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The influence of additives and calcination on the pigment properties of titanium dioxide:

Part III The influence of some rutilisation catalysts
Part IV The influence of some titanium compounds as rutilisation catalysts

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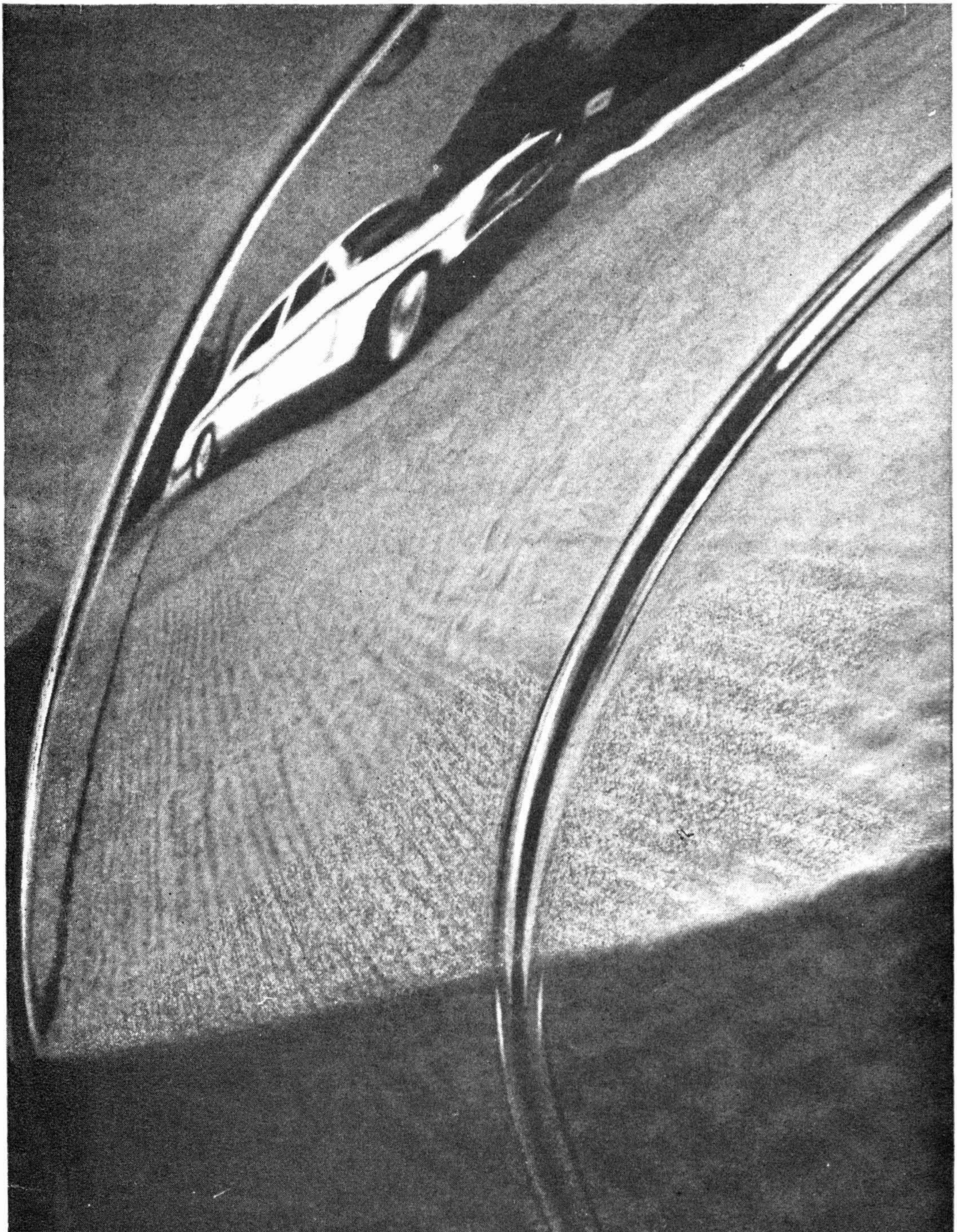

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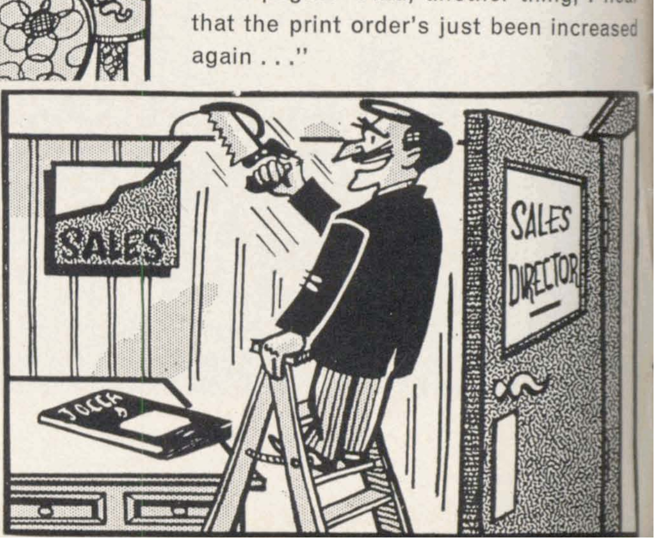

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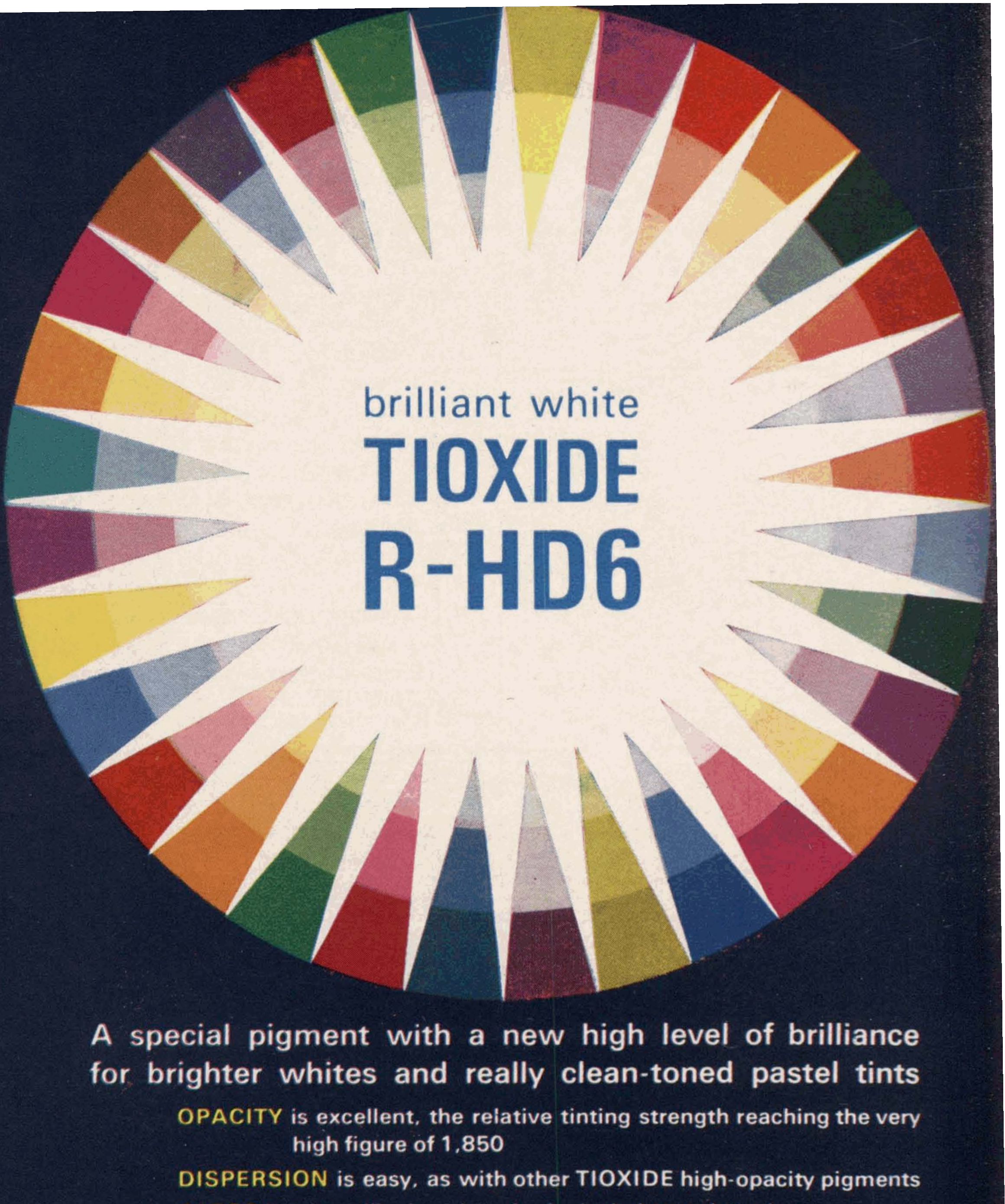

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Transactions and Communications

The influence of additives and calcination on the pigment properties of titanium dioxide: Part III. The influence of some rutilisation catalysts

By Vladimír Blechta, Miloš Lavička and Zdirad Blechta

Inorganic Chemistry Research Institute, Ústí nad Labem, Czechoslovakia

Summary

The influence of zinc and aluminium sulphate, phosphoric acid, and antimony trichloride, in combination with potassium sulphate, on the pigment properties of the product obtained by calcination at temperatures of 825° to 1,000°C has been studied. Zinc sulphate is a very good positive rutilisation catalyst. Products, however, obtained by impregnation with $ZnSO_4+K_2SO_4$ are of unsatisfactory tinting strength. Aluminium sulphate is a negative rutilisation catalyst. Phosphoric acid as well as antimony trichloride have no marked influence on rutilisation.

L'influence des additifs sur la calcination et les propriétés pigmentaires du dioxydede titane

III ème. Partie. L'influence de certains catalyseurs de rutilisation

Résumé

On a étudié l'influence exercée par des combinaisons du sulfate de potassium avec les sulfates de zinc et d'aluminium, l'acide phosphorique, et le trichlorure d'antimoine sur les propriétés pigmentaires du produit de la calcination de TiO_2 hydraté à des températures de 825°C à 1000°C. Le sulfate de zinc est un très bon catalyseur de rutilisation. Les calcinats que l'on obtient à l'aide d'un mélange des sulfates de zinc et de potassium sont d'un pouvoir colorant faible. Le sulfate d'aluminium est un catalyseur négatif de rutilisation. L'acide phosphorique et à la fois le trichlorure d'antimoine n'ont pas d'influence importante sur la rutilisation.

Der Einfluss von Additiven und Kalzinierung auf die Pigmenteigenschaften von Titandioxyd

Teil III: Der Einfluss Einiger Rutilisierungs-Katalysatoren

Zusammenfassung

Die Beeinflusssung der Eignung des Erzeugnisses als Pigment durch Zusätze von Zink- und Aluminiumsulfat, Phosphorsäure und Antimontrichlorid in Kombination mit Kaliumsulfat, mit Hilfe des Kalzinierens bei Temperaturen zwischen 825 und 1000°C wurde untersucht. Zinksulfat ist ein sehr guter, positiver Rutilisierungskatalyst. Dagegen besitzen Erzeugnisse, die lediglich durch Imprägnierung mit $ZnSO_4+K_2SO_4$ erhalten wurden, ungenügende Farbstärke. Aluminiumsulfat ist ein negativer Rutilisierungskatalyst. Phosphorsäure sowie Antimontrichlorid beeinflussen Rutilisierung nicht merklich.

Влияние добавок и кальцинации на пигментые свойства двуокиси титана Часть III. Влияние некоторых катализаторов рутилизации

Резюме

Изучалось влияне сульфатов цинка и алюминия, фосфорной кислоты и треххлористой сурьмы в соединении с сульфатом калия, на пигментные свойства продукта полученного кальцинацией при температурах от 825°C до 1000°C. Сульфат цинка является очень хорошим положительным катализатором рутилизации. С другой стороны продукты полученные пропитыванием $ZnSO_4 + K_2SO_4$ обладают неудовлетворительной интенсивностью окрашивания. Сульфат алюминия является отрицательным катализатором рутилизации. Фосфорная кислота и треххлористая сурьма не имеют заметного влияния на рутилизацию.

Introduction

In their preceding work the authors were studying the influence of additions of ammonia and sulphuric acid[1] as well as of sodium and potassium salts[2]. The latter improve the pigment properties of the calcinate.

Rutilisation catalysts play an important role among the impregnation agents. With regard to their chemical composition, they may be classified either as titanium compounds or as compounds of other metals ; and, with regard to their effect, positive or negative rutilisation catalysts. A large number of positive rutilisation catalysts have been described both in patents and in journals[3]. The group of negative rutilisation catalysts includes K_2SO_4 (studied previously[2]) and H_3PO_4. Since very little has been known about the specific influence of catalysts containing no titanium, these studies have been aimed at some of the most important ones.

Experimental

The initial material was hydrated titanium dioxide of anatase structure containing 0.0913 g H_2SO_4/g TiO_2, obtained by thermal hydrolysis of sulphate solutions from ilmenite on an industrial scale. The experimental methods, i.e. the method of preparing samples for calcination, the calcination in a grate-less fluidisation furnace[4], the method of determining the tinting strength of the calcined samples by means of an objective method, and the determination of rutile in the final product, have been described earlier[1]. The impregnated samples were calcined in every case for 30 minutes at a temperature of 825° to 975°C. The rutile content and the tinting strength of the ground samples were determined and are shown in the figures.

Results and discussion

The influence of zinc sulphate

The best known positive rutilisation catalyst is zinc sulphate, disclosed in 1938 by Dupont[5] and in a series of following patents[6-9]. Its influence both acting alone and in combination with potassium sulphate has thus been investigated, see Fig. 1.

The following conclusions may be drawn from Fig. 1 : Potassium sulphate in conformity with its properties determined earlier[2], is a negative rutilisation catalyst. It improves, however, the tinting strength of the calcinate. Zinc sulphate is a strong positive rutilisation catalyst. The optimum of its tinting strength is shifted towards lower temperatures. At temperatures about 900°C the product

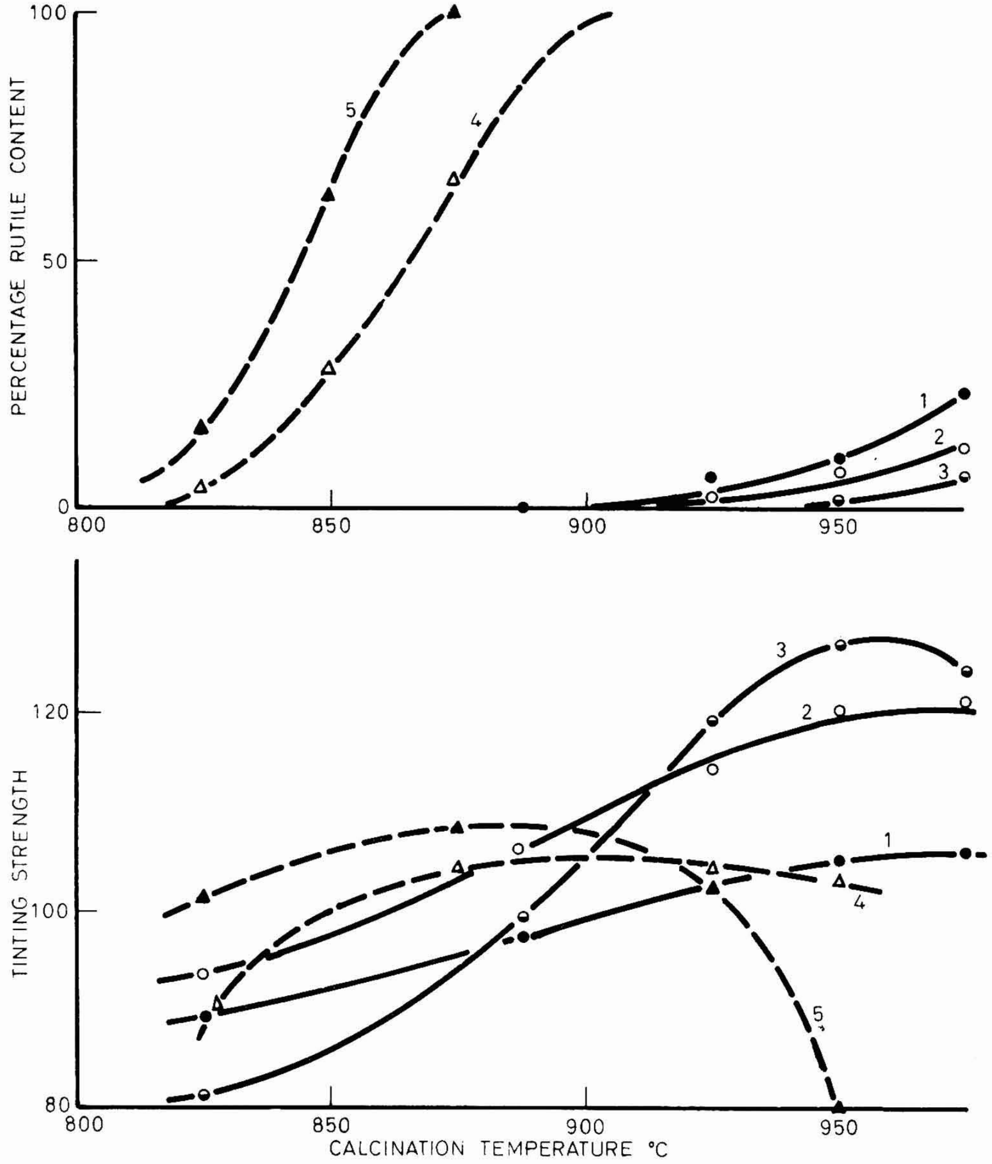

Fig. 1. Influence of potassium and zinc sulphate on the pigment properties of the calcinate : calcination time 30 minutes

Curve	Notation	Impregnation [g/100 g TiO_2] K_2SO_4	$ZnSO_4$
1	●	0.0	0.0
2	○	0.5	0.0
3	◒	1.0	0.0
4	△	0.0	1.85
5	▲	0.0	3.70

is 100 per cent rutile, but its tinting strength is lower than that of an anatase, obtained from a gel impregnated with K_2SO_4.

The strong rutilisation effect of zinc sulphate, and the marked effect of potassium sulphate in improving tinting strength, were sufficiently striking to warrant examination of the joint use of these salts. Results of the tests using a constant 0.5g K_2SO_4/100g TiO_2 with gradually increasing additions of $ZnSO_4$ are given in Fig. 2.

Fig. 2 shows that gradually increasing additions of $ZnSO_4$, up to about 2g $ZnSO_4$/100g TiO_2, greatly increase rutilisation. Further increases of the zinc content have a far smaller effect on rutilisation. The influence on the tinting strength is more complicated. A small amount of zinc greatly decreases the tinting strength of the product, whilst larger additions shift the optimum for the tinting strength to slightly lower temperatures and higher tinting strength values. A similar conclusion follows from Fig. 3, showing the influence of increasing additions of $ZnSO_4$ at simultaneous impregnation with 1g K_2SO_4/100g TiO_2.

The influence of an increasing addition of K_2SO_4 in combination with a constant amount of $ZnSO_4$ is shown in Figs. 4 and 5.

Fig. 4 shows an interesting interaction between the impregnation salts. Material impregnated with 0.5g K_2SO_4/100g TiO_2 (curve 6) rutilises better than unimpregnated material (curve 4). Material containing 1g K_2SO_4/100g TiO_2 (curve 8) shows the same rutilisation strength as material not impregnated with K_2SO_4 (curve 4). A similar conclusion may be drawn from Fig. 5. The interaction of impregnation salts causes the same rutilisation effect as if no K_2SO_4 had been added. Only a higher addition of potassium (curve 9) causes a lower rutilisation. As to the tinting strength of the resulting calcinate, the influence of K_2SO_4 addition attains its optimum close to the values for the 0.5g K_2SO_4/100g TiO_2 addition.

The influence of aluminium sulphate

Besides zinc sulphate, the patent literature recommends aluminium sulphate as a positive rutilisation catalyst[6]. The influence of aluminium sulphate alone and in combination with potassium sulphate is shown in Figs. 6 and 7.

Both figures show that aluminium sulphate is a negative rutilisation catalyst. The negative rutilisation effects of aluminium sulphate and potassium sulphate are additive. A small addition of aluminium does not appreciably influence the tinting strength while larger amounts decrease it. This decrease may be compensated by larger additions of potassium sulphate.

Influence of antimony trichloride and phosphoric acid

According to the patent literature, antimony compounds ought to exert a positive effect, and phosphoric acid a negative effect on rutilisation[7]. The influence of antimony trichloride and phosphoric acid in combination with K_2SO_4 is shown in Fig. 8.

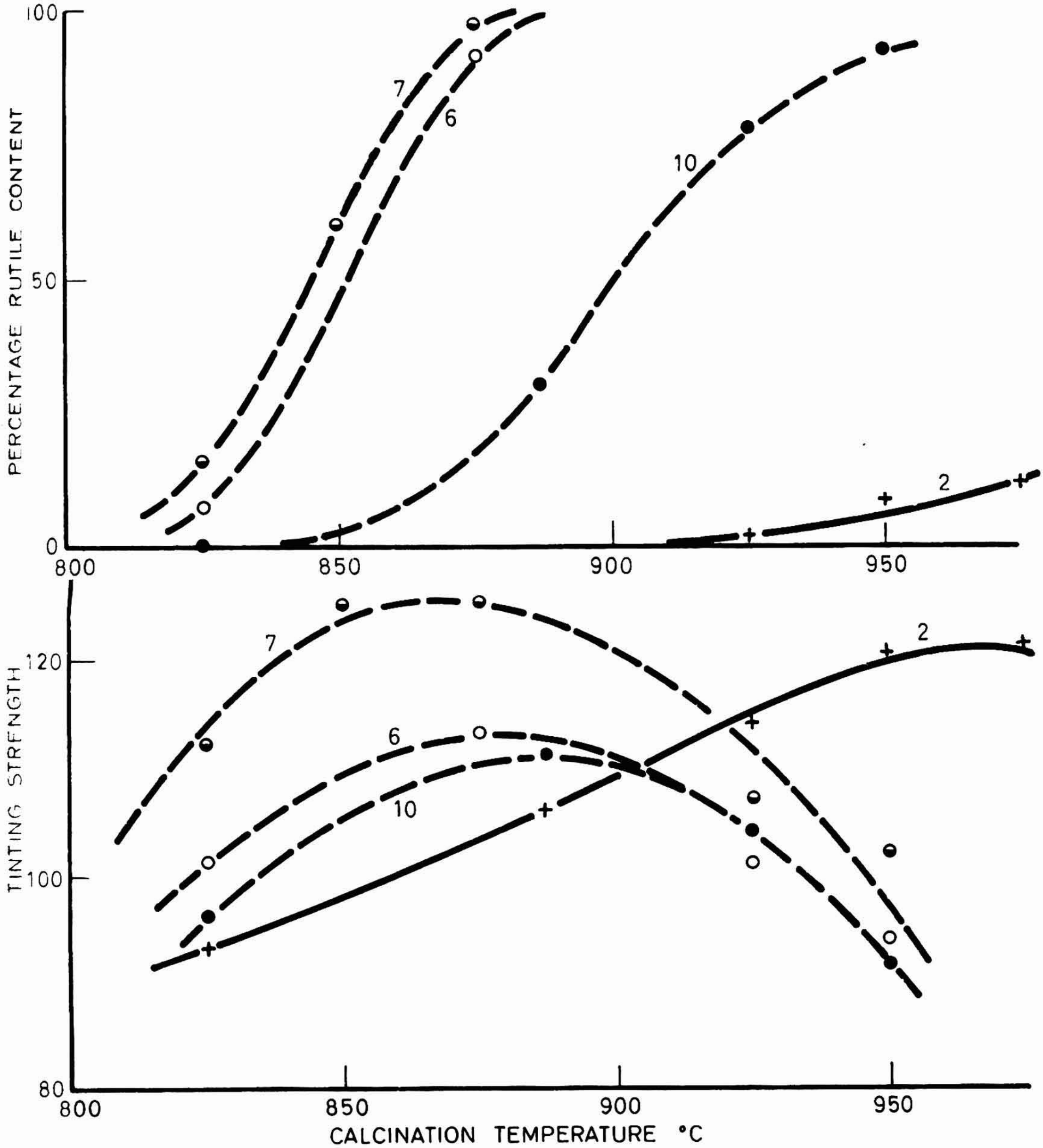

Fig. 2. Influence of increasing amounts of $ZnSO_4$ combined with impregnation with 0.5g K_2SO_4/100g TiO_2 : calcination time 30 minutes

Curve	Notation	Impregnation [g/100 g TiO_2] K_2SO_4	$ZnSO_4$
2	+	0.50	0.0
10	●	0.50	0.92
6	○	0.50	1.85
7	◒	0.50	3.7

