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Composition and some uses of tall oil products K. S. Ennor

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The effect of zeta potential on the optical properties of paints *M. J. B. Franklin*

An investigation into the relationship between the nature of surface defects and gloss

J. H. Colling, W. E. Craker and J. Dunderdale

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Transactions and Communications

Composition and some uses of tall oil products*

By K. S. Ennor

British Oxygen Chemicals Ltd., Chester-le-Street, Co. Durham

Summary

Scandinavian tall oil fatty acids of low rosin content and soya bean oil give alkyds with similar air drying times, but American tall oil fatty acids give slower dry. Tall oil fatty acids contain no linolenic acid and give less yellowing in the dark than soya bean oil. In durability, alkyds from tall oil fatty acids compare favourably with alkyds from soya bean oil. A maximum of about 30 per cent of the tall oil fatty acids can be replaced by linseed oil without using an alcoholysis step, thus saving processing time.

Tall oil rosins of Scandinavian and American origin are both composed mainly of abietic and dehydroabietic acids. A simple gelometer test for the measurement of rosin crystallisation is described. Reaction of tall oil rosin with a minor proportion of paraformaldehyde is the most effective way to inhibit crystallisation.

In distilled tall oil, about 25 per cent of the fatty acid portion is similar to tall oil fatty acids and the remainder contains non-yellowing higher fatty acids plus some dimers. The rosin acid portion contains very little abietic acid, but is rich in pimaric acid. This is relatively resistant to autoxidation, which may explain why alkyds from distilled tall oil show rather better durability than gum rosin-modified alkyds.

La composition et quelques applications de tall oil

Résumé

Les acides gras de tall oil en provenance de la Scandinavie ayant une faible teneur de colophane et celles de l'huile de soja rendent des résines alkydes qui sèchent aux pareilles vitesses, mais les acides gras de l'Amérique sèchent moins vite. Les acides gras de tall oil ne contiennent pas d'acide linolénique et provoquent moins de jaunissement à l'abri de la lumière que l'huile de soja. Au point de vue de durabilité, les résines alkydes aux acides gras de tall oil se comparent favorablement des alkydes contenant d'huile de soja. Sans besoin d'utiliser une étape d'alcoolyse, on peut remplacer au maximum 30 pour cent d'acides gras de tall oil par huile de lin et par conséquent effectuer une économie du temps de fabrication.

Les colophanes de tall oil d'origine scandinavienne et américaine sont également composées largement des acides abiétique et déshydroabiétique. On décrit un facile essai gelométrique pour la détermination de la crystallisation de colophane. La réaction de la colophane de tall oil avec de petites quantités de paraformaldéhyde donne la possibilité la plus effective pour inhibiter la crystallisation.

En tall oil distillé 25 pour cent de la part des acides gras ressemblent les acides gras de tall oil et le reste contient d'acides gras plus élevés non-jaunissant, ainsi que des dimères. La part des acides de colophane contient tres peu d'acide abiétique, mais beaucoup d'acide pimarique. Ceci est assez résistant à l'autoxydation, qui peut expliquer pourquoi les alkydes à partir de tall oil distillé démontrent une durabilité plutôt mieux que celle des alkydes modifiées à la colophane.

^{*}Presented to the Scottish Section on 14 December 1967.

Zusammensetzung Sowie Einige Anwendungsgebiete von Tallölprodukten

Zusammenfassung

Skandinavische Tallölfettsäuren von niedrigem Harzgehalt, sowie Sojaöl ergeben Alkydharze, die gleiche Trockeneigenschaften besitzen; amerikanische Tallölsäuren ergeben dagegen langsamere Trocknungsresultate. Tallölfettsäuren enthalten keine Linolensäure und vergilben im Dunkeln weniger als Soyaöl. Hinsichtlich Dauerhaftigkeit verhalten sich Alkydharze aus Tallölfettsäuren im Vergleich mit solchen aus Sojaöl günstig. Eine Höchstmenge von etwa 30Prozent Tallölfettsäuren kann, ohne dass die Alkoholysenstufe eingestzt zu werden braucht, durch Leinöl ersetzt werden, woduch Fabrikationszeit eingespart wird.

Tallölharze sowohl skandinavischen als auch amerikanischen Ursprungs bestehen hauptsächlich aus Abietin-und Dehydroabietinsüren. Eine einfache Gelometer-Prüfung zur Messung der Harzkristallisation wird beschrieben. Die Kristallisation von Tallölharzen wird am wirksamsten durch geringe Zusätze von Paraformaldehyd vermieden.

In destilliertem Tallöl ähneln etwa 25 Prozent des Fettsäureanteils den Tallölfettsäuren; der Rest enthält nichtgilbende höhere Fettsäuren sowie etwas Dimere. Der Harzsäureanteil enthält sehr wenig Abietinsäure, aber viel Pimarsäure. Diese ist verhältnismässig widerstandsfähig gegen Antoxidation, wodurch sich die grössere Dauerhaftigkeit von Alkydharzen aus destilliertem Tallöl verglichen mit Kolophonium-modifizierten Alkydharzen erklären dürfte.

Состав и некоторые применения продуктов таллового масла

Резюме

Скандинавские жирные кислоты таллового масла с малым содержанием канифоли и соевое масло дают алкиды с похожими временами воздушной сушки, но американские жирные кислоты таллового масла дают более медленное время сушки. Жирные кислоты таллового масла не содержат линоленовой кислоты и дают меньше пожелтения в темноте чем соевое масло. В отношении стойкости, алкиды из жирных кислот таллового масла дают благоприятное сравнение с алкидами из соевого масла. Максимум в приблизительно 30 процентов жирных кислот таллового масла могут быть заменены льняным маслом без применения алкоголиза, что дает экономию во времени обработки. Канифоли таллового масла скандинавского и американского происхождения состоят главным образом из абиетиновой и дегидроабиетиновой кислот. Описывается простое гелиметрическое испытание для измерения кристаллизации канифоли. Реакция канифоли таллового масла с малой пропорцией параформальдегида является наиболее эффективным методом подавления кристаллизации.

В дистиллированном талловом масле около 25 процентов жирных кислот подобно жирным кислотам таллового масла а остаток содежрит нежелтеющие жирные кислоты высокой кислоты и некоторые димеры. Доля канифольной кислоты содержит очень мало абиетиновой кислоты но богата в пимаровой кислоте. Последния сравнительно устойчива против самоокисления что возможно объясняет почему алкиды из дистиллированного таллового масла проявляют существенно более удовлетворительную устойчивость чем смольные алкиды модифицированные канифолью.

Introduction

Crude tall oil is a by-product from the sulphate or kraft paper process¹. The most valuable products of fractionated tall oil are tall oil fatty acids and rosin. Tall oil fatty acids are composed mainly of linoleic and oleic acids and tall oil rosin is a mixture of mainly abietic and dehydroabietic acids¹. Distilled tall oil is a mixture of tall oil fatty acids and rosin. This paper considers the applications of tall oil fatty acids and distilled tall oil in the preparation of alkyds. The durability and drying times of these alkyds and the crystallisation behaviour of tall oil rosin is explained by the chemical composition of the constituent fatty acids and resin acids.

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Alkyds from tall oil fatty acids

Alkyds modified with crop oils must contain glycerol, but fatty acids impose no such restriction on the amount and type of polyol. The reactants are cooked together, for example, by the solvent process in xylene at 240-250°C. In alkyd manufacture, tall oil fatty acids compete mainly with soya bean oil, and some typical long oil length formulations are shown in Table 1.

		10	able I		
Long	oil	length	alk yd	formulations	

					Weight %				
					Alkyd (1)	Alkyd (2)	Alkyd (3)		
Tall oil fatty acids				•••	58.5	·	_		
Soya bean oil fatty acids	s		••			58.5	-		
Soya bean oil	••				_	—	63.0		
Phthalic anhydride					22.0	22.0	23.8		
Pentaerythritol		•.•			19.5	19.5	13.2		
Fatty acid content, %		••.			62.5	62.5	62.5		
Reaction time, hour	•••		••		10	11	21		
Acid value, mg KOH/g			••		5	5	5		
Solids content of 5 pois at 25°C, %	e solut	ion in	white s	spirit	61	63	60		

Air drying rates

It is well known that tall oil fatty acids of Scandinavian origin promote faster air dry in alkyds than American tall oil fatty acids of the same rosin content. This reflects the higher proportion of acids with multiple unsaturation in the Scandinavian tall oil fatty acids¹. To study these effects, Scandinavian and American tall oil fatty acids of different rosin contents were evaluated in comparison with soya bean oil and soya fatty acids, in the formulations given in Table 1.

Varnishes were prepared from solutions of the alkyds in white spirit by addition of 0.5 per cent of lead and 0.05 per cent of cobalt metals, as naphthenates, based on alkyd solids. Films of 0.001 in dry thickness were applied to steel and the drying times (shown in Table 2) were measured with the ICI drying recorder at 22°C and 60 per cent relative humidity. The same drier system and drying conditions were employed for all the resins described in this paper. Ballotini times are a measure of surface dry and the needle times are a measure of through-dry. Scandinavian tall oil fatty acids of low rosin content gave drying times similar to soya bean oil.

Yellowing in the dark

White gloss paint films based on the alkyd formulations given in Table 1 were kept in a dark room for four months and the relative yellowing results are shown in Table 3.

K. S. ENNOR

	711	un y	18 mile	o oj u	nya rarmsnes	4	
Fatty a	icid or o	il	Rosin content, %	Ballotini time, hour	Needle time, hour		
Scandinavian tall oil fat	ty acids	••	1.3	1.5	4.75		
American tall oil fatty a	ncids	••	••		1.3	3.0	5.0
Soya bean oil	••	••	••		0	1.75	4.75
Soya fatty acids	••	••			0	1.25	4.25
Scandinavian tall oil fat	ty acids				3.8	2.0	6.0
American tall oil fatty a	acids	• •			3.8	3.5	5.5

Table 2 Air drying times of alkyd varnishes

Table 3										
Relative	yellowing	of	white	gloss	alk yd	paint	films			

	Fat	ty acid	or oi	1		Rosin content, %	Relative yellowing
Scandinavian tall	oil fa	tty aci	ds			 1.3	Slight
Scandinavian tall	l oil fa	tty aci	ds	••	••	 3.8	Slight
American tall oil	fatty	acids		••	••	 1.3	Moderate
American tall oil	fatty	acids				 3.8	Slight/moderate
Soya bean oil	••	••	••	••	••	 0	Severe
Soya fatty acids			••	••	••	 0	Severe

The absence of linolenic acid explains why tall oil fatty acids, especially those of Scandinavian origin, produce significantly less yellowing in the dark than soya fatty acids. This confirms the report² that cis-5,9,12-octadecatrienoic acid does not promote yellowing, probably because it does not readily form a fully conjugated system³.

Durability

White gloss paints were prepared from the alkyd formulations (Table 1) and two coats were applied to mild steel and exposed for two years, at 45° facing south, in a rural and an industrial atmosphere in County Durham. All the coatings showed equivalent excellent colour retention and chalk resistance. The tall oil alkyd paints showed slightly less dirt retention and slightly better gloss retention than the soya bean oil alkyd coating.

Alkyds from blends of tall oil fatty acids and linseed oil

When the price of linseed oil is low, alkyd manufacturers sometimes use a mixture of tall oil fatty acids with linseed oil. It has now been found that, in the preparation

1968 (6)

of long oil length alkyds, a maximum of about 30 weight per cent of the tall oil fatty acids can be replaced by linseed oil, without using an alcoholysis step. Table 4 shows a typical formulation (4).

				Weight %
			-	Alkyd (4)
Tall oil fatty acids (1.3 % ro	osin)			41.8
Alkali refined linseed oil	••			17.9
Phthalic anhydride				22.5
Pentaerythritol	••			17.8
Total fatty acid content, %	.•			62
Reaction time, hour	•••			7
Acid value, mg KOH/g			••	6
Solids content of 5 poise spirit at 25°C, %	solutio	on in v	white	56
Ballotini time, hour				3
Needle time, hour		••		6

 Table 4

 Tall oil fatty acid/linseed oil alkyd

The tall oil fatty acids, phthalic anhydride and pentaerythritol were cooked together by the solvent process, in xylene, for one hour at 190-250°C. Then about one third of the linseed oil was stirred in rapidly and the resulting clear solution was cooked for one hour at 250°C. The remaining linseed oil was added, in two equal proportions, after hourly intervals. The reaction solution was then cooked for four more hours at 250°C. This unusual reaction procedure has the distinct advantage of retaining the shorter processing time of the fatty acid process (Table 4). Under the reaction conditions employed, interesterification probably took place since the resulting alkyd was quite different from a medium oil length tall oil fatty acid alkyd which had been cold blended with linseed oil to give a similar oil length. In particular, alkyd (4) was air dried in thick films which were free from wrinkling under conditions where the alkyd cold blended with linseed oil showed severe wrinkling.

Two coats of a white gloss paint from alkyd (4) were applied to mild steel and evaluated against tall oil fatty acid alkyd (1) for one thousand hours in a weatherometer according to Defence Specification DEF 1053 Method 26. Both coatings showed similar gloss retention and chalk resistance. Alkyd (1) gave very good colour retention, but, as would be expected, alkyd (4) gave somewhat more yellowing. A similar pattern was obtained when the white coatings were kept in a dark room, when the coating from alkyd (4) showed relatively severe yellowing.

Chemical composition of tall oil rosin

Gas liquid chromatography of the methyl esters of tall oil rosin confirmed that the main components were abietic and dehydroabietic acids. The methyl esters were conveniently prepared from the tetramethylammonium salts of the rosin acids⁴. In contrast to tall oil fatty acids, little difference in chemical composition was found between Scandinavian and American tall oil rosin. However, the sample of American tall oil rosin contained more palustric acid, as shown in Table 5.

7	able	2 5
	uvic	

R	osin acid	s		Scandinavian rosin, weight %	American rosin, weight %
Tetrahydroabi	etic				3
Pimaric		••	••	2	5
Dihydroabietic	·			5	3
Palustric				4	12
Isopimaric				9	5
Unknown				8	6
Abietic		••		36	35
Dehydroabieti	c	••		29	26
Neoabietic	• ••			8	5

Chemical	composition	of	tall	oil	rosins
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Crystallisation of rosin and modified rosins

Tall oil rosin crystallises more readily than gum rosin or wood rosin. Separation of abietic and dehydroabietic crystals takes place most rapidly from molten rosin at 90-120°C. However, no crystallisation takes place at 150°C or at higher temperatures, so that tall oil rosin is normally stored and transported at about 150° C.

A gelometer with a slowly rotating $probe^5$, as well as solution⁶ and melt⁶ techniques have been described for the measurement of rosin crystallisation. A simple and reproducible gelometer test has now been developed. The test sample of rosin must be freed from surface-oxidised powder because this inhibits crystallisation. Then a 30gm portion is powdered and allowed to melt, during 15 minutes, in a 50ml beaker held in a thermostat at 110°C. The plunger of a Tecam gelometer is inserted into the molten rosin so that it reciprocates not less than 0.5in from the bottom of the beaker when at the lowest point of its stroke. When crystallisation takes place the movement of the plunger is arrested. The time of operation, which is recorded automatically, is a measure of the crystallisation test in less than 15 minutes at 110°C. However, tall oil rosin can be modified in

TALL OIL PRODUCTS

several ways to make it less prone to crystallisation. As shown in Table 6 an effective method is to react tall oil rosin with a minor proportion of paraformal-dehyde⁷.

Type of rosin	Gelometer time, hour	
Scandinavian tall oil rosin		0
American tall oil rosin		0
American FF wood rosin		28
Portuguese gum rosin		62
Tall oil rosin reacted with 3% of paraformaldehyde	7	37
Tall oil rosin partially neutralised with NaOH to a value 129 mg KOH/g	cid	27
Tall oil rosin reacted with 3% of maleic anhydride		. 8
Tall oil rosin reacted with 5% of saligenin ⁸		1.5
Tall oil rosin blended with 5% of dimerised rosin ⁹		0.5
Tall oil rosin after seven hours at 260°C under nitroge	n ¹⁰	0.2

Table 6

Tecam gelometer tests on different rosins and modified rosins

Chemical composition of distilled tall oil

Distilled tall oils are mixtures of tall oil fatty acids containing from ten to about 60 weight per cent of rosin. In the United Kingdom, Scandinavian distilled tall oil of approximately 30 per cent rosin content is widely used and the chemical composition of such a sample, as revealed by gas liquid chromatography of methyl esters, is shown in Table 7.

