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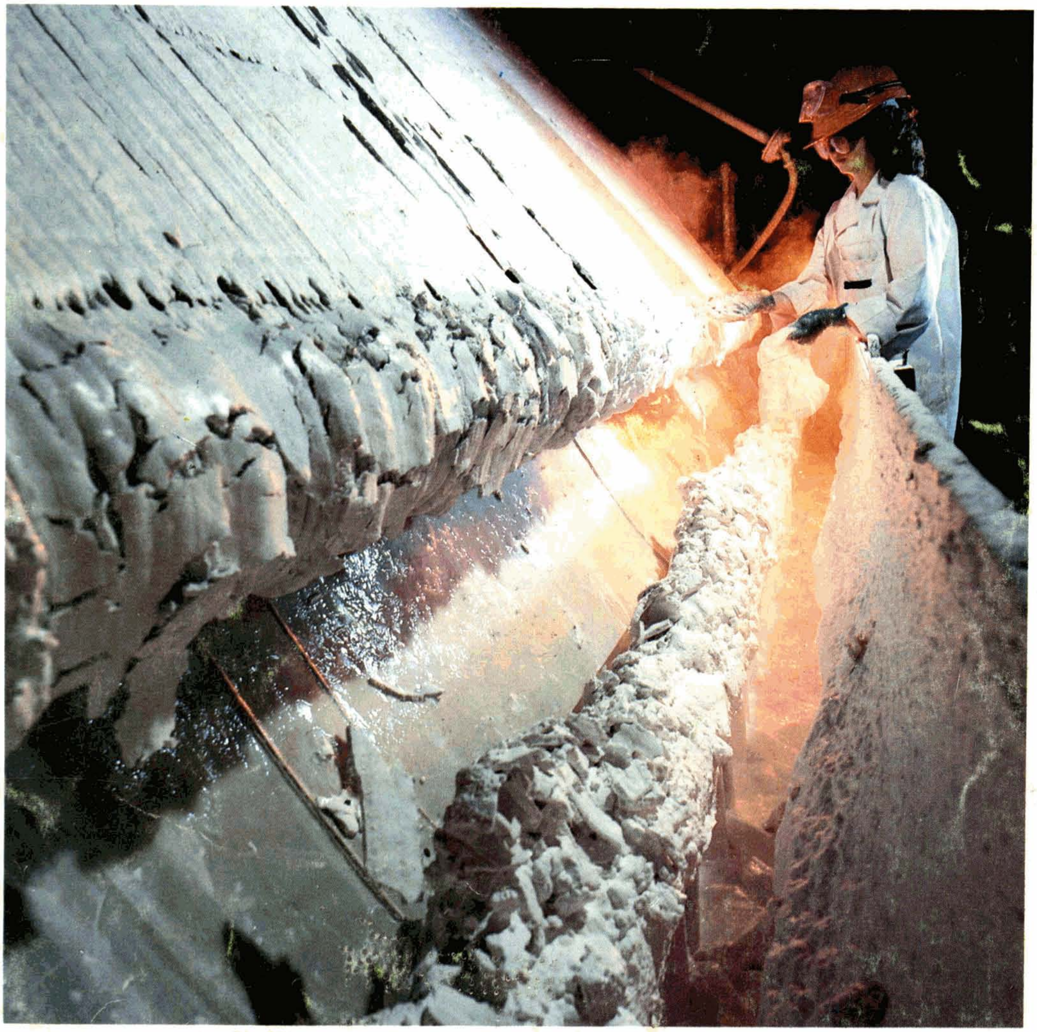

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JOCCA

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Contributions are welcomed at least five weeks prior to publication date.

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Vinamul registered for BS 5750

Vinamul, the UK market leader in synthetic resin emulsions, has gained registration to BS 5750. The registration is in accordance with BS 5750: Part 2, 1987, and covers 'The manufacture and supply of synthetic polymer emulsions' produced at the company's manufacturing site at Warrington, Cheshire.

Berberi Freres open up Cyprus office

E. G. Berberi Freres Ltd has opened up a new office in Larnaca dealing with liquid waste disposal and solvent recovery.

ASTM announces new standard test methods for inks

Philadelphia, PA — ASTM D01.56 on Printing Inks has announced the approval of five standard test methods for the evaluation of printing inks and prints.

The test methods are: D 4942, Water Take-up of Lithographic Printing Inks, D 4713, Determination of the Non-Volatile Matter of paste-type Inks and Varnishes, D 4361, Apparent Tack of Printing Ink, D 4040, Falling Rod-type Viscometer.

News in brief

Deltech Corporation USA has named **Goodyear Chemicals Europe** as a European distributor of Paramethylstyrene (PMS).

The National Physical Laboratory are setting up a **Spectrophotometry and Colorimetry Club.** For further information contact Dr G. H. C. Freeman on 081-977 3222.

Rhône-Poulenc is to invest FF 500 million at Roussillon (France) to increase the capacity of its phenol plant to 150,000 tons a year.

Harrisons & Crosfield has purchased **Pfizer Pigments Inc,** the largest producer of iron oxides in N. America, for $65m.

SCM major plant investment

SCM Chemicals Limited has announced an investment of over £14 million at the Company's Stallingborough, South Humberside, factory to ensure that its modern high technology Chloride Process Titanium Dioxide Plant will continue to meet its waste reduction targets well into the future. The plant produces SCM Chemicals' TiONA® rutile titanium dioxide pigments, major raw materials for the paint and plastics industries. In operation since the late 1960s, the plant was renovated with a multi-million pound investment to install SCM Chemicals' chloride process technology after the plant was acquired in late 1984. Waste is currently discharged under a NRA/Anglia Consent into the River Humber. This investment will significantly reduce the quantity of solids and dilute acid discharged keeping the plant in full compliance with EC Harmonisation Directives regulating waste from the titanium dioxide industry.

The chloride route is one of the two main processes available for the manufacture of titanium dioxide pigment. It has long been regarded as the environmentally preferred approach, and SCM Chemicals has gradually moved the majority of its worldwide operating capacity to this more advanced technology, reserving its older sulphate process plants for specialist products which cannot be made by the chloride process. SCM Chemicals is the world's second largest producer of titanium dioxide by the chloride process with the manufacturing operations in the United States and Australia as well as the United Kingdom.

SCM Chemicals is proposing to introduce novel technology developed at Stallingborough, to convert waste materials from the chloride process into by-product hydrochloric acid and metal oxides consisting mainly of iron. The company has developed substantial markets for hydrochloric acid in metal pickling, and this environmental protection investment will further supplement supplies.

It is hoped that the iron values in the metal oxides can ultimately be re-used, and various opportunities are currently being investigated. Initially the metal oxides will be landfilled – they are inert with extremely low dusting and leaching characteristics, prime considerations for acceptable landfilling.

The new technology has been developed and tested at the Stallingborough site over the last two years, with emphasis on recycling/re-use in combination with minimum production of material for landfill. Engineering and design work has been in progress for several months and the construction project will begin as soon as the appropriate planning permits and regulatory aspects are approved. Construction of the new plant will then take place over the next two years achieving compliance with the EC Directive ahead of the December 1992 deadline. Approximately 100 construction jobs will be created over the two-year project, followed by a small number of operating jobs.

Volstatic opens advanced demonstration laboratory

A new demonstration and laboratory facility, the most advanced of its kind in Europe, has been opened by Volstatic at their Slough headquarters. The facility enables potential and existing customers to carry out coating trials under production conditions, using a wide variety of electrostatic powder coating equipment. The laboratory contains four contrasting spray booths: Colourspeeder, Combination Autocoater, Speedcoater and Compactcoater, all fed by overhead conveyor tracks. A diverse combination of application equipment can also be demonstrated. These include Volstatic Waggler units and reciprocating units, featuring the newest Volstatic automatic powder guns, as well as electrostatic generators and the Solidspray 90XC manual powder coating system. The laboratory also includes de-greasing and a product curing oven.

Home Secretary opens new Flexcrete premises

Home Secretary David Waddington recently visited Flexcrete Limited, Preston-based world leaders in concrete repair technology, for the official opening of their new premises, housing production lines, laboratory, office and conference facilities.

The company's expansion into the new, purpose-designed, single-storey unit stems directly from the outstanding sales success of Flexcrete's high performance products, used worldwide to provide the most cost-effective and durable repair systems for defective or deteriorating concrete.

An associate company of polymer coatings manufacturer Liquid Plastics Limited, Flexcrete manufactures an extensive range of corrosion protectors, polymer modified cementitious repair mortars, screeds, renders and specialist surface coatings used on multi-storey buildings, low rise housing stock, road bridges and all structural concrete.

Following sustained sales growth, and with demand from Government Departments, local authorities and consulting engineers soaring, a significant increase in production capacity became essential. The new plant has enabled Flexcrete to double its original manufacturing capacity and will allow the company to develop and exploit further market opportunities for its products.

Unveiling a plaque to commemorate the opening of the new Flexcrete building, Mr Waddington commented "Given the scale of the problem of deteriorating concrete, the Government welcomes the introduction of repair materials of such high quality, and Flexcrete are to be congratulated on the excellence of their products and their outstanding achievements in this field."

Flexcrete Opening (L to R): R. L. Gorick, Chairman & Joint Managing Director of Flexcrete Ltd, Paul Bennison, Joint Managing Director, Flexcrete Ltd, and the Rt Hon David Waddington, QC, MP

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US Focus

By Abel Banov
Co-publisher
American Paint and
Coatings Journal

Air quality rules still up in the air

Leaders of the coatings industry have been hoping for some time that the uncertainty about air quality rules would finally be resolved last month by Congress.

But the tricks of parliamentary rules led to disappointment.

The industry's leading organization, the National Paint and Coatings Association, has been beating the legislative bushes for the past year trying to get one nationwide set of air quality rules; the purpose is to avoid having every state, small and large, set its own, frequently misguided and unnecessarily harsh regulations. The idea is to have what is called Federal preemption, which means the national government would set rules, and the states' intentions would be quashed.

In April, the upper legislative body, the US Senate, failed to include Federal preemption in the legislation it passed, mainly because of some sort of complicated rule of order. While that isn't encouraging, it's not hopeless, because the lower house still can include such a measure in the bill that it passes. If so, the two houses will get together and come up with a bill full of compromises that usually passes both legislative bodies. Senate members have expressed support for the idea, when the time comes, if some technicality doesn't mess matters.

Industry leaders are still optimistic that a set of nationwide bills will emerge from the effort.

Not unanimous support

Not everyone here wants Federal preemption, just as it isn't likely everyone in England would want a rule that would apply all over the new European Community.

Paint companies in states where the pollution problem is slight object to having to hew to the lines set nationally to assure that the worst states are adequately controlled. Understandable. It's the kind of situation likely to be encountered after 1992 in Europe.

Fight to reduce VOCs

While some battle to limit controls on volatile organic chemicals (VOCs), others are struggling to provide products that will reduce them drastically. One route is to develop reactive diluents, which serve to dilute liquid products and then react with some component to avoid evaporation. A new one was recently introduced by Union Carbide. It's hydroxyethylethylene urea, which has been found capable of improving product performance while markedly reducing VOCs.

HEEU reacts with amino resins and enhance performance of the solids in an amino coating. Gloss is enhanced, and the product has more open time when it is used as an additive for thermoplastic formulations. A white baking enamel cured with a melamine had excellent hardness after a 20-minute bake at 350°F.

Corrosion inhibitors in waterborne epoxies

A recent study by Hi Tech Polymers showed that care must be taken in selecting corrosion inhibitors to be used with waterborne epoxy.

Found acceptable were zinc phosphate; a co-precipitated blend of zinc phosphate and a proprietary organic corrosion inhibitor; basic lead chromate; and strontium chromate.

The report on the study was made at the Annual Meeting of the Southern Society for Coatings Technology last month by Mike Jackson, who said that the research undertaking found that formulations were consistent with a ratio of 88 per cent epoxy and 12 per cent inhibitive pigment at a Pigment Volume Concentration of 38 per cent and a Q-value of 0.7. The anticorrosive pigment level was one lb per gallon.

He reported that although waterborne epoxies are sensitive to humidity and are subject to flash rusting. These problems can be overcome with available additives, he claimed.

New TiO_2 grades on their way

While no-one seems to be complaining about titanium dioxide – especially in the last few years of shortages – but SCM Pigments Div. isn't waiting for complaints. It has developed new grades, one a medium durability grade (MDHG), and the other a high durability high gloss grade (HDHG), which will give both durability and gloss in one product.

The new improved grades have been achieved by narrowing the particle-size distribution of the pigments and by eliminating whatever harms gloss and durability.

The MDHG grade is better for latex because it is alkaline, and HDHG, also alkaline but less so. MDHG is optically equivalent to present gloss grades, while HDHG has improved tint strength, so less is needed for given opacity.

People

New Director for the Paintmakers

*M*oira T. McMillan BSc has been appointed the Director of the Association. She is an honours graduate in Chemistry from Southampton appointment. PA Members' interests, and those of the industry at large, Britain's £1.5 billion paint turnover; they employ some 20,000 people.

Mrs McMillan (41) was formerly Manager of Corporate Development and Head of International Trade with the UK Chemical Industries Association. She is an honours graduate in Chemistry from Southampton University. Before joining CIA in 1976 she worked for Mallory Duracell, where she specialised in R & D on body-implanted batteries for heart pacemakers.

She is married to Bill McMillan, who heads a specialist chemical federation based in Brussels. They live in Turners Hill, West Sussex, where she is a Parish Councillor.

The former Director of the Association, Michael Levete, who retired earlier this year, said, "I am delighted with the news of this appointment. PA Members' interests, and those of the industry at large, will be very well served by Mrs McMillan. I believe that under her direction the Association will continue to adapt itself to change and solve all the challenges of the nineties." Bill Moffat has taken over as acting Director until Mrs McMillan arrives in mid-June.

Equipment

New Eiger electronic drive

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EXDRIVE

*T*he first of a range of "Variable Speed AC Electronic Drives" for use in Hazardous Areas has been introduced by Eiger Torrance. The unit called "EXDRIVE" features a compact, purpose designed enclosure containing an "AC Single Phase Input Inverter" with three phase output. The enclosure is a cast body to a modern design suitable for wall mounting or can be fixed from the rear to a free standing panel.

For further information Enter F101 ■

Back to basics:
Opacity and titanium dioxide pigments

by J. G. Balfour, Tioxide UK Ltd, Central Laboratories, Portrack Lane, Stockton-on-Tees, Cleveland, TS18 2NQ, UK

Summary

Opacity is a very complex subject which has been described in many publications. Very often these have been difficult to fully comprehend by newcomers to the field, because of the large mathematical content. This paper is an attempt to describe the basics of opacity in a relatively simple, non mathematical fashion. It considers factors affecting opacity with particular reference to titanium dioxide pigments in paint systems.

What is opacity?

In many instances opacity is a desirable, or even necessary, property in a large number of materials encountered in everyday life. For example, if the paper on which this is printed was not opaque, it would be very difficult to read because the print from the subsequent pages would show through. If the ink used was transparent, it would be even more difficult to read. Opacity in clothing is a vital means of covering embarrassment!

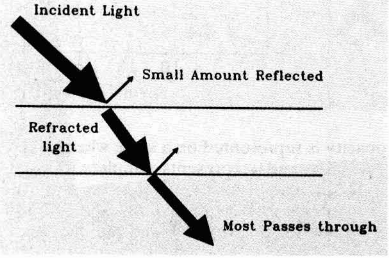
What is opacity?

Opacity, sometimes known as hiding or covering power, is the capability of a material to obliterate whatever is behind it from view. It is achieved by preventing light from passing through the material by either reflecting it back or absorbing it.

Considering the example of a paint film, in order to maximize opacity, the aim is to minimize the amount of light passing through it.

Figure 1 is a schematic diagram of a paint film which has virtually no opacity because it contains no pigments.

Figure 1
Unpigmented paint film



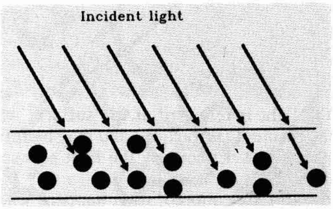
Light strikes the surface at which some is reflected giving a little opacity, but most travels through. A further amount is reflected at the bottom surface. The quantity reflected depends on the angle of the incident light, the refractive index of the film and the substrate to which it is attached. None of these parameters are readily controlled by the paint formulator.

What are pigments?

Pigments are small insoluble particles which affect light. They are incorporated into materials to impart opacity and colour and do this by absorption and reflection of light.

Figure 2 shows a paint film which contains a black pigment which absorbs all light. If enough black is present, this gives a high opacity through absorption alone.

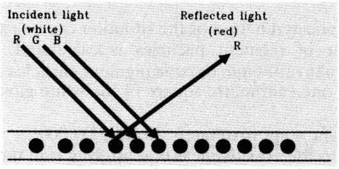
Figure 2
Paint film pigmented with black which absorbs all the light allowing none to pass through



Under normal lighting conditions, light can be considered to be a mixture of constituent lights, as seen when looking at sunlight which has been separated by rain droplets into the constituent colours of a rainbow. This concept can be simplified further by considering "white" light to be made up from three coloured lights, red, green and blue.

Figure 3 shows a paint film containing a red pigment.

Figure 3
Paint film pigmented with red pigment



The green and blue parts of the incident light are absorbed by the pigment whilst the red is reflected. The reflected light is what an observer sees and, in this case, he would see a red paint. The wide range of colours seen in surface coatings are achieved through various combinations of pigments but the principle described above remains the same. Some of the light is absorbed and that which remains and is reflected dictates the colour which is seen. With coloured pigments, the opacity achieved is normally much greater with inorganic, rather than organic pigments but, because of limitations on the shades that can be obtained with inorganics, the use of organic pigments is often a necessity.

Very often white pigments are also used, not only to give the desired shade, but to impart opacity through multiple reflections and refractions of light

White pigments

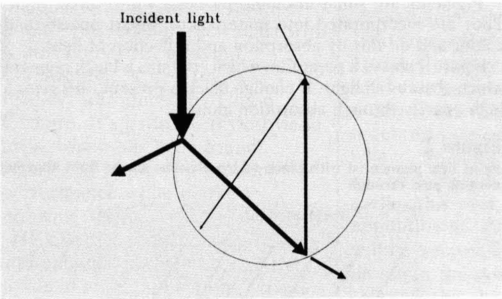
What makes a good white pigment?

The primary requirement is that it should be efficient at scattering light. Scattering is merely a series of multiple reflections and refractions that take place at the interface between the pigment and its surroundings, normally a resin.

Figure 4 shows how light can be reflected and refracted at the surface of the pigment which is represented here as a sphere.

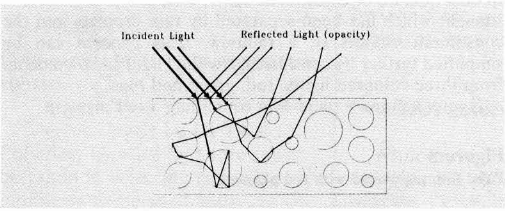
Figure 4

Light scattering by a white pigment particle



Some of the light is reflected at the surface, whilst some passes into the pigment (refraction) and may be refracted out or internally reflected. Effectively the light gets scattered in many directions.

Figure 5 gives an indication of what happens when there is a concentration of pigment particles.



The complicated nature of the situation can be envisaged if the number of pigment particles is calculated. A Question–How many titanium dioxide pigment particles would you expect in a one centimetre square of the white gloss paint on your door?

The answer – approximately 30,000,000,000!

The key to the effectiveness of scattering is in the property known as refractive index (RI), the higher the RI, the higher is the scattering power of the pigment. The RI of a material can be considered as the extent to which light is bent when it passes through its surface. See Figure 6.

Figure 6

RI is related to the amount the light is bent

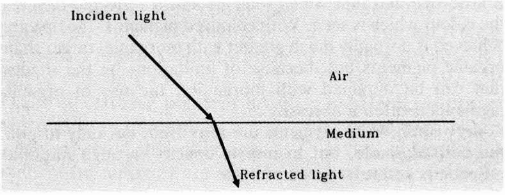
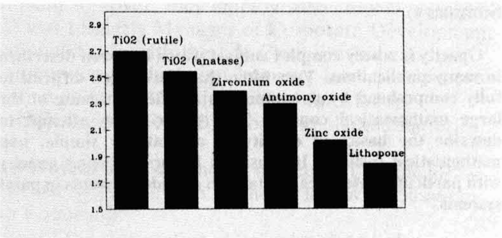


Figure 7 shows the RIs of several white pigments. The degree of scattering depends on the difference in RI between the pigment and the medium surrounding it which, in a paint, is normally about 1.5. Thus, a pigment with a RI of 1.5 gives virtually no opacity to a paint whilst one of 2.7 gives high opacity. This puts the relative values for these pigments in perspective and explains one of the reasons for the dominant position of titanium dioxide as a white pigment.

Figure 7

Refractive indices of some white pigments



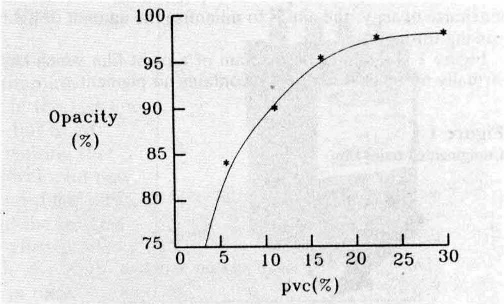
Pigment concentration

What effect does TiO_2 pigment concentration have on opacity? It is useful at this stage to define the units of concentration. As the optical properties are more closely connected to the spatial characteristics of pigment particles at is preferable to think in terms of volume. The concept of pigment volume concentration (pvc) is useful for this. The pvc, normally expressed as a percentage, is the volume of pigment relative to the total volume of the dry paint film.

Figure 8 shows the effect on opacity of a white gloss paint when the concentration is increased from zero to a pvc of 30%.

