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JOURNAL OF THE IL & COLOUR CHEMISTS' ASSOCIATION

Don't waste your money on research

G. de W. Anderson

Internal reflection spectroscopy: application to organic coatings
and plastic sheeting

J. D. Frazee

New developments in wallcoverings

A. Burton

Zeta potential—organic pigments

W. Carr and J. A. Long



*'Picture of my father'
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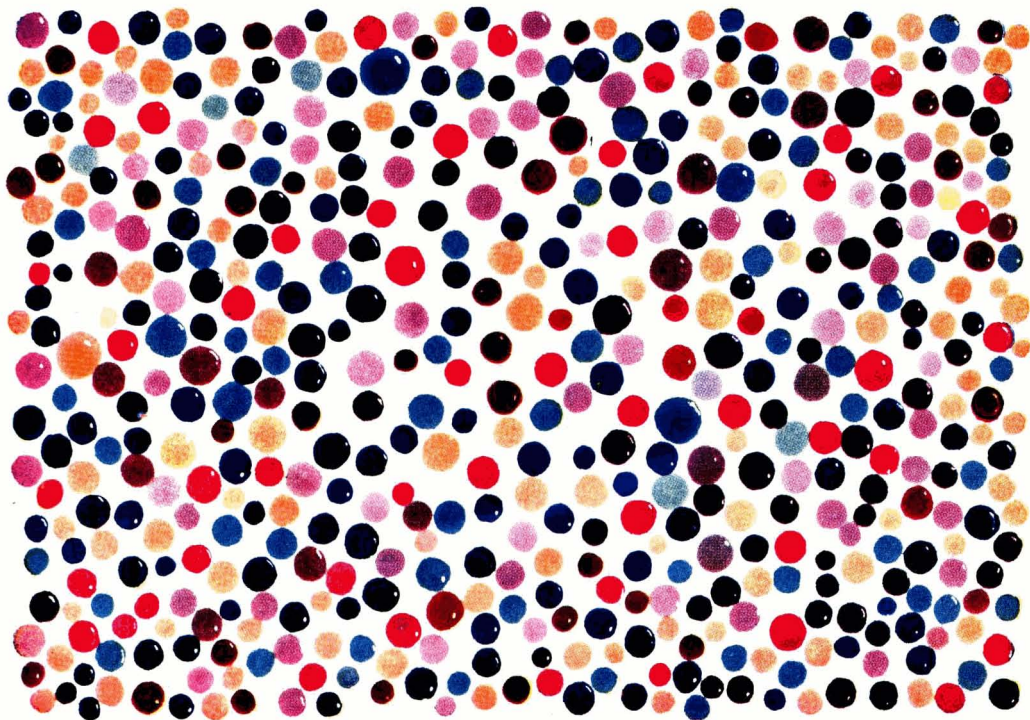
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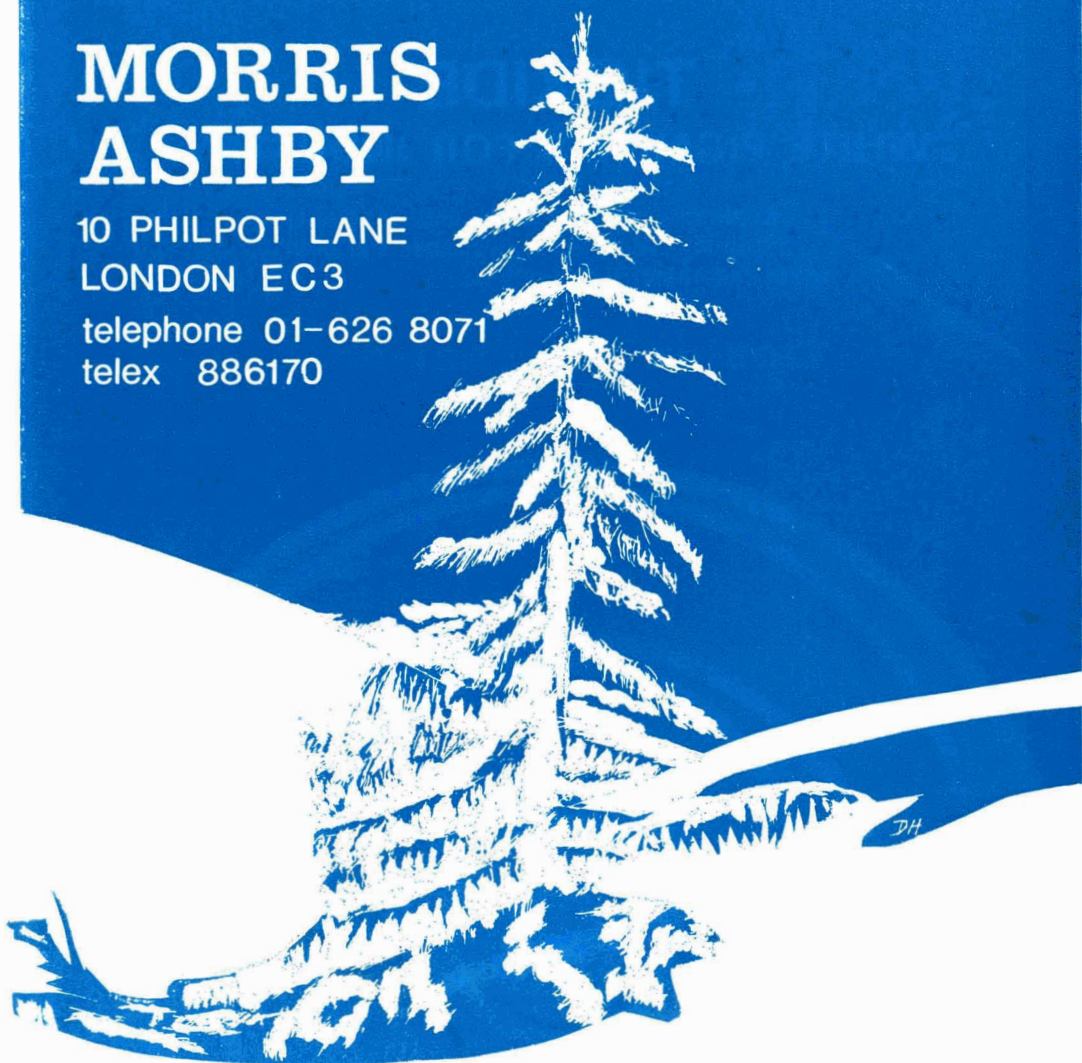
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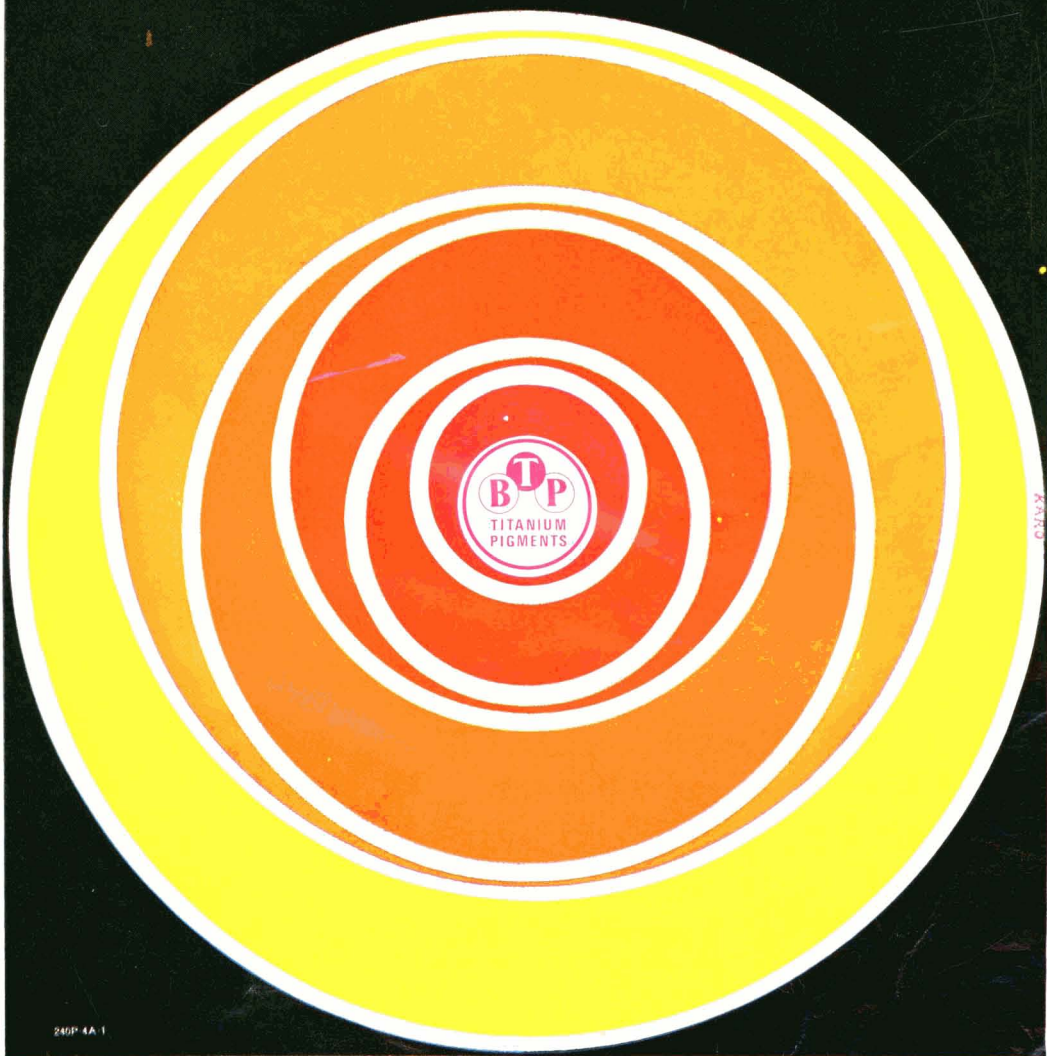
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Transactions and Communications

Owing to the illness of the translator, the papers published in this issue do not include translations of the summaries in Russian.

В виду болезни переводчика нет возможности публиковать выдержки статей на русском языке.

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Transactions and Communications

Don't waste your money on research*

By G. de W. Anderson

Paint Research Association, Waldegrave Road, Teddington, TW11 8LD

Summary

It is shown that, in general, the output of British industry is increasing at a rate proportional to the rising costs of research, but that this is not so in the paint industry.

The volume of paint produced increased substantially during the years 1963 to 1970, but prices remained almost static and any improvement in quality resulting from research work was not reflected in the revenues obtained for the product.

A review of the patent and technical literature suggests that a great deal of effort is put into investigations not having any clear benefit to the companies supporting it. Means by which research projects could be better selected and the amount of unprofitable work reduced are put forward.

The research projects undertaken at the Paint Research Association in recent years are described and it is suggested that, if properly applied, the results should be of benefit to the industry.

Ne gaspillez pas votre argent sur la recherche

Résumé

On démontre, qu'en général, le rendement de l'industrie britannique s'augmente au fur et à mesure des prix en hausse de la recherche, mais ce n'est pas le cas à l'industrie de peintures.

Entre 1963 et 1970 la quantité de peinture produite s'augmentait sensiblement, mais les prix restaient presque statiques et toute amélioration de qualité qui parvenait des recherches, n'exerçait pas d'influence sur les prix que l'on obtenait pour le produit.

En raison d'un aperçu de la littérature technique et des brevets

d'invention, on suggère que des efforts importants sont consacrés aux investigations qui ne rendent aucune bénéfice bien définie aux entreprises intéressées. On propose des moyens par lesquels on saurait choisir, dans une manière plus efficace les projets de recherche, et réduire le taux de travail inutile.

On décrit les projets de recherche entrepris par la Paint Research Station au cours des années récentes, et l'on suggère que les résultats devraient être au bénéfice de l'industrie de peintures, pourvu que l'on les utilise justement.

Verschwendet kein geld für Forschungsarbeiten

Zusammenfassung

Es wird aufgezeigt, dass mit Ausnahme der Lackindustrie sich die Produktionsrate der britischen Industrie proportional zu den ansteigenden Kosten für Forschung erhöht.

Während der Jahre 1963 bis 1970 vergrößerte sich das Volumen produzierter Anstrichmittel erheblich, das Preisniveau blieb jedoch beinahe statisch, und aus Forschungsarbeiten resultierende Verbesserungen in der Qualität spiegeln sich nicht in den für ein solches Produkt erhaltenen Einkünften wieder.

Eine Betrachtung der Patent- und technischen Literatur legt nahe, dass ein grosser Teil der Mühe für Untersuchungen aufgewandt wird, welche den diese unterstützenden Firmen keine klar erkennlichen Vorteile bieten. Es werden Mittel und Wege vorgeschlagen, wie Forschungsprojekte besser geplant, und unprofitable Arbeit reduziert werden kann.

Die von der Paint Research Association im Verlauf der letzten Jahre unternommenen Projekte werden beschrieben, und es wird nahegelegt, dass die Resultate, sofern richtig ausgewertet, der Industrie zugutekommen würden.

The power of research

Ref. 1

How often has one heard or even used the phrase "the technological revolution"? Yet few people, companies or governments recognise the literal truth of the idea expressed in this phrase, or the necessity for taking appropriate action.

Until about 1750, the sources of a country's prosperity depended on its natural resources, the number of good harbours and its military strength. From that date onwards the industrial revolution consolidated the position of those nations which already had progressive craft industries, some mechanical ability and the will and financial resources to utilise the two.

Dr J. Werner, of the GAF Corporation, in receiving the 1972 Chemical Industry Medal observed¹ that the technological revolution in this century had been "the great leveller"

among nations. Already the USSR has risen from a predominantly agricultural nation in the 1920s to become one of the two leading world powers in less than half a century. Even more striking is the case of Japan, a craft nation in the 1930s, a vanquished nation in 1945—a nation which in a mere quarter century since then has already become the third industrial world power.

The vastness of the new international scientific resource created is embodied in the observation that 90 per cent of the scientists who ever lived are alive today and again in the phrase "the information explosion." The aptness of the explosion metaphor is borne out by the figures. The number of patents and papers on pure and applied chemistry abstracted by "Chemical Abstracts" has for some time been doubling every seven years, reaching 300,000 items last year. The growth of new knowledge has been similar in other sciences. Thus, a vast and still rapidly increasing body of knowledge is available to any nation or any industry with the will to use it.

*Shortened version of the paper presented to the Scandinavian Paint Conference on behalf of OCCA at Sandefjord, 1 to 3 October 1973

The low effectiveness of paint industry R and D

The author's thesis is that despite the still increasing cost of science and technology, the paint industry internationally is not using research effectively as a business tool. Table 1

Table 1
Cost and use of science and technology in the UK

	Annual cost per graduate at the PRA	Turnover of UK paint industry*	UK Gross National Product*
1950	£1,800	£102 × 10 ⁶	£11,752 × 10 ⁶
1960	£3,750	£152 × 10 ⁶	£22,816 × 10 ⁶
1970	£4,950	£160 × 10 ⁶	£42,819 × 10 ⁶
Increase between 1950 and 1970	175%	57%	265%

*Data from Annual Abstracts of Statistics of the Department of Trade and Industry.

indicates the increased cost of maintaining a qualified scientist in the UK in 1950 compared with 1970 and the hopefully related growth of the UK paint industry and the GNP. This shows clearly that whilst the business of "UK Ltd", as a whole, is more than keeping pace with the increased research costs, the UK paint industry is falling far behind. Table 2 gives the volume and the value of various types of paint made by UK companies in 1963, 1970 and 1971, showing that the volume of paint made increased substantially in the seven-year period 1963-70, but that any improvement made was rewarded by static, and in some cases even falling, prices. That this was not fully corrected by the small increase in prices obtained in 1971 is seen from the fact that average profits on turnover in each of the three years to April 1972 were 0.2, 6.0 and 6.9 per cent.

Table 3 shows the volume of paint produced in other countries between 1964 and 1970. In some cases, this shows substantial increases but again, an improving quality is not reflected by any increases in price per gallon, which has on occasion driven Presidents of overseas national paint associa-

tions to write to the author referring to "our beleaguered industry".

Thus, paint manufacturers, in general, have been failing to derive demonstrable benefit from science and technology. Some reasons for this can be examined first by looking at the list of successful paint industry innovations. Four senior members of the Paint Research Association (PRA) assisted

Table 3
World production of paints, enamels and varnishes*
(Figures in thousand metric tons)

Country	1964	1965	1966	1967	1968	1970
USA	3,287	3,517	3,800	3,500	3,800	3,800
Western Europe	2,681	2,890	3,011	3,064	3,405	3,893
Germany	740	827	846	885	992	1,144
Japan	569	583	669	785	882	—
France	552	575	603	629	644	684
UK**	532	529	531	535	564	599
Italy	217	226	255	270	340	480
Netherlands	133	145	150	156	156	177
Spain	113	123	133	137	177	209
Sweden	115	126	123	127	134	138
Belgium	90	92	95	103	107	116
Austria	52	57	71	78	84	95
Switzerland	48	50	51	51	—	—
Denmark	49	51	—	—	67	81
Norway	46	46	48	—	51	56
Portugal	19	20	22	19	25	35
Ireland	13	13	13	13	15	15
Greece	12	12	—	—	—	—
Turkey	—	9	—	15	—	24
Finland	38	39	36	40	36	40
Canada	232	234	—	—	—	—
Russia	1,810	—	—	—	—	—
Czechoslovakia	99	—	—	—	—	—

*Source: Organisation for Economic Co-operation and Development quoted by Ernest Benn Ltd, Chemical Industry Handbook 1972.

**Figures for companies employing 25 or more persons.

Table 2
UK paint manufacturers' sales, 1963-1970*

Year		Oil or synthetic based		Emulsion	Cellulose	Water paints	Others	Total
		Decorative	Industrial					
1963	Volume (1,000 gals)	30,857	19,160	9,485	12,275	4,605	8,921	85,303
	Value (£ thousands)	55,232	26,114	15,370	13,734	3,356	10,765	124,571
	Price (£/gallon)	1.79	1.36	1.62	1.12	0.73	1.20	1.46
1970	Volume (1,000 gals)	36,088	24,494	21,910	13,116	1,087	9,319	106,014
	Value (£ thousands)	64,255	35,083	31,467	15,562	830	10,753	157,949
	Price (£/gallon)	1.78	1.43	1.44	1.19	0.76	1.15	1.49
1971	Volume (1,000 gals)	35,080	23,717	26,067	11,575	—	14,964	114,403
	Value (£ thousands)	69,815	36,393	41,791	16,776	—	22,437	187,212
	Price (£/gallon)	1.99	1.53	1.60	1.45	—	1.50	1.64

*Data from Department of Trade and Industry Business Monitor and Ernest Benn Ltd Chemical Industry Handbook, 1972.

the author in drawing up the list given in Table 4.