The composition of about one quarter of the fatty acid portion of Scandinavian distilled tall oil is similar to that of Scandinavian tall oil fatty acids¹. However, the greater part consists of higher fatty acids, which have not yet been completely separated, plus dimerised fatty acids. A trienoic acid with 20 carbon atoms has now been isolated by chromatography on a column of silica gel impregnated with silver nitrate. This trienoic acid is very probably cis-5,11,14-eicosatrienoic acid which has been identified in Finnish crude tall oil¹¹.

Table 7 shows that the rosin acids in distilled tall oil are chemically different from the constituent acids of tall oil rosin (Table 5). Pimaric acid accounts for over one half of the rosin acid portion and the other major component is tetrahydroabietic acid. In contrast to abietic acid, the carbon-carbon double bonds in pimaric acid are not conjugated and are relatively resistant to autoxidation.

		0.13				
	Weight %					
Oleic			•••			9
Linoleic	••	••	•••	••		13
cis-5, 9, 12-Octa	decatr	ienoic	••	••		4
Higher fatty aci	ds+di	mers	•••			74
	Rosi	n acids				Weight %
Tetrahydroabiet	ic	••		••		28
Pimaric	•••	•••		••		52
Dihydroabietic	••	••	••	••		8
Palustric	• •	••	••	••		5
Unidentified	••	••	•••	••		1
Isopimaric		••	••	••		3
Abietic+dehydi	roabiet	ic	••	••		3

		Ta	ble 7			
Chemical	composition	of a	Scandinavian	distilled	tall oi	1

÷.		Table 8		
Medium	oil length	rosin-modified	alkyd	formulations

							Weig	sht %
							Alkyd (5)	Alkyd (6)
Distilled tall oil (30% ro	sin)	••	••	•••	••		70.9	
Tall oil fatty acids (1.3%	rosin)	•••	••	••				49.6
Gum rosin		••	•••					21.3
Phthalic anhydride	••	••		••			13.5	14.0
Pentaerythritol	••	••	• •	••	•••		15.6	15.1
Fatty acid content, %	••			•••			54	54
Reaction time, hour	••	••	••	••			8	12
Acid value, mg KOH/g	•••	••					9	10
Solids content of 5 poise	solutio	n in v	white sp	oirit at	25°C, 9	%	53	74
Ballotini time, hour	••	• •	• •	• •	••	••	4	3
Needle time, hour		••		••	••	••	10	10

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Rosin-modified alkvds

Distilled tall oil offers an economical route to rosin-modified alkyds. Table 8 shows a typical medium oil length alkyd formulation (5) from distilled tall oil. For comparison, a gum rosin-modified alkyd formulation (6) of the same oil length is shown and both alkyds were prepared by the solvent process at 250°C.

Yellowing in the dark

White undercoat paints were prepared from alkyds (5) and (6) and single coats were applied to mild steel primed with a conventional calcium plumbate coating. The coatings were stored in a dark room for four months, together with a white alkyd coating based on tall oil fatty acids. In all cases the degree of yellowing was slight. This demonstrates that the higher fatty acids in distilled tall oil do not cause yellowing.

Durability

The coating systems from alkyds (5) and (6) were exposed for 1,000 hours in the above mentioned weatherometer. As expected, cracking took place in both undercoats, but the distilled tall oil alkyd (5) showed least cracking and also the least yellowing. This improvement in durability may reflect the superior oxidation resistance of the pimaric acid in distilled tall oil compared with the more reactive abietic acid in gum rosin.

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Antifouling paints based on organotin compounds Part I. Colorimetric determination of microgram amounts of organotin compounds in aqueous solutions

By L. Chromy and K. Uhacz

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Summary

A method for the determination of microgram amounts of organotin compounds in aqueous solutions has been developed. The method is based on extraction of the compound from the aqueous phase with carbon tetrachloride, followed by absorptiometric measurements of the complex formed with dithizone.

The method is suggested as a means of studying the leaching of organotin compounds from antifouling compositions.

Peintures anti-fouling à base des composés organostanniques

Première partie. Le dosage colorimétrique des quantités de l'ordre de microgrammes de composés organostanniques dans des solutions aqueuses

Résumé

On a mis au point une méthode pour la dosage des quantités de l'ordre de microgrammes de composés organostanniques dans des solutions aqueuses. La methode s'agit de l'enlèvement du composé à partir de la phase aqueuse par le tetrachlorure de carbone, suivi par le dosage absorptiométrique du complexe formé avec dithizone.

On propose la méthode pour étudier la dissolution des composés organostanniques à partir des enduits antifouling.

Auf organischen Zinnverbindungen Aufgebaute Antifoulingfarben

Téil I. Kolorimetrische Bestimmung von Microgrammengen organischer Zinnverbindungen in wässrigen Lösungen

Zusammenfassung

Es wurde eine Methode zur Bestimmung der Microgrammengen von organischen Zinnverbindungen in wässrigen Lösungen entwickelt. Die Methode beruht auf der Extraktion der Verbindung mit Tetrachlorkohlenstoff aus der wässrigen Phase mit nachfolgender Bestimmung des mit Dithizon gebildeten Komplexes mit Hilfe des Absorptionsmessgerätes.

Die angewandte Methode wird zur Verwendung bei Studien des Auslaugens von organischen Zinnverbindungen aus Antifouling-Kompositionen vorgeschlagen.

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Необрастающие краски на основе органотинных соединений. Часть 1. Колориметрическое определение микрограммных количеств органотинных соединений в водных растворах

Резюме

Выработан метод определения микрограммных количеств органотинных соединений в водных растворах. Метод основан на извлечении соединения из водной фазы с четыреххлористым углеродом с последующими абсорбционными измерениями комплексного соединения образованного с дитизоном. Метод предлагается как средство для изучения выщелачивания органотинных соединений из необрастающих составов.

Introduction

Antifouling paints containing organotin compounds are being increasingly used in place of compositions based on inorganic toxic agents such as compounds of copper and mercury. Routine tests of antifouling compositions, based on leaching of the toxins from the coatings, are very useful, both for research purposes and for production control.

Laboratory testing of antifouling paints containing organotin compounds is, however, difficult. There is a lack of suitable analytical methods for determining the concentration of such compounds in water and solutions of electrolytes. Few methods have been proposed for the determination of organotin compounds, and all of them have disadvantages for the routine testing of antifouling compositions. The procedure is usually carried out by decomposition of the compound, followed by estimation of inorganic tin by colorimetric, gravimetric, or volumetric methods.

The colorimetric methods available for the determination of tin using dithiol and phenylfluorone permit estimation of amounts in the order of $100\mu g$ and $10\mu g^1$. Leaching rates of certain organotin compounds from paint films have been measured by analysis for tin in the films after soaking in sea water for various periods².

The reactivity of dithizone with organo-metallic compounds has been used for determination of di- and trialkyltin compounds in mixtures³. The method based on selective extraction of organotin compounds from mixtures by a solution of dithizone in chloroform in the presence of a suitable buffer solution, and measuring the absorption spectra of the yellow or pink complexes allows the compound to be determined in amounts of *ca*. $5\mu g$. A.C. polarography has also been used for direct estimation of organotin compounds⁴.

The main difficulty in applying the foregoing methods to study the leaching of toxic compounds from paint films is the need to estimate organotin compounds in aqueous solutions at concentrations of about 10^{-6} g/l.

In this paper a method for the direct quantitative determination of organotin compounds in aqueous solutions is described.

The analysis was carried out by extraction of the organotin compound from the aqueous solution with carbon tetrachloride, followed by absorption measurements of the dithizone complex.

Experimental

All colorimetric measurements were made with a Speker Photoabsorptiometer, using Filter No 7, maximum transmission 570nm.

Reagents

Carbon tetrachloride A.R. Chloroform A.R. Diphenylthiocarbazone, (dithizone), A.R. *bis*-(tri-n-butyltin) oxide, (TBTO), distilled (b.p. 180°C at 2mm Hg). tri-n-butyltin acetate, (TBTA), recrystallised from methanol (m.p. 118-119°C).

Solution of dithizone

125mg of dithizone was dissolved in 5ml of chloroform and diluted to 250ml with carbon tetrachloride. This solution (5mg/ml) was diluted 25-fold with carbon tetrachloride, and the solution containing 0.02mg/ml was used for the analysis.

Solutions of organotin compounds

Solutions of *bis*-(tri-n-butyltin) oxide containing 0.1 mg/ml and 0.01 mg/ml, and tributyltin acetate (0.1 mg/ml, and 0.01 mg/ml) in carbon tetrachloride were used for preparing the calibration graphs.

Preparation of calibration graphs

Volumes of the solutions of organotin compounds, containing increasing amounts of compound from 0.01mg to 0.2mg, were added to 5ml of dithizone solution (0.02mg/ml), and diluted to 10ml with carbon tetrachloride. After ten minutes the absorption of the solution in a 1cm cell was measured against a 0.01mg/ml solution of dithizone. Thus the influence of excess of dithizone on the absorption of the sample was eliminated.

Procedure

50ml of the solution of organotin compound in water was extracted twice with 5ml of CCl_4 . In the combined extracts the concentration of organotin compound was determined as follows. To 5ml of dithizone solution (0.02mg/ml) the solution of organotin compound in CCl_4 was added dropwise from a micropipette, until a slight change of green colour occurred. The volume of CCl_4 solution taken in the analysis was noted. After diluting the sample to 10ml with CCl_4 the absorption of the sample was measured against 0.01mg/ml solution of dithizone in 1cm cell. The amount of organotin compound in the sample was deduced from the calibration graph, and the concentration of organotin compound in the analysed solution was calculated from the formula:

$$C = \frac{10}{V} \times A \times 20 \times 1.04$$
 where

C=concentration of organotin compound in analysed water solution as parts per million.

V=volume of CCl₄ extract, taken in the analysis (ml)

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A=amount of organotin compound deduced from the graph (mg).

1.04 = constant calculated from the distribution coefficient between water and CCl_4 .

Results

Using the method described it is possible to determine organotin compounds present in the analysed sample in amounts from 0.01 mg(see Fig. 1), corresponding to concentrations of 2ppm in CCl₄ solution, and 0.4 ppm in aqueous solutions.



From the shape of the calibration graphs, the linear parts of which were used for quantitative determinations, it is obvious that organotin compounds $(nBu_3Sn)_2O$ and nBu_3SnAc form complexes with dithizone.

The dithizone complexes are formed with the R_3Sn cation in equimolar proportions. Increasing the amount of organotin compound in the sample above the equimolar value (with respect to dithizone used) causes no significant change in the optical density of the formed complex.

The method described was used to determine the concentrations of organotin compounds in aqueous solutions. The solutions of TBTA and TBTO were prepared by diluting with water the 0.1 per cent solutions of the compounds in ethanol. The concentrations of the analysed solutions were 1, 15, 50, and 200ppm.

The results of these determinations are given in Table 1. Taking into account the low concentrations of organotin compounds in the analysed solutions, the results of quantitative determinations are considered satisfactory.

Concentration of TBTO taken (ppm)			1	15	50	200
Concentration of TBTO found (ppm)			0.93	14.3		_*
Concentration of TBTA taken (ppm)			1	15	50	200
Concentration of TBTA found (ppm)	••	••	0.95	14.2	52	215

*At concentrations of 50 and 200 ppm, a dispersion is formed, and the determination was not carried out.

The method described can be used to follow the leaching of tributyltin oxide and tributyltin acetate from antifouling paint films by various aqueous solutions.

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The effect of zeta potential on the optical properties of paints

By M. J. B. Franklin

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Summary

The significance of zeta potential as a factor affecting pigment dispersion is examined. A novel method for the determination of zeta potential in paints is discussed and applied to titanium dioxide pigmented air drying alkyd paints. It is concluded that in such systems the zeta potential of titanium dioxide contributes to the stability of pigment dispersion, but that this effect is small compared with stabilisation imparted by adsorption on the pigment surface of molecules from the medium. The zeta potential of the pigment does, however, become important when two or more pigments (extenders) are incorporated into the paint. Pigments of opposite zeta potential co-flocculate; this phenomenon can markedly affect the tint efficiency in coloured paints.

L'effet du potentiel-zèta sur les caractéristiques optiques de peintures

Résumé

On a examiné l'importance du potentiel-zèta en tant qu'un facteur ayant une influence sur la dispersion de pigments. On discute une nouvelle méthode pour déterminer le potentiel-zéta en peintures et l'on l'applique aux peintures glycérophtalliques, contenant de dioxyde de titane et qui sèchent à l'air. On conclut que dans tels systêmes le potentiel-zèta du dioxyde de titane fait-il une contribution à la stabilité de la dispersion pigmentaire, mais que cet effet est assez faible en comparaison de la stabilisation à cause de l'absorption sur la surface pigmentaire des molécules en provenance du liant. Cependant, le potentiel-zèta du pigment devient important lorsqu'on introduit deux ou plusieurs pigments (matières de charge) dans la peinture. Les pigments ayant des potentiels-zèta opposés deviennent co-floculés; ce phénomène peut produire un effet assez grave sur le rendement pigmentaire dans des peintures colorées.

Die Wirkung des Zeta-Potentials auf die Optischen Eigenschaften von Anstrichfarben

Zusammenfassung

Die Wichtigkeit des Zeta-Potentials als die Pigmentdispersion beeinflussender Faktor wird untersucht. Eine neuartige Methode zur Bestimmung des Zeta-Potentials in Anstrichfarben wird besprochen und bei lufttrocknender mit Titandioxid pigmenttierten Alkydlacken angewandt. Es wird gefolgert, dass das Zeta-Potential des Titandioxides in solchen Systemen zur Stabilität von Pigmentdispersionen beiträgt, dass aber diese Wirkung, verglichen mit der durch Adsorption auf der Pigmentoberfläche von Molekülen des Bindemittels erzielten Stabilisierung, gering ist. Wenn jedoch zwei oder noch mehr Pigmente (Streckmittel) in eine Anstrichfarbe einverleibt werden, wird das Zeta-Potential wichtig.Pigmente von entgegengestztem Zeta-Potential bilden eine Flockenmischung; dieses Phänomen kann in Buntemaillen die Ausgiebigkeit beim Abtönen merklich beeinflussen.

Влияние зета-потенциала на оптические свойства красок

Резюме

Изучается значение зета-потенциала как фактора влияющего на дисперсию пигментов. Обсуждается новый метод определения зета-потенциала в красках, который применяется в двуокиснотитановых пигментированных алкидных красках высыхающих на воздухе. Выводится заключение, что в таких системах зета-потенциал двуокиси титана содействует устойчивости дисперсии пигментов, но что этот эффект мал по сравнению с стабилизацией сообщаемой адсорбцией на пигментной поверхности молекул среды. Зета-потенциал пигмента однако становится существенным, когда два или более пигмента (наполнителя) входят в состав краски. Пигменты противоположных зета-потенциалов со-флоккулируют; это явление может существенно повлиять на эффективность оттенка цветных красок.

Introduction

The extent of light scattering by a pigment is determined by the refractive index of the material and the size and size distribution of the pigment particles. The manufacturing process controls the size and size distribution of the pigment, and the degree of dispersion of these particles in any given medium determines the hiding power. One of the factors which determines the degree of dispersion in medium is the charge residing on the pigment surface. It is the object of the present work to measure the magnitude of this surface charge and to assess its effect on dispersion stability in air drying alkyd systems.

Zeta potential

In a colloid system such as paint, redistribution of electrical charges takes place at the boundaries between the disperse phase and the continuous phase. This is due to selective adsorption of ions or polar molecules from the continuous phase, and gives rise to an electrical charge on the particles. Since the system as a whole is electrically neutral, an equal and opposite charge carried by counter ions appears in the continuous phase. The concentration of counter ions around the single charged particle decreases with increasing distance from the particle¹.

By reason of the charge on a particle there is a potential difference between a point at infinity and a point a finite distance from the particle-medium interface. This potential difference increases as the distance between the particle and the second point decreases. Its maximum value, at the interface, is called the surface potential. In an assessment of the contribution of charge to the properties of the dispersion it would be preferable to use the surface potential as the criterion. This is not possible, however, since the surface potential cannot be measured directly. If an electrical field is applied to a dispersion, the electrostatic force on the particles causes them to move along lines of force and the counter ions, with their solvated layers, move in the opposite direction. The layer of the continuous phase next to the interface is not mobile, and moves with the particle; thus the potential measured by observation of any of the electro-kinetic phenomena (electrophoresis, electro-osmosis, streaming potential) is not the true surface potential, but the potential at the shear plane that separates the fixed from the mobile parts of the continuous phase. This is called the zeta potential, and is used instead of the surface potential as a measure of particle charge.

