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THE NORDIC PAINT INDUSTRY

ALSO IN THIS ISSUE:

- High binders in decorative emulsion paints
- Preparation of ionomer coatings from water-soluble polymers
- Durability of anti-carbonation coatings

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stop press

Crown Paints acquired by Williams Holdings

Williams Holdings the diversified industrial group (which includes Duport, Rawlplug and Fairey Engineering) has acquired Reed's paint and do it yourself division (Crown and Polycell) for £285 million. Williams plans to keep the business intact and retain the existing managers who were behind the £240 million management buyout offer (JOCCA June p.174).

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The Nordic paint industry

A. Saloranta

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When I am talking in this lecture, which for many reasons is rather general, about the Nordic Countries I am referring to the paint industry in Denmark, Finland, Norway and Sweden. Since the facts and figures which I will be presenting are based on statistics from a number of sources, as well as the information published in the annual reports of various companies in the paint business, there may be some errors.

The combined production of paint in the Nordic Countries is equivalent to about 10% of the total production of Western Europe. West Germany, the UK, France and Italy account for 70% of Western European production.

None of the paint companies operating in the Nordic Countries can be placed among the group of 10 largest paint manufacturers in the world. However, the Swedish company AB Wilh. Becker, and the Finnish company Tikkurila Oy, are two of the top 10 companies in Western Europe.

Market structure

The paint industry in the Nordic Countries is characterized first of all by the small number of manufacturers compared to other countries in Western Europe, as well as by the fact that one or two of the paint companies are the clear market leaders in their own country.

The paint producers are independent, rather pure coating manufacturers, and are not usually owned by the concerns which manufacture the basic raw-materials used by the paint industry.

In Denmark there are four major paint companies, with a combined market share of 70%. In Finland there are four companies active in the paint field, two of which have a combined market share of 70%. Sweden has three companies with a combined market share of 80%, and Norway one large paint manufacturer with a share of about 65% of the market.

The major companies in the Nordic paint industry

Denmark

The three largest paint manufacturers in Denmark are Sadolin & Holmblad A/S, Hempel's Marine Paints A/S and S. Dyrup & Co A/S. They are all internationally important companies.

Sadolin & Holmblad A/S was founded already in 1777. It has specialized in trade and retail paints, industrial and automotive coatings. The parent company consists of three companies representing paint, printing ink, glue and chemical units. The paint unit is the largest, accounting for almost one half of the concern's turnover in 1985.

The Sadolin concern operates in almost 20 countries, and has a number of licence agreements. Its largest paint-manufacturing subsidiary is in Finland, and has about 180 employees and a turnover of about GBP 23 million. The turnover of the concern in 1985 was GBP 187 million, the parent company's contribution being GBP 62 million. Exports accounted for 46% of the parent company's turnover. The size of the concern's workforce was 2,196, and that of the parent company 843. Almost 70% of the whole concern's turnover came from exports.

Hempel's Marine Paints A/S is the world's second largest producer of marine coatings. The company was founded in 1915 by J. C. Hempel. Hempel is an extremely international company which has a manufacturing base in Denmark and 28 production units around the world. In addition, it has about 270 sales and marketing units, and a large number of licence agreements abroad. As well as marine coatings, the company also manufactures industrial and decorative coatings. The turnover of the concern in 1985 was GBP 150 million, only 20% of the whole production is in Denmark. The average size of the concern's workforce was 1,700, of which about 400 were employed in Denmark.

S. Dyrup & Co A/S was founded in 1928. It is a part of the larger group Mohnberg & Thoren, which is one of the biggest construction and construction material companies in Denmark. Dyrup has specialized in trade and retail paint, this sector accounting for about 70% of the company's sales. Industrial paints on metal surfaces and anti-corrosion paints are accounting for 20% of the sales. The company has business activities in eight countries. Exports accounted for over 40% of the concern's turnover in 1985, the most important exports having for long been wood preservatives. The turnover of the Dyrup concern in 1985 was GBP 43.5 million, the parent company's contribution being GBP 34 million. The size of the parent company's workforce was 449.

In addition to these three there are two other important companies, Flügger A/S and Hygaea A/S in Denmark. They are specialized in trade and retail paints and the export is 5-20% of the turnover. The turnover of Flügger was in 1985 GBP 25.5 million and the turnover of Hygaea was GBP 11.5 million.

Finland

The two largest paint manufacturers in Finland are Tikkurila Oy and Teknos-Winter Oy. Other major companies are the Danish-owned Sadolin Oy and the Swedish-owned Becker.

Tikkurila Oy was founded in 1862, and has been a subsidiary of Kemira Oy since 1972. Tikkurila Oy moved in one stroke into the international field following the takeover in 1984 of the larger British company Donald

Macpherson Group. Today Tikkurila has production and/or sales companies in nine different countries. Tikkurila's main product group is trade and retail paints, but it is also the largest manufacturer of industrial coatings in Finland. The industrial lines are woodfinishes, coil coatings, industrial light coatings, heavy duty coatings and automotive coatings. Tikkurila Oy has earned a special name for itself as the developer of tinting systems for Trade and Retail and Industrial use. The concern's turnover in 1986 was GBP 190 million and the size of the workforce 2,900. The corresponding figures for the parent company were GBP 80 million and 840 employees. Exports accounted for 28% of the parent company's turnover.

Teknos-Winter was formed in 1986 when the paint manufacturer Teknos Maalit Oy, founded in 1948, bought the Winter Oy paint factory, which had been established in 1892. The estimated turnover of the new company for 1986-87 is around GBP 39.5 million. The company has 470 employees. Teknos-Maalit Oy is specialized in the production of industrial light coatings, heavy duty, marine and powder coatings. Following the takeover, Teknos-Winter Oy is now also an important producer of trade and retail paints. The company has no international subsidiaries. The value of the company's exports is about 10-15% of the turnover. Most of the exports go to neighbouring countries.

Norway

The Norwegian paint market is dominated by A/S Jotun, which is the largest paint manufacturer of international standing in Norway. Jotun's proportion of Norwegian paint production is between 60-70%. The Jotun Concern was formed in 1971 following the fusion of four paint manufacturers.

Jotun manufacturers decorative products—this is the largest and most profitable paint division—as well as marine and offshore coatings that are marketed worldwide through subsidiaries, associated companies and agents. Jotun is the world's third largest producer of marine coatings. Jotun industrial coatings are sold merely on the Norwegian and Swedish markets. Two to three of the products of the Polymer Division are sold outside Norway. Associated companies include Corrocoat, which produces powder coatings.

The market of A/S Jotun are very international, and it has 14 subsidiaries in 13 countries and operations in almost 40 countries. The turnover of the whole concern in 1985 was GBP 152.1 million, the parent company accounting for GBP 110 million. 41% of this figure was derived from exports. The size of the parent company's workforce was 1,060, and that of the concern 1,665.

Sweden

The three largest companies in the paint sector in Sweden are Ab Wilh. Becker, Ab Alfort & Cronholm and Casco Nobel.

The turnover of the Ab Wilh. Becker's concern in 1985 was GBP 228.8 million—64% coming from abroad. The concern's turnover has doubled in five years. The concern has 28 subsidiaries in 12 countries. The concern has 3,525 employees. Becker's major product group is industrial coatings, especially woodfinishes, coil coatings, automotive

and powder coatings, accounting for about half of the whole concern's turnover. The largest market area outside Sweden is the UK, where Becker has a significant share in the powder coatings market.

Ab Alfort & Cronholm, also known as Alcro, was founded in 1906. The turnover of the parent company in 1985 was GBP 64.2 million, and that of the concern GBP 82.3 million. The parent company had 697 employees, and the concern 944. Alcro has concentrated on trade and retail paints. The parent company is divided into paint, wall and wholesale divisions. The products manufactured by the subsidiaries include automotive coatings, woodfinishes and heavy duty coatings. The concern's manufacturing capacity has been concentrated in Sweden; foreign trade is channelled through sales representatives.

Alcro and Becker combined their production of trade and retail paints in 1986. Each company has a 50% share in Alcro-Becker Ab and the company has a combined share of the trade and retail market of 50%. The joint company has made it possible to rationalize production, distribution and administration.

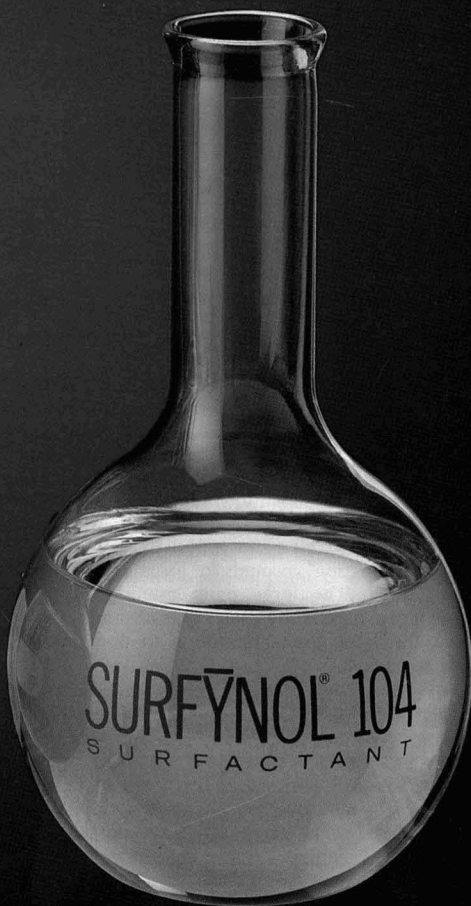
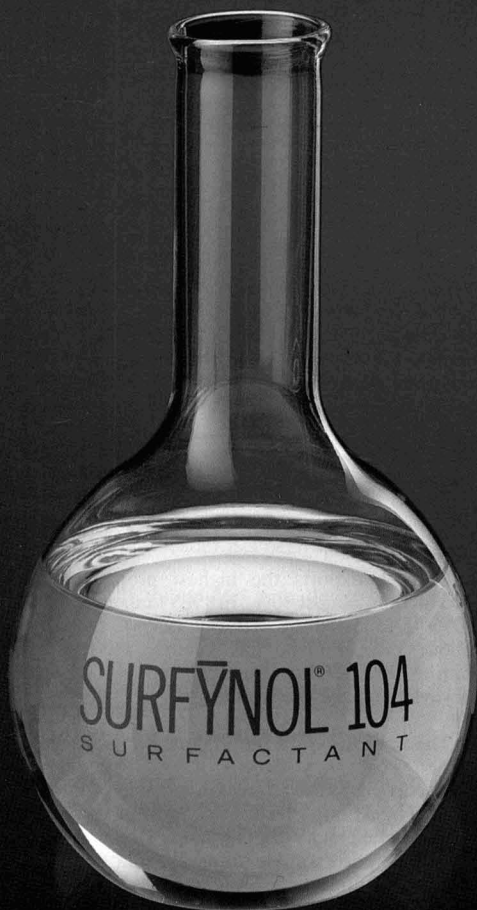
Casco-Nobel, in turn, is a part of the Nobel Industrier Concern. Nordsjö Ab was founded in 1903. Casco bought the company in 1982 from Bayer Ab. Nordsjö is a division of Casco-Nobel which manufactures mainly trade and retail paints, the market share is of 35% in Sweden. A separate industrial paints division produces industrial and automotive paints. The major marketing areas of these divisions are the Nordic countries. The turnover of Casco Nobel in 1985 was GBP 210 million. The number of employees was 2,144. The turnover of Nordsjö was about GBP 73 million and that of Casco Nobel industrial paints was about GBP 82 million. Nordsjö and Casco Nobel industrial paints have about 1,600 employees.

Development of the paint industry

One reason for the centralization of the paint industry is the falling volume of sales which has been a common characteristic of paint markets in Western Europe. This, in turn, had resulted in unsatisfactory profitability for both the paint manufacturers and the raw-material suppliers. The latter group includes major chemical concerns such as BASF, Hoechst, ICI, which are also among the world's largest paint manufacturers. Although these companies can improve their profitability by increasing the price of raw-materials, this in turn brings about an unfavourable situation for those in the paint industry who are not integrated with a raw-materials supplier.

The Nordic paint manufacturers are not usually raw-material manufacturers, and hence they have had to concentrate strongly on product development, on acquiring new technology, and on the rationalization of their production and business operations. This, in turn, has led to the merging of companies in order to make full use of the benefits of mass production. It is thus difficult for foreign and new companies to gain a foothold in the markets in question. The markets in the Nordic Countries have thus developed into ones characterized by a small number of companies and a high degree of dependence between the individual paint manufacturers.

The major paint companies at the Nordic level respect each other's domestic markets to some extent, thus



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preventing the development of unfavourable price competition. The small companies naturally exploit price competition, and their narrow product range is usually built around special products.

Paint production

Paint production in the Nordic Countries, 1979-1985 (1,000 tonnes)

	1979	1981	1982	1983	1984	1985	79/85%
Sweden	196	187	192	192	189	187	-4.6
Denmark	111	112	113	124	133	140	+26.1
Finland	68	107	(110)	78	81	85	+25.0
Norway	71	70	72	74	75	76	+7.0
W Germany	1331	1317	1285	1308	1321	1330	+/- 0
UK	774	707	716	747	772	800	+3.4

Production in Finland and Denmark has seen the strongest increase during this period. The development in Norway has been slow, while in Sweden it has varied from year to year, and has fallen towards the end of the period.