Table 4
Surface coatings innovation

Material or method	Date of appreciable use	Remarks, companies involved, etc.
1. Nitrocellulose finishes	1920	Material and method are complementary
2. Conventional spray gun application	1920	
3. Oil-modified alkyds	1935	Albert Chem. Werke, Beck Koller, ICI
4. Titanium dioxide (anatase)	1932	Sulfate process; Du Pont, Nat. Lead, British Titan Products
5. Titanium dioxide (rutile)	1942	In 1959 consumption of TiO ₂ and lithopone was about the same. Thereafter TiO ₂ went rapidly ahead
6. Chlorinated rubber	1935	ICI
7. Phosphating	1935	Pyrene
8. Phthalocyanine pigments	1936	ICI
9. Urea resins in finishes	1940	Am. Cyanamid, British Industrial Plastics
10. Melamine resins in finishes	1945	Ditto
11. Pva emulsion paints	1948	After development and extensive use in Germany during the war
12. Micronising	1949	—
13. Unsaturated polyesters	1950-1	Am. Cyanamid, PPG Industries
14. Electrostatic spray	1953-4	Ransburg Electro-Coating Corporation
15. Slurry grinding	1955	Smith & Walton Ltd
16. Epoxide resins	1956	Shell
17. Thixotropic alkyds	1955-6	Washburn Co, Cray Valley Products
18. Airless spray	1957	J. A. Bede, Aerograph de Vilbiss
19. Quinacridone pigments	1958	Du Pont
20. Urethane oils	1959	Cargil, Beck Koller
21. Siliconised resins	1960	Dow Corning, Midland Silicones, Berger, Jenson & Nicholson
22. Thermoplastic acrylic automotive finishes	1960	ICI
23. Chloride process titanium dioxide	1960	Du Pont; all new USA TiO ₂ plants since 1960 have used this process
24. Sand mill	1960	Du Pont
25. Thixotropic emulsion paints	1960-1	British Oxygen using sodium silicate; other companies using metal chelates in late 1960s
26. Electrophoretic painting	1961-2	Ford/Glidden/PPG in USA
27. Curtain coating	1962	Bürkle & Co; developed first on Continent
28. Coil coating	1962	Pre Finish Metals Inc, etc.
29. Computer colour control	1962	COMIC
30. Electrostatic powder spray	1964	SAMES initiated process in France in 1962. Process in direct competition with solvent thinned finishes
31. Thermosetting acrylic automotive finishes	1965	PPG
32. Zinc phosphate anticorrosive pigment	1967	Goodlass Wall, Imperial Smelting Co
33. Non-aqueous dispersions	1970	Notably ICI but also Du Pont, BASF and one or two others. British car industry took up ICI Dispersymers in 1972

The list of 33 items is rather a short one, when considered as the significant achievements of worldwide paint research, especially as it is extended back to 1920, instead of being limited to the highlights of post-war research as originally

intended. Secondly, the dates given are those of the first significant use rather than the dates of discovery, which usually preceded this by far too many years; thus ensuring that the profits to the inventing company were of "me also" rather than "me only" dimensions. Thirdly, if restricted to innovations made by paint companies, the list would be very short indeed. Fourthly, and very notably, not one of these innovations has significantly increased the market for paint manufacturers either by extension or by diversification.

Not all research is, however, innovative but virtually all successful research is eventually published either in the form of patents to obtain protection, or in scientific or technical journals to obtain publicity for the authors or their organisations. At present, the technical work of the surface coatings industry is reported in 12,000 publications annually in 357 national journals and the patent literature of major industrial countries. Mr E. F. Redknapp, editor of "World Surface Coatings Abstracts," analysed the January and July 1972 issues, comprising about 2,000 abstracts to give the data reported in Table 5. This shows that 50 per cent of all surface coatings industry publications are now patents, whose annual number has doubled in the last decade, but that 85 per cent of these are patents of improvement, mostly of a relatively minor character. Other publications of claim-

Table 5
World Surface Coatings Abstracts 1972
(based on January and July issues)

Category	Percentage of total abstracts	Remarks and motives for publication
<i>Useful to company</i>		
New products or processes	8.6	7.9% patents (for protection), 0.7% papers (for publicity)
Improved products or processes	42.5	40.8% patents, 1.7% papers
Sales promotion	7.2	Papers written round company products or easily identified proprietary materials
Analytical or test methods	7.1	Useful in production control, technical service, analysis of competitor products, standards, etc.
Background scientific data	9.3	Prestige value to companies, sponsors, etc., who sanction work
Defence of products	0.2	Estimate. Not encountered in WSCA sample
	74.9	
<i>Not useful to company</i>		
Review articles	5.6	To assist competitors?
Experimental study of technical problems to define in scientific terms and assist solution	3.3	To assist competitors?
Miscellaneous	16.2	Motive for work or publication difficult to identify
	25.1	

Note—(a) WSCA contained 2,174 patents in 1962 and 4,791 in 1972, i.e. the number has more than doubled during the last decade. However, about 85 per cent of new patents concern improvements rather than real innovations and it is estimated that some 80 per cent of these improvements are of a relatively minor character. (b) Number of non-patent abstracts has been held constant from 1962 to 1972 at 5,300 by not abstracting more trivial publications in recent years.

able value to the company carrying out the work make up the total to 75 per cent of all publications. Statistics can, of course, be dangerous, but in the light of the present very high costs of R and D, two conclusions seem very clear. First, the proportion of work without a very clear usefulness to the company is, at 25 per cent, much too high. Second, inventions at a rate of 92 issued patents per week should be making the rate of technical progress (and profitability) very clear indeed—if the research projects were sufficiently ambitious in the first place and the company concerned seriously intended to exploit new technology from its selected research projects.

Present cost and benefits of paint industry R and D

Consider now the cost of producing exploited inventions and published papers at this rate.

British paintmakers spend about 2 per cent* of their turnover on R and D. For an industry operating at high profitability of, say, 20-25 per cent an expenditure of 2 per cent on R and D would be worthwhile purely for maintaining the market. For an industry with much smaller profit margins, say 10 per cent, an ambitious R and D programme must seek to expand the market by more than the 20 per cent per annum needed merely to recover the cost of the R and D. The UK paint industry rate of expansion between 1950 and 1972 averaged 4 per cent by volume and 6 per cent by value per annum.

The research publications and highlights considered above were, however, the product of the paint industry worldwide with a paint turnover approximately twenty times that of the UK industry or £4,600 millions per annum and if spending at the same rate as the UK, a combined R and D budget of £92 millions per annum. There is, in addition, the cost of research by chemical raw material concerns and makers of paint manufacturing and application equipment to a total unlikely to be less than £200 millions per annum. Against this, the list of highlights seems very short indeed.

Why not put science to work more effectively?

Ref. 2

It has been noted that the effective use of science and technology can make a profound difference not merely to one business, but to the industrial welfare of whole nations. Why is it not used more effectively to create a more profitable and expanding paint industry? Is paint an obsolescent industry, where R and D is merely fighting a rearguard action against overwhelming competition from other surface finishes? The author thinks not, for despite small inroads in to paint markets by laminated plastics and vinyl wall coverings (both of which could have been products of a more adventurous paint industry), the volume of paint manufactured continues to rise. Is there too much production capacity and too many manufacturers chasing too few customers? Yes, but in such a situation really aggressive research by the leaders could set performance characteristics and production levels which would drive the inefficient quickly out of business and at the same time deserve higher profit margins. Strong world competition in steel-making, shipbuilding, glassmaking, scientific instruments, industrial electronics and watchmaking did not prevent the Japanese

* (a) J. M. Butler, "A Profitable Paint Industry", PA 4th Annual Conference 1966, quotes 2.7 per cent for "laboratory costs"; (b) *Paint, Oil and Colour Journal*, 1973, p. 118, quotes DTI Statistics showing 1.8 per cent of paint industry turnover spent on R and D.

from entering these markets with sufficient success to become world leaders in several of these industries. Indeed, the will to achieve a leading position was probably necessary for successful entry to these competitive markets. In the surface coatings industry, itself, overproduction has not prevented one very profit-conscious US company (not previously a paint manufacturer) from entering the market with "Scotch-lite" reflective road signs and reflective paint available in aerosol can form. The same company is also reputed to have built up epoxy powder coating business worth £8 millions per annum for pipe linings. That company is, however, dedicated to new approaches and a rate of research and its exploitation, which achieve a succession of "me only" type developments with consequent high profitability.

As the author has a vested interest in research as a business tool, he must observe that research is, of course, only one of the means available to management for improving the business, which must be considered in context and used as purposefully as other more drastic methods listed in Table 6.

Table 6
Methods for improving paint company performance

1. Rationalise product range; to eliminate loss-makers and low profit items.
2. Amalgamation/takeover; to reduce overheads and create stronger technical and marketing units.
3. Asset stripping; to ensure that financial, site and equipment resources are fully used.
4. Improved management techniques; optimisation of factory layout, inventory control, production planning, distribution and marketing to reduce overheads.
5. Vertical integration; to offer a total systems approach to paint manufacture and application by the same company as convenience to customers and means for minimising technical service and trouble-shooting.
6. Licensing patents and know-how; to avoid high costs in imitative research and gain rapid market entry.
7. Aggressive research; to improve present profits and generate new business.

The first four methods have been a feature of the UK paint trade for 20 years and have since become common in Continental Europe and Scandinavia. In the last five years, several UK paint manufacturers have become substantially involved in industrial paint application (method 5) with very favourable effect on their profits. However, detailed consideration of these methods is outside the scope of this paper, except for the observation that, in general, these devices work only once in improving the business and none of them is rapidly effective.

The beneficial effect of exploiting new technology, either other people's by licensing (method 6), or one's own by really aggressive research (method 7), can be applied time and time again in order to have improved products ready before sales of the existing range start to suffer from increasingly strong competition, and to diversify in providing new business opportunities within the company's capital resources and its plans for the future. Indeed, if these are not the objectives of building up a strong research team in the company—don't indeed waste your money on research!

The techniques for managing research have improved notably in the last 20 years, indeed with increasing costs they had to do so. There are now methods such as the "technical audit" for assessing the relative merit of alternative research investments, the technique of "network analysis" to estimate time for completion of the project and to ensure

that the time-table is met, and "discounted cash flow" to ensure that exploitation is undertaken rapidly enough to derive full benefits from the research. The usefulness of such techniques was reviewed in the author's lecture to the Midlands Section OCCA Symposium three years ago.²

However, the choice of alternative research/exploitation investments is too important a matter to be left to the Research Director alone. His job is to ensure that present projects are successfully completed on time and within the budget allocated, to lead and stimulate his staff to produce the maximum number of worthwhile proposals for further research, to predict the time and money needed for their completion, and with his colleagues in top management to select those in which company money, enthusiasm and expectations will be invested. If scientists and technologists are not telling these people what can be done within the stated time and budget, they have got the wrong scientists and technologists. If, thereafter, top management does not decide what is going to be done, it is the wrong top management.

The problem and some solutions at the Paint Research Association

Refs. 3-10

It is only fair that an industrial research institute should share the difficulties experienced by the industries it serves. Rising research costs, however, have their effect on the institute even more severely than they do on industry, for research is the institute's only product and it is dependent on the effective and beneficial use of developments by the industry to justify, and pay for, continuing support. In recent years, many institutes have been experiencing difficult times, particularly in Britain where the still developing policy of successive governments has been that industrial research should not need government subsidy and, even if conducted in government laboratories, should be funded on a strictly customer/supplier basis.

In these critical circumstances, it is of more than theoretical interest to the PRA to achieve and demonstrate the maximum value of research per pound invested, to attract new Members and sponsors. Its success, so far, is indicated by growth of income from 1966 to 1973; over this seven-year period, despite a diminishing rate of government grant, now comprising only 12 per cent of total income, and increased subscriptions from existing Members of less than 30 per cent, a growth was achieved of 106 per cent with major progress in overseas membership (470 per cent increase) and research contracts (550 per cent increase).

Choice of projects

The changes which the increasing cost of science and the information explosion have made to the conduct of work at the PRA over the last few years and methods for attempting not to waste the money on research are determined basically by use of the seven disciplines enumerated below.

Strictly mission-orientated research

Projects selected for the annual Research Programme must, of course, generate either scientific or commercial excitement; naturally in today's difficult economic climate, the commercial criterion is the more important; science for science's sake, or rather paint for science's sake, is left to

those who can afford it, or those funded by society for instructing the young in techniques for industrial research. Certain background science studies are necessary, of course, from time to time to complete a capability for a major commercial project.

Each project in the annual Research Programme states, in two or at most three sentences, a clearly defined objective and indicates the methods the Association expects to use to reach that objective. This clear definition of specific targets and consequent limitation of the work enables the PRA to undertake many more projects than previously.

A planned timetable for completion of work

In view of the vast body of knowledge and the range of sophisticated research tools and methods available today, a Research Director must accept responsibility for both a high degree of success and for predicting the number of "man-months" effort needed to achieve it. Smaller projects, therefore, are defined for completion within the year, whilst for larger projects an intermediate stage of accomplishment is defined as the year's work.

Constructed invention³

With the multitude of new compounds, new materials, new machines, new techniques and new ideas available in science and the technologies, the Research Director must also accept responsibility for putting existing capabilities together in new ways to construct inventions. This could be called "exploratory development" work; it may not be Research with a capital "R" as practised in the "ivory towers", but it certainly enables research of high challenge to produce useful results extremely quickly. In passing, it is worth noting that several recent studies of industrial innovation indicate that highly qualified scientists are not the best or most frequent performers in invention, but that this frequently comes from well-trained technicians of near graduate qualifications.³ The author hopes that in time there will be fewer narrow specialist PhD technicians and more true research scientists with imagination and broader interests.

Co-operative projects with other industries

Involving the customer in the research as a sponsor for the work, a partner in the research or in order to evaluate its results

The above two items do not require comment, but less common for an industrial Research Institute is the following discipline:

Maintaining a high proportion of innovatory and improvement projects

The first page of the PRA published programme each year indicates the distribution of technical effort, which for the past three years has averaged 30 per cent on technical services and 70 per cent research (including 29 per cent on new products and processes, 23 per cent on improvements and 18 per cent on background science studies).

With approximately half the technical effort on innovation and improvement, recent programmes are clearly aggressive and highly commercial in intent.

Promotion of research results

Only a few years ago this would have been regarded as scientific heresy, and even today promotion of research results is still regarded by some as an unorthodox procedure unbecoming to the dignity of science and technology. An even greater indignity, however, is the neglect by lack of attention to a new product, process, compound, capability or theory. Such neglect is only too easy these days when the surface coatings scientist or manager with wide interests has the choice of 240 new publications or patents every week as reading material, in addition to internal reports.

The PRA continues to publish in the technical journals and the patent literature. Increasingly, however, it has come to use press handouts, with radio and television coverage to notify major achievements to a larger business audience. A wide scientific and business readership in the UK now includes the technical page of "The Financial Times" as one means to keep the industry informed of the highlights of its own and other people's science and technology.

Examples of typical projects

With the exception of project selection and timing, the above disciplines cannot be applied systematically, but rather by a process of continuous applied opportunism. Examples of their use are indicated in the following brief accounts of typical projects from PRA work in the last few years.

*Conductive paints and paint-on-electric-heating*⁴

This was a constructed invention aiming at new markets for the paint industry. Nearly all the technical capability for conductive paints already existed, and was simply waiting for someone to have the idea. The PRA was able, therefore, to prepare a full range of conductive paints based upon inorganic systems, emulsion systems, solvent-soluble resins (even convertible coatings) and many different applications within two years of the first experiment. This gave material for patent completion in 26 countries. It also illustrates the use made of publicity on television, radio and worldwide press to stimulate an immediate market for these new paint products and applications.

*Mirror-making paints*⁵

These provide another example of a constructed invention using existing knowledge of colloidal silver making and paint manufacture. Once again, publicity on television and in the press stimulated many customer enquiries. Mirror paint is very easily and rapidly applied to textured glass and plastics giving pleasing effects which could extend paint markets in the architectural field.

*Non-polluting antifungal and antifouling paints*⁶

These researches illustrate co-operative projects with another industry. Four years ago a number of major pharmaceutical companies were approached on a basis of scientific "waste-not—want-not" proposing joint research projects to use the rapid screen-testing methods developed at the PRA and the companies' chemical compound collections. Six major companies have joined in these projects for the discovery by screen testing of new paint biocides of low mammalian toxicity.

In the paint fungicide project, the PRA multipoint inoculator enables an agar plate containing the compound under test to be simultaneously inoculated with the fungal spores of all 16 important "paint fungi." Active compounds identified by this screen-test (on average 3 out of every 100 compounds examined) are then evaluated in paints in the PRA fungal test cabinet.

Three years ago a background science project developed the capability for laboratory reproduction and culture of *Enteromorpha* and *Ectocarpus*. This enables screen-testing of potential weed antifoulants to be carried out accurately and reproducibly all the year round. Active compounds identified by this screen-test (on average one out of every 100 compounds examined) are then tested in paints.

Chemicals can now be tested for both antifungal and antifouling action at a rate of 200 compounds per month. The first PRA patents on new, metal-free paint fungicides and paint antifoulants were lodged in September 1973.^{6f,g}

*Sucrochemical resins*⁷

These projects provide another example of co-operation with another industry, in this case by sponsorship from its trade association, the International Sugar Research Foundation. The work has already given interesting new sucrochemical paint resins whose price/performance characteristics justified patent application early this year.⁷

Other sucrochemical resins are now being developed for application in wood stabilisation. These show promise in preventing the expansion/contraction cracking damage that can occur on wetting and drying out, and also in considerably hardening softwood timber.