Measurement of zeta potential by micro electrophoresis

The movement of charged particles through a medium when an electric field is applied to the system is called electrophoresis, and this affords a means of measuring zeta potential². Individual particles of a dilute dispersion contained in a suitable cell are observed by means of a microscope, and the electrophoretic mobilities are found by timing particles over a fixed distance, and dividing the calculated velocity by the value of the potential gradient applied to the cell. A number of precautions must be taken to ensure that the velocity observed is the electrophoretic velocity of the particles³; among these is the requirement that the velocity should be directly proportional to the applied field. If the applied field is too high, dielectric effects occur, which are proportional to the square of the voltage, and vary in different parts of the cell, thus making accurate measurement impossible. Crowl⁴ states that the applied field strength should not exceed 100 volts per cm; it is felt that this figure should not be regarded as a fixed value, as it depends on the conductivity of the system under examination. For example, field strengths of up to 500 volts per cm have been used with acrylic systems in a micro electrophoresis apparatus (conductivity 3.2×10^{-9} mhos). Fig. 1 shows the dependence of velocity on applied voltage for a titanium dioxide pigment dispersed in a 5 per cent solution of an acrylic resin (D2101/U9192, British Resin Products Ltd.) in xylene and butanol (xylene : butanol=4:1 by weight). It can be seen that there is no departure from linearity even at high field strengths.



Fig. 1. Relationship between mobility and potential gradient

Pigment dispersions used in micro electrophoresis experiments must be dilute (about 0.1g/l) for it to be possible to observe individual particles. Furthermore, the electrophoretic mobility is inversely proportional to the viscosity of the medium through which the particle moves, hence it is difficult to measure the mobility of a particle in a medium of the same resin concentration as is normally employed in paints; more dilute resin solutions must be used so that the mobilities are high enough to be conveniently measured, i.e. greater than about 10^{-2} micron/sec volt⁻¹ cm⁻¹. In the present work, using a micro electrophoresis cell similar to that described by Parfitt⁵, resins were diluted with suitable solvent to 5 per cent solids content and two methods were used to prepare samples:

(1) a very small amount of pigment was shaken with about 10ml of the dilute resin solution.

(2) a drop of paint was shaken with about 10ml of the dilute resin solution.

In each case the suspension was allowed to stand for about three minutes to clear the bubbles before the micro electrophoresis cell was filled. It was found that the mobility values obtained for the same pigment using the two methods of preparation of the sample did not agree, but that the values changed slowly with time tending to approach the same limiting value. This is probably due to the slow adsorption or desorption of resin, approaching equilibrium (Fig. 2).

The worth of electrophoretic methods for the measurement of zeta potential of pigment in paints is questioned because of the initial dependence of results on the method of preparation of the sample and the long period of time required before equilibrium values are obtained. Further, the equilibrium mobilities do not represent the conditions in the paint. As the change in mobility is most rapid immediately after dilution of the paint, it is not considered that extrapolation of mobility results to instant of dilution is a permissible procedure.

When white spirit thinned air drying alkyd systems are used, the conductivity is very low ($\sim 3.8 \times 10^{-11}$ ohm⁻¹cm⁻¹); hence applied voltages must be low in order to avoid undesirable dielectric effects, and therefore mobilities are small and difficult to measure accurately. This complication can be regarded as a further disadvantage of micro electrophoretic methods in such systems.

Measurement of zeta potential by electrodeposition

To overcome these difficulties, a method of measuring zeta potential has been developed which makes use of electrodeposition. Electrodeposition of paint films from water based paint is well known⁶, and in the present work the same principle has been applied to non-aqueous paints.

An apparatus was devised in which pigment particles in a paint migrate under the influence of an applied field and deposit on to an electrode suspended from the arm of an analytical balance. The increase in weight of the electrode is followed on the milligram scale of the balance, and plotted against time (Fig. 3). The gradient of such a plot may be used to calculate the zeta potential of the pigment in the paint, assuming that all the particles which reach the electrode stick to it. An important difference between this process and electrodeposition from aqueous paints lies in the resistance characteristics of the







systems. With an aqueous paint the electrical resistance of the circuit is initially low and builds up to high values as deposition proceeds. In white spirit thinned alkyd paints used in the present work, the electrical resistance is initially very high (about 10¹⁰ohms) and does not vary significantly during the deposition.



Fig. 4. Relationship between deposition rate and applied potential

As with micro electrophoresis, it is important to ensure that the velocity of the particles is directly proportional to the voltage applied. The deposition rate is a measure of particle velocity and Fig. 4 shows that the deposition rate is proportional to the voltage within the range observed.

Experimental

Materials

In the course of the present work a number of different pigments, resins and other paint components were required.

Pigments: (a) Titanium dioxide pigments.

The pigments used are listed in the table below. These two series of experimental rutile pigments were specially selected because of the wide range in zeta potential which is readily obtainable with relatively minor modifications to the coating composition. In each series the base material was the same throughout. These pigments do not necessarily possess any particular commercial attractions.

Sulphate Pigments			Chloride Pigments		
Pigment reference	Coating composition Wt % Al ₂ O ₃ Wt % SiO ₂		Pigment reference	Coating of Wt % Al ₂ O ₃	omposition Wt % SiO ₂
1	0.0	1.62	16	0.08	2.29
2	0.04	2.69	17	0.24	2.48
3	0.09	2.14	18	0.37	2.29
4	0.14	2.03	19	0.59	3.06
5	0.25	2.35	20	0.93	2.76
6	0.29	1.98	21	1.32	2.37
7	0.48	2.38			
8	0.68	2.36			
9	0.88	2.29			
10	1.25	2.00			
11	1.64	1.73			ŧ
12	1.98	1.51			
13	2.38	1.18			
14	2.86	0.84			
15	3.21	0.60			

List of titanium dioxide pigments used

In addition three commercially available sulphate process rutile pigments, designated as A, B and C, were used to study the effect of driers and solvents on the zeta potential of pigments. A was post treated with alumina, phosphate, silica and titanium dioxide, B and C were post treated with alumina and titanium dioxide. All pigments were equilibriated to 60 per cent relative humidity, 21°C. This ensured that all work would be carried out under conditions approximating to the normal conditions of use.

(b) Coloured pigments.

Table 2 lists the various commercially available coloured pigments which were used.

Colour In Part II refe	dex rence	Pigment	Manufacturer
Blue 15	74160	Fastona Blue RFR 55	Smith, Cornbrook and Cromford Colours Ltd.
Green 7	74260	Monastral Fast Green GNS	Imperial Chemical Industries Ltd.
Green 41		Monastral Fast Green GYS	,,
Green 10	12775	Monolite Fast Green YS	,,
Red 9	12460	Monolite Fast Red LFS	,,
Red 8	12335	Monolite Red 4RS	,,
Black 9	77267	Drop Black No. 300	Columbian International
Black 6 or 7	77266	Dixie Carbon Black • "Perfecto"	Anchor Chemicals Co. Ltd.

List of colour pigments used

Resins: In much of the work Wresinol W9951 (Resinous Chemicals Ltd.) was used for the preparation of the paints. Other commercial resins used were Paralac 10W (Imperial Chemical Industries Ltd.), Crestalkyd 119WS (Scott Bader and Co. Ltd.) and Wresinol W25000 (Resinous Chemicals Ltd.). All the resins were pentaerythritol-drying oil modified alkyd resin (63-68 per cent fatty acid). The viscosities (75 per cent resin in white spirit, 25° C) were: Wresinol W9951, 40-60 poise; Paralac 10W, 60-80 poise; Crestalkyd 119WS, 20-25 poise; and Wresinol W25000, 12-16 poise.

For some aspects of the present work a series of alkyd resins was required having a regular gradation of properties; since such a series was not readily commercially available, the resins were prepared in the laboratory. Two series of resins were prepared; in the first series the oil length was kept constant and the molecular weights were varied by stopping the reaction at different times, giving resins with a wide range of acid values; in the second series, the oil length was varied in order to alter the molecular weight, and the resins were prepared with acid values within a narrow range.

The materials used in the preparation of the alkyd resins were: Soya bean oil, bleached alkali refined grade supplied by S. Banner and Co., Liverpool (resins of constant acid value); linoleic acid (Frederick Boehm Ltd.) (resins of different acid value); glycerol, "Analar" grade (Hopkin and Williams Ltd.); pentaerythritol, laboratory reagent grade (British Drug Houses Ltd.); phthalic anhydride, commercial (Imperial Chemical Industries Ltd.); sodium hydroxide, "Analar" grade (British Drug Houses Ltd.).

The preparation of the resins was carried out in two stages in accordance with the recipe given in "Paint Technology Manuals," Part 3 (OCCA, 1961).

Table 3

		At 75% solids		
Resin	Acid value mg KOH/g	Viscosity (poise)	Specific gravity	Oil length
В	7.2	30.6	0.980	61.3
С	7.5	23.2	0.978	61.8
D	6.6	18.5	0.972	62.2
Ε	7.2	14.5	0.971	62.7
F	7.6	11.6	0.970	63.4
G	7.6	8.3	0.969	64.2
н	7.0	6.1	0.965	64.6
I	7.5	5.4	0.967	65.0
J	19.7	2.9	0.953	67
K	9.4	3.3	0.951	67
L	3.8	3.4	0.951	67
М	5.3	3.4	0.951	67
N	6.5	3.2	0.950	67
		l		

Table 3 lists the relevant properties of the resins.

The calculated hydroxyl numbers for resins B to I were within the range 33.5-36, and for resins J to N, within the range 58-61mg KOH/g.

Other materials used were:

"Nuodex" lead/cobalt naphthenates (Durham Chemical Groups Driers: Ltd.)

Solvents: High flash white spirit (Flash point 115°F) (Shell-Mex and BP Ltd). and n-butanol, "Analar" grade (Hopkin and Williams Ltd.).

Experimental methods and apparatus

Pigmentation of paint: Titanium dioxide paints for reflectance and zeta potential measurements were made up according to the following formulation:

Pigment	45g (after being stored humidity for 24 hours)	at	60	per	cent	relative
Resin (75 per cent nv)	12g					
High flash white spirit	21g					

The components were milled in a $\frac{3}{8}$ pint jar with 120g of 8-10mm ballotini for 16 hours. After milling, the following additions were made to 60g of the millbase:

Resin (75 per cent nv)	115g (This figure is adjusted according to the specific gravity of the dried resin, so that the PVC of the dried paint is 10 per cent)
Lead-cobalt driers	6.5 ml (i.e. Cobalt .05 per cent, Lead .5 per cent on the weight of dry resin)
Methyl-ethyl ketoxime	2ml

(10 per cent solution in white spirit).

The paints were allowed to stand for 24 hours before use.

The formulation was similar for paints containing coloured pigments in addition to titanium dioxide, but the colour was introduced as a separate millbase with the second resin addition. The ratio of titanium dioxide to colour pigment was 20:1 by weight.

Reflectance measurements: Five panels were spun at different film thicknesses (from about 20 to about 35 microns dry film thickness) from each paint for reflectance measurement. The thickness was controlled by the amount of extra solvent added. The paint thrown (during spinning) from the five panels was collected, and used to measure the zeta potential of the pigment. The reflectances were measured on a Harrison colorimeter, using the green filter. A black tile was placed behind each panel during the measurement, and glycerol was used to ensure a good optical contact between the glass panel and the black tile. A value for the reflectances at 30 micron film thickness was interpolated from the results.

Zeta potential determination: The determination of the zeta potential of a pigment required measurements of viscosity, dielectric constant, density of the paint and deposition rate. These measurements were performed on paints collected after reflectance panels had been spun, so that the reflectance and zeta potential results for each pigment were obtained from the same paint.

Viscosity was measured by the falling sphere method, with $\frac{1}{16}$ in diameter steel balls. Two coils were placed round the viscometer tube, 19.3cm apart, and impulses from two metal detector units connected to the coils were used to start and stop an electronic timer as a steel ball passed through the upper and lower coil respectively. The timer measured to 0.04 seconds, and results were reproducible to ± 0.5 per cent. To ensure that the velocity of the steel ball was

constant between the two detectors, the viscometer tube was filled to 10cm above the upper coil. Balls were dropped through a small funnel, and the tube was set vertically using a small plumb line, to ensure that the balls travelled along the axis of the tube.

The dielectric constant was calculated from the capacitance of a cell containing the paint: The cell was calibrated with "Analar" nitro-benzene and nitro-toluene.

The densities of the paints were measured with a hydrometer.

The apparatus used to measure the deposition rate of pigment from a paint consisted of a 4cm square of 22 swg brass, suspended by two wires (.02in diameter) from the arm of an analytical balance, and completely immersed in paint held in a rectangular cell (Fig. 5). The two inner surfaces of the cell



Fig. 5. The electrophoresis cell

parallel to the suspended plate were 5cm squares of brass, and the distance between them was 2.07cm. The two fixed plates were connected to a terminal of a high tension dry battery (120 volts, with tappings at 24, 48, 72 and 108 volts); the floating plate was connected to another terminal of the battery by means of a fine wire, allowing the plate complete freedom of vertical movement. The current was switched on and the weight of the freely suspended electrode plotted against time. (Fig. 3). Zeta potentials calculated from these measurements were reproducible to within ± 1.5 mv ($\sim \pm 3$ per cent). All experimental work was performed at 21°C in a constant temperature laboratory.

Calculation of zeta potential for deposition data

The particle velocity, v, is calculated from the deposition rate as follows:

$$v = \frac{D_p}{A \times C} \text{ cm/sec}$$

where D_p is the deposition rate of pigment (g/sec)

A is the area of the electrode (32cm²)

C is the pigment concentration (g/ml) in the paint.

C is calculated from the measured values of the densities of the pigment, resin, solvent, and paint, and the weights of the pigment, resin and solvent used. D_p , the true deposition rate of pigment, is calculated from the observed deposition rate, D_o , as follows:

$$\mathbf{D}_{\mathbf{p}} = \mathbf{D}_{\mathbf{o}} \times \mathbf{F} \times \frac{\mathbf{\rho}_{\mathbf{f}}}{\mathbf{\rho}_{\mathbf{f}} - \mathbf{\rho}_{\mathbf{p}}}$$

where F is the weight fraction of the pigment in the electrophoretic deposit ρ_f is the density of the deposit,

 $\rho_{\rm p}$ is the density of the paint.

The term $\frac{\rho_f}{\rho_f-\rho_p}$ is a correction for the buoyancy of the deposit in the paint.

F was determined for a number of pigments by applying 120 volts to a paint in the deposition cell for 24 hours, after which time sufficient deposit had formed for gravimetric analysis. After the dip coat had been removed, the deposit was weighed into a crucible, and ashed. The value of F was found to be independent of the duration of the deposition.

Run 1	0.81
Run 2	0.79
Run 3	0.83
Run 4	0.82

The average value of 0.81 was used throughout subsequent calculations. The density of the deposit, ρ_{f} , was calculated from the equation

$$\rho_{\rm f} = \frac{\rho_{\rm m} \times \rho_{\rm T}}{\rho_{\rm m} \times F + \rho_{\rm T} \left(1 - F\right)}$$

where ρ_T is the density of the pigment,

and ρ_m is the density of the medium.

 ρ_m is calculated assuming that the ratio of resin to solvent is the same in the deposit as in the bulk of the paint. This is obviously not true when adsorption of resin on to the pigment surface takes place, but the correction necessary

when a reasonable level of adsorption is assumed (i.e. about 2 per cent on the pigment, by weight) is so small that it is ignored.

Much work has been done in elucidating the theoretical relationship between the mobility of the particle and the zeta potential. If the dimensions of the particle are very much larger than the thickness of the ionic atmosphere surrounding it, the equation given by Von Smoluchowski⁷ holds:

$$\frac{v}{x} = \frac{\varepsilon \zeta}{4\pi \eta}$$

where v is the electrophoretic velocity,

x is the field strength,

 ε is the dielectric constant

and η the viscosity of the medium within the double layer,

and ζ represents the zeta potential.

If CGS units are used ζ and x should appear as ESU volts and ESU volts per cm respectively.

If the dimensions of the particle are very much smaller than the thickness of the ionic atmosphere, the equation of Huckel⁸ should be used

$$\frac{v}{x} = \frac{\epsilon \zeta}{6\pi \eta}$$

The conductivity, and hence the ionic concentration, of the alkyd paints used in the present work were very small. Under these conditions the thickness of the ionic atmosphere is very large compared with the size of the particles, and hence the equation of Huckel should be used⁵.