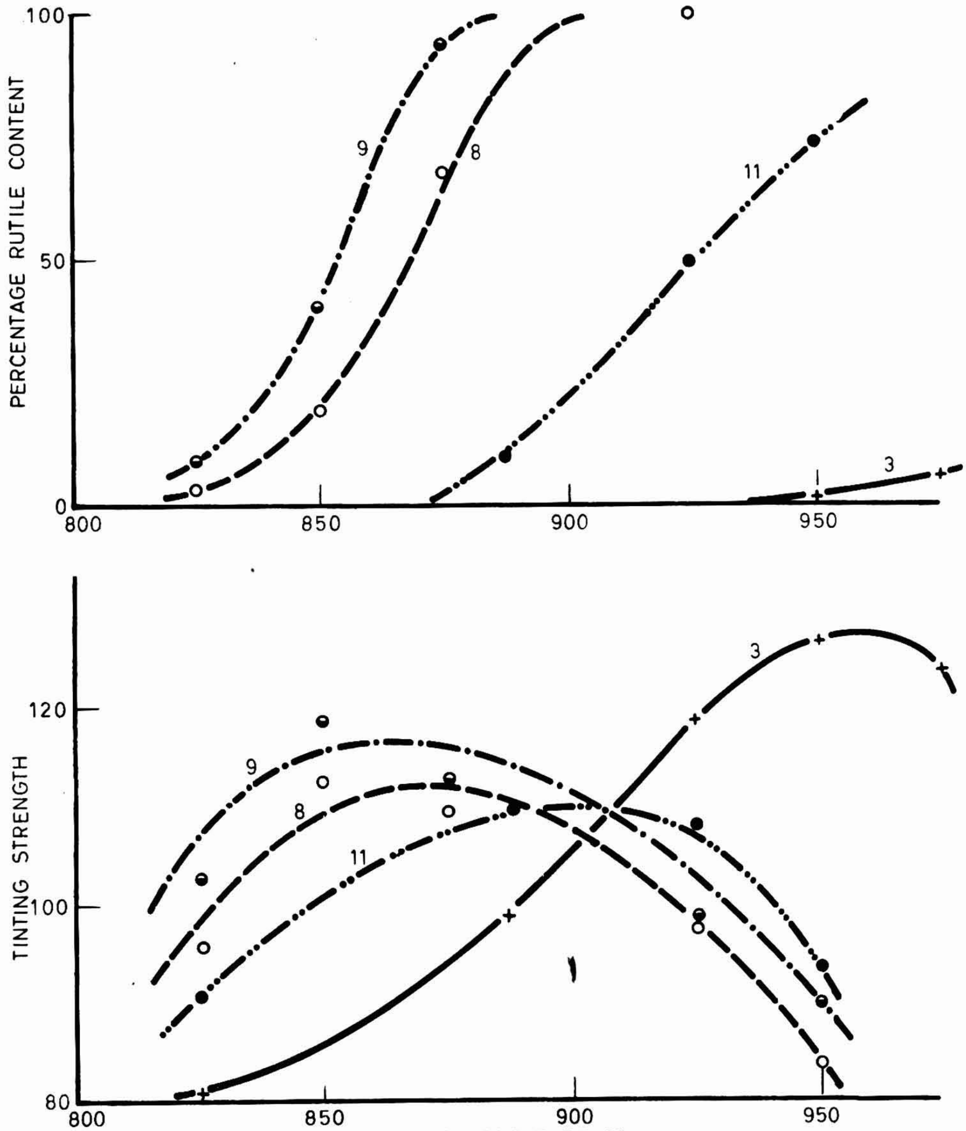

Fig. 3. Influence of increasing amounts of $ZnSO_4$ with simultaneous impregnation with 1.00g K_2SO_4/100g TiO_2 : calcination time 30 minutes

Curve	Notation	Impregnation [g/100 g TiO_2] K_2SO_4	 $ZnSO_4$
3	+	1.0	0.0
11	●	1.0	0.92
8	○	1.0	1.85
9	◓	1.0	3.70

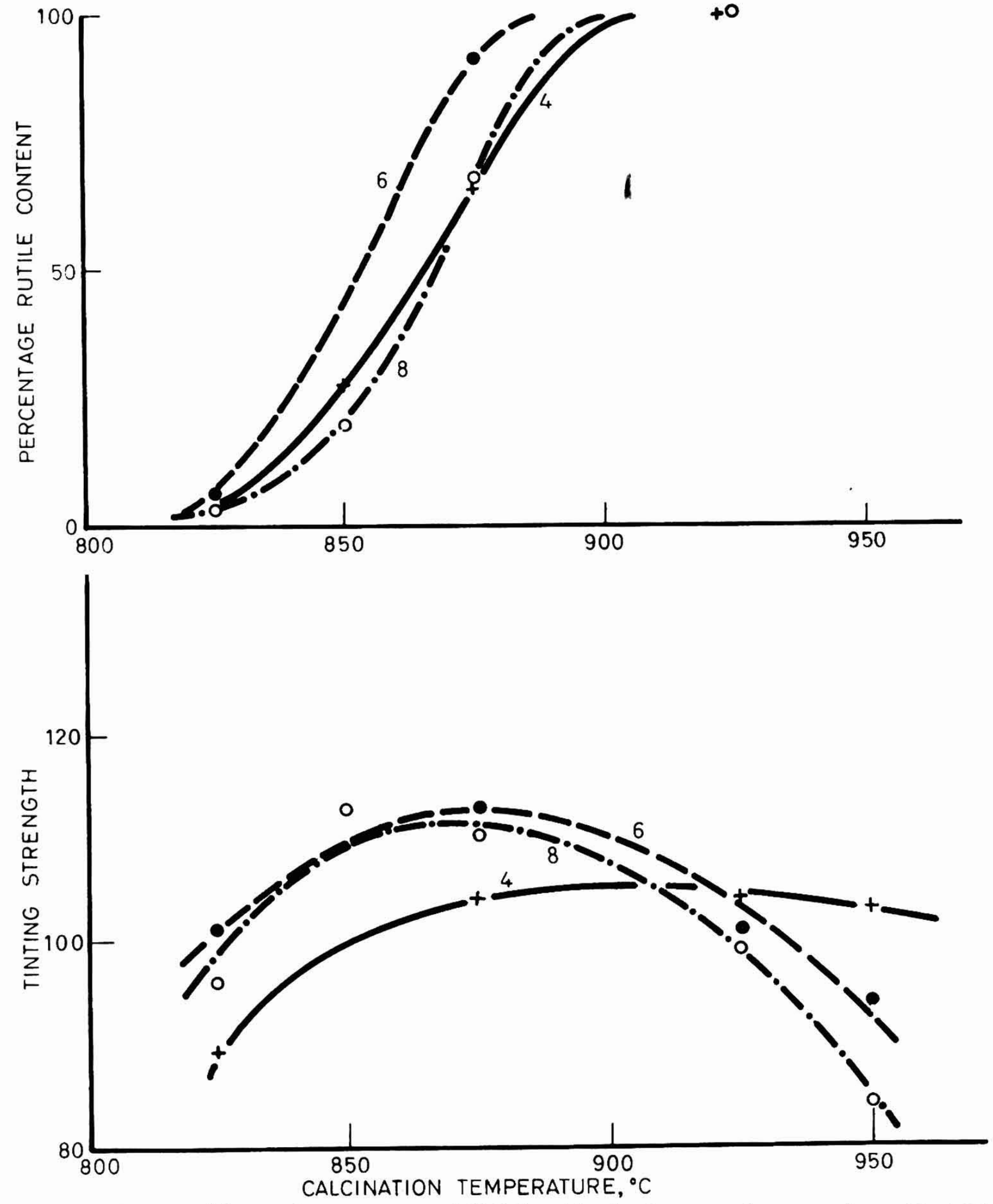

Fig. 4. Influence of increasing amounts of K_2SO_4 with simultaneous impregnation with 1.85g $ZnSO_4$/100g TiO_2 : calcination time 30 minutes

Curve	Notation	Impregnation [g/100 g TiO_2] K_2SO_4	$ZnSO_4$
4	+	0	1.85
6	●	0.5	1.85
8	○	1.0	1.85

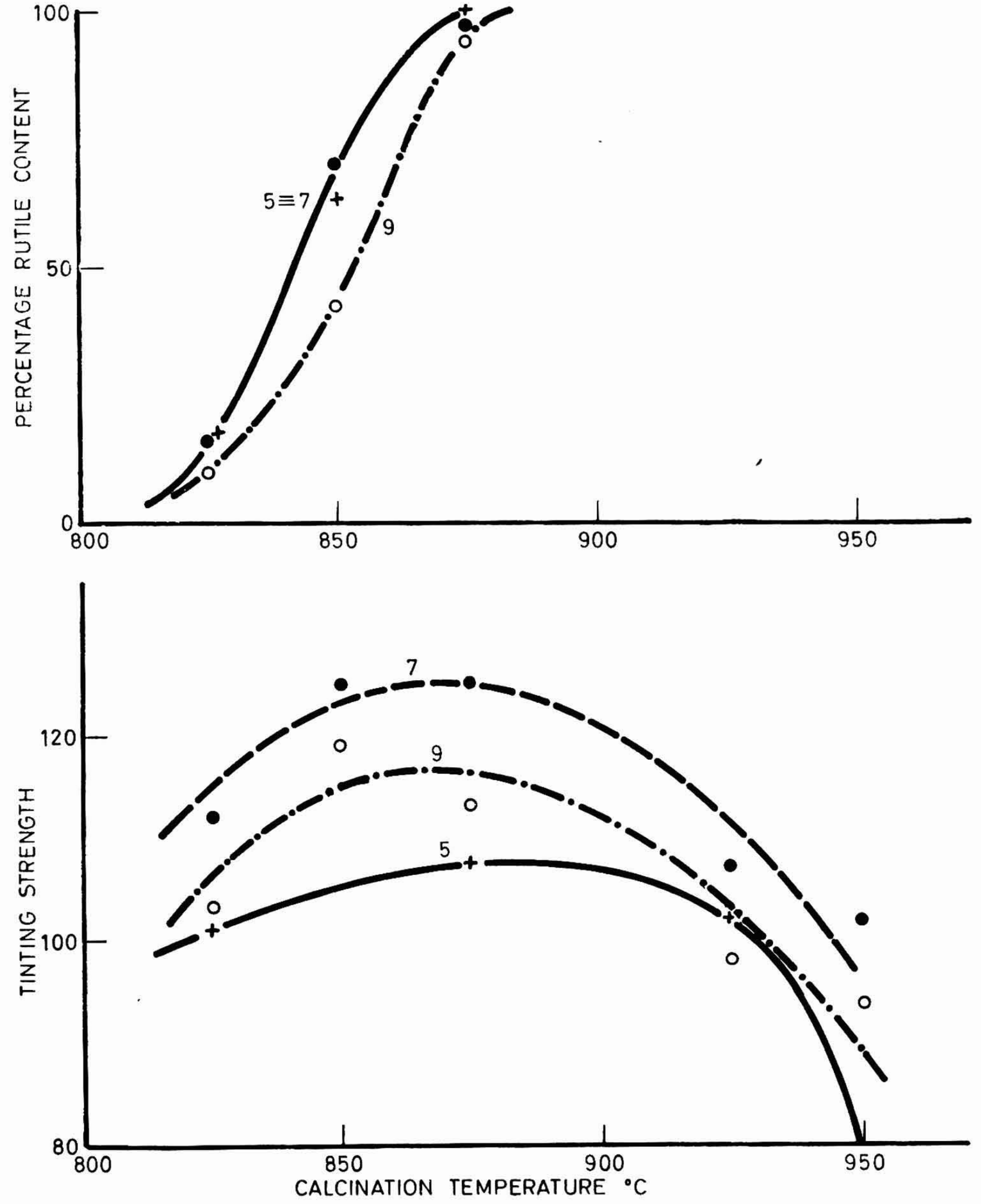

Fig. 5. Influence of increasing amounts of K_2SO_4 with simultaneous impregnation with 3.7g $ZnSO_4$/100g TiO_2 : calcination time 30 minutes

Curve	Notation	Impregnation [g/100 g TiO_2] K_2SO_4	$ZnSO_4$
5	+	0.0	3.7
7	●	0.5	3.7
9	○	1.0	3.7

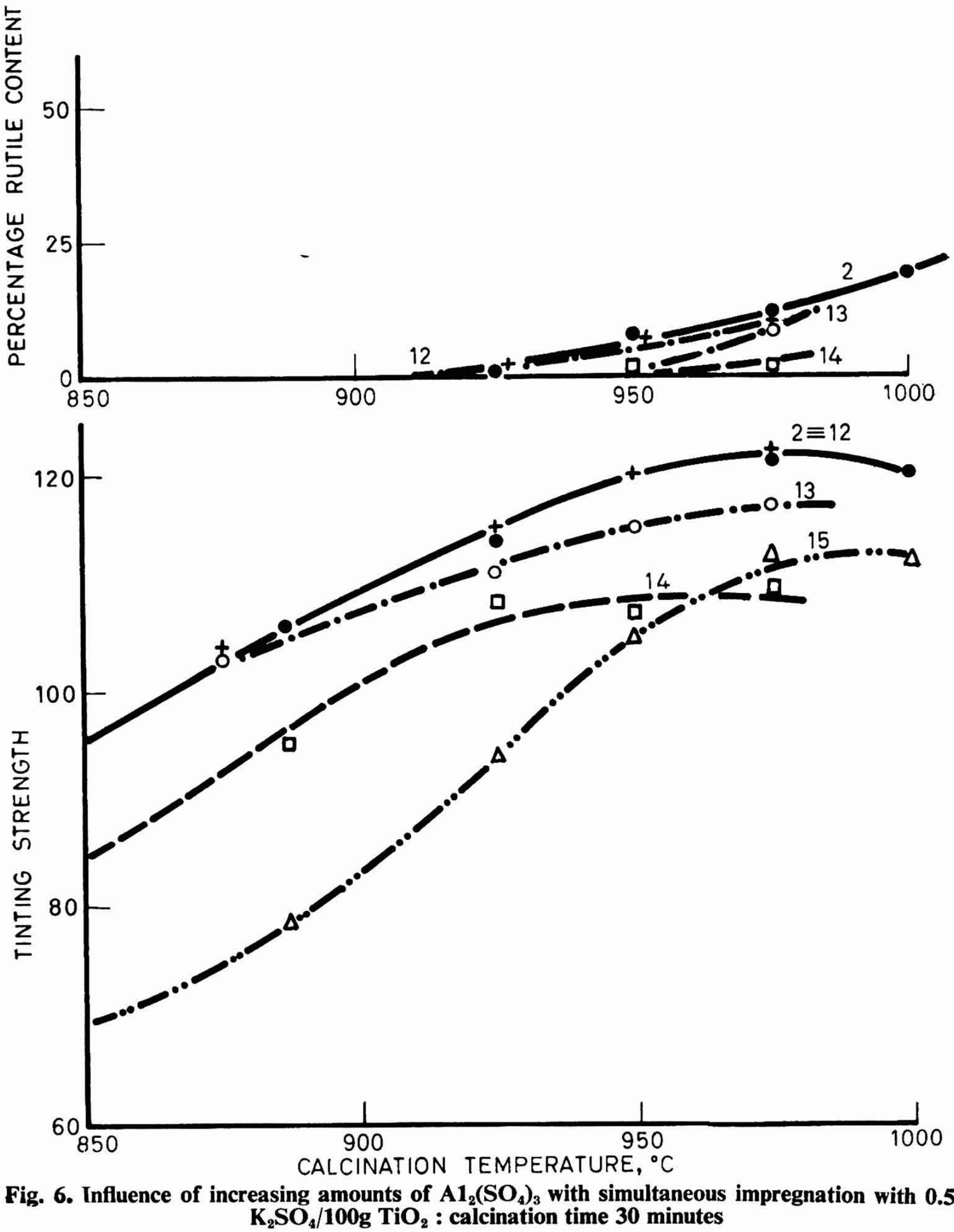

Fig. 6. Influence of increasing amounts of $Al_2(SO_4)_3$ with simultaneous impregnation with 0.5g K_2SO_4/100g TiO_2 : calcination time 30 minutes

Curve	Notation	Impregnation [g/100 g TiO_2] K_2SO_4	$Al_2(SO_4)_3$
2	●	0.5	0.0
12	+	0.5	0.32
13	○	0.5	0.63
14	□	0.5	1.97
15	△	0.5	4.06

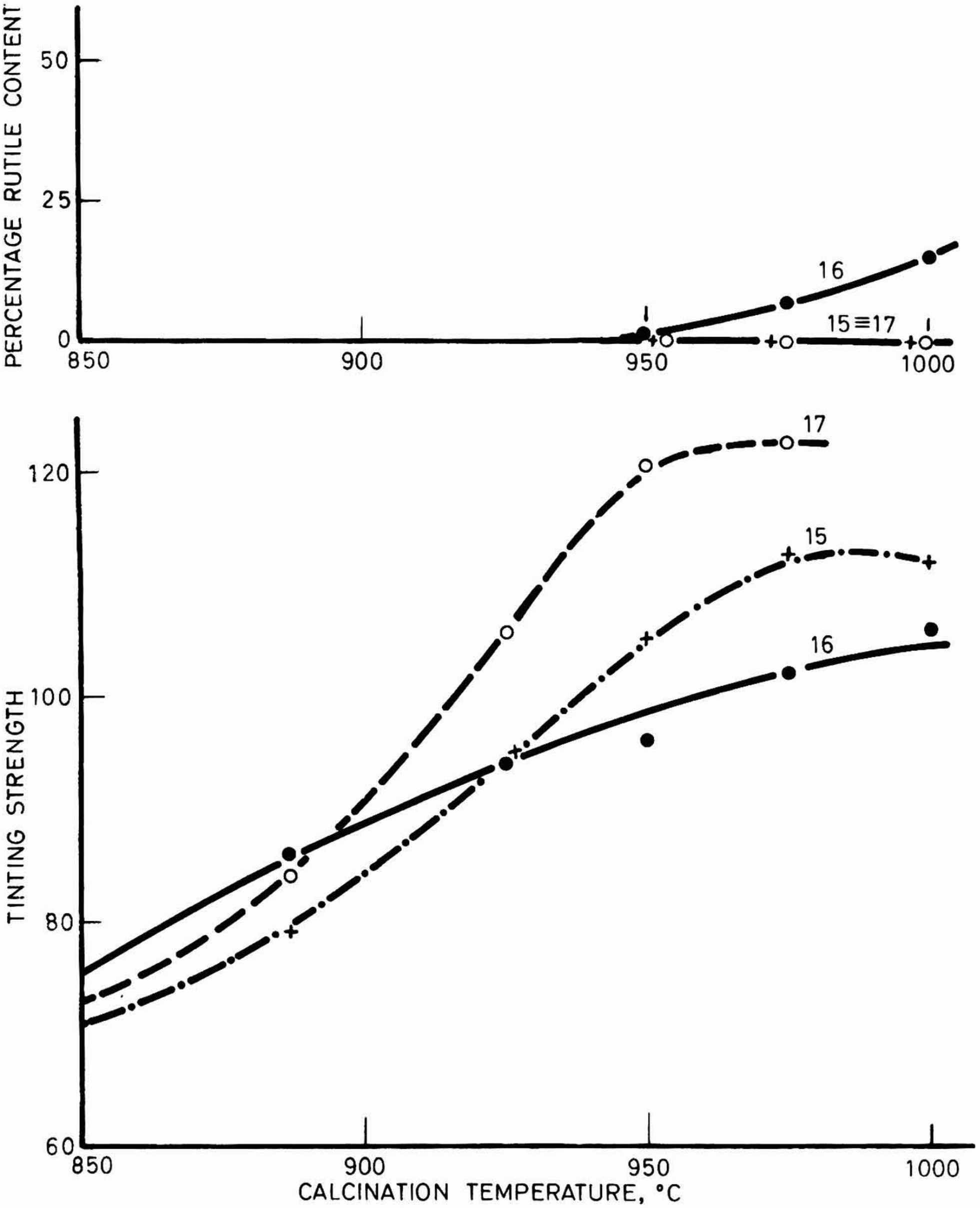

Fig. 7. Influence of increasing amounts of K_2SO_4 with simultaneous impregnation with 4.06g $Al_2(SO_4)_3$/100g TiO_2 : calcination time 30 minutes

Curve	Notation	Impregnation [g/100 g TiO_2]	
		K_2SO_4	$Al_2(SO_4)_3$
16	●	0.0	4.06
15	+	0.5	4.06
17	○	1.0	4.06

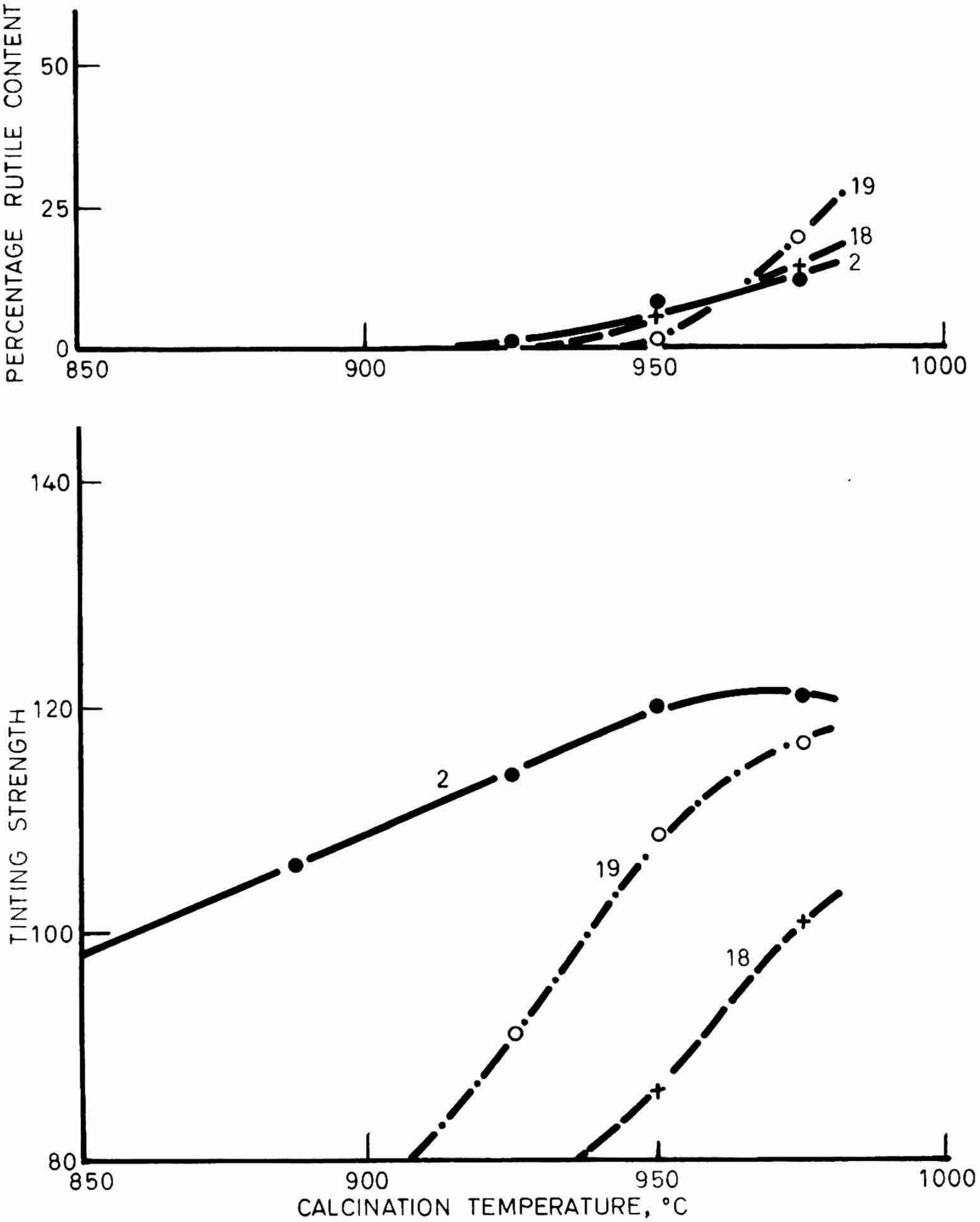

Fig. 8. Influence of antimony chloride and phosphoric acid : calcination time 30 minutes

Curve	Notation	Impregnation [g/100 g TiO_2]		
		K_2SO_4	H_3PO_4	$SbCl_3$
2	●	0.5	0.0	0.0
18	+	0.5	0.0	5.23
19	○	0.5	2.25	0

From Fig. 8 it may be seen that antimony trichloride and phosphoric acid have no marked effect on rutilisation. Both compounds decrease the tinting strength optimum, shifting it to higher temperatures. This conclusion results also from Fig. 9 where another sample of hydrated titanium dioxide, containing 7.67g H_2SO_4/100g TiO_2, was used as initial material.

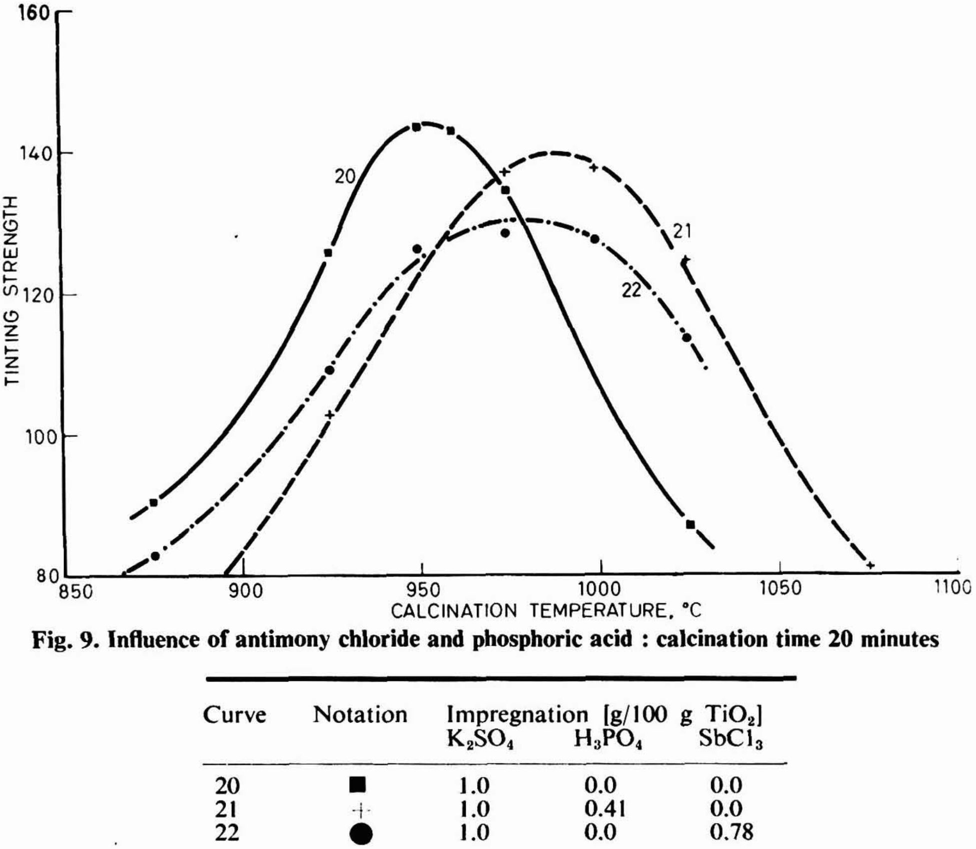

Fig. 9. Influence of antimony chloride and phosphoric acid : calcination time 20 minutes

Curve	Notation	Impregnation [g/100 g TiO_2] K_2SO_4	H_3PO_4	$SbCl_3$
20	■	1.0	0.0	0.0
21	+	1.0	0.41	0.0
22	●	1.0	0.0	0.78

Conclusion

The effect of zinc and aluminium sulphates, phosphoric acid and antimony trichloride in combination with potassium sulphate on the pigment properties of a product obtained by calcination at temperatures of 825°C to 1000°C has been studied. The results lead to the following conclusions :

(a) Zinc sulphate is a very good positive rutilisation catalyst. It shifts the tinting strength optimum to lower temperatures. However, the tinting strength resulting in this way, although that of a 100 per cent rutile, is lower than that of any products obtained by impregnation only with K_2SO_4. $ZnSO_4$—K_2SO_4 combinations interact, decreasing both rutilisation and tinting strength of the calcinate. By a mere combination of $ZnSO_4$ and K_2SO_4 as impregnation salts it is impossible to obtain a calcination product of a satisfactory tinting strength from a normal anatase hydrolysate.

