Table 1) are indicated in the Figure. The dashed curves correspond to the products R<sub>Zs</sub>, z<sub>s</sub> being the specific conductivity of the salt solution.

Discussion

Refs. 1-8

It is known<sup>4</sup> that the permeability of various gases and small solutes through polymer films depends to a large extent on the ability of polymer segments to move co-operatively; the glass transition temperature being the most significant single parameter in expressing chain mobility. The factors affecting the mobility of polymer segments have been summarised by Kumins<sup>5</sup>; those bearing directly to the permeation through paint films are: degree of cross-linking, homogeneous distribution of cross-linking, intrinsic rigidity of polymer backbone, presence of plasticisers and fillers in the film, crystallinity of the polymer. Plasticisers produce an enhancement of permeability since they increase the mobility of the polymer segments. In the case of epoxy paints, the presence of coal tar as a plasticiser explains why the permeability of ions is greater through epoxy coal tar than that measured by Murray<sup>2</sup> for Na<sup>+</sup> and Cl<sup>-</sup> ions through films of epoxy-polyamide clear varnish. When paint films are equilibrated in aqueous solution, some water is taken up by the films. It has been observed<sup>1</sup> that even hydrophobic films, such as epoxy coal tar, change their properties appreciably when wet. Water could be considered to act just as another plasticiser and an explanation of its influence in altering the permeability of solutes could be given. However, when the diffusing species are ions or other hydrophilic particles, the role of water is more complicated.

The value of the diffusion coefficients of small solutes through hydrophilic membranes, having a larger water content, is governed essentially by the water content of the membrane<sup>3</sup>. According to Yasuda<sup>6</sup>, the relationship between the diffusion coefficient of species i, D<sub>i</sub>, and the volume fraction of polymer, V<sub>p</sub>, in the hydrated membrane, is given by

$$D_i = D_i^0 \exp(-b_i V_p / (1 - V_p)) \dots \dots \dots (3)$$

where D<sub>i</sub><sup>0</sup> is the diffusion coefficient of i in electrolyte solutions and b<sub>i</sub> is a constant which depends on the diffusing species<sup>6</sup>. The water content of epoxy coal tar films was found<sup>1</sup> to be between 5.2 and 2.4 per cent depending on the particular membrane portion being employed. For Na<sup>+</sup> diffusion<sup>2</sup>, b<sub>i</sub> = 1.42, and eqn. (3) predicts that for a water content of 5 per cent, D<sub>Na+</sub> < 10<sup>-16</sup> cm<sup>2</sup>s<sup>-1</sup>. Since the salt concentration inside the paint film will be smaller than the concentration of salt in the external solution<sup>2</sup>, Q < 1, the permeability of Na<sup>+</sup> should be less than 10<sup>-16</sup> cm<sup>2</sup>s<sup>-1</sup>. This value is much smaller than any of the values measured in the present work. It may be concluded then, that the water absorbed by epoxy coal tar films is not homogeneously distributed throughout the membrane, and consequently, the mechanism of solute transport appears to be different from that in hydrophilic membranes. However, the fact that in Table 1, P<sub>THO</sub> is observed to be of the same order of magnitude as P<sub>22Na+</sub> would imply that the mobilities of both species, which are equal to the reciprocal of the friction coefficients, are nearly the same. This would confirm the impression that sodium ion is distributed in the same regions of the film as water and that the transport pathways may be considered to be the same.

The macroscopic heterogeneity of the membranes is evident from the values of the permeability coefficients in Table 1 and also from the values of the electrical resistance<sup>1</sup> of different regions of a given epoxy coal tar film. This heterogeneity complicates the interpretation of small changes in the properties of the film, making it impossible to describe quantitatively a set of properties which may be considered typical of an epoxy coal tar film. Quantitative conclusions

can be drawn with some certainty only when comparing the properties of the same film portion under different experimental conditions.

Mayne<sup>7</sup> has described two types of variation of the electrical resistance of varnish films with external salt concentration,  $C_s$ ;  $D$ -type areas have electrical resistances that decrease with  $C_s$ , and  $I$ -type areas in which  $R$  increases with  $C_s$ . He proposed that the first type corresponded to electrolyte flooding the paint film, whilst the second one would be due to water desorption from the paint film when the osmotic pressure of the salt solution increases. These two types of behaviour depend on the degree of cross-linking of the varnish in the area being examined.

In epoxy coal tar films, it was found<sup>1</sup> that the most typical behaviour corresponded to that of a charged membrane (almost constant  $R$  until the external salt concentration is great enough to overcome Donnan exclusion, thereafter  $R$  decreases with  $C_s$ ), or to that of a membrane having an electrical resistance which is almost concentration independent. This latter behaviour is shown by the membrane  $A$  in Fig. 2. No  $I$ -type areas have been observed in epoxy coal tar paint and a few films had  $D$ -type areas, like membrane  $B$  in Fig. 2. If electrolyte penetrates through membranes of  $D$ -type, the product  $R \times S$  should remain almost constant as shown in Fig. 2 for membrane  $B$ . In 0.01 molar NaCl the resistance of the membrane  $A$  is 100 times greater than that of membrane  $B$ . The electrical resistance ratio increases over 1,000 times at higher NaCl concentration. It is notable that the permeability of NaCl in membrane  $A$  is only 5.7 times smaller than in membrane  $B$ .

It may be considered that in membranes  $B$ , NaCl permeates through micropores in the film. According to the value of  $R \times S$  for that film, the free area should be of about  $800 \mu\text{m}^2$ . It is likely that the free area is not concentrated in a single diffusion channel, but rather due to a larger number of smaller pores throughout the membrane area.

This interpretation is supported by the fact that the measured electrical resistances of membrane  $B$  gave results independent of the pH of the solution (see Fig. 2), whilst epoxy coal tar films have a small fixed positive charge in acid and neutral solutions, but not in alkaline solutions<sup>1</sup> due to the amino groups of the cross-linking agent. Homogeneous transport of ions through a charged membrane would not be expected to produce a decrease of  $R$  with  $C_s$  as observed. Furthermore, if the transport of salt takes place through channels flooded by the external salt solution, it would be expected that ionic conductivity would yield a value of permeability near to the observed value employing the Nernst-Einstein relation<sup>8</sup>. A rough estimate of the permeability of  $\text{Na}^+$  through membrane  $B$  may be calculated employing the experimental value of the electrical resistance and the cation transport number<sup>1</sup>. The calculated value obtained is about  $4 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$  for the permeability coefficient, showing a correspondence between the observed permeability and that calculated with the Nernst-Einstein relationship.

On the other hand, for membrane  $A$ , the permeability calculated from the measured resistance was 100 to 1,000 times smaller than the observed value. The fact that the

Nernst-Einstein relation does not hold in this case is evidence in favour of the view that there must be a strong interaction between the charged epoxy matrix, either with the diffusing species or with the external electric field<sup>8</sup>. At present, it is not possible to distinguish between these two alternatives, because the heterogeneous nature of the paint films makes quantitative comparison possible only within the same film section. A further complication is due to the fact that epoxy coal tar films have been observed occasionally to become persistently polarised; hence the presence of reactive electric fields in the films due to polarisation of the resin when subjected to an external electric field during the resistance measurements cannot be completely excluded.

If such a reactive field exists, the relationship between permeability and ionic conductivity would not be given by the Nernst-Einstein relationship.

## Conclusions

Permeability measurements through epoxy coal tar films confirm the heterogeneous nature of these films, probably due to non-uniform cross-linking. Through normal membrane regions the transport of ions and small solutes corresponds to that through a membrane bearing a small positive (weak) charge.  $D$ -type areas would allow transport through micropores flooded by external electrolyte solution.

This work indicates the need for further study of electrochemical properties of paint films measured on the same film section, so that quantitative information may be obtained. These measurements must be performed with the films in equilibrium with the liquid medium, if its results are intended to explain the function of protective paint for immersed structures.

The presence of heterogeneities in applied coatings seems to be a general feature of paint films and a likely cause of deterioration of the coatings.

## Acknowledgment

The authors are grateful to the Consejo Nacional de Investigaciones Científicas y Técnicas (Argentina) for partial financial support in this research.

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# THE NEW TECHNOLOGIES FOR INDUSTRIAL FINISHING PAINT R.A.'s THIRD



**LONDON 23-25 MAY 1978**

Stimulated by environmental restrictions, energy considerations and economic pressure, a wide range of new products and techniques for industrial painting have been developed during the last 15-20 years, including:-

- Water-Borne Paints for conventional and electrocoat application
- Powder Coatings - conventional and thin film types
- High - Solids paints including conventional, solventless and non-aqueous dispersions
- Coatings for Radiation Curing by UV, electron beam, glow discharge and plasma arc.

None has achieved the market penetration at one time predicted for it; some falling short by only a little but others by a large margin.

The aim of this Conference is to bring together Raw Materials Suppliers, Paint Manufacturers and

Users for an up-to-date and realistic assessment of the present situation and future prospects.

Invited papers from seven countries will feature:-

- Needs of society and requirements for successful innovation
- Product Finishing Technology: Products – application, performance
- Markets and Marketing - what went wrong in market prediction
- Users' views - what they will be using during the next ten years  
– ending with a
- Debate on whether advanced technology is necessary for profitability in the surface coatings industry.

The conference will cater for scientists, technologists, marketing and managing directors of paint making and paint using companies.

Organised by:-

## The Paint Research Association

# THE NEW TECHNOLOGIES

Opening Ceremony  
(13.45 – 14.00)

Chairman:

*Paper 1*  
(14.05 – 14.30)

*Paper 2*  
(14.45 – 15.10)

*Break for Tea*

*Paper 3*  
(15.55 – 16.20)

*Paper 4*  
(16.35 – 17.00)

OPEN FORUM  
(17.15 – 17.40)

*Paper 5*  
(09.15 – 09.45)

Chairman:

*Break for Coffee*

*Paper 6*  
(10.30 – 11.00)

*Paper 7*  
(11.15 – 11.45)

*Paper 8*  
(12.00 – 12.30)

OPEN FORUM  
(12.40 – 12.50)

*Break for Lunch*

Chairman:

*Paper 9*  
(14.15 – 14.40)

*Paper 10*  
(14.55 – 15.20)

*Break for Tea*

## PROGRAMME – FIRST DAY

Tuesday, 23 May 1978

**The Rt. Hon. the Earl of Shannon** – Director, CDRA

### SESSION ONE

**Francis Smith** – President, Paint R.A.

#### Perspectives

**Duncan Davies** – Chief Scientist,  
Department of Industry

#### Innovation & Achievement – Marketing New Technologies

**Karl Krøyer** – Inventor, Denmark

#### Why Didn't Grandfather Do It This Way

**George Anderson** – Managing Director,  
Paint R.A.

#### Marketing – Observations on Market History of the New Technologies

**John Bickers** – Managing Director,  
Goodlass Wall

Discussion on Session One

## PROGRAMME – SECOND DAY

Wednesday, 24 May 1978

### SESSION TWO

**Austin O'Malley** – Deputy Managing Director, Industrial Coatings Division  
International Paint

#### Powder Coatings: Technical Status

**Sid Harris** – Powder Coatings  
Consultant

#### Coil Coating – Its Role for the Future

**Bill Peachey** – Director, Packaging &  
Coil Coatings Division  
International Paint – Industrial Coatings

#### Industrial Water-Borne Paints

**Jerome Levy** – Research & Development  
Manager  
European Laboratory for Polymers &  
Resins  
Rohm & Haas, France

#### Progress in Electropainting

**Marco Wismer** – Vice President of  
R & D  
PPG Industries, USA

Discussion on Session Two

### SESSION THREE

**Leslie Valentine** – Director of Research & Development  
Berger, Jenson & Nicholson

#### Industrial High – Solids Paints

**Gerd Walz** – Manager of Development  
Department  
Hoechst AG, Wiesbaden, West Germany

#### Non-Aqueous Dispersions & their Market in the Automotive Industry

**Michael Waghorn** – R & D Department  
ICI Paints Division

# FOR INDUSTRIAL FINISHING

*Paper 11*  
(16.00 – 16.25)

*Paper 12*  
(16.40 – 17.05)

OPEN FORUM  
(17.05 – 17.20)

19.00 for  
19.30

Chairman:

*Paper 13*  
(09.15 – 09.45)

*Break for Coffee*

*Paper 14*  
(10.30 – 11.00)

*Paper 15*  
(11.15 – 11.45)

*Paper 16*  
(12.00 – 12.30)

OPEN FORUM  
(12.40 – 12.50)

*Break for Lunch*

Chairman:

14.15 – 14.35

14.40 – 15.00

15.00 – 15.30

15.45

*Tea*

**Radiation Curing: Materials & Methods**

**New Industrial Finishing Systems Throughout Europe**

Discussion on Session Three

CONFERENCE DINNER

Guest Speaker: **Ted Schoeters**  
Editor, Technical Page, Financial Times

PROGRAMME – THIRD DAY

Thursday, 25 May 1978

SESSION FOUR

**Gianni Varasi** – General Manager,  
Colorificio Italiano Max Meyer, Italy

**Options for Automotive Industry Finishing**

**Graham North** – Managing Director  
Cray Valley Products

**Werner Burckhardt**  
Head of Department,  
Less-Polluting Paint Systems,  
AKZO Coatings, Stuttgart,  
West Germany

**Ian Walker** – Co-ordinator,  
Product & Process Improvement  
Ford Europe, Köln, West Germany

**Can Coatings Requirements**

**The Varied Needs for Finishing Domestic Appliances**

**Finishing of Agricultural Tractors**

Discussion on Session Four

**Fred Fidler** – Manager, Metals R & D  
Metal Box Packaging

Speaker from Industry

**Thomas Sheppard** – Chief Chemist  
David Brown Tractors

SESSION FIVE

**Rex Chester** – Executive Chairman, Donald Macpherson Group  
Debate on the motion

“ADVANCED TECHNOLOGY IS NOT NECESSARY FOR PROFITABILITY”

For the motion: **Leslie Silver** – Managing Director  
Silver Paint & Lacquer

Against the motion: **Clive Cook** – Technical Co-ordinator  
ICI World Paint Group

Discussion on the Debate

The President of Paint R.A. will close the Conference

END OF CONFERENCE

# CONFERENCE ARRANGEMENTS

The Conference will be held at the Forte Suite, Excelsior Hotel, London Airport and will start at 13.30 on May 23 and will end at 16.00 on Thursday May 25.