Results

This work is primarily concerned with the effect of the pigment surface on zeta potential and the contribution made by zeta potential to the dispersion of the pigment and hence to hiding power. A brief examination of the effects of the presence of driers, the acid value of the resin, and the polarity of the solvent on zeta potential have been included, since the zeta potential developed at the surface of a pigment particle in a paint depends upon all these factors.

Driers

The presence of a small amount of driers may alter the charge. This effect was demonstrated by measuring the zeta potential of three commercial pigments and paints with and without the addition of lead/cobalt driers. The results are shown in Table 4.

These results emphasise the importance of including driers in the present work.

Table 4				
Pigment	Zeta potential with driers (mv)	Zeta potential without driers (mv)		
A B C	22 46 38	7 47 40		

511

512

Resin

The effect of molecular weight and acid value were considered. Table 7 shows the relationship between zeta potential and viscosity of resin (taken as measure of molecular weight). It is evident that zeta potential is independent of this variable.

The effect of the resin on the charge of the pigment is apparently due to the acid number of the resins; paints were made up using one pigment and five resins of different acid values, and the zeta potential of the pigment in each paint was measured. The results, in Table 5, show that the charge tends to become more positive as the acid value increases. This is analogous to aqueous systems, where the zeta potential of an oxide such as titanium dioxide becomes more positive (or less negative) as the pH decreases², although the mechanism of charge formation in the two systems is not necessarily the same.

Zeta potential (mv) 66
66
71
70
70
78

7	ahl	P	- 5
•		-	-

Solvent

If some of the high flash white spirit in the paint is replaced by butanol, a more polar solvent, the charge of the pigment tends to become more positive. Table 6 gives the zeta potential of three commercial rutile pigments in paints with and without butanol. Table 6

Pigment	Zeta potential with butanol replacing 10% of white spirit (mv)	Zeta potential without butanol (mv)
Α	13	12
В	54	49
С	53	48

This confirms the work of Tamaribuchi and Smith⁹.

Pigment treatment

In the present work, it has been found that the contribution of the pigment to the charge depends upon two factors:

- 1. The composition of the pigment prior to any surface treatment.
- 2. The composition of the coating put on to the particles in the course of the surface treatment.

A coating composed of silica and alumina was chosen for these experiments as by altering the silica: alumina ratios large changes in zeta potential were obtained. The total coating remained substantially constant throughout.

Fig. 6 shows zeta potential as a function of the alumina content of the pigment coating for pigments prepared from both a sulphate and a chloride process pigment. It can be seen that in both cases there is a relationship between the composition of the coating and the zeta potential; the two series are not identical, due to a difference in base pigments.



A number of experimental pigments (all prepared from the same sulphate process pigment) were used to make paints with each of the eight soya-bean-oilmodified alkyd resins which had been prepared in the laboratory. Hiding power and zeta potential measurements were determined on each paint and the results are shown in Table 7. A graph of zeta potential of the pigment is shown as a function of the pigment coating for one of the resins in Fig. 7. All eight resins showed very similar trends.

	in E 4.5	Hiding power	432.8 435.4 435.4 431.6 431.6 431.6 431.6 449.4 1
	Res 1	Zeta potential (mv)	
	in D 8.5	Hiding power	429.5 433.5 433.5 433.5 433.5 433.5 461.5 461.5 466 1 1
	Res 1	Zeta potential (mv)	1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 -
Table 7	sin C 23.2	Hiding power	437.5 437.5 433.5 442 459.5 459.5
	Re	Zeta potential (mv)	12 12 14 15 0 0 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
	sin B 0.6	Hiding power	431 4335.5 4335.5 4335.5 462.1 462.1 462.5 1 462.5 1 462.5 1 462.5 1 462.5
	3 3	Zeta potential (mv)	$\begin{array}{c} -16\\ 0\\ 1\\ 1\\ 1\\ 1\\ 1\\ 1\\ 1\\ 1\\ 1\\ 1\\ 1\\ 1\\ 1\\$
	ty, poise	Coating (% Al ₂ O ₃)	0.0 0.04 0.25 0.25 0.25 0.29 0.29 0.29 0.29 0.29 0.29 0.29 0.29
2	Viscosi	Pigment	-96420800111645

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EFFECT OF ZETA POTENTIAL

Table 7 (continued)

in I 4	Hiding power	424.0 429.5 432.5 432.5 432.5 436.5 466.5 466.7 466.5 466.5
Res 5	Zeta potential (mv)	8 ¹ ⁰ ⁸ ² 22 ⁸ ⁰ ⁶ 62 62 62 62 62 62 62 62 62 62 62 62 62
H U	Hiding power	428 434.5 433.5 433.5 434.5 435 436 456 463 4635 4656 4656 4655 4655
Resi	Zeta potential (mv)	
in G	Hiding power	426.5 126.5 430 466 466 466 467.5
Res 8	Zeta potential (mv)	63 58 8 3 2 1 0 0 1 1 0 1 1 0 0 1 1 0 0 0 0 0 0 0
iin F 1.6	Hiding power	429.5 432 432 459 465 465 468 468 470.5
Res 1	Zeta potential (mv)	3888433 0 0 9
ty, poise	Coating (% Al ₂ O ₃)	0.0 0.04 0.25 0.25 0.28 0.29 0.29 0.29 0.29 0.29 0.29 0.29 0.29
Viscosit	Pigment	-96400800155545

515



Fig. 7. Relationship between coating composition and zeta potential. Resin C

Fig. 8 shows hiding power as a function of zeta potential for one of the resins. The increase in hiding power with increasing charge indicated by the graph was a feature common to the results from all eight resins. However, the hiding power at zero charge varied. This is illustrated in Fig. 9, where the zerocharge hiding power, interpolated from the graphed results shown in Table 7, is shown as a function of the viscosity of the resin (which may be taken as a measure of molecular weight).

Paints containing more than one pigment

A number of tinted paints were prepared to examine effects occurring when the coloured pigment carried a charge of sign either the same as or opposite to the titanium dioxide pigment. A simple test of the sign of the charge of a coloured pigment in a particular system is to dip two wires about 0.5cm apart into a small sample of millbase, and to apply about 120 volts across the two wires for a few minutes. On removing the wires, it is found that one or other carries a deposit of pigment; a negatively charged pigment will deposit on the wire connected to the positive of the voltage supply, and vice versa.

Initially, two coloured pigments were selected; a blue (Fastona Blue RFR55; SCC Colours Ltd.) carrying a positive charge in the alkyd system used, and a green (Monastral Green GNS, ICI Ltd.) negative charge. These pigments were used to tint four paints, two containing a positively charged and two a negatively charged titanium dioxide pigment. The compositions of the four paints are shown in Table 8.





Plate 1. Positive TiO₂ in centre left: Monastral Green GNS (-ve) right: Fastona Blue RFR 55 (+ve)



Plate 3. Mixtures of Fastona Blue RFR 55 (+ve) and Monastral Green GNS (-ve)



Plate 2. Negative TiO2 in centre

Negative colours Monastral Fast Green 6 YS Dixie Carbon Black Monolite Red 4 RS Positive colours Monolite Fast Green YS Drop Black No. 3000 Monolite Fast Red LFS



Fig. 10. Thin film electronmicrographs

top left: +ve TiO_2 , -ve colour top right: +ve TiO_2 , +ve colour bottom right: -ve TiO_2 , -ve colour bottom right: -ve TiO_2 , +ve colour bottom right: -ve TiO_2 , +ve colour

			Sign of charge on titanium dioxide	Sign of charge on coloured pigment (5% on pigment weight)
Paint 1	••		+	+
Paint 2		• •	+	-
Paint 3				-+-
Paint 4	••		-	

Table 8

Paints 1 and 3 were drawndown together, as were paints 2 and 4. The drawdowns are shown in Plate 1. In both cases, the paint in the positively charged titanium dioxide pigment is in the centre. Electron micrographs of thin films of the four paints are shown in Fig. 10.

This experiment was repeated with a wider range of coloured pigments (3 negative and 3 positive) and the drawdowns (Plate 2) showed the same behaviour as the original set.

Discussion

The medium

It has been demonstrated that the various components of the medium may all affect the charge developed by a pigment. The addition of lead-cobalt driers may affect the charge on the pigment surface, as shown in Table 4. The charge tends to be increased by using resins of higher acid values, or by replacing some of the solvent by one which is more polar (e.g. white spirit by butanol).

The pigment

In the manufacture of titanium dioxide pigments, controlled addition of various chemicals is used to determine such properties as crystal size and size distribution, or crystal allotropy. Also there are two distinct methods of manufacture, known as the sulphate process and the chloride process. Thus a variety of pigments is available for surface treatment, and although all the pigments arising are titanium dioxide, their surface properties and hence zeta potential in any given medium will differ. This is illustrated for two base pigments in Fig. 6.

The surface treatment of titanium dioxide pigments is essential for improving pigmentary properties such as ease of dispersion and durability. The treatment often involves the precipitation of a coating of hydrous metal oxides on to the particle surface; in much of the present work, experimental pigments coated with silica and alumina were used. As has already been mentioned, alteration of the silica : alumina ratio affords a convenient means of varying the zeta potential of the pigment in a given medium. The effect of pigment coating on charge is illustrated in Table 7 and Fig. 7. It will be seen that as the alumina content of the coating increases, the charge becomes more positive. This is analogous to aqueous systems, where basic oxides such as alumina carry positive charges when dispersed in water, and acidic oxides such as silica carry negative charges¹⁰.

In the present work, the hiding power for a paint at 10 per cent PVC is taken as a measure of the degree of dispersion of the pigment particles. It has been shown, in Fig. 8 and Table 7, that the hiding power improves as the charge on the pigment increases, irrespective of the sign. This is to be expected if the charge on a pigment contributes to its dispersion.

It will be noted that the minima in hiding power/zeta potential graphs do not occur at zero charge, but at small negative zeta potentials; furthermore, the hiding power achieved at a given zeta potential is greater if the charge is positive than if it is negative. This means that some other dispersion stabilising mechanism is either absent or reduced when the charge of a pigment is negative in an alkyd paint. Supporting evidence is derived from the observation that rapid sedimentation occurs with paints based on less viscous resins containing negatively charged pigment. A few days after the preparation of the paint a clear pigment-free layer appeared, being approximately quarter of the volume of the paint. Similar paints containing positively charged pigments, on the other hand, remained well dispersed over this period. It is believed that one factor involved is the adsorption of resin polymers from the medium on to the pigment surface. The adsorption isotherms for positive and negative pigments are completely different¹¹, and the orientation of the adsorbed molecules may also be different.

The viscosity of the resin, which is taken as a measure of its molecular weight¹², is shown in Fig. 9 to be of considerable importance: increasing molecular weight of the resin is shown to result in improved dispersion (hiding power) to a substantially greater extent than increasing zeta potential. The effect of zeta potential on hiding power becomes less as the molecular weight of the resin increases: this is believed to be due to the fact that the pigment dispersion is already stabilised by adsorption of long chain resin molecules.

Paints containing more than one pigment

When, however, more than one pigment is present in the paint, then the zeta potential becomes very important.

The signs of the zeta potentials were determined of a number of colour pigments, typical of those used to produce pastel colours in titanium dioxide alkyd paints. Among those examined approximately half carried positive charges, the rest being negative. It will be seen from Plates 1 and 2 that where the charges of the two pigments in paint have opposite signs, a dark colour is produced. When the two pigments have the same sign charge (whether positive or negative) the colour is lighter. The electron micrographs (Fig. 10) show that very heavy flocculation of the titanium dioxide occurs when the signs are opposite, but not when the signs are the same. Although the coloured pigments are not visible on the electron micrographs, it is believed that the observed flocculation is the result of co-flocculation of white and colour pigments.

Thus, whenever pigments of opposite charge are mixed flocculation will result, giving rise to dark tints in the case of coloured pigments. It must be emphasised that the charge of individual pigments must be measured under conditions as close as possible to those occurring in the paints, in particular, in the presence of the driers which are to be used in the paints. For this purpose,



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the charge is most conveniently measured by the electrodeposition techniques described.

The viscosity at low shear of paints containing more than one pigment is considerably increased if the pigments carry charges of opposite sign. Plate 3 shows a glass slide on which 11 drops of mixtures of millbases of positively and negatively charged pigments have been allowed to run down. This is another illustration of the flocculation which occurs under these conditions. (The slide was kept at an angle of about 10° to the horizontal in an atmosphere of nitrogen saturated with solvent vapour for about 24 hours. It will be seen that flow occurs hardly at all where the mixture of millbase is about even, because of the gross flocculation which has occurred.)

Conclusions

The most efficient use of titanium dioxide as sole pigment in an alkyd paint is achieved when the pigment has a large positive charge (greater than about 40mv), and when the alkyd resin has a high molecular weight (i.e. a viscosity at 75 per cent ny greater than about 40-50 poise). The pigment charge becomes progressively less important as the molecular weight of the resin increases.

In paint containing more than one pigment, it is essential that all pigments in the final paint carry the same sign charge, if heavy flocculation is to be avoided.

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An investigation into the relationship between the nature of surface defects and gloss*

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Summary

The intensity distribution in specularly reflected beams has been studied as a function of wavelength and angle of incidence. Paints prepared at a number of PVC's have been examined and the results are compared with measurements obtained with a fixed head gloss meter. Although several forms of energy distribution across the specular beam have been observed, it is suggested that in general these probably arise from combinations of two distinct types of defect:

- (1) Macro defects. These are of such a size that angular divergence of the specular beam is brought about by geometric optical effects.
- (2) Micro defects. These are of the order of size of the wavelength used and radiation is removed from the beam by diffraction or Mie type scattering.

The energy distributions around the specular angle corresponding to these defects give rise to broad curved peaks and narrow triangular peaks respectively. Other peak shapes appear to arise from combinations of these extremes.

A tentative explanation for the different types of energy distribution is proposed.

Une recherche sur le repport entre la noture d'imperfections superficielles et le brillant

Résumé

On a étudié la répartition de l'intensité des rayons réfléchis spéculairement en fonction de la longueur d'onde et de l'angle d'incidence. Peintures preparées à quelques CVP ont été examinées et les résultats comparés des cotes d'un brillancemètre à tête fixe. Bien qu'on ait noter plusieurs espèces de répartition d'énergie à travers le rayon spéculaire, on suggère qu'en général celles proviennent des combinaisons de deux types différents d'imperfection.

- (1) Macro-imperfections. Celles-ci sont de telle grandeur que les divergences angulaires sont provoquées par des effets d'optiques géometriques.
- (2) Micro-imperfections. Celles-ci sont de même gradneur de la longueur d'onde utilisée et par conséquent la radiation est enlevée à partir du rayon par diffraction au par diffusion du type Mie.

Les répartitions d'energie autour de l'angle spéculaire correspondante à ces imperfections produisent respectivement de larges maxima courbés et d'étroites maxima triangulaires. Maxima d'autres formes semblent provenir des combinaisons de ces extrêmes.

On propose une explication tentative pour les différents types de répartition d'énergie.

Eine Untersuchung der Beziehungen Arten von Oberflächenschäden und Glanz

Zusammenfassung

Die Helligkeitsverteilung in durch Spiegelung reflektierten Strahlenbündeln wurde als Funktion von Wellenlänge und Einfallwinkel untersucht. Geprüft wurden Anstrichmittel mit verschiedenen P.V.Ks. Die Ergebnisse werden mit Messungen verglichen, die mit einem Glanzmesser

*Read by Mr D. M. D. Stewart at the 1967 Australian OCCA Convention, Broadbeach, Queensland.

mit feststehendem Kopf vorgenommen wurden. Obwohl verschiedene Arten der Energieverteilung im Bereich des mittles Spiegel reflektierten Strahlenbündels beobachtet wurden, wird vorgeschlagen, dass diese wahrscheinlich als Folge von Kombinationen zweier ganz verschiedener Oberflächenfehler entstanden sind:

1. Makrodefekte. Diese sind so gross, dass eckige Divergenz des zurückgespiegelten Strahlenbündels durch geometrische optische Effekte zustande kommt.

2. Mikrodefekte. Diese besitzen die Grössenordnung der benutzten Wellenlänge, und Strahlung wird durch Beugung oder Mie-artige Streuung entfernt.

Die Energieverteilungen um den spiegelnded Winkel herum rufen analog deh obigen Defekten ausgedehnte, gekrümmte Höhen, beziehungsweise enge, dreieckige Spitzen hervor. Andersartig geformte Höhen scheinen durch Kombinationen dieser Extreme zu entstehen.

Versuchsweise wird für die verschiedenen Arten der Energierverteilung eine Erklärung vorgeschlagen.