(b) Aluminium sulphate is a negative rutilisation catalyst. Small additions have little effect on tinting strength, while larger amounts decrease it. This decrease may be compensated by larger additions of potassium sulphate.

(c) Antimony trichloride and phosphoric acid do not influence rutilisation markedly. They decrease the tinting strength optimum and shift it toward higher temperatures.

[*Received 19 December 1966*

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The influence of additives and calcination on the pigment properties of titanium dioxide: Part IV. The influence of some titanium compounds as rutilisation catalysts

By Vladimír Blechta, Miloš Lavička and Zdírad Blechta

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Summary

The influence of gel additions, prepared from $TiCl_4$ and peptised with hydrochloric acid in various combinations with potassium, sodium and zinc sulphates, to hydrated TiO_2 on the pigment properties of a product obtained by calcination at temperatures of 775°C to 975°C has been studied. Similarly the influence of sodium titanate peptised with hydrochloric acid has been studied. Both titanium compounds are very good positive rutilisation catalysts. They decrease the rutilisation temperature and improve the pigment properties of the calcinate.

IVème. Partie. L'influence de certains composés du titane en tant que catalyseurs de rutilisation

Résumé

Des gels ont été préparés du $TiCl_4$ et peptonisés par l'acide chlorhydrique en diverses combinaisons avec les sulfates de potassium, sodium, et zinc. On a ajouté ces gels à TiO_2 hydraté avant de'n calciner à des températures de 775°C a 975°C et l'on a etudié leur influence sur les propriétés pigmentaires du produit de calcination. Egalement on a etudié l'influence du titanate de sodium peptonisé par l'acide chlorhydrique. Tous ces composés du titane sont de bons catalyseurs de rutilisation. Ils diminuent la température de rutilisation et améliorent les propriétés pigmentaires du calcinat.

Teil IV: Der Einfluss Einiger Titanverbindungen als Rutilisierungskatalysatoren

Zusammenfassung

Objekt der Untersuchung war es, festzustellen, welchen Einfluss Gel-Zusätze, die aus $TiCl_4$ hergestellt und mit Salzsäure in verschiedenen Kombinationen mit Kalium-, Natrium und Zinksulfaten peptisiert worden waren, zu hydratisiertiertem TiO_2 hinsichtlich seiner Eignung als Pigment ausüben, das durch Kalzinieren bei Temperaturen zwischen 775 und 975°C gewonnen worden war. Das Studium erstreckte sich gleichfalls auf mit Salzsäure peptisiertes Natriumtitanat. Beide Titanverbindungen sind sehr gute positive Rutilisierungskatalysatoren. Sie erniedrigen die Rutilisierungstemperatur und verbessern die Eignung des kalzinierten Produktes für Pigmentzwecke.

Влияние добавок и кальцинации на пигментные свойства двуокиси титана Часть IV. Влияние некоторых соединений титана как катализаторов рутилизации

Резюме

Изучалось влияние гельных добавок, приготовленных из $Ti\ Cl_4$ и пептизованных соляной кислотой в различных соединениях с сульфатами калия, натрия и цинка в гидратное TiO_2, на пигментные свойства продукта полученного кальцинацией при температурах от 775°C до 975°C. Подобным же образом изучалось влияние титаната натрия пептизованного соляной кислотой. Оба титановых соединения являются очень хорошими положительными катализаторами рутилизации. Они понижают температуру рутилизации и улучшают пигментные качества кальцината.

Introduction

The earlier study[1] was of the influence of some rutilisation catalysts, added to the hydrated TiO_2, on the pigment properties of the calcinate. Titanium compounds form a separate group, e.g. a titanium compound formed by neutralisation of aqueous $TiCl_4$ solution with alkali hydroxide or ammonia, followed by peptisation with hydrochloric acid, is assumed to be a positive rutilisation catalyst.[2] The compound obtained by peptisation of sodium titanate with hydrochloric acid[3-5] is assumed to have a similar effect. Since very little has been published on the effects of these compounds on rutilisation and pigment properties of the final product, their influence in combination with potassium, sodium and zinc sulphates has been investigated.

Experimental

As in the former work[1], the initial material was hydrated titanium dioxide of anatase structure, containing 0.0913g H_2SO_4/g TiO_2, obtained on the industrial scale by thermal hydrolysis of sulphate solutions from ilmenite. The experimental methods, e.g. the method of preparing the sample for calcination in a grate-less fluidisation furnace[6], the method of determining the tinting strength by an objective method, and the determination of rutile in the final product were described earlier[7]. Samples impregnated with the respective additives were calcined for 30 minutes at temperatures of 775°C to 925°C. The rutile content and tinting strength were determined on every final product.

Preparation of the TiO_2 gel from the $TiCl_4$ solution

The solution of $TiCl_4$ in dilute hydrochloric acid was poured slowly under agitation into a dilute NaOH solution until the pH of the mixture dropped to 8.5, so as to obtain a final concentration of about 40g TiO_2/l. in the suspension, keeping the temperature during neutralisation below 30°C. Hydrochloric acid was then added in a weight ratio of $HCl : TiO_2 = 0.7$ and the suspension was heated to 85°C. After peptisation, the gel was coagulated by means of a NaOH solution and washed with water until disappearance of Cl^- in the filtrate.

Preparation of the peptised titanate

The suspension of the hydrated titanium dioxide, containing 350g TiO_2/l., was mixed with 40 per cent NaOH solution in weight ratio of $TiO_2 : NaOH = 1 : 1.6$. The resulting suspension was heated to boiling under reflux for two hours. The reaction mixture was then washed to remove excess NaOH and neutralised with hydrochloric acid to pH 3. The mixture was washed again with water until disappearance of Cl^- in the filtrate. The titanate thus prepared was analysed by the X-ray method and was found to be a 1:1 mixture of anatase and rutile. The titanate was then mixed with hydrochloric acid in a weight ratio of 1:1, heated to 80°C and kept at this temperature for 30 minutes. The suspension was then diluted with cold water to a final concentration of 50g/l. The product was analysed again and was found to be 100 per cent rutile.

Results and discussion

The behaviour of TiO_2 gel prepared from $TiCl_4$ solution

The behaviour of this compound in combination with potassium, sodium and zinc sulphates is shown in Fig. 1.

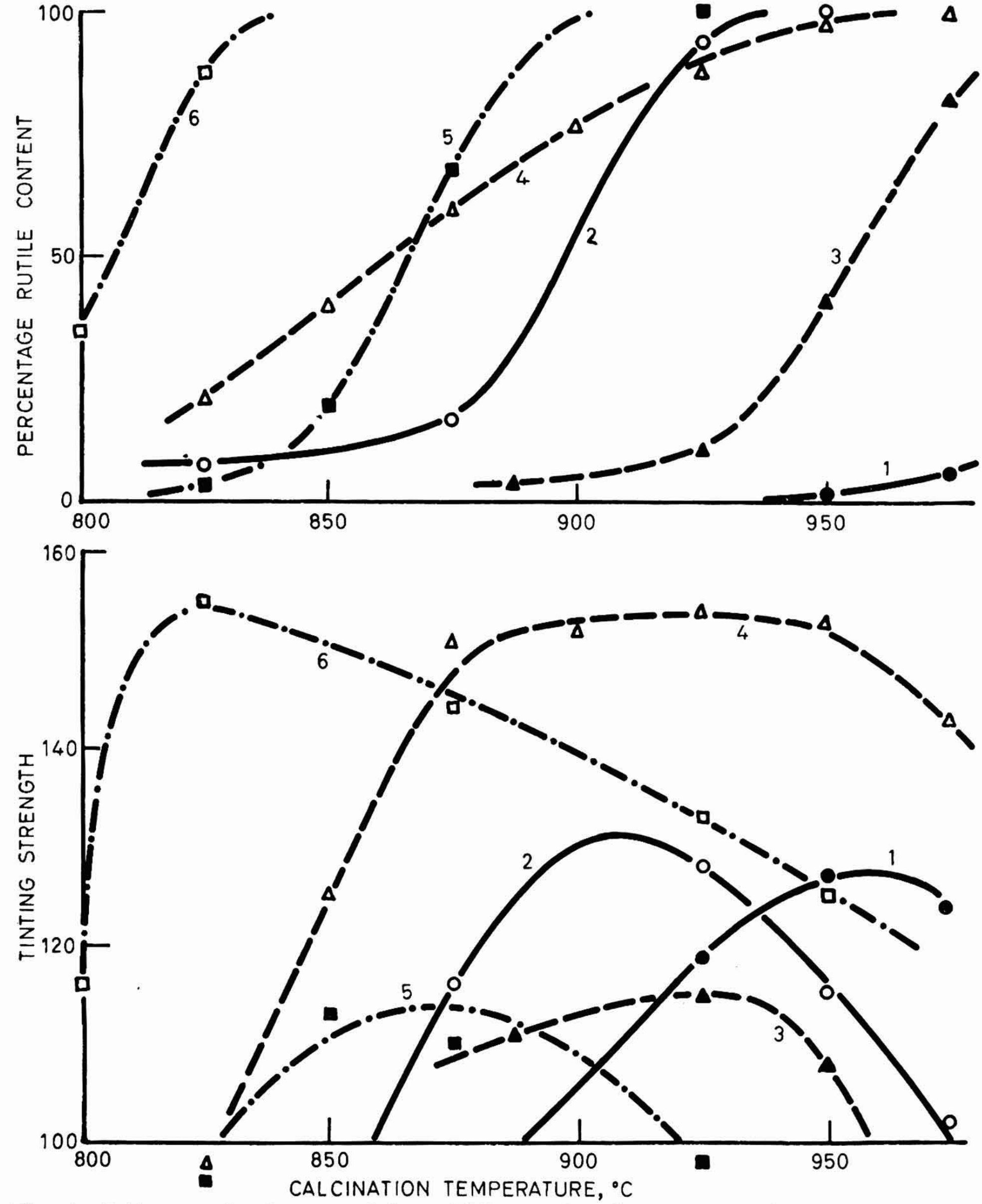
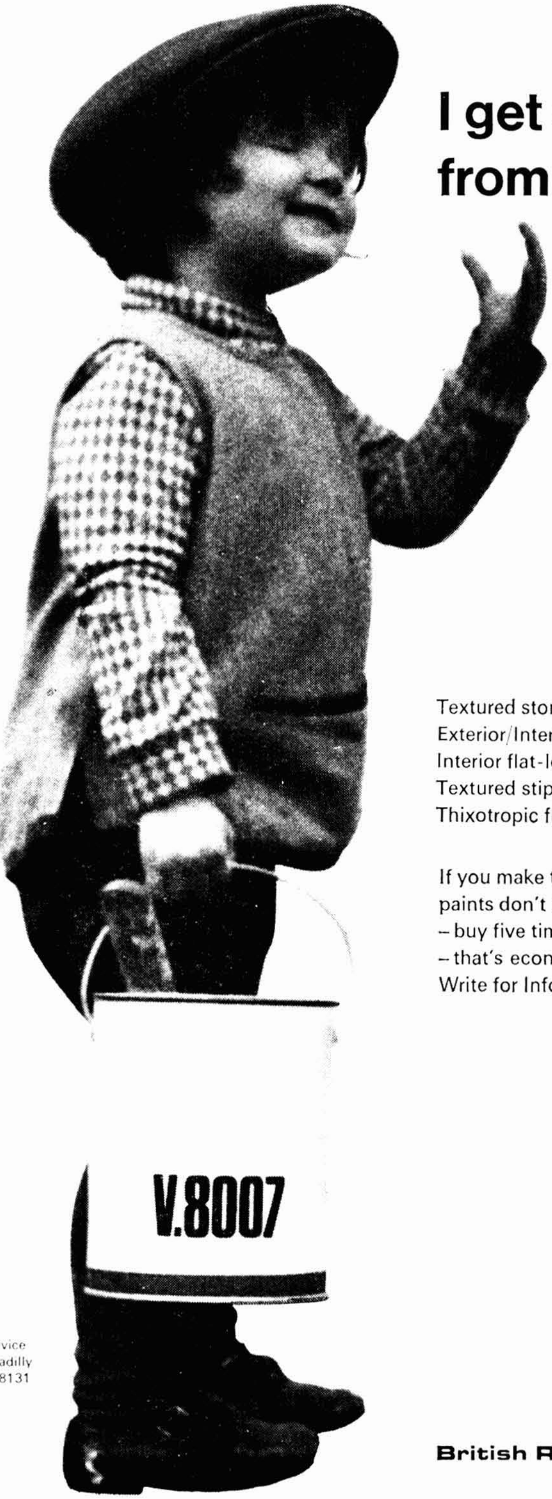


Fig. 1. Influence of gel prepared from $TiCl_4$ on the pigment properties of the calcinate: calcination time 30 minutes

Curve	Notation	Impregnation [g/100g TiO_2]			
		K_2SO_4	$ZnSO_4$	Na_2SO_4	TiO_2-gel
1	●	1.0	0	0	0
2	○	1.0	0	0	6.0
3	▲	0	0	0.8	0
4	△	0	0	0.8	6.0
5	■	1.0	1.85	0	0
6	□	1.0	1.85	0	6.0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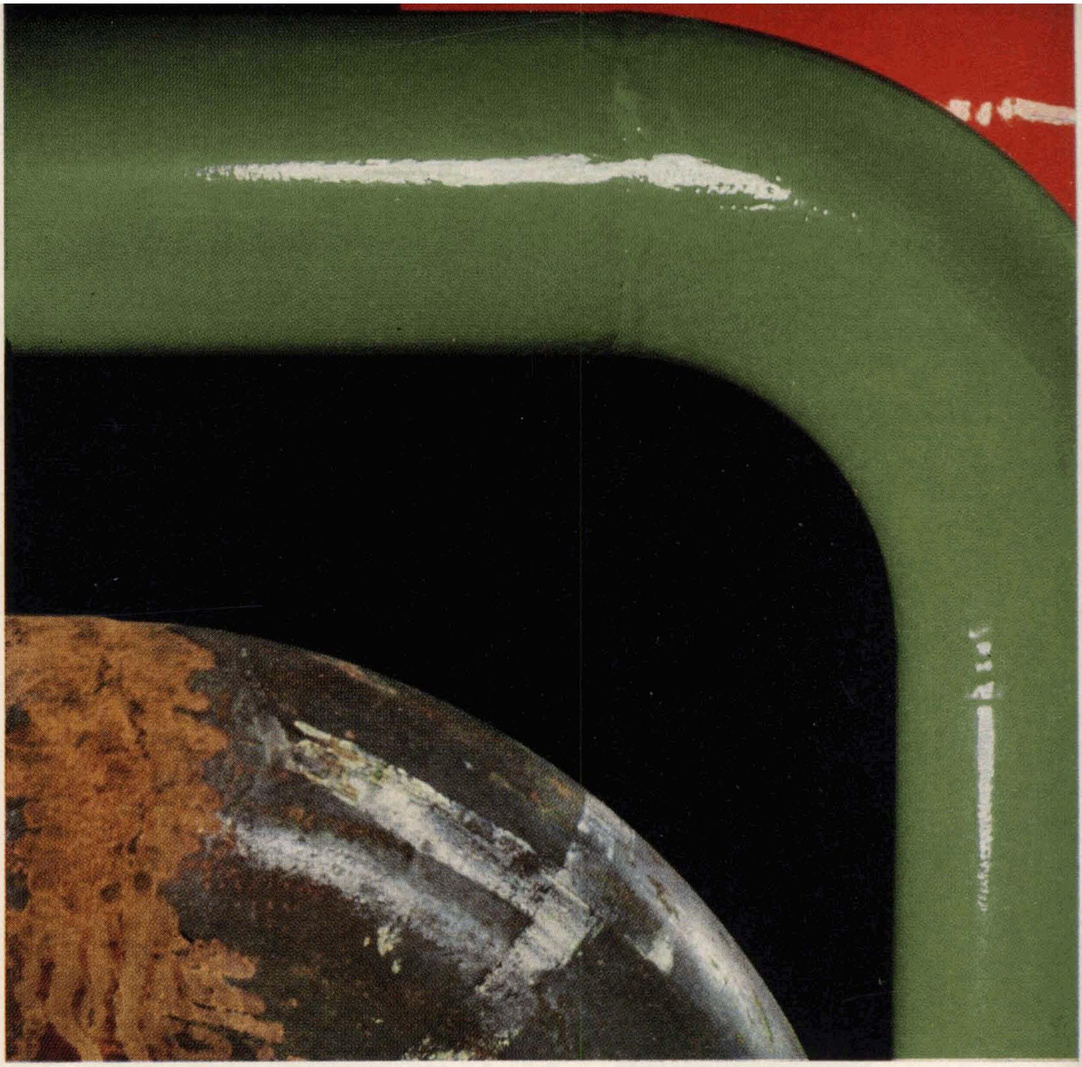

A comparison of the respective pairs of curves which differ in each case only in addition of the TiO_2 gel from $TiCl_4$ (Fig. 1 : curves 1,2 ; 3,4 ; 5,6) shows that the gel addition in all cases markedly decreases the rutilisation temperature. When another positive rutilisation catalyst is present besides the TiO_2 gel, the effect of both catalysts is additive (Fig. 1 : curves 3,4 and 4,5). The TiO_2 gel shifts the tinting optimum towards lower temperatures and higher tinting strength values. A combination of the TiO_2 gel with Na_2SO_4 (curve 4) is interesting in that, within the temperature range of 880° to 950°C, the tinting strength is but little dependent on the temperature. Furthermore, the rutilisation curve shows a substantially lower dependence on temperature.

The behaviour of peptised titanate

The behaviour of this titanium compound in combination with potassium sulphate, and the influence of ageing of the peptised titanate is evident from Fig. 2.

This shows the peptised titanate to be a very good rutilisation catalyst. The catalytic effects of zinc sulphate and the peptised titanate are additive. Similarly, as in the case of TiO_2 gel from $TiCl_4$, the peptised titanate shifts the tinting strength optimum towards lower temperatures and higher values. Since the curves 10, 11, 12 are superimposed, one may deduce that the peptised titanate does not age quickly and that the peptisation process itself is not particularly critical.

The influence of sodium sulphate compared with potassium sulphate in combination with the peptised titanate is shown in Fig. 3. Thus the sodium sulphate *ceteris paribus* increases the degree of rutilisation and slightly shifts the tinting strength optimum towards lower temperatures. In the presence of zinc sulphate the differences between sodium and potassium sulphates practically disappear.

It had previously been shown[7] that the addition of ammonia to the hydrated TiO_2 gel before calcination yielded a product which was easy to grind. It was necessary to verify whether this effect of ammonia addition would be observed in the case of impregnation with zinc sulphate and the peptised titanate. The results are shown in Fig. 4.

The ammonia addition, as expected, leads to a product with better grindability. As to the rutilisation and tinting strength of the final product, the properties of the ammonia-impregnated product were only slightly inferior, this fact agreeing with the earlier results[7].

It is interesting to note that TiO_2-based rutilisation catalysts distinctly differ from the other positive rutilisation catalysts, e.g. sodium and zinc salts. Sodium and zinc salts decrease the rutilisation temperature substantially, but at the same time they influence the growth of the particles, yielding a highly polydisperse product, generally having a lower tinting strength (in comparison with the anatase obtained without the addition of these rutilisation catalysts).

Thus the TiO_2-based rutilisation catalysts distinctly decrease the rutilisation temperature without unfavourably influencing the particle size in calcination. From the technological point of view this is a very favourable property which is, moreover, retained in the presence of zinc salts, which further decrease the rutilisation temperature.

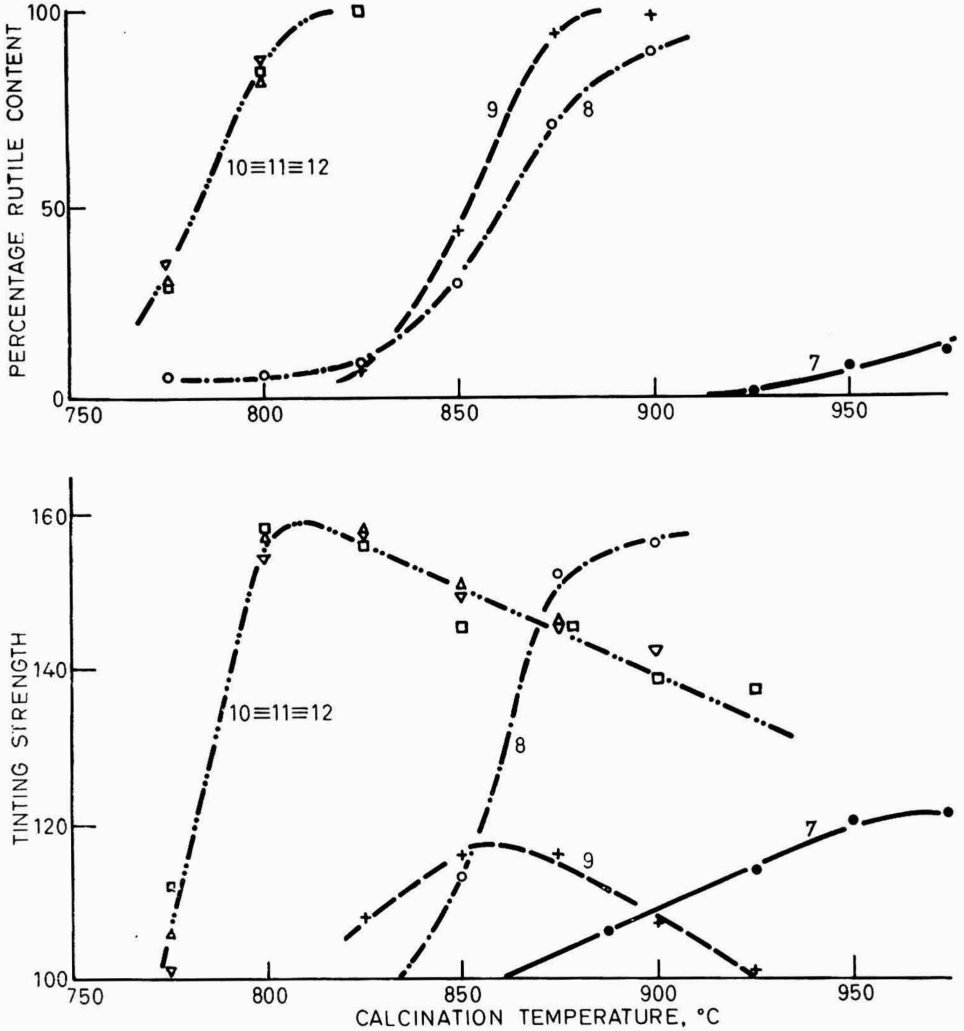

Fig. 2. Influence of peptised titanate in combination with potassium sulphate and zinc sulphate : calcination time 30 minutes. Note : Curve 12 is a reproduction of curve 10

Curve	Notation	Impregnation [g/100g TiO_2]			Age of peptised titanate (days)
		K_2SO_4	$ZnSO_4$	pept. tit.	
7	●	0.5	0	0	—
8	○	0.5	0	2.0	1
9	+	0.5	3.7	0	—
10	□	0.5	3.7	2.0	1
11	▽	0.5	3.7	2.0	26
12	△	0.5	3.7	2.0	1