Figure 8

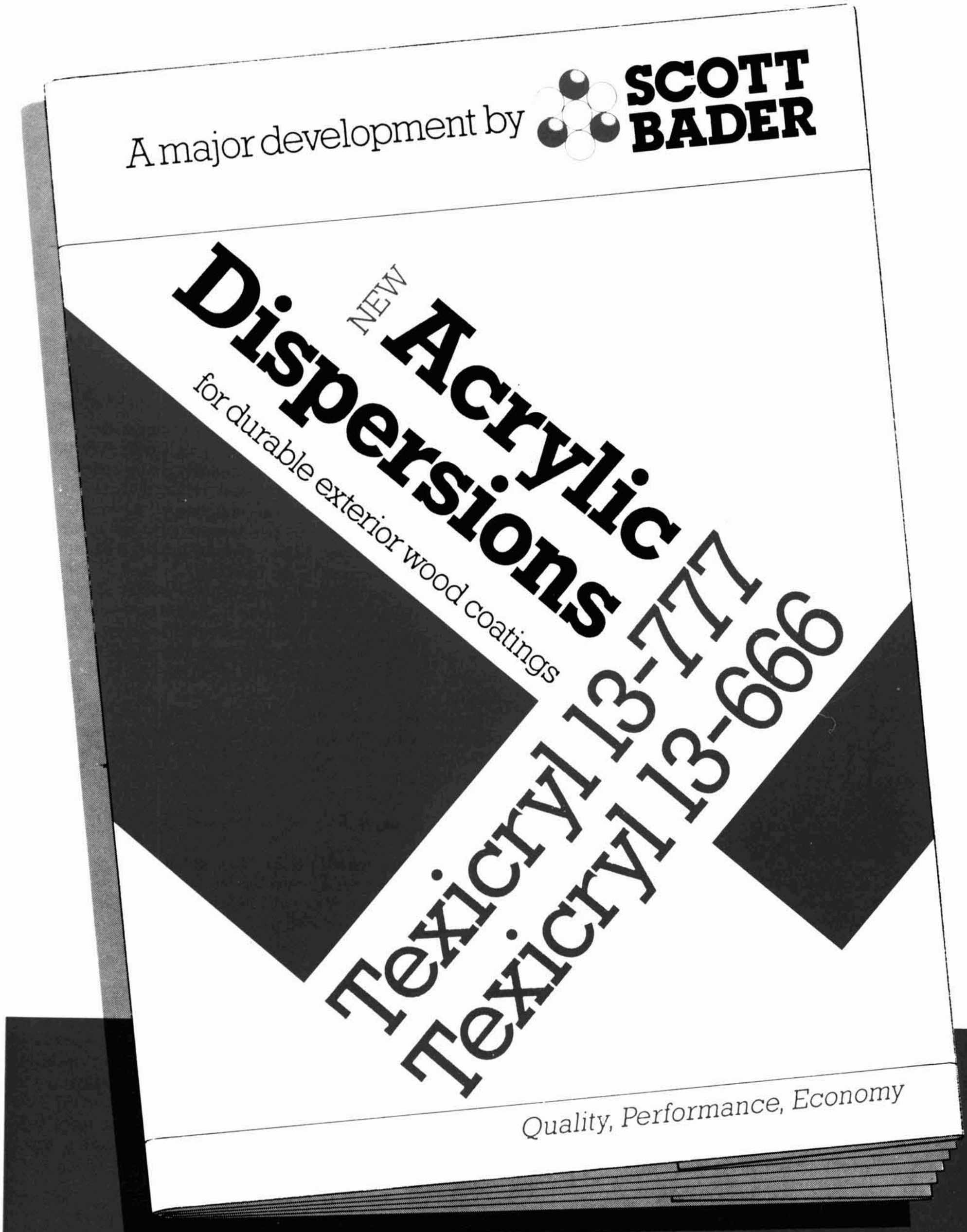
Effect of pigment concentration on opacity



The opacity is represented on a scale where 100 represents complete opacity and 0 represents complete transparency. Up to about 10% pvc the opacity increases in proportion to the amount of pigment but above this level the individual particles do not act as efficiently and the increase in opacity becomes less than proportional. Eventually the opacity reaches a maximum and further increases in concentration above about 30% can lead to a decrease in opacity.

Crowding effect

The above loss of scattering efficiency is due to what is known as the crowding effect. Because light is in the form of waves, and TiO_2 particles are small, about half the wave-



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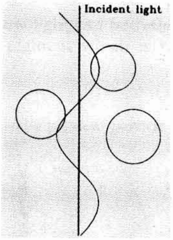
length of light, the light interacts with the pigment particles and makes them act as if they are bigger than they really are as shown in Figure 9.

Figure 9

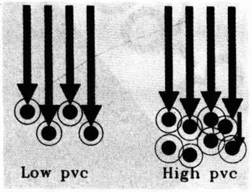
Because of the wave nature of light it impinges on particles offset from the straight line



Thus the pigment particles can be considered to have what is described as a sphere of influence surrounding them and when the concentration reaches a certain level these spheres overlap and consequently each of the particles scatters less light which gives rise to the loss of scattering efficiency as shown in Figure 10. Also, it can be seen that particles further into the film are hidden from the incident light and do not have the opportunity to scatter it.

Figure 10

Individual pigment particles can scatter light more effectively when well spaced from each other (low pvc)



To summarize, increasing the pvc upto about 10% will give a proportional increase in opacity. In the 10%-20% region the opacity will still increase but at an ever decreasing rate. From approximately 20%-30% the increase in opacity will be even less making it, very probably, uneconomic to use this level. Above 30% the opacity is likely to decrease. The precise effects will vary depending on the pigment grade used and the formulation it is used in.

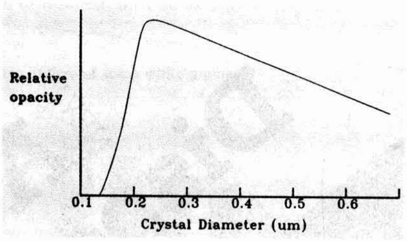
Crystal size and particle size

The terms, crystal size and particle size, are often used interchangeably which is incorrect. Crystal size refers to the fundamental size of the crystal and is controlled solely by the TiO_2 manufacturer. Particle size refers to the overall size of the particles in a given system. These particles may comprise either single crystals or particles containing a number of crystals which are bound together. The particle size is thus controlled by the pigment user and is related to how well he has dispersed the pigment. In an ideal world all the pigment agglomerates would be broken down to single crystals during dispersion but this is never achieved. Because particle size is such a variable it is easier to relate optical performance to crystal size and Figure 11 gives an indication of its effect on opacity.

To put precise figures on such a diagram is misleading because of the influence of so many other factors involved, especially concentration, but it does indicate that the optimum size should be just over 0.2 microns for normal paint applications and that to move far away from this size, either higher or lower, would have a severely detrimental effect on opacity.

Figure 11

An indication of the effect of crystal size on opacity



In some applications, notably plastics, where the concentration of pigment used can be much less, smaller crystal size pigments are used in order to optimize the opacity. For example, if the size of crystal was reduced from say 0.24 microns to 0.18 microns the number of crystals would increase by 2.4 times for the same weight or volume of pigment. This increase would give an opacity advantage at very low pvc's because of the increased number of scattering sites even though each individual site was less efficient. This is known as the population effect. If, however this lower size was used in a higher pvc paint, the opacity would suffer as the crowding effect would be much greater because of the greater number of particles. The nett effect would be a loss of opacity.

It should be mentioned that the crystal size also has an effect on colour. A larger crystal size tends to give a slightly brown tone, whilst a lower size will give a tendency towards a bluer tone.

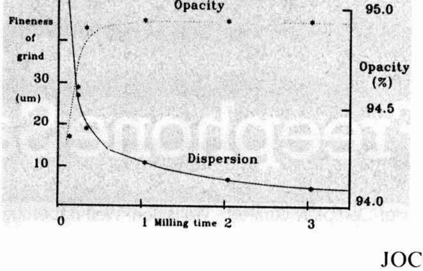
State of dispersion

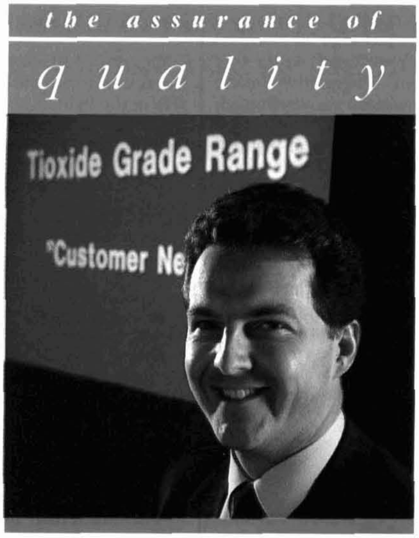
It was mentioned earlier that pigment has to be incorporated or dispersed into the medium in which it is going to be used. The state of dispersion is of fundamental importance. What is the state of dispersion? It is the extent to which pigment particles are broken apart by milling and remain separated afterwards. This is affected by the degree of milling and the tendency towards pigment flocculation.

The effect of milling on opacity is relatively slight. Most of the agglomerates are broken up very quickly and the majority of the milling time is spent breaking down a small number of larger particles. This number is so small that it has little effect on opacity. However, it is still necessary to do this as this small number will be readily visible in a paint film in the form of nibs, affecting the gloss and appearance of the finish. Figure 12 shows the opacity development with milling time.

Figure 12

Effect of milling time on opacity and fineness of grind





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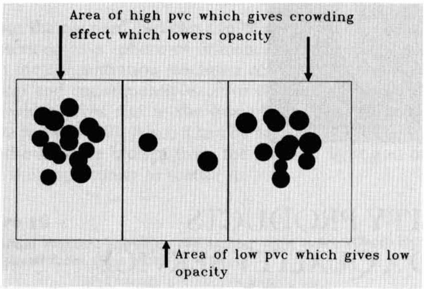
It also shows that much longer is required to achieve a satisfactory dispersion rating (perhaps less than 10 microns) for the same paint. No time units are included as the time would depend on the milling conditions. The relative time to achieve good dispersion and optimum opacity is unaffected

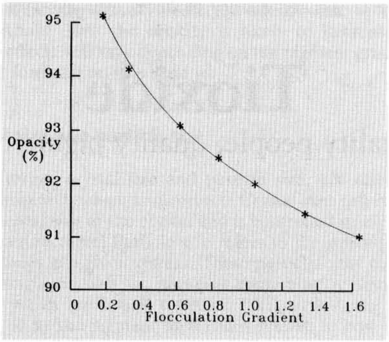
The extent of flocculation has a considerable effect on opacity. Flocculation is the formation of clusters of pigment particles after they have been milled. In most circumstances the pigment manufacturers will treat the surface of the pigments such that flocculation is kept to a minimum. However, there are many circumstances in which it is impossible to predict what the pigment user's conditions will be and the possibility for flocculation to occur may be high. When these pigment clusters are formed, areas of low and high pvc are generated as shown in Figure 13.

Figure 13
Pigment flocculation in a paint film


Area of high pvc which gives crowding effect which lowers opacity
Area of low pvc which gives low opacity

The areas of low pvc have low opacity because there is insufficient pigment and in the areas of high pvc the particles are close together and the crowding effect comes into play again causing a loss of opacity. It is possible to measure the extent of flocculation through a technique which gives what is called a flocculation gradient, the higher the value, the greater is the degree of flocculation. Figure 14 shows the effect that flocculation has on opacity for a typical gloss paint formulation.

Figure 14
Effect of flocculation on opacity

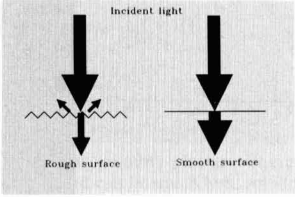


To put the numbers in perspective, values for flocculation gradients from about 0.2 up to 0.9 can be found in commercially available paints. Apart from having adverse effects on other properties such as colour, gloss and durability, flocculation means the inefficient use of the available scattering power of the pigment and, in most cases, means that significant raw material cost savings or quality improvements could be made if flocculation was minimized.

Nature of the film surface

Opacity is affected by the surface roughness of the film. Because a rough surface has a greater surface area and can reflect the light at a variety of angles, less light goes into the film and, consequently, the opacity is greater than with a smooth film. This is shown diagramatically in Figure 15.

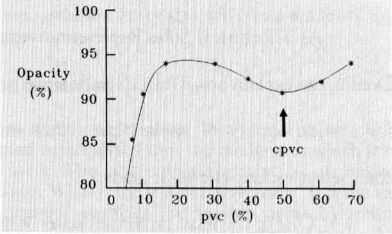
Figure 15
Effect of surface roughness on opacity



Incorporation of air

The scattering power of a pigment depends on the difference in refractive index between the pigment particles and the medium surrounding them. If this difference is increased through lowering the RI of the surrounding medium, for example through the inclusion of air, an opacity increase would occur. Figure 16, a continuation of Figure 8, illustrates this.

Figure 16
Effect of pigment concentration on opacity



The opacity increase at about 50% pvc occurs because there is insufficient medium to completely surround the pigment and, consequently, pockets of air are included in the film increasing the scattering power of the pigment. This phenomenon is often exploited with emulsion paints but in this situation most of the particles present would be extenders. Extenders have a RI similar to most paint media and would not contribute to opacity in a completely bound paint. When air is included, however, the RI difference between extender and air is sufficient to give significant opacity. The concentration at which air becomes included in the film is known as the critical pigment volume concentration (cpvc) and is a point at which a number of other properties change. For example a deterioration of film integrity normally occurs. Paints formulated above the cpvc also show a reduced wet opacity which can cause decorators problems. When the paint is wet the pigment and extender is surrounded by medium and water and it is only when the water evaporates that the RI difference becomes significant through the inclusion of air. Thus, such a paint is often characterised by a large increase in opacity on drying.

Some products are available on the market which contain encapsulated air and operate using the same principle.

Continued on p.245

OCCA Chester Conference Paper

Profitable application of research and development for novel anticorrosive pigments

by O. Leblanc, Colores Hispania S.A., Josep Pla 149, 08019 Barcelona, Spain

Abstract

The methodology involved in a search through the cumulative evidence of suitable replacement products for chromate based anticorrosive pigments is discussed. Tests included strictly chemical experiments with candidate materials, and an extensive use of conventional and improved accelerated and outdoor exposure of painted panels. Useful information was drawn from a thorough examination of a water immersion test originally regarded as a quality control method. The search resulted in three products being made commercially available, of which one showed a specially broad application potential, this is further stressed by an innovative approach to evaluating cost effectiveness.

Why launch a programme?

Most self-respecting authors start papers on anticorrosive pigments by stressing the incidence that corrosion control has on the overall economics of their country, their continent—or the world. Let this writer also be allowed to admit this, the company he works for has for many years been making a sizeable part of its living out of chromate based anticorrosive pigments. It was therefore only natural that the company should seek and make available replacement materials should the time come when chromates were no longer required by the market.

Zinc Phosphate vs Zinc Chromate

Zinc Phosphate has for a long time been available as the most acceptable alternative to chromate based anticorrosive pigments (at least in Europe). Colores Hispania was among the many companies who once thought this material would have a bright future, thus helping to contribute to the European production overcapacity of a pigment that in the end did not fulfil expectations.

Nevertheless, the obligation was felt to identify as closely as possible the reasons for the lack of success of Zinc Phosphate, and at the same time get a better understanding of its actual performance in relation to Zinc Chromate, the most widely used of the chromate based anticorrosive pigments. Accordingly, a preliminary study was launched, in which the performance of Zinc Phosphate and Zinc Chromate would be assessed, together with that of a true extender (Barytes) and a far lesser soluble, non-carcinogenic, possibly less effective chromate pigment: Lead Chromate. The candidate "anti-corrosive" pigment compositions tested are as listed in Table 1. Several approaches to paint formulation were tried:

a) A deliberate very low loading of pigments, keeping the ratio of Pigment Volume Concentration to Critical Pigment Volume Concentration (referred to as Reduced Critical Pigment Volume Concentration by some authors[1], henceforth referred to throughout this paper as Fraction of CPVC—or FoCPVC for convenience) to 0.25.

b) A compromise PVC of 25%, representative of a likely standard procedure for pigment evaluation irrespective of more accurate data being available. (FoCPVC not taken into account, as sometimes met in practice.)

c) A FoCPVC value of 0.80 representing a closer approach to desirable formulating practice for air drying alkyd based primers which are normally to be top-coated.

All paints were applied to two different dry film thicknesses, namely 8 and 20 microns for single coat systems. Besides this, duplicate panels of each kind were topcoated with a white air drying alkyd finish of PVC 20% to allow for total dry film thicknesses of respectively 18 and 35-40 microns (primer plus top coat). Panels were then exposed to several testing environments, as detailed in Table 2.

Table 1

Pigment compositions used in preliminary Zinc Phosphate vs Zinc Chromate tests.

1. 100% Zinc Chromate
2. 100% Zinc Phosphate
3. 100% Lead Chromate
4. 100% Barytes
5. 10:90 Zinc Chromate + Zinc Phosphate
6. 10:90 Lead Chromate + Zinc Phosphate
7. 20:80 Zinc Chromate + Iron Oxide
8. 20:80 Zinc Phosphate + Iron Oxide
9. 20:80 Lead Chromate + Iron Oxide
10. 20:80 Barytes + Iron Oxide

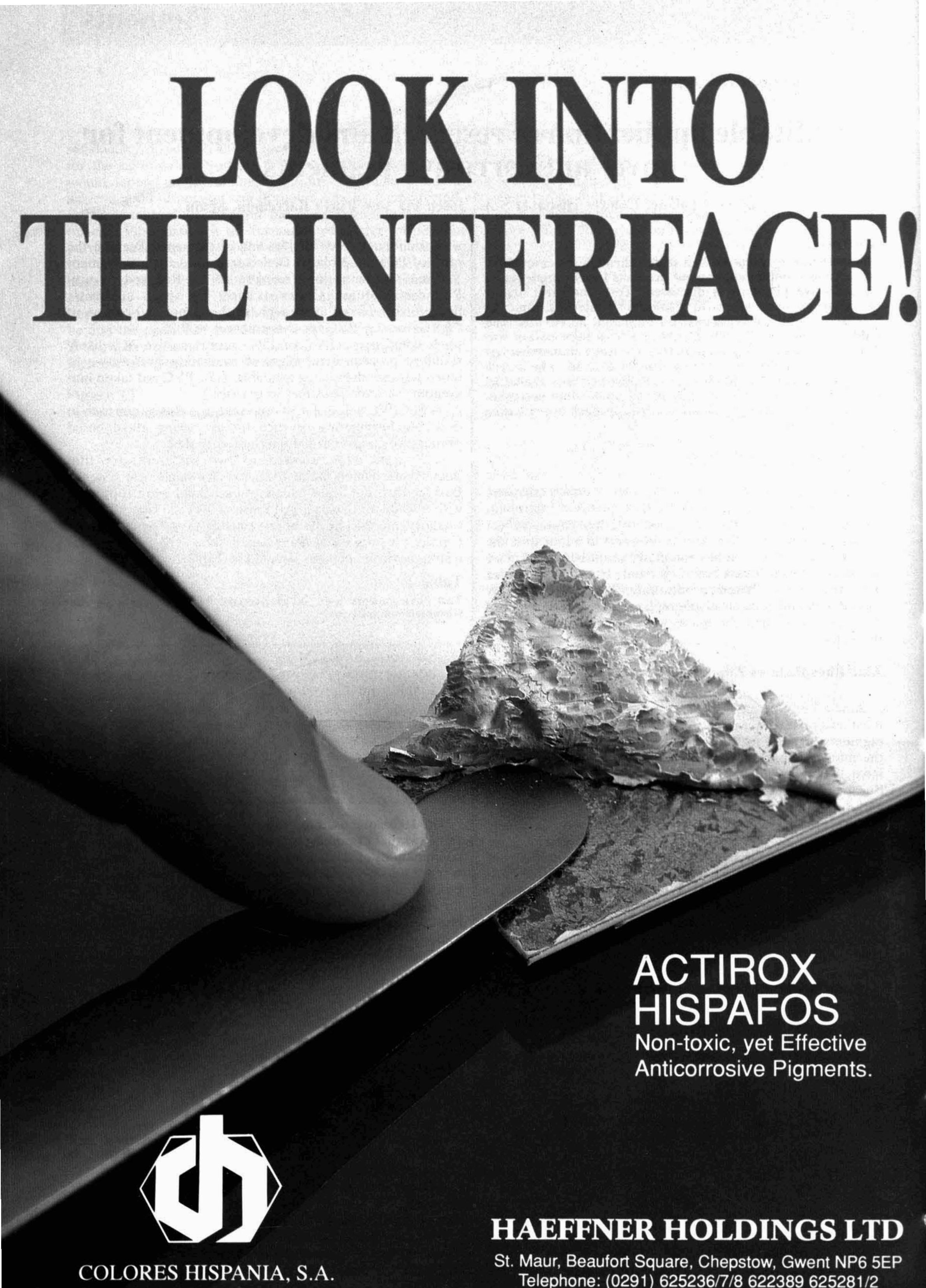
Table 2

Test environments used in preliminary Zinc Phosphate vs Zinc Chromate comparisons.

(a) Salt spray to ASTM B-117, cyclic test consisting of 20 hours exposure followed by 4 hours during which the panels were allowed to dry.
(b) Salt spray to ASTM B-117, cyclic test consisting of 20 hours exposure followed by 4 hours during which the dry panels were exposed to UV radiation.
(c) Outdoor exposure, in a mild industrial/rural environment at Colores Hispania's factory in Martorelles, near Barcelona.

The technique used to draw meaningful results from these tests was that of ranking all panels in each class or in selected combinations of classes, arranging them in order from best to worst results by visual examination. As examples of the use of this technique, complete results are given in Appendices AA through to AD for some of the relevant combinations. The most useful findings of this preliminary study were the following:

1. Zinc Phosphate alone does not stand up to the performance of Zinc Chromate or Lead Chromate when tested by the salt spray test. This is especially true for dry film thicknesses below 20 microns, or for pigment/extender combinations where anticorrosive pigment accounts for only a small fraction of the total. (Figure 1.)
2. In an outdoor mild environment, the performance of Zinc Phosphate is even better than that of chromates, provided that the primer is protected from UV radiation, be it by means of a highly UV absorbent pigment (Iron Oxide) or by topcoating with an opaque finish. (Figure 2.)
3. It is self evident from the above points that there is a complete lack of correlation between the results of accelerated salt spray tests (the standard ASTM B-117 version) and performance in a mild outdoor environment. (Figure 3.)
4. Paints formulated to lower FoCPVC values perform best to accelerated tests only when Zinc Chromate is used as the sole pigment in single coat application. For other pigments or pigment/extender mixtures, best results with regards to



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corrosion protection (as rated by visual examination of panels prior to and after striping the paint coating) are obtained from the use of higher values of FoCPVC. Only when adhesion alone is checked after outdoor exposure, irrespective of general corrosion protection, does advantage fall again to the lower FoCPVC side.

Figure 1

Performance of Zinc Phosphate to Salt Spray depending on thickness. Top row: 40 microns. Bottom row: 18 microns. Primer plus top coat systems. Coatings removed to show appearance of substrate after 28 cycles of Salt Spray. Pigments (left to right): Lead Chromate, Zinc Chromate, Barytes, Zinc Phosphate.

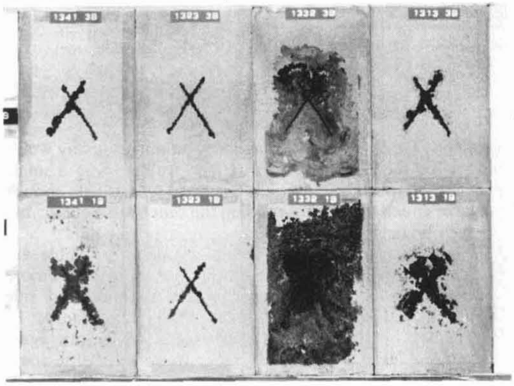


Figure 2

Incidence of UV on the performance of Zinc Phosphate. Panels with primer only exposed to weathering in Martorelles. Top row: 100% "Anticorrosive" Pigment. 13 months exposure. Bottom row: 20:80 "Anticorrosive" Pigment/Iron Oxide. 25 months exposure. Pigments (left to right): Lead Chromate, Zinc Chromate, Barytes, Zinc Phosphate.