The trade and retail paint industry, which has a high volume of production, accounts for around half of the value of paint sales. The large paint manufacturers try to maintain a firm base in their sales of trade and retail paints, while at the same time attempting to dominate certain product segments.

The relative importance of the decorative and industrial sector by country (1985)

	Decorative		Industrial and others	
	(1000 tonnes)	%	(1000 tonnes)	%
Denmark	58.5	50	59	50
Finland	33	47	37	53
Norway	34	40	51	60
Sweden	67.5	42	92.5	58
West Germany	502	42	693	58
United Kingdom	300	48	323.5	52

The Danish and Finnish markets are strongly centred around trade and retail paints. The strong emphasis in the Swedish market on industrial coatings, as in West Germany, is due to the car industry and the overall strong industrial basis of these two countries. The high percentage for industrial coatings in Norway is mainly a result of sales of marine and offshore coatings.

About 30-40% of the decorative paints are sold to do-it-yourself enthusiasts.

Paint consumption

Paint consumption per capita in 1976 and 1984, kg

	1976	1984
Sweden	23.8	19.9
West Germany	21.2	19.2
Denmark	19.6	21.7
Norway	19.3	23.6
Finland	15.2	18.0
United Kingdom	12.2	10.0

Consumption in Norway and Denmark has grown. The

consumption of paint in Finland is, internationally speaking, relatively high.

The annual national growth rates for the production of paints and allied products

	Annual change (%) on a tonnage basis	
	1984/83	1985/84
Sweden	-1.50	-1.06
West Germany	+1.00	+0.52
Denmark	+7.60	+5.26
Norway	+1.80	+1.33
Finland	+4.10	+4.94
United Kingdom	+3.40	+3.63
Western Europe	+0.60	+0.64

According to the annual change %, the level in the Nordic Countries, apart from Sweden, is higher than the average for Western Europe.

Foreign trade

The proportion (%) of exports out of total production.

Denmark exports the highest proportion of its paint production, almost 40%. In 1985 Finland is in second place (35%), followed by Norway (25%). Sweden's share is about 15%. Finland has strongly increased its exports during this period, although Denmark's percentage has always remained the highest.

The proportion (%) of imports out of total production.

According to the relative proportion of imports, Norway is the largest importer (32%), most of the imports coming from Sweden and West Germany. Denmark is next (24%), with its imports coming primarily from West Germany and Sweden, followed by Sweden (15%), with exports from West Germany and the other Nordic Countries, and finally Finland (12%), with exports mainly from West Germany and Sweden.

Sweden is mostly involved in foreign trade between the Nordic Countries, and it exports 60% of the value of its total paint exports value to these countries. Exports to the Soviet Union are of special importance to Finland, and in 1984 they accounted for about 60% of the total value of paint exports (primarily automotive coatings and special coatings). Of the Nordic Countries, Denmark exports the most to countries outside this bloc. About 25% of Denmark's exports go to other Nordic Countries, and 50% to the other EEC countries. UK's exports to the Nordic Countries are of only minor importance.

Rationalization of activities

The paint manufacturers in the Nordic Countries have, during the past decade, maintained an investment level of 3-8% of their turnover. The investment level in Finland has been 7-8%, and hence is on quite a different level to that of the other countries.

The product range and size of the company have a considerable effect on the figures. However, we can conclude from the following data that considerable advances have been made in the rationalization of production in the Nordic Countries and during the last two years in the UK.

Annual productivity rates for paint (1979-1985), yearly tonnes/employee

	1979	1982	1984	1985
Denmark	46.2	53.2	63.5	62.8
Sweden	66.1	71.1	64.1	62.9
Finland	45.7	65.5	47.7	50
Norway	37.5	40	44.1	44.1
West Germany	49.3	47.6	55	55.4
United Kingdom	32.5	34.1	33.6	43

Research and development, internationalization

Every Nordic country is a small market area, but the product range is large. The exceptionally large market shares of the individual paint manufacturers have resulted in a situation in which each producer makes all the paint products. This has especially been the case in Finland, Sweden and Norway. The principles of specialization and division of tasks have not been applied in the Nordic Countries. Division of tasks has mainly taken place through the competitors strengthening their product ranges in those areas where the market leader has been weaker.

This has resulted in a situation where, due to the fact that extensive research activity is needed to maintain a product range and to develop new products meeting the needs of the constantly changing domestic and foreign markets, the cost of product development has become very high. The Nordic paint manufacturers plough back 3-4% of annual turnover into research and product development.

The research workers employed by the paint industry are usually university graduates, and the other personnel engaged in product development usually have a technical training lasting for a number of years.

The paint manufacturers in the Nordic Countries have had to acquire market shares in larger markets in order to ensure that they retain their technical know-how in product development and production. A company which has taken on an international form is also in a better position to choose the key points for its activities, while at the same time obtaining additional production capacity without having to make investments in its own country. Technical development is nowadays so fast that not even a large company can master everything—well, at least no better than the rest.

A rather profound structural change has taken place in the European and American paint industry during 1985-1986. For this reason, the companies in the Nordic paint industry will have to become large enough to possess, under changing conditions, the qualifications required for growth and international operations.

The Nordic paint industry has always paid particular attention to occupational health and environmental aspects. The strict legislation in force in these countries has seen to that. The companies have usually been first in Europe to introduce raw-materials which are less hazardous to health. A code system for marking the labels of compounds harmful or hazardous to health was introduced already at the beginning of the 70's.

The paint companies have also strived to develop painting systems which, while being of as high a quality as

possible, are also economical from the point of view of both the paint manufacturer and the customers. This policy also includes overall responsibility and an emphasis on technical service.

NIF (Scandinavian Paint and Printing Ink Research Institute) which started its activities on 1/7/1969 and is financially supported by Sweden, Denmark, Finland and Norway, is an internationally known research centre whose prime aim is to serve the Nordic paint and printing ink industry. Its field of operations includes various pure research projects, testing and method research, analyses, environmental protection, documentation, standardization etc. NIF also represents the Nordic paint industry in different international joint research projects.

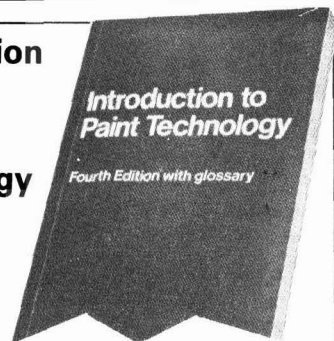
NIFAB, which arranges courses and carries out on commission inspection, analyses and other services, was set up in connection with the NIF in 1974.

The Nordic paint manufacturers work in close co-operation with the universities, technical high schools, and research centres in the individual countries. These joint projects have dealt with a wide spectrum of questions, ranging from the surface to be painted to the durability of the paint surface, and of course occupational health.

Summary

The Nordic paint industry is a relatively mature industrial field whose profitability is susceptible to a variety of factors, including the weather conditions during the painting season and economic cycles. The fact that competition in the Nordic Countries remains strong sets considerable pressure on their economic viability. The Nordic paint industry has made considerable effort in rationalizing and investing in its activities. The industry is in a strong position to further internationalize its position.

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High binders in decorative emulsion paints

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Abstract

The contribution being made by higher performance vinyl acetate based copolymer dispersions to the cost effective formulation of decorative emulsion paints is explored. A brief outline of the technology used to achieve the enhanced binder performance is described and comparisons made with other advances in binder technology made in recent years. Potential future developments of the technology and its applications are discussed.

1. Introduction

Since the introduction of decorative emulsion paints the emulsion polymer binder has played a crucial role. Strictly speaking, 'emulsion polymers' is a misnomer, since the products are dispersions of predominantly spherical particles of solid polymer in an aqueous phase.

The earliest widely used types were polyvinyl alcohol stabilised polyvinyl acetate emulsions manufactured in Germany¹. These polymers were externally plasticised with dibutyl phthalate and other plasticisers. Internally plasticised copolymers using a variety of flexibilising comonomers such as maleate and fumarate esters, acrylic esters and higher vinyl esters were introduced in the late 50's.

The introduction during the 1960's of the "Veova®" range of monomers by Shell led to new vinyl acetate copolymers with improved alkali and water resistance².

The Veova® monomers are vinyl esters of synthetic branched chain fatty acids, the branched chain being responsible for the improved alkali resistance.

Concurrently with these developments a steady growth in the use of styrene acrylic and 'all acrylic' emulsion polymers took place where their superior weathering and binding power could be justified despite appreciably higher costs.

More recently, during the period 1965-1975 vinyl acetate/olefin copolymers were introduced, eventually leading to vinyl acetate/ethylene/vinyl chloride terpolymers of generally similar marketplace cost and technical performance to their Veova® counterparts.

In summary, by the early 1980's paint manufacturers had

available a range of polymers suitable for vinyl silk and vinyl matt paints, the latter generally in the region of 50-65% pvc. For higher pvc styrene acrylic emulsions tended to be used because of their higher binding ability.

2. Development of 'high binding' emulsion polymers

In general, the term 'high binding' can be used to describe any emulsion polymer capable of producing paints of good film integrity at high pigment volume concentration. Until recently only styrene acrylic or acrylic copolymers would have merited such a description, albeit with their inherent cost penalty. From 1984 however, a new range of vinyl acetate copolymers has been introduced whose performance is much improved compared to their conventional 'general purpose' precursors.

Desirable performance targets for the high binding emulsion polymers can be listed as below in Table 1. The required paint properties compare with those of conventional general purpose polymers apart from the significantly improved scrub resistance.

Scrub results are expressed as the percentage of paint film removed at the number of cycles reached when the test was terminated. In the tests quoted in this paper the film removal was assessed visually.

It must be appreciated that binder evaluation in an ideal paint formulation could well mask the factors influencing polymer performance. Consequently the test systems referred to in this paper were deliberately designed to enhance differences in binder performance by (a) formulating matt paints with high demand pigments beyond the cpvc and (b) testing matt and silk paints in the absence of gellants to ascertain the rheology contribution of the polymer.

Results comparing a high binding Vinyl Acetate/Veova® copolymer, namely VIKING 2420 with a traditional general purpose Vinyl Acetate/Veova® copolymer are shown in Figure 1, for typical commercial formulations at 65% pvc and 85% pvc.

It can be seen that at 65% pvc the high binder is virtually unmarked after 2,000 cycles whereas the traditional copolymer suffers about 40% removal after only 1,000

Table 1

Targets for high binding polymers

Paint Property	Conventional Vinyl Acetate Copolymer	High Binding Vinyl Acetate/Veova® Copolymer
Opacity (Contrast Ratio)	ca. 95.0	No change
Gloss, (Vinyl Silk 60°)	ca. 60%	No change
Natural Gel Strength (gm/cm)	40-150 (25% pvc)	No change
	20-25 (High pvc)	No change
Rotthinner Viscosity, poise, 25°C	2.5-4.0 (25% pvc)	No change
	4.0-5.0 (High pvc)	No change
Scrub Resistance (% removed @ 75% pvc)	Total removal at 50 cycles	Less than 25% at 500 cycles

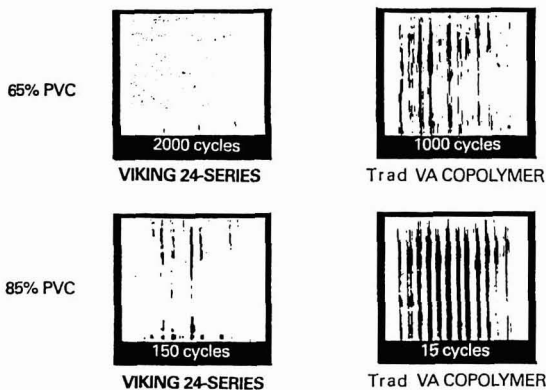


Figure 1.

cycles. Similarly at higher pvc (85%) the high binder has markedly less erosion even at ten times the number of cycles for the traditional copolymer.

The development of the VIKING 24-Series, and similar copolymers thus represents a significant increase in performance compared with binders used hitherto.

To obtain the increased performance the emulsion polymer technologist has, inter alia, the following formulation variables available, as shown in Table 2.

Table 2

Component	Function/Effects
Colloid type and level	Rheological properties, stability
Surface Active Agents:	
a) Non-ionic	Stability, particle size control, rheology, colour acceptance
b) Anionic	Particle size control, rheology, stability, interaction with "associative thickeners"
Initiators	Reaction time, conversion efficiency, reaction temperature, reaction profile, molecular weight control
Buffer(s)	pH control, reaction rate
Co-monomers e.g. (VeoVa® 10)	High levels (25-30% give good alkali/water resistance, good weathering for exterior use. Lower levels (20%) for general purpose interior use

In addition the following process variables can influence performance as shown in Table 3.

Table 3

Process Variable	Function/Effects
Temperature	Molecular weight, viscosity, particle size and shape
Processing Time	Molecular Weight, viscosity
Pre-emulsion of Monomer	Particle size distribution
Agitation	Rheology, heat dissipation, reaction control, particle size

To illustrate the effects of some of the variables in a typical development programme Tables 4-7 compare the results obtained with a series of Vinyl Acetate/VeoVa® copolymers, all of which were stabilised using constant

levels of hydroxy ethyl cellulose, non-ionic surfactant and anionic surfactant. All the polymers contained 20% VeoVa® 10, 80% Vinyl Acetate, standard initiator levels were used throughout, and all polymerisations conducted at 75-80°C.