Extended Abstracts of papers will be issued in advance. Each paper will be followed by a full discussion and there will be an 'Open Forum' at the end of each Session. Conference Proceedings will be published. Early booking is recommended in view of the anticipated demand for places at the Conference.

## REGISTRATION FEES

£100 + VAT per delegate to Paint R.A. Members

£120 + VAT per delegate to others.

Applications should be made on the attached registration form giving full details. Do not send Remittance with this form. Invoices will be issued within two weeks after the receipt of the registration form.

Fees include Extended Abstracts of Papers, one copy of Conference Proceedings, luncheon on 24 and 25 May, tea and coffee as in the Programme. The fees do not include hotel accommodation and Conference Dinner

## LADIES PROGRAMME

All delegates' wives and accompanying guests are invited.

Provisional programme: afternoon tea and welcome 23 May, trip to London on 24 May comprising one or more of the following: Victoria and Albert Museum, Harrods, Royal Academy and shopping, Conference Dinner on 24 May (optional). Trip to Hampton Court on 25 May morning.

Apart from Conference Dinner and Hotel accommodation all other items are free of charge. Please indicate your choice on the registration form.

## VENUE

The Conference will be held at:

The Excelsior Hotel, Forte Suite,  
London Airport (Heathrow),  
Bath Road, West Drayton,  
Middlesex.

Telephone: 01-759 6611; Telex: 24525

The Hotel (Four Star) features two Bars and two Restaurants. Transport is provided from the Airport together with a free regular coach service to and from the West End. There are 660 rooms (with bath, shower, colour TV etc.) and free parking space for 600 cars.

## ACCOMMODATION

The Paint R.A. has reserved a large number of single and twin-bedded rooms for the nights of May 23 and 24 at the Excelsior Hotel. A special reduced rate has been negotiated for delegates wishing to book their accommodation through the Paint R.A. For further details see the attached Registration Form.

## CONFERENCE DINNER

The Conference Dinner will be held at 19.30 on Wednesday May 24 at the Excelsior Hotel.

Charge: £10 per delegate  
£10 per delegate's guest

Dress: Informal

Guest Speaker: Ted Schoeters,  
Editor, Technical Page,  
Financial Times

# WHO'S WHO

**ANDERSON, GEORGE de WINTER, B.Sc.,** Ph.D., C.Chem., F.R.I.C., A.R.P.S., worked with I.C.I. Dyestuff Division for fifteen years where he carried out research on photographic chemistry, reactive textile dyes and electrochemical routes to polymer intermediates. As Director of Research with 3M Research Ltd., he was responsible for chemical research of a company with wide ranging interests. He joined the Paint R.A. as Director (now Managing Director) in 1968.

**BICKERS, JOHN.** After a brief flirtation with textiles, followed by fourteen years in the food industry, Mr. Bickers moved into general management as M.D. with Jeyes, Ireland. He returned to the U.K. as Marketing Director of the parent Company and then as M.D. of another Jeyes Group Co. — Brobat. Mr. Bickers is at present Managing Director of Goodlass Wall & Co. Ltd.

**BURCKHARDT, WERNER,** was educated in the University of Stuttgart where he studied chemistry and biology. Mr. Burckhardt joined Deutsche AKZO Coatings (also known as Lesonal) in 1959. Mr. Burckhardt is at present Head of Department of Less-Polluting Paint Systems (water-borne and high-solids) and Project Manager for Water-Borne Paints for the whole AKZO Coatings Group.

**CHESTER, REX, M.A. (Oxon),** educated in Winchester College and New College, Oxford, with first class Honours Degree in Philosophy, Politics and Economics. Mr. Chester joined Donald Macpherson Group Ltd., in 1958 where he became Managing Director in 1965, Chairman and M.D. in 1968 and Executive Chairman in 1972.

**COOK, CLIVE, B.Sc.,** educated in London University, spent all his working life with I.C.I. In R. & D. he has worked on physical and chemical methods of analysis, emulsion polymers, electrodeposition and NAD. As Research Group Manager for long-term programmes Mr. Cook has been closely associated with innovation in the surface coatings and allied industries. As Technical Co-ordinator, I.C.I. World Paint Group he is responsible for long-term technical needs.

**DAVIES, DUNCAN, B.Sc., M.A., D.Phil.,** educated in Trinity College, Oxford, was Research Director of various I.C.I. Divisions. He was the founder Director of I.C.I. Petrochemical and Polymer Laboratory. He was a visiting professor at Imperial College and a visiting Fellow, St. Cross College, Oxford. Dr. Davies is now Chief Scientist at the Department of Industry.

**FIDLER, FRED, B.Sc., M.I.P., A.I.F.S.T.** After graduation he joined Metal Box Ltd. in 1955. His experience has covered work in various development areas leading to his transfer to R. & D. Department in 1961. Mr. Fidler's initial work on freeze drying led to wider interests in food technology and packaging. Appointed Manager Metals R. & D. in 1976.

**HARRIS, SID, B.Sc.,** worked in the Paint Industry for more than 30 years specialising in the development of synthetic resins for decorative and industrial coatings. He has been directly concerned with the growth of the Powder Coatings industry in the U.K. from its early beginnings. His close contacts with the end user have provided a sound commercial insight into the needs of this rapidly expanding market. He is now Director of S.T. Harris (Powder Coatings Consultant) Ltd.

**KRØYER, KARL, M.C.I.F., M.Ing.F.,** Danish inventor, has established an inventors' institute at Århus, Jutland employing some 80 technicians. A list of Karl Krøyer's inventions includes some 300 patents which are used by more than a hundred industrial firms throughout the world. They include a method of producing glucose in the consistency of granulated sugar directly from corn, methods for dry production of paper, a continuous automatic refrigeration system, water filters and many others. In 1969 the German Inventors' Association awarded him its most distinguished award, the Diesel Medal, previously awarded to such eminent scientists as Wernher von Braun and Professor Picard.

**LEVY, JEROME, B.S. (Michigan, U.S.A.), Ph.D. (Wisconsin, U.S.A.),** joined Rohm and Haas in 1963. Initial responsibilities were organic synthesis oriented and involved basic study concerned with speciality functional monomers and new cross linking mechanisms intended for high performance coatings applications. In 1969, Dr. Levy was appointed Head of Laboratory charged to provide new technical leads in the leather field, historically a market in which Rohm and Haas has played an important role. These activities were expanded to encompass developments directed towards the textile industry. Following promotion to Research Department Manager, Dr. Levy became responsible for a converted products research group involving film and plastics based composites. In 1976 he assumed his present position as Research and Development Manager for European Polymers, Resins and Monomers Business Group. In that capacity he supervises technical support provided out of the European Laboratory in Valbonne, France.

**NORTH, GRAHAM, B.Sc.,** educated in London and Harvard Business School, has spent all his working life at Cray Valley Products where he is now the Managing Director. He has lectured extensively in the U.K. and some fifteen other countries on diverse subjects, ranging from thixotropic alkyls to electrodeposition and financial analysis. Mr. North was Chairman of the British Resin Manufacturers' Association and is currently Hon. Treasurer of the Paint R.A.

**O'MALLEY, AUSTIN,** a Member of the Institute of Marketing, won the George Drexler Travelling Scholarship. This is awarded annually by the Institute of Marketing to the most successful finalist of this professional examination. He is at present Deputy Managing Director, International Paint Co. Ltd., Industrial Coatings Division.

**PEACHEY, ARTHUR WILLIAM** has spent his business life in the Pinchin Johnson Group — now International Paints — Industrial Coatings. He originally joined the marketing organisation of Robt. Ingham Clark, a Pinchin Johnson company, in 1933, and set up the industrial coatings operation in Bristol and South Wales in the post-war years. In 1968 he assisted in the formation of the Packaging & Coil Coatings Division and became Director in 1974. He is a member of the European Coil Coating Association and is keenly enthusiastic about the scope of coil coating in industry.

**SCHOETERS, EDWARD,** educated in Belgium and England, Mr. Schoeters joined Reuters in 1950. He spent four years with the U.K. Atomic Energy Authority as Senior Information Officer. In 1961 he joined the Financial Times as Science Correspondent. Mr. Schoeters is now Editor of Technical Page, Financial Times.

**SHANNON, The Rt. Hon. the Earl of.** Educated at Eton College, Regular Army (Irish Guards) 1942-54, a Cross-Bencher, i.e. non-Party member, Lord Shannon is a Deputy Speaker and Deputy Chairman of Committees in the House of Lords. A member of sub-Committees of the House of Lords in the fields of Research and the Environment. Past Vice-President and present Deputy Chairman of the Parliamentary & Scientific Committee. Director of the Committee of Directors of Research Associations (CDRA) since 1969. Secretary and Treasurer of the Federation of European Industrial Co-operative Research Organisations (FEICRO) since 1973.

**SHEPPARD, THOMAS.** Born in Gloucestershire and educated in Buckinghamshire and at Wellingborough, and subsequently a part-time student at various Colleges of Technology in this country, Mr. Sheppard claims no academic qualifications, but has a lifetime of experience in Industry as an Industrial Chemist. He has been Chief Chemist of David Brown Tractors Limited since 1946, responsible for all metal finishing plant and process planning and control in that company's own operations, and for advisory work to associated companies. Mr. Sheppard was elected an Honorary Member of the Chemical Coaters' Association of America in 1976 'In tribute to the quality achievement of David Brown Tractors'.

**SILVER, LESLIE,** on leaving the R.A.F. in 1947 formed his own company - Silver Paint and Lacquer Company Limited. This is now one of the largest privately-owned paint companies in the U.K., with sales of over £12m per year, and with interests in a wide variety of chemicals and polymers. Mr. Silver was President of OCCA from 1973-1976 and President of the Paint Industries Club from 1975-1977.

**SMITH, FRANCIS, B.Sc., Ph.D.** completed his 1st Class (Hons.) B.Sc. and Ph.D. in the Colour Chemistry Department of Leeds University in 1948. He joined the Scottish pigment manufacturer, James Anderson & Co. (Colours) Ltd., as a Research Chemist, and has held several posts in the Technical and Marketing Departments prior to his appointment as Technical Director, Pigments Division in 1965, when the company was The Geigy Company Limited, and subsequently Pigments Division, CIBA-GEIGY Plastics & Additives Company. Dr. Smith is a long-standing member of the P.R.A. Panels, and has been a Member of Council since 1968, and President since 1975.

**VALENTINE, LESLIE, B.Sc., Ph.D.** graduated in chemistry at Aberdeen University. This was followed by research on polymerisation at Aberdeen and Birmingham Universities. He was Lecturer on the chemistry of high polymers at Leeds University. Dr. Valentine joined the Paint R.A. as Director, 1960-67, and is now Director of R. & D., Berger, Jenson & Nicholson Ltd.

**VARASI, GIANNI,** after completing studies in Italy, joined Harvard Business School and acquired management experience in the United States with several important companies. Back in Italy, Mr. Varasi began to work in his family's company, Max Meyer, in positions of growing responsibility and became its General Manager. He is also a member of the Board of Directors of Max Meyer, Saver and other important companies. Mr. Varasi is at present President of both the Paint Manufacturers group of the Italian Association of the Chemical Industry and European Committee of the Association of Paints, Printing Inks & Artists' Colours Manufacturers.

**WAGHORN, MICHAEL JOHN, C.Chem., M.R.I.C.,** joined I.C.I. Paints Division in 1949 and after working in analytical, fundamental research and production departments became associated with I.C.I.'s early work on resin dispersions in 1961. For the last ten years he has been working on all types of finishes for the automotive industry, with a special interest in non-aqueous dispersion paints.

**WALKER, IAN, M.I.M., F.I.M.F.,** started his industrial career with the Rootes Group (now Chrysler) where he became Chief Metallurgist and Chemist. He joined Ford Motor Company in 1955 and became Manager of Materials Development and Technical Services. He has been associated with several major developments in Paint Technology. After the formation of Ford - Europe he moved to Germany where his responsibilities included the quality control of paints, plastics, fabrics and other organic materials throughout Europe. Currently he is responsible for the coordination of product & process improvement investigations for a group of body components, which include paint and paint materials. He has been a member of several Industry Committees, national and international, and was Chairman of the Organic Finishing Group of the Institute of Metal Finishing.

**WALZ, GERD, M.Sc., Ph.D.,** educated in the University of Saarbruecken and University of Mainz where he obtained Diplom Physiker and Doctorate in physical chemistry respectively. Dr. Walz joined Hoechst in 1970 where he is now Manager of Development Department in the Resins Division. At present he is doing basic research on new resins and dispersions. Dr. Walz has published and presented many papers on resin chemistry.

**WISMER, MARCO, M.Sc., D.Phil.,** born and educated in Switzerland, joined PPG Industries in 1956 as a Research Associate in the Coatings and Resins Division, where he became Director of Advanced Research in 1964, a post he held until he was named Vice President of R. & D. in 1974. Dr. Wismer has published widely in coatings industry technical journals and has contributed chapters for seven textbooks. He holds more than 100 U.S. and foreign patents pertaining to coatings and resin products, and has won two IR-100 Awards and the 1973 American Metal Society Award. Dr. Wismer is a member of several academic and professional societies.