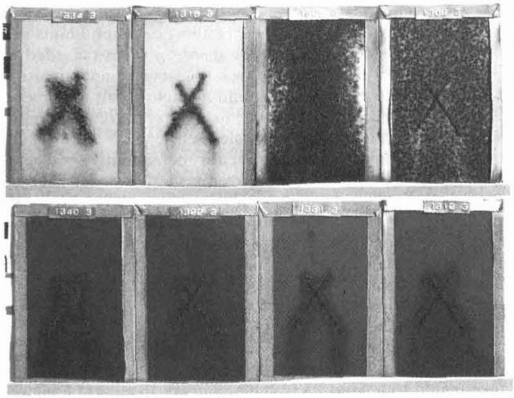
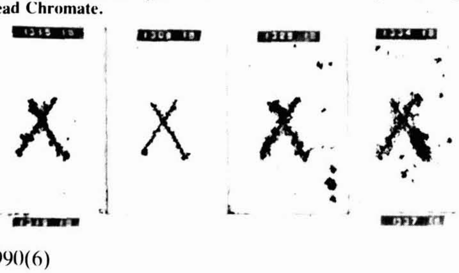


Figure 3

Good performance of Zinc Phosphate by actual weathering, under a top coat. Panels shown after removing the coating after 25 months at Martorelles. Left to right: Zinc Chromate, Zinc Phosphate, Barytes, Lead Chromate.



A conclusion could be drawn from the preliminary study: Zinc Phosphate did not deserve to be rated as an "expensive extender", as some authors[2] might have done, nevertheless non-toxic products with improved performance would very likely find a niche in the marketplace. These improved products should ideally:

☐ Take advantage of the proven outdoor performance of Zinc Phosphate pigments.

☐ Perform well at lower film thicknesses.

☐ Perform well at lower ratios of anticorrosive pigment to pigment/extender mixture.

☐ Be selected after cumulative evidence in several paint systems and several FoCPVC levels.

☐ Be selected after both accelerated and outdoor tests.

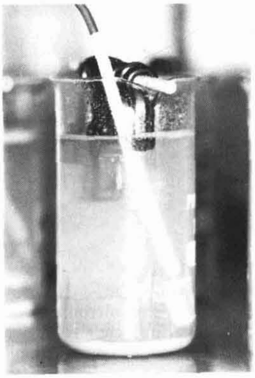
What experience tells

Many years of testing anticorrosive paints had sufficiently taught us not to draw conclusions from any single test. A number of ideas as to materials with potential for anticorrosive protection or ways to enhance the potential of already better known substances were available. A working scheme was needed that would transfer these ideas into commercially worthy anticorrosive pigments.

Monitoring the loss of weight of steel coupons immersed in aerated salt solutions to which candidate anticorrosive materials had been slurried (Figure 4) was a technique we had resorted to some years previous[3], without thereafeter never really ceasing to do so. It is an easy and inexpensive method that readily shows evidence of chemical activity—if any—in connection with anticorrosive protection (Figure 5). It has a drawback in that, the more soluble a compound is, the bigger the chances are that a good performance to this test does not mean a good performance when it made into paint[4]. On the other hand, this method leaves obviously undetected anticorrosive capabilities explained by mechanisms other than the solubilization of inhibiting ions. Nevertheless it continues to prove useful and results obtained by this technique provided some of the materials to be tested in the paints. Depending on their solubility, some of the candidate materials were to be tested alone or as enhancers to the better known Zinc Phosphate.

Figure 4

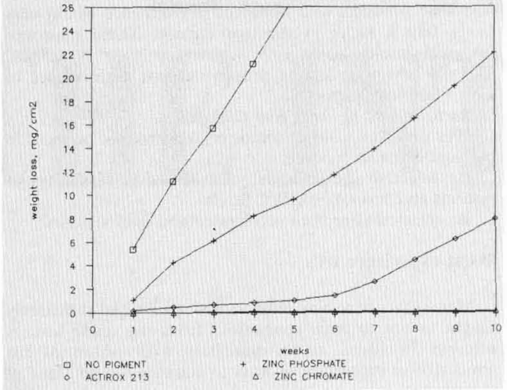
Weight loss of steel coupons immersed in aerated salt solutions to which anticorrosive pigments have been slurried. Layout of experiment.



Another way of trying to enhance Zinc Phosphate, or more generally anticorrosive pigments, was through surface treatment of their particles in order to make them more easily coatable by binders, thus eliminating paths for water penetration to the substrate/coating interface, or also to make available minor amounts of functional ligands thought to be

Figure 5

Weight loss of steel coupons immersed in aerated salt solutions to which anticorrosive pigments have been slurried. Typical results.

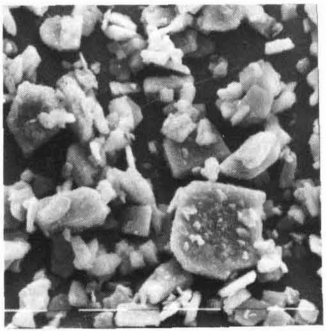


of interest to the anticorrosive action.

A further way of trying to enhance Zinc Phosphate, and a most obvious yet difficult one, was to make it into smaller particles. Zinc Phosphate consists, as is widely known, of large laminar particles, sized up to 12-20 microns (Figure 6).

Figure 6

SEM picture of standard Zinc Phosphate.



It is not possible by means of micronization to get a product with significantly smaller particle size, at least to the extent that would make the pigment useful for thin film applications or for moderately active pigment loadings. A number of methods had been developed at our laboratories to make small particle sized Zinc Phosphate pigments, and most of these pigments showed promise as improved materials, nevertheless it was not until well within the project we are reviewing that a reproducible, efficient, original method[5] was developed that allows for a small particle sized, spherical Zinc Phosphate pigment with high active surface properties to be manufactured (Figure 7).

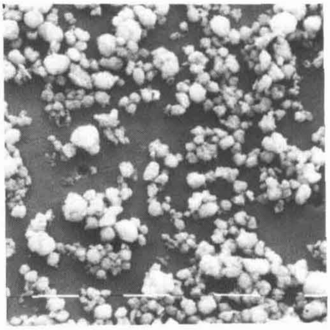
State of the art

Having examined in the course of our studies most of the non-toxic or lesser-toxic alternative materials that have been proposed, I would like only to bring the attention of the reader three facts:

1. No single universal replacement material has been achieved. Most suppliers in Europe, America and Japan have either proposed ranges of products for specific applications right from the beginning, or have gone the way from one single product to the next single product, to be followed by successive single products or eventually by a range of products. Of course the management in our company would have liked the outcome of this R&D project to be a single product. We never set out to do that, and surprisingly enough we have ended up by almost going the other way round...but this will be dealt with later.

Figure 7

SEM picture of new Zinc Phosphate of high active surface area.



2. Most enhanced Zinc Phosphate pigments available are based on one of two techniques: either the addition of a more soluble compound, which often results in undesired side effects, like heavy blistering under some circumstances, or formulation of the pigment with excess ZnO, with again undesirable effects in the form of reactivity with some binders.
3. Some of the proposed products do indeed show very good performance in accelerated tests, and others do so only in outdoor exposure. Still, lack of consistent cross-testing is often experienced (Figure 8).

Searching through cumulative evidence

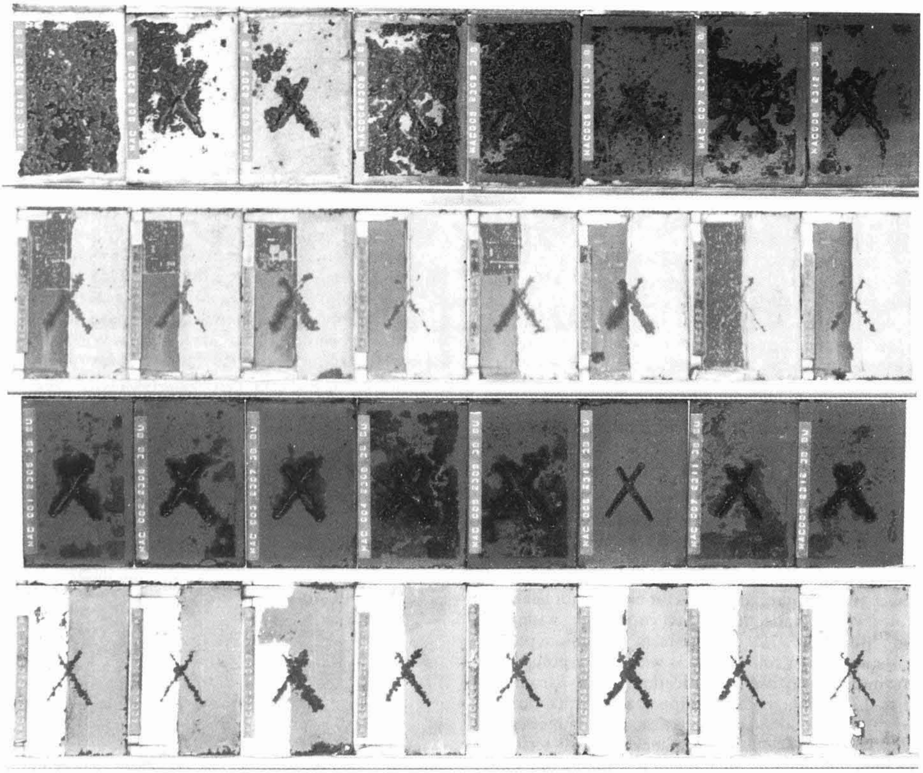
As already pointed out earlier, pulling out useful hints out of large numbers of anticorrosive paint tests was regarded as one of the difficulties in our task. Testing of anticorrosive paints is not an exact science, and a single result may mean anything. This is well known to both frustrated sample submitters and over-aggresive salesmen.

The methodology chosen to identify consistently promising materials or performance enhancing methods was that of grouping together candidate materials in series of 10-12 samples, and then comparing their performance in a wide range of paint formulating conditions and to different environments. All paints in this early screening stage were based on an air drying phenolic-modified alkyd resin, of short-medium length in linseed/wood oils, a type widely used for maintenance primers.

For the screening of these series of samples, two levels of Pigment Volume Concentration were chosen: a lower level formulated to a fixed PVC value, namely 10%, and a higher level formulated to a FoCPVC value of 0.80. For the lower level, candidate anticorrosive materials were tested at 80% and 25% of the total pigment/extender mixture, whereas for the higher level 100% and 25% were used. All systems were tested as a single coat application, at 8 and 30 microns dry film thickness. Besides this, replicate panels of the higher level systems were topcoated in two ways: with an air drying white alkyd finish, made to a PVC of 20%, and with paint used for the "lower level/low active pigment" test, that is PVC 10% with 25% candidate anticorrosive material on total pigment/extender. This was done in order to check the possibility of "in-depth protection" through the availability of active pigment in both primer and top coat. A complete layout of this experimental design is shown in Appendix B for better understanding.

Figure 8

Salt spray (wholly stripped off coating) and weather (half-stripped) performance of 8 market supplied alternative anticorrosive pigments. Top two rows, primer only application. Bottom two rows, primer plus top coat. Note that products performing best to salt spray do not coincide with those performing best to weathering.



Each group of 10-12 panels of uniform conditions was exposed to both the standard and the UV modified ASTM B-117 salt spray test, performed in the cyclic mode as earlier discussed, and to actual outdoor weathering at Colores Hispania's factory in Martorelles.

At scheduled periods along exposure (normally every 12 cycles in accelerated tests, every 6 months in outdoor exposure, more often when appropriate) all panels in a group were visually examined, and ranked within their group from best to worst in three ways:

1. With regard to qualitative deterioration (bulk of rust, staining) visible in the scratches usually made to the panels prior to exposure.
2. With regard to the area around the scratch which was in one way or another damaged (blistering, cathodic delamination).
3. With regard to the overall appearance of the panel, especially areas other than those adjacent to the scratches.

Depending on the relevance with which each mode of damage showed to every set of conditions, the three values obtained for each panel at every examination were combined, most often as the geometric average of two, three, or one with respect to the other two values. This demanded of course some judgement from the researcher.

Once a balanced ranking could be obtained for a group, it was weighted by the number of cycles elapsed, or the number of months, so that better performance to the end of the test added more to overall ranking than better performance at an earlier stage of the experiment. When the experiment was over, adhesion tests were performed on each panel wherever feasible, followed by the removal of the paint coating and examination of the appearance of the underlying substrate. This in turn was again made into values by the ranking method, and weighted in the final performance ranking by a factor related to the length of the test and the relevance of the observed facts. This again demanded some judgement from the researcher. Eventually a global more or less arithmetic ranking could be elaborated for every group. Appendix C shows an example of a typical evaluation procedure form.

Rankings obtained from each of the different paint systems, film thicknesses, pigment loadings, and test methods were finally combined by means of arithmetic and judgement to reach conclusions, this process I describe as based upon a "Search Through Cumulative Evidence". This technique will be further dealt with later under the heading "Shaping a novel anticorrosive pigment" and in Appendix D.

Among the information that this part of the project contributed, the following can be highlighted:

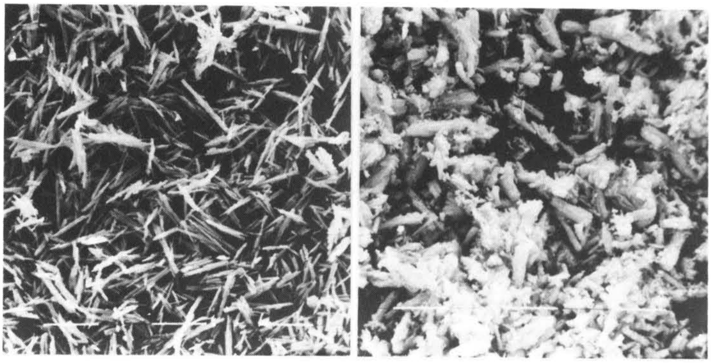
☐ Small particle size Zinc Phosphates are preferred for lower PVC or FoCPVC values, while pigments with a broad particle size distribution are advantageous for higher FoCPVC values.

☐ Enhancement of Zinc Phosphate by "the right amount of the right coupling agents added in the right way" results in outstanding long term outdoor exposure results, especially when high FoCPVC values and high ratios of active pigment to extender blend are used.

☐ Zinc Molybdate, when made sufficiently insoluble, adds significantly to the performance of Zinc Phosphate based

Figure 9

SEM pictures of two Strontium Chromate pigments. The sample shown in the left gives much more tendency to blistering than the sample in the right, in spite of substantially identical chemical characteristics.



pigments, especially when the primer is not topcoated with a highly impervious finish. "In-depth protection" is a suitable technique with this material.

☐ Other more soluble products give good results during outdoor exposure of primer alone applications, although not in accelerated testing.

From quality control into R&D

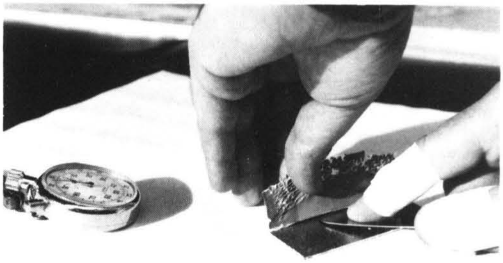
Following concern expressed by some customers about the performance of Strontium Chromate pigments from different suppliers in coatings systems intended for aircraft application, several tests were made to paints complying with US specification MIL-P-23377D. In these tests, aluminium panels coated to 20 microns dry film thickness with epoxy-polyamide primers formulated to the specification, with Strontium Chromate as the main pigment, and top coated with a further 70 microns of a white polyurethane finish, were immersed in distilled water at 50° for 4 days, to be checked for blistering at the end of the experiment. Some pigment samples did show much heavier blistering than others, as previously reported by researchers from the US Navy, but, as opposed to what had been suggested[6], we found that the differing performances were not related to impurities in some of the samples, but rather to the size and shape of the pigment particles (Figure 9).

This proved to be a finding of paramount importance, not to the success of any Strontium Chromate pigment but to the success of our R&D project. Having realized how important particle size and shape could be to the anticorrosive performance of a chemically proven material, we wanted to know how would Zinc Phosphate and other candidate materials perform in a similar test.

After some laboratory work, we reached the point where by adjusting the paint formula to a lower epoxy:polyamide ratio (1.1:1) we were able not only to check differences in blister formation between different pigments but also their effect on the wet adhesion of the coating to the substrate. An immersion test followed by an assesment of blistering, and then by carefully removing—or unsuccessfully trying to remove—the coating system with the help of a knife, under as standardized conditions as possible (same knife, same pattern of attacking the interface, fixed period of time allowed, etc,—see Figure 10)—turned out to produce a wealth of information about a pigment. The amount and appearance of blistering or its absence, wet adhesion, appearance of both the substrate and the coating interface, even the "feeling" of trying to remove the coating helped characterize candidate materials and anticipate their performance in more standard tests. The best performance of a pigment was achieved when samples were tested at a fixed PVC, usually 28%, with three primers made, one with 100% candidate material and the other two with 50:50 and 15:85 blends of candidate material and micronized talc, these primers were applied to 10 and 25 microns dry film thicknesses and always topcoated with 90 microns of polyurethane finish (Figure 11).

Figure 10

Removing the coating after water immersion test.



The influence of paint formulation factors such as Pigment Volume Concentration could also be studied by this technique (Figure 12). The well known fact that the FoCPVC value used is most relevant to adhesion could be explored, and subsequently the importance of playing with the ratio between anticorrosive pigment and extenders in order to bring FoCPVC to a desirable range while keeping fixed PVC or active pigment loadings. Another test that proved to yield good results in assessing the possibilities of candidate materials was that of comparing the same pigment, at a fixed PVC and 100% candidate material loading, in primers formulated to several epoxy:polyamide ratios (Figure 13).

The most relevant finding obtained through this technique was that of identifying some iron/zinc phosphate candidate materials as showing excellent adhesion on non-ferrous metals, namely aluminium, aluminum-copper alloys and galvanized steel, whilst at the same time showing no tendency at all to generate blistering under the circumstances of the test.

Shaping a novel anticorrosive pigment

Once some candidate materials and enhancement methods had been selected by both the Cumulative Evidence and the Immersion Test techniques, new, larger groups of varying size, up to 30 samples for the biggest, were formed. Materials forming these groups consisted of Positive Control chromate based pigments, Negative Control inert pigment blends, Standard Zinc Phosphate, a number of candidate material samples which included chemical compositions and manufacturing processes as an alternative to those showing promise after the screening stage, and a number of samples of materials from other sources available on the market. Selection of the chromate pigment kind, inert pigment blend, candidate materials and samples from other sources to form each group was suited to each specific application; similarly, paint formulations were used at this stage that approached common practice for the systems under test.

Zinc Chromate was the control for alkyd primers, which were formulated to a FoCPVC value of 0.80 with 25% active pigment on the total pigment/extenders blend, and were tested both as single coats, to a dry film thickness of 35 microns, and topcoated with a standard white air drying alkyd finish, to 30 and 50 microns total dry film thickness.

Strontium Chromate was the control for epoxy-polyamide primers formulated to PVC 28%, with 50:50 ratios of active pigment to talc. They were tested as single coats to 25 microns dry film thickness, and as complete primer plus top coat systems, one with 15 microns primer and 20 microns polyurethane top coat, another with 25 microns primer and 50 microns top coat. Zinc Tetraoxychromate was the control for polyvinyl-butyral shop primers and wash primers formulated to PVC 17%, with candidate materials accounting for 70% and 50% of the pigment/extender blend.

Panels were exposed to the two cyclic salt spray tests already discussed and to actual weathering in Martorelles, but this time further tests were included for panels with the complete primer and top coat system which comprised a weak cycle of the Kesternich Test prior to exposure to salt spray or outdoors.

This produced again a mass of data which was turned into conclusions by carefuly ranking all of the panels in each group according to the same method as discussed under the heading "Search through cumulative evidence", equally followed by combination of the results of all groups to produce a "figure-supported" outcome. When doing this process, all controls, candidate materials and market-supplied samples were indiscriminately considered together, and later conclusions as to which products should be manufactured were heavily based on the results of this classification. As an example, the results of the Strontium Chromate group are outlined in Appendix D, where the names of candidate materials other than those retained for further work and market-supplied samples have been obscured for obvious reasons. What we want to stress here is only the methodology used in our

Figure 11

Performance of a Zinc Phosphate pigment via the Immersion Test. Above: Reverse side of removed coatings shown, corresponding to primer dry film thickness of 10 micron. Time needed to remove coating increased (left to right, 45, 67 and 105 seconds) as number of rust spots in the interface increased as well with decreasing pigment/talc ratio (100:0 – 50:50 – 15:85). Below: Only part of the coatings could be stripped off the panels when using thicker primer coats (25 micron) and the same top coat as above. Efforts were abandoned after 60 seconds.

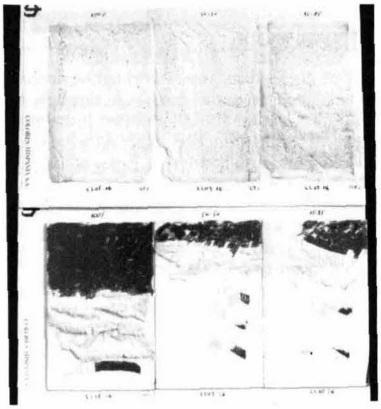


Figure 13

Performance to the water immersion test of primers with the same pigment and different epoxy-polyamide ratios. (Top row: 1.1:1 and 1.3:1. Bottom row: 1.7:1 and 2:1.)

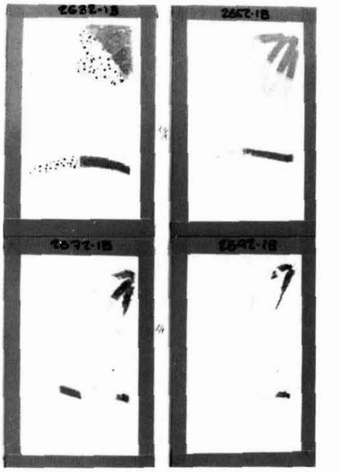
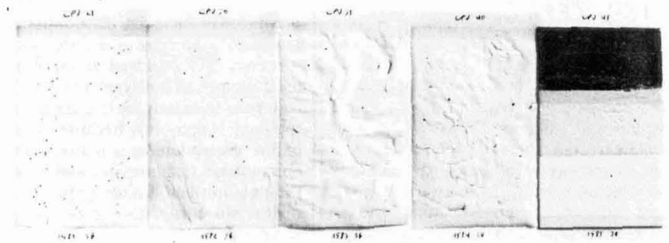


Figure 12

Adhesion of paints formulated to a ladder of values of PVC for a Zinc Phosphate pigment. Left to right: PVC 25, 30, 35, 40 and 45. Increasing adhesion shown through increased difficulty to remove coating.



designing ("shaping") of the pigments to be manufactured.