Two types of process were examined. For emulsions A-G a non pre-emulsion technique was used, the mixed monomer being fed to an aqueous phase containing all the colloid together with varying proportions of surfactants. Modifications were made by apportioning the surfactants and buffer between reactor, monomer feed or aqueous feed as described in Table 4.

Conventional polymer performance in this system, particularly designed to differentiate between binders, would give total removal at only 50 cycles.

All of the emulsions A-G perform satisfactorily in silk paints.

Whilst the scrub performance demonstrated in Table 7 is a marked improvement over conventional polymer performance it still does not meet the target level at 500 cycles for this system.

A further series of emulsions H-K were prepared, of the same composition as emulsions A-G but using a pre-emulsion technique. Variations as described in Table 8 were obtained by apportioning surfactants and buffer between the initial reactor aqueous phase and the aqueous phase of the pre-emulsion. Tables 8-11 list emulsion and derived paint properties for these emulsions.

Of the four emulsions in this series only 'I' meets all the requirements stated in Table 1 for a commercially viable high binding emulsion. It is of interest that though deficient in silk paints the relatively coarse particle size emulsion 'H' performs very satisfactorily in terms of scrub resistance. In our experience emulsions similar to 'H' are liable to greater inconsistency in performance compared with products of more uniform particle shape.

By using similar techniques for optimising performance, coupled with theoretical considerations the VIKING 24-Series was developed.

To meet the requirements of a broad spectrum of paint manufacturers it is necessary to produce a variety of polymers with varying comonomer ratios. Thus at 20%, 25% and higher VeoVa® levels the span of interior to exterior high binders is catered for. By incorporation of minor proportions of acrylic ester monomers softer, easier filming products may also be obtained.

3. Comparisons of high binding polymer types

Currently, four principal types of polymer emulsion are used as high binders. A qualitative comparison of these types is given in Table 12.

One of the principal variations in properties between the four types of emulsion of Table 12 lies in the rheological properties of derived paints, and in the performance of silk paints. Generally styrene acrylic and acrylic emulsions can be formulated into rheologically satisfactory matt paints but problems were traditionally encountered in silk paints with styrene acrylics due to the poor flow of the (usually) fine

Table 4
Variations A-G

Emulsion	Proportion of Non-Ionic in reactor (%)	Proportion of Anionic in reactor (%)	Proportion of Buffer in reactor (%)
A	33	100	100
B	66	100	100
C	100	0	100
D	60	60	100
E	0	60	100
F	100	100	10
G	0	100	100

Table 5
Emulsion Properties A-G

Emulsion	Non-Volatiles (%) Content	Average Particle Size (microns)	Particle Shape	Viscosity	
				Rotothinner 21°C (p)	Haake, 13 secs ⁻¹ 25°C (p)
A	52.0	0.37	Poor (aggregated)	2.15	8.4
B	51.5	0.38	Good	2.15	9.4
C	52.5	0.35	Good	2.65	11.3
D	51.3	0.48	Moderate (aggregated)	2.25	7.6
E	51.4	0.55	Poor (aggregated)	2.15	6.3
F	52.0	0.30	Moderate (aggregated)	2.0	8.2
G	52.5	0.55	Poor (aggregated)	2.05	5.3

Table 6
Paint Properties, Emulsions A-G, 25% pvc Vinyl Silk

Emulsion	pH	Viscosity (Rotothinner p)	Natural Gel (gm/cm)	Dry Contrast Ratio (%)	60° Gloss (%)	Visual Assessment
A	7.96	3.5	47	93.8	60.5	Standard
B	8.08	3.7	50	93.8	61.4	Standard
C	8.20	3.6	57	94.2	63.4	Better than standard
D	8.43	5.1	68	94.0	59.4	Standard
E	8.11	4.5	58	94.0	59.6	Standard
F	8.68	4.4	58	94.0	60.9	Standard
G	8.11	3.9	58	93.6	59.5	Standard

Table 7
Paint Properties, Emulsions A-G, 75% pvc Vinyl Matt

Emulsion	pH	Viscosity (Rotothinner p)	Natural Gel (gm/cm)	Dry Contrast Ratio (%)	Scrub Resistance, % removed @ 500 cycles
A	8.06	4.9	28	97.8	70
B	8.07	5.0	26	97.6	80
C	8.1	4.7	24	97.7	80
D	8.08	5.5	33	97.6	50
E	8.18	5.5	32	97.3	50
F	8.42	5.0	23	97.5	40
G	8.09	5.35	30	97.4	60

particle size emulsions used. In our experience the 'pressure polymers' are broadly comparable to vinyl acetate/VeoVa® polymers.

65% pvc with their contribution to paint properties, including cost. These costs are those appertaining at the end of 1986.

4. Economic benefits of high binders

Tables 13 and 14 illustrate the effects of the principal components present in emulsion paints at 27% pvc and

It can be seen that the principal cost contributions derive from the binder and the titanium dioxide pigment. High binders therefore offer the paint manufacturer two principal means of achieving economies. Firstly, by allowing customary performance levels to be achieved with

Table 8
Variations H-K

Emulsion	Proportion of Non-Ionic in Reactor (%)	Proportion of Anionic in Reactor (%)	Proportion of Buffer in Pre-emulsion (%)
H	100	60	90
I	33	Nil	90
J	100	Nil	90
K	100	60	Nil

Table 9
Emulsion Properties H-K

Emulsion	Non-volatiles content (%)	Average particle size (microns)	Particle shape	Rotothinner 21°C (p)	Viscosity Haake, 13 secs ⁻¹ 25°C (p)
H	51.8	1.04	Poor (aggregated)	1.2	1.5
I	51.9	0.35	Good	2.2	8.9
J	51.7	0.76	Moderate (aggregated)	1.8	3.7
K	51.8	0.35	Good	1.9	7.8

Table 10
Paint Properties, Emulsions H-K, 25% pvc Vinyl Silk

Emulsion	pH	Viscosity (Rotothinner p)	Natural Gel (gm/cm)	Dry Contrast Ratio (%)	60° Gloss (%)	Visual Assessment
H	8.74	4.9	63	92.7	50.8	Poor
I	8.61	3.8	47	93.5	58.4	Equal Std.
J	8.76	4.9	76	93.6	56.8	Poor
K	8.16	3.7	50	93.0	61.2	Equal Std.

Table 11
Paint Properties, Emulsions H-K, 75% pvc Vinyl Matt

Emulsion	pH	Viscosity (Rotothinner p)	Natural Gel (gm/cm)	Dry Contast Ratio (%)	Scrub Resistance, percentage removed
H	8.21	5.6	22	97.4	15% at 1,000 cycles
I	8.38	4.8	23	97.4	18% at 500 cycles
J	8.40	5.2	30	97.2	12% at 500 cycles
K	8.11	5.0	28	97.5	80% at 500 cycles

lower binder levels and secondly taking advantage of 'dry hiding' contributions at high pvc's if slightly lower wet opacity levels are acceptable.

Table 12
Comparison of high-binding emulsion polymers

Emulsion Type	Typical Critical pvc (%)	Scrub Performance	Weathering
Vinyl Acetate/ Ethylene/Vinyl Chloride	62	Good	Good
Vinyl Acetate/ Veova®	65	Good	Good
Styrene-Acrylic	75	Excellent	Good
Acrylic	72	Very Good	Excellent
Conventional VA Copolymer	50	Moderate	Good

The relative contribution to paint costs at three pvc levels are shown in Table 15 for a variety of binders, while Table 16 gives binder costs for the same binders at equivalent performance levels.

Though the costs shown in Tables 15 and 16 relate to particular paint formulations, the authors believe they are typical. They illustrate the raw material cost savings available with all binders as the pigment volume concentration is increased, and the relatively greater costs attributable to styrene acrylic copolymers. The ability of high binding polymers to achieve good performance at e.g. 65% pvc when a conventional emulsion is beyond its critical pigment volume concentration clearly enables paint manufacturers to achieve substantial cost savings.

Table 13

Effect of Major Components—27% pvc Silk Vinyl

Property	Emulsion Polymer	Titanium Dioxide	Extender	Thickener	Coalescing & Wet Edge Solvents	Dispersants
Wet Opacity	*	***	*			*
Dry Opacity	*	***	**		*	**
Colour	*	***	**			*
Gloss	***	**	**		*	*
Storage Stability	*	*	*	*		***
% of Total Paint RMC	37	50	4	2	5	<1

*** signifies most influential

Table 14

Effect of Major Components—65% pvc Matt Vinyl

Property	Emulsion Polymer	Titanium Dioxide	Extender	Thickener	Coalescing & Wet Edge Solvents	Dispersants
Wet Opacity	*	***	*			*
Dry Opacity	*	***	**		*	**
Colour	*	***	**			*
Wash Resistance	***	*	**	*	*	*
Exterior Durability	***	***	*		*	
Storage Stability	*	*	*	*		***
% of Total Paint RMC	22	53	14	4	4	<1

*** signifies most influential

Table 15

Binder costs versus pvc, pence/litre of paint, and as percentage of total raw material cost

Binder type	50% pvc		65% pvc		85% pvc	
	p/l	%	p/l	%	p/l	%
1. Conventional vinyl acetate/acrylate copolymer (55% NV)	16.5	27.0	11.0	22.5	6.5	17.0
2. Conventional vinyl acetate/VeoVa® copolymer (55% NV)	16.0	26.5	10.5	22.0	6.0	16.5
3. High binding vinyl acetate/VeoVa® copolymer (52% NV)	17.0	27.5	11.5	23.0	6.5	17.5
4. High binding vinyl acetate/ethylene/vinyl chloride copolymer (52% NV)	17.0	27.5	11.5	23.0	6.5	17.5
5. Styrene acrylate copolymer (50% NV)	23.0	34.0	15.5	29.0	9.0	22.0

Further cost savings are available if products are formulated at slightly above the critical pigment volume concentration. By taking advantage of 'dry hiding' contributions at these pvc levels savings can be made by reducing titanium dioxide content, albeit with some loss of wet opacity at the highest reductions. These possibilities are illustrated in Table 17.

In practice, it is our experience that those paint manufacturers taking advantage of the opportunities available achieve actual raw material cost savings of 8-10% in total using moderate pvc changes.

Table 16

Binder Costs at Equivalent Paint Performance

Formulation	pvc (%)	% Savings on Binder Cost	Binder Cost p/litre
1. Conventional Vinyl Acetate/Acrylate	50	Nil	16.5
2. Conventional Vinyl Acetate/VeoVa® 10	50	Nil	16.0
3. High Binding Vinyl Acetate/VeoVa® 10	65	28	11.5
4. High Binding Vinyl Acetate/Ethylene/Vinyl Chloride	62	22	12.5
5. Styrene/Acrylate Copolymer	75	23	12.3

5. Comparison with other recent advances in emulsion paint technology

How does the introduction of high binding emulsion polymers compare with other recent advances? Some of the more recent principal advances are:

1. Plastic pigments
2. Vinyl Acetate/Ethylene/Vinyl Chloride ('pressure polymers')
3. Wet adhesion promoted polymers

Of these, plastic pigments, e.g. 'Ropaque' are certainly being used to offset titanium dioxide costs. Pressure polymers compete on equal terms with their Vinyl Acetate/VeoVa® counterparts despite earlier claims to potential savings as a result of lower raw material costs.

Table 17
Cost savings and properties for Titanium Dioxide reductions

	Conventional VA/VeoVa® Copolymer (55% NV)		High binding VA/VeoVa® 10 Copolymer (52% NV)		
	A	B	C	D	E
% pvc	50	50	68	68	68
% Non-volatiles (weight)	54	54	54	54	54
% Non-volatiles (volume)	35	35	35	34	34
% TiO2 (weight)	20	20	20	17.5	15
% Extenders (weight)	19.5	19.5	26	28	30.5
Wet Opacity	Standard	= to Standard	= to Standard	= to Standard	-1
Dry Opacity	Standard	= to Standard	+3	+2	+1
Scrub Resistance	Standard	+3	= to Standard	+1	+1
Raw Material Cost (p/litre)	60	61	57	54	50
% change in cost relative to standard (A)	Standard	+1	-5	-10	-17

Wet adhesion promoted polymers have been produced and made available for some time, and have achieved some penetration in in speciality products. By contrast, the relatively less glamorous high binders have achieved significant penetration of the emulsion paint binder market, and the rate of adoption by the industry is a further indication of the successful marketing of these products.

6. Future Developments

Emulsion paints are applied to a variety of surfaces, under differing climatic conditions. Frequently, the conditions are not ideal, particularly where painting is carried out at low temperatures. Many paint manufacturers seek to lessen the potential difficulties associated with low temperatures by increasing coalescent solvent levels. As coalescent level is

increased there is a tendency for performance as measured by scrub resistance to deteriorate. Recent development polymers using slightly modified polymer types have given indications that the problems associated with high coalescent levels can be overcome, that is to say that scrub resistance can be maintained at levels similar to paints containing lower coalescent levels at equivalent pvc's. It is intended to illustrate these developments at the Conference.