This work has special importance in view of the rate at which world resources of coal, oil and other mineral sources of energy and chemical raw materials are being exhausted. Agricultural chemicals, such as sugar, can be renewed or even increased next harvest time and are likely to have increasing importance in the chemical industry.

*Organosilicon resins*⁸

This recent project illustrates another challenging mission-orientated research with which success is rapidly being achieved. Silicon is the most abundant element in the earth's crust and is present in different mineral silicates in differing stereochemical (chain, ladder or sheet) forms. Such rocks and clays thus offered considerable temptation as starting materials for organosilicon resin synthesis, despite their previously intractable nature.

A method has now been devised which, in a single-stage, room-temperature reaction, converts mineral silicates into organopolysilicate resins, soluble in a wide range of solvents including even white spirit. The products vary from colourless viscous liquids to solids depending on the mineral starting material and the reaction conditions.

Applications for this remarkable chemistry are being explored, now with contract support from the National Research Development Corporation, who will also considerably assist in arranging exploitation. Recently several of these products have been found to give excellent water-proofing action, particularly on cotton, wool, nylon and polyester fabrics. Patent applications have been lodged for

the manufacture of these new resins and their use in waterproofing a wide range of textiles and building materials.⁸

*Fibre optics colorimeter*⁹

This instrument, now widely known from published patents, papers and publicity,⁹ has been on sale since January 1974 with an associated wet-paint-bench for virtually simultaneous monitoring of six batches of paint.

This is another example of a constructed invention which used existing knowledge of fibre optics and photomultipliers to make a new colorimeter with a remote sensing head. It makes fully automatic colour control, even for continuous paint manufacture, a practical prospect.

*Painting of joinery timber*¹⁰

This background technology research defined guidelines for selection of integrated systems of preservative and paint among existing commercial products. Its immediate aim was to provide the means for achieving savings in the maintenance costs of replacing rotted wood and repainting (for which figures as high as £300 million per annum have been mentioned and £100 million per annum is the probable UK bill). A second important aim was to set the standards for future research on improved wood protection products. This research also devised a wood porosity meter able to detect rapidly and non-destructively "overporous timber" for which premature paint failure in external use can be predicted confidently, whether or not the wood is pretreated with preservative. The use of such wood should be avoided for external joinery.

For this project, the PRA involved the largest UK building contractor (the Ministry of Public Building and Works—now the Department of the Environment) as sponsor. Once the work was successfully completed, the sponsor readily accepted responsibility for publicity, including arranging two symposia for the three trades involved as well as for architects.

Conclusion

The Paint Research Association does not have all the answers—far from it. As the author has shown, however, it is trying

to offset increased research costs by the full and most effective use of modern science and the technologies. Research projects aim in very direct manner to meet the urgent needs of the industry for increased profitability and for expanded markets.

For Research Institutes such as this the problems differ slightly from those of industry, for the PRA is dependent on Member companies exploiting its science and invention. Indeed, the continuing existence of industrial Research Institutes can be justified only if Member companies truly recognise and use them as extensions of their own technical capability.

In this technological age, companies must use both their own research and that of the industrial Research Institutes much more purposefully and effectively. Research must be on carefully selected projects and must anticipate success and rapid exploitation, otherwise . . . don't waste your money on research.

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Internal reflection spectroscopy: application to organic coatings and plastic sheeting

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Summary

The application of infrared internal reflection spectroscopy to the analysis of organic coatings and multilayered plastic sheeting is discussed in terms of the available literature, elementary theory and several analytical problems.

Any surface that is reasonably pliable can be examined by internal reflection spectroscopy (IRS). The sample is mounted on a crystal and inserted in the beam path of an infrared spectrophotometer. The resulting infrared spectrogram can be used to identify the

components in films such as retro-reflective sheeting, paint films, and so forth. IRS is also useful in identifying powders, such as additives and pigments. Several of the advantages of IRS over transmission spectroscopy are discussed. The more important of these are the ease of sample preparation and the fact that the surface features can be studied.

Specific uses of IRS by the Texas Highway Department as a quality control procedure are described.

Keywords

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

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

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

La spectroscopie à réflexion interne: Son emploi dans le domaine de revêtements organiques et de plastiques en feuille

Résumé

En faisant appel à la littérature disponible, à la théorie élémentaire et aux divers problèmes analytiques, on discute l'emploi de la spectroscopie à réflexion interne de rayons infra rouge pour analyser les revêtements organiques et les plastiques en feuilles multicouches.

Toute surface d'une souplesse raisonnable peut être analysée par la technique de spectroscopie à réflexion interne (IRS). La prise d'essai se fait monter sur un cristal et l'ensemble est interposée dans la marche de rayons d'un spectrophotomètre à l'infra rouge. On peut utiliser la spectrogramme infra rouge qui en résulte pour

identifier les constituants des feuilles retroréfléchissantes, des feuillets de peintures et le reste. La IRS se montre utile d'ailleurs pour l'identification des poudres telles que pigments et adjuvants. On discute certains des avantages que possède la IRS auprès de la spectroscopie par transmission. Les plus importants parmi ceux-là ce sont la facilité de préparation de la prise d'essai et la possibilité de faire une étude des caractéristiques de la surface.

On décrit des exemples spécifiques de l'emploi de la IRS par le Texas Highway Department pour effectuer les essais de contrôle.

Inner—Reflektionsspektroskopie: Anwendung auf organische Beschichtungen und Kunststoffolien

Zusammenfassung

Die Anwendung der Inner-Reflektionsspektroskopie auf die Analyse organischer Beschichtungen und mehrschichtiger Kunststoffolien wird mit Bezug auf zur Verfügung stehende Literatur, Elementartheorie und verschiedene analytische Probleme besprochen.

Irgendeine, einigermaßen geschmeidige Oberfläche kann mittels der Inner-Reflektionsspektroskopie (IRS) untersucht werden. Das Muster wird auf einem Kristall montiert und in den Strahlenkegel eines Infrarot-Spektrophotometers eingeführt. Das resultierende Infrarotspektrogramm kann zur Identifizierung der Filmkom-

ponenten, z.B. in retroréfléktiven Folien, Lackfilmen etc. benutzt werden. IRS ist auch zur Identifizierung von Pulvern, wie Zusatzmitteln und Pigmenten brauchbar. Einige Vorzüge der IRS gegenüber der Transmissionsspektroskopie werden erwähnt. Am wichtigsten in dieser Beziehung ist die Einfachheit der Herstellung von Mustern und die Tatsache, dass Oberflächencharakteristika beobachtet werden können.

Die spezielle Verwendung von IRS zur Qualitätskontrolle seitens des Texas Highway Department wird dargelegt.

Introduction

The purpose of this report is to demonstrate the utilisation of the internal reflectance accessory of the infrared spectrophotometer for paint and plastic sheeting analysis. A summary of the pertinent literature is given. The theory of internal reflection spectroscopy (IRS) is briefly covered in order to point out several generalisations useful in IRS experimentation. Several analytical problems are discussed in which IRS was employed to identify or quantify paints, plastic sheeting and raw materials.

Background and theory

Refs. 1-8

The use of the infrared spectrophotometer in the internal reflection mode was introduced about a dozen years ago.^{1, 2} Since that time, several application papers have appeared in the paint and plastics literature. Additionally, much important work has been reported by IRS instrument manufacturers (notably, Wilks Scientific Corporation and Barnes Engineering Company).^{3, 6} The general theory of IRS has been well



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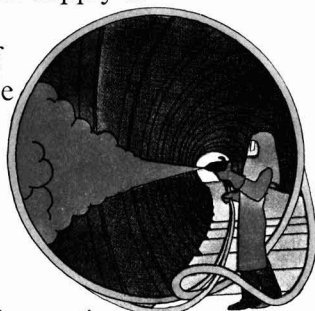


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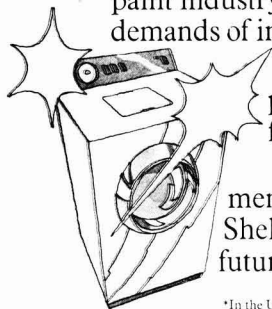
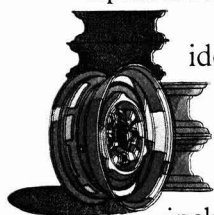
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covered by Wilks and co-workers.^{3, 7} The mathematical aspects have been developed by Harrick.⁸ The references should be consulted for more rigorous expositions.

Physical processes involved in IRS

Ref. 9

An adequate description of internal reflection phenomena can be based on Newton's "Opticks,"⁹ first published in 1717. Fig. 1 shows a refractive prism called an internal

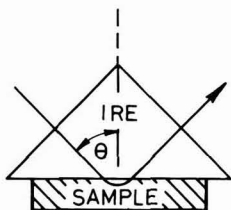


Fig. 1. Path of light through an internal reflection element (1 reflection IRE)

reflection element (abbreviated IRE). Let a light beam (in this case infrared light) be directed towards one face of the IRE. If the angle of incidence (θ) is greater than the critical angle, the beam is totally reflected as though the back were silvered. It can be easily demonstrated that this totally reflected beam penetrates into the space beyond the back face before returning to the prism. The amplitude of this beam decreases exponentially with distance from the back surface and is consequently called the "evanescent" wave. When a sample is placed against this back surface the evanescent wave undergoes selective attenuation. This attenuation is related to the infrared activity of the sample. A plot of wave length versus transmittance yields a spectrum similar to that of regular transmission spectroscopy. (This description of "internal reflection spectroscopy" conforms to the definition in ASTM E 131. One of the originators of the analytical method, Fahrenfort, used the term "attenuated total reflection" (ATR) and, thus, the literature contains both phrases.)

Penetration of the evanescent wave

Refs. 8, 10, 11

The depth of penetration d_p of the evanescent wave is defined by Harrick⁸ as:

$$d_p = \lambda_1 / 2\pi (\sin^2 \theta - n_{21}^2)^{0.5}$$

where λ_1 is the wavelength of light in the IRE, θ is the angle of incidence (Fig. 1), and n_{21} is the ratio of the refractive indices of the optical element n_1 and of the sample n_2 .

The value of d_p is one of the factors that determines the strength of absorption in the spectrogram. The relation shows that d_p :

1. *Increases with wavelength.* As the scan moves from 2.5 to 40 microns (4000 to 250 wavenumber cm^{-1}) the depth of penetration in a typical case increases from 0.75 to 15 μm . This wavelength dependence produces some distortion in IRS peaks compared to transmission spectra. It is apparent that the IRS method samples only near the surface of most paint films (i.e., films 100 to 200 μm thick).

2. *Decreases with increasing θ .* The incidence angle is easily varied and this can be used to control the depth of penetration. This is useful in studying effects, such as weathering, plasticiser migration, multilayered films, and so forth.
3. *Increases with closer refractive index matching.* From the equation, it is seen that the depth of penetration increases as n_{21} tends to unity. However, the index of refraction of the IRE must be greater than the sample in order to obtain undistorted spectra. Since KRS-5 (thallium bromide-iodide, $n_1 = 2.38$) is the IRE usually available to the analyst and is, generally, an excellent reflector, this variable (the IRE) is utilized only in unusual cases. Silver chloride ($n_1 = 2$) and germanium ($n_1 = 4$) are sometimes used where index matching presents a particular problem. Sapphire is the only currently available IRE for ultraviolet and visible work.^{10, 11}

Effective depth of penetration

Refs. 4, 8

Assuming that the depth of penetration d_p is satisfactory, it is still necessary that several other variables be controlled in order to obtain a satisfactory IRS scan. For example, the sample should be in intimate contact with the back face of the IRE. The amount of interaction or coupling can also be changed by changing to a multiple reflection IRE.

Several variables are contained in the concept of the effective penetration depth:^{4, 8}

$$d_e = n_{21} E_o^2 d_p (2 \cos \theta)^{-1}$$

This approximate equation contains four factors affecting the strength of coupling of the evanescent wave with the sample: E_o is the electric field amplitude of the evanescent wave; the other factors are defined above. The term $(1/\cos \theta)$ is proportional to the sampling area. This variable, as well as E_o and d_p , decreases in magnitude with increasing θ . (The n_{21} term is independent of θ .) Thus, strongest coupling is obtained when the incidence angle is very nearly equal to the critical angle for the particular IRE.

Variations in scans with wavelength

In the above equation, when d_e is greater than the film thickness, the d_p and θ terms are no longer significant. However, for most films the effective depth of penetration of the evanescent wave d_e is less than the film thickness. In this case, the band profiles are affected by the wavelength. The value of d_e increases with λ_1 and the bands become stronger, broader, and show an apparent shift to longer wavelengths as compared to transmission spectra.

Dispersion effects

Refs. 8, 12

A second effect that distorts bands and displaces them to longer wavelengths is the change in sample refractive index that the instrument sees as it passes through an absorption band. Dispersion effects occur in both transmission and reflection spectroscopy, but in the former case the beam angle is constant and the effect is not noticed. Chromatic aberration in lenses is another illustration of dispersion. Dispersion is the effective increase in the refractive index of a material as the frequency of the source light increases.

In the simplest case, where n_1 is nominally equal to n_2 , the effect becomes apparent when n_2 changes as the scan passes through a molecular absorption band. This creates a displacement and distortion of peaks that is additional to the effects of penetration depth. This distortion is greatly minimised by keeping several degrees (5° to 10°) above the critical angle and using a high refractive index IRE ($n_1 > n_2$). A detailed knowledge of dispersive effects is not necessary in order to obtain good laboratory results (for detailed analysis, see Harrick's monograph⁸).

In view of the discussions of penetration depth and dispersion, it is evident that a compromise between peak height (coupling) and peak distortion must be made.¹³ This is best determined for each particular case by running the sample at several θ angles above the critical angle (see Results below).

An IRS scan is generally similar enough to a regular transmission scan to permit a direct comparison.

Advantages and limitations of IRS

Refs. 8, 13

In Isakson's paper on infrared specular reflectance,¹³ a comparison is given of several sampling techniques. To a certain extent, IRS is replacing the use of free films, cast films, and salt pellets. The principle shortcoming of IRS is its failure to match transmission spectra exactly. The advantages^{8, 13} of IRS are:

1. *Applicability to a wide variety of samples.* Some examples are (a) a variety of solids, such as plastics, rubbers, etc; (b) very minute samples, such as those obtained by gas or gel permeation chromatography; (c) organic and inorganic powders usually handled as mulls or pellets which can be prepared as dry paste; (d) pigmented samples such as paints; (e) liquids. Liquids can be handled with special liquid cells. This has proved useful with aqueous solutions, highly concentrated solutions, and viscous solutions.
2. *Ease of sample preparation.* The primary requisite for a good IRS specimen is close sample-to-crystal contact. Paint solids serve as a good example of IRS sample preparation. A solid, such as titanium dioxide powder, can be mixed with a volatile liquid (methanol) into a paste, allowed to dry, and scanned. The preparation of a halide pellet or mull is avoided. Furthermore, the powdered samples do not exhibit the scattering associated with transmission spectra.

Hard, thick sheets with uneven surfaces (such as a rough cut wood) are usually difficult to study with IRS. Also, it is important that the preparation procedure does not contaminate the IRE with plasticisers, residues, etc.

3. *Films do not produce interference fringes.* Unlike transmission spectra, IRS does not produce the confusing interference waveforms associated with films and liquids. This problem is often noticed in the 4 to 7 micron region of transmission spectra.
4. *The spectra are independent of the sample thickness* (for sample thickness $> d_c$). The film can have any convenient thickness and still be amenable to quantitative analysis providing good sample contact is obtained.

5. *Can be used to study surface reactions.* The fact that the beam penetrates only a few microns permits a study of many surface reactions, including cure reactions (using either surface or bulk catalyst), plasticiser migration, weathering, and ageing effects.

The disadvantage of IRS compared with transmission spectra of free films, cast films, mulls, and pellets lies primarily in the lower quality of the spectra. Consequently, the sections on Theory and Procedures are stressed in this paper. Good spectra can be obtained on a variety of samples when proper techniques are used. For example, both the pigments and the resin show up in the spectra of whole paint films and this will work as an advantage or disadvantage depending on whether there is an interest in the pigment itself. In liquid paint samples, the pigment can be readily removed by prior centrifugation.

Literature survey: IRS studies on coatings and plastics

Refs. 14-26

Harris and Svoboda used IRS to determine the aromatic constituents of modified alkyd resins without prior chemical treatment.¹⁴ Quantitative analysis for phthalic anhydride, isophthalic acid, vinyl toluene, and styrene was made at 13.5, 13.7, 12.3, and 14.3 microns, in turn. The concentrations (25 to 75 per cent range) were determined using calibration curves of per cent constituent versus absorbance.

McGowan has reported on the use of IRS for the quantitative evaluation of alkyd resins.¹⁵ Whilst the "absorbance ratio" method¹⁶ can be used in many applications involving transmission spectra of free films, the method will often give better results with IRS samples (lower variability) with fewer calculations. In most infrared analysis a simple percentage result is sufficient and quantitative results are not necessary. An example of this method of data reporting is the ratio or per cent of oil in an alkyd. The peak at 2 950 cm^{-1} is associated with the oil, whilst the peak at 1 725 cm^{-1} is related to both the oil and the phthalate ester content. The relative peak heights of a sample are compared to a calibration curve of relative peak height versus per cent oil.¹⁶

An IRS study has been made of the oxidative-polymerisation of drying oils.¹⁷ The top and bottom surface spectra and the bulk transmission spectra were recorded for a period of eight days. The quantitative data were obtained by a variation of the internal standard method¹⁶ in which the C—H absorption of the oils served as the reference. The results were consistent with an oxidation (rather than a diffusion) rate-controlling process. That is, the oxygen diffused through the film more rapidly than it was utilised for the cross-linking reaction.

Polchlopek and Harris compared the spectra of several whole paints and their alkyd base.¹⁸ Most inorganic components of paint have a fairly high detection threshold and rather broad peaks. Titanium dioxide gives a characteristic "halo" from 12 microns up and, at high concentrations, from 2.5 to 5.5 microns. Calcium carbonate, clay, and talc can be detected by IRS. Toluidine red, hydrated yellow iron oxide, ultramarine blue, and iron blue are compounds that have sharper and stronger absorption bands.

The IRS method can also be applied to both dried¹⁸ and liquid latex paints.¹⁹ In the latter case, liquid IRS cells

are used. The intensity of water absorption bands are reduced by this method and dispersed solids do not cause significant light scattering. Liquid cells are capable of handling more viscous emulsions than are transmittance cells. Liquid cells sometimes require highly concentrated emulsions (20 per cent or more).