**Paint  
Research  
Association**





# REGISTRATION FORM

*International Conference on*  
**THE NEW TECHNOLOGIES**  
**FOR**  
**INDUSTRIAL FINISHING**  
 23-25 May 1978

A Please reserve places for the Conference & Dinner for the delegates listed below:

Serial No	Name in Full (Surname followed by Christian name)	Title (Dr, Mr, Miss or Mrs)	Present Position	Places for Dinner YES or NO
1				
2				
3				
4				
5				
6				

B Accompanying Guest

Please indicate in boxes below which functions you wish to attend

Serial No	Name in Full (Mrs/Miss " <i>First name</i> " " <i>Surname</i> ")	May 24					May 25
		Victoria & Albert Museum	Harrods	Shopping	Royal Academy	Conference Dinner	Hampton Court
1L							
2L							
3L							
4L							
5L							

## HOTEL ACCOMMODATION

A number of single and twin-bedded rooms have been reserved in the Excelsior Hotel. The Paint R.A. has negotiated a special reduced rate for the delegates (23-25 May) with the hotel as follows:

Name of the Hotel	Price per day per delegate <i>(inclusive of VAT &amp; Service charge, but no breakfast)</i>	
	Single room + bath (A)	Twin-bedded room + bath (B)
Excelsior Hotel London Airport (Heathrow) Bath Road, West Drayton, Middlesex, England. Telephone: 01-759 6611 Telex: 24525	<b>£16.00</b>	<b>£23.00</b> <i>(Double Occupancy)</i>

PLEASE TURN OVERLEAF

**C** Please reserve accommodation as detailed below:

Delegate's Serial Number	Accommodation needed – for the nights of	Total No. of nights	Accommodation (A or B)

Name .....

Position .....

Please print  
or  
Type

Company ..... *(PRA Member or Non-Member)\**

Full Address .....

.....

*\*Please indicate*

Tel. No. .... Telex .....

Date ..... Signed .....

*DO NOT SEND REMITTANCE* with this form. Invoices will be issued in due course covering the fee, VAT and Dinner.

The completed form should be sent to:

Mrs Gill McDonald,  
Secretary to the Head of Information Department,  
Paint Research Association,  
Waldegrave Road, Teddington, Middlesex TW11 8LD.  
England.  
Telephone: 01-977 4427 Telex: 928720

*For Paint R.A. Use*

Acknowledged .....

Extended Abstracts

List of Delegates

Instruction

.....

Amount to be invoiced

Fees ..... £

VAT @ 8% ..... £

Dinner ..... £

Total ..... £

Invoice sent .....

Remittance received .....

# The ultraviolet screening behaviour of pigments

By P. Marvuglio, R. F. Sharrock and R. J. Kennedy

The Hilton-Davis Chemical Company., 2235 Langdon Farm Road, Cincinnati, Ohio 45237, USA

## Summary

The recent surge of interest in plastic packaging, particularly for plastic beverage containers and medicine bottles, has resulted in the development of new grades of polymers.

The gaining of acceptance by the packaging industry, however, requires proof that the coloured plastic compound will protect the contents from harmful radiation at a price competitive with other

materials now being used.

This paper discusses the ultraviolet screening behaviour of transparent pigments, and suggests the use of transparent synthetic iron oxide pigments, which effectively screen out harmful radiation at levels as low as 0.0313 parts per hundred of resin whilst maintaining transparency.

## Keywords

*Types and classes of coatings and allied products*

clear coating

*Raw materials for coatings binders (resins, etc.)*

polymer

*prime pigments and dyes*

synthetic iron oxide

*miscellaneous paint additives*

ultraviolet screening agent

*Processes and methods primarily associated with analysis, measurement or testing*

accelerated testing

*Properties, characteristics and conditions primarily associated with materials in general*

clarity

*the environment*

solar radiation

*Specifications, standards and regulations*

Food, Drug and Cosmetic Act

## Le caractère protecteur contre l'action des rayons ultra-violets de pigments

### Résumé

La poussée d'intérêt dans le domaine des emballages en plastique, surtout à l'égard des bouteilles en plastique pour boissons et pour médicaments, avait comme résultat l'évolution de nouvelles qualités de polymères.

Pourtant, afin de gagner l'approbation de l'industrie de conditionnement, on est obligé de fournir les épreuves démontrant que le produit en plastique coloré peut protéger les contenus contre les radiations nuisibles et à un prix de concurrence à l'égard d'autres

produits actuellement utilisés.

Dans cet exposé les auteurs discutent les caractéristiques protectrices contre l'action des rayons ultra-violets des pigments transparents, et ils proposent l'emploi des pigments transparents de l'oxyde de fer synthétique qui éliminent en grande partie les radiations nuisibles et maintiennent la transparence, même où la concentration ne dépasse pas 0,0313 parties sur cent de résine.

## Das Verhalten von Pigmenten hinsichtlich UV-Ausfilterung

### Zusammenfassung

Das erneute Aufleben des Interesses in Kunststoff-Getränkebehältern und Medizinflaschen, führte zur Entwicklung neuer Qualitäten von Polymeren. Um aber von der Verpackungsindustrie akzeptiert werden zu können wird Beweis dafür verlangt, dass farbige Kunststoffverbindungen den Inhalt vor schädlichen Strahlen schützen, und dies zu Preisen in Konkurrenz mit den anderen bereits benutzten Materialien.

In dieser Abhandlung wird das Ultraviolet-Ausfiltern transparenter Pigmente besprochen, und die Verwendung transparenter, künstlicher Eisenoxidpigmente vorgeschlagen, welche harmvolle Strahlen selbst bei so niedrigem Gehalt, wie 0,0313 Teilen Harz ausfiltern und dabei transparent bleiben.

The recent surge of interest in plastic packaging, particularly for plastic beverage containers, has led to a detailed study of transparent pigments for plastics.

The Food and Drugs Administration (FDA) acceptability, durability and unique shade features of transparent iron oxides, coupled with the earlier recognition of their UV screening characteristics in coatings, suggested that these pigments would find utility in this emerging plastics application.

In general, plastic packages and their contents are susceptible to degradation as a result of prolonged exposure to UV radiation. Sunlight or solar radiation is comprised of a 6 per cent UV radiation component which lies in the 290nm

to 400nm range. Of this, only the 300nm to 400nm wavelength range penetrates the atmosphere. Therefore, for the purpose of this study, only the 300nm to 400nm range wavelengths were considered.

The absorption of UV radiation and its concomitant degradative effects vary for each individual polymer. Stability is greatly dependent on the specific chemical and molecular structure of the polymer. Since the molecular structure governs the absorption ranges of each polymer, variations in structure lead to differences in the absorption ranges of individual polymers.

The UV radiation absorption of various polymers and the most harmful wavelengths and peak absorptions are shown

in Table I. The absorption picture is not limited to these specific wavelengths. The absorption profile of a polymer encompasses a wide, rather than a narrow, range of wavelengths. Again, turning to specific polymers, it is found that those with absorption maxima in the 290nm to 400nm range are the polysulfones, polyesters (terephthalate types) and some polyurethanes. Those with absorption maxima outside the 290nm to 400nm range, but with significant absorption within this region are polystyrene, polyester (aliphatic types), cellulose esters, acrylics (PMMA) and polyamides. Polymers that, in theory, should not be affected by UV radiation are the polyolefins (PE, PP) and polyvinyl chloride, but due to defects in their polymer matrix, they are also susceptible to UV degradation.

Table I

Ultraviolet radiation absorption wavelengths for various polymers

	Most harmful	Peak absorption
Polyethylene	254nm	<200nm
Polypropylene	375nm	<200nm
Polystyrene	254nm	210–260nm
Polyvinyl chloride	245nm	200nm
Acrylic (PMMA)	254nm	214nm
Polycaprolactam	254nm	—
Polycarbonate	254nm	260nm
Polyester (PET)	280–360nm	240–290nm
Cellulose acetate	254nm	<250nm

With respect to packaging applications, Figure 1 illustrates the significant differences in transmission which can be obtained with three commercial plastic packaging resins. For this study, a crystal polystyrene resin was selected, because of its high degree of clarity and its relatively greater percentage transmission of UV radiation in the desired wavelength ranges.

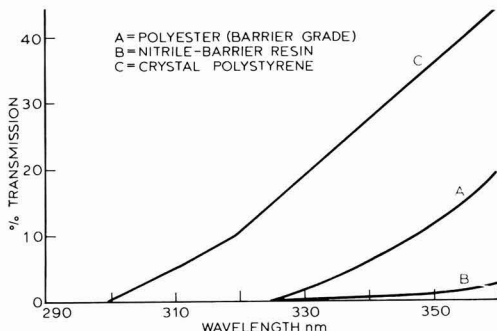


Fig. 1. Percentage transmission of unpigmented polymers

Organic compounds which are recognised as producing a stabilisation effect with regard to UV radiation when incorporated into polymeric materials have the following characteristics:

- Their peak absorption are within the 290nm to 400nm range.
- They exhibit minimal absorption in the visible, i.e. the 400nm to 700nm range.

The effect of incorporating a typical UV absorber into crystal polystyrene is illustrated in Figure 2.

In conducting this study, the following procedure was employed in the preparation of test plaques. First, a colour

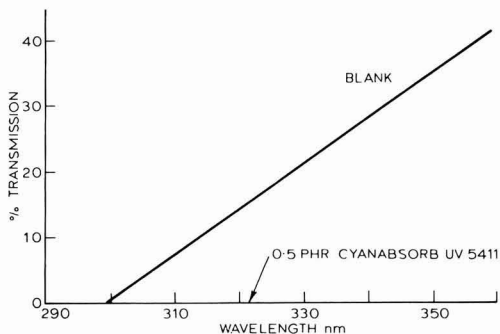


Fig. 2. Percentage transmission of polystyrene containing 0.5phr UV absorber

concentrate was compounded into a masterbatch by extrusion. This masterbatch was then injection molded into 2'' × 3'' flat test plaques with an average thickness of 116 mils. In addition to the transparent iron oxide pigments, similar masterbatches were prepared from transparent organic pigments.

All transmission curves were obtained using a Perkin-Elmer Model 323, UV/Vis-NIR Recording Spectrophotometer in the 210–360nm wavelength range. The sample transmission was taken relative to air at 100 per cent. The scale used was the 0–100 per cent, with a photometric transmittance accuracy ± 0.5 per cent of full scale.

Figures 3 to 8 represent a series of transmission curves for varying concentrations of the transparent red and yellow iron oxides and a variety of organic pigments. It can be noted that the incorporation of the transparent iron oxides at levels of 0.03 to 0.50 per hundred of resin (phr) effectively screened out harmful UV radiation. The transparent yellow iron oxide was slightly the more effective in this respect than the

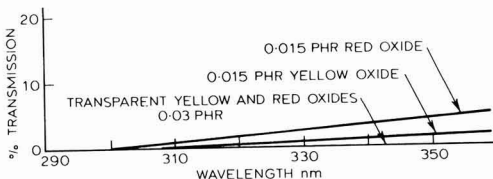


Fig. 3. Percentage transmission of polystyrene pigmented with transparent iron oxides

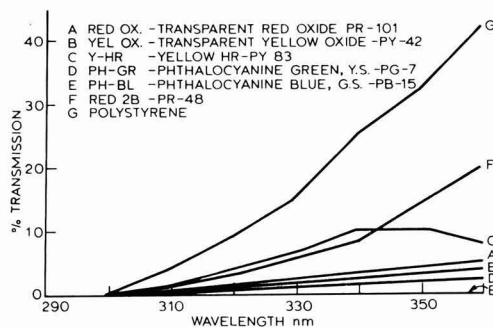


Fig. 4. Percentage transmission of various pigments at 0.015phr in polystyrene

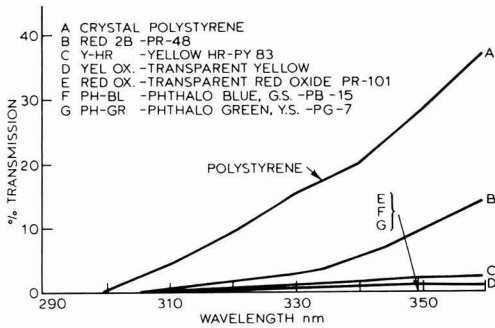
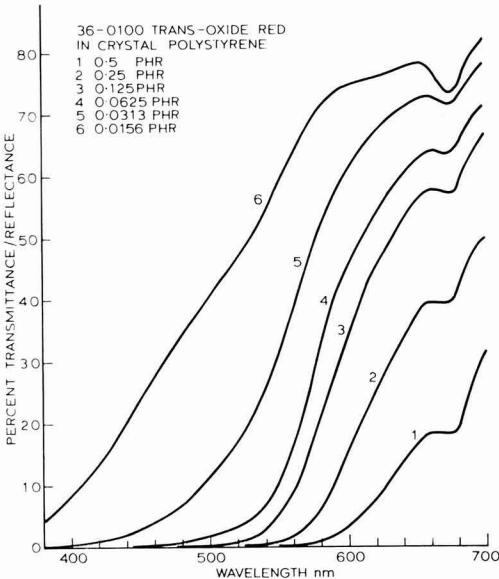


Fig. 5. Percentage transmission of various pigments at 0.031phr in polystyrene



Figs. 6-9. Percentage transmission of pigments at various concentrations in polystyrene

transparent red iron oxide. At the 0.015phr pigment level, at which the first UV transmission of the oxides occurs, almost all of the pigments which were tested showed some degree of UV transmission. Whilst several of the organic pigments show equivalent UV transmission characteristics when compared to the oxides (particularly the phthalocyanine blue and carbon black), the colour contribution of these pigments in the visible range is very significant, thus reducing their utility to only highly coloured items.