References

1. BIOS 1102
2. Aten, W. C. and Vegter, G. C., "New copolymer latices on the basis of VeoVa® monomer in paint applications", *JOCCA*, 1970, 53(6), 448.

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Preparation of ionomer coatings from water-soluble polymers

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Summary

The preparation and properties of a series of waterborne coatings, cured by a newly discovered process, are described. The crosslinking reaction involves carboxylic acid groups on the polymer backbone, some of which are neutralized with sodium ions. The action of heat on such a polymer brings about a two-step process, comprising dehydration then decarboxylation, and yields water-stable ketonic crosslinks. The resulting coatings contain a minority of ionic species in an otherwise organic matrix, hence this belongs to the class of materials known as "ionomers". The simplest coating system of this type is based on partially neutralized sodium poly(acrylate). In this paper, various modifications to the basic system are described, including the use of alternative counterions, and the effect of additional crosslinkers on the properties and performance of the final films.

Introduction

As waterborne coatings have grown in importance in recent years, two distinct themes have emerged in the fundamental research being carried out in this field¹. These are:

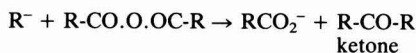
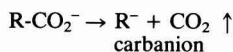
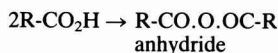
1. The development of novel methods of solubilizing (or dispersing) polymers in water.
2. The application of novel curing processes to coatings, aimed at minimising the water sensitivity of the final films.

Examples of the first kind of work include Thames² on polymers containing aminoethanethiosulphuric acid functional groups, Tirpak and Markush³ on polyurethane ionomers, and Richardson⁴ on the discovery of a group of additives capable of both dispersing and catalysing crosslinking in waterborne epoxy resin systems.

In the second group come such developments as the use of zirconium compounds to crosslink carboxylated polymers⁵, thereby imparting much improved solvent resistance to stoved films. The work of Thames also falls partly into this second group, since his polymers undergo a novel crosslinking reaction, generating sulphur bridges when heated⁶. Finally, within this group comes our own recent work^{6, 7}, in which partial neutralization of carboxylic acid groups in poly(acrylic acid) is used to catalyse thermal decarboxylation, and thereby to produce films showing excellent water resistance.

It has been established that this ionically catalysed thermal decarboxylation takes place as the second step in a two-stage reaction⁶⁻⁸. The first step is dehydration to form polymeric anhydrides, a reaction that has been extensively studied for poly(acrylic acid)⁹⁻¹³. These anhydride groups may be inter- or intra-molecular, depending on the temperature at which the reaction is carried out. Higher temperatures favour the formation of intermolecular anhydride groups, thus forming a crosslinked material¹², films of which have been used for the protection of tinplate¹⁴.

In our previous studies of the formation of coatings from partially neutralized poly(acrylic acid), we found that where sodium ions were present at a level of 10% neutralization, heating at 250°C for 10 minutes caused almost all of the anhydride crosslinks to undergo decarboxylation, to yield keto groups. Not being susceptible to hydrolysis, these films had very good resistance to aqueous media, such as 3% sodium chloride solution, or boiling 5% acetic acid^{6, 7}. The loss of anhydride groups was clearly demonstrated using reflectance infrared spectroscopy^{6, 7}. This technique was also used to study the kinetics of the decarboxylation reaction, which was found, after the first three minutes or so, to be first order with respect to loss of anhydride groups, and this result has been shown to be consistent with the following reaction scheme⁵:



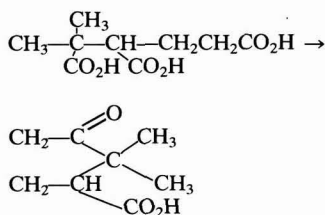
The cured films belong to the class of materials known as "ionomers", i.e. substances containing a minority of ionized groups in an otherwise organic matrix. The term "ionomer" was originally applied to a group of hydrocarbon and fluorocarbon compounds containing minor amounts of a neutralized acid function, generally in the range 5-10%¹⁵. The term has since been extended to cover any polymeric material with similar structure, including the present coatings⁷.

Ionomer films with levels of neutralization significantly above 10% were found to be no longer stable in water^{6, 7}; at levels above 25%, they no longer formed films on metallic substrates, but rather simply reticulated into discontinuous globules. The first result was to be expected, since neutralization is generally used to confer aqueous solubility on polar but otherwise insoluble polymers¹⁶. The second result would not necessarily have been expected in advance, but is a reflection of the mismatch between surface energies of the increasingly polar polymer (caused by greater degrees of neutralization) and the substrates.

Other ions have also been used to neutralize poly(acrylic acid), and attempts made to prepare chemically resistant coatings from them. The ions used have been lithium, potassium, copper, cobalt zinc¹⁷ and ammonia⁸. Of these, both lithium and potassium were found to promote thermal decarboxylation, while all the rest proved ineffective. The behaviour of the ineffective ions fell into two classes: the metal ions all formed some kind of covalent bond by coordination to the carboxylate groups, and thus became site-bound¹⁷, while the ammonium ion appeared to be lost from the films mostly as free ammonia, although some

reacted to yield covalent structures such as imido groups⁸. The results for the metal ions are significant in that they throw additional light on the mechanism of the crosslinking reaction, since they show that, while preserving the overall electro-neutrality within the films, the actual sites of the carboxylate groups need to be labile in order for decarboxylation to occur. These results provide additional evidence that carbon dioxide is lost from the carboxylate groups themselves, rather than directly from the anhydrides, and this is what was proposed in the mechanism illustrated.

The combination of the two reactions used in this crosslinking process was originally thought to be novel and although both anhydride formation by carboxylic acids and decarboxylation from sodium carboxylates are well-known reactions, it was thought that they had not previously been put together. However, we have since discovered one previous case of the use of these combined reactions, by Perkin and Thorpe in 1904¹⁸, where the sodium salt of 4-methylpentane-1, 3, 4-tricarboxylic acid was refluxed in acetic anhydride at 140°C to give the keto-acid 2, 2-dimethyl-3-oxocyclopentanecarboxylic acid:



In the present paper, results are reported for two kinds of modification to the original ionomer system, namely the use of hydroxylated compounds to create additional crosslinks within the structure of the films, and the use of copolymers containing, in addition to acrylic acid units, hydrophobic segments of the acrylate ester type. Both modifications were introduced in order to try to improve on the properties of the original coatings and to extend the scope for application of this type of coating.

Experimental

1. *Materials*: The following were used:

(a) Poly(acrylic acid), "Versicol E7" (ex. Allied Colloids, Bradford, W. Yorkshire), Molar mass 30,000. It is supplied as a 25% solution in water, and was diluted to 15% concentration for use in the present work.

(b) Copolymers of the butyl acrylate/acrylic acid type. Copolymer A consisted mainly of acrylic acid with 15-20% *iso*-butyl acrylate units in the polymer. Carbon-13 nmr showed that it also contained about 2% residual acrylic acid monomer. Copolymer B consisted of substantially more ester, some of which was *n*-butyl rather than *iso*-butyl (ratio of *N*- to *iso*- approximately 3:1). ¹³C nmr spectroscopy revealed that it contained no trace of monomer. Both were neutralized with ammonia in order to prepare aqueous solutions, as opposed to dispersions, copolymer A being at 15% solids and copolymer B at 10%.

(c) Sodium hydroxide ("AnalaR" grade, ex. BDH Ltd, Poole, Dorset).

(d) Ethylene glycol, butane-1, 4-diol and pentane-1, 5-diol (all ex. Aldrich Chemical Co Ltd, Gillingham, Dorset).

(e) Triton X-114 (ex. BDH Ltd), a non-ionic surfactant, was incorporated in small amounts (less than 1%) to improve substrate wetting.

Two groups of formulations were prepared, one based on poly(acrylic acid), the other based on the copolymers.

Formulations in the former group were prepared by first partially reacting the poly(acrylic acid) with sodium hydroxide to give 10% neutralization, and then adding sufficient diol to esterify 25, 50 or 75% of the carboxylic acid groups originally present in the polymer. Surfactant was then added to each mixture.

Formulations in the latter group were prepared by adding sodium hydroxide at levels of 1% or 5% of the weight of the polymer, in order to give materials which would retain some of their ionic character on heating. To some of these copolymer formulations, pentane-1, 5-diol was added at 10% by weight of polymer to give the potential for additional crosslinking. Again, surfactant was added to each formulation.

2. *Application and cure*: As before⁷ coatings were applied by aerosol spray to aluminium or tinplate panels (dimensions 100 mm × 150 mm), after which cure was brought about in a forced air oven at 200 or 250°C for 10 minutes. The films were generally about 5 μm thick.

3. *Test procedures*: The following tests were carried out, the British Standard number of the method being shown where appropriate:

(a) Bend test round 3 mm mandrel (BS 3900, Part E1: 1970).

(b) Cross-cut adhesion (BS 3900, Part E2: 1970).

(c) Exposure to some of the following, under the conditions specified:

1) Soak in distilled water, room temperature, one hour.

2) Soak in 3% NaCl solution, room temperature; 24 hours.

3) Soak in 5% acetic acid solution, boiling, one hour.

4) Soak in carbonated lemon drink ("Seven-Up") 37°C, two weeks.

5) Soak in citrate/brine buffer at pH 5.5, 37°C, two weeks.

6) 50 rubs with a tissue soaked in the organic solvent 4-methylpentan-2-one (methyl *iso*-butyl ketone, MiBK).

In all cases film resistance was expressed on a five point scale, running from 0 (the best) to 4 (the worst), defined as before⁷.

Results and discussion

Use of diols

In preliminary studies, two diols were used, namely ethylene glycol (ethane-1, 2-diol) and butane-1, 4-diol. It

was felt originally that the latter, with its longer carbon chain, might confer greater flexibility to the cured films. In practice, however, neither this compound, nor pentane-1, 5-diol, gave any detectable improvement in flexibility.

Diols were considered for inclusion because it was known that they would react with carboxylic acid groups on the polymer, thereby forming ester links, and it was hoped that this process might occur sufficiently readily for the cure conditions to be eased from the fairly severe 250°C/10 minutes used previously⁶⁻⁸. This, too, did not prove to be the case in practice: it was found that coatings cured at temperatures significantly below 250°C (for example, 200°C for 10 minutes), were still seriously disrupted by water, often dissolving completely in distilled water at room temperature within an hour. Thus, like the very simple ionomers, these systems were shown to require a minimum temperature of 250°C in order to bring about a satisfactory cure in 10 minutes.

The formulations employed in this study are listed in Table 1.

Table 1

Ionomer formulations containing diols

Code	Na ⁺ content of PAA	Diol*	Amount of diol (% esterification)	Resistance to 3% NaCl
1	10%	EG	25%	0
2	10%	EG	50%	1
3	10%	EG	75%	0
4	0%	EG	50%	3
5	10%	BD	25%	1
6	10%	BD	75%	0
7	10%	—	0%	0
8	0%	BD	75%	3

*EG = ethylene glycol, BD = butane-1, 4-diol

Coatings, prepared from these formulations, were applied to aluminium and cured at 250°C for 10 minutes. All were insoluble in distilled water, and showed excellent adhesion, flexibility (bending without cracking around a 3 mm mandrel) and resistance to rubbing with MiBK. Resistance to soaking for 24 hours in 3% NaCl was more discriminatory, as the results in the final column of Table 1 show.

While there was no clear advantage in using diols in the coatings, there was equally no disadvantage. Films three and six, which contained significant amounts of diol, showed the same properties of adhesion, flexibility and chemical resistance as the simple ionomer system, film seven in the Table 1. In addition, as found previously⁶⁻⁸, it was apparent that films which contained no sodium ions (i.e. 4 and 8) did not develop acceptable resistance to 3% NaCl, and in this regard were inferior to films which did contain sodium ions. This implies that, despite the existence of the competing esterification reaction, anhydride formation followed by decarboxylation, still took place in these films.

To confirm that thermal decarboxylation was still able to occur alongside esterification, a study was carried out using reflectance infrared spectroscopy to examine films of the related system containing 75% pentane-1, 5-diol, the

analogue of films three and six. For these experiments, coatings were applied to polished tinplate, because the technique requires highly reflective substrates. The results of this study are shown in Table 2, and as before^{7, 8} the anhydride bands are normalized to the carboxylate band at 1,570 cm⁻¹, which thus acts effectively as an internal standard.

Table 2

Reflectance infrared study of 10% Na⁺ PAA/75% pentane-1, 5-diol cured at 250°C

Time of cure/minutes	Ratio of anhydride: carboxylate bands
2	0.89
10	0.18

Decarboxylation appeared to have taken place, in that there was a significant reduction in intensity of the anhydride band at the longer heating time. Hence, it has been confirmed that the primary cure reaction continues in these systems, despite the presence of diols seeking to react competitively with the acid and anhydride groups. Diols are thus seen to be compounds which could be included in ionomer formulations, should it be necessary, in order either to add bulk to the film, or possibly to improve final film properties by the choice of sufficiently hydrophobic diols, such as neopentyl glycol (1, 3-dihydroxy-2, 2'-dimethylpropane).

Use of carboxylated copolymers

Formulations prepared from the two copolymers are listed in Table 3, together with results of test on coatings on aluminium prepared from them.