Анализ зависимости между характером поверхностных дефектов и лоском

Резюме

Изучалось распределение интенсивности зеркально отраженных лучей как функция длины волны и угла падения. Рассматриваются краски изготовленные с различной пигментной объемной концентрацией (P.V.C.) и результаты сравниваются с измерениями полученными при помощи измерителя лоска с постоянной головкой. Хотя наблюдалось несколько форм распределения энергии поперек зеркального луча, выдвигается мнение что в общем случае они вызываются сочетанием дефектов двух определенных типов.

- 1. Макро дефекты. Эти дефекты такого размера—что угловое расхождение зеркального луча вызывается геометрическими оптическими эффектами.
- Микро дефекты. Эти дефекты порядка размера длины применяемой волны и излучение устраняется из луча диффракцией или рассеянием типа Мие.

Распределеиня энергии вокруг зеркального угла соответствующие этим дефектам вызывают широкие кривые пики и узкие треугольные пики соответственно. Другие формы пиков повидимому вызываются сочетанием этих экстремальных величин. Предлагается предварительное объяснение различных типов распределения энергии.

Introduction

Gloss is generally accepted as a subjective phenomenon and it has been customary to assess the relative values of different finishes by direct visual comparison. In such assessments, the observer is influenced by several factors, which he does not always recognise, in arriving at his judgment. Consequently, it is not possible to make strictly comparable instrumental assessments by means of a single physical measurement. However, it has become common practice to attempt to place gloss measurements on a more quantitative basis by measuring the specular reflectance (from paint film surfaces) with instruments such as the EEL gloss meter. Unfortunately, although the agreement between the subjective assessment and the instrumental method is generally good, there are exceptions, and instrumental measurements do not always rank paints in the same order as the subjective method.

The two most important factors in assessing the gloss of a paint film seem to be the total energy content of the specular beam and the sharpness of the image. A third factor of some importance is image contrast. Apart from the fact that many conventional gloss meters are capable of measuring only one of these factors (total specular energy), many of the instruments have optics with wide angles of acceptance and beams which are not accurately parallel



or uniform. Hence, the instruments are capable of detecting only gross distortions. The amount of information obtained can be increased by using a variable angle gloss head with high quality optics and small aperture to scan the reflected energy distribution. The area under such a scan is a measure of the total energy contained in the specular beam and the shape is a measure of the sharpness of image. Furthermore, as it may be supposed that many gloss phenomena are related to imperfections of the same order of size as the wavelength of the radiation used for assessment, it would be useful to obtain information which contained wavelength as a factor. Therefore, an instrument was constructed which would permit variation of the angle of incidence, angle of detection, wavelength and slit widths independently.

Spectro-goniophotometer

Fig. 1 is a diagramatic representation of the instrument, which is based on a student spectrometer. A Unicam SP500 provides monochromatic radiation of fairly wide band width, which is focussed on to the entrance slit of the spectrometer. The spectrometer table was adapted to provide a suitable mounting for the painted panels, such that the axis perpendicular to its plane (i.e. the axis of rotation) can be contained in the front surface of the paint film. Table levelling screws may be adjusted to achieve this coincidence, thus permitting the angle of incidence and/or detection to be varied without movement of the image centre. Reflected radiation falling on the telescope is focused on the exit slit, behind which is mounted a photomultiplier tube, fed by a stabilised EHT supply. The amplified signal from the photo tube is fed to a linear pen recorder. The telescope assembly can be rotated by a synchronous motor through a gearbox at a minimum rate of $\frac{1}{2}^{\circ}$ per minute, or more rapidly as required. Thus, for any angle of incidence (within the geometric limitations imposed by the instrument design), the telescope can be driven to scan through the angular energy distribution of the specular beam and the resulting peak shape is plotted by the recorder.

Method of use

Absolute reflectance measurements have not been attempted, although these could be made by setting the telescope at 180° to the collimator and removing the specimen. The normal procedure has been to compare peak shapes with each other and with those obtained from a standard black glass plate. The entrance and exit slits are adjusted to the same width, under which condition the scan of an unreflected beam produces a perfectly triangular peak. (For any other slit width relationship, the plot of the energy distribution would be trapezoidal.) The peak width at half the peak height (measured in degrees) corresponds to the acceptance angle of the instrument which, in the case of all the work reported here, was $\frac{1}{6}^{\circ}$. Hence, a perfect surface would produce a reflected beam giving rise to a perfectly triangular peak of half width $\frac{1}{6}^{\circ}$. Any deviation from this shape must result from surface irregularities.

The sensitivity of the instrument was normally adjusted by varying the EHT of the photo tube, or amplifier gain, so that under whatever conditions the instrument was used, the standard black plate produced a peak with a height roughly corresponding to the full chart width. The traces obtained from the

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standard black tile are very nearly perfectly triangular, there being only slight broadening and curvature at the base of the peak. (There is no doubt that the base of the peaks would show marked curvature if examined at high amplification.) The background level of radiation, per unit solid angle, arising from diffuse scattering within the body of the film, is so low (relative intensity is $<10^{-4}$ of the specular maximum) that for the acceptance angles used, it is undetected and does not affect peak shape.

Two quantities can be obtained from the recorded peaks; these are peak height and peak area. They are expressed as percentages of the corresponding values obtained from scans of the standard black plate and are referred to as peak height ratios and peak area ratios. The height ratios were found to be generally reproducible to $\pm \frac{1}{2}$ per cent. The peak area ratios are equivalent to the measurements obtained with a fixed angle gloss head, provided that the specularly reflected beam has not been so broadened that it extends over a greater angle than the acceptance angle of the fixed head (ca. 2° in the case of the EEL gloss head). It is clear that, in the case of perfectly triangular peaks, the peak height ratio and peak area ratio should be identical. Areas were measured in all cases by cutting the peaks out and weighing them, and are consequently less precise than the peak height ratios.

Results

The effects of different methods of paint application

For this part of the investigation, a set of paints prepared from a variety of pigments made up in long oil alkyd at 18 per cent PVC were applied to duplicate test panels. Three different methods of application were used:

- (i) Bar applicator giving a 3mil wet film.
- (ii) Spinning. The paints were reduced to a standard viscosity. $15\frac{1}{2}$ mls of paint were left for two minutes on the centres of the plates which were then spun at 550rpm for three minutes. The dry film thicknesses obtained were about 1mil.
- (iii) Brushing. The paints were brushed on to the panels in one direction only.

All panels were air dried for seven days before commencing measurements.

The peak height and peak area ratios were determined at 550nm for 45° incidence and the specular reflectances were measured with a 45° EEL gloss head. The information from the plates prepared by spinning and by the applicator is presented in Table 1. In all cases there is excellent agreement between the gloss head measurement and the peak area ratio. This is to be expected as the general level of specular reflectance is high, the peaks are all triangular, and each measurement is an estimate of the total specularly reflected energy.

Many of the peak height ratios (groups a and c) show excellent agreement with the area ratios and the EEL gloss head results. In none of these cases did the surfaces show distortions which were visible to the naked eye, and the energy distribution reflected from these surfaces gave rise to triangular peaks, that is the surfaces were plane by geometric standards. Some of the plates prepared with the applicator (group b) produced peaks which showed a slight

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Peak and gloss characteristics for spun and applicated plates (550nm and 45°)

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Group		9			l	Ī		ſ							l		- p -		
Pigment	1	-	7	7	e	e	4	4	2	5	4	4	-	5	5	9	9	7	1
Application		Appli	icator			Appl	cator				Spin	ning				S	pinnin	50	
Peak height ratio (%)	90	87 <u>1</u>	88 <u>1</u> 88 <u>3</u>	89	87	87 <u>1</u>	91	89	83 <u>1</u>	$85\frac{1}{2}$	68	92 <u>4</u>	90	91	69	70 <u>1</u>	71	80	62
(Two parts of same plate)	$89\frac{1}{2}$	88 <u>1</u> 882	$88\frac{1}{2}$	89	87 <u>1</u>	87 <u>1</u>	16	68	84 ¹ / ₂	84 <u>1</u>	90 ¹ / ₂	89	88 <u>1</u> 88 <u>1</u>	88	67 <u>1</u>	67½	73	801	71
Peak area ratio (%)	88	89 <u>1</u>	68	88	96	$89\frac{1}{2}$	94	95	85	85	16	91	89	96	94	86	85	92 <u>4</u>	892
EEL Glosshead value (%) Mean of six Readings	91.0	87.8	89.6	87.7	91.9	91.4	91.3	90.5	84.2	84.2	9.09	91.3	88.8	91.0	91.7	86.7	85.4	92.9	92.6
Plate examination	Sr	nooth	surfac	9	×	few sl irregul	ight lo arities	cal		Genera	ully sm	nooth s	urface		W	ore or effe	less or ects vis	ange p ible	eel
Peak shape	Per tria	fectly' ngular			Slig tails othe triar	ht smø srwise ngular	ار =	\triangleleft	÷	'Perfe triang	ctly' ular	\bigtriangledown			Mo bro: peal	re or l adenec ks	ess 1		

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departure from triangularity associated with a small amount of distortion that was visible in the surface. Here the peak height ratios are somewhat less than the peak area ratios. The peaks obtained from the panels in group d showed considerably greater deviation from the triangular shape and a correspondingly greater reduction in the peak height ratio as compared with the area ratio. Visual examination of the paint surfaces in this group revealed a pronounced orange peel effect and also some radial lines, presumably produced by the spinning.

To present a picture of this type of visible defect, the reflection of a rectangular grid in the surface of the plate being studied was photographed. Surface distortions large enough to be visible to the naked eye are shown up by the corresponding distortions caused in the photographed image of the grid. The grid image obtained from one of the plates from group d is shown in Fig. 2, alongside that obtained from the standard black glass plate, and comparatively large surface distortions are clearly visible.

The good reproducibility of peak height ratios in groups a, b and c is a further indication of the lack of gross surface distortions which affect peak shape. Conversely, the poor reproducibility of group d is a result of surface distortions which are present and which cause deviations from triangularity by geometric divergence of the specular beam.

Gross surface distortions were studied in more detail using the brushed plates, which had more obvious lack of uniformity of surface, the brush marks being more pronounced in some areas than in others. Four positions on each plate were measured, two with the axis of rotation parallel to the brushing direction and two with it perpendicular to that direction. These results, together with conventional gloss measurements, are presented in Table 2.

Once again, there is agreement between the conventional EEL measurement and the peak area ratio, but the peak height ratios show a considerable amount of variation and difference from the area ratios. Further, the peak shapes differ quite markedly from the simple triangular shapes which we associate with plane surfaces. In general, visual observations showed that those parts of the panels where the differences between peak height and peak area ratios were the greatest were those showing the most pronounced brush marks. Despite the gross nature of these distortions, the total reflected energy, as measured by either the peak area ratio or the conventional gloss meter, is still high and compares well with those values obtained from either applicated or spun panels prepared from the same paint.

This is illustrated by the grid photographs in Fig. 3 where two plates, one prepared by brushing and the other by application, but with similar gloss (EEL readings 87 per cent and $89\frac{1}{2}$ per cent), are compared. It is clear from the photographs that one surface contains considerable distortion, whereas the other does not. The peak height ratios are quite different, being 87 per cent for the applicated plate and varying from 57 per cent to $82\frac{1}{2}$ per cent, depending on the orientation of the brush marks and the area of the plate examined, for the brushed plate.

Fig. 2. Surface distortions in a spun paint film



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	EEL glosshead value (%) Mean of 6 readings	94.1	93.1	87.6	91.4	90.1	90.4	97.1	97.8	91.6	91.3
	allel to direction Position 4	95	06	85	92	60	89	97	67	90	84
and at 45°)	ratios (%) Axis par brushing Position 3	961	861	86 <u>1</u>	93 <u>1</u>	$90\frac{1}{2}$	93 <u>1</u>	$97\frac{1}{2}$	102	$93\frac{1}{2}$	88
tes (550nm c	Peak area endicular g direction Position 2	92 <u>4</u>	87	(73)	86	85	89	86	96	87	84 <u>1</u>
ıble 2 · brushed pla	Axis perp to brushing Position 1	93	87	881	95	87 <u>1</u>	89	96	$100\frac{1}{2}$	84	68
Tc ea ratios for	allel to lirection Position 4	76	80	42	41	53 <u>1</u>	67	77 <u>1</u>	78	70	65
height and a	ratios (%) Axis part brushing c Position 3	62	71	552	475	65 <u>1</u>	$73\frac{1}{2}$	$62\frac{1}{2}$	59	57	70 <u>1</u>
Peak	Peak height endicular g direction Position 2	80	85 <u>1</u>	67	6712	76	$74\frac{1}{2}$	95 <u>‡</u>	94	81	86
	Axis perp to brushing Position 1	88 <u>1</u>	89	79 <u>5</u>	86	831	79 <u>4</u>	95	91	75 <u>1</u>	$87\frac{1}{2}$
	Pigment		1	2	2	3	3	5	5	8	ø

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Fig. 3. Comparison of surface distortions in brushed and applicated paint films

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Without exception, the peak height ratios obtained when the instrument axis was parallel to the brushing direction were lower, and the corresponding peaks less sharp, than those obtained when the axis was perpendicular to that direction. This difference in energy distribution across the specular beam for the two orientations is to be expected from the type of surface irregularity known to be present. See Fig. 4.

Furthermore, in the case of perpendicular orientation of the axis to the brushing direction, there should be a small quantity of energy specularly reflected out of the plane containing the incident beam and the detector; this will be lost from the system. Whilst there are indications that this may be so, results to date do not prove it.

These results indicate quite clearly that although large surface distortions can affect the angular distribution of specularly reflected energy, the total quantity is not affected.

Relationship between gloss and PVC

Four sets of paints covering a wide range of PVC were made from two different pigments in an alkyd and an acrylic medium. Measurements obtained with the authors' instrument at 45° incidence and 550nm monochromatic radiation, together with the readings obtained from a conventional gloss meter, are presented in Table 3.

With the exception of the paint made from pigment B at 58 per cent PVC, the peaks are very nearly perfect triangles, with peak height and peak area ratios in very close agreement. The surfaces were extremely flat (in the macro sense) as demonstrated by Fig. 5, which was obtained by the method described previously. For these two plates there is a large difference in gloss, one plate having a value of 63 per cent and the other 33 per cent, even though there is no surface distortion visible in either plate. Clearly, the loss of gloss in this case does not arise from large scale surface distortions, as a considerable and variable amount of radiation has disappeared from the specular beam without modifying the general shape of the peak. The process involved must be one which produces a discrete peak of energy at some other angle, or is capable of diffusing the energy fairly uniformly through a large solid angle. In the latter case, the level of energy falling within the solid angle subtended by the detector system would be sufficiently small, in comparison with peak height, for broadening of the triangle to be undetected. No secondary peaks have been found, therefore a general scattering phenomenon is considered to be responsible for the energy loss. This is consistent with the lack of visible irregularities since the size of imperfections responsible for such a phenomenon would be expected to be extremely small.

A standard method for studying small imperfections in plane surfaces relies on the use of an interference microscope, by means of which irregularities as small as 50nm can be detected. Interference micrographs of the paint surfaces studied have been taken and typical examples are shown in Fig. 6, the plates used being the same as those shown in Fig. 5.



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Fig. 4. The effect of scan direction on unidirectionally brushed panels

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	Pigment volume concn (%)	Peak height ratio (%)	Peak area ratio (%)	EEL glosshead value	Peak shape	Pigment volume concn (%)	Peak height ratio (%)	Peak aren ratio (%)	EEL glosshead value	Peak shape
<u> </u>	10	96 <u>4</u>	96	100	V	10	651	66	73	\ \
	19	8212	82	89	<	19	562	56	57	\leq
igment A	28	552	56	56		30	491	49	47	
	36	63	63	70		36	324	33	39	peaks
	46	113	113	100	e.g.					c.g.
	26	65 <u>1</u>	66	70	\Box	5	72 <u>4</u>	73		<
C transit	36	57	58	62		10	. 55	55	55	\leq
Ignicili D	50	652	66	71	<	14	45	4	36	1
	58	33 <u>5</u>	11	70						

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Using the method described in the Appendix, the degree of irregularity of the interference fringes has been analysed and estimates of the micro-roughness obtained. The results are presented in Fig. 7, which shows the gloss head value plotted against the roughness factor. It is immediately evident that in general terms the peak height ratio and the gloss decrease as the micro roughness increases. Within the authors' experience, this micro roughness is always less than the wavelength used for the examination (550nm).