Prolonged exposure to direct, accelerated sunlight (100,000 Langley) on the EMMAQUA (equatorial mount; mirrors and water) machine and Fadeometer tests (300 and 500 hours) were conducted. The effect of UV radiation on the percentage transmission of an unprotected crystal polystyrene blank is shown in Figure 10 after 300 and 500 hours Fadeometer exposure and 100,000 Langley of solar radiation. Addition of a UV absorber at levels ranging from 0.015phr to 0.50phr eliminates all of the UV transmission.

Generally, prolonged exposure results in a progressive loss in percentage transmission, as polymer degradation proceeds,

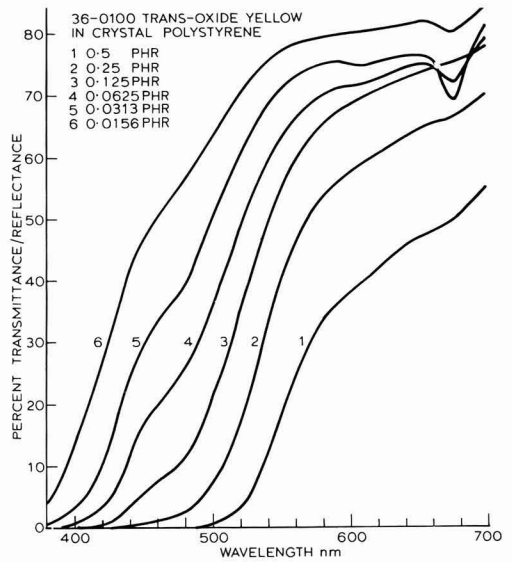


Fig. 7.

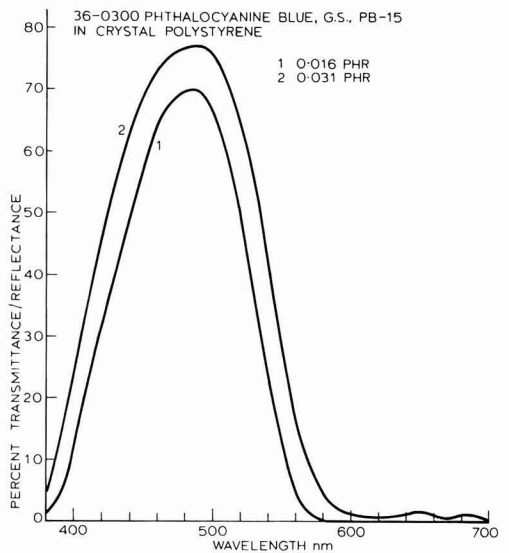


Fig. 8.

and assumes the classical degradation profile obtained with fractionally pure polymeric materials. This phenomena enabled the evaluation of the permanency of the UV protection afforded by various pigments. For example, carbon black, which is a well known stabilising pigment, yielded the results shown in Figure 7 in which low concentration levels of carbon black show similar behaviour after exposure, i.e. a gradual decline in transmission on continued exposure.

Figures 3-8 show the percentage transmission of crystal polystyrene pigmented with transparent red and yellow iron oxides, phthalocyanine green (PG7), permanent red 2B

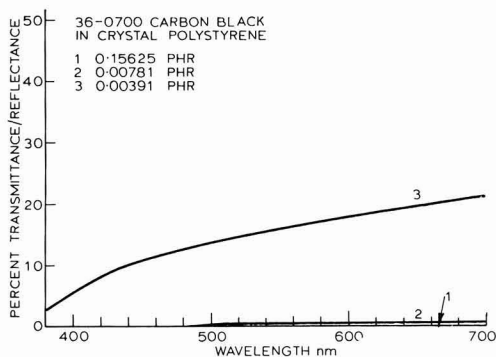


Fig. 9.

(PR-48) and yellow HR (PY-83) and phthalocyanine blue (PB-15) at levels of 0.015phr and 0.030phr after prolonged exposure to artificial and solar radiation. At a level of 0.015phr all of these pigments showed similar degradation profiles. When the pigment level is increased to 0.03phr the degradation is still evident in the organic pigments, but is no longer evident in the transparent oxides. Since it was demonstrated earlier that a pigment level of 0.03phr completely screened the UV radiation, it can be concluded that at this pigment level, a transparent oxide pigmented plastic package would effectively protect the contents from the harmful effects of UV radiation.

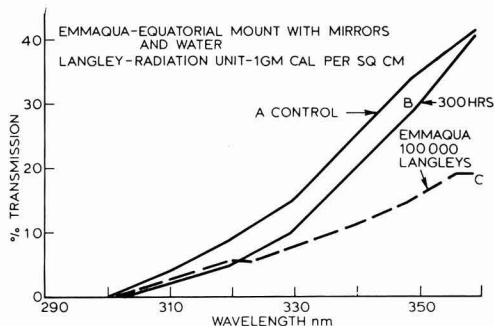


Fig. 10. Percentage transmission of polystyrene after exposure

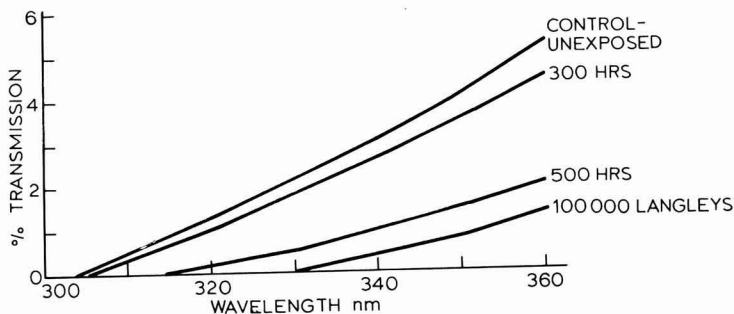


Fig. 11. Percentage transmission of black pigmented polystyrene after exposure. Pigment concentration 0.0039phr

The effect of prolonged exposure on the visible properties of the various pigmented plastics is demonstrated in Figures 10-18. After 200,000 Langley's exposure, which can be equated to approximately 16 months outdoor exposure in southern Florida, it is observed that, in general, all of the polystyrene samples exhibited significant colour changes. The unpigmented polystyrene sample exhibited the familiar yellowing, i.e. a change in the yellowness index of 8.67 contributing to a  $\Delta E$  of 9.4 units. The pigmented samples exhibited the following colour changes:

	Parts per hundred of resin	$\Delta E$
Phthalocyanine blue, G.S.	0.031	4.4
Phthalocyanine green, Y.S.	0.031	5.6
Organic red 2B	0.031	99.9 +
Organic yellow HR	0.031	0.8
Carbon black	0.004	18.2
Transparent red oxide	0.031	5.4
Transparent yellow oxide	0.031	8.6

Whilst all of the pigments exhibited colour changes in the visible range, the transparent iron oxides, carbon black and phthalocyanine blue were the only ones which did not exhibit a reduction of the UV screening characteristics on prolonged exposure. This permanency is parallel to the behaviour which is observed in polystyrene containing an effective UV absorber at a concentration of 0.25phr.

Having established that the transparent oxides demonstrated a superiority over the organic pigments in affording UV protection whilst maintaining transparency, the pigment loading requirements needed to provide this same level of protection at various thicknesses of plastic for five distinct shades were determined. The particular pigmentation levels and shades of colour they represent are those thought to be most useful in packaging applications, particularly the transparent red oxide for the manufacture of beverage (beer) and medicine bottles.

Plotting the thickness versus percentage transmission gave a series of curves which are shown in Figure 19. These curves exhibit sufficient flatness between 15 mils and 120 mils thickness permitting the calculation of regression curves with reasonable accuracy (95 per cent confidence level). (Table 2).

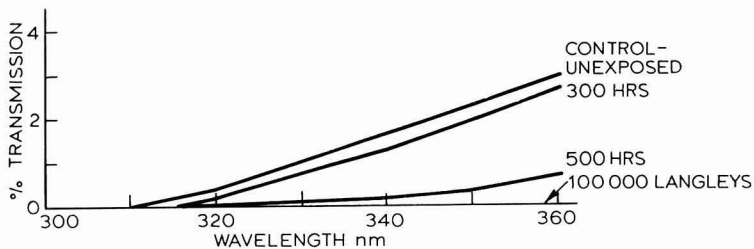


Fig. 12. Percentage transmission of black pigmented polystyrene after exposure. Pigment concentration 0.0078phr

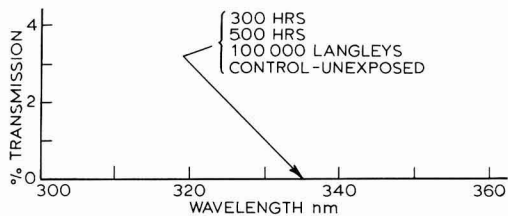


Fig. 13. Percentage transmission of black pigmented polystyrene after exposure. Pigment concentration 0.0156phr

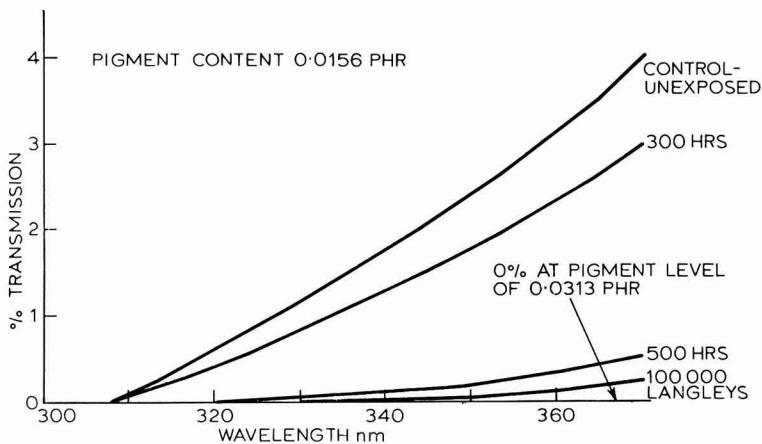


Fig. 14. Percentage transmission of polystyrene pigmented with various levels of transparent red iron oxide

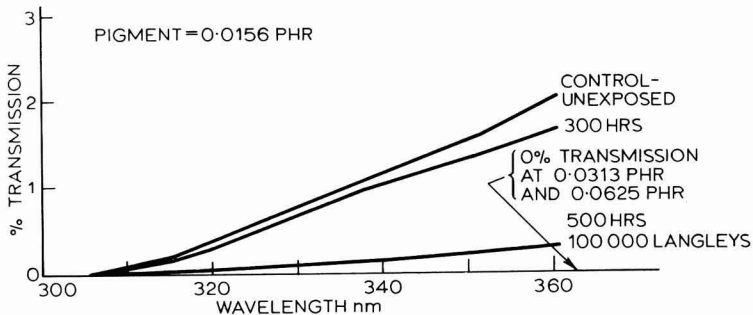


Fig. 15. Percentage transmission of polystyrene pigmented with various levels of transparent yellow iron oxide

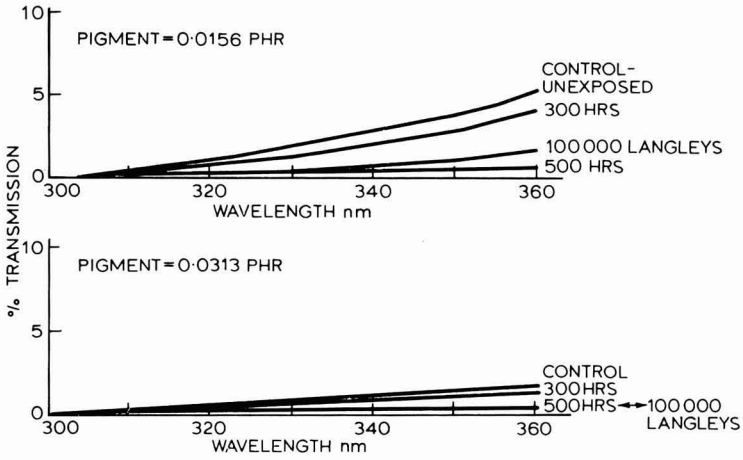


Fig. 16. Percentage transmission of polystyrene pigmented with various levels of phthalocyanine green

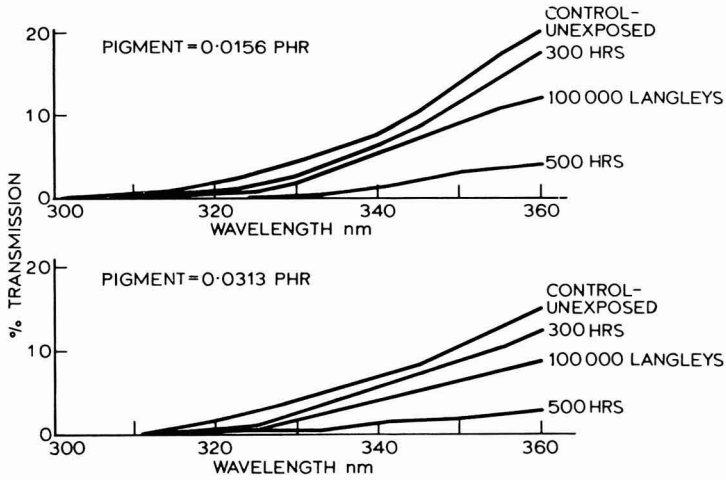


Fig. 17. Percentage transmission of polystyrene pigmented with various levels of permanent red 2B