Table 3

Copolymer formulations and properties of coatings

Coatings	A	A1	A2	A3	B	B1	B2	B3
Copolymer	A	A	A	A	B	B	B	B
NaOH (wt %)	—	5	1	1	—	5	1	1
Pentane-1, 5-diol (wt %)	—	—	—	10	—	—	—	10
Cross hatch adhesion	0	0	0	0	0	0	0	0
Cold water soak	0	0	0	0	0	0	0	0
Acetic acid, boiling 1 hr	2	1	0	0	2	2	0	0
NaCl, 3%, 24 hrs	3	0	0	0	4	0	0	0
"Seven-Up", 37°C, 2 weeks	2	1	0	0	0	0	0	0
Citrate/brine buffer, 37°C, 2 weeks	4	4	4	4	4	2	1	1

A number of conclusions are apparent from the data in Table 3. First, as for the simple homopolymer of acrylic acid, the presence of a small percentage of sodium ions gave films with superior chemical resistance on curing at 250°C. Second, coatings based on copolymer B were superior to those based on copolymer A. Since they were known to contain fewer hydrophilic segments, and no water-soluble residual monomer, this was to be expected. Third, resistance to the various aqueous media was better at lower ionic content, i.e. 1 wt% Na⁺, than at higher ionic content, i.e. 5 wt% Na⁺. Finally, the presence of diols had very little effect on the performance of these films.

Overall, the tactic of introducing hydrophobic segments

into the film forming polymer was successful. The best performance of the films of all the ionomer coatings produced were for formulations B2 and B3.

Infrared studies of reaction mechanism

As before⁶⁻⁸, reflectance infrared spectroscopy has been used to examine the chemistry of the cure reaction. Films were applied to reflective substrates (generally polished tinplate) and cured for various times at 250°C. Results from this study are shown in Table 4, the ratio of the anhydride band at 1,795 cm⁻¹ to the methylene band at 1,440 cm⁻¹ being given for various times of heating. The methylene band was chosen as the "base" absorption because in these films the band due to carboxylate was harder to distinguish than for the simpler systems. Otherwise, the principle of choosing a band that is both prominent and essentially unchanged by the cure process is the same as used previously.

Table 4

Anhydride: methylene ratios for the infrared spectra of coatings of B and B1 on polished tinplate.

Sample	Heating time/min	Anhydride/methylene ratio
B	2	0.59
	10	0.71
	15	0.75
B1	2	0.55
	10	0.41
	15	0.34

Although the ratios for B and B1 are similar after two minutes heating, there is considerable divergence as the heating time is extended. The sodium-free films (B) show a gradual build up in the amount of anhydride present, and no indication of any decarboxylation, while the sodium-containing films (B1) show a maximum after two minutes heating, and subsequently a decrease as decarboxylation occurs. Unlike the simple partial sodium poly(acrylate), decarboxylation does not appear to be quite so extensive after heating for 10 minutes or so. Nonetheless, the reaction was found to occur to a sufficient extent to confer improved resistance to aqueous media. One can therefore conclude that the ionically catalysed decarboxylation reaction, described previously, is applicable to the curing of films consisting of carboxylated copolymers. This is likely to be of significance in extending the range of potential uses of these "ionomer" coatings, since the possibility exists of controlling film properties, such as durability and flexibility by including various appropriate monomer units in the polymer in the same way as is done for "emulsion" paints¹⁹.

Conclusion

In this paper, the use of two methods of modifying the properties of ionomer films are reported, namely the use of diols to bring about additional crosslinking, and the inclusion of hydrophobic monomers in the polymer backbone. In both cases, it was found that the primary cure reaction, i.e. anhydride formation followed by decarboxylation, took place essentially unimpeded by the presence of the other molecular species. The success of these two approaches means that a number of possible variations have been demonstrated for the formulation of ionomer coatings and that in principle these coatings may be tailored to suit particular application requirements.

References

- Nicholson, J. W., "Waterborne Coatings", OCCA Monograph No. 2, Oil & Colour Chemists' Association, London, 1985.
- Thames, S. F., *J. Coat. Tech.*, 1983, **55** (704), 87.
- Tirpak, R. E. and Markush, P. H., Paper presented at the 12th Waterborne and High-Solids Coatings Symposium, University of Southern Mississippi, New Orleans, 13-15 February, 1985. Quoted in "Waterborne and High-Solids Bulletin", 1985, **7** (9), 1.
- Richardson, F. B., US Patent 4,526,721, (2 July 1985).
- Moles, P. J. and Byram, J., *PPCJ*, 1984, **174**, (4122), 440.
- Nicholson, J. W. and Wilson, A. D., *Chem. & Ind.*, 1986, 530.
- Nicholson, J. W., Scott, R. P. and Wilson, A. D., *JOCCA*, 1987, **70**, 157.
- Nicholson, J. W. and Wilson, A. D., paper submitted to *British Polymer Journal*.
- Crugnola, A., Pegoraro, M. and Severini, F., *J. Polym. Sci., Part C*, 1969, **16**, 4547.
- Lleras, J. and Combet, S., *J. Chim. Phys. Physicochem. Biol.*, 1972, **69**, 1620; *Chem. Abs.* **78** (1973) 125080.
- Frank, A. and Weunscher, K., *Int. Congr. Automat. Instrum. Pap., Rubber, Plast. Ind. Pap.*, Antwerp, October 1966; *Chem. Abs.* **69** (1967) 1737.
- Eisenberg, A., Yokoyama, T. and Sambalido, E., *J. Polym. Sci., Part A-1*, 1969, **7** (7), 1717.
- McGaugh, M. C. and Kottle, S., *J. Polym. Sci., Part B*, 1967, **5**, (9), 817.
- Nishihara, T., Hirotsaki, Y. and Tsukamoto, Y. (Nippon Steel), *Jap. Pat.* 74 31604; *Chem. Abs.* **82** 159358.
- Longworth, R., in "Developments in Ionic Polymers", Vol 1, *Applied Science Publ.*, London, 1983.
- Nicholson, J. W., *JOCCA*, 1987, **70**, 1.
- Nicholson, J. W. and Wilson, A. D., *Brit. Polym. J.*, 1987, **19** (1), 67.
- Perkin, W. H. Jnr. and Thorpe, J. F., *J. Chem. Soc.*, 1904, **85** (1), 128.
- Paul, S., *Prog. Org. Coatings*, 1977, **5**, 79.

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Durability of anti-carbonation coatings

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Abstract

This paper provides an extension to the author's previous work on coatings for concrete protection, by assessing the gas barrier properties for a range of generically different coating materials after periods of up to 3,000 hours accelerated weathering. In total 19 coatings comprising of methacrylates, alkyds, emulsions, chlorinated rubbers, urethanes, styrene acrylates, ethylene co-polymer and water-based acrylics were evaluated in terms of their long term protection against carbon dioxide penetration. This in turn provides useful information regarding the long term protection offered by such coatings against carbonation and potential reinforcement corrosion.

Introduction

Coatings for exterior concrete and masonry have been in use for decades primarily performing a decorative function. More recently however, there is a growing awareness that coatings should complement aesthetic appeal with protective performance.

Today the use of coatings for concrete protection has been stimulated by the increasing number of concrete structures showing signs of deterioration. Reinforcement corrosion can be caused by the ingress of atmospheric carbon dioxide, oxygen, water and aqueous chloride ions. The use of barrier coatings to prevent the incursion of such deleterious species can play a key role in an overall repair specification. Hence concrete repair has become a potential market growth area for suppliers of polymers and manufacturers of polymeric based coatings impregnations, polymer modified mortars and bonding coats.

The vast number of commercially available repair materials only serves to confuse the specifier. There is always an obvious appeal to use materials with a successful track record, however that is not to say that new development products may not be as trustworthy or indeed provide a better option. Thus it is apparent that there exists an urgent requirement for ways and means of evaluating the behaviour and properties of materials, particularly new products, with a view towards their long term performance and durability.

Coating performance has to be assessed in terms of its ability to provide adequate penetration resistance after exposure to the environment. Therefore in order to evaluate the long term performance of barrier coatings the degradation processes encountered in practice have to be simulated in the laboratory, via accelerated weathering trials.

Several publications can be cited which refer to the degradation processes of building materials particularly polymer materials. Eurin¹ reviews the main degradation processes relating to mineral, metal and polymeric materials, discussing elementary phenomena—thermo-oxidation, photo-oxidation and hydrolysis—which are responsible for the weathering of polymeric materials.

Fukushima and Motohashi² discussed the deterioration

processes of polymeric materials, presenting a theoretical model to explain the dynamic processes of polymeric degradation relating the significance of such mechanisms to the durability of reinforced concrete. A paper by Browne³ examines the philosophy behind the deterioration of building materials and shows how understanding this complex subject can lead to service life predictions for concrete structures. Boyd⁴ discussed early attempts to predict the effect of weathering on building materials, emphasising the inadequacy of test data and pointing out that more complex relationships involving several synergistic factors must be more clearly understood before the in-situ performance of a material can be fully explained.

Whiteley et al⁵⁻⁷ had been particularly active looking at the long term performance of exterior coatings. In one of his articles⁵ he examines the long-term action of water as a factor in the degradation of saponifiable paint films by measuring the change in extensibility and breaking load of detached films. Loss of extensibility for detached films of alkyd and polyurethane alkyd paints is explained in terms of alkali sensitivity and hydrolysis when immersed and embrittlement when exposed to the air caused by continuing oxidative degradation.

The Building Research Establishment has been studying the long term weathering performance of coatings for many years and have established several natural exposure sites worldwide. Crowder and Ali⁸ recently reported on the performance of a number of building materials exposed for three to four years in Dubai. Several surface coatings were evaluated in terms of colour change/ soiling, chalking and cracking. A review by Davis and Sims⁹ is fairly comprehensive in its treatment of the weatherability of polymers.

Today's advanced technology enables the degradation of polymeric materials to be studied in greater detail, which provides access to quantitative data¹⁰. This paper attempts to quantify the effect of accelerated weathering on the protective performance of a range of coatings used commercially for concrete protection. One of the main causes of concrete reinforcement corrosion is by a neutralisation process called carbonation, whereby atmospheric carbon dioxide penetrates the concrete, reacting with the calcium hydroxide present¹¹. This carbonation front becomes a major problem when the zone of neutralized concrete (pH 8.5) reaches the depth of the embedded reinforcement. The steel may start to corrode when the thin oxide layer around it, formed fortuitously by the high alkalinity of the concrete, (pH 12.5), is no longer stable because of reduced alkalinity.

Thus the performance of 'anti-carbonation' coatings in terms of their effectiveness at preventing the ingress of carbon dioxide and halting the progress of carbonation, is a vitally important factor in today's strategy for providing long term protection and increased lifetime for reinforced concrete structures.

A limited number of publications¹²⁻¹⁴ have examined the

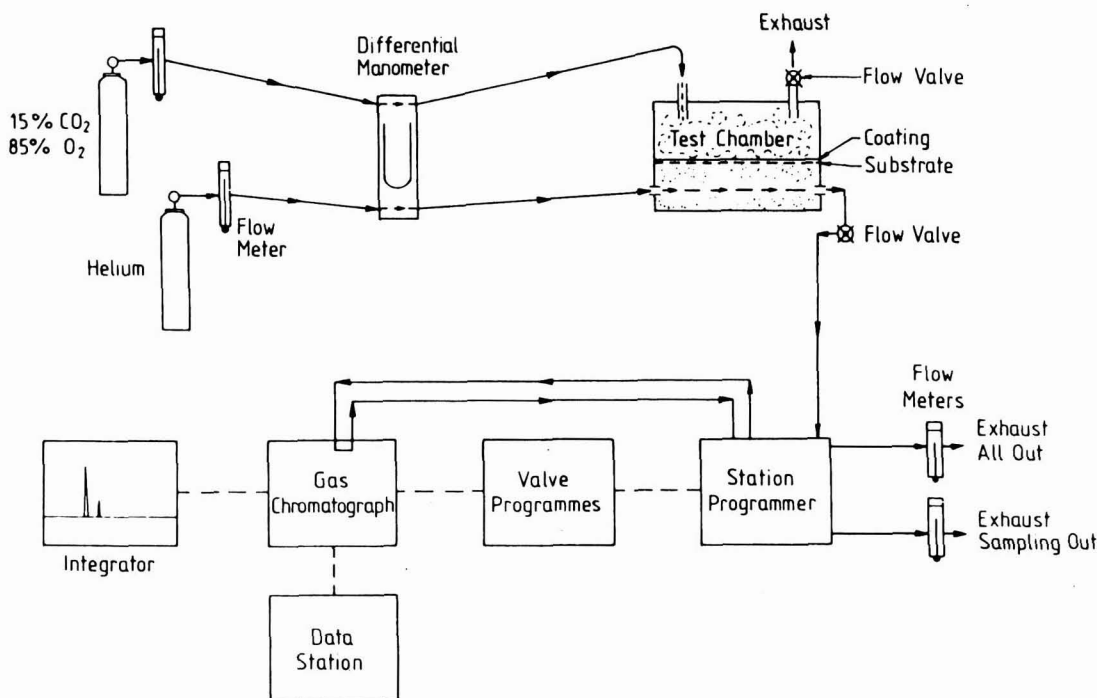


Figure 1. Diagram of gas chromatography apparatus.

barrier properties for coatings of different generic types, without evaluating the effect of weathering on their performance. This paper extends a previous study¹⁴ by measuring the resistance of coatings to carbon dioxide diffusion after subjecting them to periods of accelerated weathering.