As the salt spray tests for epoxy-polyamide systems so far mentioned had been all done on steel substrates, the need was felt for complementary tests on non-ferrous metals. Further clarification between the merits of the Iron/Zinc and Zinc only based products was also needed. The primers this time were formulated to PVC values of 28% and 20%, with respectively 50:50 and 15:85 ratios of active pigment to talc, and topcoated as usual with a white polyurethane finish. Only complete primer plus top coat systems were tested, at total dry film thicknesses of 100 and 115 microns, of which 90 were contributed by the top coat. Salt spray tests (not inclusive of UV radiation) were performed on steel, aluminium (non-chromatized surface) and aluminium/copper alloys. This supported the evidence previously obtained from water immersion tests of the advantage of Iron/Zinc Phosphate based products on non-ferrous metals.

More to outdoor testing

The informed reader will surely have noticed that I have repeatedly referred to outdoor exposure tests in a mild industrial/rural environment near Barcelona. This should not be regarded by the reader as a rural area since many industries are there, heavy traffic runs nearby and, most importantly, the panels are wetted with dew and mist every morning, to be dried by the sun at noon. Nevertheless we did feel the need to carry further testing under more severe conditions, this is why some runs of tests with panels previously exposed to SO_2 (the Kesternich test) have been included in our scheme. Searching for more aggresive environments, evidence was found[7] of the harbour at Bilbao, in northern Spain, being a most suitable place, where both natural and man-made conditions (salt spray, rainy weather, orography forcing winds drive the pollution of the city and its industrial area twice a day over this site) promotes the corrosion of metals. We arranged for a testing site to be built at the very edge of the outer breakwater, next to which incidentally a coal fired power station helps to complete the picture (Figure 14). The only drawback of this testing site is that we occasionally happen to miss a panel after a storm.

Since this site is now available we have been able to re-assess the performance of the new pigments with respect to Zinc Chromate and Zinc Phosphate, the latter being no longer able to hold comparison in such an environment (Figure 15).

Final push

At this point we had achieved a clear enough indication as to the product that should be pursued for Strontium Chromate replacement, but we were still left with too many promising candidate materials for Zinc Chromate replacement.

A last study was planned which comprised Zinc Chromate and Zinc Phosphate as controls, and 17 candidate materials based on those more promising to date together with samples of modified composition and alternative manufacturing process—already with a view to cost considerations. A right decision seemed to be to search for the most universal product, so that for this approach the whole group was tested both in air drying alkyd and epoxy-polyamide primers. Also to provide for wider compatibility, two ratios of active pigment to total pigment and extender blend were tested, namely 25 and 80%, while overall pigment level was kept to a FoCPVC value of 0.80. Panels were exposed with primer only and primer plus alkyd top coat systems to the usual cyclic salt spray tests, with and without UV modification, and to weathering both in Martorelles and at the new site in Bilbao.

Figure 14

Weathering site on the breakwater at the harbour of Bilbao.

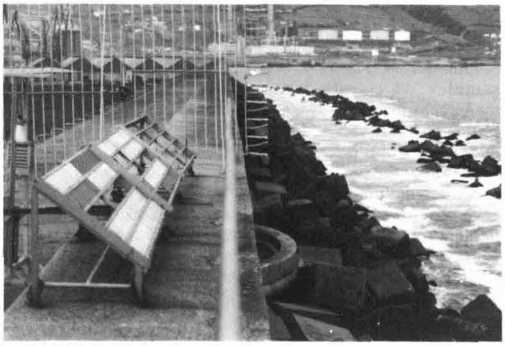
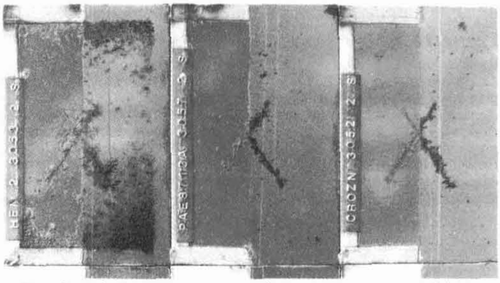


Figure 15

Alkyd primers based on Zinc Phosphate–Hispafos NZ (left) and Zinc Chromate (right) after 7 months on the breakwater at Bilbao. Shown in between is a primer made with the Iron/Zinc Phosphate pigment–Actirox 213 developed during the project discussed in this paper.



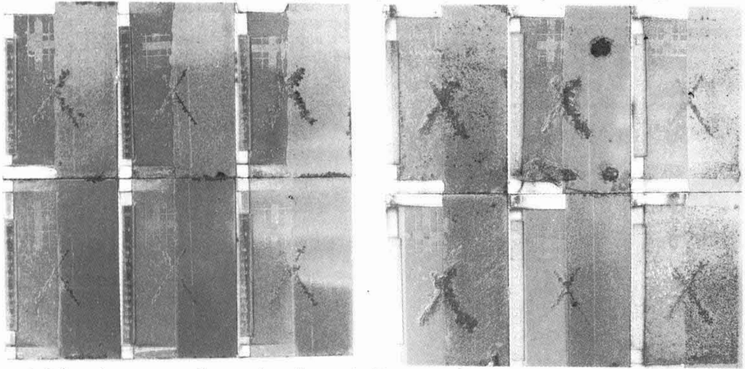
Results of these tests were thoroughly processed in the manner described in appendices AA through to D. Very interesting information could be drawn this time depending on whether all results from each pigment were considered, or alternatively only results for the amount of pigment best suited to each application (primer only or two coat systems) were considered. No disclosure will be made here of the detailed results, as research is continuing into the further development of some of the materials, but it is interesting to note that, depending on the way results for air drying alkyds were combined, Zinc Phosphate ranked from "11th Best" for "salt spray only, all results" to "19th Best" for "outdoor only, all results", meaning that more of the candidate products gave improved results to outdoor exposure than to accelerated tests. As to epoxy-polyamide systems, Zinc Phosphate ranked from "2nd Best" to "5th Best". This shows that the more soluble materials that perform best in air drying systems do not exhibit the same high standard when used in better crosslinked systems.

Three interesting products have emerged from this extensive research project:

1. A Zinc Phosphate/Zinc Molybdate based pigment[8,9], with optimized particle size distribution and coupling agent surface modification. This product, commercially launched as "Actirox 102", showed its merit in air drying alkyds. When used at higher levels of FoCPVC values, it gave excellent results to salt spray and outdoor exposure with and without a top coat. Apparently because of the relatively high solubility of the molybdate ion, it did not give such good results in epoxy-polyamide primers where blistering was noticed under the polyurethane finish. Probably for the same reason it has on the contrary shown excelent results when alkyd systems were tested by the "in-depth protection" method, that is with

Figure 16

Actirox 102 compared to Zinc Phosphate and Zinc Chromate, in air drying alkyd primers exposed to weathering at Martorelles (left block) and the breakwater at Bilbao (right block). Top row: 25% anticorrosive pigment on total pigment blend. Bottom row: 80% anticorrosive pigment on total pigment blend. For each block, left to right: Zinc Phosphate–Hispafos NZ, Actirox 102, Zinc Chromate.

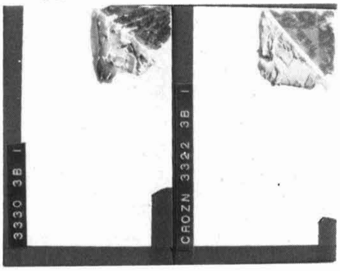


the finish coating containing also some anticorrosive pigment. The most remarkable feature shown by this pigment was the extremely good result of panels exposed to actual weathering when again higher FoCPVC values and high active pigment loadings were used. This could perhaps be credited to the improved mechanical properties afforded to the primer by the coupling between pigment and binder (Figure 16). This same reason, on the other hand, accounts for a loss of wet adhesion at lower PVC values, as found out by the Immersion Test method, as for a pigment like this of very high CPVC, this means lower FoCPVC values than those for non-surface treated pigments.

2. An Iron Phosphate/Zinc Phosphate pigment[10], of very low solubility and small particle size, which gave excellent results in epoxy-polyamide systems under polyurethane top coats (Figure 17), and most interestingly in non-ferrous metal substrates. This product, launched as Actirox 213, shows a rather low CPVC, and was regarded in principle as a most suitable replacement for Strontium Chromate. Chemical composition of this pigment, specially the balance between zinc, iron II and iron III phosphates, proved to be of utmost relevance to performance, so it was further finely tuned with the help of some more loss-of-weight-in-slurry tests. See Figures 18 and 19 for examples of relevance of such fine tuning.

Figure 17

Actirox 213 (left) showing adhesion comparable to Zinc Chromate (right), and no sign of blistering, after 4 days immersion in distilled water at 50°C of panels coated with epoxy-polyamide primer and polyurethane top coat. Primers formulated to PVC 28%, with 15:85 ratio anticorrosive pigment:talc.



3. A spherically shaped small particle sized Zinc Phosphate pigment, without any other ion addition and substantially stoichiometric ZnO/PO_4 ratio (less than 5% disproportion), the process for manufacturing which had been instrumental to the development of the three new products[5]. This unique pigment, launched as "Hispafos SP", shows much better performance that standard Zinc Phosphate, especially at low thickness and lower PVC values or lower active pigment to pigment/extender ratio. (Figure 20).

Figure 18

Relevance of Fe++ to Fe+++ ratio, with no Zn present, as shown by the loss of weight of steel coupons immersed in salt solutions containing pigment slurries.

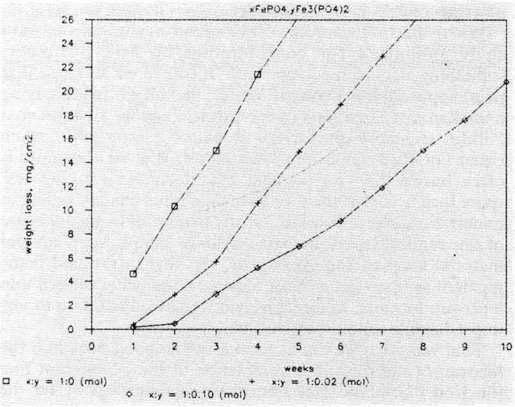
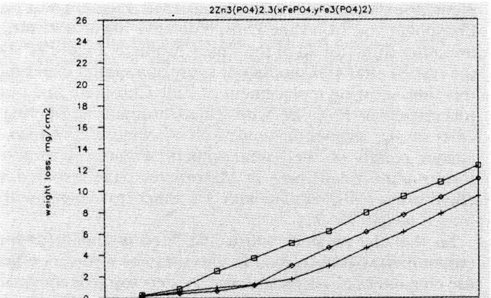


Figure 19

Relevance of Zn++/Fe++/Fe+++ ratios, as shown by the loss of weight of steel coupons immersed in salt solutions containing pigment slurries.



Characteristics of these three pigments are given in Table 3, together with those of standard Zinc Phosphate and relevant chromate pigments.

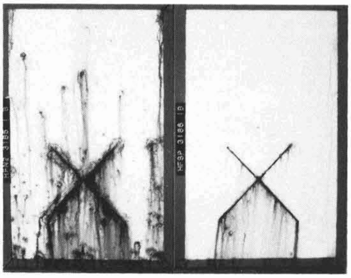


Figure 20

Hispafos SP (right) against standard Zinc Phosphate (left). Panels coated with 20 microns of an air drying alkyd paint formulated to PVC 35%, with 27% anticorrosive pigment on the total pigment/extenders blend. 300 hours salt spray.

Surprise: A universal replacement?

So much for Research and Development. Let's indulge now for a while into Profitability.

When the first samples of our brand new pigments were shyly submitted for consideration by Mr. Customer, something astonishing happened: Of course we all know that paint application is a volume matter, that all we do is applying a thickness of something over a surface, and we all know that faithful technical comparison of paints is only made when equal FoCPVC values are resorted to!. But Mr Customer is often busier than we pigment manufacturers are, has less spare technical staff than we have, and is not exactly willing to undertake such tremendous efforts like we did—just because of our request (specially when a dozen sample suppliers per material keep calling every year). So that in the end many pigment samples get at most the chance of being slipped into a proven formula, in direct weight/weight substitution of any unpredictable amount of chromate pigment.

That was what we did as soon as we stepped back into the laboratory...to find after completion of the experiment that the Iron Phosphate/Zinc Phosphate pigment was by far the one which performed best under this approach. Figure 21 shows the results after 400 hours salt spray of paints of which one has been formulated with Zinc Chromate to PVC 35, with Zinc Chromate accounting for 27% of the pigment/extender blend, while an inert pigment mix, Zinc Phosphate and Iron/Zinc Phosphate have been substituted in the other three for all of the Zinc Chromate. Figure 22 shows the results after 1000 hours salt spray of a similar experiment, this time showing replacement of Zinc Chromate in a primer formulated to PVC 45, with Zinc Chromate accounting for 28% of the pigment/extender blend; Figure 23 shows top coated panels of the same primers. Figure 24 shows the results after weathering in Martorelles panels coated with alkyd primers formulated with 3% anticorrosive pigment, on a total weight basis.

So that the pigment which had been intended for highly crosslinked systems turned in the end to be also very efficient for conventional alkyd systems. A step towards universality had been achieved.

Formulating into paints: Cost effectiveness re-evaluated

Now that we were faced with two "most suitable" pigments for air drying systems, the need was apparent to decide which of them should be commercially promoted.

Figure 21

Direct weight/weight replacement of Zinc Chromate (bottom right) by respectively an inert blend of TiO2 and extenders (top left), Zinc Phosphate (top right) and Actirox 213 (bottom left). Panels shown after stripping off half of the coating after 17 cycles in the salt spray (approx. 400 hours). PVC for Zinc Chromate based paint: 35%, with 27% anticorrosive pigment on the total pigment/extenders blend. Dry film thickness 35 micron.

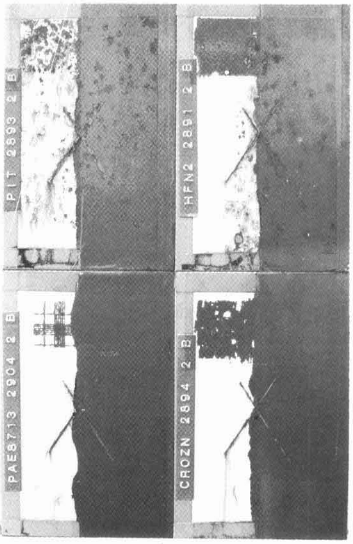


Figure 22

Direct weight/weight replacement of Zinc Chromate (left) by respectively Actirox 213 (centre) and Zinc Phosphate (right). Panels coated to 70 micron dry film thickness, shown after 1,000 hours salt spray. PVC for Zinc Chromate based paint: 45%, with 28% anticorrosive pigment on the total pigment/extenders blend.

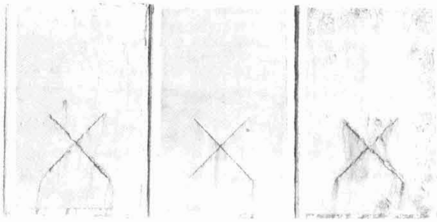
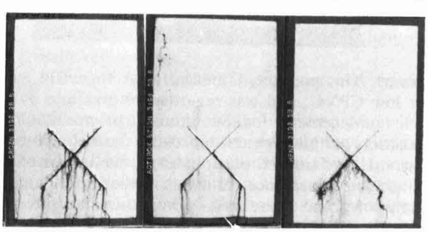


Figure 23

Same primers as shown in Figure 22, top coated with an air drying alkyd finish. 1,000 hours salt spray. Total dry film thickness: 70 micron. Left to right: Zinc Chromate, Actirox 213, Zinc Phosphate.



On purely technical grounds, some of their characteristics, namely specific gravity, oil absorption, CPVC and solubility were different enough (see Table 3) not only to leave relative merits to be expected uncertain but also to allow for possibly optimized results if both were used in combination: Figure 25 shows the CPVC values of blends of the two "most suitable" pigments with an inert mix of constant composition, while

Figure 24

15 months outdoor exposure at Martorelles of primers with 3% anticorrosive pigment on total paint formula. Left to right: Zinc Chromate, Actirox 213, Zinc Phosphate.

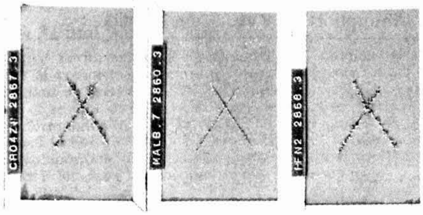


Figure 25

CPVC values of blends of Actirox 102, Actirox 213 and an inert iron oxide/extenders mix. (Diagram shows blends in volume %.) Composition of inert mix (volume): Iron oxide, micronized=25.7%, Barytes, micronized=38.6% and Talc, micronized=35.7%.

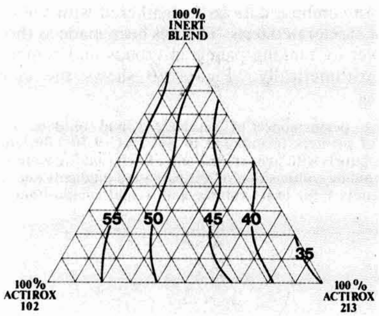


Figure 26

Solubility (mg/100 ml)* of blends of Actirox 102, Actirox 213 and an inert iron oxide/extenders mix.
***Active anticorrosive material extracted when 20 g of pigment are stirred in 1 litre of distilled water at 23°C. (Diagram shows blends in volume %.) Composition of inert mix (volume): Iron oxide, micronized=25.7%, Barytes, micronized=38.6% and Talc, micronized=35.7%.**

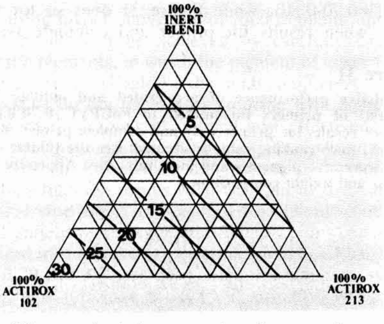


Figure 27

Estimated raw materials cost (per litre) of paints formulated to a FoCPVC=0.80 for blends of Actirox 102, Actirox 213 and an inert iron oxide/extenders mix, relative to the cost of the inert mix only paint. (Diagram shows blends in volume %.) Composition of inert mix (volume): Iron oxide, micronized=25.7%, Barytes, micronized=38.6% and Talc, micronized=35.7%.

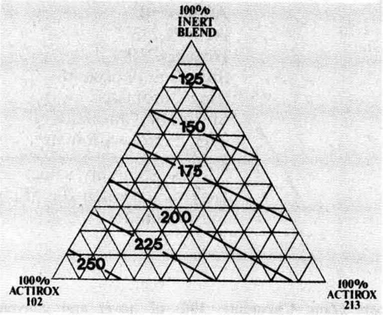


Figure 26 shows solubility values for the same blends. It is apparent that in principle the paint formulator can choose a balance of CPVC and solubility values that best suits a prospective application. On the other hand, relative costs were also different, both between the pigments themselves (see Table 4) or between paints formulated from them (Figure 27 shows the estimated total raw material costs of primers formulated to a constant FoCPVC value of 0.80 with blends of variable volume composition, relative to the cost of a "primer" with an inert mix only).

Trying to make technical merits meet profitable use, we designed a test scheme in which paints would be formulated for ranges of blends of Actirox 102 and Actirox 213 at either fixed paint raw materials cost or fixed volume ratio between anticorrosive pigments blend and inert mix. Figure 28 shows the relative costs chosen for primers formulated to FoCPVC values of 0.70 to 0.80 (to be tested as single coat and as complete primer and top coat system), and Figure 29 shows the relative costs of primers formulated to FoCPVC=1.00 (to be tested only as complete systems). In these figures, solid and dotted lines tie respectively points of fixed cost or of fixed

Figure 28

Figures in the diagram are the costs relative to that of an inert mix only primer of paints formulated at FoCPVC=0.70-0.80 chosen to be tested both as single coat and complete primer plus top coat system. Each cost is situated over the volume composition of anticorrosive pigments and inert mix. (See Appendix F for exact volume and weight composition.)

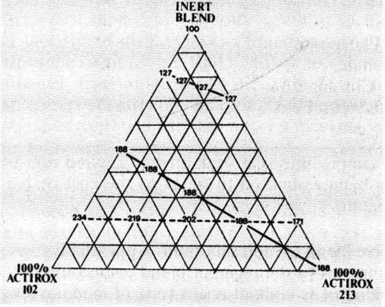


Figure 29

Figures in the diagram are the costs relative to that of an inert mix only primer of paints formulated at FoCPVC=1.00, tested only as complete primer plus top coat system. Each cost is situated over the volume composition of anticorrosive pigments and inert mix. (See Appendix F for exact volume and weight composition.)

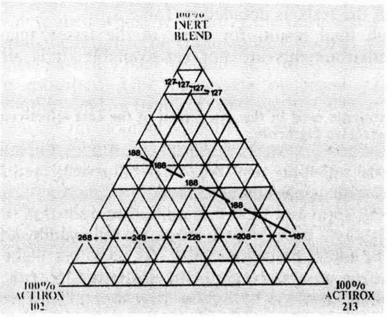


Table 3

Characteristics of novel and standard anticorrosive pigments.

	Specific Gravity	Oil Absorption	CPVC	Solubility*, mg/100 ml
Actirox 102	3.1	21	58	31.0
Actirox 213	3.0	57	35	7.3
Hispafos SP	3.4	60	31	5.2
Std. Zinc Phosphate	3.3	20	58	2.8
Zinc Chromate	3.5	20	57	113.6
Strontium Chromate	3.7	27	47	92.8
Zinc Tetroxychromate	3.6	59	30	9.2

* These solubility values correspond to the active anticorrosive material which is extracted when 20g of pigment are stirred in 1 litre of distilled water at 23°C for 15 minutes.

Table 4

Relative costs (Zinc Chromate=100) of novel and conventional anticorrosive pigments (subject to minor variations depending on national market characteristics, nevertheless orientative).

	1 Kg Pigment	1 litre Pigment	1 litre Dry paint at CPVC*
Actirox 102	118	104	104
Actirox 213	103	88	73
Hispafos SP	118	114	82
Std. Zinc Phosphate	84	79	84
Zinc Chromate	100	100	100
Strontium Chromate	170	180	143
Zinc Tetroxychromate	143	147	95
Red Lead	36	91	92

* As an example, the cost of 1 litre of applied non-volatile binder has been estimated to be ⅓ or the cost of 1 litre of Zinc Chromate.

anticorrosive blend to inert mix ratio. Appendix F gives more precise figures as to the pigment blend compositions.

A 1:1 blend of two alkyd resins (one of medium length in linseed oil and wood oil, and one of short-medium length in dehydrated castor oil and modified with phenolic resin) was used. An in-house computer software programme was instrumental in handling all of the paint formula and cost calculation involved in this part of the project.

All primers were applied to 25 microns dry film thickness to cold rolled steel panels, and topcoated where applicable with a white air drying alkyd finish to a total dry film thickness of 45 microns. Panels were then scratched in the usual way, and exposed to the tests as detailed in Table 5.

Table 5

Test environments used in the assessment of the cost effectiveness of novel anticorrosive pigments.