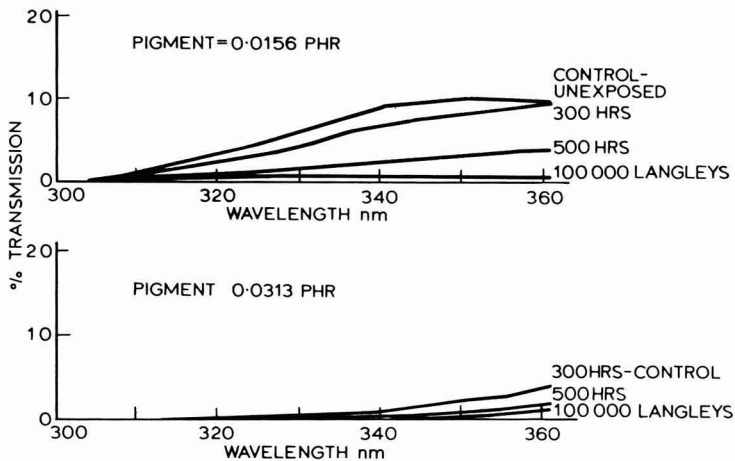


Fig. 18. Percentage transmission of polystyrene pigmented with various levels of organic yellow HR (PY-83)



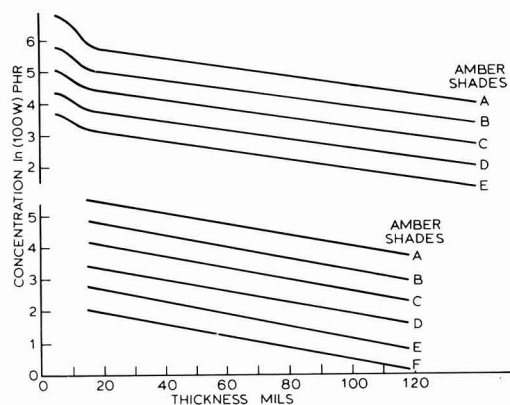


Fig. 19. Thickness vs. concentration: Polystyrene pigmented with transparent red iron oxide

In conclusion, it has been demonstrated that the transparent iron oxides, which offer the transparency of a dye and the permanency to light attributed to regular iron oxides, effectively screen out harmful ultraviolet light at concentrations low enough (0.03phr) to maintain transparency in plastics, such as acrylonitriles, polyesters, polystyrene, vinyls and polycarbonates. The absorption of the transparent yellow oxide is slightly superior to the red oxide. The oxides, whilst maintaining desired transparency, afford UV protection

Table 2

*W (grams phr) to match shade at various mil thicknesses*

Mils	A	B	C	D	E	F
10	9.90	4.95	2.48	1.25	0.619	0.309
15	3.94	1.97	0.984	0.492	0.246	0.123
20	2.95	1.48	0.738	0.369	0.184	0.092
25	2.36	1.18	0.590	0.296	0.148	0.074
30	1.96	0.983	0.481	0.246	0.123	0.061
35	1.68	0.843	0.421	0.211	0.105	0.053
40	1.48	0.738	0.369	0.184	0.0922	0.0461
45	1.30	0.650	0.325	0.1625	0.0813	0.0406
50	1.18	0.590	0.295	0.148	0.074	0.0369
60	0.985	0.493	0.246	0.123	0.062	0.031
100	0.590	0.295	0.148	0.074	0.037	0.018
118	0.500	0.250	0.125	0.0625	0.0313	0.0156

which is superior to the organic pigments with the exception of the phthalocyanine blue and carbon black. However, the colour contributions of these pigments at effective levels are considerable. When compared to a typical UV absorber, the oxides perform equally as well with the exception of some colour contribution in the visible range. Thus, it can be stated that the transparent oxides provide the plastic package manufacturer with effective pigments. The transparent red oxide, for example, provides a transparent amber similar to that required for beer and medicine bottles and food oil packaging. A myriad of amber shades are possible by blending with other transparent pigments.

[Received 31 March 1977]

## Next month's issue

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

Exciplex interactions in photoinitiation of polymerisation by fluorenone-amine systems by A. Ledwith, J. A. Bosley and M. D. Purbrick

Recent developments in photoinitiators by G. Berner, R. Kirchmayr and G. Rist

Present status of ultraviolet curable coatings technology in the United States by J. Pelgrims

The design and construction of ultraviolet lamp systems for the curing of coatings and inks by R. E. Knight

## Review

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### Liquid Chromatography of Polymers and Related Materials

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By J. Cazes

Marcel Dekker, Inc.

Pp. viii + 180. Price 65 SFrs

This book contains the proceedings of the International Symposium on Liquid Chromatographic Analysis of Polymers and Related Materials held in October 1976 in Houston, Texas. It contains 13 contributions, which include descriptions of some previously unpublished techniques. The term liquid chromatography is taken to include both high-performance liquid chromatography (HPLC) and gel-permeation chromatography (GPC) and six of the papers likely to be of most interest to research workers in the coatings field are the following:

Vivilechia *et al* report on the gel-permeation chromatography of hydrophilic polymers using silica packings modified by reaction with organosilanes. These can be used with mobile phases from hexane to water.

Hellman examines the feasibility of using GPC to obtain

intrinsic viscosities, since both are dependent on hydrodynamic volume.

Drott indicates the value of hexafluoro-2-propanol as a GPC solvent for hydrogen-bonded polymers, particularly polyamides, polyesters and polymethyl methacrylate.

Crabtree and Hewitt report on the use of both HPLC and GPC for the analysis of epoxy resin formulations for epoxy oligomer, curing agent and minor components, and thereby following changes on storage.

Nuss investigates the capability of GPC for evaluating thermosetting epoxy resin/anhydride systems through the B-stage curing cycle.

Ambler and Mate, in a study of the analysis of oligomers of various polymer types, suggest that universal calibration approaches may be used to extend molecular weight calculation techniques to lower levels than previously thought possible.

This volume is valuable for those wishing to extend the frontiers of their liquid chromatographic techniques.

L. A. O'NEILL

## Section Proceedings

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### Bristol

#### Films for packaging

A meeting of the Bristol Section took place on Friday 25 November when Mr C. R. Oswin, of British Cellophane Ltd, gave a lecture on "Films for packaging", with Mr Brooks deputising for Mrs Harper in the chair. The lecturer demonstrated the close similarity of problems associated with the use of cellophane as a packing material and the surface coating of such substrata as wood in the paint industry.

The lecturer discussed the range of films now used in industry and the difficulties when modern high class printing was required. Graphs showing the properties of these materials associated with the work of Salamee *et al*, clearly demonstrated a means of choosing the correct material for any particular conditions of use.

The Question Time was opened by J. R. Taylor and there followed a very lively discussion by all the members present. A vote of thanks was proposed by Mr A. C. Lageu and carried with acclamation.

### Hull

#### Subjective comparisons—what does influence you?

The Third Ordinary Meeting of the 1977-78 Session was held at the "George Hotel", Land of Green Ginger, Hull, on Monday 5 December. Mr T. W. Wilkinson, the Hull Section Chairman, introduced the lecturer, Dr W. E. Craker, who gave a lecture entitled, "Subjective comparisons—what does influence you". Dr W. E. Craker was aided by Mr S. P.

Smart, the co-author of the paper, in a subjective assessment of film glosses of preprepared panels before the lecture and, during question time, after the lecture.

Dr Craker began by discussing the relationship that exists between objective gloss measurements and subjective gloss rankings, with reference to the published work in this field. This led to the role played by the paint film/air interface in the optical assessment of paint films. He stated that the subjective appraisal of the film is influenced not only by the total energy which is diffusely scattered and specularly reflected at the paint/air interface, but also by factors such as image contrast, definition of image and the colour of the image. Dr Craker went on to describe viewing conditions which had resulted in operators reversing their judgments. He stressed the need for a controlled viewing condition.

After a lively discussion period, Mr J. Wenham proposed the vote of thanks. The lecture was attended by 25 members and guests. The Hull Section were pleased to welcome a group from the Newcastle Section.

#### Prediction of performance—fact or fiction?

The Fourth Ordinary Meeting of the 1977-78 Session was held at the "George Hotel", Land of Green Ginger, Hull, on Monday 9 January. The lecturer was Mr D. M. Bishop of The Railway Technical Centre, Derby, who gave a talk entitled "Prediction of performance; fact or fiction".

Mr Bishop reminded the audience of his previous lecture given to the Hull Section in February 1971, when he described the micro indentation techniques developed at the Centre and, from the results, their prediction of performance of coatings for containers and rolling stock. He stated that, seven years

A man in a dark suit and red tie is shown from the chest up. He has a serious expression. Bright green paint is splattered all over his face, including his forehead, cheeks, and chin. The paint is also on his dark top hat, dripping down the sides. The background is plain white.

# Pity he didn't know about Proxel preservatives!

What a waste – the paint stinks, so do the profits, and that's the end of a valuable customer. But with Proxel preservatives ICI has discovered the formula to save time, energy and money. They're the special preparations which give maximum protection against a wide range of paint spoilage organisms. Proxel preservatives are environmentally safe, low in toxicity, come in easy to handle liquid form and have long term chemical stability.

Compatible with both emulsion paints and latex emulsions, the range includes a variety of formulations. For details of the Proxel preservative that you need, contact your local ICI sales office.



**Organics Division** 

Hexagon House, Blackley, Manchester M9 3DA

# Looking at the water from which paint can grow

A tin of water-based paint that doesn't contain a totally effective in-can preservative can escalate into quite a nightmare. Gassing, loss of viscosity, fouling odours, modification of pH and coagulation of the latex are all the results of in-can degradation.

Dow has done something about it. We spent years researching antimicrobials for paint. Correlating laboratory data with field results. Comparing our bactericides with our competitors' on a stringent cost-performance basis.

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Painstakingly developing Dowicil<sup>®</sup> 75, the high water soluble preservative that stops in-can degradation before it starts. And concentrations from 0.05 to 0.15% are all you need.

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between a good paint and a lost reputation.

Our Technical Service and Development Department will be pleased to supply you with further information.

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c) Swan Office Centre, 1508 Coventry Road,  
Yardley, Birmingham. Tel: 021-707 2525.

Please attach this coupon to your letterheading, stating your name and send to one of the addresses above for further details of Dowicil 75.

**Dowicil<sup>®</sup> 75**  
Helps keep paint, paint.



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AK BUTTEN

later, these coatings were still sound and confirmed the expected performance based on the micro indentation work.

He continued that, in recent studies, they had found no correlation between micro indentation values and the expected performance of modern long life coatings. In fact, he doubted whether coatings were necessary, when they had evidence of a 0.004 inch thick sprayed zinc coated structure lasting 15 years, and, of a galvanised steel bridge structure, still sound after 10 years. However, where coatings were applied there was great difficulty in predicting the performance of precoated metals and PVC plastisols on treated steel.

With respect to long life coatings, he suggested ten criteria which should be considered before selecting the system. He followed by describing the range of chemically resistant paints available; specifying their intrinsic properties, and their application properties, linking these, in a table, with the criteria mentioned. He also quoted £36–£52 per tonne of steel as the cost range for these coatings.

With regard to testing, he was of the opinion that the B.S. salt spray test was too severe and recommended a half or quarter strength "Harrison solution"\*. Using this solution, they had converted a Marr Weatherometer into a large salt spray cabinet and obtained good correlation with natural exposure conditions. He then posed the question, "Which comes first, loss of adhesion, or corrosion?", claiming optimising the adhesion minimised the corrosion.

Finally, he described a test referred to as the "Pop test". In stating the principles behind the test, he said that traces of solvents left in a film are excellent plasticisers. Therefore, the coated films used in the test were cured at an elevated temperature for 30 days to ensure solvent free films. The coatings are then taken down to  $-10^{\circ}\text{C}$  and impacted immediately. Panels were removed and impacted after leaving for 2 minutes and 5 minutes at room temperature; and, after the panel had reached room temperature.

It was hoped to be able to predict the performance of long life coatings using this test.

The vote of thanks by Mr F. Gay closed the meeting after a lengthy question and discussion period. There were 20 members and guests at the lecture.

F.D.R.

\*("Harrison's Solution": 3.25 per cent ammonium sulphate, 0.25 per cent sodium chloride.)

## West Riding

### Printing ink system for textile colouration

On Tuesday 6 December, a Meeting of the West Riding Section was held at the Mansion Hotel, Leeds, when Mr F. D. Hough of Coates Bros. Ltd, presented a lecture entitled, 'Printing ink systems for textile colouration by sublimation and diffusion transfer methods'.

Mr Hough started off his lecture by giving a brief history of how he became involved in this relatively new technology of textile printing and the ways in which he overcame the initial patent problems.

Two transfer methods were detailed, the dry transfer process and the wet transfer ("Fastran") process. With the aid of a heated press, the former process was demonstrated on a piece of polyester fabric.

In discussing each process, Mr Hough outlined the types of fibres which may be printed, the application conditions, and the class of dyestuffs employed. Also mentioned, were the methods of printing used to manufacture the different types of paper transfers and the difficulties encountered in manufacturing the printing inks.

Mr Hough concluded by stressing the practical and commercial reasons for the rapid growth of transfer printing methods.

A very lively question time followed which reflected the considerable interest that had been generated. Dr Watson was called upon to give the customary vote of thanks on behalf of the Section.

### Flexible solvent free epoxy resin systems

A Meeting of the West Riding Section was held on Tuesday 3 January, 1978 at the Mansion Hotel, Leeds and the lecture was presented by Mr A. G. McKay and Mr P. T. Brown of Ciba Geigy Plastics Division.

Solvent free epoxy systems are traditionally employed in cold cure systems, such as in adhesives and flooring compositions. Laboratory studies had suggested that an increase in flexibility of a system can improve adhesion. Work on particular systems showed that adhesion improved up to the glass transition temperature of the resin and then fell away.

A programme of work was undertaken to investigate failures being experienced with epoxy mortars used as "road nosing" compositions. Originally these were formulated for high compressive strength but high modulus and transverse cracking was occurring in the nosings.

Several systems were examined and one utilising a flexible epoxy resin system, showed better stress/strain behaviour, better stress relaxation behaviour, less deformation under compression and better recovery from compressive forces. It was also shown that stress/strain behaviour for different resin systems is a function of temperature and related to the glass transition temperature. It was established in practical tests that the system which showed up best in the foregoing tests also performed best in road nosing compositions.