In the case of powders, it has been found that the strength of absorption can be related to the particle size through the packing fraction.²⁰

As the following examples will show, IRS is particularly well adapted to the study of coated or layered materials, such as adhesive tapes, coated paper, and retro-reflective sheeting.

An adhesive tape may have as many as four surfaces requiring analysis: the adhesive layer, the adhesive-backing interface, and both sides of the backing. For example: a common, pressure sensitive, clear tape has been shown to have a natural rubber adhesive with kaolinite and dioctyl phthalate plasticiser. The backing was primed with natural rubber latex. The glossy side and the adhesive side of the backing produced spectra indicating cellulose acetate with phthalate plasticiser.²¹ Other adhesives for tapes include polyethylacrylate and styrene-butadiene rubbers with various tackifiers. The IRS spectra of rubber and rubber formulations have been reported.²² Other backing materials include cellophane, paper (cellulose), and glass fibre.

Coatings and impregnates for paper have been studied with IRS. These materials can greatly complicate a spectrum. In one reported case, the urea-formaldehyde-alkyd impregnate dominated the cellulose spectrum.²¹ The use of clay, calcium carbonate, starch, protein, and dicyandiamide paper coating materials has been studied with IRS.²³ Barnes Engineering Co. has reported that DuPont's "Corfam" shoe leather has five distinct layers and several additives.²⁴

IRS has been used to study the adhesion of paint to wood.²⁵ It was shown that the oxirane ring of epoxy resins reacts with the hydroxyl groups of reconstituted cellulose.

Pyrolytic analysis is sometimes useful for polymer samples which contain a high solids loading (pigment in paint; carbon, clay in rubber). It is often desirable to use IRS to analyse the pyrolyzate, particularly if the sample is small.²⁶

This review of the literature indicates the scope of analytical problems that are amenable to internal reflection spectroscopy. IRS is a versatile tool which should find wide application to paint and sheeting materials.

Experimental 1: IRS of retro-reflective sheeting

Ref. 27

Retro-reflective sheeting is widely used in information and warning signs on public highways. A complicated but, nonetheless, fairly typical design is shown in Fig. 2. A detailed description of retro-reflective sheeting design can be found in the patent literature.²⁷

It is apparent that the upper portion of the plastic sheeting in Fig. 2 is too complex to be readily studied by infrared transmittance spectroscopy. Furthermore, plastics are becoming increasingly complex mixtures of plasticisers, antioxidants, fillers, etc. This study was undertaken to see whether a

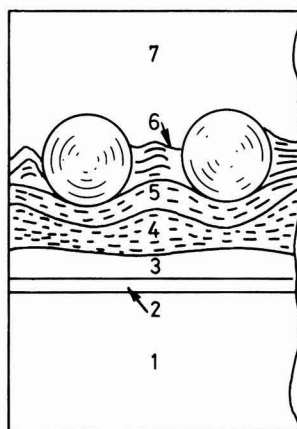


Fig. 2. Cross-sectional representation of a retro-reflective sheeting (1. Paper backing; 2. Release layer; 3. Dry adhesive; 4. Aluminium; 5. Spacer-colour layer; 6. Bead-binder layer; 7. Top coat.)

"fingerprint" of each layer of such a sheeting could be obtained by IRS as a quality control or product uniformity check over a continuing period of time. It is an axiom of infrared spectroscopy that if two samples have identical spectra, the samples are identical. Under these circumstances, it is not necessary to identify every component in each layer. The pinpointing of changes in the spectra could be used to monitor product uniformity.

Procedure

All of the following experiments were conducted with a Perkin-Elmer Model 521 grating infrared spectrophotometer and a P-E standard IRS unit with a KRS-5 prism, one reflection and three reflection types. The operating conditions of the infrared spectrophotometer were quite usual: slit programme-1000, gain-4, attenuation-1100, scan time-16 to 32. In other tests, discussed later, the slits were opened wider and an expanded scale was used.

All of the outer layers of the sheeting (backing paper, dry adhesive, plastic back and top surface) were prepared for analysis simply by cutting the sample to size. Several approaches were used to expose the inner layers: knife peeling of dry rubber adhesive, solvent treatment of pressure sensitive adhesive, sanding paper for plastic layers, and a silicone carbide grinding wheel for the beaded layer.

The procedure for obtaining IRS spectra is well documented. The instruction manual that accompanies the IRS unit is usually the best source of information (in the present case, P-E manual 990-9417). Good sample to crystal contact is very important for a sharp spectrum. This is improved by having a smooth surface; heating the sample and sample holder to some convenient temperature (65° C for retroreflective sheeting); and then allowing the sample 30 to 40 minutes to reach laboratory ambient temperature.

Results

Table 1 lists the types of retro-reflective sheeting materials covered in this report. The samples include flat surfaced sheeting (such as depicted in Fig. 2), exposed lens sheeting,

undipped license plate sheeting, dipping resins, screening inks, and auxiliary samples such as slip-sheets (sheeting cover sheets). Five suppliers, both domestic and foreign, are represented.

Table 1

Samples and the tentative classification of their exposed surface

Brand	Alkyd/melamine	Predominately alkyd	Poly (vinyl) resin
A	First grade, flat surface, sheet*	Regular grade, flat surfaced sheet	Regular grade, license plate sheet, undipped
B	First grade, license plate, dipped resin	Screening ink*; First grade, license plate sheet, undipped; Regular grade, license plate, dipping resin; Open beaded* sheet (exposed lens)	
C	First grade**, flat surfaced, sheet		
D			First grade, flat surfaced, sheet** Open beaded sheet
E		First grade**, flat surfaced sheet*	

* Two or more colours tested for these samples

** Cellulosic slip sheets tested for these samples

Flat surfaced sheeting

Ref. 29

Brand A first grade, flat surfaced sheeting, such as that shown in Fig. 2, is widely used and was closely examined in this study. Note that layers 5, 6, and 7 may be composed of the same or different plastics depending on the application.

The following evaluation was obtained for this layered sample:

Layer 1 is a brown, heavy paper, 40.0 μm thick and weighing 0.0081 g cm^{-2} . It shows absorption peaks typical of cellulosic materials (1021, 665, and 1150 cm^{-1}) (Fig. 3).

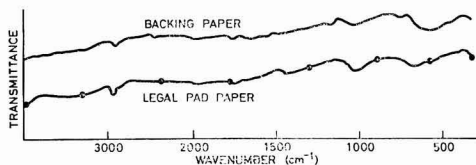


Fig. 3. "Brand" side of backing paper and a paper reference (1 reflection IRE)

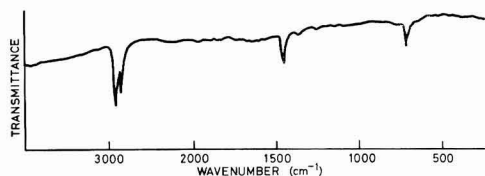


Fig. 4. Release side of backing paper (3 reflection IRE)

Layer 2 is a thin, bluish coating that can be scraped off the brown paper with an Exacto blade. It is probably a low molecular weight polyethylene. Its main absorption peaks are at 2910, 2843, 1458, and a doublet at 718 and 728 cm^{-1} (Fig. 4).

Layer 3 can be stripped from layers 1 and 2 without difficulty and from 4 to 7 with some effort. This dry adhesive layer is a yellowish brown, highly stretchable, but not tightly cured material, about 25 μm thick. It has essentially the same IR spectra on both sides. The numerous absorption peaks (1600, 1450, 1220, 820 and 757 cm^{-1}) shown in Fig. 5 indicate a butyl type rubber. Note the unsaturated bonds ($\text{C}=\text{C}$) at 967 cm^{-1} which are available for heat-pressure curing.

Layer 4 is aluminium deposited as vapour. The presence of some hydrocarbon material is evident from the structural integrity of this layer. This plastic material also shows up in the spectra (Fig. 6) of this thin layer.

In some retro-reflective sheeting, a reflective pigment (such as titanium dioxide) is substituted for the aluminium layer (which is infrared inactive). Inorganic pigments also have some applications in the layers above the aluminium.

Layers 5 and 6 were exposed by buffing of the aluminium layer. It appears from the spectra that these layers contain polyvinyl butyral. Note the peaks at 983, 1090, 1130, and 1261 cm^{-1} (Fig. 6). A similar spectra was obtained on the surface of regular grade license plate sheeting.

Layer 7 is used for protective, colour and optical purposes. This flat-surfaced layer gives an IRS plot that indicates the presence of alkyd (740, 1600 cm^{-1}). Characteristic bands of the triazine ring (1545, 1467, 811 cm^{-1}) are also present. An alkyd/melamine mixture is indicated (Fig. 7). Hensley and McGinty give typical coating formulations of this type where the alkyd/HMMM (hexamethylmelamine) ratio is 80/20.²⁹ The same spectral pattern was also obtained for an extended life, license plate dipping resin manufactured by the same company.

Better results can usually be obtained on clear solutions by the transmission technique (Fig. 9). Both methods used

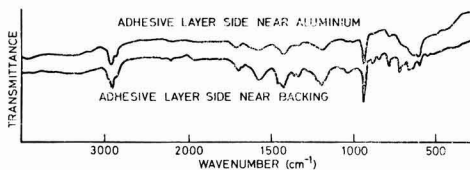


Fig. 5. Backing side and aluminium side of dry rubber layer of adhesive

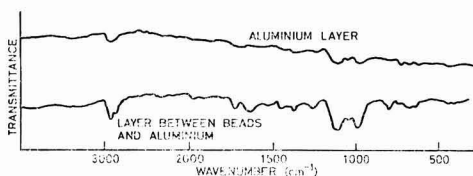


Fig. 6. Aluminium layer and layer between beads and aluminium

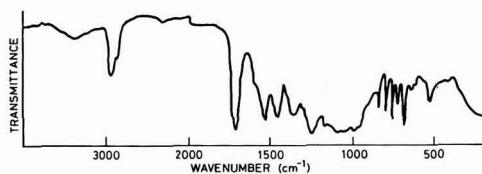


Fig. 7. Top plastic layer (Brand A)

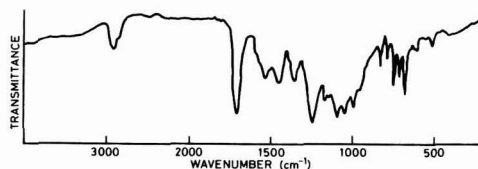


Fig. 8. Top plastic layer (Brand B)

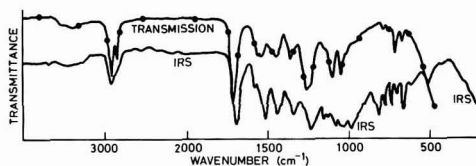


Fig. 9. License plate dipping resin

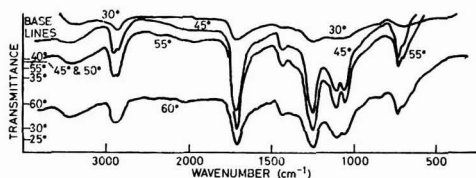


Fig. 10. Effect of incidence angle on absorption peaks

together sometimes provide a more complete analysis. Recent IRS and transmission scans of the adhesive layer of Brands *A* and *B* show nitrile groups in the layer's interior.

The spectra of the top layer of competitive brand *B* is quite similar to sample *A*'s top layer. (Fig. 8).

Many plastic samples are difficult to analyse because copolymers, plasticisers, anti-oxidants, etc., complicate the interpretation of the spectrogram. Samples *C* and *D* are examples of this (see brand listings in Table 1). The top surfaces of both samples are apparently vinyl polymers, but the detailed composition of the polymers has not been worked out.

Table 2

Principal IR bands of outer surface of retro-reflective sheeting

Brand C		Brand D	
Absorption peak cm ⁻¹	Characteristics	Absorption peak cm ⁻¹	Characteristics
2800-3000	M	2800-3000	S
2310	W	1740	M
1720	S	1435	M
1440	M	1230	M
1372	W	968	M
1225	W	680	Sharp
1131	S		S, Broad
1015	W		
841	W		
748	M, Sharp		

S = Strong; M = Medium; W = Weak

License plate sheeting

Refs. 16, 27, 28

The principal IR bands of a regular grade license plate sheeting, undipped surface, are given in Table 3. It appears that this is a polyvinyl butyral with an ester plasticiser. An attempt was made to leech out the plasticiser, but the results were limited. Patent literature indicates that dioctyl phthalate ester is a commonly used plasticiser in this application.²⁷

Table 3

Principal IR bands—regular and first grade license plate sheeting, uncoated

Regular grade		First grade	
Absorption peak cm ⁻¹	Characteristics	Absorption peak cm ⁻¹	Characteristics
3200-3500	M, Broad	3200-3550	M, Broad
2800-3000	M	2800-3000	M
1732	M	1725	S
1645	M	1580-1600	M, Doublet
1377	M, Sharp	1490	W
1097-1130	S	1450	M
975-1050	S	1376	M
808	M, Sharp	1250	S
		1115	S
		1062	S
		815	W
		740	S, Sharp
		703	S, Sharp
		650	M

S = Strong; M = Medium; W = Weak

The absorption bands listed in Table 3 for first grade license plate sheeting are typical of a phthalate alkyd.^{16, 28} There is a very small peak at 815 cm⁻¹, indicating the possibility of some triazine (melamine) copolymer.

If a plastic sample is available as a clear solution, then a better spectrum can usually be obtained by the transmission technique. Note the detail shown in the transmission spectra in Fig. 9 for regular grade license plate dipping resin. This is the same or similar to the plastic used in screening inks.

Table 4

Summary of effects of incidence angle
(typical results on an alkyd sample)

Incidence angle	Relative peak height at 1245 cm ⁻¹ (% T)	Base line at 4000 cm ⁻¹ (% T) with reference beam constant
60°	15	42
55	20	73
50	32	80
45	35	81
40	37	83
35	15	16

Screening inks

The IRS for a clear screening "ink" (toner) is shown in Fig. 10. The spectra of the various coloured inks differ very little from this example. The curves are for the same air dried sample at several incidence angles. Note how the base line and relative peak height vary if the energy to the reference port is not adjusted (Table 4).

Less energy is available for presentation of spectra at the low and high incidence angles. The base line of the curves shown in this report were adjusted to about 85 per cent T at 2.5 microns. The curves in the Figs. were subsequently shifted vertically for the sake of clarity.

For KRS-5 an incidence angle 45 to 50° is usually best, but a higher angle (50 to 55°) sometimes gives less distortion at long wavelengths (above 10 microns). This sample had sufficient absorption to produce a well-defined spectrum. If the effective sampling area is small, then scale expansion is often useful. The sample appears to be an alkyd/melamine mixture.

Adhesive materials

It has already been mentioned that first grade, flat surface sheeting employs a heat-pressure activated rubber adhesive. The adhesive layers of regular and first grade licence plate sheeting gave similar scans with the principal peaks given in Table 5.

Table 5
Principal IR bands of licence plate adhesive (cm⁻¹)

2920	1375
1730	1250
1457	1156
1450	969

The key bands are at 1450, 1375, and 1250 cm⁻¹. The adhesive is tentatively classified as a plasticised polyvinyl.

Slip sheets

In addition to maintaining quality control of the retro-reflective sheeting, it is necessary to check the spacer or slip sheets used to separate sheets. Slip sheets of brands *A*, *B* and *E* were analysed by IRS. The samples were all paper based materials but with a heavy coat of sizing. In the case of brand *A* this sizing shielded out the strong, broad cellulose peak at 980 to 1080 cm⁻¹. Tentatively, it is concluded that brand *A* has an alkyd sizing. Brand *B* appears to be sized with a simple waxy hydrocarbon. Brand *E* appears to be a polyvinyl resin.

Table 7
Paint work sheet and spectral data: yellow traffic paint

Grams	Material	Important infrared bands (cm ⁻¹)
158.4	60% traffic alkyd	1640, 1600, 1275, 1125, 1070, 740
0.8	Butanol	3350, 1459, 1071
0.8	Oxime type ASA	3420, 1165, 939
4.0	24% lead tallate	3050, 1150, 1459, 1399
1.2	6% cobalt naphthenate	1580, 1420
65.6	VM & P naphtha	2850, 2970, 1460, 1380, 770
4.0	Anatase titanium dioxide	660, 540, 360
0.8	Bentone 38	1135 (shoulder), 1091
120.0	Talc (3MgO · 4SiO ₂ · H ₂ O)	1021, 461, 450
60.0	Lithopone (BaSO ₄ · ZnS)	1245, 1125, 1060, 685, 655
80.0	Medium chrome yellow (PbCrO ₄)	840, 400

Table 6

Principal IR bands of slip sheets (cm⁻¹)

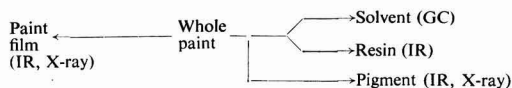
Brand A	Brand B	Brand E
1720	1460	1260
1265	1152	1010
1246	1022	900
1170	680	790
1140	655	515
1020		450
965		
857		
745		

Experimental 2: IRS of paint materials

Refs. 16, 18, 29

Paint pigments and additives

When considering the analysis of a whole paint system, a logical first step is to think of the analysis in terms of three main components: vehicle solids, solvents, and pigments. The last of these can be separated from the liquid materials by centrifugation. The volatile solvent can be removed by evaporation. The remaining resin can be analysed by regular infrared techniques. The centrifuged solid components may be amenable to infrared or X-ray analysis. The paint film (resin plus solids) can sometimes be analysed by infrared directly:



Afremow and Vandenberg have reported the infrared spectra of virtually all inorganic paint pigments and extenders using CsI pellets to reach the 200 cm⁻¹ range.^{16, 29} Inorganic absorptions primarily occur in the lower wavenumber region (1500 to 200 cm⁻¹). Polchlopek and Harris used IRS in whole paint analysis down to the 650 cm⁻¹ range.¹⁸ Since the analysis of paint solids can utilise X-ray, flame emission, and atomic absorption spectroscopy, etc., this section does not consider in detail components where IRS has only a minimal usefulness.

For the purpose of this study, a yellow traffic paint (YPT) was selected. The materials for this paint batch (Table 7) were obtained from regular commercial sources.