(a) Standard salt spray test, ASTM B-117, performed in the cyclic mode as already described.
(b) Cold salt spray test (23°C), modified composition (4.1 g/l $(NH_4)_2SO_4$ + 0.3 g/l NaCl), 16 hours followed by 8 hours in QUV test cabinet (at 45°C).
(c) Outdoor weathering, mild industrial/rural site. Martorelles.
(d) Outdoor weathering, heavy industrial/marine site. Breakwater at the harbour of Bilbao.

Although final results for some of the lesser aggresive outdoor environments are not yet available, it is already possible to combine data so far gathered with the complete results of accelerated tests. This has been made as throughout the project by ranking panels in groups and combining the results arithmetically. Figure 30 shows the cumulative performance (1=best) in primer only panels (F of CPVC=0.70-0.80), while Figure 31 does so for the same group when results for primer and complete systems are

Figure 30

Cumulative performance of accelerated and outdoor weathering (1=best) of primers formulated to FoCPVC 0.70-0.80, considering results for panels with primer coat only. Each ranking value is situated over the volume composition of anticorrosive pigments and inert mix. (See Appendix F for exact volume and weight composition.)

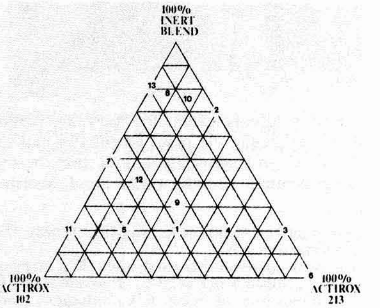
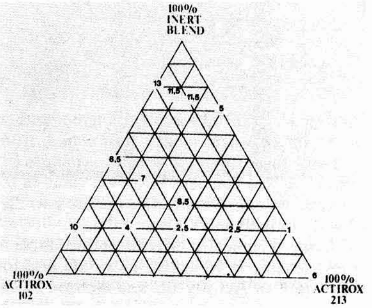


Figure 31

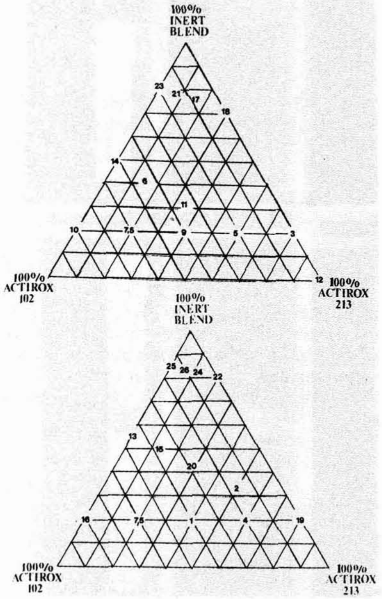
Cumulative performance of accelerated and outdoor weathering (1=best) of primers formulated to FoCPVC 0.70-0.80, adding together results for primer only and complete primer plus top coat systems. Each ranking value is situated over the volume composition of anticorrosive pigments and inert mix. (See Appendix F for exact volume and weight composition.)



added together. Figures 32 and 33 (which should be examined jointly) show the ranking of all panels in complete system application. It is thus possible to check the relevance of FoCPVC value with regards to success of primer plus top coat systems.

Figures 32 and 33

Cumulative performance of accelerated and outdoor weathering (1=best) of complete primer plus top coat systems for all primer compositions as per Figures 28 and 29 and Appendix F. For better analysis of results, ranking values are split between Figure 32 for primers formulated to FoCPVC 0.70-0.80 and Figure 33 for primers formulated to FoCPVC 1.00. Each ranking value is situated over the volume composition of anticorrosive pigments and inert mix. (See Appendix F for exact volume and weight composition.)



The following conclusions can be tentatively drawn:
1) When lower active and/or total pigment amounts are used, it is more economically effective to use the pigment with the lower CPVC and solubility values (here, Actirox 213).
2) When using higher active and/or total pigment amounts, optimized results can be achieved by carefully choosing blends of the pigments, in which the pigment of lower CPVC and solubility values should be the main component.
3) Best results do not necessarily coincide with higher raw material costs, and zones of optimal cost effectiveness are identified which should be further restricted in future work (Figure 34). As throughout this paper, it is more the methodology than the results what we want to stress here.
4) For air drying alkyd primers based on blends containing the novel anticorrosive pigments studied here, good results are achieved in single coat application when FoCPVC values between 0.70 and 0.80 are used, while for complete systems of primer plus top coat a FoCPVC around 0.90 is to be preferred.

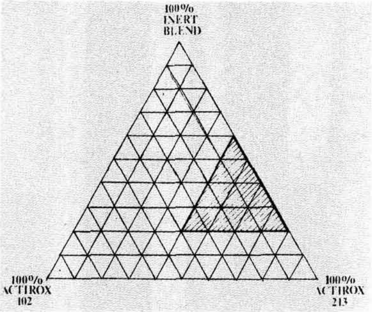
According to these results, the strategic decision was made to commercially promote Actirox 213 with preference to Actirox 102, leaving with the paint formulator the choice of deciding on further work for optimal use of both products.

Food for thought (some more)

When doing the part of the project we have just discussed, some commercial primers were used in lieu of the customary controls. These included a number of red lead primers and also a number of lead-free do-it-yourself primers. All were picked up at random from retail dealers. We found that most of the tentative formulae we examined clearly outperformed all of the lead-free and some of the red lead controls; some examples are shown in Figure 35. In fact, the overwhelming advantage of the tentative over the commercial lead-free materials made us re-check the performance of the inert pigments mix which was being used together with the novel anticorrosives. Figure 36 shows the result of such a test.

Figure 34

Area of optimal cost effectiveness for air drying alkyd primers based on blends of two anticorrosive pigments and an inert mix. (Diagram shows blends in volume %.) Composition of inert mix (volume): Iron oxide, micronized=25.7%, Barytes, micronized=38.6% and Talc, micronized=35.7%.



Still, a distinct advantage was found in some of the test modes on the side of some Red Lead primers, because of the traditional use of linseed oil and resins by paint manufacturers (Figure 37). The results of applying such skills to formulating primers with the novel anticorrosive pigments remain to be seen.

The use of improved accelerated testing may help such studies progress. We have already stressed under the heading "Zinc Phosphate vs Zinc Chromate" the lack of correlation between results of the standard salt spray test and actual outdoor performance. Elaborating on work by previous workers[11] we have been able to assess the improved correlation with reality of some of the modified salt spray tests[3]. Based on this older work, our own new experiences with cyclic tests inclusive of UV exposure, and suggestions by Sherwood[12], and Skerry[13], we have been able to standardize two sets of cyclic test conditions which are detailed in Appendix E for the convenience of other researchers.

Summary

A search for novel non-toxic anticorrosive pigments has been described which resulted in the development of three materials believed to be commercially worthy: a small size, spherical particle Zinc Phosphate, a Zinc Molybdate/coupling agent modified Zinc Phosphate of broad particle size distribution, and an Iron/Zinc Phosphate. Of these, the latter shows some remarkable potential because of its wide scope of application, both in terms of binder compatibility and adhesion to ferrous and non-ferrous substrates, and economy when the complete paint formula raw material cost is properly considered.

The methodology used to identify and characterize candidate materials has been discussed, which comprised a screening step consisting of purely chemical tests, a further step in which paints were submitted to accelerated and actual outdoor corrosion tests, trying to make use of candidate materials in many different ways in order to gather cummulative evidence of promising results. Extensive use

Figure 35

A primer based on Actirox 213 (bottom row in each picture) compared to 3 commercial red lead primers (upper block) and 3 DIY lead-free primers (bottom block). All panels half stripped after 7 cycles of salt spray exposure. Left panel in each pair with 35 microns primer only, right panel 50 microns primer plus top coat.

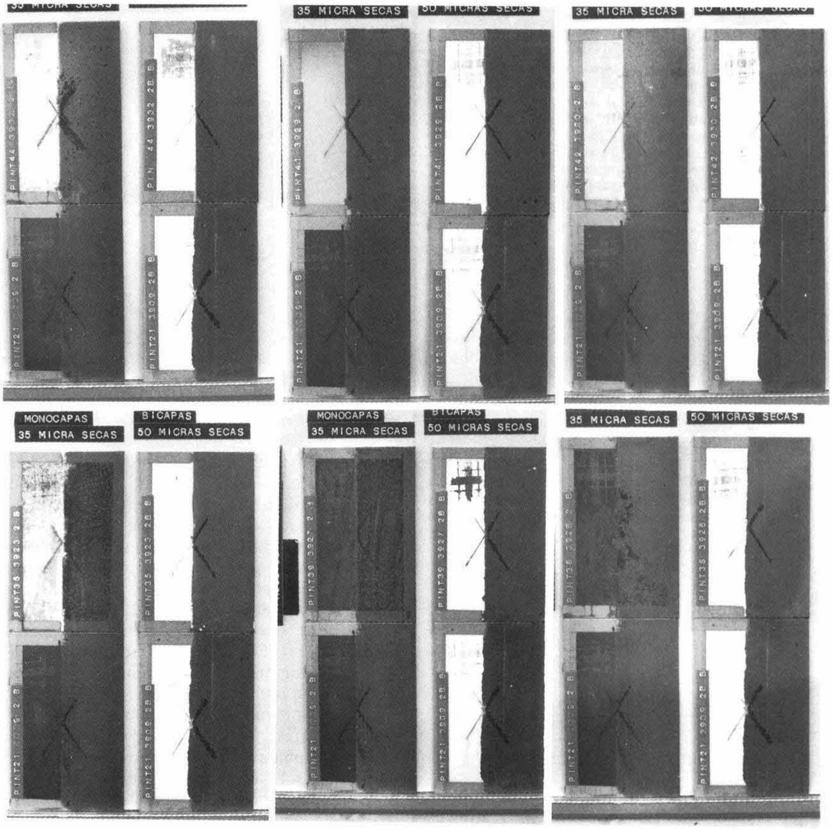


Figure 36

Air drying alkyd primer with 18.2% Actirox 213 on total formula (centre) compared to red lead primer (left) and blank test formulated to same FoCPVC and same inert pigment composition. Panels with primer only exposed to 10 cycles of salt spray, panels with primer and top coat exposed to 25 cycles.

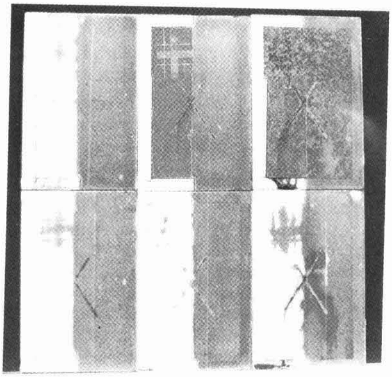
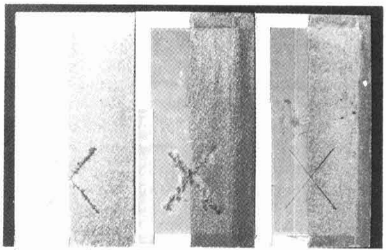


Figure 37

Red lead primer showing better resistance to special double cyclic salt spray/QUV test (see Appendix E, mode b) than alkyd primer formulated with Actirox 213 (centre). Shown at right, linseed oil primer formulated with Actirox 213.



was made of a water immersion test, which yielded many useful ideas contributing to the success of the project. At a later stage, new standard and modified accelerated and weathering tests helped the final design of new products and assessment of their potential as compared to conventional and other innovative pigments on the market.

Based on our company's knowledge of anticorrosive pigments built up over decades, the project itself which has been discussed took five years of effort, during which more than 200 candidate materials were examined, more than 800 steel and non-ferrous panels were probed for adhesion and blistering of coatings after immersion tests, and more than 12,000 steel panels have been rusting indoors or outdoors.

Acknowledgment

This paper could have never been written without the guidance and advice of Mr Carles Martorell. I am truly indebted to him.

I also wish to thank Mr Juan Manuel Somoza for his help throughout the project, he did most of the hard work on the bench. My gratitude goes through him to all other laboratory staff who have collaborated.

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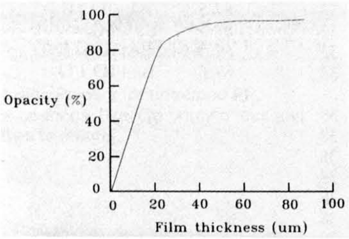
Appendices▷▷▷

Balfour, J. continued from p.230

Film thickness

The thickness of the material containing the TiO_2 will very often dictate the necessary concentration. This is why, for example, many plastic applications use a low concentration because the thickness is relatively high. Figure 17 shows the relationship between film thickness and opacity for a typical gloss paint.

Figure 17
Effect of film thickness on opacity



The increase in opacity is initially high but as the thickness increases a value is eventually reached where the sample is completely opaque and further increases in thickness have no effect.

Conclusion

The above has described opacity and the factors influencing it, with particular reference to systems containing TiO_2 pigments. Factors considered have included refractive index, pigment concentration, crystal size, state of dispersion, the inclusion of air and film thickness.

Acknowledgement

The author would like to acknowledge the permission of the directors of Tioxide UK Ltd to publish this paper.

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Appendix AA

Examples of the procedure for ranking anticorrosive material, system used in preliminary work of "Zinc Phosphate vs Zinc Chromate".

Variables:
☐ 10 "anticorrosive" pigments or pigment blends (Table 1).
☐ 3 fractions of CPVC level.
☐ 2 film thicknesses (primer only).
☐ 2 systems (single coat and top coat over primer, for each film thickness).
☐ 3 test environments (Table 2).
which makes 60 panels (30 of each primer film thickness) in each complete batch of 1 test environment and 1 system (single coat or primer plus top coat). That is, 360 panels in all.

Rankings were performed before and after removing the paint film from the panel after exposure in order to see the appearance of the substrate, and when feasible after adhesion tests. As an example, results of the cyclic test inclusive of salt spray to ASTM B-117 and UVA radiation are given for the system consisting of primer only:

Explanatory notes:

* The numeral at the end of each Panel Number refers to the thickness of primer dry film: 1 means the lower value and 3 the higher value.

† For the convenience of this Appendix, "Materials" have been abbreviated as follows:
ZC=Zinc Chromate
ZP=Zinc Phosphate
LC=Lead Chromate
IO=Iron Oxide
Ba=Barytes
blends when indicated by "+" are those listed in Table 1.

Fraction of CPVC levels are:
LO (FoCPVC=0.25)
ME (PVC=25%)
hi (FoCPVC=0.80)

‡ In this ranking, a "Pigment Composition" is the combination of one of the materials in Table 1 and one of the three Fractions of CPVC level used.

Panel Number*	Order in batch of 60 panels	Rating	Rating together thickness −1 and −3	Material† & FoCPVC level	Ranking‡ (per Pigment Composition)
1320-3	1	2	40	ZC+ZP ME	4
1316-3	2	2	6.5	ZC ME	1
1317-3	3	2	6.5	ZC LO	1
1317-1	4	4.5			
1316-1	5	4.5			
1315-1	6	6.5	21	ZC HI	2
1321-3	7	6.5	52.5	ZC+ZP LO	2
1337-3	8	14.5	52.5	LC+ZP HI	6
1322-3	9	4.5	40	ZC+IO HI	4
1324-3	10	14.5	52.5	ZC+IO LO	6
1323-3	11	14.5	52.5	ZC+IO ME	6
1334-3	12	14.5	29	LC HI	3
1341-3	13	14.5	60.5	LC+IO ME	7
1340-3	14	14.5	60.5	LC+IO HI	7
1309-3	15	14.5	52.5	ZP HI	6
1315-3	16	14.5			
1334-1	17	14.5			
1310-3	18	14.5	60.5	ZP ME	7
1335-3	19	14.5	52.5	LC ME	6
1311-3	20	14.5	70	ZP LO	9
1339-3	21	14.5	60.5	LC+ZP LO	7
1319-3	22	25.5	51	ZC+ZP HI	5
1319-1	23	25.5			
1338-3	24	25.5	63.5	LC+ZP ME	8
1336-3	25	25.5	71.5	LC LO	10
1342-3	26	25.5	81	LC+IO LO	12
1313-3	27	25.5	71.5	ZP+IO ME	10
1314-3	28	25.5	81	ZP+IO LO	12
1322-1	29	25.5			
1332-3	30	32	78	Ba+IO ME	11
1331-3	31	32	87.5	Ba+IO HI	13
1326-3	32	32	87.5	Ba ME	13
1327-3	33	32	87.5	Ba LO	13
1333-3	34	32	87.5	Ba+IO LO	13
1309-1	35	38			
1337-1	36	38			
1323-1	37	38			
1324-1	38	38			
1335-1	39	38			
1320-1	40	38			
1338.1	41	38			
1325-3	42	46	101.5	Ba HI	14
1340-1	43	46			
1310-1	44	46			
1313-1	45	46			
1332-1	46	46			
1341-1	47	46			
1336-1	48	46			
1339-1	49	46			
1321-1	50	46			
1325-1	51	55.5			
1312-3	52	55.5	111	ZP+IO HI	15
1331-1	53	55.5			
1312-1	54	55.5			
1326-1	55	55.5			
1327-1	56	55.5			
1311-1	57	55.5			
1342-1	58	55.5			
1333-1	59	55.5			
1314-1	60	55.5			

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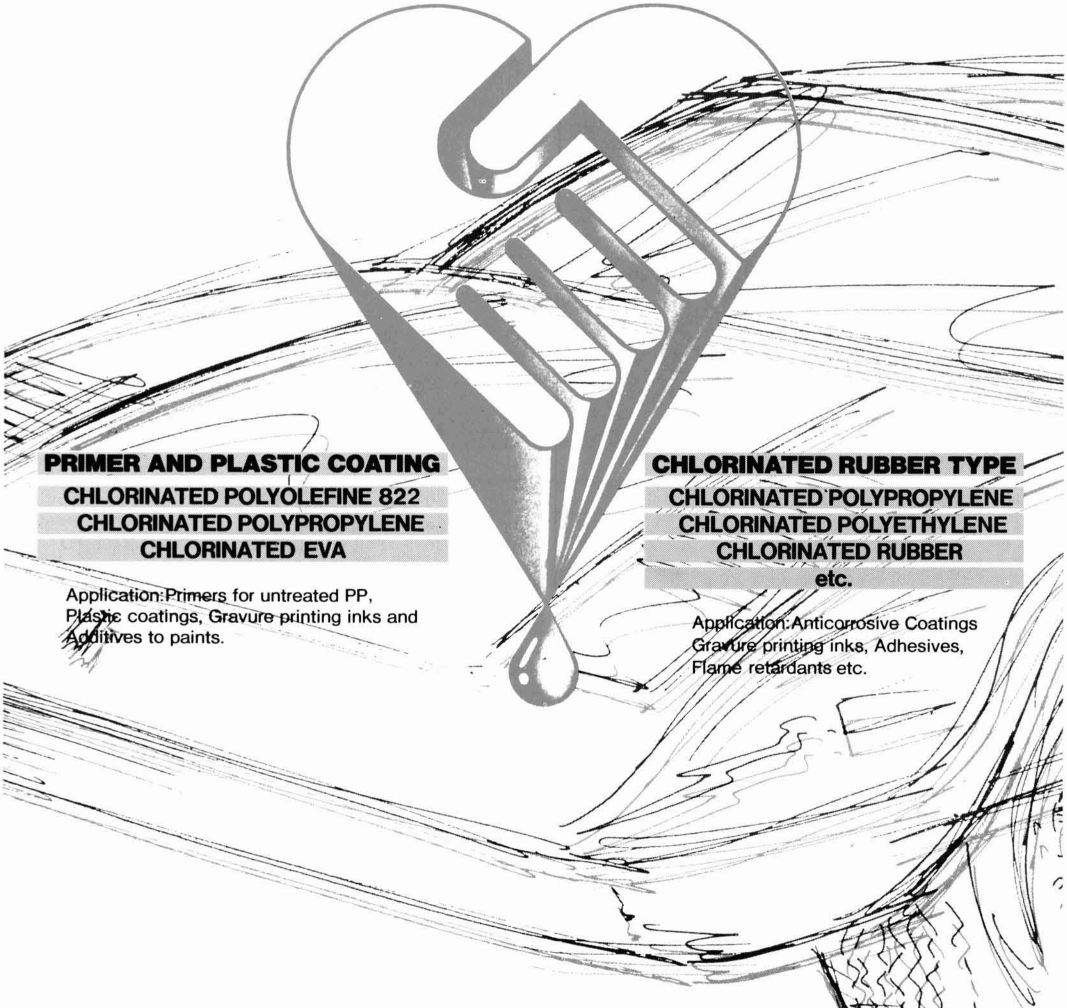

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Appendix AB

Preliminary work "Zinc Phosphate vs Zinc Chromate".

Combined ranking for all primer only panels exposed to the two modes of salt spray test, obtained by adding rankings for each mode as obtained for different variables as shown through the example given in Appendix AA:

For the convenience of this Appendix, "Materials" have been abbreviated as follows:
ZC=Zinc Chromate, ZP=Zinc Phosphate, LC=Lead Chromate, IO=Iron Oxide and Ba=Barytes

Blends when indicated by "+" are those listed in Table 1.

Ranking	FoCPVC=0.25	PVC=25%	FoCPVC=0.80
1		Zinc Chromate	
2	Zinc Chromate		
3			Zinc Chromate
4			ZC + ZP
5		ZC + ZP	
6			Lead Chromate
7			ZC + IO
8			LC + ZP
9	ZC + ZP		
10		LC + IO	
11		ZC + IO	
12			Zinc Phosphate
13	ZC + IO		
14	LC + ZP		
15		LC + ZP	
16			LC + IO
17	Zinc Phosphate		
19	Lead Chromate	Lead Chromate	
19		Zinc Phosphate	
21		ZP + IO	
22	LC + IO		
23		Ba + IO	
25	ZP + IO		ZP + IO
25	Barytes		
28	Ba + IO	Barytes	Ba + IO
30			Barytes

Appendix AC

Preliminary work "Zinc Phosphate vs Zinc Chromate".

Combined ranking for all primer plus top coat panels exposed to the two modes of salt spray test, obtained by adding rankings for each mode as obtained for different variables as shown through the example given in Appendix AA:

For the convenience of this Appendix, "Materials" have been abbreviated as follows:
ZC=Zinc Chromate, ZP=Zinc Phosphate, LC=Lead Chromate, IO=Iron Oxide and Ba=Barytes

Blends when indicated by "+" are those listed in Table 1.

Ranking	FoCPVC=0.25	PVC=25%	FoCPVC=0.80
1			Zinc Chromate
2	Zinc Chromate		
3		Zinc Chromate	
4			ZC + IO
5			ZN + ZP
6		ZN + IO	
7		ZN + ZP	
8	ZC + ZP		
9	LC + ZP		
10		LC + IO	
11	ZC + IO		
12	Zinc Phosphate		
13			LC + ZP
14		Zinc Phosphate	
15		LC + ZP	
16			Zinc Phosphate
17			Lead Chromate
18	LC + IO		
19		Lead Chromate	
20			LC + IO
21		ZP + IO	
22			ZP + IO
23	ZP + IO		
24	Lead Chromate		
25			Ba + IO
26	Barytes		
27		Ba + IO	
28.5	Ba + IO	Barytes	
30			Barytes

Appendix AD

Preliminary work "Zinc Phosphate vs Zinc Chromate".