Fig. 7. Percentage gloss in relation to roughness (i.e. measure of micro defects)

Assuming that each defect acts as a scattering centre, a connection between roughness and specular reflectance would be expected. Clearly, the greater the number of scatterers and the greater the efficiency of each, the greater the proportion of energy removed from the specular beam. Considering the size of defect involved in this scattering phenomenon, it is likely that the process will be similar to Mie scattering, in which case the efficiency of the defects as scatterers will be a function of their size and wavelength.

To examine this hypothesis, the variation in specular reflectance of the same panels was studied as a function of wavelength. All the panels were examined at 45° incidence at nine wavelengths in the range 350-750nm. The results for pigment A in alkyd resin are shown in Fig. 8. All of these surfaces produced triangular peaks, so that the results have not been confused by broadening of the specular beam by geometric effects.

The results show that:

1. Each curve possesses a slight minimum which, as the PVC increases, moves towards shorter wavelengths.

2. As the PVC increases, there is first of all a decrease in gloss followed by an increase; alternately it decreases again.

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This pattern is quite consistent with Mie type scattering if one considers that the final setting in a paint film causes the surface to contract on to an underlying layer of pigment (Fig. 9). At lower PVCs, the point defects are relatively few and will, therefore, scatter less radiation; hence, at very low PVCs the gloss will be high. As the PVC increases, the number of scattering points will increase, causing more scattering and reducing the gloss. Some change of efficiency will also arise because the distance between particles decreases; hence, the upper surface has a lesser distance between particles over which it can sag, effectively reducing the size of the scattering defects. This correlates with the movement of the gloss minimum to shorter wavelengths as the smaller defects would be expected to scatter more efficiently at shorter wavelengths. It is also consistent with a stage being reached such that the defects become so closely crowded, and hence so small, that their scattering efficiency in the visible region is low and the gloss rises again. This appears to take place in the present instance between 28 per cent and 36 per cent PVC.

Fig. 9. Diagrammatic representation of paint film surfaces at various pigment volume concentrations

Reverting to Table 3, it will be noticed that for most paints the agreement between the gloss head and peak area ratios is not nearly as good as it was in the earlier experiments. The panels scanned for Tables 1 and 2 had relatively high gloss; beam broadening was produced by a geometric process and there was little evidence of diffuse scattering. These geometric effects would be independent of wavelength. The effects demonstrated in Table 3 are predominantly wavelength dependent, hence there are differences between the gloss head, which uses white light, and the peak area ratios for 550nm monochromatic radiation.

Combinations of both types of defect

The two different types of defect—a macro defect which produces broadening of the specular beam by geometric effects, and a micro defect which is responsible for loss of energy from the specular beam by diffuse scattering—are shown diagrammatically in Table 4.

peak shapes	Comment	Triangularity and base width unaffected, but peak height and area reduced with increase in micro defects.	Peak area decreases as micro defects increase. The spread of the specular beam increases (i.e. the peak height decreases) with increasing slope of the irregularity : either by decreasing defect base width (ii), or by increasing defect height (iii).	A longer "tail" is produced by increasing the range of defect slope in the distorted regions (ii). With more local areas of irregularity present, energy is transferred from the triangular part of the peak to the "tail," which therefore becomes thicker (iii). The total peak area decreases as micro defects increase.	lead to peaks which show general broadening with tesses.
m of surface irregularities and resulting	Peak shape	Triangular peaks	(i) (ii) Feaks (iii)	(i) Peaks triangular (ii) (iii) (iii	proportions of different macro defects tails of various lengths and thickne
Diagra	Surface	(a) " Plane "	(b) Macro defects : ・ ・ ・ ・ ・ ・ ・ ・ ・ ・ ・ ・ ・ (i) ヘ・ ヘ・・ ヘ・・ ヘ・・ ・ ・ ・ ・ (i)	(c) Combination ; Areas of plane surface with local regions of macro distortion. (i) (i)	(d) Appropriate combinations of various 1

Table 4

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There must be an intermediate surface defect, too large to scatter and too small to be geometric, which distorts the specular beam by a diffraction type of effect. This will also produce wavelength dependent effects.

A third type of surface which gives rise to a characteristic peak shape is also included. This is a predominantly plane surface which has local regions of distortion and gives rise to peaks which are obviously triangular but possess tails. Such surfaces can still be regarded as combinations of the two basic types—micro defects, causing changes in overall peak height, and relatively large local macro irregularities with a low frequency of occurrence, producing the tails. This particular type of surface is very common, as the irregularities which we now consider are often produced by dust and bubbles formed during drying. It is a consequence of this type of defect that surfaces giving rise to perfectly triangular peaks can only be produced under very stringent conditions.

To illustrate the range of peak shapes which can be produced, six plates were prepared by modifying the milling conditions during the paint preparation in order to produce paint films with a wide range of nibby finishes.

After classification in order of nib count, the plates were scanned and the results are presented in Table 5. In addition to the measurements previously quoted, the base width of the peak and the peak width at half height are included.

The peak area ratios and the gloss head measurements indicate that the specular reflectance is sensibly constant for the first four plates in the series. In the case of the sixth plate there is a reflected energy distribution in which the peak area ratio is appreciably different from the gloss head measurement. This is because the angular width of the specular beam exceeds the acceptance angle of the gloss head. The first plate in the series gives a peak which is generally very broad and has the characteristics of a surface with gross distortions. In fact, visual observations showed that the main defect was a series of ripples across the surface. The second peak is almost typical of the low PVC peaks shown in the previous series, but with a slight broadening at the tail which is due to the presence of the nibs. The peaks further on in the series follow the general pattern arising as a result of the increasing number of surface nibs, producing geometric beam broadening and hence long tails. Finally, we have so much gross distortion that there is insufficient plane surface to give rise to a triangular component. It should be stressed that the lower gloss level of the last two plates relative to the others arises from loss of radiation from the specular beam by the scattering phenomenon.

As a further example of the analysis of deficiencies from the appearance of the peak shape, we can refer back to the 58 per cent PVC alkyd paint which was made from pigment B (Table 3). The peak was very far from being triangular and the peak height ratio of $33\frac{1}{2}$ per cent was very much lower than the gloss meter reading of 70 per cent. This result is consistent with there being a gross irregularity of the surface causing beam spread; at the high PVC used the paint flow would be inhibited during drying and a plane surface would not be produced.

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Peak and gloss characteristics for a series of nib plates (550nm and at 45°)

	,				(
Plate number	(1)	(2)	(3)	(4)	(5)	(9)
Nib count (per sq. cm.)	20	26	68	130	310	830
Plate examination	Plate surface considerably rippled. A few small nibs.	Plate surface slightly rip- pled. $\sim 5\%$ covered by medium nibs.	Apparently flat surface. ~25% cov- ered by med- ium and small nibs.	Surface flat $\sim 50\%$ covered by small nibs.	$\sim 80\%$ covered by small and very small nibs.	Surface covered by very small and extremely small nibs.
Resulting peak shape	\triangleleft	\bigtriangledown		\triangleleft	\langle	
Peak height ratio (%)	$49\frac{1}{2}$	74	70	56 <u>1</u>	24 ¹ / ₂	4
Peak area ratio (%)	85	87 <u>1</u>	89	85	70	24
EEL glosshead mean value (%)	90.6	87.0	91.7	82.9	73.0	35.4
Width of peak base (cms)	П	2	12	20	21	24
Peak half height width (cms)	2.95	2.15	2.15	2.35	4.2	10.0
(Black gl	ass plate : triang	ular peak; base v	width 4 cms ; wid	Ith at half peak l	height 1.9 cms)	

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Fig. 10. Diagrammatic representation of an interference photograph

Conclusions

The presence of two types of surface defect has been discussed.

- (i) A micro defect which removes energy by a scattering process and is responsible for loss of reflectivity.
- (ii) A macro defect which is responsible for beam spreading by geometric reflection.

Combinations of these two types of defect have been shown to be capable of accounting for the various types of gloss phenomena observed.

Acknowledgment

The authors wish to thank the Directors of Laporte Industries Limited for permission to publish this work.

[Received 8 February 1968

Appendix

Estimation of surface roughness from interference photographs

The methods of studying surface defects by interferometry are well known and can be applied to obtain estimates of surface roughness. In our case, the spacing of successive fringes, S, measured along a line drawn perpendicular to the general fringe direction, was used as the basis of a roughness estimate. Fig. 10 depicts two regions of a typical interference photograph and alongside it the sort of surface configurations which produce them. Let Δ be the height difference between two adjacent points on the plate. This is positive when the (n + 1)th fringe corresponds to an increase in surface height when compared to nth fringe and negative when there is a decrease in height.

From the diagram it is obvious $Z_1' - Z_1 = \lambda/2$ and

that $Z_1' - Z_1 = S_1 \tan \beta - \Delta_1$

i.e. $\Delta_1 = S_1 \tan \beta - \lambda/2$ (Δ_1 -ve)

and $\Delta_2 = S_2 \tan \beta - \lambda/2$ ($\Delta_2 + ve$) i.e. $\Delta = S \tan \beta - \lambda/2$ (in general).

Whilst it is obvious that the mean value of Δ is zero and cannot be used to estimate surface roughness, the value of σ_{Δ} (the standard deviation of Δ) can.

But
$$\sigma_{\Delta} = \frac{\sigma_{\rm S}}{S} \cdot \frac{\lambda}{2}$$

so the roughness, as defined here, can be found simply from the standard deviation of the distribution of fringe spacings, σ_s , the mean spacing S and the wavelength used for the measurement λ .

In our work the largest value of σ_{Δ} which was recorded was 0.06μ . This implies that 99.9 per cent of the height differences are less than 0.36μ (i.e. $6 \times \sigma_{\Delta}$).

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Short Communication

The durability of paint systems Standard laboratory testing compared with painting time schedules on the building site

Final Report*

By T. A. Banfield

Introduction

In 1961 the Research Liaison Sub-Committee of the Newcastle Section of the Oil and Colour Chemists' Association commenced a project to determine whether any marked effects on the outdoor performance of a paint system are caused by different painting time schedules and different seasonal climatic conditions at the time of painting. A report on this project was presented by Dr A. J. Seavell on behalf of the Sub-Committee at the Association's 1963 Conference, Scarborough—see "JOCCA" 1963, **46** 719. At the time of that report the paint systems had been exposed for 18 months to 24 months according to the time of painting; exposure was continued for another two years and the present report summarises the results obtained in this period.

The materials and methods used are detailed in Dr Seavell's 1963 report. Briefly, British Columbian pine panels were painted with four paint systems (acrylic emulsion, PVA copolymer emulsion, penta-alkyd gloss, VT-alkyd gloss) in accordance with seven time schedules representing laboratory and building site conditions, and exposed at eleven exposure sites representing a wide range of temperate weather conditions. The reporting procedure was to compare each test panel with its own control prepared in accordance with the laboratory time schedule (24 hours between coats applied indoors and seven days ageing indoors), the test panel being described as "equivalent," "worse," or "better" than the control under headings such as chalking, crazing, flaking, etc. This avoided difficulties arising from observers at the eleven exposure sites having different ideas as the extent of breakdown, but precluded any numerical comparisons. In continuing the exposure tests, it was decided to ask the observers to report the condition of the test panels and control panels in accordance with the ASTM numerical scale. This revised reporting procedure enabled numerical comparisons to be made between the different painting time schedules, which was the objective of the experiment. Admittedly there are inevitable differences between observers at the various sites, but it was considered that these could be eliminated by taking the average results for the eleven sites; the results show that this is the case.

*Prepared by Dr Banfield on behalf of the Research Liaison Sub-Committee of the Newcastle Section of the Oil and Colour Chemists' Association.

Results

In the earlier report, Dr Seavell listed three main conclusions—see "JOCCA" 1963, p. 746—and it is proposed to consider how these are affected by the later observations.

(i) The objective of the project was to determine the effects of different painting time schedules on paint performance, and the interim conclusion was that these are not marked. The later results reinforce this conclusion, the average of the eleven sites showing a difference of only 2 per cent between the seven painting time schedules. Individual sites showed differences greater than 2 per cent but no trends as to the effects of polluted or non-polluted atmospheres were shown by the figures.

(ii) Comparing artificial weathering cycles with natural weathering, the four-year results confirm the interim conclusion that the DEF1053 Method 26 cycle develops blistering to an unrealistic degree. No significant blistering has appeared under conditions of natural weathering, and this is in accord with the results of the modified artificial weathering cycle. (It may be noted that the cycle of BS3900, F3 of 1966, is essentially the same as the modified cycle used in the present project.)

(iii) The effect of environment was found to be appreciable in respect of chalking, dirt retention, and overall appearance; the interim conclusion was that it had no effect in respect of film failure affecting the protective properties. Longer exposure has confirmed these findings.

Conclusions

The conclusions given in Dr Seavell's interim report in 1963 have been confirmed by the result after four years' exposure. With the four paint systems used in the project, there were no appreciable differences in paint durability resulting from seven different painting time schedules representing laboratory and building site conditions. An artificial weathering cycle essentially the same as BS3900 caused paint deterioration more in accordance with natural weathering than did the earlier DEF 1053 Method 26 cycle.

[Received 5 April 1968

Next month's issue

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

International Liaison Lecture—"Co-operation—a necessity for paint and printing ink research," by H. K. Raaschou Nielsen.

"The identification of pigments," by D. McClure, J. Thomson, J. Tannahill.

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Reviews

HARDNESS TESTING OF ORGANIC COATINGS

By P. FINK-JENSEN. London: Butterworth & Co., 1967. Pp. 51. Price 10s.

This booklet is the co-ordination by Mr Fink-Jensen of individual papers given by four eminent authors. It is in five chapters in good English and is sponsored by the International Union of Pure and Applied Chemistry.

Initially it deals with the concept and definition of hardness and the purpose and use of hardness testing.

Chapter 2 amplifies this definition with physico chemical considerations.

The sections dealing with mechanised and hand testing compare the methods available and this sums up the admirable purpose of this booklet.

The reader is left to form his own criticism of a well written and documented comprehensive guide to European hardness tests, with good tabulation and bibliography.

E. ESHER

RECOMMENDED METHODS FOR THE ANALYSIS OF DRYING OILS

Analytical Methods Sub-Committée of the Organic Coatings Section, Applied Chemistry Division, International Union of Pure and Applied Chemistry London: Butterworth & Co. Ltd., 1967. Pp. ix+47. Price 10s.

The sub-committee was formed in 1956, with representatives from Belgium, Denmark, France, Germany, Holland, Sweden and the United Kingdom, to undertake a review of the existing methods of analysis of drying oils and to edit a collection of such supplementary methods as were considered most suitable for adoption as international standards. Their findings were published in the third issue of "Pure and Applied Chemistry" of 1965 and a reprint is now made available in booklet form. It contains details of one physical and eight chemical methods of drying oil analysis with French and English texts printed on opposite pages. In contrast to previous IUPAC publications, the English version is to be taken as official in cases of dispute and, although this is generally clear and precise, it is not entirely free from certain peculiarities of construction which convey the impression that its author's knowledge of the language was not quite perfect.

The methods proposed for the determination of acid value, saponification value, unsaponifiable matter and Wijs iodine value are widely known and can be dismissed with the observation that some indication of the difficulties encountered when they are applied to the analysis of modified drying oils ought to have been included. The main interest of the booklet lies in its treatment of conjugated unsaturation, including ultraviolet spectrophotometry and the determination of Woburn iodine value, diene and pandiene values. These techniques are probably less familiar to many engaged in oil analysis and their relative advantages and shortcomings are fully discussed.

The remaining sections, concerned with the determination of polymeric fatty acids in stand oils and the detection of fish oil in linseed oil, and of linseed oil in linseed stand oil, are of lesser importance, since they should soon be replaced by chromatographic methods. These were not considered by the sub-committee owing to the difficulty of standardisation, but their possible inclusion at a later date was envisaged.

In general, it can be said that the booklet provides a useful contribution within the rather narrow terms of reference governing its production. It cannot, however, be recommended as a treatise on drying oil analysis, as it tells only a part of the story.

M. R. MILLS

PROTECTIVE COATINGS FOR METALS

By R. M. BURNS and W. W. BRADLEY. Third edition. New York: Reinhold Publishing Corporation, 1967. Pp. 735. Price £11 13s 6d.

This is No. 163 of the American Chemical Society's Series of Chemical Monographs, the present volume following the first edition of 1939 by R. M. Burns and A. E. Schuh, and the second edition of 1955 by the present authors. Dr Burns had a distinguished career at the Bell Telephone Laboratories and is now Scientific Advisor to the Stanford Research Institute; Dr Bradley was formerly on the staff of the Bell Telephone Laboratories and is now Associate Professor at the Institute of Colloid and Surface Science, Department of Civil Engineering, Clarkson College of Technology.