Little, if any, work has been carried out into the use of this type of resin system in surface coatings. However, the authors postulated that many of the properties relevant to the particular application studied also bore relevance to paint systems.

Despite marginally inferior chemical resistance compared with conventional epoxy resins, they could well prove worthy of examination for use in high build, solvent free coatings.

Following a lively discussion Mr Mike Cochrane proposed a vote of thanks for an interesting and stimulating lecture.

R.A.C.C.

# Information Received

## Increased output

A 20 per cent increase in output is claimed by the Hengrove, Bristol, factory of Berger following the installation of a fully automatic plant for water thinned paints, in addition to a considerable improvement in the working environment. The whole installation, producing up to two and a half million gallons a year, is believed to be the most advanced in the UK, and was designed and built by York based Portasilos Ltd. The installation provides for the bulk storage of pigments and extenders in powder form, various types of conveying, weigh, transfer and blowing hoppers and a punch card control system equipped with a manual override facility.

## Extended services

A new 220 MHz proton nuclear magnetic resonance spectrometer extends the range of facilities available at the Physico-Chemical Measurement Unit at Harwell. The new instrument, a Perkin Elmer R34, has just been installed and has a superconducting magnet and offers improved variable temperature and spin-decoupling facilities, which extends the range of analytical services being offered as part of the Harwell service.

## Acquisition by Kratos

As a further part of the programme of international expansion, Kratos Ltd has acquired Schoeffel Instrument Corporation of New Jersey, U.S.A. This is the third major acquisition by Kratos within the last two years. Schoeffel are manufacturers of instruments for the biochemical, analytical chemistry, medical and physical science markets and has plants in New Jersey, U.S.A. and near Hamburg in Germany.

## Rationalisation

Akzo Chemie UK Ltd have announced that they will cease to produce UK Stecatols (paint driers) from the end of January, as a part of their rationalisation programme. This product range will be available from Manchem Ltd, an RTZ Chemicals company who are one of the major manufacturers of metallic soaps in the U.K.

## 25th anniversary

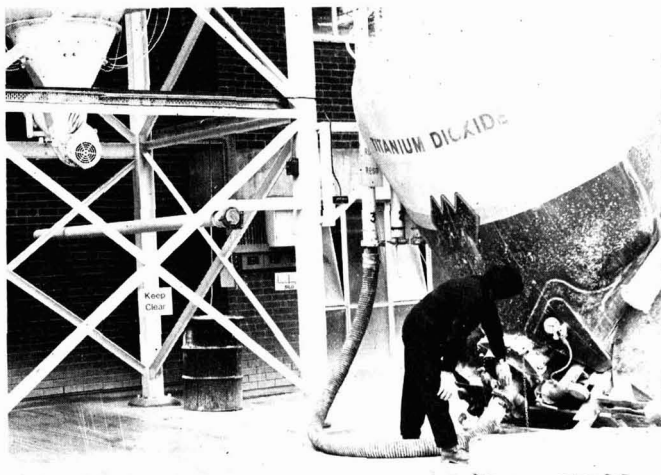
After twenty-five years on the market and with more than 450,000 tons having been sold, Du Pont has authorised additional production capacity of its Mylar polyester film with the objective of increasing total world-wide capacity 60 per cent by the early 1980s.

## Gurr products from Hopkin & Williams

Hopkin & Williams, of the G.D. Searle group, have taken over the production and marketing of the complete up-to-date range of Gurr dry stains and indicators, stain and indicator solutions, embedding and mounting media, fixatives and allied reagents and chemicals.

Hopkin & Williams have been associated with the Gurr range of dyes, stains and accessories since 1915 when a Hopkin & Williams employee, George Gurr, went into business himself on a part-time basis.

The high quality of the Gurr products will be maintained, whilst the adoption of



A bulk delivery of TiO<sub>2</sub> being fed into Portasilos at Berger Paints

Hopkin & Williams' trading terms will offer positive advantages to customers.

## New trading company

TR International (Chemicals) Ltd and Grillo Werke AG of Duisburg have formed a jointly-owned chemical trading company known as Grillo Chemikalien GmbH based in Duisburg. TR and Grillo each have a 50 per cent shareholding in the new company, which will operate under the overall supervision of the Grillo management.

The joint venture is regarded by TR as an important extension of their world-wide chemical trading activities.

## U.K. distributor

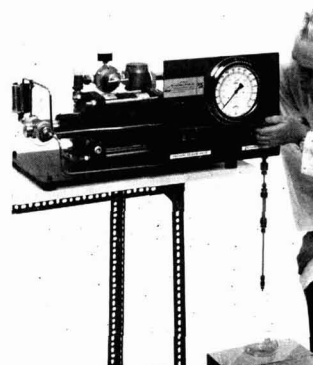
The Garrick Chemical and Equipment Company Ltd has been appointed exclusive distributor in the U.K. by Chemplast Inc. of New Jersey and will become suppliers of Chemplast's full line of high-performance plastic products. Chemplast is a leading processor of high performance plastics such as Teflon fluoropolymers, which have wide application in industrial and commercial markets throughout the world.

## New products

### Liquid chromatograph column packing

High performance liquid chromatography is used throughout industry to analyse virtually any substance which can be dissolved in a solvent. All liquid chromatographs have a column of fine particles which act as a strainer to break down substances being analysed, and one of the disadvantages is that the pre-packed columns can be contaminated and add considerably to the cost of analysis. A new system available from Olin Energy Systems Ltd, the Haskel model 29426 pump system which has been designed specifically for column packing, enables contaminated columns to be recovered and customers to

make up columns to their own specifications, using the wet packing or slurry technique.



The Haskel liquid chromatography column packing system

### New furnace blacks

The Pigments Division of Degussa, has developed two high-quality furnace blacks, called Printex 80 and Printex 90, which are recommended for the deep black colouration of plastics. Available in powder or bead form, they show improved dispersing properties which give a higher tinting strength and improved colouring efficiency.

### New Curie point pyrolyser

Orme Scientific Ltd have announced the introduction of a new Curie point pyrolyser manufactured by Fischer Instrumentation Ltd. The samples are shock heated to the Curie point temperature in only a few milliseconds using a high frequency generator and induction coil in a special pyrolyser chamber.

The sample is coated on to a ferromagnetic conductor, inserted into the pyrolysis chamber, which is then fitted through the centre of the induction coil directly into the gas chromatograph injection port. Power to the induction coil, from the high frequency generator, is automatically programmed and timed and causes eddy currents in the ferromagnetic conductor, producing the heating effect, and the almost instantaneous heating to the Curie Point eliminates the production of spurious intermediate compounds.

#### New powder coating resin

A new Beetle polyester resin for use in the production of powder coatings is now available from the Chemicals Division of British Industrial Plastics Ltd. The resin, reference L5232, is a carboxyl terminated saturated polyester resin and has been formulated for use, primarily, with epoxy resins to give a good balance of properties. Use of the resin can offer reduced curing schedules and improved mechanical properties in the form of flexibility and impact resistance. The finish obtained using L5232 will also exhibit resistance to corrosion, humidity and a wide range of proprietary household chemicals.

#### New Din cup

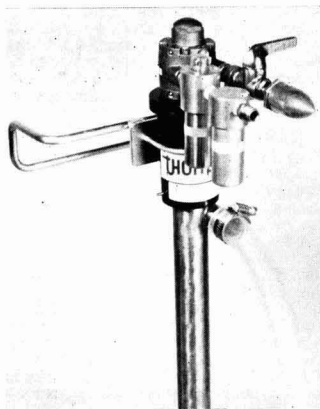
A new Din cup has been introduced by Gray-Campling Ltd, distributors of paint spraying and other equipment. The stainless steel paint viscosity measuring cup conforms to standard specifications and is supplied with an adjustable hammer finish stand.

#### New electrometer

A new combined electrometer and Model P152 power supply is now available from Analysis Automation Ltd, for the HNU Photoionisation PI 51 GC Detector. The detector and electrometer together give a significant improvement in analytical performance.

#### Portable drum transfer pumps

The Thompson range of portable drum transfer pumps with capacities of up to 20 g.p.m. has just been introduced to the



The Thompson air driven pump

U.K. for the first time by Amafilter (UK) Ltd. Easy to handle, safe and highly efficient, the pumps are of chemical-resistant construction, with a variety of material options, and are available with either electric or air drive.

#### New blender

Lightnin Mixers Ltd have introduced the Series 50 In-Line Blender which consists of a helix manufactured in equal elements that can be indexed to change blending rates or formulations quickly without the need for special tools – a feature never before offered with motionless mixers. The flow pattern required for a particular processing is created by fitting three bladed elements together into a conventional or opposed helical pattern, which offers a greater variation in blade alignment.

#### Constant power supply

For electrophoresis, constant power is essential for the optimisation of separations of sensitive macromolecules. The new Buchler 3-1501 power supply from Baird & Tatlock (London) Ltd offers this facility with output up to 200 watts as well as modes for constant voltage and constant current. The required mode is push-button selected and there is a clear digital readout of power output or voltage.



The new Buchler constant power supply with digital readout

#### Conferences, courses etc.

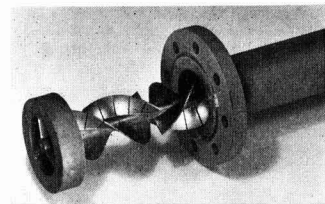
##### Paint Research Institute Symposium

The Paint Research Institute of the F.S.C.T. are organising a Symposium on photochemical processes in film formation and degradation to be held at Battelle Columbus Laboratories, Columbus, Ohio on May 1-2 1978.

##### Rheology course

A course on applied rheology for industrial chemists will be conducted for the third year at Kent State University on June 26-30 1978,

and a coatings and polymer characterisation conference will be held at the University on July 24-28 and will cover the use of many instruments for the characterisation of coatings and polymers.



The Series 50 in-line blender from Lightnin Mixers

#### Coatings Conference

A conference on protective paint coatings has been organised by Loughborough University to be held on April 5-7 1978.

#### Building handbook

The British Standards Institute has now available BS Handbook 3, the new building handbook which is an essential source of reference for architects, consulting engineers, builders etc. It contains summaries of more than 1,300 British Standards, codes of practice and drafts for development relating to building and construction.

#### Pigments and plastics

BTP Toxide Limited have published a new fifty-two page booklet which replaces their publication BTP 165 covering the most important aspects of pigmentation and the main properties of pigmented plastics.

#### Standard grades summary

Vinyl Products Ltd have recently published a new summary list of their standard products, which includes 54 grades and include pressure polymerised emulsions.

#### Printing open days

The London College of Printing has announced that visitors will be welcome to view the College at work on open days during 1978. The College buildings at the Elephant and Castle will be open daily from 13-15 June and visitors will be welcome to tour the College, see students at work and visit the various exhibitions which are to be arranged.

#### Colour technology courses

Instrumental Colour Systems Ltd are organising two residential courses on Applied Colour Technology at the Aldermaston Court Conference Centre near Reading. Courses will be held on Tuesday 28 March to Friday 31 March and Tuesday 25 April to Friday 27 April 1978.

The courses are of interest to people involved in the fields of colour management, colour specification and colour matching at all levels, and the syllabus covers the subject from an introductory level right up to the level of colorimeters and spectrophotometers linked on-line to computers.



# OCCA-30 Exhibition

18-21 April 1978 at Alexandra Palace, London

★ Belgium ★ Canada ★ Finland ★ France ★ East Germany ★ West Germany ★ Holland ★ Hungary ★ Italy ★ Japan ★ Poland ★ Spain ★ Sweden ★ Switzerland ★ UK ★ USA ★

## The continuous dialogue between suppliers and manufacturers

### New Exhibitors

The Exhibition Committee is pleased to report a number of additions to the list of Exhibitors published in the January and February issues of the *Journal*, and these organisations are mentioned below.

Any company still wishing to apply for Exhibition space should contact the Director & Secretary immediately, since there is only a very limited amount of stand space left in the hall.

It is particularly pleasing to note the return of many exhibitors from previous years, as well as new exhibitors, thus showing the strength of the support for this annual focal point for the surface coating industries. At present, there will be participation by organisations in the following 16 countries:

Belgium, Canada, Finland, France, East Germany, West Germany, Holland, Hungary, Italy, Japan, Poland, Spain, Sweden, Switzerland, the UK and the USA.

### Theme of the Exhibition

The Committee emphasises that whilst it naturally encourages the showing of new products it does not stipulate that new products have to be shown by exhibitors each year and it attaches equal importance to the advantage to personnel at all levels of meeting and discussing their common technical problems.

### Dates and times

The 1978 Exhibition will take place at Alexandra Palace, London, N.22 on the following dates and times:

Tuesday	18 April	..	09.30 - 17.30 hrs.
Wednesday	19 April	..	09.30 - 17.30 hrs.
Thursday	20 April	..	09.30 - 17.30 hrs.
Friday	21 April	..	09.30 - 16.00 hrs.

Since the lists of Exhibitors were published in the January and February issues of the *Journal*, the Association has been informed that the following companies' products will also be on display:

A. L. Process Equipment Co. Ltd (*manufacturing equipment*)  
Cornelius Group (*resins, additives, pigments*)  
Daniel—USA (*additives*)  
Flare (*pigments*)

Flavell & Churchill (*manufacturing equipment*)

Hilton-Davis—USA (*pigments*)

Kemira Oy Vuorikemia—Finland (*pigments*)

Mearl (*pigments*)

Methylon—USA (*resins*)

Oulu—Finland (*additives*)

Plastic Pumps Ltd (*manufacturing equipment*)

Red Devil Inc. (*manufacturing equipment*)

Roehm GmbH—Germany (*resins*)

The Exhibition provides an excellent annual opportunity for the technical personnel in the supplying industries to meet their counterparts in the manufacturing industries and to discuss their common technical problems. The advantage both to exhibitors and visitors of meeting in an informal atmosphere needs hardly be stressed, since the cost to exhibitors sending representatives to all the countries from which the visitors are drawn might well be prohibitive, particularly to smaller companies.