Combined ranking for all primer plus top coat panels exposed to actual outdoor weathering at Colores Hispania's factory in Martorelles. Panels have been classified after striping the coating in order to asses the appearance of the substrate:

For the convenience of this Appendix, "Materials" have been abbreviated as follows:
ZC=Zinc Chromate, ZP=Zinc Phosphate, LC=Lead Chromate, IO=Iron Oxide and Ba=Barytes Blends when indicated by "+" are those listed in Table 1.

Ranking	FoCPVC=0.25	PVC=25%	FoCPVC=0.80
1			ZC + ZP
2			Zinc Phosphate
3		Zinc Phosphate	
4			LC + ZP
5.5		ZC + ZP	ZP + IO
7			Zinc Chromate
8		ZP + IO	
9.5	Zinc Phosphate	LC + ZP	
11		Zinc Chromate	
12	Zinc Chromate		
13.5		ZC + IO	Barytes
16.5	LC + IO	LC + IO	
16.5	LC +	ZP	
16.5	ZC + ZP		
19.5	ZC + IO		ZC + IO
21	Barytes		
22			LC + IO
23	ZP + IO		
25		Barytes	Ba + IO
25		Ba + IO	
27		Lead Chromate	
28	Ba + IO		
29			Lead Chromate
30	Lead Chromate		

Appendix B

Layout of the experimental design used for screening candidate materials as described under the heading "Searching through cumulative evidence". A reproduction of a typical form used for putting ratings together for this purpose.

Form for putting together ratings of relative anticorrosive performance.

Test:

	Fraction of CPVC = 0.80 Primer only						Pigment Volume Concentration = 10 One coat only					Fraction of CPVC = 0.80 Primer plus top coat (see boxes below)			
Candidate material	100% Candidate material			25% Candidate material 55% Barytes 20% Iron Oxide			25% Candidate matrl 55% Barytes 20% Iron Oxide		80% Candidate matrl 20% Iron Oxide			100% Candidate matrl		25% Candidate matrl 55% Barytes 20% Iron Oxide	
	PVC	DFT 8 micron	DFT 30 micron	PVC	DFT 8 micron	DFT 30 micron	DFT 8 micron	DFT 30 micron	DFT 8 micron	DFT 30 micron		Top coat TiO2	In-depth protection	Top coat TiO2	In-depth protection
1	*			*											
2	*			*											
3	*			*											
4	*			*											
5	*			*											
6	*			*											
7	*			*											
8	*			*											
9	*			*											
10	*			*											

Appendix C

Form used for ranking every group of panels with the same conditions of paint system, thickness and mode of exposure.

Form for ranking panels in a group during follow-up of a test:

Paint system:
Thickness:
Top coat:
Test:

		Ratings during evolution of the test																														Adhesion		Rating after striping of coating						Overall ranking	
		n(1)					n(1)					n(1)					n(1)					n(1)					n(1)					f(7)		f(7)						F(8)	
Candidate material	**Panel number**	QDS (2)	ADS (3)	OAP (4)	Ave (5)	x n (6)	QDS (2)	ADS (3)	OAP (4)	Ave (5)	x n (6)	QDS (2)	ADS (3)	OAP (4)	Ave (5)	x n (6)	QDS (2)	ADS (3)	OAP (4)	Ave (5)	x n (6)	QDS (2)	ADS (3)	OAP (4)	Ave (5)	x n (6)	QDS (2)	ADS (3)	OAP (4)	Ave (5)	x n (6)		x f	QDS (2)	ADS (3)	OAP (4)	Ave (5)	x f (6)			x F (6)

(1) n = number of cycles or months elapsed
(2) Qualitative Deterioration in Scratch
(3) Area Damaged around Scratch
(4) Overall Appearance of Panel
(5) Average of (2), (3), (4)
(6) weighed average
(7) weight given to test (worker decided)
(8) weight given to group for addition to other groups (worker decided)

Appendix D

Putting together the results of a large group of control and candidate anticorrosive materials tested on steel in epoxy-polyamide primers, as explained under heading "Shaping a novel anticorrosive pigment".

Example of adding weighted results for several modes of salt spray exposures and water immersion tests, for a large group of materials tested in epoxy-polyamide primers applied to steel:

Test mode (Salt Spray, Kesternich, Immersion)	SS	SS	K+SS	IMM	SS	K+SS	IMM		
System (Primer Only, Top Coat)	PO	PO+TC	PO+TC	PO+TC	PO+TC	PO+TC	PO+TC	TOTAL	RANKING
Thickness (microns)	25	15+20	15+20	15+20	25+50	25+50	25+50		(1=BEST)
Weight (number of cycles)	11	36	36	36	60	48	54		
MATERIAL									
Strontium Chromate	247	72	144	454	420	336	524	2197	21
Zinc Phosphate (standard)	209	144	108	281	120	48	432	1342	23
Zinc Phosphate (small particle)	22	900	684	576	1410	1200	659	5451	3
Iron Oxide (synthetic)	192	36	36	151	180	96	92	783	25
Candidate material PAE 8510	82	288	252	115	540	528	373	2178	22
Candidate material PAE 8511	82	504	540	576	660	864	869	4095	13
Candidate material PAE 8512	82	180	576	288	480	768	724	3098	17
Candidate material PAE 8513	137	540	720	238	330	1104	508	3577	15
Iron Phosphate PAE 8514	220	828	864	490	1500	1152	432	5486	2
Candidate material PAE 8517	192	612	324	238	780	720	238	3104	16
Candidate material PAE 8524	82	396	216	749	1200	960	1118	4721	8
Iron/Zinc Phosphate PAE 8525	22	792	396	799	1140	816	1118	5083	5
Candidate material PAE 8526	137	216	612	749	600	672	1118	4104	12
Iron/Zinc Phosphate PAE 8527	82	468	432	799	1410	912	1118	5221	4
Iron/Zinc Phosphate PAE 8528	82	864	828	799	1260	1008	1118	5959	1
Iron/Zinc Phosphate/Molybdate PAE 8529	165	648	468	799	1320	576	805	4781	7
Candidate material PAE 8531	231	252	288	799	1080	432	1118	4200	10
Market-supplied sample MAC 001	82	756	900	342	1020	1056	664	4820	6
Market-supplied sample MAC 002	247	360	756	259	240	288	254	2404	18
Market-supplied sample MAC 003	154	720	648	338	720	480	1118	4178	11
Market-supplied sample MAC 004	176	324	180	259	840	144	292	2215	19,5
Market-supplied sample MAC 005	22	576	504	385	960	624	772	3843	14
Market-supplied sample MAC 006	264	684	792	547	900	192	1118	4497	9
Market-supplied sample MAC 007	275	432	360	115	330	384	319	2215	19,5
Market-supplied sample MAC 008	82	108	72	162	60	240	140	864	24

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Appendix E

Standardized accelerated tests proposed for further work:

a) Moderate industrial/rural environment:

Each cycle consists of 16 hours salt spray cabinet, at 23°C, with 4.1 g/l $(NH_4)_2SO_4$ and 0.3 g/l NaCl, followed by 8 hours under UVA 351 lamps at 45°C. With air drying alkyd systems, significant results are obtained after 15 such cycles for a single coat primer and 30 cycles for a primer plus top coat system.

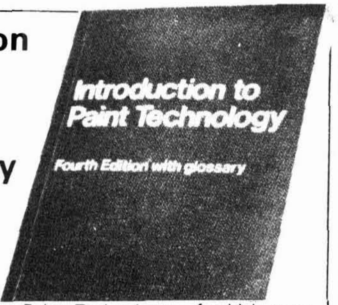
b) Heavy industrial/marine environment:

Each cycle comprises the following: 16 hours in the salt spray cabinet, under the same conditions as above, followed by 8 hours during which panels are allowed to dry but not removed from the cabinet. This is repeated the next day. Then panels are transferred to the QUV test cabinet, where they undergo cycles of 4 hours UVA 351 at 45°C followed by 4 hours water vapour condensation at the same temperature during 2 more days. At weekends, one of the two modes is alternatively extended a third day. Significant results are obtained after 10-15 of these long cycles.

Appendix F

Paint formulating parameters, pigment compositions by volume and by weight, relative paint raw material costs and results corresponding to the heading "Formulating into paints: Cost effectiveness re-evaluated".

		Pigment blend % volume composition					Pigment blend % weight composition					Anti-corrosive Pigments in Total Paint (%weight)	Relative cost of paint raw materials	Performance (1=Best)		
Fraction of CPVC	PVC %	Actirox 102	Actirox 213	Barytes	Iron Oxide	Talc	Actirox 102	Actirox 213	Barytes	Iron Oxide	Talc			Primer Only	Primer & Primer + Top Coat	Primer + Top Coat Only
0.8	42.40			38.60	25.70	35.70	0.00	0.00	44.86	29.60	25.54		100			
0.7	39.20	19.00		31.27	20.82	28.92	15.81	0.00	37.77	24.92	21.50	7.00	127	13	13	23
0.7	35.70	14.00	7.00	30.49	20.30	28.20	11.72	5.67	37.06	24.45	21.10	7.00	127	8	11.5	21
0.7	32.90	8.00	16.00	29.34	19.53	27.13	6.76	13.08	35.96	23.73	20.47	8.00	127	10	11.5	17
0.7	30.80		27.00	28.18	18.76	26.06	0.00	22.27	34.87	23.01	19.85	8.00	127	2	5	18
1	55.00	15.00		32.81	21.85	30.35	12.38	0.00	39.31	25.94	22.38	7.00	127			25
1	52.00	11.33	5.66	32.04	21.33	29.63	9.40	4.55	38.60	25.47	21.98	8.00	127			26
1	48.00	6.00	12.00	31.65	21.07	29.27	5.00	9.67	38.28	25.26	21.79	8.00	127			24
1	46.00		20.00	30.88	20.56	28.56	0.00	16.23	37.58	24.80	21.39	8.00	127			22
0.8	46.40	52.00		18.53	12.34	17.14	46.45	0.00	24.02	15.85	13.68	23.00	188	7	8.5	14
0.8	42.40	44.00	15.00	15.83	10.54	14.64	40.10	13.23	20.94	13.82	11.92	24.00	188	12	7	6
0.8	37.60	34.00	34.00	12.35	8.22	11.42	31.81	30.79	16.78	11.07	9.55	25.00	188	9	8.5	11
0.8	33.60	20.00	60.00	7.72	5.14	7.14	19.41	56.35	10.88	7.18	6.19	28.00	188	4	2.5	5
0.8	28.00		98.00	0.77	0.51	0.71	0.00	97.43	1.15	0.76	0.66	29.00	188	6	6	12
1	57.00	43.00		22.00	14.65	20.35	37.65	0.00	27.97	18.46	15.92	20.00	188			13
1	52.00	36.00	12.00	20.07	13.36	18.56	31.98	10.32	25.88	17.08	14.74	22.00	188			15
1	48.00	28.00	28.00	16.98	11.31	15.71	25.44	24.62	22.40	14.78	12.75	22.00	188			20
1	43.00	16.00	50.00	13.12	8.74	12.14	14.97	45.28	17.83	11.76	10.15	26.00	188			2
1	35.00		80.00	7.72	5.14	7.14	0.00	75.60	10.94	7.22	6.23	28.00	187			19
0.8	46.40	80.00		7.72	5.14	7.14	76.20	0.00	10.67	7.04	6.08	36.00	234	11	10	10
0.8	42.40	60.00	20.00	7.72	5.14	7.14	57.51	18.55	10.74	7.09	6.11	33.00	219	5	4	7.5
0.8	37.60	40.00	40.00	7.72	5.14	7.14	38.58	37.33	10.81	7.13	6.15	30.00	202	1	2.5	9
0.8	28.00		80.00	7.72	5.14	7.14	0.00	75.60	10.94	7.22	6.23	24.00	171	3	1	3
1	58.00	80.00		7.72	5.14	7.14	76.20	0.00	10.67	7.04	6.08	41.00	268			16
1	53.00	60.00	20.00	7.72	5.14	7.14	57.51	18.55	10.74	7.09	6.11	39.00	248			7.5
1	47.00	40.00	40.00	7.72	5.14	7.14	38.58	37.33	10.81	7.13	6.15	35.00	226			1
1	42.00	20.00	60.00	7.72	5.14	7.14	19.41	56.35	10.88	7.18	6.19	33.00	208			4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For further information contact Dr Peter Fyne Tel: 081-908 1086; Fax: 081-908 1219.

OCCA Chester Conference Paper

Dispersion behaviour of plasma-treated pigments in aqueous paint systems

by T. Kobayashi, T. Terada and S. Ikeda, Nippon Paint Co. Ltd., 19-17, Ikedanaka-Machi, Neyagawa-City, Osaka, Japan

Abstract

Surface modification of pigments was carried out using a low temperature plasma method. The dispersion behaviour of such plasma treated pigments in water soluble acrylic resins was studied. Surface properties of such treated pigments were investigated, by measuring the heat of immersion in water and their acidity-basicity. The dispersion rate of plasma treated pigments was increased and its dispersion stability improved.

1. Introduction

A water-borne paint is a non-polluting coating system, and is already widely used, for example as wall or electro deposition coatings. But in some cases, there are still technical problems to be solved. Typical problems are flooding and flocculation of the pigment dispersion. This is a drawback to the gloss of paint films and the rheological properties of the paint.

In this study, we shall prove that plasma surface treatment of pigments was an effective means to obtain a finely dispersed pigment in the aqueous coating.

In our previous paper[1], the dispersibility of hydrophilic pigments (TiO_2) and hydrophobic pigments (Cu-Phthalocyanine blue) in water soluble acrylic resins was studied from the viewpoints of "wetting" and "stabilization" of pigments. We reported the following conclusions about how to obtain a well or finely dispersed pigment in an aqueous coating:

(1) As for the dispersion of hydrophilic pigments, "wetting" of pigments by the aqueous solution of resins was easily obtained. In this case, the "stabilization" process (that is, an adsorption process of resin on a pigment surface through hydrophobic interaction between the resin and pigment) was the rate determining process of dispersion. A certain degree of hydrophobicity given to the hydrophilic pigment surface increased the amount of resin adsorption on the pigment, and a finely dispersed pigment was obtained.

(2) On the other hand, for the hydrophobic pigments, the "wetting" process was the rate determining process of dispersion. Since the hydrophobic pigment was not easily wetted by the aqueous solution of resin. Therefore in order to disperse the hydrophobic pigment finely in the aqueous solution of resin, a certain degree of hydrophilicity had to be given to the surface of the hydrophobic pigment.

(3) From (1) and (2), we can say that "wetting" and "stabilization" contradict each other. In other words, selection of a hydrophilic pigment leads to a higher rate of "wetting" but results in lower level of "stabilization". For the fine pigment dispersion in aqueous solution of acrylic resins, the most favorable hydrophilicity value of pigment, which was measured by the heat of immersion in water, was between 0.1 and $0.2 J/m^2$. This occurred because appropriate levels of both "wetting" (of pigment by an aqueous solution of acrylic resin); and "stabilization" (caused by the adsorption of resin on the pigment surface) were achieved by the pigment.

Also, we have previously reported[2] that the low-temperature plasma treatment can give hydrophilic and acidic (or basic) functional groups to an organic pigment surfaces, according to plasma species used. Such plasma-treated pigments showed excellent dispersibility in conventional alkyd resin systems, because of the enhanced acid-base interaction between pigments and resins.

In this study, we applied NH_3-plasma and O_2-plasma treatments to give the favorable hydrophilicity to the hydrophobic surface of carbon black and quinacridone red pigments. Dispersibility of these plasma-treated pigments in water soluble acrylic resin systems was examined.

2. Experimental

2.1 Plasma surface treating apparatus

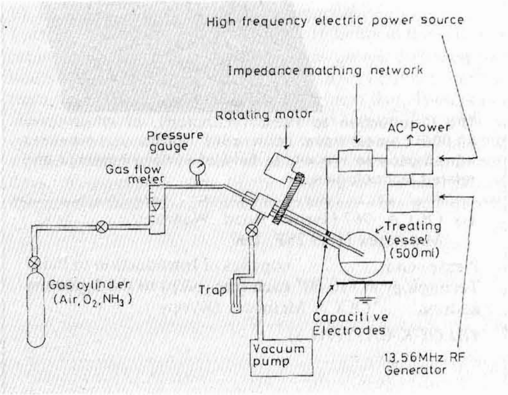
2.1.1 Laboratory-scale apparatus

The schematic diagram of a laboratory-scale plasma surface-treating apparatus is shown in Figure 1. RF power (13.56 MHz) was applied through the impedance matching network to one of capacitive electrodes. The other electrodes was grounded.

The treating vessel (500 mL) containing pigment was rotated at 30 rpm. The vessel was pumped down to a base pressure of 20 Pa. by a vacuum pump. Then NH_3 or O_2 gas was supplied by gas cylinder and the pressure was increased to 100 Pa. The gas flowmeter and pressure gauge were placed in the circuit in order to adjust the experimental conditions.

Figure 1

Schematic diagram of the laboratory-scale plasma-treating apparatus.



Paper presented to OCCA Chester Conference 1989 on behalf of the Japan Society of Colour Material

The plasma was generated in the treating vessel between the two electrodes.

2.1.2 Pilot-scale apparatus

The schematic diagram of a pilot-scale plasma treating apparatus is shown in Figure 2. RF power (13.56 MHz) was applied through the impedance matching network to the lower part of a 45 L treating vessel. The upper part of the vessel was electrically isolated from the lower part and grounded.

The vessel containing 2.5 Kg of pigment was pumped down to a base pressure of 20 Pa by vacuum pump. Then NH_3 gas was allowed to flow in and the pressure was increased to 150 Pa.

Plasma was generated inside the vessel, which was vibrated by the oil pressure equipment.

2.2 Characterization of plasma-treated pigments

2.2.1 Measurement of the heat of immersion

The heat of immersion of pigment in water was measured by twin isoperibol calorimeter (TIC-221, Tokyo Ricoh Co. Ltd.) for the quantitative evaluation of the degree of hydrophilicity of the pigment surface.

2.2.2 Measurement of acid (base) amount

Two grams of pigment were immersed in 30mL of 0.01N Dimethyl Ethanol Amine / aqueous solution (0.01N Acetic Acid / aqueous solution) and dispersed by ultrasonic vibration.

The pigment was separated from the solution by a centrifugal separator.

The residual clear solution (10 mL) was back-titrated by 0.01N Hydrochlolic acid / aqueous solution (0.01N Potassium Hydroxide / aqueous solution).

The acid (base) amount of pigment was calculated from the back-titrated base (acid) amount.

2.2.3 Measurement of zeta-potential

Twenty-five grams of Dimethyl Ethanol amine (DMEA) and 12.3 grams of Acetic Acid were dissolved in 900 grams of water, and the pH value of this solution was adjusted to 9, which is the pH value of the aqueous resin solution used for the dispersion. The pigment (0.1 g) was dispersed in 50mL of this solution by applying the ultrasonic vibration.

Then the zeta-potentials of the pigment in the above solution were measured by the electrophoretic method using the Laser Zee Model 500 (PEN KEM Co. Ltd.).

2.3 Materials

Quinacridone red (Cinquasia Red Y RT-759D, Ciba Geigy) and carbon black (Mitsubishi Carbon #1000, Mitsubishi Chem. Ind. Ltd.) were selected for the experiment.

Acrylic resin was synthesized from Methyl Methacrylate (MMA), Hydroxyethyl Acrylate (HEA), Ethyl Acrylate (EA) and Methacrylic Acid (MAA). The acid value and the number average molecular weight (measured by GPC based on the Poly Styrene Standard) of the acrylic resin were 60 and 6000, respectively.

The acrylic resin was dissolved in water by neutralizing the carboxylic acid groups of the resin with DMEA. The molar ratio of DMEA to MAA was 1.1 and the pH value of the resin solution was approximately 9.

2.4 Procedure of pigment dispersion

The mill used for this experiment is shown schematically in Figure 3. This was specially developed to control the temperature of the dispersing medium and the speed of rotatory disc. The dispersing temperature was 20°C and the rotation speed was 2000 rpm. The paste formulations are shown in Table 1.

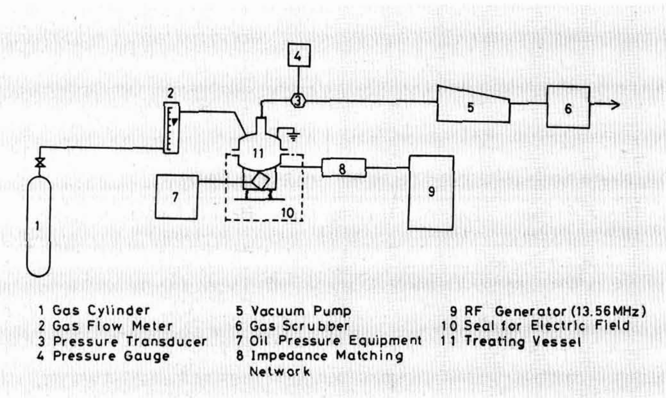
Table 1

Pigment paste formulations

Pigment	Carbon Black	Quinacridone Red
Acrylic Resin Solid	34	22
Butyl Cellosolve	26	19
Water	22	41
DMEA	3.6	2.3
Carbon Black	18	–
Quinacridone Red	–	18
Glass Beads	100	100
Total	203.6	202.3

Figure 2

Schematic diagram of the pilot-scale plasma-treating apparatus



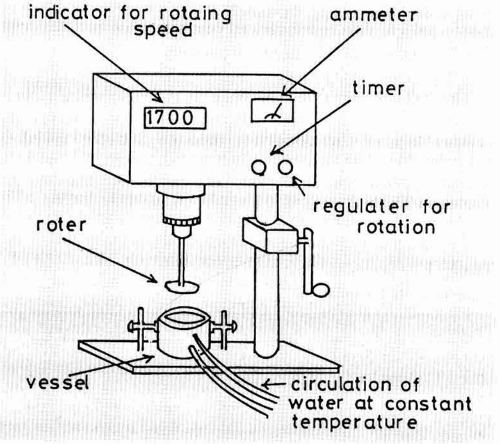
2.5 Evaluation of the dispersibility of pigment

The dispersibility (or the degree of flocculation) of pigment in the resin solution was measured by the yield value. Shear stress at various shear rate, ranging from 1.92 sec^{-1} to 384 sec^{-1}, was measured by a cone/plate type of viscometer (E Type Viscometer, Tokyo Keiki Co. Ltd.). The temperature was kept at 25°C. Yield value was calculated from the Casson's plot[3]. The viscosity of the pigment dispersed paste in this study followed the Casson's plot quite well.

2.6 Evaluation of the degree of dispersion[4]

The degree of pigment dispersion was measured by the gloss of grind gauge drawdowns. The procedure of measurement was as follows: (1) the dispersed paste was drawn down on the grind gauge, with a 0-25 micron scale; followed by (2) the measurement of 60 degree gloss at the position of 17.5 microns on the grind gauge readings.