Experimental

Carbon Dioxide Diffusion

The test method is described in detail in the author's previous work¹⁴, hence is discussed only briefly in this paper.

Concrete was not chosen as the test substrate because of inherent surface irregularities hindering the formation of a defect free film. Instead a porous ceramic plate (100 mm × 100 mm × 5 mm) with a uniform pore size distribution of the order 10^{-3} to 10^{-4} Angstroms, offering a flat surface and consisting of a mixture of Boulder/China clay, 25% ground silica, 10% limestone was adopted. The test plates were characterised for their diffusion resistance to carbon dioxide and thoroughly dried to constant weight before applying the coatings. The application techniques were designed to minimise the number of defects in the cured films. Low viscosity systems i.e. impregnations, were all applied by a dip method, more viscous coatings applied by a blade technique, whilst high build systems with small aggregate particles of the order 1 mm were applied carefully by brush.

After application each system was subsequently conditioned at $60\% \pm 5\%$ RH, 24°C , to constant weight, normally taking 6-8 weeks. This ensured that all the systems

were fully cured prior to test with consistent internal humidities.

After the conditioning period the samples were sealed in a circular steel rig with the coated and uncoated faces exposed. Carbon dioxide (15% in oxygen) at a known pressure and flow rate was passed over the coated face of the plate and helium gas purged over the opposite face at the same pressure and flow rate. The helium gas stream was continuously monitored by gas chromatography and analysed for carbon dioxide. Equilibrium conditions were achieved after approximately 24 hours, upon which the steady state flow of carbon dioxide was calculated from the percentage of carbon dioxide detected in the helium stream and the flow rate of the gas. A flow diagram of the test apparatus is shown in Figure 1.

Diffusion coefficients, indicating the rate at which carbon dioxide diffuses through the coatings, were calculated using Ficks first law.

Accelerated Weathering

After evaluating the coatings initial barrier properties, the next stage involved subjecting them to periods of accelerated weathering in a purpose-built QUV weatherometer. There are obvious limitations using such a technique when trying to correlate in-situ performance with laboratory data, however the results obtained provide a useful indication of long term performance and also a method of qualitatively ranking coatings in order of performance. It must also be noted that certain polymers will be more susceptible to accelerated cycling than others which may provide misleading results when using accelerated test data to predict in-situ performance.

Table 1

Carbon dioxide diffusion parameters through coatings after periods of up to 3,000 hours accelerated weathering

System	t_0					t_{500}		t_{1000}		t_{2000}		t_{3000}		CO ₂ Resistance vs Ageing
	μm	$\text{Dcm}^2\text{s}^{-1}$	$\mu_0 \times 10^6$	R(m)	Sc(cm)	$\mu \times 10^6$	Rm	$\mu \times 10^6$	Rm	$\mu \times 10^6$	Rm	$\mu \times 10^6$	Rm	
1	300	3.9×10^{-7}	0.38	115	28.7	1.49	417	2.01	482	-	-	-	-	Improved
2	300	3.0×10^{-7}	0.50	150	37.6	0.75	210	0.49	127	-	-	-	-	Maintained
3	170	3.5×10^{-7}	0.42	71	17.9	1.7	289	1.49	253	2.25	383	4.1	656	Improved
4	200	7.0×10^{-7}	0.21	42	10.6	0.75	150	1.66	332	1.49	283	-	-	Improved
5	110	7.6×10^{-8}	1.96	216	54.0	2.55	281	4.59	505	2.21	221	-	-	Maintained
6	200	8.1×10^{-8}	1.83	367	91.7	1.04	208	0.84	168	1.37	247	-	-	Slight deterioration
7	240	1.2×10^{-7}	1.29	310	77.6	-	-	0.3	72	0.75	165	-	-	Slight deterioration
8	160	2.1×10^{-7}	0.72	115	28.8	0.01	14	0.03	1.5	-	-	-	-	Complete deterioration
9	150	4.2×10^{-7}	0.35	53	13.3	0.14	21	0.02	1	-	-	-	-	Complete deterioration
10	150	2.2×10^{-7}	0.67	100	24.9	0.2	30	0.50	75	0.75	90	-	-	Maintained
11	100	2.5×10^{-7}	0.61	61	15.2	0.75	75	1.49	134	3.35	268	-	-	Improved
12	140	1.5×10^{-7}	1.0	143	35.7	2.71	379	2.59	363	-	-	-	-	Improved
13	300	1.0×10^{-7}	1.45	436	109	0.19	57	0.51	153	1.49	447	-	-	Maintained
14	140	7.9×10^{-8}	1.87	262	66	1.13	158	2.26	316	3.03	364	1.49	-	Slight Improvement
15	200	7.7×10^{-8}	1.93	385	96	0.45	90	1.33	266	2.56	461	-	-	Maintained
16	900	8.8×10^{-6}	0.02	15	4	0.06	54	0.04	34	-	-	-	-	Slight deterioration
17	1000	2.6×10^{-6}	0.06	57	14.3	0.01	10	0.02	19	0.05	45	-	-	Maintained
18	200	2.1×10^{-7}	0.7	145	36.2	0.75	150	1.49	298	-	-	-	-	Maintained
19	200	6.9×10^{-8}	2.14	428	107	1.92	384	1.49	298	-	-	-	-	Improved

The exposure cycle adopted in this work was one recommended by the Q-Panel Company and Tioxide UK Ltd. Both companies have considerable experience in this field with regard to correlating natural with accelerated weathering¹⁵ and the cycle; four hours UV at 50°C followed by four hours condensation, (no UV), at 40°C, is designed to simulate UK conditions. It is important to subject the coatings to realistic cycling so as to obtain meaningful results. Many thermoplastic coatings for example will be particularly susceptible to unrealistic damage at temperatures above say 55°C.

Results and discussion

Test data for the coatings gas barrier properties, listed in Table 1, are discussed in several terms:

1. Diffusion Coefficient, (DCO₂), cm²s⁻¹.
2. Diffusion Resistance Coefficient, (μ), comparing the diffusion of CO₂ gas through coatings with the diffusion of CO₂ through air under the same conditions.
3. Equivalent Air Layer Thickness, (R), in metres, which is the product of μ and the coating thickness, i.e. $R = \mu \cdot s$.
4. Equivalent Thickness of Concrete, (Sc) in centimetres. This term is the product of μ coating/ μ concrete multiplied by the coating thickness. A typical μ value for a C25 grade concrete would be approximately 400.

$$Sc = \mu \text{ coating} \times \text{coating thickness (cm)} \\ \mu \text{ concrete}$$

Each coating is designated a reference number and is described generically in Table 2. All the diffusion parameters for zero hours weathering and the μ and Rm values after periods of accelerated weathering, are listed in table 1. The R value is dependent on both the μ value and

the coating thickness, the latter being reduced by the weathering process. In this study the coating thicknesses were measured using an Erichsen Paint borer Model 518 which is accurate to $\pm 10 \mu\text{m}$. Hence for this reason, where no significant reduction in film build was detected, the initial dry film thickness, (S μm), listed in Column 2, Table 1, was used to calculate the R values after varying periods of accelerated weathering. Table 3 lists both the change in the coatings visual appearance and approximate reduction in film build with ageing. A number of the systems listed in Table 3 had yet to be tested after 3,000 hours, (t 3,000), at the time of writing.

Suffice to say that a successful anti-carbonation coating must maintain $R \geq 50$ metres¹¹, to effectively halt the carbonation front, allowing for a reduction in film thickness with prolonged weathering. For example if two coatings have the same initial diffusion coefficient but different R values, then the thicker coating will have a longer protective lifetime than the thinner coating, assuming identical chalking rates, by maintaining $R \geq 50$ m for a longer period. Of all the coatings evaluated for CO₂ diffusion after 1,000 hours accelerated weathering, only systems No 8, 9, 16 and 17 failed to maintain $R \geq 50$ m. The results listed in Table 1 are plotted in Figures 2 and 3, highlighting the weathering characteristics and relative coating performances.

Based on these results the most successful coatings in terms of initial CO₂ resistance and long term performance appear to be those based on methacrylates, urethanes, pigmented styrene acrylates, water-based acrylics, emulsions and ethylene co-polymers. The alkyd system No. 17 maintained its performance but its initial diffusion resistance was low compared to other coatings. Also the chlorinated rubber system No. 19, maintained, indeed showed improved barrier properties, however its appearance deteriorated drastically because of UV degradation.

Table 2
Coating Systems

1. Water based emulsion, 80% solids, heavily filled with TiO₂ and Mica.
2. Water based emulsion, heavily filled with TiO₂ and Mica + Low viscosity unpigmented methacrylate/siloxane pretreatment.
3. Moisture curing urethane, pigmented, solvented, heavily filled.
4. Methyl methacrylate, solvented, pigmented, externally plasticised, 18% PVC.
5. Urethane, two-pack, D-D, solvented, pigmented.
6. Acrylic, water-based, translucent, low PVC.
7. Styrene acrylate, pigmented, 65.2% PVC, high build, solvented.
8. Styrene acrylate, unpigmented, water-based.
9. Styrene acrylate, unpigmented, water-based.
10. Styrene acrylate, pigmented, 57% PVC, solvented.
11. Styrene acrylate, pigmented, 14% PVC, solvented.
12. Methyl methacrylate, pigmented, 30% PVC, internally plasticised, solvented.
13. Ethylene co-polymer, water-based, pigmented, 21% PVC + solvented acrylic pretreatment.
14. Methyl methacrylate, pigmented, 43% PVC, solvented.
15. Acrylic, water-based, pigmented.
16. Styrene acrylate, pigmented, solvented, high build.
17. Alkyd, high build, solvented + low viscosity sealer coat.
18. Acrylic, water-based, pigmented, fibre reinforced + epoxy water-based pretreatment.
19. Chlorinated rubber, high build, pigmented, solvented.

Table 3

Approximate coating thicknesses after periods of accelerated weathering

System	$\mu\text{m } t_0$	$\mu\text{m } t_{500}$	$\mu\text{m } t_{1000}$	$\mu\text{m } t_{2000}$	$\mu\text{m } t_{3000}$	Final Appearance
1	300	280	240	-	-	1 + 3
2	300	280	260	-	-	1 + 3
3	170	170	170	170	160	1 + 2 + 3
4	200	200	200	190	170	1 + 2 + 3a
5	110	110	110	100	100	1 + 3
6	200	200	200	180	120	1 + 4 + 5
7	240	240	240	220	200	1 + 3
8	160	140	50	-	-	4a + 6 + 7
9	150	120	50	-	-	4a + 6 + 7
10	150	150	150	120	110	1 + 3
11	100	100	90	80	60	1 + 2 + 3a
12	140	140	140	120	-	1 + 2 + 3
13	300	300	300	300	260	1 + 3
14	140	140	140	120	100	1 + 3
15	200	200	200	180	170	1 + 2 + 3
16	900	900	850	800	-	1 + 3
17	1000	1000	950	900	-	1 + 2
18	200	200	200	180	-	1 + 3
19	200	200	200	180	-	1 + 2 + 6

Key to final appearance: 1 = Maintained coherent film; 2 = Colour fade; 3 = Slight chalking; 3a = Moderate chalking; 4 = Severe chalking; 4a = Erosion; 5 = Bleached; 6 = Cracking; 7 = Cracking.

The obvious benefits to be gained by using coatings are highlighted in Figures 4 and 5. Figure 4, predicts the time taken to corrosion activation caused by carbonation and chlorides, for a range of different grade concretes³. Figure 5 relates the application of a coating of varying film thickness to improved concrete quality, because of the increased resistance to CO₂ diffusion. Hence by applying a coating with an initial R value of approximately 50 metres and increasing coating thickness, it is possible to up-grade a C25 concrete to an equivalent C45 concrete. Figure 6 indicates in general terms the different performances for a range of generic coatings. For example silanes/siloxanes have been shown to have negligible diffusion resistance^{16, 17}, whilst urethanes, epoxies, acrylics etc, can improve a C25 concrete up to C45 grade, depending on the coatings film thickness and diffusion resistance. This latter factor, i.e. diffusion resistance can vary dramatically for coatings within one generic class¹⁴. Thus it can be dangerous to assume that because one coating performs well then all others based on the same generic resin will perform equally as well.

The form of the curves as seen in Figures 2 and 3 may be attributed to several factors, including: plasticiser migration, loss of surfactant, varying pigment volume concentration, pigment particle size distribution, pigment particle geometry and temperature effect whilst in the weatherometer. Any combination of the above factors may be of critical importance in controlling the response to weathering. Further research is required to elucidate the precise role of each factor.

Conclusions

A method for evaluating the long term weathering behaviour of anti-carbonation coatings has been described. All but two of the 19 coatings evaluated appeared to maintain their initial performance, indeed a few actually exhibited slight improvement. The two failed systems were unpigmented styrene acrylates, however other pigmented styrene acrylates performed comparatively well. This indicates the variability in performance within a given generic type and emphasises the importance of critical pigment volume concentration, (PVC), when discussing the gas barrier properties of coatings.