### Refreshments on stands

Exhibitors were allowed for the first time in 1977 to serve alcoholic refreshments on their stands and this innovation will be continued at OCCA-30. Many exhibitors expressed their appreciation of this as it allowed their personnel to remain on the stands with visitors for the whole period of the Exhibition.

### Information in foreign languages

As in previous years the Association will be circulating information leaflets in six languages which will contain application forms for those wishing to purchase copies of the Official Guide and season admission tickets before the Exhibition.

### Official Guide

The Official Guide to the Exhibition is now being printed and copies will be available in March for sending to all members of the Association and those requesting copies as a result of the Association's widespread publicity.

Each Member of the Association, at home and abroad, will be sent a copy of the "Official Guide" and free season admission ticket.

Members are asked to ensure that they bring their tickets to the Exhibition since otherwise the charge for admission will be made and no refund will be applicable in these cases.

As in 1977, several Sections will be organising coach parties to visit the Exhibition and any Members interested should contact their local Section Hon. Secretary. (Full Section Committee lists for 1978 were published in the January 1978 issue of the *Journal*.) For example, the Manchester Section has already organised group travel to the Exhibition by train and has negotiated a fare of just over one-third of the normal day return fare. It is also hoped that several parties will be organised from overseas to visit the Exhibition. As in previous years the Official Guide and season admission tickets will be available several weeks in advance of the Exhibition (prepayment only) from the Association's offices but they will also be available for purchase at the entrance to the Exhibition Hall. A charge is made for both the Official Guide and the season admission tickets to the Exhibition. The policy was introduced several years ago to deter casual visitors who otherwise collected large quantities of technical literature from exhibitors' stands; the policy has been welcomed by exhibitors and has in no way acted as a deterrent to bona fide visitors to the Exhibition.

### Facilities at Alexandra Palace

The Association has full use of the facilities at Alexandra Palace during the period of the Exhibition which include restaurants, two bars, a cafeteria and an exhibitors' bar. Another facility which is of considerable benefit to those travelling to the Exhibition by car is the ample free car parking space within the Palace grounds.

The Heathrow Central Terminal of the Piccadilly Line was opened by Her Majesty the Queen on 16 December. The advantage to overseas visitors travelling to OCCA 30 is enormous, as it now greatly simplifies the travelling both to hotels in Central London where they may be staying and to the Exhibition. Visitors arriving at Heathrow Airport will now be able to board a Piccadilly Line train at the Airport building itself which will take them directly to Turnpike Lane Station from where the Association will be running a free bus shuttle service to and from the Exhibition. The travelling time from Central London to Turnpike Lane Station is approximately eighteen minutes.



## News of Exhibitors at OCCA-30

### Stand 35

## Laporte Industries Ltd

Confidence in chloride process technology as the route to high performance TiO<sub>2</sub> pigments has been emphasised by the recent expansion to Europe's only proven chloride plant at Laporte's Stallingborough complex. New developments will be featured in addition to information relating to current trends in the surface coatings industry. Data will be available on many grades of the Runa TiO<sub>2</sub> pigments and Laporte's technical staff will be available for discussion during the exhibition.

### Stand 25

## Montedison Group

Montedison's Industrial Products Division is mainly engaged in the fine chemicals sector. Among the wide range of products that represent its activity in the specific field devoted to the paint and varnishes industry, special emphasis will be placed on many titanium dioxide grades for various applications, and resins and intermediates for paints.

From *Acna*, a subsidiary of Montedison, a wide range of organic pigments will be shown for use in paints, printing inks and plastics.

### Stand 80

## Cordova Chemical Co

Cordova Chemical Co., a California based firm, is presenting to the coatings industry, poly functional aziridines as crosslinkers, additives, modifiers or reactive intermediates.

Cordova's products are of interest to producers of surface coating adhesives, and other polymeric based materials. The high reactivity of the aziridines can result in rapid low temperature curing in carboxylated polymers, giving coatings greatly improved solvent resistance, water sensitivity and excellent adhesion.

### Stand 17B

## Draiswerke GmbH

Draiswerke, of Germany, are the only company which can offer mills which can either operate vertically or horizontally as the customer requires.

PM 250 TEX is designed particularly for pigment dispersion and many hundreds of

this machine are operating throughout the world; it has proved to be a most economical and reliable unit.

The Drais PM 25 STS triple cooled mill has proven itself to be a most efficient and reliable mill, with simplicity of design, ease of operation and competitive price together with an unmatched product quality on both oil and liquid inks.

The Drais disperser with patented S.T.A.R. head, has made possible, for the first time, the manufacture of offset inks and paints to a fineness below 5 microns without the necessity of further milling.

### Stand 3

## Roban Engineering Ltd

Roban will be continuing their theme of previous years by specialisation in liquid storage, pumping and metering applications. The new products on display will include the 807 AT flowmeter and the air motor driven version of the famous R300 series of positive displacement solvent pumps.

It is hoped that a Mark Two version of the R400 tanker offloading pump will also be on show.

Engineers will also be present to discuss any aspect of Roban's Turnkey project construction service for liquid, raw materials, bulk storage and distribution schemes elsewhere in the world.

### Stand 38

## Emser Werke AG

In collaboration with the U.K. subsidiary company, Grilon (U.K.) Ltd, Emser Werke AG will be exhibiting at OCCA with the theme 'Grilonit epoxy resins—nature's partners for the future', and will be demonstrating the latest Grilonit resin and curing agent developments for water and solvent-free epoxy coatings and Grilonit powder coatings based on epoxy and epoxy and polyester combinations. Powder coatings based on Grilanid Nylon 12 will also be shown.

### Stand 36

## Hercules Powder Company Ltd

Products of the Resin, Water Soluble Polymers and Pigment Departments of the Hercules Powder Company Ltd will be particularly emphasised on Stand 36 at OCCA 30. As well as improved products in the existing range, new products in all

three departments will be highlighted. In the resin group, water white resins will be featured as will higher melting, more reactive, phenolic modified resins. The increasing range of Dresinol resin based emulsions, completely solvent free, will also be displayed. Water soluble polymers from both European and U.S. sources will be featured together with initial information on the Xanthan gums to be manufactured in the U.K., and the continuing advances in pigment technology together with the fluorescent pigments from Radiant Colour will also be shown.

### Stand 47

## British Industrial Plastics Ltd

A new Beetle powder coating resin is being shown by British Industrial Plastics Ltd on Stand 47. The resin reference L5232 is a carboxyl terminated saturated polyester resin and has been formulated for use with epoxy resins to give an excellent balance of properties. It is based on recent development work carried out by BIP Chemicals Division showing the incorporation of zinc oxide into epoxy, and polyester powder coating systems results in a number of significant improvements, the most important of which are:—

Reducing curing schedules, and improved mechanical properties in the form of flexibility and impact resistance.

The main applications for powder coatings employing the new resin are expected to include car wheels, domestic appliances, light fittings and tubular furniture.

### Stands 65 and 66

## S. A. Floridienne NV

In association with:

## Micro Products Co

Floridienne is the exclusive European agent for Micro Products Inc., Yonkers, New York, a leading U.S. manufacturer of micronised waxes, and for S. C. Johnson & Son Inc., Polymer Dept, Racine, U.S.A. manufacturers of Joneryl and Versacryl acrylic polymers for printing inks and water based paper coatings. The full range of Micro Powders Inc. synthetic and polyethylene waxes, with applications in liquid and paste inks finish and wood finishes and industrial finishes, will be shown and their unique high slip range of Polyfluos will be demonstrated. From S. C. Johnson & Son Inc. the full range of

*Joneryl* acrylic polymers will be shown with applications in ink manufacture and a range of acrylic water based coatings for the packaging industry will also be demonstrated.

### Stand 51

## Neville Cindu Chemie B.V.

*Neville Cindu Chemie* will be showing their range of hydrocarbon resins including *Necires LX*, *Nevchem* and *Nevroz*. Also available will be petroleum derived hydrocarbon resins, namely *Necires L. F.* and *Nevchem*, coumarone-indene resins which go by the name of *Necires RF* and *Necires ALX-100*, low viscosity epoxy-extenders known as *Necires EPX-L* and a range of coal tar compounds having good compatibility with epoxies and polyurethanes.

### Stand 17

## KWR Chemicals Ltd

The exhibits from *KWR Chemicals Ltd* will fall into two categories:

#### Raw materials from CdF Chimie

Epoxy resins and curing agents for the paint industry. Together with alkyd resins designed for specific paint applications.

#### Products from Societe Francaise D'Organo-Synthese

(a) For paints—*Orsol* phenolic resins. For can coatings—drum linings and use as electro-phoretic primer coatings for the automobile industry.

Modified *Orsol* resins for can coatings.

(b) For printing inks—Acrylic vehicles for water based inks and coatings for water alcohol flexo and gravure printing inks.

### Stand 62

## Capricorn Chemicals

*Capricorn Chemicals* will be exhibiting at the OCCA Exhibition for the first time as a result of their take-over of the U.K. agency for the *Georg M. Langer* range of products.

They will be exhibiting the *Langer* range of additives for the paint and printing ink industries including *Lanco* waxes, *Lanco Glidd* wax dispersions, antibubble compounds, antifoat compounds and aqueous thickeners and suspending agents. Also on show will be *Allplas* Thermal Insulation Blankets which are used in industry to suppress fumes and obnoxious odours, to reduce evaporation losses and to act as a splash retardant and cut process tank heating costs by as much as 70 per cent.

## Bristol Section

### Ladies' evening

The Ladies' evening lecture was given on 28 October, 1977 by Miss Jane Wehner, who spoke on "Wines from the hedgerows". The meeting was well attended and the lecturer gave a very comprehensive survey of all the naturally occurring berries and flowers suitable for wine making found in the hedgerows during the year. Warning was also given against the use of other plants which are poisonous. The general principle of wine making was also discussed and the importance of the correct choice of the yeast used in the fermentation was emphasised. The lecturer had brought many examples of the various wines described and there was enthusiastic sampling of these products by the members present. Question time was opened by Mr J. R. Taylor and was well supported by the members present.

## Obituary

### L. Bowden

Mr Leslie Bowden, for twenty-five years Hon. Auditor of the Manchester Section, died on 13 January. The Association was represented at the funeral service by Mr H. Gosling (President 1953-55) and other Manchester Section Members.

### News of members

Mr R. Duckett, a past Chairman of the Bristol Section, has been appointed Field Service Manager, Western Region, for the Industrial Paints Division of Berger Paints. He will be responsible for technical service to the wide range of operations of the Western Region including Scotland and Northern Ireland and will operate from Bristol.

In a reorganisation of the management at Burrell Colours Limited, Mr B. R. Howe, an Ordinary Member attached to the London Section, has been appointed Director responsible for purchasing and planning, and Dr E. R. Inman, also an Ordinary Member attached to the London Section, has been appointed as Director responsible for research and development.



Mrs E. N. Harper, Chairman of the Bristol Section, is shown receiving a Certificate of Membership of the Berger Quarter Century Club, Western Section, and a gold watch for twenty-five years service with Berger Paints. Presenting the award is a former Chairman of the Bristol Section and a former Vice-President of the Association, Mr V. C. Thompson, who is President of the Western Section Club.

## OCCA 60th Anniversary



### Celebrations

11—12 MAY, 1978

As members will be aware, the Association celebrates the 60th Anniversary of its foundation in May 1978, and it is felt that members would like some details of the proposed celebrations which will take place on 11 and 12 May 1978.

The actual date of the foundation of the Association was 16 May 1918, but it has been decided that the Thursday and Friday are more appropriate times to hold the celebrations.

The May 1978 issue of the Journal will contain an article by Dr S. H. Bell, OBE (President 1965-67) on main Association events since the 50th Anniversary in May 1968. Already many companies have reserved advertising space in this important issue in order to congratulate the Association on this achievement, and others wishing to do so can obtain full details from the Assistant Editor at the Association's offices at the address on the contents page.

#### Commemorative Lecture and Dinner

The Commemorative Foundation Lecture (instituted in 1963 in memory of the late H. A. Carwood, Esq., the first Honorary Secretary of the Association) will be given in the Court Room at the Painters' Hall, Little Trinity Lane, London EC4, on the



Sir John Methven

evening of Thursday 11 May by Sir John Methven, Director General of the Confederation of British Industry. The title he has chosen is "The place of business in our society". Admittance to the Lecture will be

by ticket only and will be followed by a short reception. Dinner will be taken in the Dining Hall of the Painter Stainers' Company at 8.00 p.m. Informal dress will be worn.

Immediately following the lecture, a special commemorative silver medal will be presented to Sir John Methven by the Master of the Worshipful Company of Painter-Stainers, Sir Ralph Perring Bt., to mark the occasion.

Tickets for the Lecture and Dinner will be available from the Association's offices at a cost of £12.00 plus VAT, and members will be sent an application form giving details in due course. The price of the ticket also includes the reception between the Lecture and Dinner, wines with the meal, and port or brandy after the meal. Past Presidents, Past Honorary Officers of the Association and Honorary Members will be invited as guests of the Association.

#### Commemorative Dinner Dance

The Association's Dinner Dance will be held at the Savoy Hotel, London WC2, on the evening of Friday 12 May, and Presidents of other societies, together with their ladies, will be invited to attend.

The reception will take place in the River Room at 7.00 p.m. and Dinner will commence at 7.30 p.m. in the Lancaster Room. Arrangements for a cabaret have been made and dancing to the Jay Langham Orchestra will continue until 1.00 a.m. Dinner Jacket will be worn.