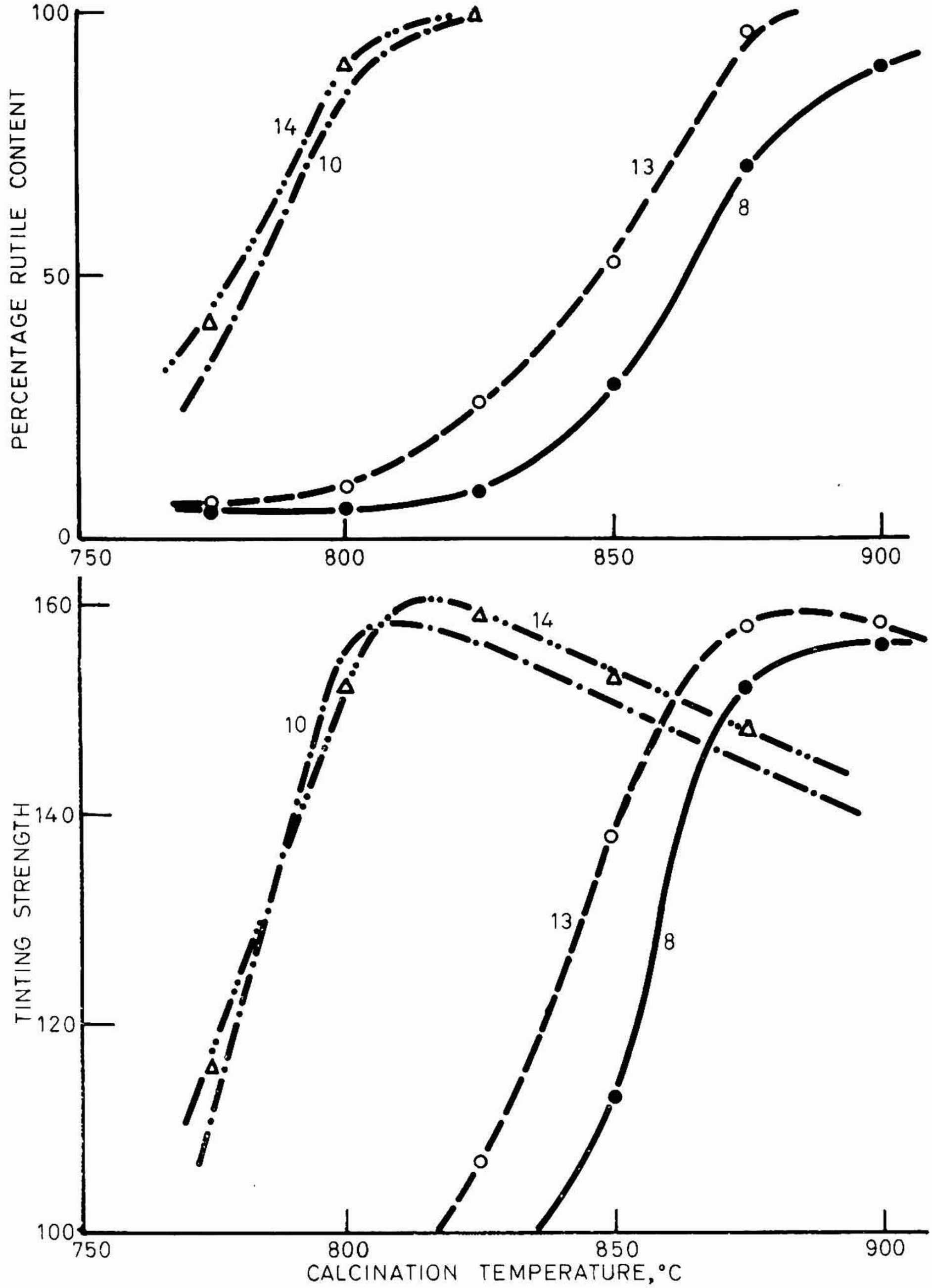

Fig. 3. Influence of sodium and potassium sulphate in combination with peptised titanate : calcination time 30 minutes

Curve	Notation	Impregnation [g/100g TiO_2]			
		K_2SO_4	Na_2SO_4	$ZnSO_4$	pept. tit.
8	●	0.50	0	0	2.0
13	+	0	0.40	0	2.0
10		0.50	0	3.7	2.0
14	△	0	0.40	3.7	2.0

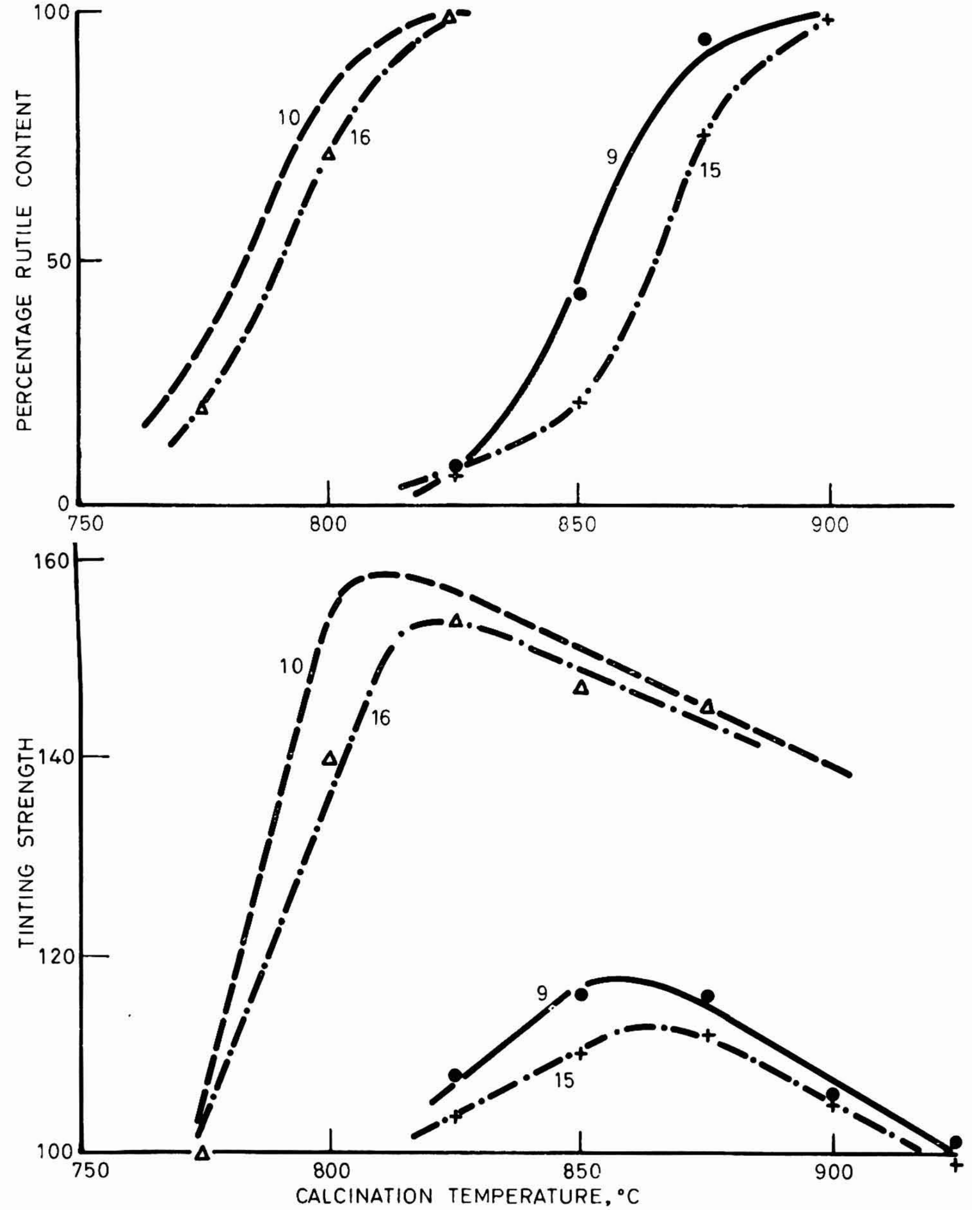

Fig. 4. Influence of ammonia in combination with potassium sulphate, zinc sulphate and peptised titanate : calcination time 30 minutes

Curve	Notation	Impregnation [g/100g TiO_2]			
		K_2SO_4	$ZnSO_4$	pept. tit.	NH_4OH
9	●	0.50	3.7	0	absent
15	+	0.50	3.7	0	present
10		0.50	3.7	2.0	absent
16	△	0.50	3.7	2.0	present

Conclusion

The influence of some titanium compounds, prepared from $TiCl_4$ and sodium titanate, on the calcination of hydrated TiO_2 has been studied. The following conclusions may be drawn.

(1) Both titanium compounds are good positive rutilisation catalysts. In presence of another rutilisation catalyst the influence of the catalysts is additive.

(2) Both titanium compounds shift the tinting strength optimum towards lower temperatures and higher tinting strength values. This is a basic difference compared with the effect of $ZnSO_4$ which also shifts the tinting strength optimum towards lower temperatures but yields final products having an unsatisfactory tinting strength.

(3) The peptised sodium titanate does not age rapidly, and the peptisation process is not particularly critical.

(4) The addition of ammonia to the hydrated TiO_2 gel before calcination in presence of the above titanium compounds and of zinc sulphate also results in a product of better grindability. As to the rutilisation of the final product, the ammonia-impregnated product is only slightly inferior.

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Formulation of fungus-resistant paints: Addition of para toluene sulphonamide

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Summary

Para toluene sulphonamide (PTSA) has been assessed as a fungicide for gloss and flat alkyd enamel coatings. Panels coated with these paints were exposed at Lae, New Guinea, and houses in Melbourne were painted indoors with a flat enamel containing PTSA. The mould growth in each case was compared with that on the same paint free of fungicide. The loss of PTSA from paint films under different conditions was also determined.

PTSA was found to be of no particular value as a fungicide for outdoor application, but tends to increase the fungus resistance of paints used indoors. Analytical results show that PTSA is quickly lost from the paint film outdoors, especially under humid tropical conditions.

La mise au point des formules de peinture resistant à végétation mycélienne

Résumé

On a apprécié, en tant que fongicide, la sulfamide de para toluène (PTSA) dans des peintures-émaux brillantes et mats. Panneaux-éprouvettes revêtus de telles peintures ont été exposés à Lae, Nouvelle Guinée et des maisons à Melbourne ont été peintes à l'intérieur avec une peinture mate contenant PTSA. La croissance de moisissure en chaque instance était comparée auprès de celle sur la même peinture exempte de fongicide. La perte de PTSA à partir des feuils de peinture exposés sous de diverses conditions a été déterminée également.

On a trouvé que la PTSA ne possède pas de valeur remarquable en tant que fongicide pour l'usage à l'extérieur, quoiqu'elle augmente la résistance à vegetation mycélienne des peintures à l'intérieur. Résultats analytiques démontrent que la PTSA se perd très rapidement à partir du feuil de peinture à l'extérieur, notamment sous des conditions de l'humidité tropicale.

Formulierung Eines Rezeptes für Anstrichmittel, die Pilzwachstum Verhüten: Zusätze von Paratoluolsulfonamid

Zusammenfassung

Paratoluolsulfonamid (PTSA) wurde auf seine Eignung als Fungizid in aus glänzenden und matten Alkydharzemaillen bestehenden Anstrichmitteln geprüft. Mit diesen Emaillelacken gestrichene Tafeln wurden in Lae, Neu Guinea bewittert; ausserdem wurden in Melbourne Häuser innen mit matter, PTSA-haltiger Emaille gestrichen. Das Ausmass des Verschimmelns wurde in jedem einzelnen Falle mit dem auf der gleichen, aber fungizidfreien Farbe verglichen. Ebenfalls wurde der sich unter verschiedenen Verhältnissen ergebende Verlust an PTSA aus den Anstrichfilmen bestimmt.

Es wurde gefunden, dass PTSA als Fungizid für Aussenanwendung keinen besonderen Vorteil bietet, dass es aber die Resistenz gegen Pilzbewuchs von Anstrichmitteln für Innen fördert. Wie analytische Resultate zeigen, geht aussen PTSA schnell, besonders unter feuchten tropischen Bedingungen, aus dem Farbfilm verloren.

Формулировка красок с сопротивлением против плесени
Добавление паратолуолсульфонамида

Резюме

Оценивается эффективность паратолуолсульфонамида (ПТСА) как средства для истребления плесени в блестящих и матовых алкидных эмалевых покрытиях. Панели окрашенные этими красками подвергались действию лучей света в Лао, Новая Гинея и жилища в Мельбурне окрашивались внутри матовой эмалевой краской содержащей ПТСА. В каждом случае нарастание плесени сравнивалось с плесенью на той же краске без фунгисида. Определялась потеря ПТСА в красочных пленках при различных условиях экспонирования.

Установлено что ПТСА не проявляет особых качеств как истребитель плесени под открытым небом, но имеет тенденцию увеличивать сопротивление против плесени в красках применяемых внутри домов. Аналитические результаты показывают что ПТСА быстро испаряется из красочной пленки на открытом воздухе, особенно при влажных тропических условиях.

Introduction

The first investigation of para toluene sulphonamide as a fungicide seems to have been by workers at the Naval Research Laboratories, Washington, D.C.[1] The purpose of their experiments was to formulate a coating that would protect electronic equipment in the humid tropics. They incorporated PTSA and many other compounds recommended as fungicides in a tung oil varnish and in a lacquer, and the coatings were applied to cotton braided wire exposed in a closed hut in the Panama Canal Zone. PTSA proved superior to all other compounds tested. PTSA was later proposed as an addition to house paints, and it was claimed that paints containing from 8 to 12 per cent (based on the solid paint vehicle) showed considerably increased resistance to mould growth.

As this compound is comparatively cheap and non-poisonous it appeared worthwhile to investigate this claim, and in accordance with the general pattern of the Division's work on fungicides[2] the stability of PTSA in a paint film under different conditions of exposure was also examined.

Experimental

Analytical work

Flat and gloss alkyd enamel paints and the corresponding blanks were brushed out on sheets (12 in × 6 in) of polyethylene terephthalate polyester film which were then attached to hardboard panels and exposed under the following conditions :

(1) Outdoors at Highett, Victoria.
(2) In a fog room at 20°C.
(3) In a constant temperature room kept at 20°C and 65 per cent RH.
(4) In a hot room at 38°C.
(5) Outdoors at Lae, New Guinea.

The panels at Highett were mounted on racks at an angle of 45° facing north ; those at Lae had the painted films attached to both sides and were mounted at 45° and facing 31° east of true north.

The concentration of PTSA on the dry paint film and on the paint vehicle is set out in Table 1.

Table 1

Concentration of PTSA in paints

Paint	Exposure*	On paint film (%)	On paint vehicle (%)
Gloss enamel	Outdoors, Highett, and under controlled conditions in laboratory	5.1	9.3
	Outdoors, Lae	6.9	12.5
Flat enamel	Outdoors, Highett, and under controlled conditions in laboratory	6.3	24.0
	Outdoors, Lae	8.5	32.7

*See text.

The analyses were carried out spectrophotometrically[3]. Instead of extracting with cyclohexane as described previously[3], extraction with water was used, as this proved more convenient and also more accurate.

Evaluation indoors

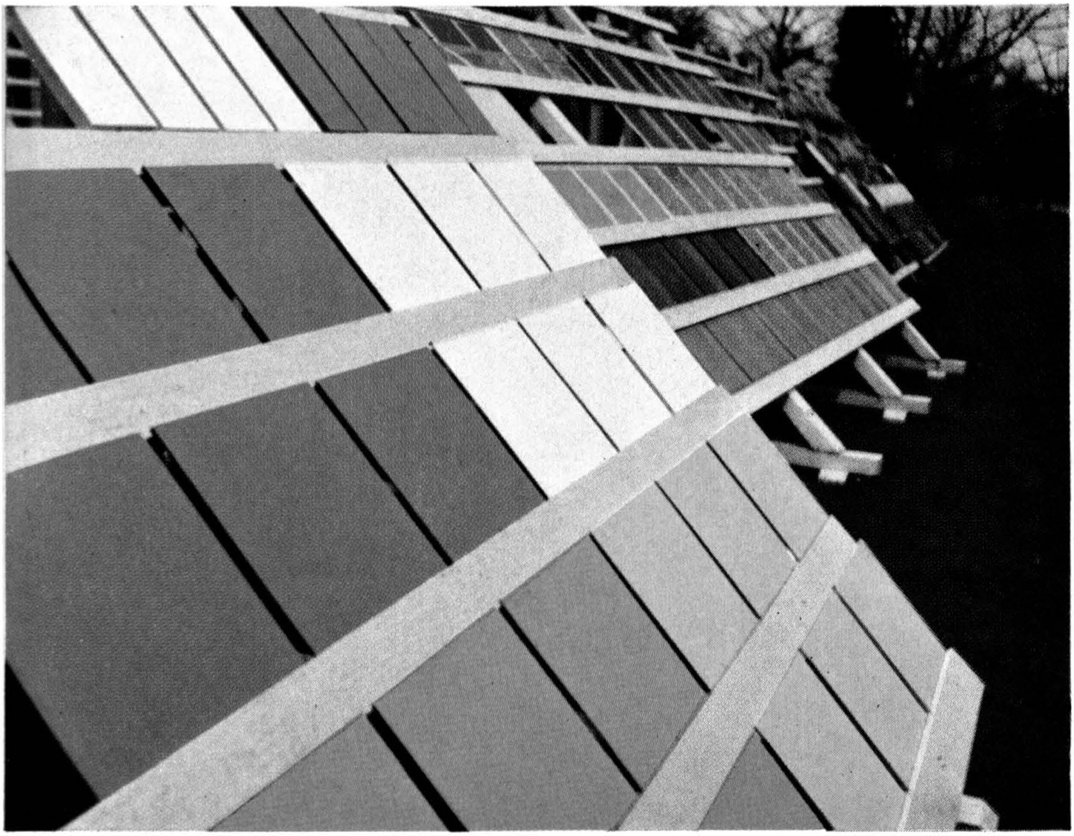
Evaluation of the paint indoors was carried out in 34 dwellings in Melbourne in which a comparatively high degree of mould growth had made repainting desirable. Nineteen houses were decorated with a flat alkyd enamel paint containing 4 per cent PTSA (PTSA content on the paint film 6.8 per cent, on the paint vehicle 26 per cent), and 15 houses were decorated with the same flat alkyd enamel without fungicide. Before painting, all walls were washed down with methylated spirits. The houses were inspected after each winter season, when mould growth is strongest, and the growth washed off with a hypochlorite solution. The results are summarised in Table 2.

Table 2

Incidence of mould growth in houses painted with a flat alkyd enamel containing PTSA

Inspection*	Control		4% PTSA	
	Number inspected	% affected	Number inspected	% affected
1	11	54.5	11	0
2	15	46.6	19	15.8
3	13	77.0	19	31.6
Average percentage affected over three seasons		59.0		18.3

*Inspection made annually after each winter season.



Exposure at Lae, New Guinea

A separate set of hardboard panels painted with gloss and flat enamel paints, and the corresponding blanks, were exposed at Lae, New Guinea. The intensity and extent of mould growth was assessed at intervals of about three months. The results are summarised in Tables 3 and 4.

Table 3

Assessment of mould growth on paint films exposed outdoors at Lae: upper side of panels

Paint	Replicate number	Exposure									
		4 months		8 months		12 months		15 months		18 months	
		I	C	I	C	I	C	I	C	I	C
G	1	1	100	2	70	3	100	4	2	1	100
	2	1	100	2	70	3	100	4	2	2	100
	3	1	100	2	70	3	100	4	2	2	100
GP	1	1	100	1-2	50	2	100	2	100	2	100
	2	1	100	2-3	80	2	100	2	100	2	100
	3	1	100	2	50	2	100	2	100	2	100
F	1	3	100	2	100	0	100	9	30	9	30
	2	2	100	2	100	0	100	1	100	1	100
	3	3	100	2	100	0	100	9	30	9	30
FP	1	4-5	30	6	90	6-8	80	5-6	100	6	100
	2	4-5	30	6	80	2-3	15	5-6	90	6	90
	3	4-5	30	6	90	5	100	5-6	100	6	100

G, gloss paint without PTSA ; GP, gloss paint with PTSA ; F, flat enamel paint without PTSA ; FP, flat enamel paint with PTSA.

Each panel was assessed by noting the percentage area " C " covered by mould and by the colour intensity " I " according to the following scale : 9 black → 0 white.

Table 4

Assessment of mould growth on paint films exposed outdoors at Lae : underside of panels

Paint	Replicate number	Exposure									
		4 months		8 months		12 months		15 months		18 months	
		I	C	I	C	I	C	I	C	I	C
G	1	3	1	3	100	2-3	90	4	60	4	50
	2	3	1	3	100	2-3	60	4	60	4	50
	3	3	1	3	100	3	70	4	60	4	50
GP	1	0	0	0	0	2	100	2-5	90	3-9	100
	2	0	0	0	0	2	100	2-5	85	3-9	100
	3	0	0	0	0	2	100	2-5	85	3-9	100
F	1	5	100	4	100	5	100	3-5	70	3-9	100
	2	5	100	3-4	100	5	100	3-5	100	2	50
	3	5	100	3-4	100	5	100	3-5	100	2-8	100
FP	1	8	10	3-7	10	2-3	100	3-4	90	3-9	100
	2	8	10	3-7	10	2-3	100	3-4	90	3-9	100
	3	8	10	3-7	10	2-3	100	3-4	95	3-9	100

G, gloss paint without PTSA ; GP, gloss paint with PTSA ; F, flat enamel paint without PTSA ; FP, flat enamel paint with PTSA.

Each panel was assessed by noting the percentage area " C " covered by mould and by the colour intensity " I " according to the following scale : 9 black → 0 white.

Discussion

The samples were analysed for PTSA and the losses from the gloss paint films graphed in Fig. 1 and from the flat enamel paint in Fig. 2. At Lae (curve 2) and in the fog room the loss of PTSA from the paint film was very fast, and

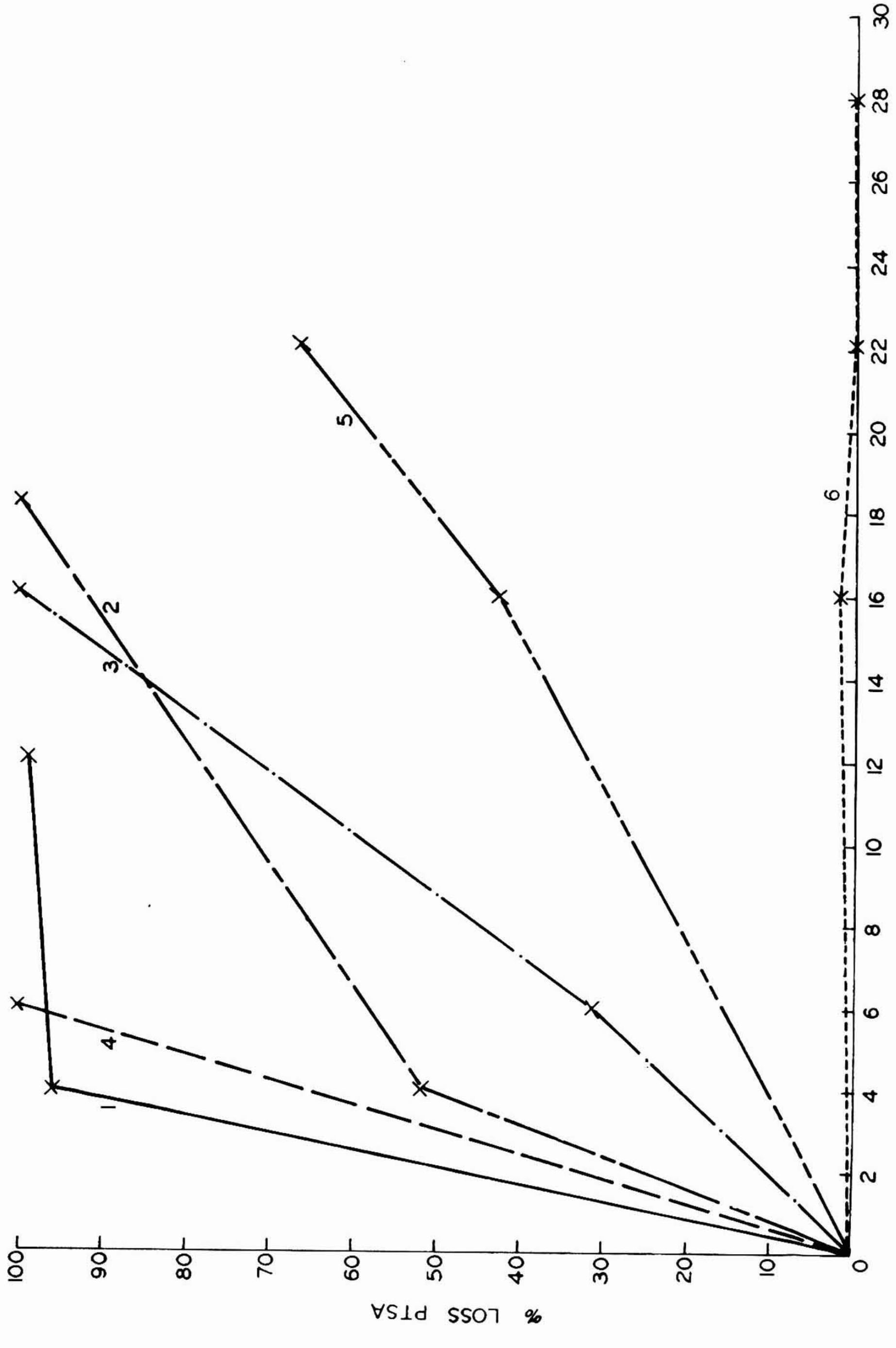


Fig. 1. Loss of PTSA from gloss enamel paint

1. Outdoors, Lae, New Guinea (upper side) 2. Outdoors, Lae, New Guinea (underside) 3. Outdoors, Highett, Victoria
4. Fog room 5. Hot room 6. Constant temperature room

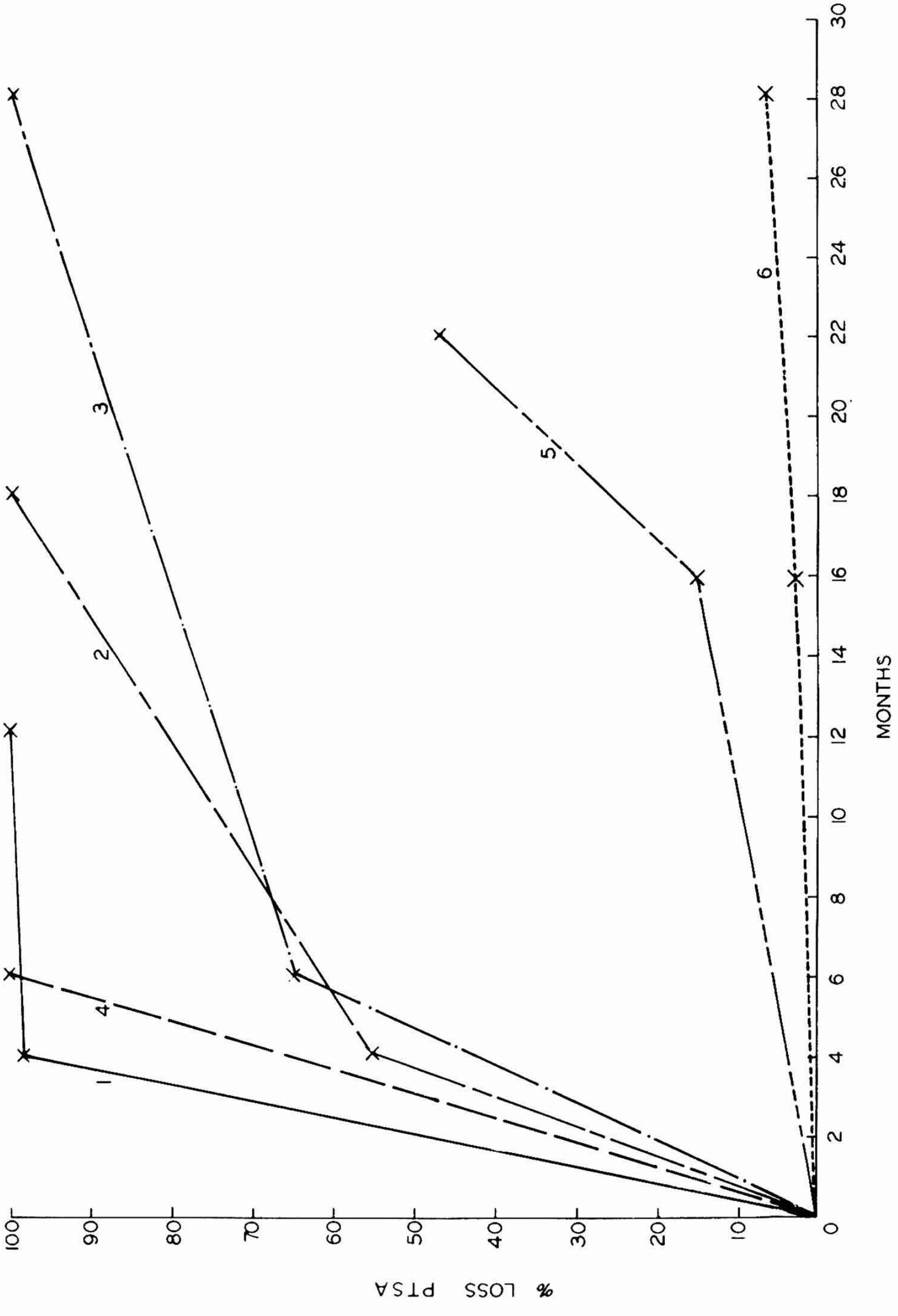


Fig. 2. Loss of PTSA from flat enamel paint
1. Outdoors, Lae, New Guinea (upper side) 2. Outdoors, Lae, New Guinea (underside) 3. Outdoors, Highett, Victoria
4. Fog room 5. Hot room 6. Constant temperature room

practically all of the fungicide was lost in from four to six months (curves 1 and 4). Loss from paint films on the underside of panels at Lae was more than 50 per cent in four months. After one year there was still some extractable compound left, but the spectrogram had already changed from that of the pure PTSA and it was impossible to say how much was left. After 18 months the spectrogram had changed so extensively that the PTSA content was assessed to be zero.