Procedure

The IRS spectrum for each component was determined in several ways: individually, with alkyd resin, and as a paint film. The paint components were dispersed on a shaker. Subsequently, the sample was separated into vehicle and solids on a 12 000 rpm Sharples centrifuge. The pigment samples were mixed with methanol to form a paste which was applied to the IRE. The samples of whole paint were applied to a draw-down card, allowed to dry, and cut to fit the IRE.

Results

Refs. 16, 16

Fig. 11 shows a spectrum obtained using an IRS sample and a salt plate film of the alkyd resin used in this study. The IRS plot has lower definition, particularly at the shorter wavelengths. In this connection, it is often useful to run scans at two angles of incidence (for example, 45° and 55°). The alkyd spectrum has been discussed in detail by Afremow, *et al.*¹⁶ The absorption bands of the solvents in YPT are almost hidden by those of the alkyd. Alcohols and naphtha can best be determined by gas chromatography (GC). Mixtures of alkyd with ASA, Bentone or driers in the proportion shown in Table 7 did not yield absorption peaks sufficiently pronounced to be analytically useful. In situations where these substances occur in stronger concentration, these peaks can be useful.

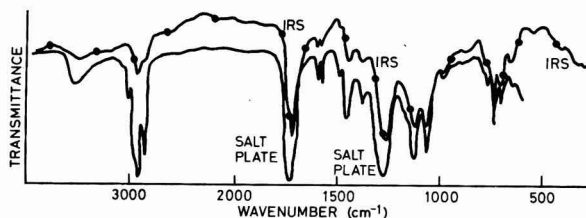


Fig. 11. Comparison of IRS and transmission spectra

The addition of increasing amounts of titanium dioxide to the alkyd affects the spectrum as follows. At low levels of TiO_2 , increased absorption occurs at the longer wavelengths (Fig. 12). As the concentration of TiO_2 increases (about

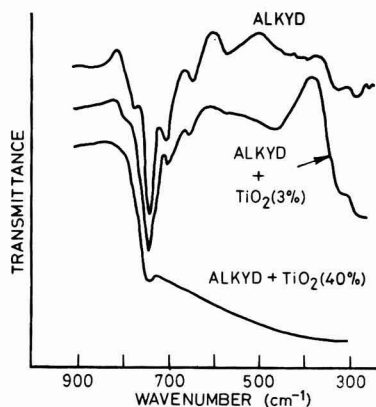


Fig. 12. The effect of anatase titanium dioxide on the alkyd spectrum at long wavelengths

10 per cent), the spectrum past 850 cm^{-1} takes on a broad curved shape, called the titanium dioxide "halo." At even higher concentrations of TiO_2 , the "halo" covers both ends of the alkyd spectrum. Although the TiO_2 absorption peaks are not very sharp for either the anatase (657 cm^{-1}) or rutile (652 cm^{-1}) forms, they are so commonly encountered that it is useful to recognise the manner in which they change the spectra of resin substrates.

Several other inorganic compounds are frequently formulated in sufficient strength to be detectable. In the present case, Lithopone, talc and chrome yellow all show up in the spectrum of the solid components (Fig. 13). The peaks interact in a mixture of this type and prior knowledge of specific peak interaction effects is necessary in order that a proper assignment of the peaks may be made. In addition, scale expansion is useful in this case. The peaks will show up in the whole paint film (Fig. 13), but they may be obscured by the resin. Talc, for example, is relatively easily seen in an alkyd substrate, but simple hydrocarbons are masked by the alkyd spectra.

The IRS technique can usefully be applied also to the analysis of pigments, and so forth, as raw materials if an X-ray spectrometer is not available. Table 7 includes a listing of the important peaks for YPT obtained by the IRS technique. A comprehensive compilation of transmission spectra has been previously cited.¹⁶ Table 8 summarises data on YPT as well as several other common pigments.

Table 8
The use of IRS with paints

Titanium dioxide ²⁹	Causes TiO_2 "halo". Can determine rutile/anatase ratio from 360 and 425 cm^{-1}
Medium chrome yellow	Moderate IR absorber
Talc, clays	Silicates fairly strong absorbers
Lithopone	600 cm^{-1} peak quite sharp
Calcium carbonate	Threshold of detectability fairly high. Good peaks at 7 and 11.5 microns
Toluidine red ¹⁸	Strong spectra of diazo compound; many bands
Hydrated yellow iron oxide	Two band near 11.2 and 12.7 microns
Ultramarine blue	A complex silicate. 10.3 microns
Iron blue (iron ammonium ferricyanide)	C=N bands strong

From these results it can be seen that IRS has a useful place in the analysis of paint solids, particularly dried films.

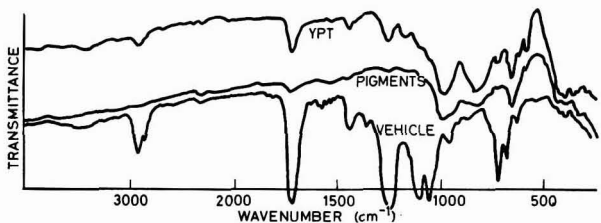


Fig. 13. Spectra of whole paint, centrifuged pigments, and vehicle

Analysis of gel permeation chromatography fractions

Ref. 31

Recent work in the author's laboratory by Rogers³¹ produced a number of gel permeation chromatography (GPC) fractions of alkyd samples. Some of these fractions were analysed by IRS techniques after it was found that in some cases the amount of sample available prevented a regular salt plate analysis.

The GPC samples were carefully evaporated on a KRS-5 three-reflection crystal (using a medicine dropper). Several photo-micrographs were taken and these showed the alkyd formed a mixture of quartz-shaped and needle-shaped crystals rather than an even film. Alkyd samples that met acceptance specifications and samples that did not were compared.

Fig. 14 shows the IRS spectra of an original alkyd and a high molecular fraction of this alkyd. It is outside the scope of this paper to consider the details of combined GPC and IRS studies. However, consider a series of tests where the alkyd "cooks" are stopped at times *t*, 2*t*, and 3*t*. A GPC analysis on these samples will indicate the change in the molecular weight distribution as function of time. Combining this information with the IRS data should show the reaction sequence that produces an alkyd. From this can

be deduced the type of GPC curves that are indicative of a substandard alkyd.

Liquid cell applications

Satisfactory infrared spectra of polyvinyl acetate emulsions can be obtained from the air dried films. However, it is not necessary to first produce a film. A satisfactory scan of pva "whole paint" can be obtained in an IRS liquid cell. As in the case of transmission spectra, the pva bands can be reduced by the addition of water. It is possible to work with an aqueous emulsion in a KRS-5 cell because of the useful infrared "windows" at 2930-1750 and 1580-980 cm^{-1} in the water spectrum.

Discussion

Internal reflection spectroscopy is used by the Texas Highway Department primarily as a quality assurance tool. In the case of retro-reflective sheeting, the various layers can be examined to see if the spectra of a sample matches those of previously accepted lots. It is not necessary to identify each polymer layer. Exact identification of complex polymer systems without some prior knowledge is rather difficult and was not pursued in depth in these studies. Retro-reflective sheeting is well suited to IRS analysis and over one hundred samples of purchased materials have been checked by this procedure.

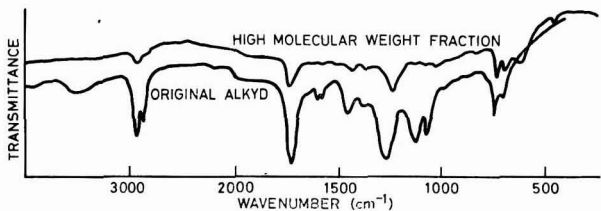


Fig. 14. IRS of original alkyd and high molecular weight GPC fraction

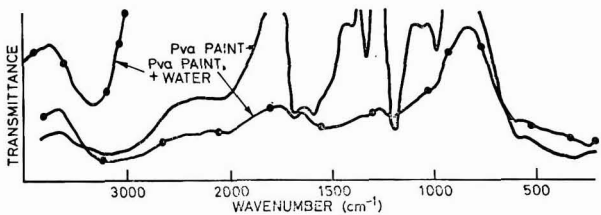


Fig. 15. IRS liquid cell: pva water emulsion paint and pva paint plus water

Paint resins are readily examined by transmission or IRS techniques, but small samples can best be handled by IRS. Whole paints or whole paint films are much more amenable to IRS analysis. The solids (pigments, etc.) can often be identified in the paint film if the concentration is fairly high.

Alkyds normally dry to form a rubbery or amorphous plastic film. Unusual drying has been observed in some samples, including a partial reversion of an alkyd to its components in a loosely capped sample. However, the presence of the quartz and needle-shaped crystals in the evaporated GPC sample is not understood at this time, but may be associated with the narrow range of molecular weights.

As in most test laboratories, the author and his colleagues are primarily interested in research projects because of some immediate problem. Studies sufficiently detailed to justify Journal reports are the exception. However, to indicate some further applications of IRS in this laboratory, several shorter projects can be mentioned:

- (a) Surface analysis of outdoor plywood for oily blemishes associated with poor adhesive qualities.
- (b) Chlorinated rubber analysis used to identify the manufacturer.
- (c) Peeled paint samples were examined before and after a solvent wipe to determine component migration to the bond interface.
- (d) Polymer identification to determine manufacture of a pavement striping tape taken from service.
- (e) Associating the viscosity rating of asphalts with their infrared spectra.
- (f) Identification of a metallo-organic rust inhibitor (diphenylguanidine—calcium chromate).

In conclusion, this report has shown that the principal advantages of IRS over other modes of infrared analysis lie in the ease of sample preparation and the surface nature of the analysis. Opaque (relatively thick) films and thin films with opaque backing can be examined. These advantages are ones that often apply to paint and film analysis.

[Received 2 March 1974

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New developments in wallcoverings*

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Summary

The printing processes used in wallpaper manufacture are described, and their individual characteristics and probable future development considered. Methods of obtaining embossed and other textured surfaces are outlined.

The various forms of backing or supporting layers of wallpaper are

described, particularly in relation to removal from the wall for redecoration.

Possible future methods both for the application and removal of wallpapers are discussed.

Keywords

Miscellaneous
wallcovering

Nouveaux développements dans le domaine de papiers peints et des matières connexes

Résumé

On décrit les procédés utilisés pour imprimer les papiers peints, et l'on considère leurs caractéristiques particulières ainsi que leur développement éventuel à l'avenir. On mentionne brièvement les méthodes de production des surfaces gaufrées ou celles d'autres textures.

On décrit les divers types des couches inférieures, qui donnent

solidité aux papiers peints, au point de vue de leur influence sur la facilité d'enlèvement du papier à partir du parois avant du retapissage.

On discute certaines méthodes éventuelles à l'avenir pour effectuer la pose et l'enlèvement des papiers peints.

Neuentwicklungen in Wandbekleidungen

Zusammenfassung

Die bei der Tapetenfabrikation benutzten Druckverfahren werden beschrieben, ihre individuellen Characteristica und ihre voraussichtliche, künftige Entwicklung betrachtet. Methoden zur Erzeugung geprägter und anderer texturierter Oberflächen werden skizziert.

Beschrieben werden auch die verschiedenen Arten von Unterlagen und Rückseitenbeschichtungen für Tapeten, insbesondere mit Bezug auf leichte Entfernbarkeit von der Wand zwecks Erneuerung.

Mögliche künftige Methoden, sowohl für die Anbringung als auch Entfernung von Tapeten werden besprochen.

Introduction

In any particular field of human activity, some change or development is always occurring, sometimes almost unnoticed by all but the most observant. In the field of wallcoverings, improvements are continually occurring to washable coatings, duplex wallpapers, and the surface printing techniques, to name but a few examples. One might regard these as small steps forward in the total wallcoverings scene.

However, it is the purpose of this paper to outline those developments in wallcoverings that in the author's opinion are likely to affect, in a significant manner, the future of wallcoverings. There is no doubt that some people will disagree with this assessment of the likely significance of some new developments but it would be surprising if it were otherwise since it must be a matter of judgement as to what changes occurring now will prove to have significant effects on the future of wallcoverings. As an illustration of this, there is no doubt that various people assessed the potential of moulded cellulose paintable bases differently when they were first introduced to the wallcoverings market a long time ago. Similarly, there were very few people around ten to twelve years ago, who were prepared to say that the intro-

duction of plasticised pvc paper backed wallcoverings would prove to be a move of great significance for the future of wallcoverings. It is convenient to consider new developments in the light of whether they concern the front or "decorative" surface, the back or "support" surface or the wall application and removal methods.

The front or decorative surface

More sophisticated printing and embossing techniques

There is no doubt that significant moves away from the traditional surface printing and cold embossing techniques are under way and that more and more wallcovering material is being produced by the more sophisticated gravure, flexographic and other processing techniques.

Gravure printing process

This process is based on the chemical or electronic etching of images in the form of concave cells below the face surface of copper coated printing cylinders. Low viscosity inks of low solids content are necessary to facilitate ink flow into

*Presented at the Manchester Section Symposium held at the University of Manchester Institute of Science and Technology on 18 September 1973.

the image areas. The excess ink not held in the engraved cells is removed from the roller by means of a flexible steel doctor blade (Fig. 1).

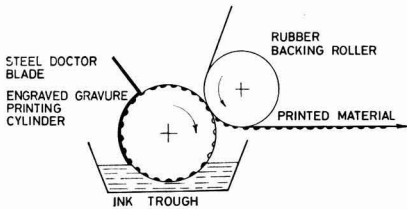


Fig. 1. The gravure process

Increasing quantities of wallpaper are being printed by gravure and the benefits of this process are being obtained, particularly in the use of printing trichromatic effects and also in the reproduction of many more delicate tone effects, particularly on solid vinyl surfaces.

Flexographic printing process

The flexographic process consists essentially of ink transfer rollers which are capable of transferring a thin film of low viscosity ink, and a raised rubber stereo roller which forms the image to be printed. Ink is transferred on to the tops of the stereo roller and then on to the wallcovering to be printed (Fig. 2).

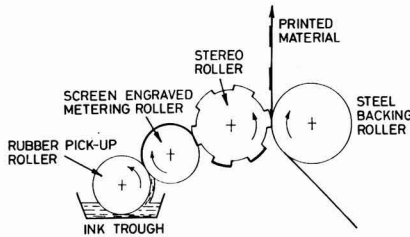


Fig. 2. The flexographic process

More and more use is being made of this process in wallpaper and plastic foam printing. Great strides have been made and further refinement is likely in the quality of tone and fine line printing that can be produced by this process. Whilst not generally recognised as capable of producing print quality fully equal to that of the gravure process, the flexographic process finds increasing justification because of the reduced cost of the basic printing machines and print cylinders. It has not so far been possible to use this process for printing solid vinyl wallcoverings, largely because of the swelling of the rubber stereotypes when in contact with the active ketone and hydrocarbon solvents required for printing vinyls satisfactorily. It is quite likely, however, that this development will occur in the foreseeable future.

Rotary screen process

This process is an adaptation of the long-established flatbed screen process and differs significantly from other printing processes by having the printing ink reservoir held inside the rotating screen cylinder. Ink is forced through holes in the metal printing screen on to the material to be printed, to form the print areas (Fig. 3).

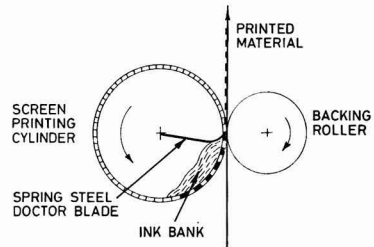


Fig. 3. The rotary screen process

Although this process has been in use for a considerable time for printing textiles it has only recently been successfully adapted to make it suitable for printing on to non-absorbent materials, and consequently the first wallcoverings printed by rotary screen are only now making their appearance on the market. This is likely to be a move of very considerable significance for the future of wallcoverings and the process will be more and more used in the future for its advantages of higher print density, thicker ink films and cheaper print cylinders.

Valley printing

This is, of course, a print-embossing process that is well known and used in the production of wallpaper. The principles of operation can be seen in Fig. 4.

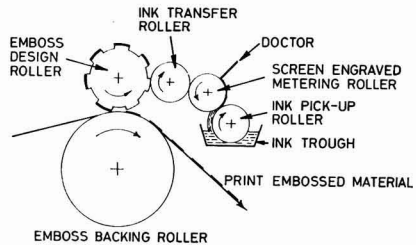


Fig. 4. The valley printing process

The valley printing process has now been developed for use with solvent based inks in the hot print-embossing of vinyls and some effects of this type have recently been marketed. Further development in this field is likely to result in the production of multicolour effects of this type.

Miscellaneous processes

In the more distant future it is likely that significant development in wallcoverings will occur in the printing of true three-dimensional effects and alongside developments in printing processes it may be that the use of radiation cured ink systems will become of importance in the production of wallcoverings.

Expanded vinyls

Expanded vinyls can be obtained by the use of compressed air to form an expanded plastisol foam which can be stabilised and then coated on to a suitable substrate. It is, however, more usual to include chemical agents in the pvc coating which decompose under the action of heat and activating agents to liberate gases that foam (or expand) the

coating to several times its original thickness. There are three main aspects to this technique as shown below.

All-over expansion

This finds application in the production of deeper all-over embossed effects with more detailed surface texture, where it helps to reduce the high coating weights that would otherwise be necessary. Effects of this kind have been observed on the wallcoverings markets on both paper and cloth backings. Print and emboss are not in register, as can be seen from Fig. 5.

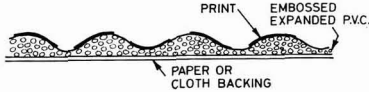


Fig. 5. All over expansion

Chemical embossing

The use of expandable vinyl coatings has now been further developed to produce fully registered print and emboss effects by various methods. Chemical embossing is one of these, and this technique can be further sub-divided according to whether the expansion is obtained by the use of activators or inhibitors in the printing inks.

In the case of the "Activation process", the activators are removed from the coating and included in the printing inks. The activators migrate into the coating and on carefully controlled heating, expansion of the coating occurs where the print has been applied (Fig. 6).

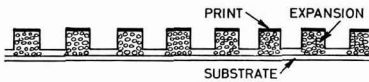


Fig. 6. The activation process

The "Inhibition process" is similar, but in this case both blowing agent and activator are included in the coating and expansion in printed areas is prevented by the use of chemical agents in the printing inks that inhibit the expansion effect (Fig. 7).