Figure 3
Dispersing mill


indicator for rotaing speed
ammeter
timer
1700
regulater for rotation
roter
vessel
circulation of water at constant temperature

2.7 Measurements of adsorbed resin amount

The amount of adsorbed resin (on pigment) was measured by the gravimetric method, using a centrifugal separator. Centrifugal separation of pigment with adsorbed resin, after dilution of DMEA / Acetic Acid solution, was repeated until its weight reached a constant value.

The amount of adsorbed resin was calculated by subtracting the weight of pigment.

3. Results and discussion

3.1 Surface properties

3.1.1 Carbon black

Surface properties of carbon black pigment treated by NH_3-plasma and O_2-plasma are shown in Table 2 together with the treating conditions.

The heat of immersion in water was increased by O_2 plasma treatment. This means the degree of hydrophilicity of carbon black pigment was increased by O_2-plasma treatment. On the other hand, almost no increase in the heat of immersion was observed by NH_3-plasma treatment.

O_2-plasma increased the acid amount and decreased the base amount of the pigment surface. While NH_3-plasma increased the base amount and decreased the acid amount of the pigment surface. The zeta-potential of pigment was changed from −30 mV to −20 mV by NH_3-plasma treatment.

These results indicate that O_2-plasma generates polar and acidic groups, and NH_3-plasma generates basic groups on the surface of the pigment[2].

3.1.2 Quinacridone red

Surface properties of quinacridone red pigment treated in NH_3-plasma are shown in Table 3, together with the treating conditions.

Table 2
Surface properties of plasma-treated carbon black pigment and treating conditions

Power (W)	Pressure (Pa)	Type of Gas	Treating Time (Hr)	Heat of Immersion (J/m^2)	Acid Amount (Mol./Kg)	Base Amount (Mol./Kg)	Zeta-potential (mV)
Non-treatment				0.067	0.15	0.05	−30
60	10^2	NH_3	2	0.069	0.11	0.08	
			6	0.067	0.09	0.11	−20
		O_2	2	0.099	0.17	0.05	
			6	0.125	0.36	0.00	−30

Apparatus: Laboratory-scale   Amount of treated pigment: 30g/batch

Table 3
Surface properties of NH_3-plasma treated quinacridone red pigment and treating conditions

Amount of Treated Pigment (Kg)	Power (KW)	Pressure (Pa)	Type of Gas	Treating Time (Hr)	Heat of Immersion (J/m^2)	Acid Amount (Mol./Kg)	Base Amount (Mol./Kg)
Non-treatment					0.11	0.004	0.009
2.5	1	150	NH_3	6	0.11	0.004	0.015
				12	0.12	0.002	0.019
				18	0.15	0.001	0.026
				24	0.17	0.000	0.030

Treating Apparatus: Pilot-scale

3.2 Dispersion behaviour

3.2.1 Carbon black

Figures 4 and 5 represent relations between dispersion time and gloss of grind gauge drawdowns of pigment dispersed pastes, which contain carbon black pigment treated in either O_2-plasma or NH_3-plasma. Thus the dispersion rate of carbon black pigment treated in either plasma was shown to increase.

After 6 hours dispersion, the yield values and amounts of adsorbed resin were evaluated. These results are shown in Table 4. Comparisons of NH_3-plasma treatment (the amount of adsorbed resin on treated pigment were increased and the yield value of the paste containing treated pigment was decreased) with those values of untreated pigment are illustrated. But only slight changes in both of these values were observed for O_2-plasma treatment.

O_2-plasma treatment of carbon black pigment increased the degree of hydrophilicity of the pigment surface. This was indicated by the heat of immersion, and enhanced "wetting" process of dispersion. However, further increases in hydrophilicity leads to a reduction of the "stabilization", since the latter is obtained by adsorption of the resin through hydrophobic interaction. After 2 hours treatment, the heat of immersion reached the appropriate level, that is 0.1J/m^2 ~ 0.2J/m^2. Further treatment (6 hours) enhanced the "wetting" but reduced the "stabilization".

The heat of immersion is not affected by NH_3-plasma treatment and the "wetting" process seems not to be enhanced. The increased dispersion rate in Figure 5 can be explained by the increased amount of adsorbed resin on the NH_3-plasma treated pigment, which improves the "stabilization" process of dispersion. This is also indicated by a decrease in the yield value in Table 4. Interaction between pigment particles seems to be lowered by repulsion between the adsorbed resin layers.

Zeta-potentials of untreated and NH_3-plasma treated carbon black pigment are shown in Table 2. Lower absolute value of zeta-potential can be seen for NH_3-plasma treated pigment. Resin molecules used in this experiment were negatively charged and the charge of carbon black pigment was also negative as shown in Table 2. The resultant electrostatic force between the pigment particles and resin molecules were repulsive. This repulsive force interfered with the attractive force (hydrophobic interaction) between them. This lower absolute value of zeta-potential of NH_3-plasma treated pigment leads to less interference of the repulsive force between pigment and resin. As a result there is an increased amount of adsorbed resin.

3.2.2 Quinacridone Red

NH_3-plasma treated quinacridone red pigment shown in Table 3 were dispersed according to the paste formulation in Table 1.

Gloss values remained constant after 2 hours dispersion.

Figure 6 represents the relationship between treating time and gloss and yield value of pigment paste after 2 hours dispersion. As shown in Table 3, the heat of immersion (degree of hydrophilicity) of quinacridone red pigments, was

Figure 4

Effect of O_2-plasma treatment on the dispersion rate of carbon black pigment

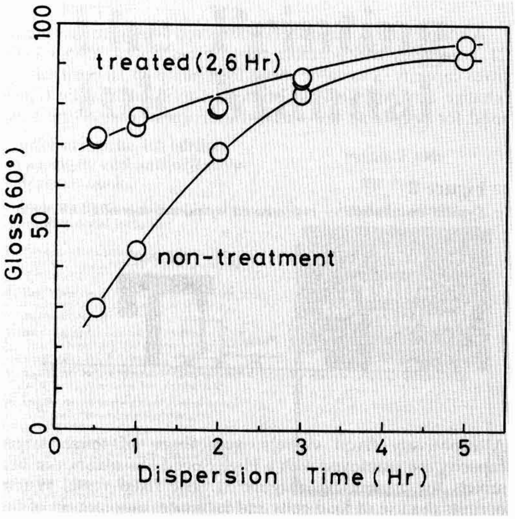


Figure 5

Effect of NH_3-plasma treatment on the dispersion rate of carbon black pigment

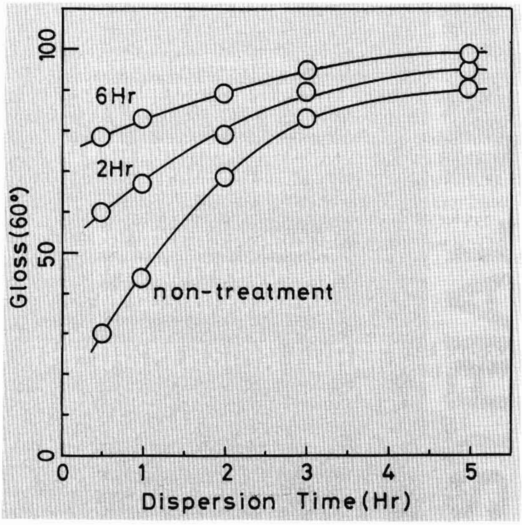


Table 4

Yield value and amount of adsorbed resin for the suspension of treated pigment

Power (W)	Pressure (Pa)	Treating Time (Hr)	Type of Gas	Amount of Adsorbed Resin (mg/g)	Yield Value (Pa)
		Non-treatment		130	3.3
60	10^2	6	NH_3	170	1.0
			O_2	120	3.5

Continued on p.261

Bead milling – a practical guide

by B. Denison, Glen Creston Limited, 16 Dalston Gardens, Stanmore, Middlesex HA7 1DA, UK

Abstract

The horizontal bead mill is now an established machine for the production of fine particle dispersions. The process is described from a practical point of view dealing with both machine variables and formulation.

The difference between primary particle milling and dispersion of aggregates and agglomerates is highlighted and a new type of dispersing agent for pigments is mentioned. An update in mill construction is included and a reference list is given for more detailed information.

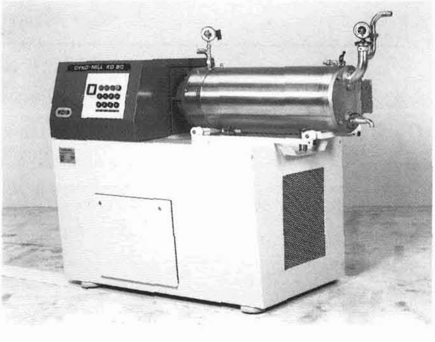
Introduction

The bead milling technique, developed for use in the paint industry more than 25 years ago has essentially replaced ball milling. The historic development of these mills has often been described in the literature[1-5] and the technique is now widely used to produce micronised dispersions in a number of industries. Dispersions of solid substances in liquids are known as suspensions. A factor common in the manufacture of these suspensions is the need for particle size reduction, however, the solid phase may comprise primary particles, aggregates, or agglomerates. The physical requirements of the mill base, especially viscosity, may differ and in general the user must aim to maximise the suspended solid concentration within the constraints of meeting product specifications, physical and practical limitations. There are now available some new types of dispersing agent to assist the pigment user in this area.

Conditions in the mill can be adapted to suit most formulations provided the feed is mobile and pumpable. The effect of changes in machine variables on milling rate, product temperature and mill pressure are generally predictable in direction but not necessarily in actual value. Mill design has improved considerably over the last two decades and Figure 1 illustrates a modern DYNO® horizontal bead mill of 60 litre chamber volume.

DYNO® — Registered trade mark of W. A. Bachofen AG, Basel, Switzerland.

Figure 1
60 Litre DYNO Mill



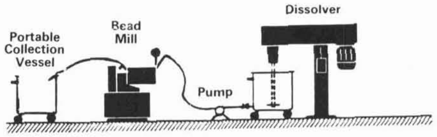
The bead mill and its rôle

The bead mill is a totally enclosed agitated ball mill with a horizontal stationary grinding container enclosing a driven shaft, with agitators which activate a bed of small, typically 1-3mm diameter, grinding beads. Suspensions are pumped through the agitated beads continuously to achieve the required reduction in particle size. A special type of filter retains the beads. The machine is designed to mill and disperse to below 20 microns, but requires the feed size to be already ground and dispersed to below 250 microns. Although particle size reduction becomes increasingly more difficult as size diminishes, bead mills are routinely employed to produce particle distributions of mean size below one micron. While some dry milling techniques may achieve sizes below 15 microns so called 'wet' techniques offer the advantages of improved temperature control, the opportunity to stabilise the micronised particles by formulation, the containment of product and the avoidance of dust formation and associated problems of powder handling. Paint and inks are of course the most common application but not all milled materials are required in liquid form, some agrochemical powders and disperse dyestuffs are formulated, milled and subsequently dried to produce wettable powders. These products when added to water, wet out rapidly and reproduce the very fine particle dispersion produced by the bead mill.

Layout and ancilliaries

A simple and commonly encountered arrangement (Figure 2), comprises two portable tubs on castors of 200 to 1,000 litres capacity, a variable speed feed pump and a bead mill. A 'change-can' mixer usually of the saw-toothed impellor type is used for preparing the initial dispersion in one of the tubs.

Figure 2
Typical installation — reproduced by permission of DIAF AG.



Alternatively fixed vessels, sometimes of much larger capacity are employed with a High Speed Dissolver or in-line mixers for pre-milling. (Figure 3). The fixed vessel system permits the use of load cells and facilitates automation of the process. Recirculation of product through a bead mill from a single feed vessel is sometimes adopted, however the "discrete pass" system is usually preferred. The feed pump must be variable speed since flow rate controls dwell time in the mill. The longer the dwell time, the finer the product, therefore pump speed is the main control exercised by the operator to meet the required size specification. Other factors to be described later are equally important but are usually optimised for specific products by plant trial under the control of chemist or project engineer.

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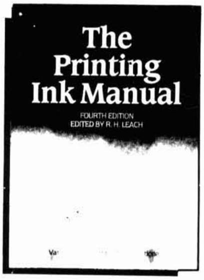

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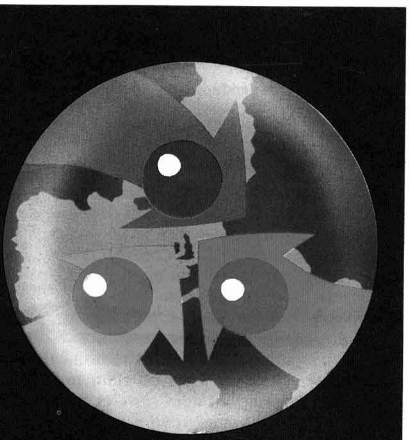

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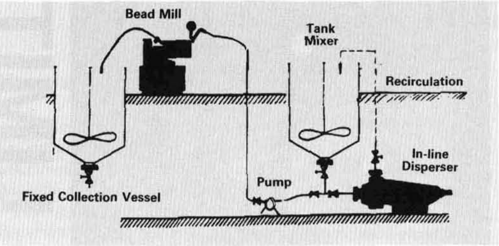
Figure 3

Typical installation — reproduced by permission of Siefer Machinenfabrik GmbH

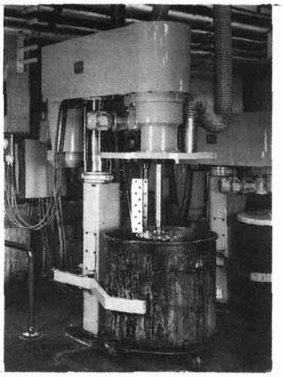


Pre-milling

The efficient operation of a bead mill is dependent on the previous stage in the process providing a lump-free pumpable suspension with an upper size limit of 1/7 to 1/10 of the bead size employed. It is, however, good practice to pre-disperse as finely as possible thereby increasing mill capacity and minimising product outlet temperature. In the paint and ink industry a high speed dissolver (Figure 4) is frequently used.

Figure 4

Diaf Dissolver with optional side scraper



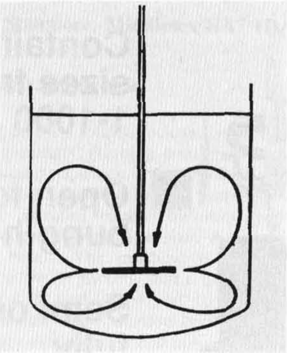
A variable speed drive system permits the incorporation of dry powders into a liquid medium at low speed to minimise dusting. When initial wetting out of the powder is complete[6], the disc speed is increased up to approximately 25 m/s, considerable de-agglomeration occurs though not primary particle breakdown. High power to volume of mix ratios are employed, typically 15 joules/litre. High viscosities, up to 10,000 cps, are needed to obtain laminar flow and good vortexing. A flow pattern known as 'The Doughnut' (Figure 5) should develop and after some 10 to 20 minutes the pre-dispersion process should be completed.

Some products will not disperse readily by this technique, having either hard gritty material or significant numbers of particles above 150 microns. Particles as large as this are often broken down in rotor/stator mixers. Batch types are often suspended from a hoist inside the mixing vessle while tooth ring mills of the Trigonal® type are used in-line. The latter has a pumping action and therefore simultaneously recirculates and grinds the suspension.

Trigonal® — Registered trade mark of Siefer Machinenfabrik GmbH, Velbert, West Germany.

Figure 5

The ideal 'Doughnut' flow pattern



Mill capacity and output

Mills are sized according to their chamber volume. This is the free volume inside the grinding cylinder with shaft and agitators in situ but without grinding beads. DYNO mills for example range from 0.3 litre to 285 litre. Mill capacity on the other hand can vary enormously with the type of product. It is often determined by trials on a mill of small volume when all variables are studied to obtain the maximum output for a given chamber volume. Both formulation and milling variables are evaluated and for paints and inks a typical output might be 7 litres per hour per litre of chamber volume. Product capacities several times this figure have been encountered while for extremely difficult materials it may be below 1 litre per hour. The low capacity figures are not met so often in paint manufacture. Multiple passes would be employed to avoid excessive temperature rise in the mill but giving the same overall output. For example 1 pass at 100 litre/hr is equivalent to 2 passes at 200 litre/hr.

Mill construction

In principle the bead mill is a simple mechanical device, however, the often abrasive and aggresive materials processed and the high shaft speeds employed necessitate a sound shaft support and bearing system together with a good seal. High viscosities, thixotropy and the use of small diameter grinding media also put special demands on the bead filter or separator. The test of a good design is simplicity combined with reliability and while some mills have proved themselves in the last two decades others have failed. It is common practice to lubricate seals by recirculation of a clean liquid which is compatible with the product being processed. Typically a 2 litre reservoir and recirculation pump are provided for this purpose or once through water.

The continuous separation of the grinding elements from the suspension is accomplished using sieves of various designs or a coaxial ring slot integrated into the shaft and support flange. The system should allow uninhibited passage of the suspension and the latter 'dynamic' system will shear thin thixotropic products as well as having a self-cleaning action. Separator gaps are set well below the diameter of the grinding elements, typically one third. The mill illustratred in Figure 1 is offered with a choice of separation system.

Mills are constructed so that wear parts are replaceable and these are usually available in stainless steel, hardened steel, hard chrome plated steel and other more specialised materials.

Machine variables

The high agitation speeds employed in a bead mill help compensate for the small mass of the grinding elements. The speed at the edge of the agitator disc is very important since this is where the high bead velocities or shear forces are generated. This velocity or "tip-speed" is calculated from Equation 1.

$$\text{Tip speed m/sec.} = \frac{\text{rpm}.\pi D}{60} \quad \ldots\ldots\ldots\ldots\ldots (1)$$

where D = disc diameter in metres

It is more usual to refer to tip speed rather than shaft speed and in practice this ranges from 6 to 16 m/sec. This range of tip speed values is adopted throughout the range of mills on the market and it is particularly important to control and note its value when conducting trials for scale up purposes. The smaller mills have higher shaft speeds than larger mills but the tip speed value employed is independent of mill size. Usually high tip speeds means higher output or finer particle size limited only by the sensitivity of the product to temperature rise. Most mills are belt driven and have the facility to select the appropriate tip speed by changing the pulley ratio. Some mills are now available with variable speed drives permitting infinite adjustment of tip speed from 8 to 16 m/sec. by the touch of a button.

The size and type of bead employed is often determined empirically but there are some useful guide lines. With increasing numbers of beads per unit volume, the number of point contacts increases and consequently the grinding intensity. Therefore the smallest beads possible should be employed eg.

1 litre holds approximately 125,000 2mm beads
1 litre holds approximately 1,000,000 1mm beads
1 litre holds approximately 8,000,000 0.5mm beads

High bead density may be beneficial if the suspension is very viscous or dense since both bead mass and tip speed determine the bead energy or shear rate developed in the mill. This energy level must exceed the critical value needed to overcome the cohesive strength of aggregates or to break primary particles as appropriate. Eg. Hard pigment particles of 100 micron diameter cannot be ground with glass beads of 0.2mm diameter.

Efficiency is also influenced by the shape and dimensions of the mill and its components. Variations in number, shape and size of agitator is a typical example. It must be noted, however, that mill design must also take account of reliability and component life in addition to operational efficiency. Good mill geometry and a horizontal format permits a high volume fill of beads of between 80 and 85% giving maximum mill potential.

Studies of milling variables have been reported for various products including paints[7], dyestuffs[8] and bacteria[9].

Mill operation

The mill is first charged with 80 to 85% beads by volume. The weight of beads can be calculated using their bulk density. This is their packing density and is not to be confused with their real density. Adherance to a volume fill avoids mistakes. Product is then pumped to the mill and when all the air has been displaced the mill may be started. The beads may need pre-wetting with a compatible liquid if the feed has a high viscosity.

The flow rate of product is often measured simply by timing the collection of a small quantity of material as it emerges from the mill. Before testing for particle size, the contents should be displaced 1.5 times to ensure the initial material has been displaced and the sample is representative. Flow rate should then be adjusted to achieve the dispersion level required.

Control and responses

It is usual to monitor, product outlet temperature, mill pressure and motor ammeter reading during milling. Temperature limitations are usually imposed by the product, not the mill and may be reduced by increasing flow rates, reducing tip speed or increasing bead size, all of which follow from the earlier descriptions of these variables.

Mill pressure originates from the screen or separator. Hence mill pressure increases as bead size decreases, but pressure also increases with product flow rate and with increasing viscosity. It is usual for mill pressures to be limited to 1.5 bar in order to avoid bead compaction and to prolong seal life, but mills do work perfectly satisfactorily at lower pressures. Excessively high mill pressure may be reduced by decreasing flow rate by reducing viscosity or by employing a larger bead size and correspondingly larger separator gap or screen.

The motor ammeter reading reflects energy consumption. It is a summation of the effects of both machine variables and formulation, and is sometimes used as an indication of how much work is being done on the product.

Formulation

This topic can only be dealt with very generally. Powder pigments, mostly comprise aggregates and agglomerates of sub micron particles and the dispersion or wetting out process pulls these particles apart. This process is favoured by the high shear developed at the tip of the agitator discs. Since shear forces diminish rapidly with distance in low viscosity systems, pigment dispersion is favoured by high viscosity. Most dyes and agrochemicals are composed of discrete particles or crystals which are physically broken by the milling process. These products not only take longer to mill but the optimum viscosity is much lower. Perhaps viscosity has a cushioning effect reducing particle and bead velocity and therefore impact energy. The viscosity limit in this case must be determined empirically but its lower level compared to pigments emphasizes the difference between dispersion and primary particle milling. Despite these differences the aim of the formulator should be to maximise the concentration of the material being ground. Additives are frequently employed to stabilise the fine particles but they may also promote the dispersion process. They can reduce viscosity significantly giving the opportunity to formulate at higher solids concentration. These special dispersing agents have been used for many years for water based dyestuffs[10] and agrochemical compositions. Products suitable for solvent based systems possessing similar properties were more difficult to develop. For many years the film forming agent in paints has acted as stabiliser and wetting agent for pigments during milling but obviously the properties of the paint film dictated their selection. Now there are some new polymeric dispersing agents[11-13], offering the same formulation opportunities previously only available for aqueous systems. Although these new compounds are used in relatively small amounts in paint compositions it is still sometimes necessary to have binder present during milling to avoid 'shock' effects when diluting the mill base. Nevertheless, the binder may be added as a fixed percentage of the total and the formulator's task is then to optimise a 3 component mixture of solid dispersant and liquid. Daniel and his flow point technique[14-15], did this for the pigment/binder/solvent system some 40 years ago, recognising that an unnecessary excess of binder denied the possibility of a further increase in solids concentration. For bead mills, the various compositions should be assessed for milling rate and dispersion stability.

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The amount of dispersant is related to the dye or pigment surface area and may vary with the degree of dispersion required. Milling rates often peak for primary particle milling but for pigments the rate may continue to rise until mill pressure or product temperature becomes limiting. Suspensions may of course be ground at lower concentrations and viscosity but some sacrifice in output must be accepted.

Shutdown and cleaning

When the batch is finished a quantity of product will remain in the mill. It is usual to push out this material with solvent and/or binder left out of the initial mix for this purpose. Additional solvent or liquid phase is then used for washing. The mill can be easily and quickly cleaned between batches but drastic colour changes are avoided whenever possible.