Outdoors at Highett (curve 3) the rate of loss was lower than at Lae, and nothing was left in the gloss enamel after 16 months. In the flat enamel the loss was 65 per cent after six months. At this time there was still an extractable compound left, but the spectrogram had started to change so that it was impossible to say how much PTSA was present. After 28 months the spectrogram had changed to such an extent that the PTSA content had to be taken as zero. In the constant temperature room (curve 6) the PTSA content was practically unchanged over a period of 28 months, but there was a loss from specimens in the hot room (curve 5).

Visual assessment—indoors

Results of the survey made over a three-year period are summarised in Table 2 and show that when PTSA is included in the paint the incidence of mould growth is reduced (significant at the <5 per cent level) to about 31 per cent of that of the control. The average area (over two seasons) covered by mould per affected house was 40 sq ft in the control and 18 sq ft in the houses decorated with a paint containing the fungicide. It has not been possible to prove statistically that this difference is significant, but these figures are given here to indicate the extent to which mould growth occurs in the dwellings under observation.

Visual assessment—outdoors

The results of the assessments are given in Tables 3 and 4. Inspection shows that on the upper side (Table 3) the addition of PTSA does not make much difference to the mould growth on the panels. On the under side (Table 4) the paints containing PTSA have a somewhat better appearance after exposure up to eight months.

Conclusions

The results show that addition of PTSA to paint, even at the high levels used in the investigation, does not increase the mould resistance sufficiently to be of any value in outdoor exposure in the humid tropics. Analytical results show that this is due to the very rapid loss of the fungicide from the paint film.

The addition of 4 per cent PTSA to a flat alkyd enamel used indoors has a significant effect by reducing the incidence of mould to 31 per cent of that of the control.

Acknowledgments

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Metallo-organic primer coatings*

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Summary

The formation of metal complex primer coatings by direct chemical interaction of the metal substrate with a drying oil type medium containing reactive groups (viz., chelating groups such as gallate, pyrogallyl or aceto-acetate, and salt forming groups such as organophosphonic or organosulphonic acids) has been investigated. Novel routes were developed for the preparation of media containing polyhydric phenol, phosphonic acid and sulphonic acid groups. With the latter two types, synthesis difficulties limited the range of media which could be prepared.

Rust-free mild steel was the most reactive substrate and the specific conditions required for promoting the formation of significant amounts of Fe complex coating *in situ* have been determined. From the practical point of view, Fe complex primers from media containing polyhydric phenol groups showed most promise and a wide range of systems were accordingly evaluated, including gallate derivatives from vegetable oils, alkyds, epoxy esters, etc., and pyrogallyl modified vegetable oils. In certain cases, e.g., a gallate modified tung/linseed alkyd, coatings deposited from dilute solution under the specified conditions were cured (via Fe complex formation) at ordinary temperatures to touch-dry films, about 0.5 mil in thickness, in about 10-15 minutes. The films, which became rub resistant after about 1 hour, exhibited very good adhesion and anticorrosive properties and were shown to be suitable for subsequent welding without toxicity hazard.

Attempts were made to elucidate the chemistry of Fe/polyhydric phenol type complexes.

Couches primaires métallo-organiques

Résumé

On a etudié la formation des complexes métaux-couches primaires par l'interaction chimique directe du support métallique et un liant siccatif contenant de groupements réactifs (à savoir des groupements chélateurs tels que gallate, pyrogallyle ou acéto-acétate, et ceux tels que les acides organophosphoniques ou organosulfoniques qui peuvent donner des sels). On a mis au point des nouvelles méthodes pour préparer des liants contenant de groupements phénoliques polyhydriques, d'acides phosphoniques ou sulfoniques. Dans le cas des deux derniers types, la gamme des liants, que l'on saurait préparer, était limitée à cause des difficultés au point de vue de la synthèse.

On a determiné les conditions particulières qu'exige la formation *in situ* des quantités importantes de complex fer-primaire dans le cas d'acier doux exempt de rouille qui était le support le plus réactif. Au point de vue pratique, les complexes fer-primaires à partir des liants contenant de groupements phénoliques polyhydriques ont démontré la meilleure allure, et par consequent on a apprécié une gamme étendue de systèmes, notamment, des gallates dérivés des huiles végétaux, des alkydes, des esters époxydiques, etc., et des huiles végétaux modifiées au pyrogallol. Dans certains cas, par exemple une alkyde, à base d'un mélange des huiles de bois de Chine et de lin, modifiée à l'acide gallique, les couches rendues par une solution étendue sous des conditions mentionnées étaient prises (par la formation d'un complexe ferrifère) à des températures ambientes sous forme des feuils d'une épaisseur de 0.5 mil environ, qui étaient manipulables après 10-15 minutes. Les feuils devenaient résistants à frottage après une heure environ, et ils démontraient de bonnes propriétés anti-corrosives et également d'adhesion. On a trouvé que des supports revêtus de ces feuils peuvent se souder sans aucun risque au point de vue de toxicité.

On a tenté d'expliquer la chimie des complexes Fe/phénol polyhydrique.

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*Read before the Newcastle Section on 6 October 1966 and before the London Section on 8 December 1966.

Metallorganische Primer-Anstrichmittel

Zusammenfassung

Die Bildung von Metallkomplex-Primern durch direkte chemische Reaktion zwischen Metallsubstrat und einem, trocknendes Öl enthaltenden Bindemittel mit reaktiven Gruppen (nämlich Chelat bildenden Gruppen, wie z.B. Gallat, Pyrogallyl oder Azetazetat und salzbildenden Gruppen z.B. Organophosphorige oder Organosulfosäure) wurde untersucht. Neuartige Wege zur Herstellung von mehrwertigen Phenol-, phosphorige Säure- und Sulfosäuregruppen enthaltenden Bindemitteln wurden entwickelt. Bei letzteren beiden Gattungen beschränkten Schwierigkeiten mit der Synthese den Bereich der Bindemittel, welche hergestellt werden konnten.

Das reaktivste Substrat war rostfreies Eisenblech. Die für die Förderung der Bildung *in situ* von einer mengenmässig nennenswerten Schicht bestehend aus Fe-Komplex erforderlichen spezifischen Bedingungen wurden bestimmt. Aus praktischen Gründen waren Eisenkomplex-primer aus Bindemitteln, die mehrwertige Phenolgruppen enthalten, am vielversprechendsten, und demnach wurden eine erhebliche Reihe von Systemen bewertet, einschliesslich der Gallatabkömmlinge pflanzlicher Öle, Alkyde, Epoxyester, usw., sowie mit Pyrogallyl modifizierte Pflanzenöle. In gewissen Fällen, z.B. bei gallatmodifiziierten Holzöl/Leinölalkyden wurden aus verdünnten Lösungen unter den spezifischen Bedingungen aufgetragene Anstriche (via Fe-Komplexbildung) bei gewöhnlicher Temperatur unter Bildung klebfreier Filme von etwa 0.5 mil. Dicke in etwa 10 bis 15 Minuten verfestigt. Die nach etwa 1 Stunde reibfesten Filme zeigten gute Haftfestigkeit und antikorrosive Eigenschaften und erwiesen sich als für späteres Schweissen geeignet und zwar ohne gesundheitsschädliches Risiko.

Es wurde versucht, die Chemie der Fe-mehrwertigen Komplexe des Phenoltyps zu erklären.

Металлоорганические грунтовые покрытия

Резюме

Изучалось образование металлокомплексных грунтовых покрытий путем непосредственного химического взаимодействия металлического подслоя со средой типа быстровысыхающего масла, содержащей реактивные группы (т.е. хелатные группы как например галлат, пирогалло – или ацето-ацетат и солеобразующие группы как органофосфонная или органосульфонная кислоты). Разработаны новые пути для изготовления сред содержащих полигидрический фенол и группы фосфонной и сульфонной кислот. В последних двух типах синтетические трудности ограничили число сред которые могли быть изготовлены.

Нержавеющая низкоуглеродистая сталь оказалась наиболее реактивным субстратом и были определены специфические условия, способствующие образованию значительных количеств комплексного Fe покрытия на месте. С практической точки зрения Fe комплексные грунтовые покрытия, для сред содержащих многоатомные группы фенола, оказались наиболее перспективными и соответственно была произведена оценка широкого класса систем, включая галлатные производные растительных масел, алкидов, эпокси эфиров и т.д. и также растительных масел модифицированных пирогаллилом. В некоторых случаях, как например в случае алкида древесного китайского и льняного масла модифицированного галлатом, покрытия осажденные из разбавленного раствора в специфических условиях подвергались сушке (путем образования Fe комплекса) при обычных температурах, без прилипания к сухим пленкам толщиной около 0,5 мм после 10-15 минут. Пленки, которые стали устойчивыми против трения через приблизительно час времени, обнаружили очень хорошие качества сцепления и противокоррозийности и оказались пригодными для последующей сварки, без обнаружения признаков разъедаемости.

Были сделаны попытки уточнить химический механизм комплексов типа Fe/полигидрического фенола.

Introduction

In this paper the term metallo-organic primer is applied to coatings formed by direct chemical reaction with a metal substrate through suitable groups introduced into the medium. For example, it is well known that vegetable tannins, which contain polyhydric phenol groups, react with rusted iron substrates to form iron tannates *in situ* which possess very good anticorrosive properties[1,11].

However, the tannin solutions require proper formulation in order to get an even, continuous film of iron tannate. Compositions of tannins in aqueous ethanol containing phosphoric acid have also been shown to react with a rust-free iron substrate[2]. The Fe complexes formed in this case were more water resistant than phosphated coatings alone and had increased anticorrosive resistance. Fe tannates have relatively low flexibility and this may be a disadvantage for some applications.

Another class of media which form metallo-organic complexes on a mild steel substrate is that containing pentavalent P^V acid groups. These groups may be attached to the polymer by P—O—C or P—C linkages, the latter type being more stable to hydrolysis. Examples of P—O—C linked products are the polymeric P^V acid phosphates prepared by reacting a high proportion of phosphoric acid with a polymer containing epoxide groups[3]. The coatings were evaluated as stoving primers on steel ; they had good adhesion and anticorrosive resistance which was ascribed to the result of interaction with the iron substrate. With respect to the application of P—C linked P^V-acid systems to steel, those based on vinyl phosphonic polymers and co-polymers[4] are of particular interest. The Fe complex primers formed had high adhesion and anticorrosive resistance.

There are also several references to the formation of metal porphyrazine (or phthalocyanine) type complexes on steel, a particular attraction being their high stability. Examples of iron and copper complex coatings of this type were those formed on the respective metal sheets by subjecting them to phthalonitrile vapour at a high temperature (300°C)[5]. In a more recent patent[6], iron complexes of a somewhat similar type were formed by heating iron sheets in phthalimide vapour at 300°C. The coating had very good adhesion, thermal stability and anticorrosive properties.

There are several other systems containing different reactive groups which have been found to form metal complex coatings on an iron surface, for example, salicylic acid condensation products with formaldehyde[7, 8], and certain phenolic resins[9]. In these cases, as with the systems above, interaction with the metal substrate has been claimed to influence the properties of the coating, e.g. adhesion, anticorrosive resistance and hardness. A recent survey of the literature relating to the general aspects of the interaction of a coating and a metal substrate, including a more detailed description of the several approaches to promote it by introducing various reactive groups and its effect on the properties, has been published[10].

The work described in this paper* was concerned with the synthesis of drying oil modified media which would undergo specific interaction with a metal substrate, e.g., mild steel, and an examination of the coatings obtained.

Based on the results of preliminary sorting tests, the main modifying groups investigated were polyhydric phenol or acetoacetate groups which react to form metal complexes (chelates) and phosphonic or sulphonic acid groups which form ionic complexes (salts). Salicylate groups, which were relatively unreactive with mild steel even when present in low molecular weight models, and carboxyl groups which react readily when present in certain simple compounds, e.g.,

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*The work was mainly carried out under a contract, Project number : UR-E-29-(40)-29 sponsored by the US Department of Agriculture Research Service. Under the terms of the contract the studies were limited to drying oil type media.

acrylic acid, were not considered further.

The extent of reaction of materials containing polyhydric phenol or acetoacetate groups with an iron substrate was judged by the formation of, respectively, a blue-black and red iron complex. With phosphonic acid modified media, however, colourless Fe complexes were formed but, in general, reaction was evident from the change in physical properties of the coating. Media containing such groups were considerably less reactive with mild steel than the corresponding simple model compounds, and it was shown that fairly specific conditions, viz., the presence of water, oxygen and a water-miscible solvent, were required to form significant amounts of metallo-organic complexes at normal temperatures. Under these conditions, the metallo-organic complex leaves the surface and diffuses into the medium and, in some cases, effects a cure to a tack-free film. The extent to which the surface coating properties are modified depends on the properties of the particular metal complex as well as on the extent of medium/substrate interaction.

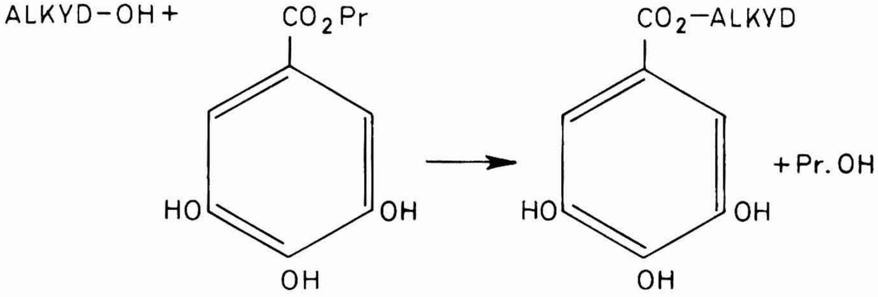
Iron complex primer coats of certain polyhydric phenol modified media were most effective, particularly with respect to their performance in corrosion tests. In some cases the coatings had high adhesion, but this was not automatically obtained. This group of materials was therefore studied in detail with respect to the formation and chemistry of the Fe complex and the evaluation of the Fe complex primers from a wide range of media. The investigations on media containing other reactive groups, viz., acetoacetate, phosphonic and sulphonic acids were largely exploratory.

Fe complex coatings from polyhydric phenol modified media

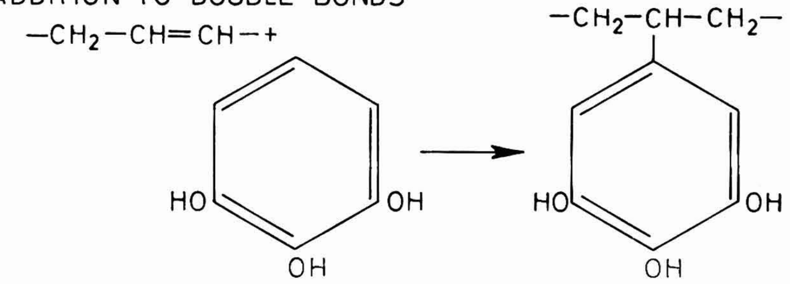
Preparation of polyhydric phenol modified media

It was found that gallate and polyhydric phenol groups could be introduced into a medium via the following reactions :

(a) ALCOHOLYSIS



(b) ADDITION TO DOUBLE BONDS



The extent of reaction obtained with various systems, and problems involved in the separation of the reaction products, are considered below.

Gallate groups were introduced using a lower gallate ester, e.g., propyl. The alcoholysis reaction is shown above but ester-interchange reactions were also possible. With drying oils, drying oil modified alkyds or epoxy media, i.e., where unsaturation in addition to ester and hydroxyl groups was present, reaction via both (a) or (b) could occur but it is not possible to determine the relative extents of each mechanism. The degree of reaction of propyl gallate with fatty unsaturation also depends on the type of unsaturation present, being significantly greater with conjugated systems. Thus, the reaction mixture of tung oil and propyl gallate contained negligible amounts of the starting materials. In contrast, the reaction of propyl gallate with a non-conjugated oil, e.g., linseed, was less extensive, although the reaction was carried out at a higher temperature.

In the tung oil/propyl gallate reaction, gelation occurred using relatively low proportions of propyl gallate, i.e., about 10 per cent based on the oil. Products with higher gallate contents, i.e., about 17 per cent could be obtained by reacting tung oil and propyl gallate in the presence of styrene or styrene containing 6 per cent divinyl benzene. Concurrent styrenation could also be applied to the reaction of isomerised linseed oil or dehydrated castor oil with propyl gallate. Methacrylation with the above systems was, however, unsuccessful, the bulk of the methyl methacrylate monomer being recovered unchanged.

Alcoholysis occurred particularly readily with primary alcohol groups such as are present in, e.g., C_{18} fatty alcohols, hydroxylated polyesters or alkyds based on glycols, pentaerythritol or trimethylol propane. Relatively less alcoholysis reaction was noted with the secondary hydroxyl groups present in glycerol alkyds or castor media. In the latter case, concurrent dehydration was a complication and reaction of propyl gallate with the diene unsaturation thereby formed could occur.

For the introduction of unsubstituted polyhydric phenol groups, e.g., pyrogallol or catechol, reaction (b) only was applicable. No apparent loss of polyhydric phenol groups was noted. As with propyl gallate, a higher degree of reactivity with conjugated systems was noted.

Titanium isopropoxide (0.1 per cent by weight based on the total reactants) was a suitable catalyst for both reactions as were aluminium isopropoxide and zirconium isobutoxide. An acid treated aluminium silicate clay (about 3 to 5 per cent by weight based on the total reactants) was also effective, particularly for reaction (b). An advantage in its use was that the unreacted polyhydric phenol was recoverable in a purer form, a disadvantage being the difficulty in removing the finely divided catalyst after the reaction.

The reactions were carried out at temperatures ranging from 150°C to 250°C for about one to four hours depending on the system. For example, the reaction between dehydrated castor oil and pyrogallol was carried out at 150-160°C for one hour whereas that between alkyds and propyl gallate required 220-230°C for about four hours.

In general, relatively high yields of gallate modified media were obtained using molar amounts of propyl gallate. The extent of reaction was determined by selective solvent extraction, separation of unreacted propyl gallate being based on its insolubility in aromatic solvents (e.g. xylene) or chloroform. With some systems, viz., those derived from a medium containing conjugated unsaturation such as a linseed/tung alkyd, an extensive reaction was obtained so that no separation was required. From the practical point of view, this would be an advantage.

In contrast, a large excess of an unsubstituted di- or trihydric phenol (at least twice molar over the unsaturated fatty medium) was generally required to obtain a sufficient degree of reaction. This resulted in difficulties in separating the product, i.e., extraction of unreacted polyhydric phenol by washing with hot water. Reactions using pyrogallol were therefore restricted to vegetable oils and vegetable oil esters since reaction with alkyds was not practicable.

With certain pyrogallol modified vegetable oils, e.g., linseed, further separation of unreacted oil was possible using petroleum ether. A similar extraction could be used for separating the products obtained from propyl gallate and castor or isomerised safflower oil.

In view of the relative cheapness of tannins, compared with propyl gallate, the possibility of preparing fatty modified hydrolysable or condensed tannins, using similar reaction conditions to those indicated above, was investigated. It was hoped to obtain Fe complexes with improved flexibility relative to unmodified Fe tannates. However, the products obtained by reacting tannins with, for example, linseed or tung methyl esters were found to be intractable.

Attempts to prepare fatty modified hydroxyanthraquinone derivatives were also unsuccessful. For example, there was negligible reaction between conjugated methyl esters and alizarin.

Formation of Fe complex coatings

Media containing polyhydric phenol or gallate groups formed characteristic blue-black complexes on an iron substrate, the main requirements being the presence together of oxygen (air), water (atmospheric moisture), a water miscible solvent, and clean, i.e. emery abraded or grit blasted, steel.

No Fe complex was formed when films were cast from bulk or from solvents immiscible with water. Only a limited amount of Fe complex was formed on slightly rusty steel and none was formed on fully rusted steel. Other important factors were the concentration of the medium and the volatility of the solvent. A suitable water miscible solvent was ethylene glycol ethyl ether (EGEE) and a suitable concentration of the solution applied to the surface was about 20-40 per cent. Highly fluid coatings were thereby deposited which allowed rapid and uniform diffusion of the blue-black Fe complex. On evaporation of the solvent, relatively thin films of the order of 0.5 mil were deposited. Other solvents, e.g., xylene or naphtha, were necessary when the medium was not completely compatible with the glycol ether. Rapid evaporation of the solvent, i.e., with solvents of high volatility, reduced the extent of formation of Fe complex ; with solvents of low volatility, extensive formation of Fe complex occurred but the films were softer due to the residual solvent. The function of the water miscible solvent was to produce a homogeneous coating containing medium, other solvents present in the solution and water condensed from the atmosphere.

With more complex media, particularly in those cases where another solvent was required to achieve compatibility, difficulty was encountered in effecting fairly rapid and even formation of Fe complex over the surface. This was presumably due to poor wetting of the iron surface. The addition of small amounts (about 1-2 per cent) of acidic substances, e.g., acetic acid, alkyl acid phosphates or ferric chloride (capable of forming soluble iron compounds *in situ*) enhanced the reaction with the surface.

The amounts of these additives had to be fairly strictly controlled, in particular ferric chloride, since excessive amounts caused too rapid formation of Fe complex resulting in powdery coatings. Relatively large amounts of ferric chloride, viz., corresponding to about 0.6-1.2 per cent Fe as ferric chloride based on the alkyd solids, yielded Fe complex coatings with reduced anticorrosive resistance, particularly in the humidity cabinet test. Thus, extensive rusting was noted after 1 day's exposure using the higher per cent addition of ferric chloride. The addition of 0.15-0.3 per cent Fe as ferric chloride gave very satisfactory results.

An idea of the extent of reaction of a polyhydric phenol modified medium with mild steel was obtained from the Fe content of the Fe complexes produced from a simple model system, viz., the reaction product of pyrogallol and methyl undecylenate. This material formed a tack-free Fe complex containing about 50 per cent Fe complex (Fe content = 14 per cent), the remainder of the coating being unreacted starting material.

With some of the Fe complexes derived from gallate modified alkyds, no reliable determination of the Fe content could be carried out since the coating could not be removed completely from the surface. However, the Fe complex from the pyrogallol/linseed oil reaction product, being relatively soft, could be completely washed off the mild steel. The Fe content for this coating was about 3 per cent, indicative of fairly extensive reaction.

The use of iron butoxide—a laboratory preparation containing chlorinated compounds—also gave excellent results in promoting Fe complex formation. Amounts ranging from 1 to 13 per cent by weight could be added, depending on the polyhydric phenol content, without affecting the film properties. Excellent results were obtained using up to 3 per cent additions. Compared with ferric chloride, there was a greater degree of tolerance with respect to the amount which could be used without causing the formation of matt or powdery films. Reaction with the iron substrate was evident from the higher Fe content of the coatings applied to steel compared with those on glass, the latter also being paler in colour and softer. For example, for Fe complexes from the linseed oil/pyrogallol reaction product, the Fe content on glass (corresponding to the amount of iron butoxide added) was 2.7 per cent, whereas the Fe content on mild steel was 5.1 per cent. The activity of the iron butoxide was presumably due to the potential acidity (i.e. HCl) of the chlorinated compounds which react with the mild steel and to reaction of butoxide groups with the functional groups (e.g. OH and COOH) in the medium. A drawback to the use of this compound is that it is not commercially available. In view of this the use of ferric chloride is preferred provided the requirements noted above are met. Other compounds derived from acids having a lower reactivity with steel than has HCl, such as iron octoate or iron napthhenate, were not effective promoters for the reaction on steel.