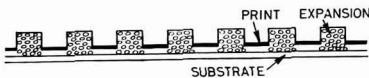


Fig. 7. The inhibition process

Both processes are capable of producing multicolour print effects in perfect register with embosses, and since the effect depends on the presence in the printing inks of either activators or inhibitors, it is evident that different levels of print raise can be obtained by including or omitting these agents, as required.

Rotary screen expanded

One of the particular advantages of the rotary screen process mentioned earlier is the ability to handle high viscosity printing inks. It is possible to use pvc plastisols containing blowing agents as the printing inks, and in this way obtain thicker ink layers that can be expanded by foaming to yield fully registered print and emboss effects (Fig. 8).

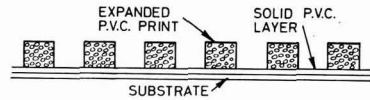


Fig. 8. Rotary screen expansion

Metallic foil effects

Over the last year or two, a considerable number of metallic foil effects has been introduced to the wallcoverings market. These are of two main types:

- Aluminium sheet laminated to paper (Fig. 9).
- Metallised plastic film laminated to paper (Fig. 10).

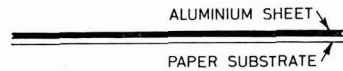


Fig. 9. Aluminium sheet/paper laminate

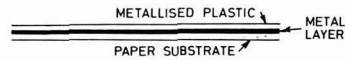


Fig. 10. Metallised plastic film/paper laminate

Being continuous coatings, the metallic layers can conduct an electrical charge under certain specific circumstances and discussions have taken place as to the risk attached to the use of these products. It is agreed, however, that the risk is small, particularly with the metallised plastic film type, but it may be that further development of this type of product will be limited because of its rather special and limited appeal.

Simulated or laminated textiles

Significant development is currently occurring in the use of textiles or textile simulations as the decorative surface for wallcoverings. There are several different types, as described below.

Woven or non-woven sheet materials

The development of woven textile wallcoverings is exemplified by the increasing use being made of materials such as hessian as the decorative facing for wallcoverings. The use of non-woven fabrics laminated to wallpaper base and suitably decorated, has also been observed in some recent wallcoverings. One factor which may inhibit development in this area concerns the difficulties associated with the lamination of light, dimensionally unstable webs for wallcoverings use. This does, however, present an opportunity for machinery manufacturers.

Laminated thread products

This type of product is characterised by having cloth or other fibres laminated to a supporting substrate. Since the fibres are essentially continuous threads, lamination is achieved by conventional creel feed to the laminating position (Fig. 11). Since many different types and qualities of threads can be used, either as single or mixed species, many different and attractive design effects can be obtained.

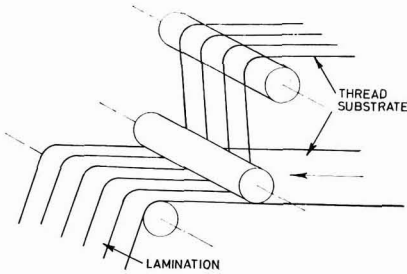


Fig. 11. Thread lamination

Flocked wallcoverings

Conventional wallpaper flocked effects have been on the market for some considerable time, but the flocking process was later developed for use with solid vinyl effects and a considerable number of flocked vinyls are now available. Most are single colour flock effects, but a few do show multicolour effects that are normally obtained either by the use of different colours of adhesive plus single colour flock, or by true two-colour flock deposition.

The flock process consists of the deposition, usually in an electrostatic field, of staple fibres of various types, to a substrate that has been adhesive printed in the required design (Fig. 12).

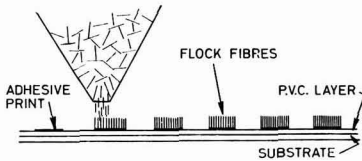


Fig. 12. The flocking process

The flock fibres stand on end and yield raised-up printed effects. Currently, there are two main types being sold. One type consists of short rayon fibres which are very well compacted and regular and which present almost a felt-like feel and appearance. The second type consists of longer nylon fibres and is less regular in appearance, but shows brighter and more attractive effects. Both types have been available for some time but currently there appears to be increasing interest in developing further the longer nylon fibre effects as single and multicolour flocked vinyls.

Paintable vinyl bases

Two different types of product have been put on the market recently. Both have certain advantages over the heavily embossed wet moulded paper effects currently monopolising a market which demands paintable wallcoverings.

1. A highly filled plasticised pvc solid coating, which is deeply embossed and is specially formulated to overcome plasticiser migration into paint films. The product has also been specially formulated to improve the paintability of the vinyl surface with the wide range of paints available. The special advantages of this type are its emboss stability, hard wearing character and easier removal than the conventional paper products.

2. A product made from foamed pvc and consequently not so hard wearing as the one mentioned above, but it too demonstrates good emboss stability and can be easily removed from a wall surface when required.

The backing or support surface

The normal backing material used in this country is, of course, a cheap paper base, the major constituent of which is mechanical wood pulp. This is adequate for many purposes, but does pose problems because of its low laminar strength. For example, it is not strong enough to dry strip from a wall and it has to be wetted and scraped when removal is necessary; if the coating happens to be washable this removal process is an extremely difficult operation. In the case of solid vinyl wallcoverings, if the pvc coating is broken then paper delamination can occur rather easily and result in severe damage. These deficiencies have led to a search for stronger backings and it is possible that further development will occur in this direction.

Strong papers

Strong papers are already being extensively used in North America with non-solid vinyl products. They usually obtain their superior strength properties from latex impregnation or they contain a proportion of strong synthetic fibres. The products made in this way are usually fully dry strippable from a wall, but the backings used are very expensive.

Plastic papers

Plastic papers are also being increasingly considered as backings for wallcoverings. An example of this is the use of "Tyvek", a spunbonded polyethylene base which, although extremely expensive, is being used as a wallcovering backing in the United States.

Synthetic wood pulp

Significant developments in the ways of producing synthetic paper-like bases are currently taking place. The most interesting are those that utilise conventional paper-making machinery for forming webs. It is well known that Crown Zellerbach are actively developing such a process, which converts monomer directly to fibre slurry. The Solvay process is similar but utilises high density polyethylene fibres for wet pulp processing.

Developments of this kind are probably of significance for the future of wallcoverings, but synthetic wood pulp is much more expensive at present than conventional paper pulps and is likely to remain so for some considerable time.

Foamed plastic films

Foamed plastic films are currently being developed as wallcovering bases. An example of these is the polyethylene film made by ICI that has recently been converted into a wallcovering and is being sold in the south of England. It is very easy to handle, being low in weight, has an attractive feel and is easily applied to and fully stripped from a wall when required. A paste-the-wall technique is recommended for application and this has some obvious advantages over traditional product pasting methods. It fulfils, therefore, many of the modern requirements of convenience in wallcoverings and must surely be one of the most significant of the new developments in this field.

Wall application methods

Very significant moves away from the traditional wallpaper pasting techniques are developing. The increasing use of ready-pasted products is a good indication of the desire for more convenient methods of applying wallcoverings. The paste-the-wall technique already mentioned is another move in the direction of convenience and since this technique is more useful with non-paper backed materials, this may well influence the development of products that are easy to apply by this method.

It may be that other methods of application, such as adhesive encapsulation, magnetic adhesion, improved contact adhesives and other dry-on/dry-off techniques, will become increasingly important in the future.

Wall panels

There are currently many different types of wall tile or panel available, but they tend to be used almost exclusively for certain areas only. Because of the possibilities they offer for convenience, it may be that wall panels warrant more serious consideration for general use. It is evidently easier to apply comparatively small squares, possibly with a dry-on/dry-off adhesive, for easy application and removal than it is to apply long lengths of wallcoverings either by separate pasting or ready pasting. Panels of this type would also be easier to replace if badly damaged or soiled. This is possibly the wall-covering of the future.

Wall removal methods

Removal of old wallcoverings prior to redecoration has for a long time been a messy and time-consuming operation involving wetting the wallcovering and scraping the material after soaking. In particular, if the wallcovering happened to be a washable wallpaper where it was difficult to soak the paper backing, the job became not only lengthy but very difficult.

Partial dry strippability

Some improvement in strippability occurred with the advent of solid vinyls because the top plastic coating was now comparatively thick and strong enough to hold together and cause backing paper delamination to occur when the sheet was pulled away from the wall. If the remaining paper is well stuck to the wall, this can be left on and redecoration started immediately. If not well stuck, removal is easily accomplished by normal soaking and scraping, but in any case this is a significant improvement over the poor strippability for so long associated with washable wallpapers.

Full dry strippability

Various possibilities exist for achieving full dry strippability:

Strong backings. The use of a strong support such as a woven cloth or latex-impregnated or fibre-reinforced paper is already in use for some products. Because of the tough nature and cost of this type of material the wallcoverings tend to be used for areas of high wear, such as public buildings, and so far have held little or no interest for normal

household use. However, it may be that products of this kind will find more general use because of the desire for more durable wallcoverings and because it may prove possible by the use of such a backing to reduce the amount of oil-based raw materials required by reducing the weight of the top or decorative coating.

Back coating. Many attempts have been made to use resin coatings on the back of wallcoverings to facilitate dry stripping by reducing the adhesion between the wall and wallcovering. So far, only limited success has been achieved and no product of this type has yet appeared on the market.

A more successful back coating utilises a highly filled coating which easily ruptures within the coating and this provides a zone of low cohesive strength between the wall and wallcovering. Products of this type are on the market and this development is of special importance in connection with washable wallpapers which, as already mentioned, are extremely difficult to remove without such treatment.

Conclusion

In conclusion, Table 1 summarises the developments that, in the author's opinion, are likely to have significant effects on the future of wallcoverings. The individual items have been rated in degrees of significance ranging from one star (low significance) to four stars (high significance).

Table 1
Significance of new developments

Development	Rating
Printing and embossing techniques	**
Expanded vinyls	**
Metallic effects	*
Textile surfaces	**
Paintable vinyl bases	***
Stronger papers	*
Plastic papers	*
Synthetic wood pulp	*
Foamed plastics	****
Ready pasting	***
Paste-the-wall	***
Encapsulation of adhesives	*
Magnetic adhesion	*
Improved contact adhesives	*
Dry-on/dry-off techniques	*
Wall panels	**
Partial dry strippability	*
Full dry strippability	***

From this Table, it is apparent that foamed plastics, ready pasting, paste-the-wall, full strippability and vinyl paintable bases are likely to be of great importance for wallcoverings in the future. These are followed closely by printing and embossing techniques, expanded vinyls, textile wallcoverings and wall panels, with the remaining developments following behind.

[Received 2 February 1974]

Errata

The athermal theory of vehicle adsorption and the structure of pigmented paints

The following corrections should be noted to the paper "The athermal theory of vehicle adsorption and the structure of pigmented paints" by H. Schütte and K. Řeháček, as published in the July 1974 issue:

Page 217, Equation 1: the two terms in brackets raised to the power m_2 should be raised to the power m^2 .

Page 217, column 1, last paragraph: the line "Essentially, the equation contains the partition functions" should read

"Essentially, K contains the partition functions".

Page 218, Fig. 8: for " $m_{20} \log K - 75$ " read " $m = 20$ and $\log K = -75$."

Page 219, column 1, item 5: the sentence should read "The large-size globule, occupying a part of the surface area of the pigment hundreds of times that of a solvent molecule, accounts for the poor desorbability of the vehicles."

Page 224: references 9 and 10, for "Rehicek, K." read "Řeháček, K."

Next month's issue

The Honorary Editor has accepted the following papers for publication, and these are expected to appear in the October issue:

Atmospheric pollution: will the paint user overcome this problem? *Including:*

The problem in context by D. J. T. Howe; **The effects of powder coating** by H. Schouten and N. Kloos; **Aqueous coatings** by R. N. Washburn and J. N. Sparrow; **The role of non-aqueous dispersions** by N. J. Waghorn; **The view of the user** by A. J. Ellis

The mechanism of the formation of crystalline bloom on paint films by G. V. G. Hill (*Short communication*)

Short Communication

Zeta potential—organic pigments

By W. Carr and J. A. Long

CIBA GEIGY (UK) Limited, Pigments Division, Wythenshawe, Manchester M23 9ND

Keywords

Processes and methods primarily associated with storage, protection or preservation

pigment dispersion
settling

Miscellaneous

zeta potential

Introduction

It is commonly accepted that there are two possible mechanisms for achieving dispersion stability of pigments in both aqueous and non-aqueous systems, namely electrostatic repulsion and steric hindrance.

Many people have felt that, in non-aqueous systems, it was unlikely that electrostatic repulsion would be a significant factor in maintaining dispersion stability because of the poor ionising properties of the media relative to water.

We recently carried out some experiments to check this view and the results may be of interest to readers. The aim of the experiments was to investigate the effect of the electrical properties of pigment surfaces on the rate of pigment dispersion and dispersion stability in non-aqueous systems pigmented with organic pigments. The particular electrical property measured was the electrophoretic mobility, which can be related to zeta-potential by known equations or tabulations.

Materials

Commercial samples of 26 pigments were used without further treatment or modification. These included:

- Phthalocyanine blues (α , β and metal-free brands)
- Calcium 4B and 2B toners
- Diarylide yellows (*m*-xylylide, anilide, and *o*-toluidide)

The pigments were dispersed in four alcohols, methanol, ethanol, propanol and butanol, by ultrasonic irradiation. It was considered that if these four systems did not show electrical effects to have a major influence, then the likelihood that less polar systems would show up electrical effects would be small. No resin or polymer was added to the systems.

Techniques

All the particle mobilities were measured on a Rank Brothers electrophoresis apparatus, using the flat cell configuration.

Rates of dispersion were measured by following the increase in optical density of the dispersion with time under a constant energy input which was provided by ultrasonic irradiation. A typical curve from these experiments is shown in Fig. 1. The slope of the initial part is higher or lower

depending on the ease of dispersion and the final value of the optical density depends on the final level of dispersion achieved. All the optical density curves measured would change with the wavelength of the incident light and for this reason the rates of dispersion were expressed as times taken to reach a final optical density.

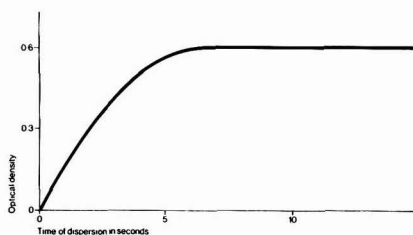


Fig. 1. Increase in optical density during dispersion

Dispersion stability experiments were carried out using gravitational hindered sedimentation. The measured parameters were the rate of fall of the pigment/solvent boundary and the final sediment volume. The pigmentation level was 2.5 per cent w/v. In concentrations of this order, pigment/solvent boundaries develop due to hindered settling where small particles are dragged down by bigger particles in a crowding effect. The rate of fall of the boundary and the sediment volume can be inserted into a modified Stokes equation to give a settling radius which provides information on the stability of dispersions on a relative basis.

Results

1. In the four solvent systems examined, all the 26 pigments have a measurable zeta-potential.
2. The zeta-potential value has no positive influence on the rate of pigment dispersion under the experimental conditions. The lack of correlation between the two parameters is illustrated in Fig. 2 for ethanol systems.
3. No general correlation was found to exist between zeta-potential value and relative settling radius. This is illustrated in Fig. 3 for ethanol systems. The relative settling radius is a guide to the stability to flocculation of the pigments. Systems are considered stable if the settling radius is ≤ 20 microns.

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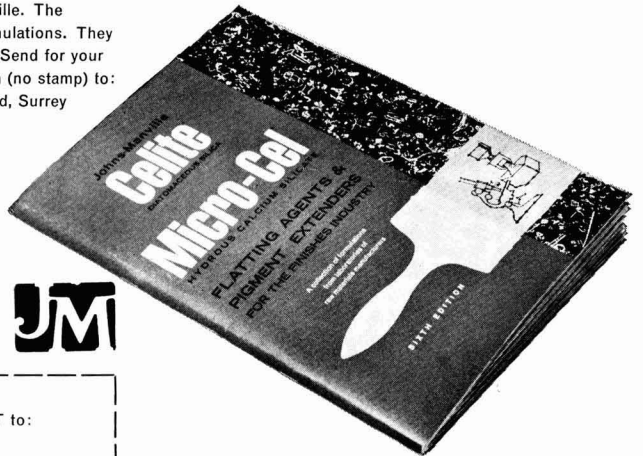
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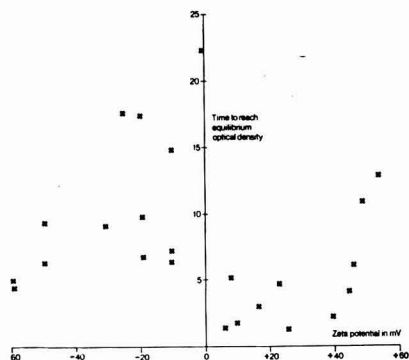


Fig. 2. Rate of dispersion versus zeta potential, in ethanol

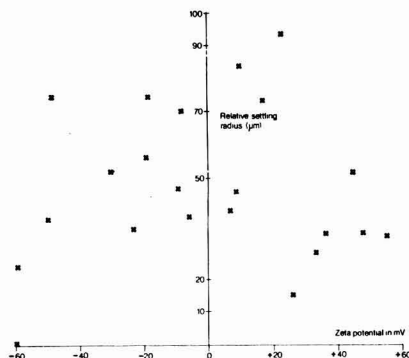


Fig. 3. Relative settling radius versus zeta potential, in ethanol

Discussion

The lack of correlation shown in Figs. 2 and 3 for ethanol systems is also found in the systems based on the other three alcohols. It confirms the view that in the properties of pigmented non-aqueous dispersions, surface electrical properties play only a minor role.

The following is put forward as a possible reason to explain the lack of importance of zeta potential.

By comparison with aqueous systems, the maxima in the potential energy/distance curves are farther away from the surfaces in non-aqueous systems. In any dispersion step, the aggregates of basic pigment particles must be broken down and the resulting fragments or particles separated by a surface to surface distance greater than that of the potential energy maximum from the surface. If this separation is not achieved, the forces operating are still attractive, leading to re-aggregation.

In the cases we examined, it is probable or possible that the necessary degree of separation was not obtained under the dispersing conditions used.