The Bell Telephone Company is a large organisation which makes a point of control of the quality and performance of all its purchases, including protective coating materials; following their experience in the laboratories of that Company the authors concentrate on the scientific aspects of quality control and evaluation of performance. Considerable information is given on the production and application of the various types of coatings so that their nature and behaviour may be understood, and there is ample information on the basic corrosion mechanisms to guide in choosing appropriate methods of prevention. As with earlier editions, this third edition is well illustrated; there are more than 2,500 references in the text to the original literature.

The first two chapters deal with the principles of corrosion and corrosion control and with surface preparation for coatings. The next ten chapters cover metallic coatings of all types: methods of application are described, a separate chapter being devoted to sprayed coatings, and zinc coatings receive special attention.

Three chapters are devoted to organic coatings. The first deals with chemistry and composition, covering the classification of organic coatings, chemistry of polymerisation, drying oils, natural resins, alkyds, phenolics, maleics, vinyls, cellulosics, silicones, epoxies, polyurethanes, bitumens, pitches, latex paints, pigments and pigmentation. The second chapter covers performance and evaluation, dealing with electrochemical aspects, inhibitive pigments, wash primers, adhesion, blistering, permeability, natural and accelerated exposure testing, physical tests and quality control. The third chapter on organic coatings deals with their application and use, describing methods for structural steel pipelines, industrial products, hot surfaces, non-ferrous metals and die cast alloys.

REVIEWS

The final section of the book deals with chemical conversion and anodised coatings, special purpose coatings, and corrosion inhibitors. There are separate author and subject indexes.

The monograph is a comprehensive and authoritative account of the theoretical and practical aspects of protective coatings for metals. As mentioned above it concentrates on the scientific approach to quality control and performance evaluation rather than on the technology of manufacture and application, and this feature makes it especially valuable to those responsible for selection of protective coatings. It can be thoroughly recommended.

T. A. BANFIELD

DIE SYNTHESE VON EINHEITLICHEN POLYMEREN

By J. H. WINTER. Berlin: Springer-Verlag, 1967. Pp. xiii+415. Price DM 89.

Einheitlich means uniform or homogeneous, but, such has been the preeminence of stereospecific polymerisation in the past decade of polymer science, that one might be forgiven for assuming that this is a book about stereoregular polymers or about *structural* regularity at least. Such, however, is not the case. Granted, these polymers and their preparation occupy a large part of the work, and constitute, perhaps, the area of greatest interest, but the author is careful throughout to treat stereoisomerism as but one source of uniformity, dealing with chemical and structural features before it, and with molecular weight distribution afterwards.

A brief first chapter introduces the concepts of uniformity, homogeneity and regularity as applied to polymers and, in 29 well illustrated pages, puts one at ease with their interpretation in terms of chemical composition and molecular structure, shape and size. This chapter deals in adequate detail with such topics as isotactic, syndiotactic, erythro- and threo-ditactic structures, conformation in general, the helical arrangement of DNA and the pleated sheet structure of polypeptides.

Chapter 2 (33 pages) provides a concise review of some relevant features of polymerisation, starting with a couple of pages on thermodynamics, and progressing through radical, ionic and Ziegler polymerisation, to a brief discussion of various heterogeneous catalyst systems and, finally, to poly-condensation, polyaddition, and enzymic processes. The treatment here is closely circumscribed by the purpose of the work as a whole, and the reader is assumed to be informed about elementary polymerisation kinetics and reaction mechanisms.

Most of the book is occupied by the third chapter (274 pages) on methods for preparing uniform polymers, and most of this deals with their synthesis from compounds of low molecular weight. The treatment is highly systematic, following the pattern set by Chapter 2; topics are divided up into sections, sub-sections and sub-sub-sections, so that a paragraph number has almost the significance of a Beilstein *Systemnummer*. Free-radical methods include polymerisation in clathrates, and many examples are given of ionic polymerisations in homogeneous systems which lead to polymers having one or other form of uniformity. Ziegler polymerisation is treated in depth and illustrated by a comprehensive series of examples which range from the obvious polyethylene and polypropylene to the less expected *trans*-polyacetylene, poly-2-*tert*-butylbutadiene-1, 3, the poly-norbornenes and the copolymers of ethylene with cyclopentene. Still following the pattern of Chapter 2, the use of "non-Ziegler" heterogeneous catalysts is illustrated by *inter alia* the silica, alumina, molybdenum oxide, chromic oxide and ruthenium carbonyl systems. Not surprisingly, the section on polycondensation is shorter and, after a brief discussion of polyesters and polyamides, is much concerned with polypeptides, polysaccharides and polynucleotides. Polyaddition is limited to a few pages on polyurethanes, polyethers having been treated earlier along with ionic and Ziegler polymerisation. Enzymic synthesis occupies 38 pages, devoted very largely to the nucleic acids, proteins and the genetic code, but the biosynthesis of natural rubber and cellulose is also discussed.

The remainder of Chapter 3, comprising some 48 pages, is concerned with chemical reactions by which uniform polymers may be modified or converted (as by isomerisation, dehalogenation, hydrolysis and etherification) and with the preparation of uniform from non-uniform polymers by chemical equilibration and various fractionation procedures.

The essentially practical nature of the book is emphasised by 17 pages on experimental methods (Chapter 4) in which brief instructions are provided for the preparation of 57 individual polymers. Almost half of these exemplify the use of *homogeneous* catalysis to produce materials exhibiting narrow molecular weight distribution or various forms of tacticity. This may be something of an eye-opener to many readers. Most of the rest are concerned with Ziegler or alternative heterogeneous catalysts, but there are a few examples embracing the stepwise synthesis of polycondensates of unequivocal structure, the preparation of a pure oligomeric urethane, a polynucleic acid and a substantially monodisperse amylose.

The last two chapters are disappointing. Methods of analysis (and characterisation) cannot be treated sensibly in 16 pages, though ample references are given the reader who really wants to pursue the subject. The final review of nomenclature is coloured by the author's opinions and, whilst there may be nothing wrong in this, the subject could well have been introduced at the beginning of the book, instead of being relegated to what is, in effect, an appendix. A summary of the patent literature from 1961 to mid-1966 and an adequate subject index complete the work. There is no author index.

To sum up, this is a book to be cherished by every polymer chemist, whatever his technological interests. To the coatings man who can see beyond the end of his nose, it will provide a fruitful source of inspiration. To the more general reader, its revelations will appear startling, even alarming (c.f. the section on the macromolecular interpretation of biological mutation). To the mere lover of books, it will grant that pleasurable if indefinable sensation of quality which, in the reviewer's experience, accrues from the handling of all Springer productions. An edition in the English language would be widely acclaimed.

Information Received

(In case of difficulty regarding addresses, members and subscribers to the JOURNAL should apply for details to the Director & Secretary of the Association at the address shown on the front cover.)

It has recently been announced that **Resinous Chemicals Limited** have decided to discontinue the manufacture of pigments. In the interests of their customers, arrangements have been made for production of these pigments by **ICI Ltd.**, **Dyestuffs Division**, who will assume responsibility for sales and servicing of these products from 1 July 1968.

Two new companies have recently been formed to deal with importing and exporting of chemicals, raw materials and additives to the paint, ink, plastics and rubber industries. The **Polymarjo Company Limited** offers group technical selling overseas, with frequent visits to the markets, specialising in Eastern Europe, the Middle East, the Far East, Australasia and Central and South Africa. All facets of technical sales and service, agency appointment, and export procedure can be handled.

Longfield Chemicals Limited handles raw materials from several overseas manufacturers, whose products are sold with emphasis on technical sales and service.

The directors of the two companies claim specialised practical experience with the problems associated with the pvc and paint industries in every major industrial country in the world.

Takdust Products Ltd. have recently introduced a chart giving details of *Takstrippers* and methods of use for various finishes.

It has recently been announced that the Queen's Award to Industry for 1968 has been received by Johnson, Matthey & Co. Ltd., and ICI Ltd., Dyestuffs Division.

Johnson, Matthey received the award for the export achievement of their operating companies, and ICI Dyestuffs for technological innovation in the synthesis and manufacture of herbicides.

Two new lightfast triaryl phosphate plasticisers, *Reofos 65* and *Reofos 95*, have recently been introduced by Geigy (UK) Ltd. These plasticisers, which are based on synthetic phenol, do not rely on supplies of tar acid products, of which there is a world shortage, as do conventional phosphate plasticisers such as tritolyl phosphate and trixylylphosphate. Superior lightfastness and reduced neurotoxilogical properties are also claimed, with equality in all other respects.

The *CVP Resin Finder* for 1968 has recently been published by **Cray Valley Products** Limited. Properties of all resins currently available from CVP are quoted.

An agreement between **Berk Limited** and **Union Camp Corporation (Chemical Division)** of the USA has been reached on the future distribution of Union Camp chemical products in the UK, it has recently been announced.

As from 3 April, Berk Limited has taken over the distribution of Union Camp products in this country. Products include *Unitol* tall oil fatty acids, distilled and acid-refined tall oils, *Unipine* pine oils, and a complete range of terpene chemicals.

Spelthorne Metals Ltd. have recently issued a new technical bulletin quoting endorsements for independent sources of the value of metallic lead primers as anticorrosive primers for steel. Copies of the bulletin, which is printed in English, French and German, are available from Spelthorne.

Bulletins on several new products produced by Beck, Koller and Co. (England) Ltd. have recently been published. The products covered are *Beckogel 1488*, *Beckurane 400*, *Beckuranes M-181*, *M-191* and 2-299, *Lustrasol 2661*, *Beckosol 1474*, *Styresol 9261* and *Styresol 9261 HV*.

Irish

Annual General Meeting

The third Annual General Meeting of the Irish Section was held in the Clarence Hotel, Dublin, on Friday 5 April 1968, with Mr Adam in the chair and 27 members attending.

The following officers were elected:

Chairman	••	••	••	Mr R. Adam
Chairman Elect		• •		Mr R. F. Cotter
Hon. Secretary				Mr G. Y. Blomeley
Hon. Treasurer				Mr J. Kerslaw
Hon. Programm	e Offic	cer	• •	Mr D. P. Godden
Hon. Publication	ns Sec	retary	• •	Mr R. B. Simon
Representative of	n Cou	ıncil	• •	Mr G. Y. Blomeley
Hon. Auditor				Mr S. McWade
Committee				Mr R. J. Clinton, Mr W. A.
				Grainger, Mr M. O'Callaghan,
				Mr M. O'Hanlan, Mr R. F.
				Patton, Mr. P. K. Smith

After the meeting an emergency Committee meeting was held. This was made necessary because, due to unforeseen circumstances, Mr Blomeley was unable to accept the position of Hon. Secretary. As a result Mr Blomeley was appointed Hon. Assistant Secretary and Representative on Council and Mr F. D. H. Sharp was co-opted on to the Committee as Hon. Secretary.

Wallpaper manufacture

This meeting was followed by the final ordinary meeting of the session, at which 31 members and six visitors were present. Mr R. Adam, in the chair, introduced Messrs. S. K. Weir, I. Weir and K. Burke, of Wallpapers Ltd., Kildare, who presented a very interesting paper on wallpaper manufacture.

Mr S. K. Weir outlined the history of wallpaper through the ages and Mr Burke then took the audience through the production of wallpaper, starting with the arrival of raw materials, through the various processing stages and concluding with the despatch of the finished product.

The paper brought forth a lively discussion. Those taking part included Messrs. Adam, Cotter, Blomeley, O'Callaghan, Grainger, Sharp, McWade and O'Hanlon.

A vote of thanks was proposed by Mr D. P. Godden and the 1967-68 session ended at 10.25 p.m.

F.D.H.S.

London

Annual General Meeting

The Thirtieth Annual General Meeting of London Section was held on 18 April 1968 at the Criterion in Piccadilly, London W1. The Committee's Annual Report and the Financial Statement were adopted unanimously; in presenting the latter the Hon. Treasurer, Mr J. Pooley, commented that expenditure during the year was somewhat higher than last year due to increased costs of printing and postage, and also of the

European Liaison Lecture in Denmark. Mr Pooley expressed the Committee's thanks to the Hon. Auditor, Mr A. H. Soane.

Mr Wheeler thanked the two retiring officers for their services to the Section, the Hon. Secretary, Mr V. Jenkins, and the Hon. Treasurer, Mr J. Pooley, who would become Vice-Chairman for the coming session, and also the three retiring members of the Committee, Mr R. E. Brightman, Mr W. O. Nutt and Mr D. G. Soar.

The Officers for the coming session were elected, as follows:

Chairman	••	•••		••	• •		Mr R. N. Wheeler
Hon. Secretary	••	• •	• •		• •	• •	Mr R. H. E. Munn
Hon. Treasurer			• •	• •	• •	••	Dr H. R. Hamburg
Hon. Publications C	Officer	••	• •	••	• •	• •	Dr V. T. Crowl
Hon. Programmes (Officer				• •		Mr D. E. Eddowes
Hon. Auditor				•••			Mr A. H. Soane

As a result of a ballot, the three new members of the Committee elected were Mr D. A. Bayliss, Mr J. K. B. Burke and Dr J. B. Ley.

After the dinner following the meeting, Mr G. M. de May, of the Institute of Patentees and Inventors, gave a talk on "The private inventor in modern industrial society."

Mr de May said that it might be thought that there was nowadays very little scope for the private inventor; this was in fact not so, although in many ways the private inventor had continually to fight for his existence, and the Institute, which was founded 50 years ago, was of great value to the individual inventor. Mr de May said that the subject could be considered in five distinct stages; the invention itself, protection of the invention, development, exploitation of the invention, and finally the encouragement of future inventions.

Concerning the invention itself, large industrial organisations were devoted to research and development, and provided with all the facilities needed in terms of equipment and manpower. Yet these organisations were each oriented towards a particular field, and it was in the areas in between that the private inventor frequently came to the fore. What he invented must be commercially viable, and not too far ahead of the time. Mr de May gave several examples of such private inventions, and referred to the assistance which the Institute gave its members. This covered professional advice, technical information, and a very valuable feed-back of problems from industry. This might take the form of lists of inventions needed to fulfil a certain need, or of new products needed as outlets for existing manufacturing processes, etc.

On the second point, protection, the private inventor was at a considerable disadvantage compared with his industrial counterpart, who would merely hand his invention over to the specialised legal department of his company. Here the Institute was of great value to the individual in the provision of skilled advice and assistance. The third aspect, development of the invention, was also easy in industry, but difficult for the private inventor.

Exploitation of inventions was a major difficulty, and the Institute could be very useful in this respect. Mr de May described the various organisations which could assist. The NRDC, which may support only those inventions which are deemed to be in the public interest, was originally formed to exploit inventions resulting from work in Government departments and Universities, but it would now also support private inventions. Other ways of achieving exploitation were described, including the use of patent brokers. Another way of getting into touch with potential users was via exhibitions, such as that at Brussels.

JOCCA

Finally Mr de May spoke of the encouragement of future inventions. Here the individual tended to have an advantage over industry in that he was not tied to a set programme of work. He was free to follow any course, and to take advantage of those occasional moments of high lucidity which occur intermittently in the inventive mind. The activities of the Institute, with lectures and technical advice, were also of great assistance to the younger inventor.

Many points were raised in the discussion, and finally Mr Wheeler expressed the thanks of the audience for a very interesting talk.

V.T.C.

Manchester

The surface treatment of organic pigments

At the fifth ordinary meeting of the 1967-68 session, held on 9 February 1968 at the Manchester Literary and Philosophical Society building, 143 members and guests heard Drs J. L. Moilliet and D. A. Plant (ICI Ltd.) deliver a lecture entitled "The surface treatment of organic pigments."

In the first half of the lecture, Dr Moilliet dealt with theoretical aspects of the dispersion of pigments in oily media, but without any involved mathematics. For such treatment, the audience was referred to a paper (A. S. Gomm et al., *JOCCA*, 1968, **51**, 143).

When separated from an aqueous medium during manufacture, pigments underwent a process of hydrophilic aggregation during drying. The normal adherent layer of water on the surface had a powerful aggregating effect, and in order to disperse such a pigment in an oily medium, it was necessary to displace the water film by resin. By coating the pigment particles suitably it was possible to modify or completely eliminate this hydrophilic aggregation and so render the pigment more easily dispersible. The organic materials used for coating did not necessarily increase the degree of deflocculation in the final pigment/oil suspension. Ingredients in the media provided the protective colloid action necessary to maintain deflocculation.