Regarding the storage stability of solutions of polyhydric phenol modified media containing 0.3 per cent $FeCl_3$, it has been found that their reactivity with mild steel was not significantly affected after about 18 months storage in glass containers. On the other hand, such solutions had considerably reduced stability on storage in unlacquered " tins." A gradual thickening of the solution was noted due to the formation of Fe complexes (initiated by attack of $FeCl_3$ on the " tin ") resulting in gelation after several months.

The possibility of obtaining Fe complex coatings by electrolytic deposition of the medium on an iron panel which was the anode of an electrolytic cell was also briefly examined. Black, but rather powdery, Fe complexes were, in fact, deposited using fairly simple polyhydric phenol derivatives e.g., propyl gallate, dodecyl gallate or decamethylene digallate. The electrolysis was carried out in water/EGEE mixtures containing ammonia to increase the conductivity of the solution. Currents of 100-200 milliamps were obtained with difficulty, using voltages of 100-200 volts. Even greater difficulties were encountered with more complex media, e.g. a gallate modified tung alkyd in water/EGEE/naphtha solution. In this case, coatings of unreacted alkyd, i.e., not complexed with Fe, were deposited on the anode.

Chemistry of Fe complexes

Information on the chemical nature of Fe/polyhydric phenol modified media complexes was obtained from studies on the reaction of model gallates, e.g., propyl and dodecyl, with mild steel, elemental analysis of the Fe complexes and spectroscopic studies.

A quantitative relationship between the amount of Fe reacted, oxygen absorbed and the Fe content of the complex was deduced from studies on the rate of reaction of propyl gallate in ethylene glycol ethyl ether containing water with mild steel chippings in the presence of oxygen at controlled temperatures, viz. 10°, 20° and 30°C. The Fe : propyl gallate ratio for Fe complexes formed *in situ* was thus found to be significantly less than unity indicating that a small proportion of Fe atoms were linked to more than one gallate group. (This would also fit the case where a Fe atom is attached to a polymerised polyhydric phenol, but the formation of such polymers by oxidative polymerisation was not substantiated in view of the absence of simple oxidation products. Also, no evidence of polymeric units in the Fe complex was obtained on breakdown with sulphuric acid). In contrast, with model Fe^{III} complexes of propyl or dodecyl gallate prepared *via* reaction with ferrous hydroxide and subsequent oxidation, it was shown from elemental analysis (C, H, direct O and Fe) that almost exactly one Fe atom was linked with one propyl or dodecyl gallate group. This ratio also applied to Fe^{III} complexes prepared in excess gallate.

The Fe complexes were extremely insoluble materials, so that molecular weight measurements were not possible. However, the corresponding butylamine/Fe gallate complexes were soluble and molecular weight determination indicated the existence of a polymeric structure.

The Fe complex is therefore in the ferric state, but the actual mechanisms involved in its formation via the ferrous complex and subsequent oxidation are not clear.

Spectroscopic studies on model compounds and the corresponding Fe complexes formed on steel have provided evidence on the structural changes involved. Although the spectra are fairly complex, they can be interpreted in terms of strongly hydrogen-bonded hydroxyl groups (associated with chelation) and C—O—Fe linkages.

There is also evidence for considerable re-arrangement of the aromatic ring and quinonoid structures (cf. Fig. 1) may possibly be present.

Suggested structures for Fe-gallate complexes, where R=propyl or dodecyl, which correspond closely to the experimental findings are illustrated in Fig. 1.

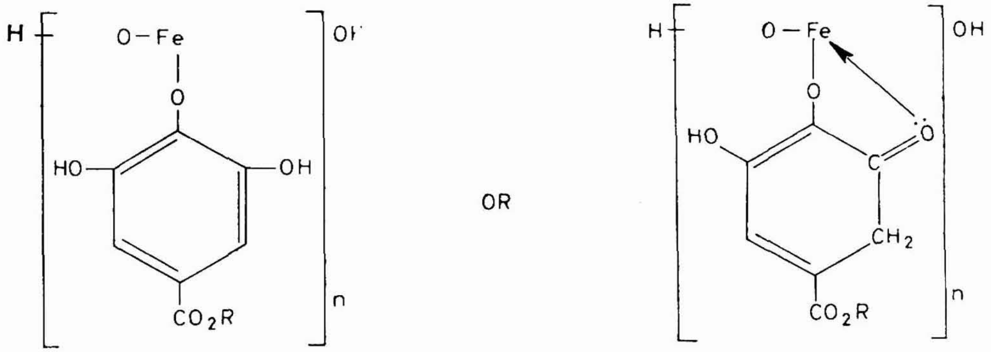


Fig. 1. Suggested structures of Fe gallate complexes

Surface Coating Properties of Fe complexes

The characteristics of the Fe complex primer coatings from a wide range of drying oil modified media were investigated and anticorrosion tests were carried out for those systems which gave tack free coatings. The coatings were applied to emery abraded mild steel (unless stated otherwise) under the optimal conditions described above. In general, the touch-dry times were about 10 to 15 minutes and film thickness about 0.5 mil. The maximum development of Fe complex as judged by the blue-black coloration was usually three to five minutes. The results are noted below.

Low molecular weight fatty gallates

The derivatives from dodecanol or C_{18} fatty alcohols gave powdery, waxy or tacky Fe complex coatings of no practical interest.

Vegetable oil/gallates

Two gallate modified oils, viz., those from castor or conjugated safflower oil, provided (as Fe complexes) good protection to steel. The results given in Table 1 for these materials relate to Fe complexes formed from the products obtained after removal of the uncombined oil fraction using petroleum ether. (Prior to extraction, the safflower oil/gallate reaction product yielded tacky Fe complex coatings whereas the castor oil/gallate gave tack-free but softer coatings than those obtained from the extracted product.) The amount of petroleum ether extract corresponded to about 20 and 35 per cent respectively of the original castor and safflower oil. From the economic point of view, an extraction stage would be a disadvantage. The subsequent application of drying oil paints to these primer coats was restricted. Paints containing zinc chromate pigment were suitable but inhibition was noted with iron oxide paints due to the antioxidant activity of residual polyhydric phenol groups. A chlorinated rubber paint or a polyvinyl chloride/acetate lacquer could not be applied due to softening of the undercoat by the strong solvents.

The hardness and anticorrosion properties of these two systems were considerably improved by stoving at 140°C for about one hour. Stoving at lower temperatures was not so effective. With the stoved primers, no difficulty was noted in applying subsequent coats of drying oil or chlorinated rubber paint.

Table 1

Fe/gallate modified vegetable oil complex coatings

Vegetable oil/gallate	Approx. wt. % unextractable gallate in product	Solvent composition (20-25 % solution)	Properties of Fe complex coating (after ageing seven days at 25°C)
Castor	32	EGEE (with 3 % Fe butoxide or 0.5 % $FeCl_3$)	Fairly hard black film ; very good performance up to 500 hours H/C or A/W, and up to five months N/W
Isomerised safflower (50 % diene)	32	1:1 EGEE/naphtha with 1 % acetic acid	Hard blue-black film ; very good performance as immediately above
Hydrogenated castor	18	EGEE with 1 % acetic acid	Soft waxy blue-black film
Linseed	28	EGEE with 0.5 % $FeCl_3$	Tacky blue-black films, not improved by stoving
Safflower	22		
Dehydrated castor (1.5 poise)	29	as immediately above	Tacky blue-black coating
Tung	8	as immediately above	Tacky dark brown coating

EGEE—ethylene glycol ethyl ether ; H/C—humidity cabinet ; A/W—accelerated weathering ; N/W—natural weathering in suburban site (Paint Research Station Roof).

The resistance to cold aqueous alkali (1 per cent) and salt spray was low for stoved as well as for unstoved primers.

With the other gallate modified oils, which yielded tacky coatings (cf. Table 1), separation of unreacted oil fraction (in order to upgrade the coating properties) was not possible due to their complete solubility in petroleum ether.

The hard, black Fe complexes formed from styrenated tung oil/gallate mixtures from a solution in 5 : 1 xylene/EGEE were, however, of interest. The product obtained with styrene/divinyl benzene had better anticorrosion resistance, viz., up to 250 hours H/C or A/W. As a result of styrenation (35 per cent by weight of the product) the resistance to cold 1 per cent alkali of the Fe/styrenated tung oil gallate complex was good. This is in contrast to the behaviour of coatings from castor or isomerised safflower gallates ; however, their anticorrosive performance in the other tests was inferior. Also, due to the high degree of styrenation, the coatings were attacked by xylol so that a chlorinated rubber paint could not be applied. However, no inhibition of drying was noted with drying oil paints.

The products obtained from the reaction of other conjugated oils, viz., isomerised linseed oil or dehydrated castor oil and mixtures of styrene and propyl gallate, however, yielded tacky coatings.

Alkyd/gallates

The results obtained on Fe complex coatings from drying oil modified alkyds are summarised in Table 2. Two systems gave coatings of technical interest, particularly the gallate modified linseed/tung alkyd. Those from the castor alkyd/gallate—whilst showing fairly good anticorrosive resistance to the H/C test (1,000 hours), A/W test (1,000 hours), N/W (up to 2 months), and exposure to SO_2—were relatively soft with poor resistance to cold water, 1 per cent cold alkali immersion, salt spray and ammonia atmosphere. The corresponding coatings stoved at 140°C for one hour were considerably better with particularly notable performance in H/C (1,000 hours) and A/W (1,000 hours) tests.

The Fe/linseed/tung glycerol or pentaerythritol alkyd gallate complexes exhibited very good protection (cf. Table 2) which was significantly better than was noted for vegetable oil/gallate or /pyrogallol derivatives (cf. below). In view of the promising results obtained with this system, a wider evaluation of the coatings was made including pigmentation and welding tests. These are discussed in detail below.

Epoxide/gallates

Hopes that these systems would show better performance than alkyd gallates were not fulfilled. The results are summarised in Table 3. Thus, with the DCO/epoxy and the soya/tung diglycidyl ether derivatives, light blue coloured, i.e., ineffectively cured, coatings were obtained even using large amounts of acetic acid to initiate reaction with the iron surface. This difficulty was overcome using iron butoxide : for example, with this additive the DCO/epoxy gallate gave a hard blue-black coating which had very good resistance to 1 per cent cold alkali but relatively low salt spray resistance. It is interesting to note that the Fe complex coatings performed very well during about three to four months natural weathering exposure, which was unexpected in view of the poor performance shown in accelerated corrosion tests. Also, the Fe complex coating did not inhibit drying of subsequent coats of drying oil paints.

Table 2

Fe/gallate modified alkyd complex coatings

Gallate modified alkyd (% oil length)	Approx. wt. % unextractable gallate in product	Solvent composition (25% solution)	Properties of Fe complex coating (aged seven days at 25°C)
Castor/ phthalic/ glycerol (45%)	10.5	EGEE (with 1% acetic acid)	Blue-black tack-free film; good performance up to 250 hours H/C or A/W and up to 2 months N/W
3:1 linseed/ tung glycerol or pentaerythritol (57%)	14	EGEE/xylene/naphtha with 3% Fe butoxide†	Hard blue-black film; very good performance up to 1,000 hours H/C or A/W or up to 6 months N/W
Lauric/ phthalic/ glycerol (31%)	14	EGEE (with 1% acetic acid)	Blue-black brittle film with poor adhesion; no evaluation made
Linseed/ phthalic/ glycerol (68%)	8	As immediately above	Soft blue-black coatings; no evaluation made
Soya/phthalic/ glycerol (68%)	6		
Dehydrated castor/ phthalic/ glycerol	12	As immediately above	Tack-free relatively soft film; no evaluation made

†Similar coatings were obtained using 0.75% FeCl$_3$ or 1 to 2% acetic acid (cf. Fig. 2).

Linoleic polyamide/gallates

The results with these systems, as with the epoxide gallates, were disappointing. Considerable difficulty was met in reacting a linoleic polyamide gallate (prepared from a polyamide with a low amine value and containing approx. 14 per cent by weight of unextractable gallate as propyl gallate) with mild steel. The choice and balance of solvents was particularly important, xylol and EGEE containing a relatively high proportion (8 per cent) of acetic acid being required. The coatings, which were blue-black, relatively soft and greasy, hardened up very slowly. The performance in the H/C test was low (severe microblistering in two days) but, as expected, resistance to cold 1 per cent alkali was good.

The product obtained by reacting propyl gallate and a polyamide with a high amine value showed little tendency to react with mild steel from a solution in EGEE/CHCl$_3$, presumably due to loss of gallate groups by reaction with amine groups.

Table 3

Fe/oil modified epoxy/gallate complex coatings

Bisphenol epoxy derivative (% oil length)	Approx. wt. % unextractable gallate in product	Solvent composition (20% solution)	Properties of Fe complex coatings (after ageing 7 days at 250°C)
Linseed (60%)	6.5	1:1 EGEE/naphtha (with 1% acetic acid)	Tack-free but relatively soft, not evaluated
Dehydrated castor (40%)	9	3:2 EGEE/naphtha (with 3% Fe butoxide)	Fairly hard coating; severe microblistering after 2 days H/C and A/W but very good performance up to about 4 months N/W
3:1 Linseed/tung (44%)	13	3:2 EGEE/naphtha (with 2% acetic acid)	Similar results to those noted immediately above
Soya (20%)	15	2:1 EGEE/naphtha (with 1% acetic acid)	Hard coatings, poor performance in H/C and A/W; very good protection up to about 3 months N/W
Soya (38%)	12		
3:1 Soya/tung (70%) diglycidyl ether	10.5	3:2 EGEE/naphtha (with 1% Fe butoxide)	Blue-black tack-free but soft, not evaluated

Pyrogallyl derivatives of vegetable oils and their derivatives

The Fe complex coatings formed from the products obtained by the reaction of pyrogallol with simple unsaturated drying oil esters or hexadecene were of no practical interest. An interesting result was obtained, however, with methyl pyrogallyl undecanoate, (the reaction product of pyrogallol and methyl undecylenate), which gave an Fe complex coating having a relatively high degree of anticorrosive protection viz., up to 0.5 month N/W and four days H/C.

The results obtained with pyrogallyl modified triglyceride oils are summarised in Table 4. The products from linseed or soya, i.e., non-conjugated oils, gave tacky, blue-black coatings on steel. It was possible to produce tack-free coatings by adding 3 per cent iron butoxide to the solution applied to steel but these were relatively soft with poor anticorrosive performance. Stoving at 140°C for one hour produced a considerable improvement in properties, the coatings then being hard and resistant to cold water during three days immersion, but attacked by 1 per cent cold aqueous alkali. The Fe complex coatings from pyrogallyl modified dehydrated castor and tung (i.e. conjugated) oils were tack-free and fairly hard in the former case. They exhibited good anticorrosive properties, particularly those from pyrogallyl modified dehydrated castor oil, although their resistance to water-immersion was poor. Significant improvements were noted with the stoved films. The Fe complex coatings from pyrogallyl modified linseed oil (after stoving) and pyrogallyl modified dehydrated castor oil (unstoved and after stoving) were judged to be the most promising.

However, in all cases the salt spray resistance was low and, with unstoved Fe complexes, appreciable inhibition of drying of subsequent coats of certain drying oil paints was noted. In view of these disadvantages, including the difficulties encountered in separating pyrogallyl modified oils, and the need for stoving in certain cases to obtain useful coatings, these systems would be of limited commercial interest.

Table 4

Fe/pyrogallyl modified vegetable oil complex coatings

Pyrogallyl modified oil	Solvent composition (30% solution)	Properties of Fe complex coatings
Linseed	EGEE with 1% acetic acid	(i) Room temp. cure :—blue-black tacky coating, not evaluated. (ii) Stoved (140°C/1 hour) :—tack-free hard coating. Very good performance up to 1,000 hours H/C or A/W and up to about 4 months N/W
Soya	As immediately above	Result as immediately above
Olive	,,	Blue-black cheesy coating, not evaluated
Dehydrated castor	,,	(i) Room temp. cure :—blue-black tack-free coating, relatively soft surface. Very good performance up to 1,000 hours A/W or 500 hours H/C, and up to 3 months N/W (ii) Stoved (140°C/1 hour) :—harder than unstoved and better anticorrosive performance, viz., up to 1,000 hours A/W or H/C and 4½ months N/W
Tung	4:1 EGEE naphtha	(i) Room temp. cure :—blue-black tack-free coating, relatively soft surface. Good performance up to 500 hours A/W or H/C ; relatively poor N/W, up to 1½ months. (ii) Stoved (140°C/1 hour) :— harder coating with improved resistance to H/C but N/W not improved

Surface coating properties of Fe linseed/tung alkyd complexes

Anticorrosive properties : the anticorrosive performance of the Fe complex primers derived from the 3 : 1 linseed/tung alkyd gallate is illustrated in Fig. 2.

Coatings were deposited from a 25 per cent solution of the alkyd/gallate containing 3 per cent iron butoxide on to grit blasted steel and exposed to natural weathering for six months in a suburban site (Paint Research Station roof). The film thickness was about 0.5 mil. For comparison with the Fe gallate/alkyd complex, steel panels coated with the corresponding pigmented Fe complex containing 10 per cent iron oxide and a butyral chromate wash primer are shown. It can be seen from Fig. 2 that pigmentation of the gallate modified alkyd did not produce a notable improvement in the anticorrosive performance of the

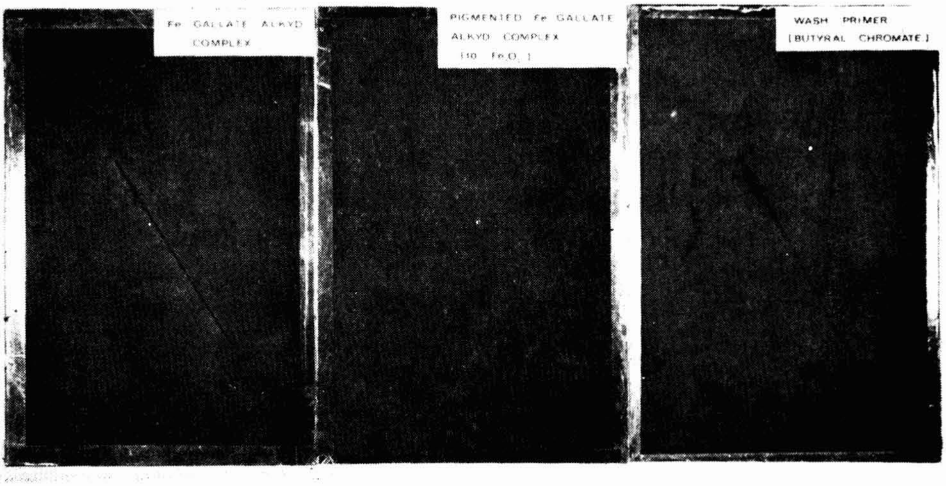


Fig. 2. Natural weathering performance of Fe complex primers

Fe complex. The wash primer showed poorer resistance to natural weathering than the Fe gallate/alkyd complex.

Similar performance by these three systems was observed during 1,000 hours accelerated weathering.

The adhesion of the Fe complex primer was examined using a pull-off technique in use at the Paint Research Station. The test discs failed at 2,500 p.s.i., which is similar to the result obtained for an alkyd with good adhesion characteristics. The failure of the Fe complex was mainly cohesional and a thin layer of the black coating was left on the test disc.

Primer coats from the gallate modified linseed/tung alkyd could be successfully overcoated with drying oil paints provided they were aged for several days. In contrast, inhibition of drying was noted with such media subsequently applied to unstoved Fe primer complex coatings from vegetable oil/gallate or vegetable oil/pyrogallol derivatives which exhibited antioxidant activity even after ageing for several weeks. Good intercoat adhesion (measured by the pull-off technique) was observed between the Fe gallate/linseed/tung alkyd complex primer and a titanium dioxide pigmented long oil alkyd paint. Adhesion failure in the test discs was noted at about 2,500 p.s.i. and there was both shear and intercoat failure.

Only a limited examination of top coats other than drying oil based paints has been made. However, a chlorinated rubber paint, a coal tar/epoxy/amine system and a polyvinyl chloride/acetate lacquer could be successfully applied.

Pigmentation of polyhydric phenol modified alkyd media presented difficulties in view of the dilute solutions required for efficient *in situ* formation of Fe complex. Thus, in addition to fairly rapid settling of pigment on storage, the diffusion of the Fe complex in the coating was impaired, leading to a reduction in the cure of the coating. The latter difficulty could be overcome by increasing the amount of solvent. Attempts to pigment a gallate modified alkyd with zinc chromate caused gelation, but no difficulties of this kind were met with red iron oxide, black iron oxide or carbon black.

Variations in anticorrosive performance were noted, depending on the pigment used and the pigment concentration. Thus, a particularly notable deterioration in properties resulted with carbon black when the pigment concentration was increased from 10 to 20 per cent. However, a high concentration of iron oxide affected the coating properties to a lesser extent. With all three pigmented systems at about 10 per cent pigmentation, the anticorrosive performance of Fe primer coats was comparable with those of the unpigmented systems. Whilst a slight improvement in touch-dry time was evident, there did not appear to be any significant advantage to be gained by pigmentation.

The resistance of Fe complex coatings to salt spray (including a laboratory test and weathering at a coastal site) and to cold 1 per cent aqueous alkali was poor. Stoving at 140°C for one hour did not lead to a significant improvement in salt spray resistance. The incorporation of 10 per cent chlorinated rubber (based on the medium), however, gave a slight improvement. Various other resins, viz., polyvinyl butyral, butadiene-styrene copolymer, polyvinyl chloride/acetate, isomerised rubber, polystyrene and polymethyl methacrylate, were considered but were found to be incompatible with the alkyd/gallate.

In addition to pigmentation and the incorporation of resins, other attempts were made to upgrade the properties of the Fe linseed/tung alkyd/gallate complex coating, particularly with respect to its resistance to 1 per cent cold aqueous alkali and salt spray. For example, the alkyd (three parts) was reacted with a linoleic polyamide (one part) prior to the introduction of gallate groups, but the corresponding Fe complex primer exhibited poorer surface coating properties and anticorrosive performance than those from the unmodified gallate/alkyd. An attempt to react a high molecular weight epoxy resin with the alkyd/gallate was unsuccessful.

The incorporation of a phenolic resin into a linseed/tung glycerol or pentaerythritol alkyd, followed by reaction with propyl gallate, gave Fe complex primers with high anticorrosive resistance to A/W and H/C tests comparable to the Fe gallate/tung alkyd complex itself. There was, however, no improvement in salt spray resistance.

Welding tests: Steel coated with the Fe gallate linseed/tung alkyd complex could be successfully welded by the submerged arc process including twin fillet welding. The results are as follows.* Mild steel plates 3 ft × 1 ft × $\frac{1}{2}$ in and 3 ft × 6 in × $\frac{1}{2}$ in were grit blasted and coated (including the edges) with the unpigmented and the corresponding iron oxide pigmented gallate modified alkyd. The uncoated control plates were stored under dry conditions prior to welding.

These plates as well as two uncoated control plates were welded in the form of T-joints by automatic twin fillet welding with the submerged arc process. The T-joints were radiographed and selected T-joints were cut and tensile tests carried out on cruciform specimens prepared therefrom. In order to emphasise the effect of the pyrolysis products of the coating on the properties of the weld, the X-ray examination was carried out through the trailing weld.

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*This work was carried out by the British Welding Research Association.

With respect to visual appearance, the surface of the weld on the control and painted paints was satisfactory : the profiles were smooth, free of surface defects and without undercut at the edges of the welds. The control specimens gave clear radiographs whereas in the painted specimens scattered porosity (indicated by dark spots in the radiograph) occurred at the roots of the trailing welds. This was considered to be within the limits for allowable amounts of porosity, a general guide of good, acceptable and bad welds being related to the extent of porosity, namely, sparse ; scattered ; or extensive.

The tensile strength of the control specimens was well above that required by BS 639 : 1952 and the presence of primers on the edge of the standing plate as well as on the faces of the plates gave no reduction in joint strength.

Toxicity tests : An examination† of the potential toxicity hazard in cutting and welding of steel plate primed with Fe gallate alkyd complex was also carried out. Under carefully controlled conditions, samples of air were taken during cutting (oxy-acetylene flame) as well as during electrical welding. These were then analysed for possible toxic constituents, namely, iron oxide, phenols, aldehydes, acrolein and carbon monoxide. Positive tests were obtained only for the presence of iron oxide and carbon monoxide ; the mean and peak concentration of these two constituents was found to be below the maximum allowable concentration values. It was therefore concluded that if cutting or welding of primed plate is carried out under good ventilation there is no danger to health.

The possible application of Fe complex coatings as prefabrication primers is evident, the main limitation being their relatively long drying time which does not meet the common requirements of existing primers, i.e., dry to handle within three minutes.

Fe complex coatings from acetoacetate modified media

The potentialities of these Fe complexes were examined using the acetoacetates from lauric-phthalic-glycerol/, castor-phthalic-glycerol/ and linseed-tung-phthalic-glycerol alkyds and a soya-bis phenol epoxy ester as models. These were readily prepared via interchange between the hydroxyl groups in the medium and ethyl acetoacetate. Mild steel was the most reactive substrate, copper, zinc and aluminium substrates being relatively unreactive. These media were, however, appreciably less reactive with ferrous mild steel than the corresponding media containing polyhydric phenol groups under comparable conditions. For example, this is evidenced by the relatively small improvement in the extent of reaction with steel which was obtained by casting films from a solution of the acetoacetates in a water miscible solvent, e.g., EGEE. However, the formation of red complex was enhanced by the addition of 2 per cent acetic acid or 2 per cent Fe butoxide to a solution of the medium in or containing EGEE. This was associated in some cases with the conversion of a tacky material to a tack-free film due to cross linking via Fe chelate bonds. On inert substrates, e.g., glass or stainless steel, light coloured coatings were obtained. (In the absence of EGEE the extent of formation of Fe complex on mild steel was greatly reduced even in the presence of Fe butoxide.) The Fe chelates formed

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†This examination was carried out by the Occupational Hygiene Unit of the North of England Industrial Health Service.

in this way are considered to be ferric derivatives, possibly with basic types present.