In the stability experiments, the particle number was high—between 10^{10} and 10^{13} per ml. This high particle concentration means that particle-particle distances are small in the dispersions. This distance becomes important when the stabilising mechanism is essentially long range, as it is here. Several authors, notably Professors Lyklema and Parfitt, have postulated that a significant reduction in the energy barriers to coagulation takes place if the particle separation is of the same order as the distances of the maxima from the surface. When taken in conjunction with the low forces of repulsion in non-aqueous media, this view would mean that at high particle concentrations, the efficiency of any long range stabilising mechanism is reduced.

Our general conclusion is that in non-aqueous dispersions of organic pigments, stability is best promoted by short range mechanisms and the example of this is steric stabilisation.

[Received 23 May 1974]

Reviews

Reactivity, mechanism and structure in polymer chemistry

By **A. D. Jenkins and A. Ledwith (Editors)**

John Wiley & Sons, London, New York, Sydney and Toronto; 1974. Pp. xvii + 613. Price £13.00

During the last few years there have been too many books on polymer science having only the old things to say with no new way of saying them, and a kindly veil is drawn over the occasional amateurish production which it has been an embarrassment to review. It is thus a pleasure and a privilege to report upon a truly professional job by two well-known polymer scientists who have here joined forces to edit a superb volume by 18 contributors each of whom writes on a topic in which he has earned international repute. These topics are treated independently but they are so skilfully assembled that the result, though not a textbook, looks more like one than a collection of review articles, and provides an in-depth treatment of the subject which omits little of current significance.

A general introduction by Billingham and Ledwith sets the scene and is followed by four chapters devoted to free radical polymerisation: Tedder on reactivity in general, Bamford on the transition metal initiators which he himself pioneered, Jenkins on propagation and transfer, and North on termination. The next two chapters, Weale on the influence of pressure and Cooper on emulsion polymerisation, form a bridge to the block of five dealing with ionic processes. Baker writes briefly on carbonium ions and is followed by a masterly exposition of reactivity and mechanism in cationic polymerisation by Ledwith and Sherrington who, evidently determined to achieve balance (which they do), nevertheless leave the impression that less than enough is said of the Liverpool work on living cations.

In reviewing a work of this quality it is easy to run out of superlatives. Another is needed for Dart's account of carbanions which, in the reviewer's opinion, shares with its successor the honours for comprehensiveness. In the latter Ledwith & Sherrington return with a discussion of polymerisation by organometallic complexes which, unlike many, is by no means restricted to Ziegler-Natta types. This is nicely complemented by Witt's account of chromium oxide catalysts.

The final three chapters show a distinct swing from predominantly organic towards more physical chemistry. De Schryver and Smets discuss photochemical processes and are perhaps a little modest in the limited treatment accorded the work of the Louvain school. Configuration and conformation are dealt with by Luisi and Ciardelli who come close to the frontiers of present knowledge and make a timely distinction between these two oft-confused terms, but the reviewer feels that 43 pages were not enough for adequate coverage of so broad a subject. The work concludes with an account by Ivin of the field he long ago made his own, the thermodynamics of addition polymerisation. There is nothing on polycondensation.

The work is strictly academic in style and content. It assumes a good basic knowledge of polymer chemistry and physical organic chemistry, but the presentation throughout is so impeccable that it will be assimilable by any graduate who has mastered a sound introductory text such as that of Billmeyer. The cover price of £13.00 seems expensive, but by today's standards the book is excellent value for money and the publishers must share in the credit for a beautiful production.

A. R. H. TAWN

A dictionary of spectroscopy

By **R. C. Denney**

Macmillan, Perkin-Elmer, London, England, 1973. Pp. xv + 161. Price £2.95

This is a handbook for the student or those with occasional contact with either the literature or the actuality of spectroscopic analysis. The aim, and in the main it is fulfilled, is to give short, lucid explanations of all the specialised terms one is likely to meet in this expanding branch of physics and chemistry. A physicist may cavil at one or two of the definitions, for example achromatic and anisotropy, which are very restricted for such widely used terms, but on the whole Dr Denney has been most successful in compressing a wealth of information into a small space. There are abundant references, happily many to original historic papers, such as those of Bouguer and Lambert in 1729 and 1760, which should set some students on a rewarding trail.

T. R. BULLETT

Section Proceedings

London

Southern Branch

Student Symposium

The first symposium which the Branch has held at the University of Surrey took place on Wednesday 8 May 1974 under the chairmanship of Mr J. Tooke Kirby. There were 54 Members, Polytechnic and London School of Printing students present in addition to 20 School of Chemistry students from the University.

Dr A. C. Healey gave the main paper, which was preceded by a tour of the University laboratories and buildings. He spoke on the subject of security printing and illustrated by the aid of slides the complex methods and precautions which

were adopted by companies engaged in this branch of the printing industry. A lively question period showed how much interest had been aroused.

A film entitled "The offset story" was then shown and Dr A. Leach spoke in detail of the opportunities which were available to graduates and others in the printing ink industry. This was adequately presented against a background of examples of the industry's end products, which showed what was currently being done in the trade. The activities of the Association were also discussed, with particular reference to the advantages of student membership.

A vote of thanks to Dr J. A. B. Genge who arranged the symposium was proposed by Mr R. Coates (retiring Branch Chairman), who mentioned that unfortunately this was the last of the Branch activities.

B.A.C.

Information Received

Mobay Chemical Corporation

Baychem Corporation, New York, which combined the various activities of Bayer AG in the USA, has changed its name to Mobay Chemical Corporation with head office in Pittsburg, Pennsylvania. The change of name and transfer to new headquarters was accompanied by some changes in personnel. Baychem, with about 4,000 employees, had a turnover of US \$330 million in 1973.

SAC centenary

The Society for Analytical Chemistry celebrates the centenary of its founding this year with an exhibition at the Science Museum, London, tracing the development of analytical chemistry from early times. The exhibition is open to the public from 10.00 a.m. to 6.00 p.m. Monday to Saturday and 2.30 to 6.00 p.m. on Sundays until about the end of this year.

Salt spray and SO₂ test cabinets

John Godrich of Ludlow, Shropshire, has been appointed agent for Gebr Liebsch of West Germany to market its range of salt spray and sulfur dioxide test cabinets in the UK. These machines are designed to carry out tests to British, American and Continental standards and are also designed for the Corrodokote test procedure and for Kesternich tests.

Tenneco Organics

Earlier this year Butler Chemicals Limited and Compass Chemicals ceased trading, and the combined operations have become Tenneco Organics Limited, a component of Tenneco Chemicals Europe. The activities of Tenneco Organics are organised in three marketing groups: Compass Industrial Products; Oil Products; and Speciality Chemicals. The main office and central facilities remain at the Rockingham Works, Avonmouth, Bristol.

Drums pass "Dangerous Goods" tests

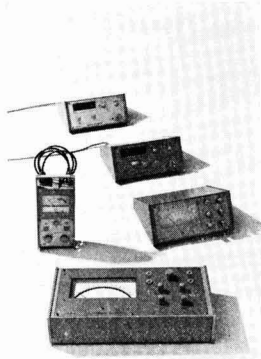
Bowater Industrial Packaging Limited has widened the market for its 210-litre (45 gallons) Bowater Mauser tight head plastic drum. The drum has passed successfully the performance tests recommended by the United Nations Group of Rapporteurs and it may now be considered suitable for the carriage of goods classified by the group as "medium hazard."

New products

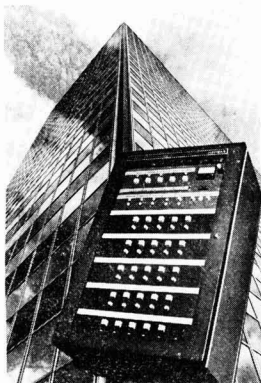
New non-dispersive X-ray analysers

Applied Research Laboratories Limited of Luton has introduced a new single element non-dispersive X-ray analyser, the N940, to complement the N900 multi-element instrument.

The N940 is intended primarily for applications where only one element has to be analysed, but in certain cases, it can analyse up to four elements, for example, sulfur in oil, silicon in polyethylene sheet and both chlorine and titanium in polyvinyl chloride.



The Knick range of laboratory and portable pH meters are now available in the United Kingdom from FT Scientific Instruments Ltd. The range covers simple, low-cost, battery operated units which are ideal for on-site testing, through to the very sophisticated digital pH meters for the most exacting laboratory work. Many models within the range have facilities for use with automatic titration equipment and for connection to a recorder. All instruments are covered by a 3-year guarantee against technical faults.



Siemens has developed a SRS 60 Fire Alarm Central Station connecting a maximum of 60 alarm lines for the quick and precise detection of fire sources. The station is suitable, in particular, for medium-size systems required in, for example, department stores, administration buildings, industrial plants etc.

New curing agent from Anchor

Anchor Chemical Company has developed a curing agent specifically for use with liquid epoxy resins in the formulation of water-dispersible coatings. Known as "Aquamine 100", this new curing agent is a modified liquid reactive polyamide containing no solvents or other additives, and so it is virtually odour-free. Aquamine 100 is a free-flowing, amber-coloured liquid which will provide a water-dispersible coating which is dry in about six hours.

NMR accessory from Perkin Elmer

Perkin-Elmer has produced a frequency counter accessory for use in conjunction with its Model R32 NMR spectrometer. This accessory will facilitate very accurate measurement of line position in the NMR spectrum and will also allow increased convenience for many applications.

Literature

Handling polymer emulsions in drums

Vinyl Products Limited, Carshalton, Surrey, has published a new leaflet, Technical Service Report G3, dealing with the main points to be considered when handling polymer emulsions in drums, and believes this is the first time that information specific to drummed supplies has been compiled.

Apart from dealing with precautions needed during drum handling and the storage of emulsions, the leaflet considers the need for filtration of emulsions before use and lists the most suitable materials for equipment in contact with emulsions. Based on practical tests, there is also a series of recommended pneumatic, electric and hand-operated pumps whose construction and method of operating are suited to withdrawing emulsions from drums.

Process industries investment forecasts

The ninth report of the Process Plant Working Party on "Process industries investments forecasts" was published recently by the National Economic Development Office, and copies are available from Nedly Books, National Economic Development Office, Millbank Tower, Millbank, London SW1P 4QX.

Textbooks for paint

Several textbooks and training manuals for paint technologists are now available from Selection & Industrial Training Administration Ltd., Lauriston Road, London. SW19 4AJ. They are detailed elsewhere in this issue.

Temperature controllers

A summary catalogue covering the full range of Jumo electronic temperature controllers has been issued by Jumo Instrument Co, Harlow, Essex.

Courses, symposia etc.

Inspection techniques for polymeric materials

A review meeting on inspection techniques for polymeric materials is being organised by the Division of Materials Applications of the National Physical Laboratory to be held on 24 and 25 October 1974.

Structural steelwork

A two-day seminar is being held by the Paint Research Association with the title "Protection of structural steelwork" on 29 and 30 October 1974 at the Paint Research Station, Waldegrave Road, Teddington, Middlesex.



OCCA—XXVII Exhibition

Olympia, London. 22-25 April 1975

* * * * *

One exhibitor's view of OCCA-26

* * * * *

Special visits for overseas delegations already being arranged for the 1975 International Forum for technical display and discussion in the surface coatings industries

Following the great success of the delegation from Osaka, Japan, on the occasion of OCCA-26 when special arrangements were made for works visits etc., requests have already been received for similar facilities for a delegation from Czechoslovakia and for a further Japanese party.

Any company wishing to be placed on the list of those willing to accept such delegations should write to the Director & Secretary as soon as possible, setting out the countries in which they are interested and the scope of the activities which would be displayed.

An exhibitor's view of OCCA-26 (April 1974)

At the twenty-sixth Exhibition, in April 1974, there were direct overseas exhibitors from 13 countries, besides many overseas companies which showed through British associates. A full review of this Exhibition, showing the countries from which visitors came and the products on display, appeared in the June issue of this journal.

We are indebted to the Editor of "Compass" for permission to quote the following:

Scott Bader was one of 120 companies from the UK and 13 overseas countries represented in the Empire Hall. Despite being staged in a period of world raw-material shortage—or perhaps because of it—the exhibition proceeded, from the start, in an atmosphere of quiet, no-nonsense, businesslike efficiency. Representatives on the Scott Bader stand recorded no less than 345 genuine technical visits—one every six minutes throughout the four days of the show.

Motif of Exhibition 1975

The motif for 1975, designed by Robert Hamblin, continues the theme of OCCA-26, in which attention was drawn to the European Economic Community, by extending it to show the world-wide interest aroused by the Association's annual Exhibitions in London, which in recent years have attracted visitors from more than 50 overseas countries.

Venue

As in 1974, the Exhibition will be of four days' duration and will open on the Tuesday morning at 09.30 and will close on the Friday at 16.00. The Exhibition of raw materials, plant and equipment used in the paint, printing ink, colour, and allied industries will take place at the Empire Hall, Olympia, London.

Invitation to exhibit

Copies of the Invitation to Exhibit are being despatched to those companies and organisations, in the United Kingdom and overseas, which have shown at past Exhibitions or have already requested information on the 1975 Exhibition. Completed application forms for stand

space must be returned to the Director & Secretary of the Association not later than 1 October 1974.

Any organisation which has not previously received an Invitation to Exhibit and wishes to do so should contact the Association's offices as soon as possible.

OCCA Biennial Conference 1975

Scarborough

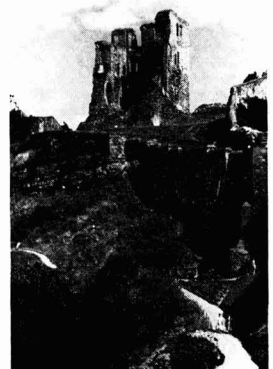
THE PERFORMANCE OF SURFACE COATINGS—DOES THE REALITY MATCH THE THEORY?

As already announced in the *Journal*, the next biennial Conference of the Association will take place at Scarborough from 17 to 21 June 1975. The headquarters will be the Grand Hotel, with overflow accommodated at the St. Nicholas Hotel. These two hotels are situated opposite each other on St. Nicholas Cliff.

The title of the Conference will be "The performance of surface coatings—does the reality match the theory?" and it is intended that as on previous occasions, full preprints will be published for despatch to delegates in advance of the Conference. It is important, therefore, that any person, whether or not a member of the Association, who feels that a report of his work could form the basis of a suitable technical paper, should contact immediately the Honorary Research & Development Officer of the Association (Mr A. R. H. Tawn, 34 Crest View Drive, Petts Wood, Kent BR5 1BY, England).

It will be recalled that it is the custom at the Association's Conference for the authors merely to outline their papers, highlighting points of interest, and for a general discussion of the paper to follow. The author will not be expected to deliver the paper *in toto*, since the object of

sending out the preprints in advance is that delegates may read these thoroughly before the Conference.



A view of Scarborough Castle

Forms for registration will be despatched to all members of the Association attached to the Sections in the United Kingdom, Ireland and the General Overseas Section early in 1975.

Joint Symposium

THE OPTIMUM USE OF RESOURCES FOR THE SURFACE
COATINGS INDUSTRIES

The one-day joint symposium organised by the Oil and Colour Chemists' Association and the Paintmakers' Association will now take place on Tuesday 17 September 1974 at University College, Gower Street, London WC1E 6BT.

The morning session will be chaired by the President of OCCA, Mr L. H. Silver, and the afternoon session by the Vice-President of the Paintmakers' Association Mr R. L. White.

The papers to be presented are as follows: "Petrochemicals", "The role of water-borne polymers", "Optimum use of organic pigments", "Utilisation of financial resources", "The role of the consultant", and "Utilisation of management resources".

The morning session will take place from 10.00 am to 12.30 pm, after which there will be a short reception and luncheon.

The afternoon session will take place from 2.00 pm to 5.00 pm. The charge for the symposium will be £22.00 (inclusive of VAT), which will include badges, folders, synopses of papers if available, and luncheon. Forms of application can now be obtained from the Director & Secretary at the Association's offices.

West Riding Section

Golf tournament

There was an excellent turn out at the Pannal Gold Club, Harrogate, on 7 August when members met to compete for the OCCA Cup and the West Riding Chairman's trophy. It was a fine day, the course immaculate, and an added interest was given to the competitions by the generosity of the following sponsors, who donated prizes: BP Chemicals International, BASF, English China Clays, R. W. Greeff, Laporte Industries, SPL Group, Smythe Morris, Tioxide International and Mr D. Morris (Section Chairman). The winners were as follows:

OCCA Cup: 1st J. J. Jackson, 2nd A. Bridgewood, 3rd J. R. Hastie, 4th J. R. Bourne.

Section Chairman's Cup: 1st R. L. Wells, 2nd R. Hardy, 3rd A. R. Curtis, 4th P. V. Jordan.

Reunion Dinner for past and present Members of the Council

Following the successful innovation last year of a Reunion Dinner for those members who have served on Council at any time, Council has decided to hold a similar event this year. The Dinner will take place on Wednesday 16 October 1974 at the Cafe Royal, 68 Regent Street, London W1, at 6.30 for 7.00 pm, and informal dress will be worn.

The price of the ticket, for the dinner and wine, will be £6.25

Register of Members

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

Ordinary Members

- CHUN, WAI-KAY, BSc, 416 Kwun Tong Road, Kowloon, Hong Kong (*General Overseas*)
 GRAYSON, FRANCIS WILLIAM, BSc, Neill Cropper & Co. Ltd., Box 9, Auckland, New Zealand. (*Auckland*)
 HART, KENNETH JOHN, FInstPet, PO Box 49413, Nairobi, Kenya, East Africa. (*General Overseas*)
 HILL, CHARLES ANTHONY, BSc, Hillbrook Printing Inks Ltd., Spa Mill, New Street, Slaithwaite, Nr. Huddersfield, Yorks. (*West Riding*)
 LANGFORD, HENRY, BSc, 25 Acacia Road, Hampton, Middlesex TW12 3DP. (*London*)
 LUI, HENRY FU-KWOK, MSc, 240A Prince Edward Road, 6/F Kowloon, Hong Kong. (*General Overseas*)

President at Royal Garden Party



The President of the Association, Mr L. H. Silver, accompanied by Mrs Silver, about to leave for the Royal Garden Party at Buckingham Palace on 18 July. On the following day, Mr and Mrs Silver left on a tour overseas which was planned to include a visit to the Annual Convention of the two New Zealand Sections at Warkai in early August (where Mr Silver presented a paper on the British paint industry) and a meeting later with the Federal Committee of the Oil and Colour Chemists' Association Australia,

(inclusive of VAT), and a cash bar will be provided at the reception and after the dinner. Past Presidents, Past Honorary Officers Honorary Members and Founder Member have been invited as guests of the Association. All other past and present Members of Council must send the necessary remittance with their completed application form. Any member with service on Council who has not received an application form and wishes to do so should write to the Director & Secretary at the Association's offices.