The next stage in developing this work involves attempting to correlate the effect of accelerated with natural ageing on the barrier properties of coatings and to examine the influence of varying PVC on CO₂ diffusion.

Regarding these latter issues, a study is currently ongoing and results are thus not available at the time of writing.

Acknowledgements

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References

1. Eurin, Ph., "Degradation Processes of Building Materials and Components: A Short Review and Some Proposals for Research", Proc. 2nd Int. Conf. on the Durability of Building Materials and Components. National Bureau of Standards, Gaithersburg, Maryland, USA, Sept. 14-16, 1981.

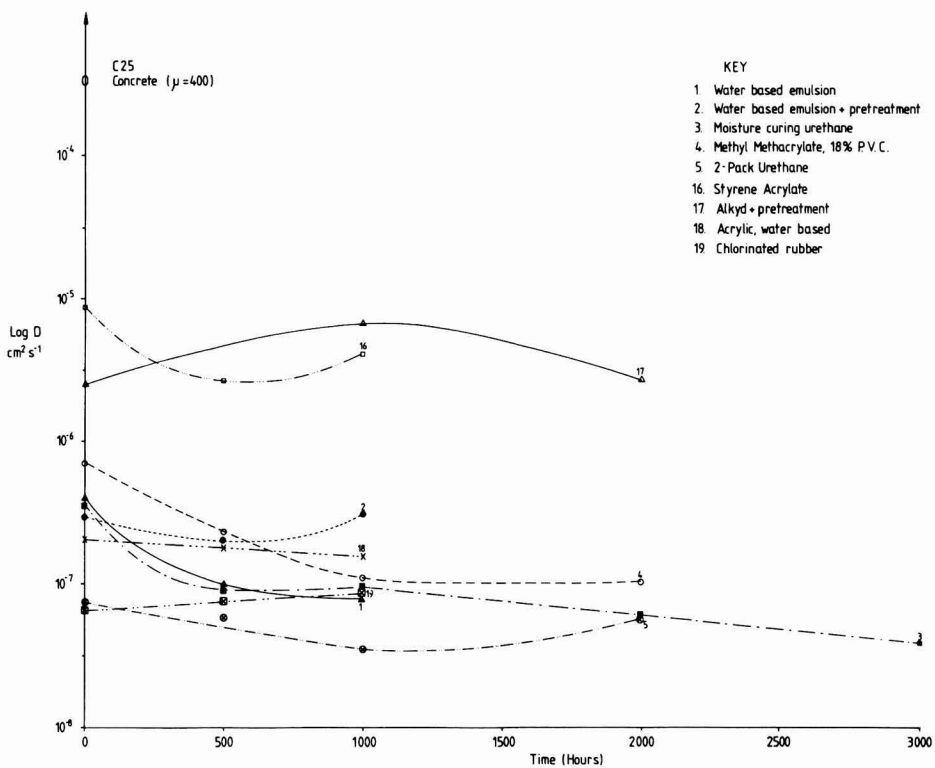


Figure 2. Effect of accelerated weathering on CO_2 resistance of coatings (Nos. 1-5 and 16-19).

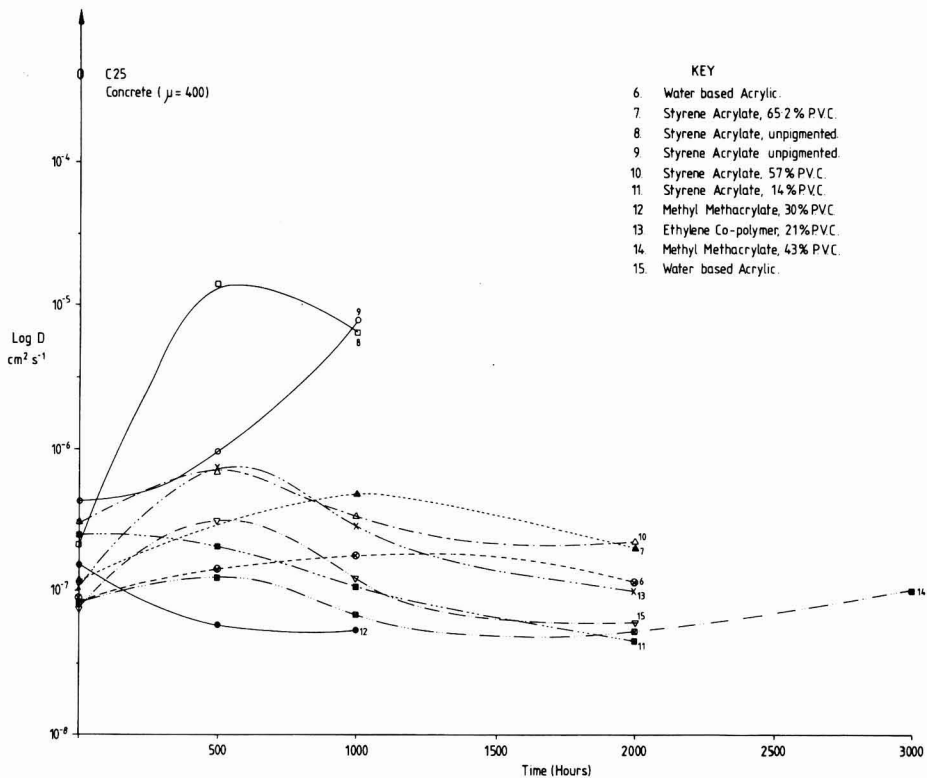


Figure 3. Effect of accelerated weathering on CO_2 resistance of coatings (Nos. 6-15).

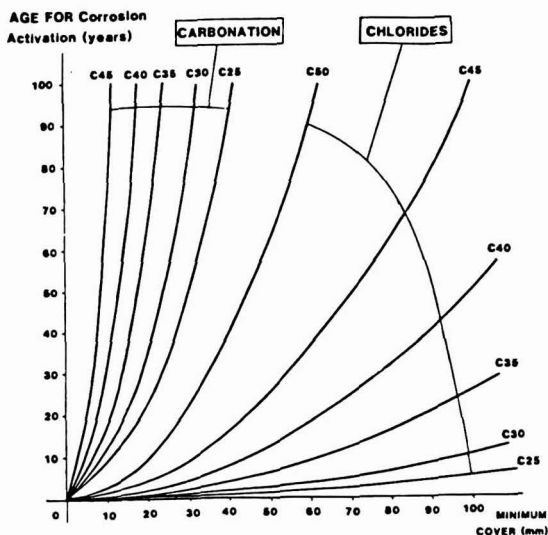


Figure 4. Predictions of time to corrosion activation (chlorides and carbonation).

2. Fukushima, T. and Motohashi, K., *Polym. Mater. Sci. Eng.*, 1984, **50**, 454.
3. Browne, R. D., "Deteriorology and life prediction—as applied to reinforced concrete", presented at "Building Deteriorology"—a one day seminar held at the Society of Chemical Industry, London, 17 April, 1986.
4. Boyd, D. W., "Weather and the deterioration of building materials", *Durability of building materials and components*, ASTM STP 691, Sereda, P. J. and Litvan, G. G., Eds., ASTM, 1980, 145.
5. Whiteley, P., Rothwell, G. W. and Kennedy, J., *JOCCA*, 1975, **58**, 200.
6. Whiteley, P., *Building Materials*, May 1970, 17.
7. Whiteley, P. and Miller, E. R., *Chem. & Ind.*, 1976, 343.
8. Crowder, J. R. and Ali, M. A., "Weathering performance of building materials in the Middle East", B.R.E. Information Paper, June 1986.
9. Davis, A. and Sims, D., "Weathering Polymers", Applied Science Publishers, Essex, England.
10. McKnight, M. E. and Byrd, W. E., "Early detection of polymeric degradation using electron microscopy", Proc. 2nd Int. Conf. on the Durability of Building Materials and Components, National Bureau of Standards, Gaithersburg, Maryland, USA, Sept. 14-16, 1981.
11. Klopfer, H., *Bautenschutz und Bausanierung*, 1978, **1**(3), 86.
12. Engelfried, R., *Farbe und Lack*, 1983, **89**(7), 513.
13. Deser, U., *PPCJ*, 1985, **175**.
14. Robinson, H. L., "Evaluation of coatings on carbonation barriers", Proc. 2nd International Colloquium on Materials Science and Restoration, Technische Akademie Esslingen, West Germany, Sept. 2-4, 1986.
15. Grossman, G. W., The Q-Panel Company, "Correlation of

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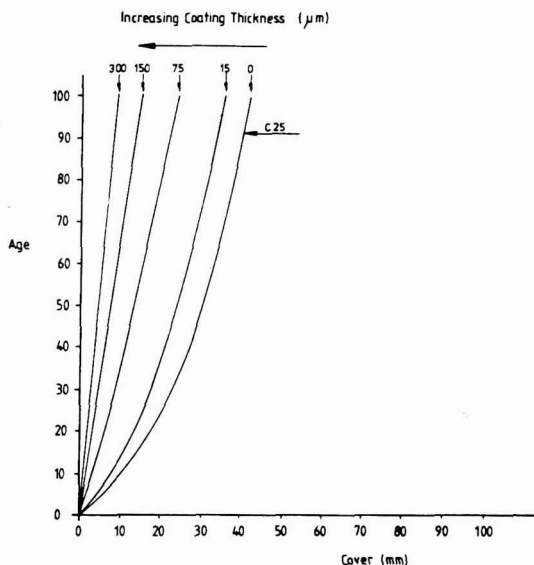


Figure 5. Effect of coating thickness on time to corrosion activation (carbonation).

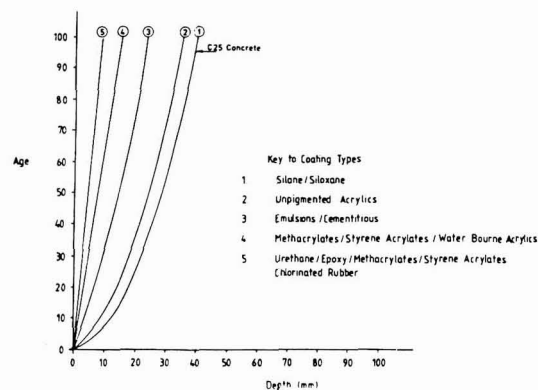


Figure 6. Effect of different coating types on time to corrosion activation (carbonation).

laboratory to natural weathering", *Journal of Coatings Technology*, 1977, Vol. 49, No. 633, pp 45-54.

16. Robinson, H. L., "An evaluation of silane treated concrete" to be published in *JOCCA*, Summer 1987.
17. Weber, H., *Element & Fertigbau*, Erschienen in Ausgabe 4/83.

Ontario Section

Pearl luster pigments and printing inks

ON 18 March Mr Eli Aschner of EM Industries (Hawthorne, NY), gave a talk on "Pearl luster pigments and printing inks".

Mr Aschner described to the 25 members and guests the four major methods of producing pearlescent effects: herring scales, lead carbonate, bismuth oxychloride, and mica encapsulated titanium dioxide. The latter method was discussed in more detail, and the physics of light absorption, transmittance and reflection were related to this type of pigment. Finally, the importance of particle size and the techniques used to control it (grinding classification and platelet isolation) were described.

After a question and answer period, the Chairman, Mr Purnell, thanked the speaker for a most informative presentation.

New demands on liquid inks

Thirty members and guests of the Ontario Section met on 20 May for a talk on "trends in liquid inks". The novel presentation featured two speakers, Mr David Hammett, Ontario Region Product Manager, and Mr Gordon Parker, Group Leader, both of BASF Inmont Canada.

Mr Parker began by outlining the history of gravure and flexo processes, the compositions of the inks, the equipment used, and the types of substrates.

Mr Hammett then described future trends in the printing process, including those towards more exotic composite substrates, high impact graphics, and greater process work. Other trends predicted were a switch from gravure and letterpress to flexo, faster press speeds, and the use of water based inks and solvent recovery systems to cope with environmental concerns.

Mr Parker ended the presentation by discussing the future demands expected of raw materials, including pigments (low dusting and easily dispersible lead chromates, higher gloss titanium dioxide, more stable metallics, and organics designed specifically for liquid inks), solvents (greater purity), resins (lower viscosity and greater water tolerance), and additives (more variety).

Following an animated question and answer session, the speakers were thanked for their novel presentations by Mr Ambury, the new Chairman.

P. Marr

General Overseas Section

Zimbabwe

Titanium dioxide

The first technical meeting of 1987, held at the CZI

Boardroom in Harare, was attended by 20 members and guests. Two film shows were presented on "Titanium Dioxide" and "Titanium Dioxide in the Alkyd Media" by Mr Robin Archer, Technical Service Consultant for Tioxide South Africa.

The first film, which lasted 20 minutes, dealt with the manufacturing processes and various quality controls found in rutile and anatase Titanium dioxide products produced worldwide. The second film outlined increased dispersability, milling and effective controls when dealing with Titanium Dioxide in the Alkyd Media with special emphasis based on flocculation.

Mr Archer concluded his presentation with a question and answer session based on the two films shown. This met with a variety of interesting questions being raised and answered.

Mr Claude Calasse proposed a vote of thanks to Mr Robin Archer and ICI Zimbabwe for sponsoring the evening.