Conclusions

Academic studies of milling and dispersion are often on simplified or dilute systems and the gap between theory and practice is widely appreciated. Far from being exclusively for paint and ink manufacture the range of application of bead mills continues to grow. Suppliers therefore look to their experience in different technological areas to understand the process and develop their products to the benefit of users generally. This paper is intended to guide both new and existing users to improve their mill performance, however there is no substitute for trial and experimentation for specific products even within the paint and ink industry.

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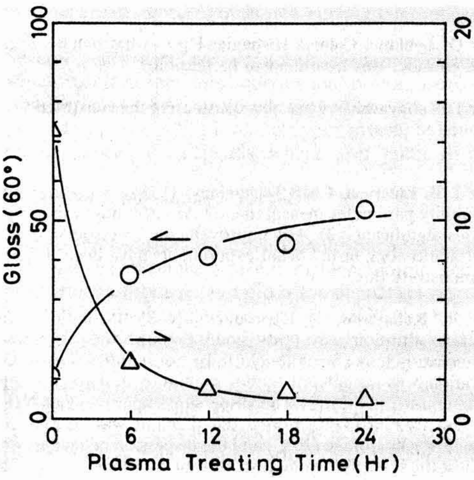
Presented at the Newcastle Section Seminar, 'Paint Manufacture', 24 April 1990, Durham University.

Kobayashi, T., et al continued from p.255

increased by NH_3-plasma treatment, which suggests that the "wetting" was enhanced. Moreover, a decrease in the yield value of pigment dispersed paste suggests that an improvement of the "stabilization" also occurred. This improvement is obtained by the same mechanism of decreasing the repulsive electrostatic force (as shown for the carbon black pigment, treated in NH_3-plasma).

Figure 6

Effect of the plasma treating time on dispersion properties of quinacridone red pigment



4. Summary

Plasma surface treatment is a simple and useful technique for improving the dispersibility of organic and carbon black pigments.

NH_3-plasma treatment can improve the wettability and / or the "stabilization" of pigments in water. This is proven by the increase in the base amount of pigment and / or the heat of immersion of pigment in water, and by the decrease in the acid amount of pigment. An increase in base amount and decrease in acid amount, leading to reduction of absolute value of negative zeta-potential, results in an increase in the amount of adsorbed resin. O_2-plasma treatment of the pigment surface can improve the wettability in water.

NH_3-plasma is more effective for improving pigment dispersion than O_2-plasma. This is because the "stabilization" is improved, and in some cases (quinacridone red), the "wetting" is also enhanced.

5. Acknowledgement

The authors are grateful for the support of the Japan Society of Colour Material. The authors also wish to thank our colleague Miss Y. Kato, for the measurements of acid/base amounts, the heat of immersion and gloss of grind gauge drawdowns.

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Chester Conference Discussions

Profitable Application of Research and Development for Novel Anti-corrosive Pigments

by Mr O. Leblanc, Colores Hispania, Spain

Published in June 90 JOCCA

Mr J. R. Taylor, JOCCA: You state that in the accelerated corrosion testing you exposed the panels to a "weak cycle" of the kesternich test before normal testing. What difference in the performance of the panels was found compared with the ASTM B117 Salt Spray test and do you show this performance of your panels in the photographs in your paper?

Mr O. Leblanc: In some of the early stages of the project we used strong cycles of the Kesternich test, with results which showed little connection with the more standard ways of testing. As a trend, chromate and molybdate containing pigments were penalised, with best results for zinc phosphate based pigments. When the standard salt spray test was done on panels previously exposed to a weak cycle of the Kesternich test, we found that results were somewhat accelerated although not too far away from those of the standard test, so it seemed reasonable to add them to the cumulative data. It is perhaps interesting to recall here that when thin (15-25 micron) alkyd top coats were used over the primers being tested. The weak Kesternich cycle seemed to deteriorate (increase the porosity) of the top coat rather than actually accelerate the attack at the scribe (except for chromate based pigments).

The influence of the Kesternich weak cycle in performance to salt spray is not shown on the photographs included in the paper. Nevertheless, some results may be found in Appendix D: 2nd and 3rd column of weighted ratings correspond to similar batches of panels (15 micron primer, 20 micron top coat) exposed respectively to salt spray only and to salt spray after one weak Kesternich cycle, while 5th and 6th column do the same for panels with 25 micron primer and 50 micron top coat (note in this case different number of cycles in each mode). Although a detailed comparison between results in the two modes should not be over-emphasized, it may nevertheless be noticed that some of the pigments do perform differently.

Mr J. R. Taylor, JOCCA: You note that particle size of the anticorrosive pigment is important regarding corrosion resistance. Is this due to the change in pigment packing and therefore difference in water and water vapour permeability and have you carried out any work on this subject?

Mr. O. Leblanc: The particle size of anticorrosive pigments may be relevant to corrosion resistance because of several reasons:

☐ solubilisation of the active chemical is made easier by increased specific surface.

☐ an increased ratio between coating thickness and pigment size prevents porosity.

☐ pigment packing may indeed improve for smaller particles (although some larger particles may also be useful!).

Besides these more or less obvious facts, we have reasons to believe, based on some unpublished work, that pigment size and shape may also influence binder degree of crosslinking and/or solvent retention, with ensuing strong influence on performance.

Dispersion Behaviour of Plasma-Treated Pigments in Aqueous Paint Systems

by T. Kobayashi, R. Terada and S. Ikeda, Nippon Paint Co Ltd, Japan (Paper presented on behalf of JSCM)

Published in June 90 JOCCA

Prof I. Macpherson, Ciba Geigy Pigments: What evidence do you have of chemical modification of the pigments' surfaces occurring during oxygen- or ammonia-ion etching?

Mr T. Kobayashi: Anthracene (as the low molecular weight model for the graphite-structure of carbon black) treated by NH_3-plasma was dissolved in MIBK and potentiometrically titrated against perchloric acid. The titration curve showed that various kinds of basic compounds had been generated by NH_3-plasma treatment of anthracene.

For NH_3-plasma or O_2-plasma treated Quinacridone red pigment, XPS analysis was carried out. XPS spectra suggested that O_2-plasma generated the acidic groups containing oxygen, such as carboxyl group, while NH_3-plasma provided basic groups containing nitrogen, probably amino, and/or imino groups[2].

Dr S. G. Lawrence, Ciba Geigy Pigments: Is there any indication that the plasma treatment penetrates into this aggregate structure of pigment powders, reducing strengths of aggregates and a finer optical particle?

Mr T. Kobayashi: Usually, plasma-treatment time to improve the wettability of materials in the shape of plate or fibre is very short (a few seconds to a few minutes). However, it took many hours to improve the wettability of pigments. Even the amount of pigment to be treated was changed in the same apparatus, the treatment time to improve the dispersibility of pigment was scarcely changed.

From this result, we consider that it takes a long time for the plasma-generated active species to penetrate or diffuse into the aggregate structure of pigment powders and that this penetrating or diffusing process is the rate determining process of plasma treatment of pigments.

Mr O. Leblanc, Colores Hispania: Up to what batch size do you consider this treatment to be feasible?

Mr T. Kobayashi: We are now considering the construction of a one ton plant.

Mr J. B. Emerson, CMB Technology: 1) How accurate is the solubility parameter measurement? Are acetone evaporation losses significant? 2) Are improvements in dispersion and wettability long term? What experiments have been done to demonstrate this?

Mr T. Kobayashi: 1) Reproducibility of the data in the acetone titration was fairly good (within 10%). Acetone evaporation losses was thought to be not significant since the titration was completed within a minute or two at room temperature (20°C). 2) The dispersion experiment of NH_3-plasma treated Quinacridone red pigment was carried out after 2 weeks storage (20°C) and the dispersion behaviour was almost the same as the one just after the treatment. ■

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2. Out With The Old - In With The New

Over the years, there has been a trend towards the increasing use of aqueous systems for all paints (industrial and decorative), driven by factors such as **Cost, Environmental Issues, Easy Clean and Convenience** etc.

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Several years ago, we set about designing pigments which would bridge this aqueous and non-aqueous gap and perform really well on both sides. With such pigments, you would rationalize your inventory or even reduce stocks (it depends where you come from!).

3. A "No Compromise" Target

The research target was a truly multi-purpose pigment for high performance and not merely another general purpose compromise. We did a lot of market research and talked to a lot of customers, who told us what they wanted. Often they told us very clearly, because if **we** were going to spend **our R & D** funds to develop what **they** wanted, then it looked like a good deal. We listened very carefully too and set about this task (or in reality the Marketing lot asked the R & D Department to get on with it - under some sort of generalised guidance, naturally!) We had an armoury of surface treatment technologies at our disposal in which we had even greater variety than the systems we set out to serve.

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From the General Secretary

D J (Don) Morris

Members will be saddened to learn of the death of Past President D J Morris on 16 May 1990. Don Morris was President during 1981-1983 and continued to serve the Association as Representative on Council for the South African Division. A full obituary will appear in the July issue of JOCCA.

SURFEX 90

SURFEX 90 has come and gone and already planning has commenced for SURFEX 92. The report on the Exhibition, including new products, visitor profile and personalities will appear in the July issue of JOCCA. In the meantime, what are my first impressions? SURFEX 90 was clearly the most successful of the new style exhibitions; a record number of exhibitors; a record number of visitors; a record turnout at the Exhibitors' Dinner. The success of the Exhibition reflects the Association and the support of those companies in which members are employed.

On the down side, space at the Harrogate International Centre is at a premium. No more exhibitors can be accommodated within the existing halls and the overflow in the International Hotel. A handful of exhibitors were disappointed that they were unable to book space in the main exhibition area of Hall D and felt that accommodation within the Exhibition Centre, the Reception, Gallery and Auditorium, was less attractive. On the other hand, regular exhibitors within these three areas were very satisfied with the more informal layout and relaxed atmosphere offered by the unconventional exhibition space and would not wish to be sited elsewhere. However, there is genuine pressure from exhibitors, many of whom wish to expand their exhibition space and this will be given urgent attention by the organising committee. Harrogate is the preferred location for the Exhibition, but there is no desire to expand the exhibition into the older halls adjoining the International Centre. There are prospects of a new exhibition hall being available for SURFEX 92 which should enable a larger exhibition to be mounted, but which at the same time continues with the traditional atmosphere and most of all the enjoyment provided by SURFEX.

The Exhibition saw the introduction, for the first time at an OCCA Exhibition, of a computer-based registration system. This innovation was not without its teething problems, exacerbated by lack of space in the Reception area. However, despite the initial congestion we hope the new system has proved a success and it will be repeated for 1992. The advantage of the computerized system is that an accurate and comprehensive visitor profile will be available by the time readers receive this Journal. Data from the survey will be available to interested companies on payment of a modest fee. Additionally, an exit poll of some 10% of the visitors will provide very useful data on visitor reaction and full details of this will be included in the report on the Exhibition. It is the intention of the organisers to provide a very comprehensive visitor poll for the 1992 Exhibition and extend this to provide services to companies participating at the Exhibition.

A report on the Exhibition would not be complete without mention of the contribution made by members of the staff and the organising committee of Fred Morpeth, Jim Hemmings and Lionel Morpeth, who provided policy direction and personal involvement in the organisation of all three SURFEX exhibitions. Particular tribute and gratitude must be paid to Fred Morpeth who has made a major contribution to the success of all three exhibitions. Fred relinquishes his position as Honorary Exhibition Officer at the AGM when he assumes the mantle of President Designate. Hopefully, he will remain a member of the Management Committee, as will his two colleagues, neither of whom although well suited to take on the Chairmanship, are available and a new Chairman is required. The Management Committee quite correctly maintain that the new Chairman must come from the ranks of exhibitors, although most of the administration for SURFEX 92 will rest with staff at Priory House. Any member who is reading this column and is interested in taking on this high profile but very rewarding task should contact Fred or myself. We would be delighted to hear from you.

Subscriptions

Regular readers of this column will recollect that my April contribution concentrated on the collection of 1990 subscriptions. In the intervening month a considerable number of members have paid their subscriptions and at the time of writing this column the number of members still to pay for 1990 has reduced to under 200. Inevitably, some members will not renew and it is particularly disappointing when these are members who have served for many years, and made significant contributions to the development of the Association. However, we must accept that through retirement, redundancy or transfer from the industry members may wish to sever their contact with the Association. In such circumstances resignations are accepted with regret, but we are always happy to welcome old friends back into the Association.

If you are reading this column and have not paid your subscription for the year, please do so as soon as possible. Budgets are drawn up on the assumption that the majority of members will pay and the shortfall in income from those members who have already paid means they do not have the full benefit of their membership of the Association.

■

Hull Section

MIO coatings

The fourth technical meeting of the session was held on Monday, 5 February, 1990, at The Duke of Cumberland Hotel, Cottingham, starting at 7.00 p.m. Members and guests heard Mr Eric Carter of Cookson Laminox Ltd give a talk entitled "Developments In Micaceous Iron Oxide Coatings For Steel".

The speaker briefly traced the history of MIO starting from its discovery as specular haematite in Devonshire at the end of the 19th century. Following its use in paints in 1902 by a London paint-maker, the protective properties of the pigment were recognised in GB, France and Germany and it became widely used in coatings for the expanding railway systems in Europe.

Mr Carter explained how the pigment, an iron oxide with the particle structure of mica but not containing it, is used in finishes and some undercoats where its lamellar structure obstructs the permeaton of corrosive ions, improves mechanical strength of the film and shields the binder from degrading UV radiation. Some MIO pigments with reduced flake-like structure performed less well as a result. The original English source is worked out, he said, main supplies are now coming from Austria. There are also souces in many other parts of the world producing pigment of varying quality.

After demonstrating by way of colour slides how microscopic examination using transmitted light was used to determine lamellar structure and hence usefulness, the speaker touched on paint formulation aspects. Binders ranged from oleo-resins, alkyds, chlorinated rubbers, vinyl copolymers, acrylated rubber (styrene acrylate) to epoxies and polyurethanes. Critical pigment volume concentration ranged from around 30-40% depending on paint type.

Mr Carter then outlined some of the main factors to be considered when deciding on paint type. Is the location mild, urban? Is the structure buried or immersed in sea-water? Is there industrial pollution present? Will the coating be subjected to intense sunlight? After emphasising the importance of local conditions he listed other factors, such as surface type and treatment and ease of access for future maintenance, affecting choice of paint type. Such choices were illustrated, again using slides, by reference to the painting of the Forth Road bridge and our local Humber bridge, the longest single span suspension bridge in the world.

The speaker then touched on properties of various types of MIO paints, where and how they would be used and specifications laid down by various bodies such as British Rail, Dept. of Transport, M.O.D., C.E.G.B. Shell, B.P., etc., referring the audience to his paper "Micaceous Iron Oxide Paints" for more detail.

Moving finally to developments in MIO paints, he explained these had been almost entirely concerned with binder development, little change in the pigment itself having occurred. However, Mr Carter's company had recently developed a synthetic MIO known as LAMINOX whose lack of impurities and particle shape and size range meant even better protective properties were assured.

Water-vapour permeability, water absorption and salt-spray tests backed up with field trials demonstrated the superiority of the new pigment, he said.

The speaker finally dealt with a number of questions from the audience. These concerned the comparative characteristics of synthetic and natural MIO, optical properties, erosion of films containing non-lamellar pigments, UV, absorption, alligatoring in chlorinated rubber paints and corrosion protection. The importance of pigment morphology and PVC was stressed, Mr Carter mentioned that other materials, for example, aluminium, graphite, glass and stainless steel in lamellar form were capable of "barrier" behaviour in coatings.

The meeting closed with a vote of thanks proposed by the secretary, Philip Bentley, and endorsed by the audience.

D. Robinson ■

Midland Section

Product development and control of quality

The January meeting of the section held at the Claredon Suite, Stirling Road, Edgbaston, heard Mr Ray Tennant of Carrs Paints present a talk entitled 'Product Development And Control Of Quality In The Automotive Industry'.

He opened by reviewing the development of automotive finishes with reference to the binders on which they were based. Gum/Oil bound coach finishes, applied by brush, were replaced by Nitrocellulose which offered a greater drying speed and was associated with the widespread introduction of spray painting technology. The replacement of N-C by Alkyd/Amino stoved coatings gave improved film build through their higher applied solids content, but they were limited to colours other than white due to poor overtake characteristics. Thermoplastic Acrylics with their increased durability replaced Alkyd/Amino binders but were themselves displaced by Thermosetting Acrylics. T-S Acrylics did not, however, give satisfactory gloss characteristics when used in metallic colours, hence the industry opted for the clear-over-base approach. More recently two pack isocyanate coatings have been presented as alternatives. However, despite their greater chemical resistance, amongst other benefits, greater health and safety measures are needed for the control of fume and vapour.

The review of coating types was used to illustrate how developments in application technique, coating systems and binder types were all closely interrelated.

Mr Tennant then turned his attention to the current coating systems, briefly outlined as Phosphate pre-treatment, Electrocoat primer/suface, Base/Colour and Clear coat.

Base coats were either Polyester/C.A.B./Melamine or Acrylic/C.A.B./Melamine whereas clear coats were predominantly Acrylic Melamine or to a much smaller extent Acrylic/Isocyanate or Acrylic/Non-Isocyanate. One coat finishes could be Alkyd, Acrylic or Polyester/Melamine systems.

The sixty-two members and guests present were reminded by the speaker that in addition to durability, ease of application, cost and performance, the ability to repair the coating and hence the development of air dry, low bake and 2-pack cured coating offering similar dry film properties to the original finish was an important part of automotive finishes.

With regard to future trends in automotive finishing paints the speaker referred to High Solids, Water Based and Powder coatings. He questioned the compatability of present High Solids systems when used in the clear-over-base systems before pointing out that Humidity Control and drying speed would be a problem with water based systems. He considered Powder coatings as not yet viable due to poor flow characteristics, high cure temperature and polishability.

The speaker then presented a

shorter discussion regarding the control of quality with reference to the quality of development and service offered. He identified for areas involved in the control of quality thus: Research And Development, Quality Control, Production and Technical Service.

The material specifications used by the Quality Control department were produced by the Research and Development department after consideration of manufacture and application requirements determined during consultation with both Production and Technical Service departments. In addition to the ordinary transfer of information between departments, use was made of in-house seminars, presented by Research and Development staff, to keep other areas of the company informed and aware of new technical developments.

The vote of thanks was proposed by Mr A. Arnold.

M. J. Round ■

Newcastle Section

Highly successful symposium

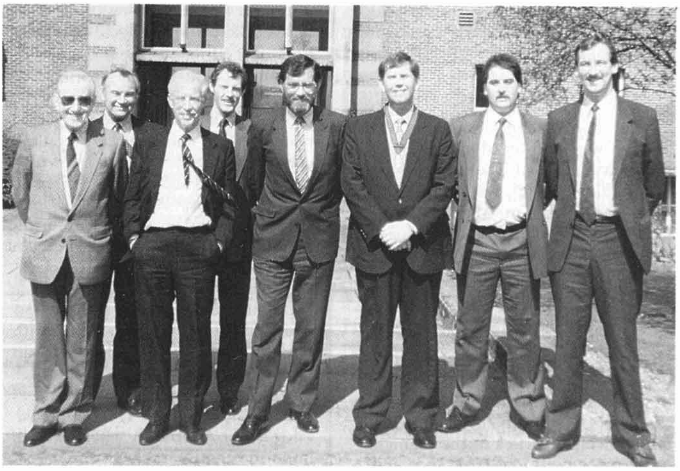
Over 117 delegates attended a one-day symposium on the Introduction to Paint Manufacture held in the James Duff Lecture Theatre, Durham University, on 24 April 1990. David Neal, Chairman of the Newcastle Section, welcomed delegates with Brian Gregory, Seminars Officer.

John Piggott, at short notice, presented the first paper of the morning session on "Planning for production and an introduction to J-i-T". In his paper he outlined the changes in production planning over the past thirty years and closed his talk with a comparison between MRP and J-i-T:

	MRP	J-i-T
Production Lead Time	Up to 4 weeks	2-4 days
Production Batch Size	20,00 litres	5-10,000 litres
Information Flow	Manual	Electronic
Forecasting Units	Monthly	Weekly
Planning Review	Weekly	Daily
Stock level	3-4 weeks	4-8 days

The second paper of the morning session was presented by Brian Denison of Glen Creston, who spoke on "Bead Milling – A Practical Guide", his paper is published in this issue of JOCCA.

The final paper for the morning session was presented by F. Hellens, Courtaulds Coatings, who spoke on "The Implications of COSHH". In his wide-ranging talk he discussed the various effects of the new legislation.



Newcastle Student Symposium Speakers (L to R): J. Bravey, B. Denison, F. Hellens, B. Gregory, J. Piggott, D. Neal – Chairman Newcastle Section, G. Green and P. Gabriel

Following an excellent buffet lunch in St Mary's College the first lecture of the afternoon session was presented by Jack Bravey, Courtaulds Coatings, who spoke on "Formulation for Manufacture". From Jack's many years of experience in the Industry he was able to highlight some of the pitfalls to be avoided and recommended several useful publications for guidance.

The second lecture of the afternoon session was presented by Guy Green and Phil Gabriel of OBS Machines. In their talk they discussed in detail the volumetric tinting system.

The final talk of the afternoon was presented by Brian Gregory, Tioxide, who spoke on "The dispersion of powders in liquids".

In his talk he described the preparation of mill bases and the dispersion of TiO_2 pigments.

Mr David Neal closed the symposium at 5 p.m. and thanked the speakers, his committee and Brian Gregory, and the companies for allowing their students to attend the symposium.

Overall an excellent set of papers were presented, and the Newcastle Committee are to be commended on their impeccable organisation.

It is planned to publish a selection of these papers in future issues of JOCCA.

P. J. Fyne ■

Scottish Section

Classical organic pigments

The final lecture of the 1989-90 session was given by Dr R. B. McKay of Ciba-Geigy Pigments. The title of Dr McKay's lecture was "Physical Character and Performance of Classical Organic Pigments."

Physical organic pigments consist of tiny molecular crystals that are essentially insoluble in the media in which they are applied. The chemical types have been established for decades now on the basis of colour general fastness properties and cost. Nevertheless, from any given chemical type a multitude of pigments each with distinctive application behaviour can be prepared by control of the crystallographic and surface properties. The key factors are size and shape of crystals, crystal lattice type, surface character and state of aggregation of crystals.

Methods of determining these factors were outlined. Specific examples were given to illustrate how they relate to dispersibility of pigments in application media, flocculation resistance and rheology of ink and paint concentrates, and optical performance of pigments in ink and paint films, plastics, etc.

The members of the Scottish Section appreciated Dr McKay standing in at short notice (24 hours) to replace the advertised lecture.

Following a question and answer session, the vote of thanks was proposed by Nigel Baird.

R. F. Hill ■

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Bristol Section Dinner Dance – top table guests (L to R): C. Pacey-Day, Mr and Mrs Stephens, Mr and Mrs Myatt, Mr and Mrs Shaw, Mr and Mrs Seymour, Mr and Mrs D. Penrice

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