- METCALF, KEITH WENTWORTH, LRIC, 49A High Street, Wealdstone, Harrow, Middlesex HA3 5DF. (*London*)
 RASHEED, ABDUR, BSc, 12 Aldin Avenue, Slough, Bucks SL1 1RS. (*Thames Valley*)
 SEN, RANEN, BSc, 244 West 99 Street, Apt. 745, New York, NY10025, USA. (*General Overseas*)
 SHAH, RAMESH NATWERLAL, BSc, Hindustan Transmission Products, Chandivali, Kurla Vihar Road, Bombay 72, India. (*General Overseas*)
 WU, CHI KIT ANDREW, ASDC, c/o Dept. of Colour Chemistry and Dyeing, University of Leeds, Leeds LS2. (*West Riding*)

Associate Members

- BUCKLEY, GLEN ALISTER, Revertex Industries (NZ) Ltd., Box 12180, Penrose, Auckland, New Zealand. (*Auckland*)
 SCHOEMAKER, KAREL JAN, 12 Dover Road, Bryanston, Sandton, Transvaal, South Africa. (*South African*)

Registered Students

- GILL, TREVOR GEORGE, 84 Huntsman Road, Hainault, Ilford, Essex. (*London*)

Forthcoming Events

Details are given of meetings in the United Kingdom up to the end of the month following publication, and South Africa and the Commonwealth up to the end of the second month.

September

Tuesday 10 September

West Riding Section: Speaker and title to be announced.

Tuesday 17 September

One-day Joint Symposium in conjunction with the Paintmakers Association. "Optimum use of resources for the surface coatings industries" University College, Gower Street, London.

Friday 20 September

Irish Section: Ladies' Night. Speaker to be announced later. Lecture followed by Cheese and Wine Party to be held at the Clarence Hotel, Dublin at 7.45 p.m.

Midlands Section: Ladies' Evening at the Westbourne Suite, Botanical Gardens, 7.00 p.m.

Thames Valley Section: Visit to Fulmers Institute, buffet etc.

Friday 27 September

Bristol Section: "Masonry coatings" by Mr P. Whiteley of the Building Research Establishment, to be held at the Royal Hotel, Bristol at 7.15 p.m.

London Section: Ladies' Evening.

Midlands Section: "The outlook for petrochemical derived raw materials for the paint industry" by Mr M. E. Robinson, ICI Ltd. Petrochemicals Division, at the Apollo Motel, Hagley Road, Birmingham.

October

Wednesday 2 October

Manchester Section—Student Group: "Titanium dioxide—its manufacture and properties" by Mr D. Charlton of Tioxide International Ltd., to be held at the Manchester Literary and Philosophical Society, Manchester, at 4.30 p.m.

Thursday 3 October

Newcastle Section: "Some examples of electrophoretic coatings for cathodic

deposition" by Dr H. Verdino, Vianova, Austria, to be held at the Royal Turks Head Hotel, Grey Street, Newcastle upon Tyne, at 6.30 p.m.

Thames Valley Section—Student Group: "Polymers" by Dr Clarke, to be held at Slough College in the main Lecture Theatre at 4.00 p.m.

Friday 4 October

Hull Section: Annual Dinner Dance to be held at Cave Castle, South Cave, Nr. Hull.

Saturday 5 October

Scottish Section—Student Group: Joint meeting in Edinburgh with Eastern Branch: "Modern phthalocyanine pigments" by Mr J. B. Blackburn, Ciba-Geigy (UK) Ltd., to be held at Three Pigeons, 573 Sauchiehall Street, Glasgow at 10.15 a.m.

Monday 7 October

Hull Section: "The protection of structural steel" by Mr J. R. Bourne, Mebon Ltd. Joint meeting with the Institution of Chemical Engineers at the Haven Inn, Barrow Haven, Lincs at 6.30 p.m.

Tuesday 8 October

West Riding Section: "Amide-imide resins" by a speaker from May and Baker Ltd.

Thursday 10 October

Midland Section—Trent Valley Branch: "Economic use of titanium dioxide in paint" by Mr J. G. Balfour of Tioxide International Limited, to be held at the British Rail School of Transport, London Road, Derby at 7.00 p.m.

Scottish Section: "The colour of azo pigments" by Dr K. Hunger of Farbwerke Hoechst AG. Joint meeting with Society of Dyers and Colourists to be held at Beacons Hotel, 7 Park Terrace, Glasgow G3 at 6.00 p.m.

Friday 11 October

Manchester Section: "High-performance violet, red, orange and yellow pigments

for automotive and industrial finishes" by Dr P. Lutz, supervisor of automotive formulations, Du Pont, USA, to be held at the Manchester Literary and Philosophical Society, 36 George Street, Manchester at 6.30 p.m.

Wednesday 16 October

London Section: "High-performance violet, red, orange and yellow pigments for automotive and industrial finishes" by Dr P. Lutz, supervisor of automotive formulations, Du Pont, USA to be held at the Polytechnic of the South Bank, Borough Road, London SE1 at 7.00 p.m.

Friday 18 October

Irish Section: "Industrial finishes" by Mr D. Pountain of Berger Paints (Ireland) Ltd., to be held at the Clarence Hotel, Dublin at 7.45 p.m.

Manchester Section: Annual Dinner Dance, Piccadilly Hotel, Piccadilly Plaza, Manchester at 6.30 p.m.

Midlands Section: "Water or what?" by Mr K. O'Hara, Cray Valley Products Ltd., to be held at the Birmingham Chamber of Commerce and Industry, PO Box 360, 75 Harborne Road, Birmingham B15 3DH at 6.30 p.m.

Wednesday 23 October

Manchester Section—Student Group: "Powder coatings" by Mr N. H. Seymour of Sterling Varnish Co. Ltd., to be held at the Manchester Literary and Philosophical Society, Manchester at 4.30 p.m.

Thursday 24 October

Thames Valley Section: "Strategy of modern purchasing" by Dr Finch, Croda Inks Ltd., to be held at the Beech Tree Hotel, Maxwell Road, Beaconsfield, Bucks at 7.00 p.m.

Friday 25 October

Bristol Section: "Design for wallcoverings" by Mr G. R. Marks of ICI Ltd. Ladies' Evening; Royal Hotel, Bristol at 7.15 p.m.

Scottish Section

Officers and Committee

At an Extraordinary General Meeting on 1 August, Mr J. D. W. Davidson was elected unanimously Vice-Chairman for the session and Mr A. S. Fraser was elected Honorary Auditor in place of Mr Davidson, who could not continue in the office.

The full list of officers of the Section for the present session, including the Committee, therefore, reads as follows:

Chairman: A. McLean, BSc, FRIC, ARCST, FTSC, 46 Lindsay Road, East Kilbride, Glasgow.

Vice-Chairman: J. D. W. Davidson, 31 Highburgh Drive, Burnside, Rutherglen, Glasgow.

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Hon. Publications Secretary: G. H. Robertson, BSc, PhD.

Hon. Auditor: A. S. Fraser, 42 Busby Road, Carmunnock, Lanarkshire.

Committee;

H. A. Munro, ATSC, Braidfield Road, Clydebank, Dunbartonshire

I. R. McCallum, 37 Burnbrae Avenue, Bearsden, Dunbartonshire

H. Glen, 4 Lombard Place, Linburn, Erskine, Renfrewshire

R. Morrow, BSc, Tioxide International, Cornhill House, 144 West George Street, Glasgow

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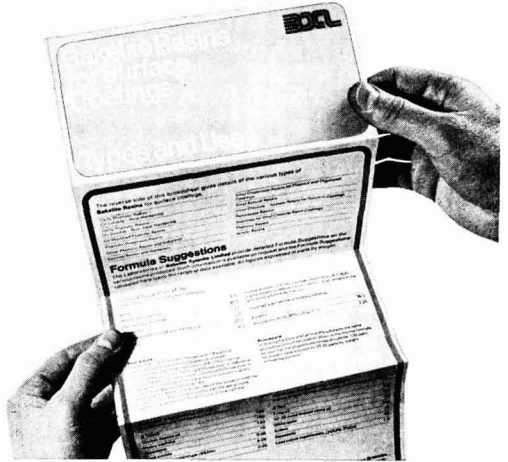
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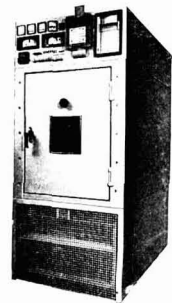


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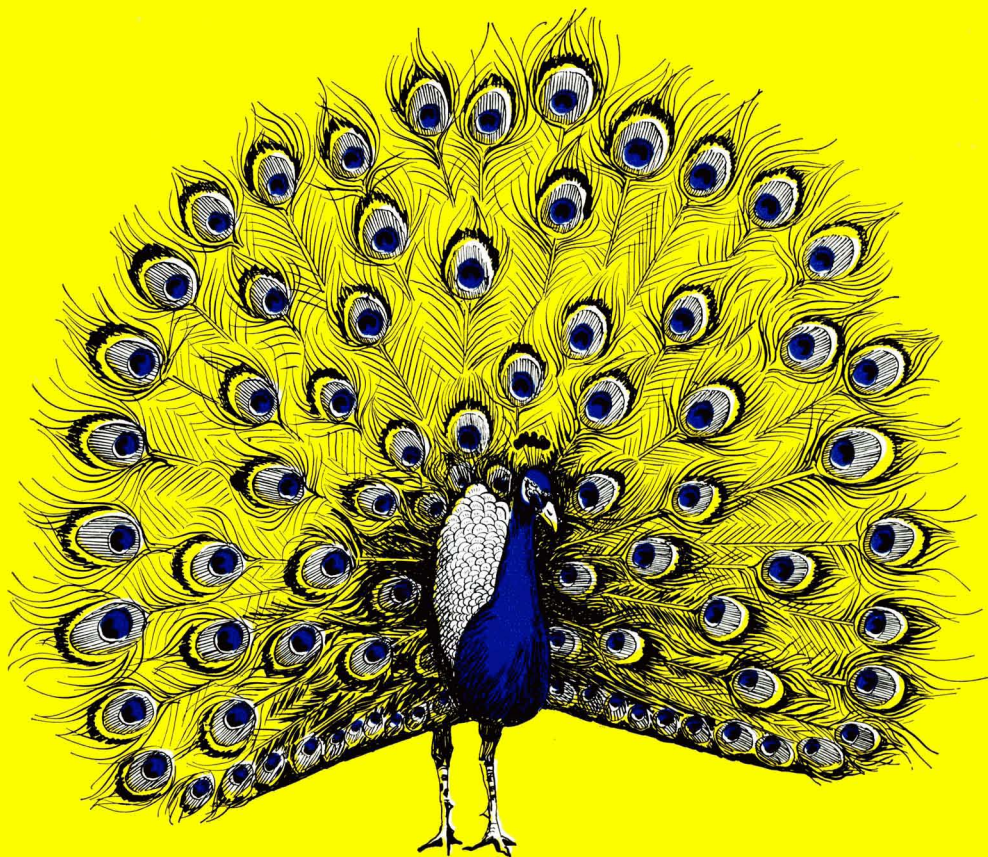
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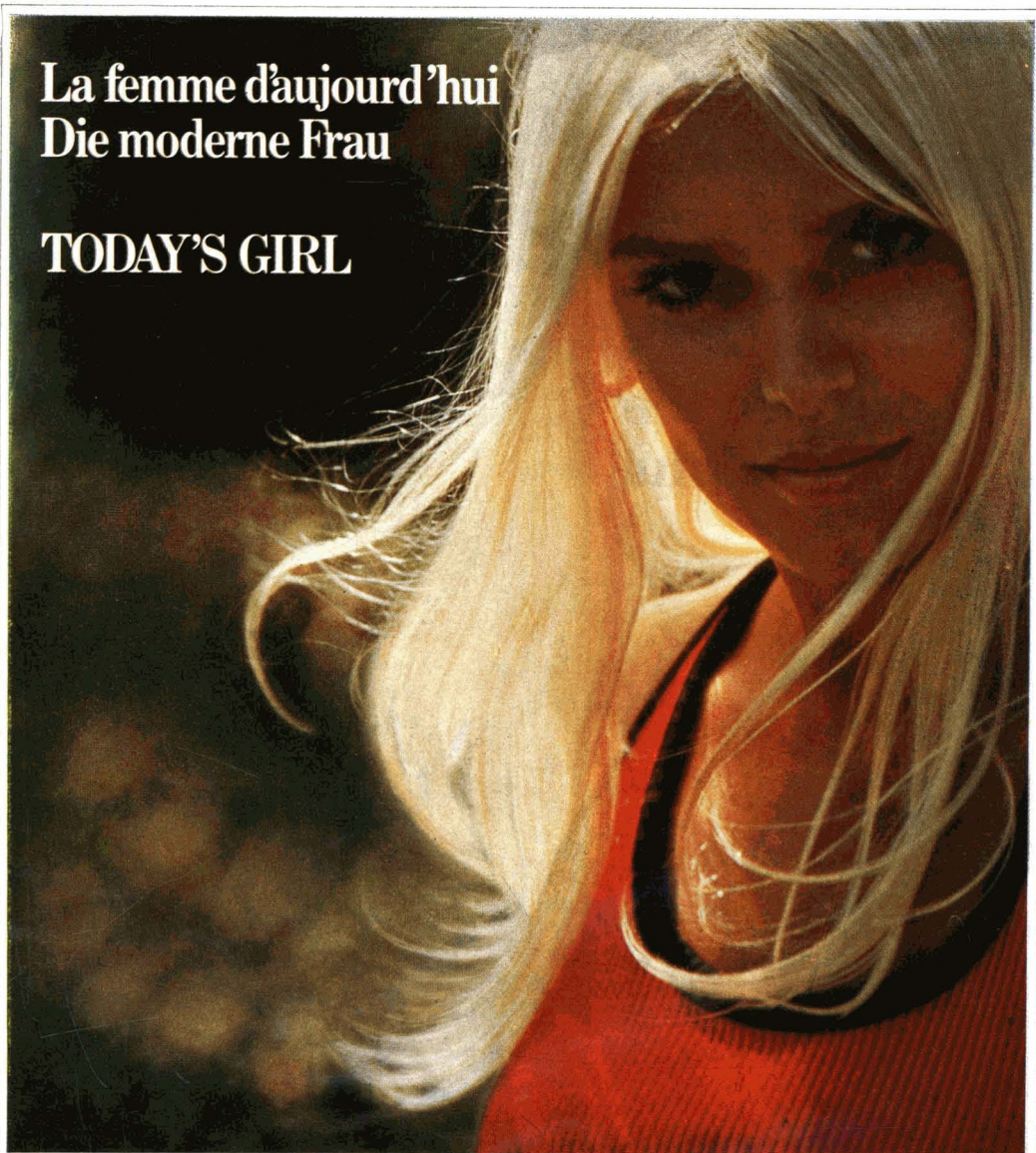
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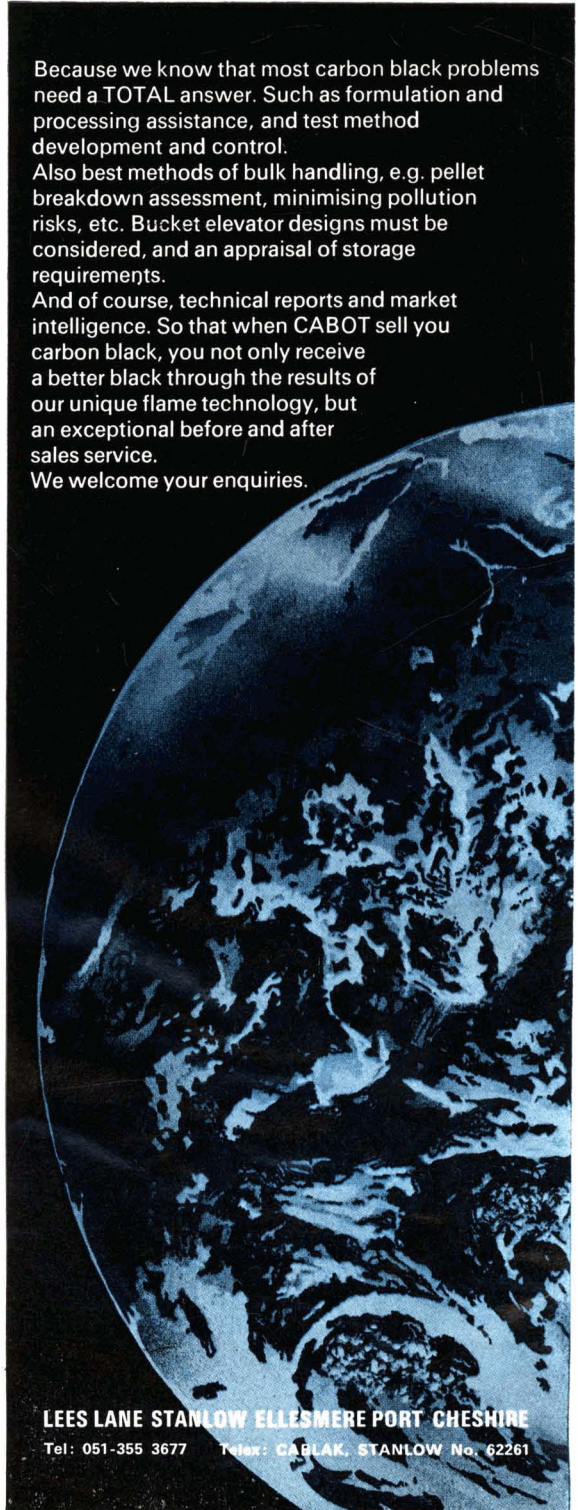
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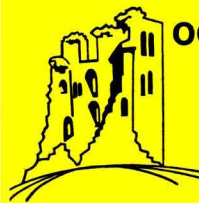
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