Although Fe complex coatings produced in the presence of Fe butoxide possessed somewhat improved properties, e.g., water and solvent resistance, hardness and adhesion, relative to coatings from the unmodified media, they were of little technical interest. The poor performance of Fe complexes from the soya epoxy ester/ and the tung alkyd/acetoacetates (both containing 0.1 per cent Co drier) was particularly disappointing. The results suggest that the acetoacetate groups interfere with the mechanism of autoxidative drying by complexing with the drier metal.

Fe complexes from media containing P—C bonded P^V acid groups

The studies were restricted to systems containing P-C bonds, viz., phosphonic acids $RP(O)(OH)_2$ and phosphinic acids $R_2P(O)OH$, since those with P—O—C bonds are more readily hydrolysable. The methods available for the synthesis of materials containing these groups are not so widely applicable as is the case with, for example, polyhydric phenols and acetoacetates. Thus, only a limited range of materials was prepared. For instance, phosphinic groups could be introduced into a triglyceride, e.g., soya oil, via published procedures involving addition of PCl_3 to olefinic double bonds using a $PCl_3/AlCl_3$ complex, but working up the product was difficult in view of the large amounts of $AlCl_3$ used. The reaction could not therefore be applied to systems, e.g., alkyds, which contain hydroxyl and carboxyl groups. A further disadvantage was that the products were thermally unstable.

Phosphonic acid groups could be fairly readily introduced into certain materials containing conjugated fatty unsaturation via a novel synthesis based on a Diels Alder addition of vinyl phosphonic dichloride at 140°C for 20 hours, followed by hydrolysis of the P-acid chloride adduct. These systems were of greater interest since working up of the product was considerably simpler than for phosphinic acids. The reaction was most readily applicable to conjugated drying oils, e.g., dehydrated castor and isomerised safflower, but difficulties were encountered with alkyd or epoxy resins. Thus with a 3 : 1 linseed-tung-phthalic-glycerol alkyd and a 3 : 1 soya-tung or dehydrated castor bisphenol epoxy derivative, reaction with vinyl phosphonic dichloride led to undesirable side reactions involving the hydroxyl groups and the formation of P—O—C bonds. This resulted in gelation, particularly with alkyds, but this could be largely overcome by acetylation of the resin prior to the reaction.

Phosphinic- and phosphonic-acid modified media were reactive with mild steel but under similar conditions there was little reaction with copper or aluminium. As with media containing polyhydric phenol or acetoacetate groups, the reaction was enhanced when coatings were applied from solutions in a water miscible solvent, e.g., EGEE alone or in admixture with another solvent to achieve compatibility. The high reactivity of organophosphorus acids such as phosphinated soya bean oil or the vinyl phosphonic adduct of isomerised safflower oil was illustrated by their ability to decolorise the blue ferric oxide layer produced by heating an iron surface. Solutions of the vinyl phosphonic adducts derived from a drying oil modified epoxy or acetylated alkyd in EGEE/naphtha, however, showed relatively less activity with a ferric oxide layer. As expected, the formation of Fe complexes on rust-free, i.e., ferrous, mild steel was more rapid as judged by the conversion of tacky materials to tack-free coatings. The properties of the coatings from the epoxy and alkyd systems were disappointing, even for films aged in the presence of Co drier. (The mechanism of drier action may have been adversely affected by the formation of cobalt/phosphonic acid complexes.)

Thus, no significant differences were noted in performance on exposure in the H/C test, between the Fe/P-acid modified soya epoxy ester complex and the epoxy ester control, whereas the resistance of the Fe complex from the P-acid modified acetylated linseed tung alkyd was, in fact, poorer than the control in this test. The coatings were of no technical interest, being fairly soft and having relatively low water resistance.

Fe complexes from media containing sulphonic acid groups

Vegetable oils containing sulphonic acid groups, which were obtained via a novel reaction between m-cresol sulphonic acid and unsaturation in the oil, reacted with mild steel, but the resulting Fe complex coatings were of little practical use. Some tests were also carried out with a sulphonated linseed/phthalic/pentaerythritol alkyd, similarly prepared by refluxing a xylol solution of the alkyd with about 2 per cent by weight of m-cresol sulphonic acid. (The reaction mixture tended to gel, especially using larger amounts of sulphonic acid.) This product had poor drying properties compared with the unsulphonated alkyd, but little difference was noted between a pigmented, e.g., titanium dioxide, paint and the control. The presence of sulphonic acid groups did not, however, significantly enhance the adhesion of the paint to iron or aluminium (determined by pull-off technique) which may have resulted from the formation of Fe complexes.

Discussion

Of the various metallo-organic coatings studied, the coatings formed by reaction of drying oil modified media containing built-in polyhydric phenol groups on an iron substrate have been shown to have the greatest technical interest. The curing mechanism, comprising the formation of Fe chelate linkages, provides a much faster cure to tack-free coatings compared with the normal autoxidative processes in conventional drying oil media. Whilst the formation of a Fe complex coating was usually associated with a relative increase in water and solvent resistance, enhanced adhesion was not automatically obtained. The results have shown, however, that with certain systems e.g., a gallate modified tung/linseed alkyd, the formation of a Fe complex coating on steel resulted in a significant improvement in anticorrosive protection and adhesion compared with coatings from the unmodified media. The reasons for the good anti-corrosive performance and good adhesion of the Fe complex coating are not very well understood. The following discussion proposes explanations of the effects observed.

Thus, it is possible that the effective physical barrier which the Fe complex coating provides, may be due, to some extent, to the fact that such coatings are formed initially from a " colloidal " solution. It may be that under these conditions coatings with low porosity are formed.


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The presence of polyhydric phenol groups may contribute to the stability of the Fe complex coating by reducing autoxidative breakdown. It is doubtful, however, whether unreacted polyhydric phenol groups in the dry film can contribute to anticorrosive performance by subsequently reacting with mild steel at rusting sites since there is no evidence for such a reaction in the absence of solvent.

Whereas a simple interaction between a modified medium and mild steel might well be expected to improve adhesion, it is difficult to explain why good adhesion is obtained with certain Fe gallate complexes under the conditions of interaction described in this paper, i.e. where there is extensive diffusion of the complex from the surface. It would be expected that, as solvent evaporates from the coating, there will be progressively less diffusion of the Fe complex so that at the mild steel-coating interface there will be a relatively high concentration of Fe complex. It could then be argued that under such conditions of limited diffusion, it may be possible for a Fe atom to link up with a polyhydric phenol group in the medium, without detaching itself from the metal substrate. In other words, adhesion would be enhanced by chemical bonding. Alternatively, the Fe atom could detach from the substrate but, under the conditions prevailing, little or no diffusion of the Fe complex could occur. Good adhesion could then be ascribed to good wetting (physical contact) of the mild steel by the Fe complex.

It is of interest to compare the behaviour of these systems with that observed for conventional alkyd coatings on zinc—a more basic substrate than mild steel. In this case, the formation of acidic oxidation products can occur more readily than with polyhydric phenol modified media. With these systems, interaction between the alkyd coating and zinc continues in the dry film, resulting in extensive formation of zinc soaps and the eventual adhesional and cohesional failure of the system.

The work described in this paper on polyhydric phenol modified media has been covered by British Patent 1,045,118 and US Patent Applications 367,262 and 442,831. Continued investigation of gallate modified drying type media has yielded, in some cases, Fe complex coatings with improved properties and anticorrosive performance over existing systems. The resistance to coastal weathering was, however, only marginally improved. In the light of further studies it appears unlikely that significant improvements in salt atmosphere resistance can be obtained with systems based on drying oil type media. The Fe complexes formed from suitable vinyl polymers containing gallate groups may show more promise in this respect.

The relatively long touch drying time (about 10-15 minutes) of the Fe complex coatings limits their application, e.g., as prefabrication primers. It may be possible to develop other systems with shorter drying times, but the limiting factor is that the coating must remain in a fluid state long enough to allow adequate diffusion of the Fe complex to obtain a cure.

Further work is obviously necessary to explore fully the potentialities of this novel method of film formation.

Acknowledgements

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Discussion at the London Section

MR. F. P. GRIMSHAW asked what types of solvents could be used with the gallate/alkyd primers. Could mild smelling solvents with low toxicity be used ?

MR. R. N. FAULKNER said that ethylene glycol ethyl ether was essential for the formation of the Fe complex but unfortunately this solvent had a fairly low maximum allowable concentration. Other available water-miscible, but less toxic, solvents, e.g. ethyl alcohol, had been tried but were found to have unsuitable solvent or volatility characteristics. Where a co-solvent e.g., xylene, was required to achieve compatibility (as was the case with a gallate/alkyd system) the choice was also limited by volatility considerations.

MR. R. R. BISHOP said that Mr. Faulkner had referred to the inhibition of air drying of the acetoacetate system by cobalt driers. Were manganese driers examined ?

MR. FAULKNER said that only cobalt driers were used, but different effects might be evident with manganese driers. It should be explained that a detailed examination of the acetoacetate system was not carried out in view of the fact that the Fe complex coatings initially formed by reaction with the substrate were softer and of little interest compared with Fe gallate/alkyd complex coatings.

DR. H. R. HAMBURG asked whether force-drying speeded up the formation of Fe complexes.

MR. FAULKNER said that force drying would remove the solvent too quickly and thereby reduce diffusion (and thereby curing) of the Fe complex.

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A micro-electrophoresis apparatus for the investigation of pigment suspensions

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Summary

A detailed description is given of the design and construction of a micro-electrophoresis apparatus which, although simple to operate and cheap to make, is able to define small changes in mobility at very high ionic strengths, and obviates errors likely to arise from use of a recently described apparatus. The detail in the description is given to fill an apparent gap in the literature in the hope that others may benefit. The apparatus has been used to study the electrokinetic properties of titanium dioxide pigments in aqueous systems, and has provided an understanding of their behaviour. The apparatus can be used to study materials and systems of lower ionic strengths, such as dilute aqueous colloids.

Un micro-appareil électrophorèse destiné à l'investigation des suspensions de pigment

Résumé

On décrit en détail le dessin et la construction d'un micro-appareil électrophorèse susceptible de signaler des petites variations de mobilité aux concentrations ioniques très élevées, bien qu'il soit facile à manipuler et économique à construire. L'appareil prévient les erreurs qui peuvent arriver pendant l'utilisation d'un appareil récemment proposé. On donne une description détailée afin de combler une lacune apparente dans la littérature en l'espoir que des autres pourront en profiter. On a utilisé l'appareil pour étudier les propriétés électrocinétique des pigments de l'oxyde de titane dans des systèmes aqueux, et également pour achever une connaissance de leur comportement. On peut aussi utiliser l'appareil pour l'étude des matériaux et des systèmes de faibles concentrations ioniques, tels que colloïdes aqueux dilués.

Ein Mikroelektrophorese-Apparat zur Untersuchung von Pigmentsuspensionen

Zusammenfassung

Entwurf und Konstruktion eines Mikroelektrophoreseapparates wird ins Einzelne gehend beschrieben, der, obwohl einfach zu handhaben und billig herzustellen, es ermöglicht, kleine Änderungen in der Beweglichkeit bei sehr hoher Ionenkraft zu definieren und Irrtümer auszuschalten, die möglicherweise bei Benutzung eines kürzlich beschriebenen Apparates auftreten können. Die Einzelheiten werden aufgeführt, um eine offensichtliche Lücke in der Literatur auszufüllen, in der Hoffnung, dass davon andere den Nutzen ziehen mögen. Der Apparat wurde zum Studium der elektrokinetischen Eigenschaften von Titandioxydpigmenten in wässrigen Systemen benutzt, er trug zum Verständnis deren Verhaltens bei. Der Apparat kann zum Studium von Materialien und Systemen niedriger Ionenkräfte wie z.B. verdünnter, wässriger Kolloide verwandt werden.

Микроэлектрофорезный прибор для изучения пигментных суспензий

Резюме

Дается подробное описание рассчета и конструкции микроэлектрофорезного прибора, несложного применения и дешевого производства, который определяет небольшие изменения в подвижности при очень высокой интенсивности ионов и устраняет погрешности возникающие в применении недавно описанных приборов. Подробное описание аппарата дается с целью пополнения существующего пробела в литературе, в надежде что это будет в пользу другим. Аппарат применялся для изучения электрокинетических свойств пигментов двуокиси титана в водных системах и дал пояснение их поведению. Прибор может применяться для изучения материалов и систем более низкой ионной интенсивности, как например разбавленных водных коллоидов.

Introduction

The effect of the surface of a titanium dioxide pigment on the stability of aqueous suspensions of the pigment is a factor of paramount importance in the manufacture of such systems for use in decorative finishes.

Studies of aqueous suspensions of pigments are being made in the Research Laboratories of British Titan Products Company Limited in an attempt to understand the factors affecting their stability. As practical systems were to be modelled, it was necessary to study the dispersion of pigments in systems of higher ionic strength than normally used in this type of work. The stability of a colloid is affected by the surface potential of the colloidal particle, but, as surface potential cannot be obtained directly, the electrokinetic, or " zeta," potential is usually measured and can be correlated with colloid behaviour.

In an electrolyte surrounding a charged non-conducting particle, a statistical excess of ions of opposite charge to that of the particle will collect so as to neutralise effectively the charge on the particle : these are called the " counter ions." The electric field at the particle surface produces an increase in the effective viscosity of the solvent by an increasing degree of solvent molecule immobilisation as the molecule comes closer to the actual interface. (This is known as the visco-electric effect.) When the particle moves relative to the medium, the " plane " of shear is not therefore the solid-liquid interface, but a narrow region where translational forces equal the combined viscous and electrical forces. This region of shear is known as the " slipping plane," and the potential in this plane is the zeta potential. The bound and more diffuse layers are collectively known as the electric double layer. The mobility of a particle moving under the influence of potential gradient is directly proportional to the zeta potential and is a function of potential gradient, dielectric constant and viscosity of the medium. The constant of proportionality depends upon the size and shape of the particle and the ionic strength of the medium. Henry[1] analysed the equation for the motion of the particle and considered various geometric shapes and the retardation effect of the electric double layer round the particle. He developed the equation

$$\zeta = \frac{6 \pi \eta \mu}{f(\kappa a) \varepsilon}$$

where f (κa) is a function of κ, the reciprocal thickness of the double layer (Ref. 2, p. 129, 208) whose value depends on the ionic strength of the medium, and a, the particle diameter (see Fig. 1). ζ is the zeta potential, η the viscosity in poises, μ the mobility in microns/sec volt^{-1} cm^{-1}, and ε is the dielectric constant. Care must be exercised to convert to cgs units (300 volts equal one esu unit of potential). Because of the approximations involved in the derivation of this equation, extreme care must be used in transforming mobility results to zeta potential. In the derivation of his equation, Henry ignored the effect of " relaxation " of the double layer on mobility, so too much reliance must not be placed on the absolute value of the zeta potential unless such detailed correction is made. The movement of such a charged particle under the influence of the potential gradient is known as electrophoresis, and the mobility of the particle is known as the electrophoretic mobility.

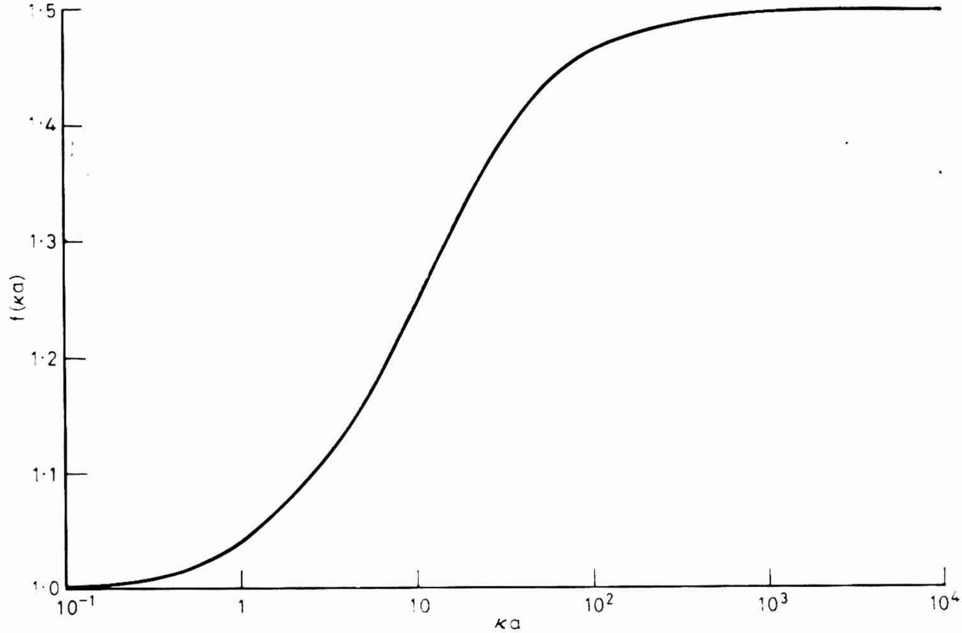

Fig. 1. The relation between f(κa) and particle diameter and ionic strength of the medium

Accounts of the theory of the electric double layer can be found in references 2, 3, 4 and many other sources.

Changes of electrophoretic mobility with ionic concentration and time give insight into the colloid chemistry of the particle, and also into the stability of its dispersions. It was therefore decided to build a micro-electrophoresis apparatus to study the mobilities of pigment particles in aqueous systems to which paint components could be added. A search of the literature failed to reveal a detailed account of the design and construction of such an apparatus and it is to fill this apparent void that this paper is mainly presented. However, a paper describing an apparatus which is purported to measure the mobility of pigment particles in aqueous systems[5] appeared in this *Journal* in March 1966. Although the author mentioned some of the errors possible in such measurements of electrophoretic mobility he considered them as insignificant. There were also other sources of error which he did not appear to have considered, the combined results of which would be to make the measurement of mobility using the simplified apparatus as described a very uncertain activity. For instance, it is critically important that the microscope used to observe the electrophoretic mobility should be focused at a level in the cell at which the electro-osmotic flow is zero, or at a level at which the electro-osmotic velocity is known accurately. The method employed whereby the microscope can be focused accurately at a layer of zero electro-osmotic flow depends entirely upon the cell being a closed system, that is that a laminar parabolic flow pattern exists between the top and the bottom surfaces of the cell with a reversal of flow at a distance 0.203 radius units from the edge of the tube. If the cell is *very* wide then accurate focusing is not so critical and it would be possible to ignore this condition, but the viewing objective used in the paper mentioned must be at least ×50, giving a maximum working distance of 0.5 mm allowing a liquid depth of 5 mm, insufficient to neglect the electro-osmotic flow. In the apparatus described it would be quite impossible, due to the open, non-symmetrical nature of the cell, to discriminate between electrophoretic and electro-osmotic motion. In addition the composition of the glasses from which the microscope objective front face and the glass slide are made will be different, giving rise to different glass/water zeta potentials, thus distorting any possible parabolic flow conditions. Furthermore, the equation for deducing zeta potentials from mobilities requires uniform potential gradients, i.e. uniform current densities, a condition which cannot exist in the apparatus described because of the variation in thickness of the sample drop, and conduction through the metal rim of the objective mount. Consequently, to produce meaningful results, the micro-electrophoresis apparatus must be constructed so as to safeguard against such errors.

Design of a micro-electrophoresis apparatus

A micro-electrophoresis apparatus has three functional units :

1. The optical system, incorporating the ultra-microscope illuminating system and the microscope viewing system ;
2. The electrophoresis cell itself and ancillary electrical equipment ;
3. The thermostatic control.

The functions of these three units are self-evident, but operational requirements depend to a marked extent on the actual colloidal system under investigation. Thus, before design of the apparatus itself can be undertaken, consideration must be given to those parameters of the experimental system which affect apparatus design, i.e. ionic strengths, likely mobilities, settling rates of particles, light scattering properties of particles and adhesion of particles to the walls of the apparatus. The ionic strengths encountered in, for example, gloss emulsion paints containing titanium dioxide pigments are far higher (i.e. 4×10^{-2}) than those previously noted as having been used in micro-electrophoresis cells, and stringent precautions must be taken to eliminate the effects of the convection currents produced in such concentrated systems. A second problem caused by the use of high ionic strengths with polyvalent electrolytes is the low mobility of particles due to the compression of the electric double layer and the attendant difficulty of defining small changes in the average mobility in a hetero-polydispersed system. The systems studied in the present work had the following major characteristics :

Mobilities probably in the range $+5$ to -5 microns/second $\text{volt}^{-1}\ \text{cm}^{-1}$; ionic strengths in the range 10^{-5} to 10^{-1} (conductivities 10^{-6} to 2×10^{-2} mhos/cm^2) ; particle sizes 0.2 to 2 microns, dispersed and also flocculent, strongly light scattering; colloid concentrations up to 10^{-2} g/l; and particles which adhered tenaciously to glass when well dispersed.

These characteristics dictate the unit requirements below.

1. *The optical system*

This, as mentioned, consists of an ultra-microscope illuminating system and a medium power transmission viewing system. The particles are not viewed directly, but as centres of scattering in a narrow intense illuminating beam of white light. In these circumstances magnification is not as important as resolution and no purpose is served in increasing the magnification beyond the level required to resolve ordinary Brownian movement. In the case of titanium dioxide particles of pigmentary size, ×200 magnification is sufficient. Optimum resolution would normally be obtained with a ×10 eyepiece and a ×20 objective, but because of the convenience of an increased working distance, a ×20 compensating eyepiece and a ×10 Achromat objective were used. In the author's apparatus this magnification means that one square on the graticule used in the eyepiece represents 44 microns at the focus of the objective, when this is immersed in water. Low mobilities mean that the observation zone at the hydrodynamic stationary layer must be narrow to eliminate the effects of particle drift, consequently the depth of focus of the viewing system must be as short as possible. This can be reduced by increasing the power of the eyepiece.

The narrow, intense illuminating beam is produced by an ultra-microscopic system using a focused projector bulb, a condenser, and a ×4 to ×10 magnification microscope objective with the usual slit system between the lenses. Interference with the observation of moving particles caused by large flocculated particles settling out of the plane of observation, and disturbing the flow pattern in the cell, is obviated by having the optical axis of the viewing microscope horizontal and the ultra-microscope axis at right angles above it. The ultra-microscope must have facilities to alter the degree of convergence, intensity, and width of the beam ; its direction, both along the axis of the cell and along the axis of the viewing microscope, is altered by mounting the objective in slides. The lamp/condenser system is built as one unit, as is the slit/objective mount, the objective focusing tube sliding into the slit support tube. The two units are independently adjustable on the main support, which is a rigid structure securely attached to a solid base, to which is fixed both the electrophoresis cell bath and the viewing microscope ; see Figs. 2 and 3.

2. *The electrophoresis cell and ancillary electrical equipment*

The first requirement of the electrophoresis cell is that laminar flow exists along the axis and that, when part of a closed system, the hydrodynamic flow

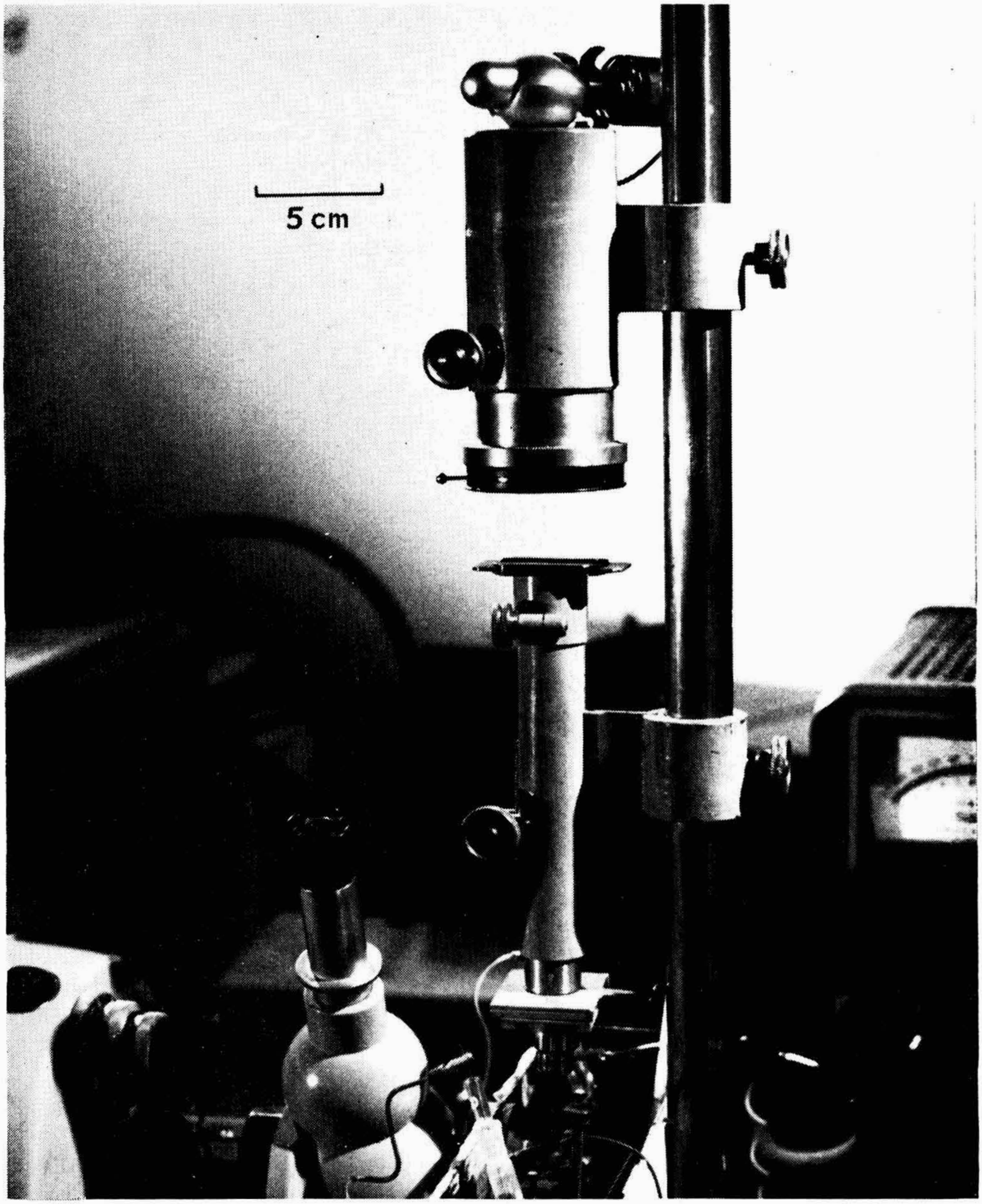

Fig. 2. Optical system

parabola condition is satisfied. This means that the cell must be constructed of one material and have a uniform cross section. Rectangular or cylindrical cells can be used, but rectangular cells must have a depth to width ratio of 1 : 20 to give the required flow conditions. As a depth of 2 mm (to give a practicable stationary level of 10 microns) would require a cell at least 4 cm wide, a cylindrical cell was chosen. The maximum useable cell width is 2.5

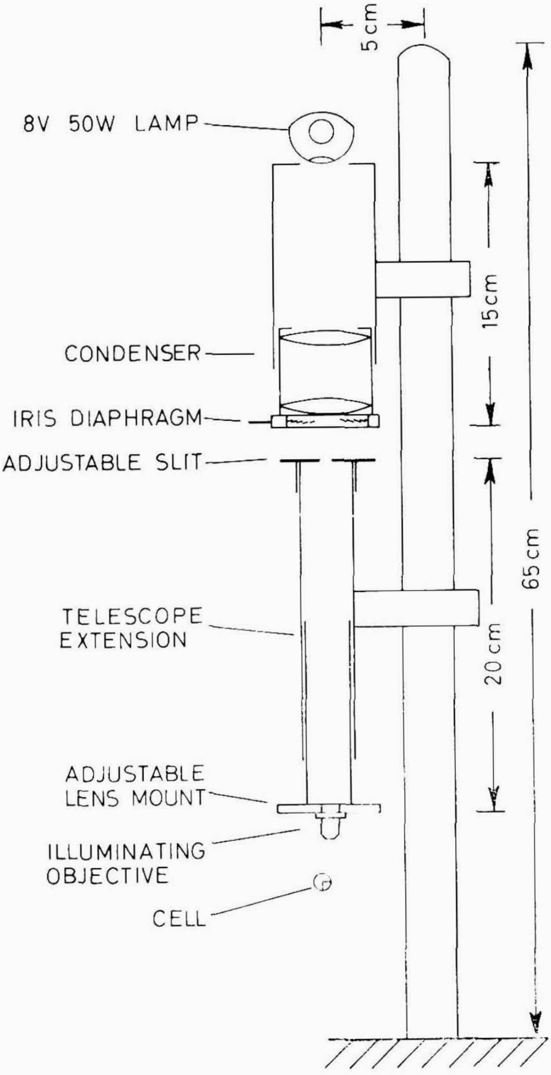

Fig. 3. Illuminating system

to 3 mm because of the working distance of the viewing objective ; normally 2.5 mm internal diameter " Viridia " precision bore capillary tubing made by Chance Bros. has been used. This tubing has very thick walls which must be ground down at the viewing position to reduce optical distortions and light absorption. The walls at these positions should have a thickness of less than 0.1 mm, produced by grinding with a diamond impregnated wheel and polishing with jeweller's rouge.