Dr Moilliet outlined the various methods of surface treating pigments with metal soaps, surface active agents, etc. He illustrated this with reference to the treatment of an Arylamide yellow and phthalocyanine blue pigment with long chain amines. From this, Dr Moilliet developed the new concept of the ED-structure of pigments in which a robust resin coating on the pigment produces an open hydrophobic structure which is easily penetrated by, and hence dispersed in, oily media. This structure could not be confirmed microscopically, but was inferred from results of compression tests and the behaviour of ED-pigments in solvents alone.

Dr Plant then described the technical effects achievable by the use of surface coated organic pigments. Benzidine yellow pigments were widely used in rotogravure inks for magazine printing. These inks were required to be highly dispersed and to exhibit excellent gloss and transparency. Benzidine yellow, surface treated with long chain amine, could be dispersed rapidly in high speed cavitation mixers and gave ink which had better flow and gloss than that from a conventional yellow. A similar surface treatment produced a flocculation resistant phthalocyanine blue, which also gave paint mill bases of improved flow. However, the main emphasis of Dr Plant's talk was on the technical and financial advantages of using the true ED-pigments.

After tracing the sequence of operations in the manufacture of both paint and inks from standard pigments, Dr Plant demonstrated how manufacture could be simplified when using easily dispersible pigments.

Structured ED-pigments were largely dispersed in the "premix" stage and only a short refining pass through a triple roll mill was necessary to achieve complete

dispersion. Where ball milling was in use, it was possible to increase the mill loading by reducing the ball content, to raise mill base concentration and also to increase the numbers of millings per day, all of which led to substantial cost savings. Similarly, only a very short dwell-time was necessary in a sand mill.

Dr Plant concluded by saying that easily dispersible surface treated organic pigments not only offered direct advantages when applied to conventional methods of paint manufacture, but also opened up possibilities of new streamlined techniques.

A long and lively discussion followed in which more than a score of the audience participated. A vote of thanks to the two lecturers was proposed by Mr S. Duckworth and passed with acclamation.

D.A.P.

Organic pigments for paints

A junior lecture was given by Mr G. T. Williams at the Manchester Literary and Philosophical Society's premises on 3 April. The subject was "Organic pigments for paints" and 45 members, junior members and guests were present.

Mr Williams commenced his talk by defining a pigment and briefly outlining the main applications of pigments in the colouring of viscose, printing inks, paper, plastics and paint. The formulation of a paint was then discussed in greater detail with most emphasis placed on the use of organic pigments and their properties.

The colour of a pigment resulted from specific chemical groups in the molecule known as chromophores; examples were azo, thio and nitroso groups. The shade of the chromophore could be modified by addition of substituent groups, known as auxochromes, to the molecule.

Pigments were classified by chemical type within the shade ranges red, orange, yellow, green, blue and violet, and their properties such as lightfastness, overspray fastness mentioned in relation to their application in decorative and industrial paints.

Mr Williams concluded his lecture with a review of the structures of pigments which fell outside the main system of classification. These included the anthraquinones, isoindolinones, thioindigoids, perylenes and quinacridones.

After a valuable period for questions in which an interesting discussion on the prediction of lightfastness from chemical structure took place, the vote of thanks was proposed by Dr Kyle.

D.A.P.

Scottish

Eastern Branch

Vinyl modified alkyd resins

The fourth ordinary meeting of the session was held at the Wee Windaes Restaurant on Wednesday 24 January 1968 with Mr G. H. Hutchinson in the chair, when Mr. A. Radcliffe lectured on "Vinyl modified alkyd resins."

Mr Radcliffe introduced his talk by saying that interest in vinyl modified alkyd resins was stimulated after the war by the ready availability of styrene monomer. It was thought desirable to combine the properties of a drying oil with those of polystyrene. Although the two were not compatible it was found that a homogeneous copolymer could be formed by heating styrene monomer in the presence of a drying oil. These products although quite useful were quickly superseded by styrenated alkyds.

Styrenated alkyds were usually produced by the previnylation or postvinylation process. Previnylation was really only an extension of the styrenated oil process in which the oil was styrenated either alone or in solution. When the styrenation was complete the monoglycerides were formed in the usual way, following through to an alkyd resin by the normal route.

In the postvinylation method an alkyd resin was produced in the usual manner and then styrenated either in 100 per cent solid form or in solution.

The catalysts employed in the process were invariably peroxides, the most common being di-tertiary butyl peroxide, tertiary butyl hydro-peroxide, or di-cumyl peroxide. Also, to prevent build up of styrene homopolymer, chain stoppers were required, especially in the previnylation process.

Although it used to be thought necessary to manufacture the system from highly conjugated oils, recent advances in technology had allowed resins to be prepared from non-conjugated oils or even oils containing no unsaturation. Also the number of monomers had been expanded from styrene itself to vinyl toluene and, more recently, to include acrylic monomers. Methyl methacrylate was the alternative hard monomer to styrene and the remaining acrylate monomers such as butyl methacrylate, 2-ethylhexyl acrylate and heptyl acrylate were used as plasticising monomers.

Mr Radcliffe concluded by saying that the main advantage of vinyl modified alkyds was their speed of dry which, in general, was dependent on the amount of monomer present. He described, with the aid of a series of paint panels, the ways to overcome the main disadvantage of these materials, namely their poor recoating properties.

Following a lively discussion, Mr C. Cochrane proposed the vote of thanks.

J.H.S.

Jordan Award

The Committee appointed by Council to consider the applications received for the Jordan Award met in February and, after long and careful consideration, decided that it was not possible to make the Award on this occasion.

It is intended, therefore, to invite further applications to be received in 1968, and the Committee will consider these early in 1969, with a view to making the Award at the Eastbourne Conference, which will be held 17-21 June 1969. The rules of the Award are appended below for the benefit of new members.

- 1. The Award will be made for the best contribution to the science or technology of surface coating by a member of any nationality working in either the academic or industrial field who is under the age of 35 at the date of application.
- 2. The final date for submission of applications will on this occasion be 1 January 1969.
- 3. The selection of the recipient of the Award will be made by a Committee

under the Chairmanship of the Association's Hon. Research and Development Officer.

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

Eastbourne Conference

17-21 June 1969

The headquarters for the Eastbourne Conference will be in the Grand Hotel, where the majority of the delegates will be accommodated, and the Technical and Workshop Sessions and Official Functions held. The remainder of the delegates will stay at the nearby Burlington Hotel.

The theme of the Conference is to be "Film formation and curing," and it is hoped that four Technical Sessions and three Workshop Sessions will be held, as in 1967.

There will be a full social programme, including a Civic Reception on the Wednesday, and the Association's Dinner-Dance on the Friday evening. Trips to places of interest will be arranged, and there will be opportunities for delegates to take part in various sporting activities.

Details will be circulated to members early in 1969. Others wishing to receive details should write to the Director & Secretary at the Association's offices.

Scottish Section

Annual General Meeting and Smoking Concert

The Scottish Section held its Annual General Meeting on Friday 5 April in the Lorne Hotel, Sauchiehall Street, Glasgow. The retiring Chairman, Mr I. S. Hutchison, in nominating Mr J. Miller as his successor, referred to his long and efficient service to the Section, first as Liaison Officer for the Student Section and then as Vice-Chairman, and to the high esteem in which he was held by the industry in general. There was no counternomination, and Mr Miller was elected with acclamation.

Other office bearers and Committee members were elected as follows:

Vice-Chairman	Mr P. Birrell
Hon. Secretary	Mr E. M. Burns
Hon. Treasurer	Mr T. B. Hannah
Hon. Education	
Officer	Mr A. McLean
Hon. Publications	
Officer	Dr J. D. Easton
Hon. Programme	
Officer	Mr R. G. Gardiner
Hon. Research	
Liaison Officer	Mr D. Rowley
Hon. Student	
Section Liaison	
Officer	Mr A. H. Smith

News of Members

Mr V. C. Thompson, an Ordinary Member attached to the Bristol Section, has been appointed Managing Director of John Hall & Sons (Bristol and London) Ltd.

Mr Thompson is a Vice-President of the Association and was a founder member of the Bristol Section and its second Chairman.

Mr A. B. Lock, an Ordinary Member attached to the Bristol Section, has been appointed technical director of John Hall & Sons (Bristol and London) Ltd. Mr Lock is a past Chairman of the Bristol Section. Committee

.. Messrs. B. G. Anderson, R. L. Barrett, G. G. Lang, C. S. MacLean, J. Mendelson, H. A. Munro.

Mr Miller made it his first duty as new Chairman to thank Mr Hutchison most warmly for all his work for the Section up to and including his term as Chairman, and to express the appreciation of the members for his leadership and organisation over the last two years.

He then thanked the 1967-68 Committee for the excellent team job they had done, mentioning particularly Messrs. W. Peden and A. Pisacane, who were retiring from the Committee.

The company then travelled to the Eglinton Arms Hotel at Eaglesham, the accustomed venue for our annual smoker. Here, 58 members and guests enjoyed a meal followed by songs and stories from Jeff Norton and Duncan Fraser, supplemented by not a few from our own members. In the course of the evening, Ian Hutchison was presented with a landing net (for the ones which do not get away) from his colleagues on the Committee.

American Oil Chemists' Society Bond Award Gold Medal

Dr R. Wood, of the Oak Ridge Institute of Nuclear Studies, received the AOCS Bond Award Gold Medal at the joint meeting of the AOCS and the American Association of Cereal Chemists on 2 April 1968. Dr F. Snyder of the Oak Ridge Institute was co-author of the winning paper, which was entitled "Quantitative determination of glyceryl alk-1-enyl and alkyl-alkylenyl ethers in neutral and phospholipids."

1968 Mattiello Lecture

The Federation of Societies for Paint Technology has recently announced that the Joseph J. Mattiello Memorial Lecture

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for 1968 will be presented by Dr F. W. Billmeyer, Jr., Professor of Analytical Chemistry at Rensselaer Polytechnic Institute, Troy, New York, the title being "Molecular structure and polymer properties."

The lecture will be given to the 46th Annual Meeting of the Federation to be held at the Coliseum, New York, 23-25 October 1968.

Thesaurus of paint and allied technology

The "Thesaurus of paint and allied technology" has recently been published by the Federation of Societies for Paint Technology. The book, which runs to 272 pages, lists some 4,000 currently important terms of paint technology. Two sections are included, Classified, where the terms are grouped into 44 main categories, and Alphabetic, where each term is displayed together with other terms which are related to it.

Our Association was pleased to give assistance in the compilation of this work, in the key-words project. Dr S. H. Bell and Messrs A. R. H. Tawn and J. L. Orpwood collated terms for, and reviewed the original draft of the book.

Symposium: Design of protective systems for structural steelwork

The Institution of Corrosion Technology is to hold a one-day symposium entitled "Design of protective systems for structural steelwork" on 19 September 1968 at Leeds University. Ten papers will be read, dealing with surface preparation, design, application and inspection and light gauge steel.

Joint 1970 Symposium Committee

A three day conference is to be held in London from 29 September to 1 October 1970.

The subject will be "Advances in the chemistry of liquid and thermoplastic co-polymers," and papers are now invited from authorities in this field.

The conference is sponsored jointly by: The Institution of the Rubber Industry, the Oil and Colour Chemists' Association, the Plastics Institute, the Society of Chemical Industry (Plastics and Polymer Group) and the Society of Dyers and Colourists.

All communications should be addressed to:

The Secretary,

The Institution of the Rubber Industry,

4 Kensington Palace Gardens, London W8.

Organic Mass Spectrometry

A copy of the first issue of a new Journal, "Organic Mass Spectrometry," has recently been received. The Journal, which is to be published bi-monthly from February 1968, has as Editor-in-Chief Professor A. Maccoll of University College, London, with Regional Editors from seven overseas countries and a large Editorial Advisory Board. The first issue runs to 190 pages and contains 14 papers, two in German, and a book review.

The publishers are Heydon & Son Ltd., of London, and the annual subscription is $\pounds 16$ 10s 0d. Reduced subscription rates are obtainable for bona fide students or private readers.

Register of Members

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

Ordinary Members

BEERE, ANDRE JAIME, 15 St. Lawrence Way, Bricket Wood, Herts.

(Thames Valley)

 BOWER, ALBAN CECIL, Kellogg International Corp., Kellogg House, Chiltern Street, London W1. (Thames Valley)
 BUIJN, K. E. C., MSc, Mesdaglaan 11, Heemstede, Netherlands. (Overseas)
 COLE, REGINALD JOSEPH, BSc, CEng, FRIC, AMIChemE, Pinelands, Beechwood Avenue, Weybridge. (London DAVIS. MICHAEL J., BAMod, PhD, site 75, Grange Park Estate, Raheny, Dublin 5. (Irish) deGRAAF, ALBERT, Verlengte Kolonieweg, Soest Z, Holland. (Overseas) FREUND, VORGE, Acevedo 2458 2PA, Buenos Aires, Argentina. (Overseas) FROGGATT, JOSHUA JOHN, 797 Wandsworth Road, London SW8. (London) HAROLD, RICHARD W., BS, 600 North 34th Street, Louisville, Kentucky 40212, (Overseas) USA. HOVAS, REIDAR, Voll Terrassa 10, Jar, Norway. (Overseas) LEMERCIER, RENE, Societe Imago, 39 Boulevar 5 de Vaugirar 5, 75 Paris (15), (Overseas) France. NIEMANN, HORST H., 4618 Kamen, Ostkamp 24, West Germany. (Overseas) PEARSON, PATRICK GEORGE, BTech, 84 Orgreave Lane, Handsworth. Sheffield (West Riding) 13. Yorkshire. ROBINSON, MATTHEW JENKINSON, BScTech, ARIC, AMCT, Moorlands, Grove Road, Tring, Herts. (London) STAGG, PETER KIDNER, The Whins, Northend, Sedgefield, Co. Durham. (Newcastle) Associate Members ASHFORD, MERVYN ALFRED, 35 Woodside Road, Downend, Bristol. (Bristol) CROCKER, FRANK HUGH, 125 High Street, Pensford, Bristol. (Bristol) JARVIE, MICHAEL ALEXANDER, Rogart, 44 Earls Way, Doonfoot, Ayr. (Scottish) LEMA, JOSE DIAS, Pinturas Honor, SL, Pontevedra—Apartado 234, Spain. (Overseas) VEGTER, LUCAS, 3 Rockfield Avenue, Terenure, Dublin 12. (Irish) Junior Members BURROW, PAUL DUMAYNE, 48 Seymour Court, Whitehall Road, Chingford, E4. (London) O'CALLAGHAN, KEVIN JOSEPH, 5 Lucan Road, Palmerstown, Co. Dublin. (Irish) POWELL, JEREMY HUGH, Industrial Development Laboratory, John Hall and

Sons Limited, Petherton Road, Hengrove, Bristol. (Bristol) REILLY, ULTAN JOSEPH, Portrane Road, Donabate, Co. Dublin. (Irish) ROGERSON, JOHN EDWARD, 48 Christchurch Road, Colliers Wood, Merton, London SW19. (London)

Forthcoming Events

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

13-16 June

Tenth Australian Convention, to be held at Hotel Florida, Terrigal, New South Wales.

Friday 28 June

Association's Annual General Meeting, to be held at the Royal Hotel, Bristol, at 7.00 p.m.

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introduction to paint technology

second edition with additional chapter

The sales of this Association publication now exceed 13,000, and because of continuing high sales of the second edition, and the need for a work of reference to be constantly abreast of the latest developments in its field, the Council of the Oil and Colour Chemists' Association has authorised the addition of an eleventh chapter to the 'Introduction to Paint Technology.' Entitled 'Recent Developments,' the Chapter incorporates up-to-date information on the latest advances in the technology of the paint and allied industries.

This addition will help the 'Introduction to Paint Technology' to maintain its position as an invaluable aid to young entrants into the industries and to marketing and other personnel requiring a basic knowledge of the principles and techniques of surface coating production and application.

new chapter

The new chapter is subdivided to three sections

resins and media

Including polyester, epoxy, polyurethane resins and developments in water based paints, vinylics, etc.

application techniques

Including electrodeposition, powder coatings, strip-coating, aerosol spraying.

instrumental testing and control methods

Including colour measurement, viscometers, brushability, hardness, film thickness, weatherometers, and use of computers.

The book contains 204 pages including 11 line diagrams, 8 photographs of common paint defects, and comprehensive index. Copies can be obtained from the Oil and Colour Chemists' Association, Wax Chandlers' Hall, Gresham Street, London E.C.2, price 20s. (post free).
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Federation of Societies for Paint Technology



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