Tickets, price £15.00 plus VAT will be available from the Association's offices, and members will again be sent full details.

Non-members who wish to receive application forms should write to the Director & Secretary at the Association's offices as soon as possible, particularly if they wish to make up parties (up to 12 per table) for the Dinner Dance.

Application forms for tickets for both functions will also be available at the Association's Information Centre (Stand 32) at the OCCA-30 Exhibition being held at Alexandra Palace, London N22, on 18-21 April.

## Forthcoming Events

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

### 1978

#### March

##### Thursday 2 March

*Newcastle Section:* "The vinyl approach to marine and maintenance coatings" by Mr J. Benson of Union Carbide to be held at St. Mary's College, University of Durham, Elvet Hill Road, Durham.

##### Monday 6 March

*Hull Section:* Ladies' Evening. Visit to the Ferens Art Gallery, Hull, conducted by Mrs L. Dunn, Senior Keeper at the gallery.

##### Tuesday 7 March

*West Riding Section:* "Calcium ferrite and zinc ferrite—two new active anti-corrosion pigments" by Dr P. Kresse of Bayer, West Germany to be held at The

Mansion Hotel, Roundhay Park, Leeds 8, commencing at 7.30 pm.

#### Wednesday 8 March

*Manchester Section:* Student Works Visit to D. Macpherson Ltd.

*Midlands Section:* One day Symposium entitled "Modern methods of paint manufacture", at the Metropole Hotel, National Exhibition Centre, Birmingham.  
*London Section:* "Metal decorating in the paint and printing industries". A day

meeting in association with the Thames Polytechnic at Woolwich, SE18, commencing at 10.00 a.m.

#### Thursday 9 March

*Scottish Section:* Title, subject and lecturer still to be advised by National Corrosion Service.

*Midlands Section—Trent Valley Branch:* A joint meeting with Institute of Corrosion Science and Technology. Suggested title "Why paint it?" to be held at the Crest Hotel, Pastures Hill, Littleover, Derby at 7.00 p.m.

#### Monday 13 March

*Manchester Section:* "Toxicological problems in the pigment-using industry" by Mr M. T. Hobbs, ICI Ltd Organics Division, to be held at Room D7, Reynolds Building, UMIST, Manchester, commencing at 6.30 p.m.

#### Wednesday 15 March

*Ontario Section:* "The anatomy of the printed dot" by Mr P. Wyskowski of McLean Hunter Ltd at the Skyline Hotel, Toronto.

#### Thursday 16 March

*Thames Valley Section:* "Rheology of pigmented systems. A new low-shear instrument" by Dr M. L. Colclough of ICI Paints Ltd, to be held at The Beaconsfield Crest Motel (White Hart), Aylesbury End, Beaconsfield, Bucks at 6.30 for 7.00 p.m.

#### Friday 17 March

*Midlands Section:* "Jewellery through the ages" a Newton Friend Lecture by Mr C. Reichsollner to be held at Birmingham Chamber of Industry and Commerce at 7.00 p.m.

#### Wednesday 22 March

*Scottish Section—Eastern Branch:* Annual General Meeting followed by a Ladies' Evening which, by the kind permission of John Haig & Co. Ltd, will involve "whisky tasting" to be held at The Alfton Hotel, 6 Grosvenor Crescent, Edinburgh 12, at 7.30 p.m.

#### Friday 31 March

*Bristol Section:* Annual Dinner Dance at the Mayfair Suite, New Bristol Centre at 7.30 for 8.00 p.m.

*Irish Section:* "Organic versus inorganic coatings" by Mr J. R. Lyon, Goodlass Wall Ltd, to be held at The Clarence Hotel, Dublin 2, commencing at 8.00 p.m.

### April

#### Monday 3 April

*Hull Section:* Annual General Meeting to be held at the George Hotel, Land of Green Ginger, Hull at 6.30 p.m.

#### Tuesday 4 April

*West Riding Section:* Annual General Meeting to be held at The Mansion Hotel, Roundhay Park, Leeds 8, commencing at 7.30 p.m.

#### Thursday 6 April

*Newcastle Section:* Annual General Meeting to be held at St. Mary's College, University of Durham, Elvet Hill Road, Durham.

#### Friday 7 April

*Midlands Section—Trent Valley Branch:* Annual General Meeting to be held at the Crest Hotel, Pastures Hill, Littleover, Derby at 7.00 p.m.

#### Wednesday 12 April

*Scottish Section:* Annual General Meeting followed by "Demonstration of Hypnotism" by A. M. Hearne, MBE, at the Bellahouston Hotel, Glasgow at 7.30 p.m.

#### Thursday 13 April

*London Section:* Annual General Meeting at Rubens Hotel, Buckingham Palace Road, S.W.1.

#### Friday 14 April

*Bristol Section:* "Uses of solar energy" by Professor B. J. Brinkworth of University College, Cardiff, at the Royal Hotel, Bristol at 7.15 p.m.

*Manchester Section:* Annual General Meeting at The Woodcourt Hotel, Sale, Cheshire, commencing at 6.30 p.m.

#### Wednesday 19 April

*Ontario Section:* Annual General Meeting.

#### Thursday 20 April

*Thames Valley Section:* Annual General Meeting and talk on "Beekeeping" by Mr H. Aplin at the Beaconsfield Crest Motel (White Hart), Aylesbury End, Beaconsfield, Bucks at 6.30 for 7.00 p.m.

#### Friday 21 April

*Irish Section:* Annual General Meeting at the Clarence Hotel, Dublin 2, commencing at 8.00 p.m.

*Midlands Section:* Annual General Meeting at the Crown Hotel, Broad Street, Birmingham at 6.30 p.m.

#### Friday 28 April

*Bristol Section:* Annual General Meeting at the Royal Hotel, Bristol at 7.15 p.m.

## Register of Members

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

#### Ordinary Members

ALDERSON, GODFREY CLIFFORD, LRIC, 12 Masham Road, Hartogate, Yorks. (*West Riding*)

ANDREWS, ROBERT ANTHONY, 33 Marton Drive, Burnley, Lancs. (*Manchester*)

BOWMER, DAVID ROGER, Kenroy Dispersions Ltd, Holt Mill Road, Waterfoot, Rossendale, Lancs. (*Manchester*)

CLARK, ARTHUR STEWART, BSc, MRIC, British Aluminium Co. Ltd., Davids Loan, Falkirk FK2 7XT. (*Scottish-Eastern Branch*)

COTTON, MALCOLM, B Tech, 15 Wharfe Bank, Collingham, Wetherby, W. Yorks LS22 5JP. (*West Riding*)

DAFFERN, DAVID, BSc, 115 Puma Drive, Agincourt, Ontario M1V 1G8, Canada. (*Ontario*)

DE RUITER, FRANS, Dr. de Snoostraat 8, Bergen op Zoom, Netherlands. (*General Overseas*)

ELLIS, JOHN CEDRIC, BSc, LRIC, Robin Hole, 10 Chadfield Road, Duffield, Derby DE6 4DU. (*Midlands-Trent Valley Branch*)

GAMON, MICHAEL HUGH, 30 St. Peter's Grove, Laceby, Grimsby, S. Humberside DN37 7HD. (*Hull*)

JAMES, DAVID MICHAEL, BSc, FRIC, 14 Beaconsfield Crescent, Low Fell, Gateshead 9, Tyne and Wear. (*Newcastle*)

MEDCALFE, TERENCE, PhD, ARIC, Kon-Tiki, 6 Nursery Lane Ripponden, Nr. Halifax, Yorks. (*Manchester*)

STONE, LIONEL WILLIAM, 2 Dale View Gardens, Kilburn, Derbys DE5 0PT. (*Midlands-Trent Valley Branch*)

THOMPSON, JOHN PHILIP, 42 Dorset Terrace, Leeds LS8 3QR. (*West Riding*)

WALSHAM, RICHARD, 48 Briggsfold Road, Egerton, Bolton, Lancs. (*Manchester*)

#### Associate Members

COPELAND, IAIN GRAHAM, 64 Adswood Lane East, Cale Green, Stockport, Cheshire SK2 6RG. (*Manchester*)

DRIVER, NORMAN, Pollard Hall, Oxford Road, Gomersal, W. Yorks. (*West Riding*)

FAIN, JEAN FRANCOIS, Lorilleux Lefranc International, 161 rue de la Republique, 92801 Puteaux, France. (*General Overseas*)

TATTERSALL, DAVID STANLEY, 37 Redwood Drive, Rawtenstall, Rossendale, Lancs. (*Manchester*)

#### Registered Student

WHITELEY, PHILIP DUNCAN, No. 1 Kirkwood Way, Cookridge, Leeds 16. (*West Riding*)

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The Hon. Research and Development Officer now invites offers of papers for presentation at this Conference. Anyone wishing to submit a paper for consideration should notify his intention as soon as possible to: The Director and Secretary, Oil and Colour Chemists' Association, Priory House, 967 Harrow Road, Wembley, Middlesex HA0 2SF, England (Telephone 01-908 1086; telex 922670).

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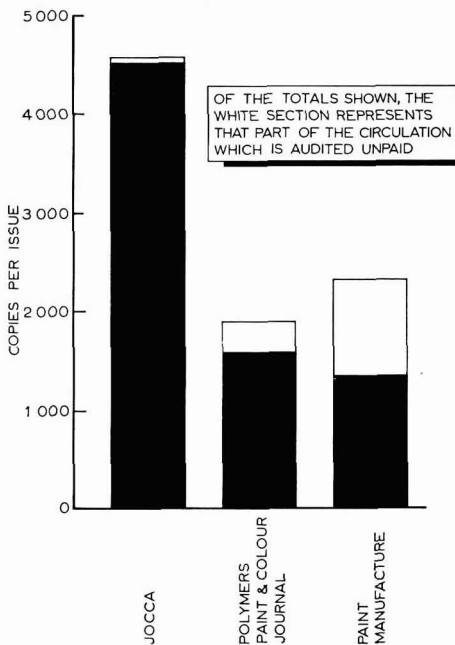
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## Comparison of circulations of U.K. publications to the paint, printing ink and allied industries



(Reference Audit Bureau of Circulations Reviews, Jan-Dec 1976)

For full details of advertising in this, and other Association publications, contact D. M. Sanders, Assistant Editor

### Journal of the Oil and Colour Chemists' Association (JOCCA)

Priory House, 967 Harrow Road, Wembley, Middx. HA0 2SF, England

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Classified Advertisements are charged at the rate of £3.00 per cm. Advertisements for Situations Wanted are charged at 80p per line. A box number is charged at 50p. They should be sent to D. M. Sanders, Assistant Editor, Oil & Colour Chemists' Association, Priory House, 967 Harrow Road, Wembley, Middlesex HA0 2SF. JOCCA is published EVERY month and Classified Advertisements can be accepted up to at least the 12th, and in exceptional circumstances the 20th of the month preceding publication. Advertisers who wish to arrange for an extension of the copy deadline should contact the Assistant Editor, D. M. Sanders, at the address given above (telephone 01-908 1086, telex 922670 OCCA Wembley).

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FRIDAY 21 APRIL	09.30	16.00

The Association will operate a free bus service to the Exhibition from (and return) Turnpike Lane Station (Piccadilly Line, London Underground).

Copies of the "Official Guide" including season admission tickets, at £2.00 each (including VAT) are obtainable in advance from the address below or at the entrance to the Exhibition.

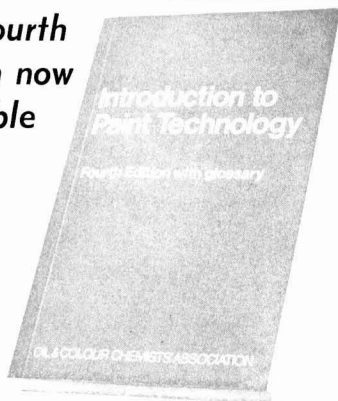
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## INDEX TO ADVERTISERS

<b>A</b>		<b>I</b>	
Ashby, Morris, Ltd.	.. .. .	iii	I.C.I. Ltd (Organics Division) .. .. . ix
<b>C</b>		<b>M</b>	
CIBA-GEIGY (UK) Ltd, Pigments (Paint) Division	.. .. .	iv	Madley, Richard, Ltd. .. .. . xii
<b>D</b>		<b>S</b>	
Dow Chemical—Methocel	.. .. .	vii	Sachtleben Chemie GmbH .. .. . viii
Dow Chemical—Dowicil	.. .. .	x	Sheen Instruments (Sales) Ltd. .. .. . i
<b>H</b>		Sub-Tropical Testing Service Inc. .. .. . i	
Highgate & Job Ltd.	.. .. .	ii	Sylvachem .. .. . vi

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## Biennial Conference PREPRINTS

The Association organises an international Conference every two years and preprints of the papers are prepared for delegates. A strictly limited number of the following are available to those who wish to have the complete bound sets of papers.

**1977 Eastbourne** *The conservation of energy, materials and other resources in the surface coatings industries.* Fourteen papers presented. **Price: £5.00**

**1975 Scarborough** *Performance of surface coatings—does reality match theory?* Seventeen papers presented. **Price: £5.00**

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CHEMISTS'

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**18-21 APRIL 1978**

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#### TRAVEL ARRANGEMENTS FOR VISITORS TO OCCA-30

For those travelling to the Exhibition by car, ample free parking space is available in the grounds of Alexandra Palace, and recent improvements to the road system include the extension of the southbound carriageway of the M1 Motorway to the North Circular Road and the flyover on that road by the new Brent Cross Shopping Centre. The extension of the Piccadilly Underground line to the Heathrow Airport Terminal gives a direct line to Turnpike Lane station from where the Association runs a free bus shuttle service to the Exhibition. The journey from central London to Turnpike Lane takes approximately 18 minutes.