M. A. Johnson

PUBLICATIONS AVAILABLE THROUGH THE ASSOCIATION

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

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

The Monograph Series:

Monograph 1 — **Marine Finishes**
by Dr. T. A. Banfield. Price £2.00 each
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Monograph 2 — **Water-borne Coatings**
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Monograph 3 — **Painting on Zinc Surfaces and Zinc Containing Anti-Corrosive Primers** by E. V. Schmid. Price £7.50 each (US \$18.00).

Ultraviolet Curing

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

Ultraviolet Curing 2

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

Special Offer

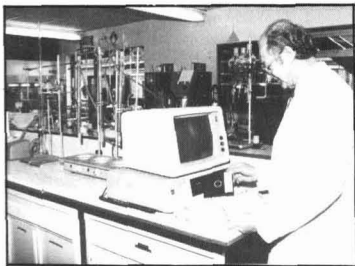
The two volumes on *Ultraviolet Curing* are offered at a special price of £10.00 (US \$24.00) for both volumes purchased together.

ITI expansion in Norway and USA

ITI Anti-Corrosion Ltd, the coatings inspection and consultancy company, is expanding its business operations in Europe and the USA. The company has formed an association with Norwegian Applied Technology (NAT), the Bergen-based company owned by Jotun A/S and Texas Eastern Engineering Ltd. ITI will provide inspection and quality control services for all NAT pipeline projects. In America, ITI has opened an office in San Francisco following a major upsurge in activities at its long-established office in Houston, Texas.

Floridienne – Italian polymers link up

Floridienne (UK) Ltd has reached agreement with R & P Italia srl, an emulsion polymer manufacturer and SAPICI a polyurethane and alkyd resin manufacturer, to market their products in the UK and Eire. Both companies have modern plants with capacity to expand into new markets.



The Exxon solvent recipe

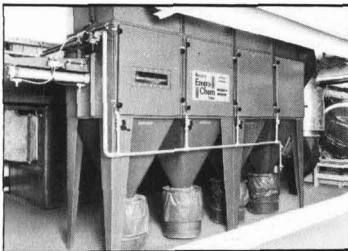
Exxon Chemical develops computer selection for solvents

Exxon Chemical Ltd has developed an innovative computerised selection procedure designed to help chemists and laboratory technicians to match the physical properties of solvents and fluids with the formulation they require. By harnessing computer technology using an IBM PC a database of information covering all Exxon Chemical products, including experimental grades, has been developed. With the aid of a simple user guide book, this system also allows for a match to be identified among Exxon Chemical products for competitive solvent mixtures.

products

New high efficiency air filtration equipment

The *Enviro-Chem Systems division of Monsanto*, Brussels, has launched a new range of high efficiency dust collection equipment. These dust collectors have



Monsanto air filtration equipment

extraordinarily high collection efficiency, especially for submicron particles which are normally difficult to capture. The essential operating principle relies on the use of modified HEPA "high efficiency particulate air" filters, in combination with a specially designed reverse air cleaning system. Each filter element is individually tested and certified to collect more than 99.97% of 0.3 micron particles. Contaminated air is drawn through the main filter to extract the dust particles. At a predetermined pressure drop or time interval, an integrated cleaning system, based on low pressure compressed air, is automatically brought into operation. This blows the dust into a hopper from where it can be discharged into a dust bin or a conveying system.

Reader Enquiry Service No. 20

Wolstenholme's new metallic finish process

Traditionally, silver, gold or other metallic finish powder coatings have always presented problems. Originally, the process used involved dry blending bronze or aluminium flakes with the resin powder. However, the different specific gravities of the two constituents caused separation problems, as well as proving expensive, as the powder could not be reclaimed and used again. There was also the danger of loose aluminium in the atmosphere.

Wolstenholme Bronze of Bolton solved these problems some years ago, by developing a process whereby the metallic pigments are bonded to the resin using a unique process. This service is provided to every powder coatings manufacturer in the UK. However, metallic finishes still presented problems, chiefly through 'chalking' when touched with the fingers and through poor weather resistance. This, in turn, was overcome by a two-coat application – consisting of the metallic coating, followed by a second pass through the oven after coating with dry powder clear lacquer.

Wolstenholme Bronze's latest technical breakthrough consists of an aluminium pigment that enables powder coating companies to apply, in one pass, a metallic silver, with highly weather-resistant properties. The durability of the process has been extensively tested on road wheels

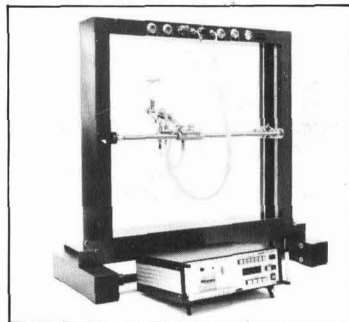
on performance cars. This finish has potential as an architectural product being particularly suitable for use on exterior surfaces of new buildings, fascias and hoardings etc.

Reader Enquiry Service No. 21

Sheen automatic test panel sprayer

Sheen Instruments of Teddington report that recent export orders for their new design automatic test panel spraying machine includes one from Hyundai Motors of Seoul, Korea. Another order has come from the Government Quality Control Laboratory in Baghdad, Iraq. The microprocessor controlled automatic test panel sprayer gives a high standard of repeatability. It is designed to spray test panels individually or in groups up to 600mm x 600mm. Standard computer programmes allow for variations in speed, lap distance, number of laps, number of successive coats, dwell time and spray cycle.

Reader Enquiry Service No. 22



Sheen test panel sprayer

meetings

Finishing '87

The *Finishing '87 Conference and Exposition* in Cincinnati, Ohio, will be held on 22-24 September 1987. This will be the largest finishing show in North America in 1987 with 114 exhibitors. For further information contact: Paula Harrington, Public Relations, Society of Manufacturing Engineers, One SME Drive, PO Box 930, Dearborn, MI, 48121, USA.

Fluid rheology

The Department of Trade and Industry's Warren Spring Laboratory (WSL) is organising a five-day course in fluid rheology to take place on 16-20 November 1987 at its laboratories at Stevenage. The course is aimed at rheologists, physicists, chemists, or engineers dealing with rheological problems. Current theory and

practice will be covered and several new concepts introduced. The course fee is £1150 (plus VAT). Further details can be obtained from: Miss P Madhvi, Warren Spring Laboratory, Gunnels Wood Road, Stevenage, Hertfordshire SG1 2BX.

literature

New particle sizer catalogue

Malvern Instruments has available a new full colour brochure describing their range of particle size analysers. Entitled "High Performance Systems for Particle Characterization", it covers Malvern's range of laser diffraction particle size analysers for powders, sprays and emulsions up to 1800 microns and photon correlation systems for submicron particles and polymer molecular weight measurements. For copies of the brochure contact: Peter McFadyen, Malvern Instruments Ltd, Spring Lane South, Malvern, Worcestershire WR14 1AQ.

Johnstone's 1987 manual and colour guide

Johnstone's Paints has published its 1987 Product Information Manual and Trade Colour Guide. The 100-page Product Information Manual gives detailed specifications and general technical advice. The latest BS4800 Colour Card provides 260 shade references for fourteen different



Johnstone's brochures

decorative paint products. Both are available from: Johnstone's Paints, Stonebridge House, Edge Lane, Droylsden, Manchester M35 6BX.

GAF protective colloids

Recent work at GAF has been established that Polyvinylpyrrolidone (PVP) polymers function effectively as protective colloids in emulsion polymerisation. Further information and a special wallchart on 'GAF Specialities for Emulsion Polymerisation' are available from: GAF Europe, Rythe House, 2 Littleworth Road, Esher, Surrey KT10 9PD.

OCCA ties at £4.25 each are now available from the Association's offices, with a single Association Insignia on either a blue or maroon background.

company reports

Wacker-Chemie GmbH

Wacker reported that at the end of 1986 the Wacker Group appeared strong and dynamic with satisfactory profits and the completion of an extensive investment programme of DM 328m in 1986. Worldwide sales decreased to DM 2.65 billion (-5.7% on 1985). In 1986 PVC and Chlorine derivatives accounted for 26% world sales and silicone, silane, fumed silica 25%, acetaldehyde and vinyl acetate derivatives accounted for 21%. In Autumn 1986 Wacker agreed with the French firm Rhône-Poulenc to take over the production-technique know-how for the manufacture of Rhodopas-resins. As a result, it was possible to expand and round-off the product range of its Vinnol' surface coating resins.

people

Alexander Williams has been appointed the Government Chemist, based at the Department of Trade and Industry's Laboratory of the Government Chemist in Waterloo Road, London SE1. He succeeds Dr Ronald Coleman who has been appointed Chief Engineer and Scientist of the Department.

Presentations

Two personal occasions of note took place during the 1986/87 session.

In November a small dinner party was held in Edinburgh, at which Mrs Bette McKendrick, wife of the late Alex McKendrick, immediate past chairman of the Section, was presented (see photo on the right) with a framed impressionist print, to mark her support for Alex during his term of office.

Recently, in March, the section arranged another dinner (see photo opposite) at the Hospitality Inn, Glasgow, in honour of Angus McLean to mark his long service for the Section and Association.

Cecil Finlay, immediate past president, in an amusing, witty and sincere speech presented the Commendation Award recently bestowed on Angus by Council for his meritorious service.

In thanking Cecil Finlay, Angus McLean

Scottish Section



Scottish Section presentation to Mrs Bette McKendrick, left to right: Mr R. L. Barrett (Chairman, Scottish Section), Mrs B. McKendrick and Mr T. McMahon (former Chairman, Eastern Branch).

gently chided the Scottish Section for considering him for this award. But, he, unwittingly, made clear the reason why, in his final remarks when he voiced his concern for the Scottish Section exhorted members to maintain standards and interest for the well-being of the industry in Scotland and the Section in particular.

R. L. Barrett

West Riding/ Manchester Section

Roses Games Evening

Once again the Scotland Inn, Birstall, on the 12th May 1987 saw renewed battle between the Red and White Roses for the coveted Games Shield with some 35 combatants attending.

The fairer weather this year paved the way to Manchester Section romping ahead to a 4-1 lead in bowls doubles matches with a particularly resounding defeat being inflicted on the West Riding Chairman by a pair of 'professionals' from Crown Paints. Whilst cribbage saw this imbalance redressed and other games scored level, a concerted effort at dominoes resulted in an unassailable lead for Manchester which even liar dice and biased scoring could not sway.

After an excellent buffet supper the Games Shield was presented to Manchester Section, with chairman, Fred Morpeth and his cohorts bearing the trophy away across the Pennines for the first time. Everyone



OCCA dignitaries with Mr Angus McLean at the Scottish Section presentation dinner in his honour. Left to right: I. J. Hutchinson (past Chairman), A. McLean (past President and past Chairman), A. S. Fraser (past President and past Chairman), Mrs A. Gibson (past Vice President and past Chairman), C. N. Finlay (immediate past President), R. G. Gardiner (past Chairman), R. L. Barrett (Chairman), D. Atherton (past Chairman) and I. R. McCallum (past Chairman).

agreed it was a 'Bitter' victory, especially for Tetley, and that the saga should continue.

J. Hemmings

Goulding, T. M., BSc (*Transvaal*)
Humphreys, B. (*Manchester*)
Mason, D. A. (*Manchester*)
Nunkissor, V. (*Natal*)
Singh, J. P., BSc (*Natal*)
Walker, G. T. (*Midlands*)

new members

Associate members

Ayres, D. S. (*Natal*)
Lowrie, P. C. (*Transvaal*)
Miniggio, G. (*Transvaal*)
Neethling, E. D. (*Transvaal*)

Ordinary members

Cochrane, R. (*Cape*)
Gill, A. W. (*London*)

Registered student

Van der Westhuizen, F., BSc (*Transvaal*)

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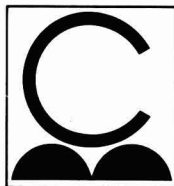
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4. **Development Chemist** for V.R., (25-30), to join small, but successful company which is becoming established in this field. S. MIDLANDS **Up to £12,000 p.a.**

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11. **O.E. Finishes Project Leader**, (Graduate 28-35), to be responsible for technical innovation advanced project work for major international company. SOUTH **£12,000 p.a. +**

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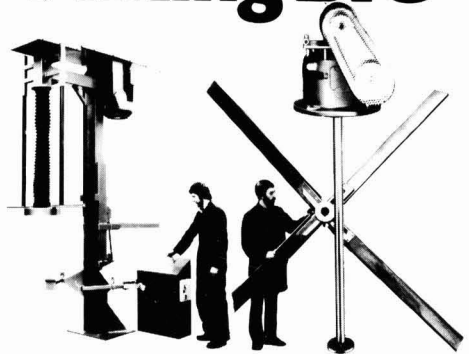
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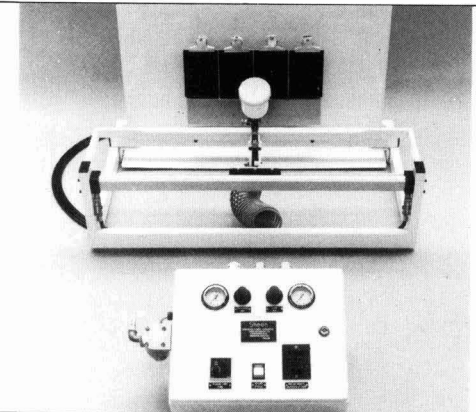


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