The electrodes are coiled platinum foil, blacked before coiling (uncoiled dimensions 1 cm × 6 cm), giving a maximum current of about 5 ma without polarisation, more than adequate to give a field strength of 2 v/cm in a system with conductivity 2×10^{-2} mhos/cm^2.

Convection currents caused by passage of such currents can never be completely eliminated, but can be reduced by grinding the cell walls as thin as possible, by using a very narrow illumination beam to facilitate observation, and by passage of current for as short as possible a time for each measurement.

Other requirements for the electrophoresis cell are robustness and rigidity combined with ease of filling, emptying and cleaning. Small platinum probes at either end of the capillary tubes are inserted to monitor the applied potential and observe fluctuations due to heating or possible polarisation of the electrodes. The final cell design is shown in Fig. 4. The electrical requirements are :

1. A stable constant voltage power supply from 0-500 volts with a good resettability factor.
2. A voltmeter with a very high input impedance to reduce the current drawn while measuring the potential applied.
3. An ammeter in the circuit to indicate cell heating load and electrode stability, reading from 0-10 milliamps in steps.
4. A pH meter reading to an accuracy of ±0.02 pH units from pH 1-12 to measure the pH of the sample in the electrophoresis cell after measurement of mobility.

The cell is filled and emptied by a vacuum line connected to one end of the cell. The cell support jig should allow separate adjustments to the position of the cell capillary as well as all the axial movements of the jig itself. It should grip the cell firmly without distortion and should be easily removable from the bath and replaceable without need for further adjustments.

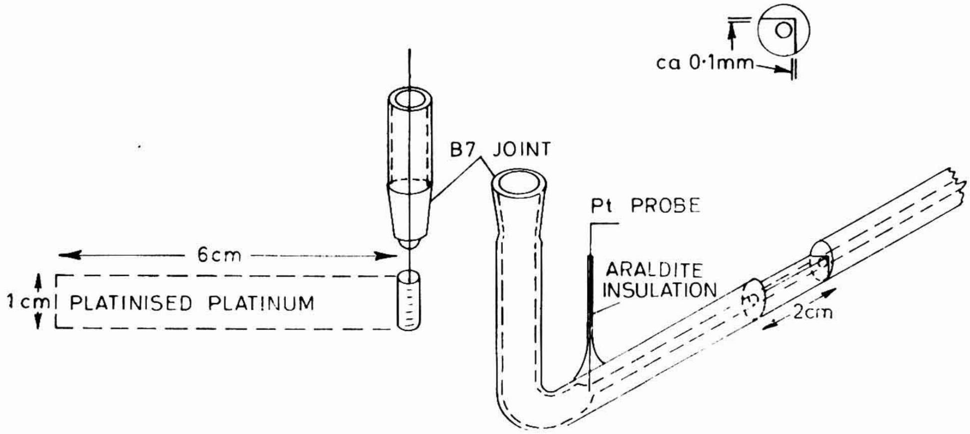

Fig. 4. Electrophoresis cell

3. *The thermostatic control*

To obtain the best optical resolution the electrophoresis cell and viewing objective should be immersed in the same liquid ; this acts also as the thermostating fluid. As the density of water changes little with temperature around 4°C the use of water at this temperature means that slightly higher currents can be handled in the electrophoresis cell, and consequently higher ionic strengths can be tolerated. The thermostat bath must be large enough to contain the electrophoresis cell and its support whilst leaving sufficient room for adjustments to the cell position.

The circulating system should contain a fine filter to remove suspended matter from the liquid.

Other equipment required is an accurate pH meter for the preparation of sample suspensions, a low power ultrasonic bath to disperse the freshly made suspensions, a well used still to prepare doubly distilled water, an electrodialysis apparatus to prepare electrolyte-free suspensions and a simple conductivity meter to measure the conductivities of the colloid suspensions. Special soluble-salt and particle-free beakers should be used to hold the colloid suspensions (e.g. nylon or polypropylene). The electrical and thermostatic circuits are shown in Fig. 5.

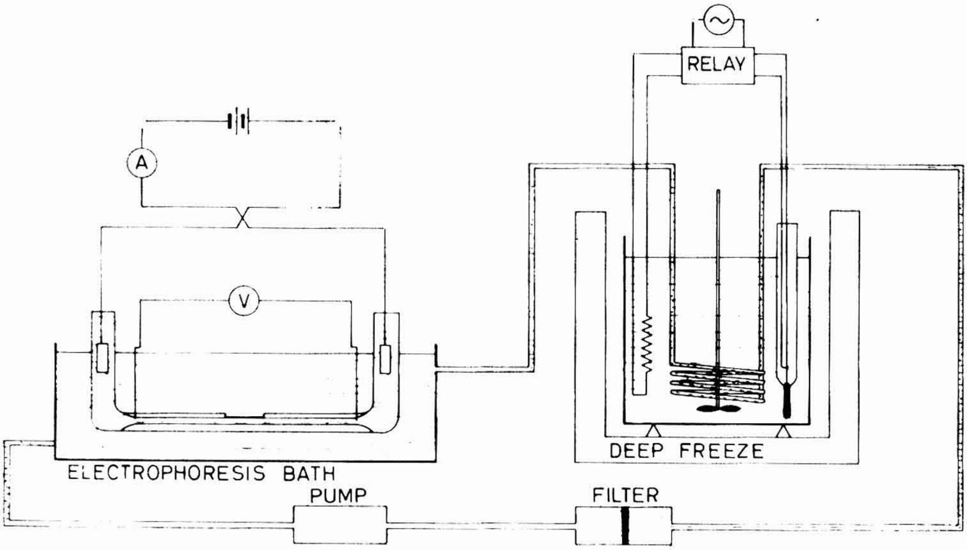

Fig. 5. Electrical and thermostatic systems

Constructional details

The optical system

The dimensions of the ultra microscope : these are shown in Fig. 3. The lamp-house is a cylindrical brass tube, closed at the top by a plate with a circular hole in the middle. Above this is an 8 volt, 50 watt, 8 mm cine projector bulb with a silvered back, held by Terry clips, which allow small adjustments to the direction of the emergent beam. The condenser system is two 5 cm focal length convex lenses 5 cm apart. The light then passes through an iris diaphragm of maximum aperture 4 cm. The unit slides on the brass support tube, located by a milled screw. The slit and objective unit is mounted similarly, the objective tube sliding inside the slit support tube, controlled by a rack and pinion. The slit consists of two bevel edged brass plates giving a slit 1 cm long and from

0 to 1 cm wide. The objective adjustment slides allow translational movement in two dimensions ±0.5 cm from the centre point. The brass support tube is held firmly to a Tufnol board which slides in grooves on the baseboard.

The viewing microscope : a Vickers " Metalette " microscope is used, with the stage mount sawn off below the level of the objective mount, and a fully silvered mirror replacing the standard half silvered mirror. This microscope was chosen because it was claimed to have an extremely linear fine focusing device working the objective rather than the stage, as is common with most other modern microscopes, and because the stage could be removed without affecting the rigidity or alignment of the instrument.

The electrophoresis cell

The grinding of the electrophoresis cell : this is an extremely tedious task as the very thin walls must be plane and at 90° to each other. The preferred method is to clamp the tubing in a " V " shaped brass channel in a heavy brass jig, and lower on to it the flat annular face of a diamond impregnated " cup "-wheel, held in the chuck of a high speed drill. The cutting face of the wheel is 2 centimeters wide on the circumferential face of the 15 centimeter wheel. Two grades of wheel are used—a coarse 700 grit wheel and a fine 900 grit wheel, made by Impregnated Diamonds Products of Gloucester, England. After a coarse cut has been made to the depth of about 1.5 mm the fine wheel is substituted and the cut smoothed off. The thickness of the wall between the bore and the outside is measured on the ultramicroscope, the tube then replaced in the grinding jig and the progress of grinding followed with a micrometer gauge. When the wall thickness is down to 0.15 mm the cutting wheels should be replaced with the polishing wheel using a liberal supply of jewellers rouge in castor oil. A B7 ground glass socket is fused to either end of the 12 cm long capillary through a 90° bend, with 4 cm of tubing. This is to accommodate the platinum electrodes, whilst the minute platinum probes are inserted at the very mouths of the capillary bore. The cell is filled and emptied by means of a vacuum tube attached to one end of the cell by a B7 coned glass tube ; suspensions are drawn up through a similar tube at the other end of the cell. When full vacuum is applied the turbulence of the liquid passing down the cell bore is sufficient to carry with it all but the most strongly adherent particles. These are dislodged occasionally by filling the cell with 5 per cent hydrofluoric acid for one minute, then washing thoroughly with doubly distilled water.

The cell support jig : a brass girder with a V-shaped trunnion at either end is used, the capillary being located in these trunnions by overhead screws. The trunnions are lined with pvc tape. The bar is supported by a vertical square-section brass tube fitting snugly into a brass bar brazed to the clamping cage of a ball and socket joint, the ball support being brazed to the cell bath floor. The square brass tube and bar provide vertical adjustments, the tube being located on the bar by means of a screw fitted with a long operating handle which protrudes out of the bath. All necessary adjustments of both the cell and the jig can be made by movement of the ball and socket joint, which is locked by another screw with an extended shaft. A small spirit level is fixed along the side of the brass girder, its true level being adjusted to that of a steel rod located in the V trunnions. The cell and supports are shown in Fig. 6.

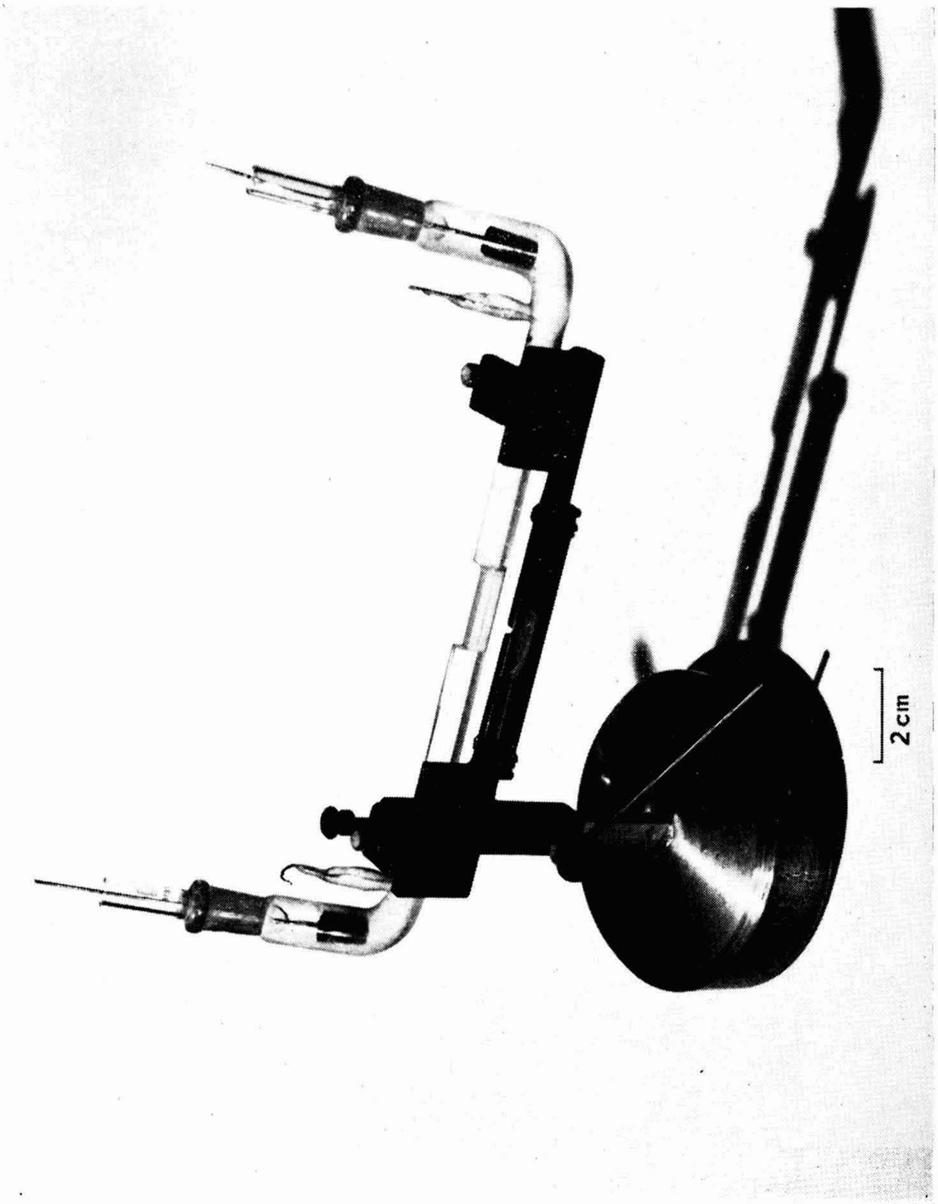

Fig. 6. Electrophoresis cell in support jig

The optical alignment of the cell and optical systems is checked by adjusting the ultramicroscope beam to glance the inner surface of the bore and focusing the viewing microscope on the fine scratches caused by the mandrel used in the manufacture of the tubing. The first scratch to come into or the last to go out of focus is exactly half way up or down the cell bore and scratches should come into and go out of focus symmetrically on either side of this scratch in the centre of the field of view. The cell jig is adjusted in any direction required to achieve this object.

The calibration of the fine focusing device of the viewing microscope must be undertaken with great care as temperature variations affect the pitch of the focusing screw. The calibration should be performed at the beginning of each measuring session by measuring the diameter of the capillary bore, corrected for immersion and refraction effects.

The thermostatic control

The temperature control : in the thermostatic bath, ± 0.1°C, this is achieved by using a Jackson regulator and " fish-tank " heater, the heat exchanging coils being contained in a deep freeze to ensure that the surroundings of the thermostat exchange bath are at a lower temperature than the bath liquid itself.

Suspension preparation and mobility measurement

Before a cell is used to measure mobilities, it must be checked to ensure that the cone and socket joints do not leak and that the hydrodynamic flow condition is satisfied. If any leaks exist, the particles will move without a potential gradient ; the parabolic condition is checked by measuring the mobility of particles at fixed intervals across the cell, plotting these on a graph, and verifying that they fit the curve $y^2=4\,ax$ (see Fig. 7).

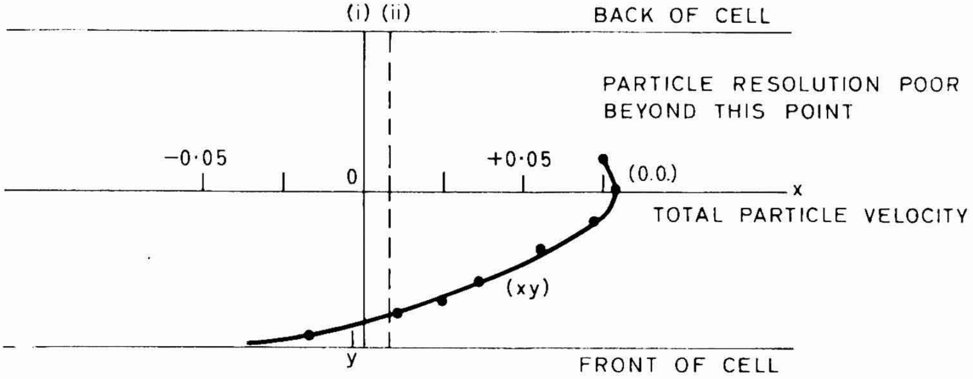

Fig. 7. Flow conditions in the cell. (i) Electro-osmotic zero. (ii) Electro-osmotic plus electrophoretic apparent zero

As the zeta potential and hence the mobility of a particle varies as a function of the ionic strength of the solution in which it is suspended, a series of samples containing an electrolyte at various concentrations will have different mobilities without any other effect being present. As this effect could be significant, the ionic strength of each sample must be made up to the level of the highest sample with an indifferent electrolyte. (The indifference of an electrolyte can be checked by increasing its concentration. The mobility should decrease, but never be reversed, i.e. the decrease should be due to compression of the double layer, not specific adsorption.) About 1 mg of pigment per 100 ml of suspension is used to prepare the samples for mobility measurements. The electrolytes are added in predetermined order depending upon any chemical reaction expected and the suspension treated in an ultrasonic bath for a few minutes. It is then allowed to reach chemical equilibrium, which may take many days, redispersed in the ultrasonic bath, and introduced to the electrophoresis cell. The sample must then be allowed to achieve thermal equilibrium before mobility measurements are performed. The pH of each suspension should be measured before and after admitting to the electrophoresis cell and after mobility determination.

The actual measurement of mobility : this is a fairly easy technique to learn. In a hetero-polydisperse system there will be particles of a wide range of sizes, and although mobility is a function of charge density and should thus be fairly constant, considerable variations do occur, and an average mobility determination must take account of this range of velocities. Extremely fast or slow particles may be ignored, but a sufficient number of particles should be timed to account for most variations present. The selective experience is easily acquired, and after 20 sets of measurements an operator will be able to determine the average mobility of a sample twice and produce the same result within 2 per cent.

The potential gradient is adjusted so that a particle in sharp focus in the centre of the field of view crosses an integral number of squares in about ten seconds. When focusing on the hydrodynamic stationary layer, a correction must be made for the refractive effect of the plano-concave lens formed by the cell wall and surrounding liquids. This correction and the equation used to calculate it are found in reference 6.

Use of potential gradients greater than 10 volts per centimeter is not advised, but if necessary the timed interval may be up to a minute. Particles which move sideways or which move out of focus should be disregarded ; a sample which has a large number of such particles has not yet reached thermal equilibrium in the cell. Particles should be timed in both directions by reversing the electrode polarity. If these times and those of other particles are within ±5 per cent of each other, ten measurements are sufficient. If not, then sufficient readings in excess of ten should be taken until each further reading does not affect the *mean* by more than 1 per cent. Twenty readings is the maximum which it is sensible to take. Some authors recommend taking these readings at three different levels in the cell and constructing the flow parabola from them, back calculating the mobility at the stationary layer. We find this procedure quite unnecessary, in that we obtain the same mobility (±2 per cent) by a single series of measurements at the stationary layer. The occurrence of polarisation or convection effects is detectable by wide variation of mobilities and non-parallel movement of the particles. With only slight heating effects, where the particle moves at less than 30° to the grid lines, it is permissible to use these particle mobilities, but the results must be treated as suspect. In practice, when such particles have been measured at a high voltage, and compared with the same sample measured without convection at low voltages, the mobilities vary by only a few per cent.

Two stop-watches are used, one for each direction of movement, so that the observer does not lose sight of the particle in view whilst recording the first measurement. Where the measured mobility of a sample is very much away from the general trend, it is advisable to check the materials used, the pH of the sample, and the equilibrium water used in making up the sample for impurities. Scrupulous cleanliness is essential in accurate mobility determination.

Results

Typical results for a series of titanium dioxide pigments in various electrolyte systems are shown in Fig. 8 and the Table. A number of such measurements have been made on titanium dioxide pigments with a variety of surface treatments in aqueous systems ; the information gained from these measurements has been important in understanding the physical and chemical mechanisms by which the pigment suspensions are stabilised. This work could be extended to non-aqueous systems if certain modifications were made to the electrophoresis cell itself to allow the use of the higher potential gradients which are necessary to produce reasonable mobilities in systems of very low conductivity such as the alkyd resin/white spirit system.

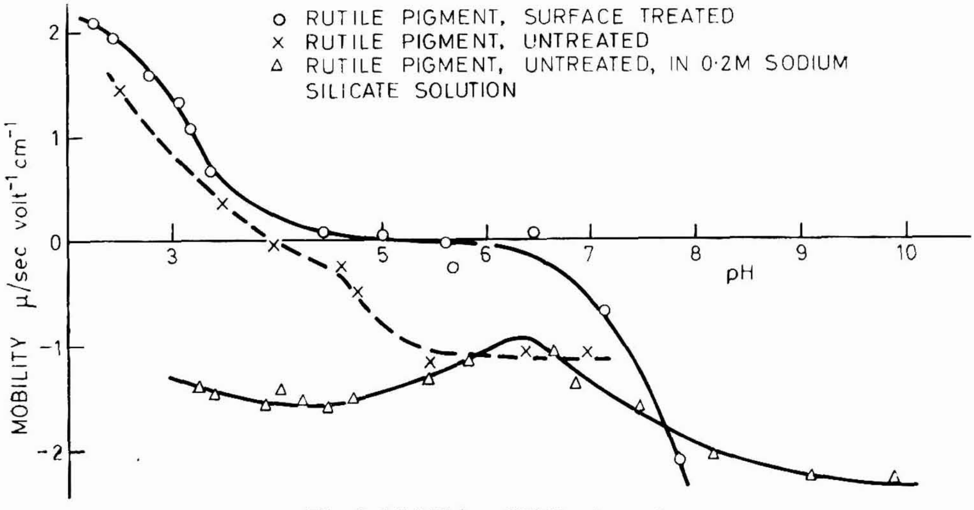

Fig. 8. Mobilities of TiO_2 pigments

Table

Measurement of mobility of untreated rutile in 2×10^{-2} M sodium silicate solution at pH 4.2

Distance traversed by particles $=44\mu$ Potential applied $=+47.2$ volts/13.5 cm
„ „ $=-46.3$ volts/13.5 cm

Charge on particles : negative Temperature of thermostat bath = 3.5°C

Timing results, in seconds :

Polarity+ve : 8.69 8.09 8.35 8.45 9.25 8.86 8.83 9.00 8.73 9.12

Polarity−ve : 9.43 7.39 7.56 8.40 9.76 7.91 9.34 9.65 9.02 9.27

Mean time, +ve polarity = 8.74 seconds. Mean mobility, +ve polarity $=44\times13.5/47.2\times8.74=1.44\mu$/sec volt^{-1} cm.$^{-1}$

Mean time, −ve polarity = 8.77 seconds. Mean mobility, −ve polarity $=44\times13.5/46.3\times8.77=1.46\mu$/sec volt^{-1} cm.$^{-1}$

$\therefore$ **Average mobility $=1.45\mu$/sec volt^{-1} cm^{-1}**

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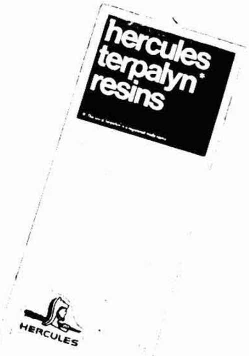

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Conclusion

The micro-electrophoresis apparatus described in this paper has enabled the investigation of the electrokinetic properties of pigment suspensions in systems of higher ionic strength than have been previously investigated elsewhere. Mobilities of $0.1 \mu/\text{sec volt}^{-1} \text{cm}^{-1}$ at an ionic strength of 2×10^{-2} have been successfully measured. Results of this type are essential to the meaningful study of pigment stability in practical aqueous systems. Accurate measurement of such low mobilities under similar conditions does not seem to have been reported previously.

Acknowledgments

The author wishes to thank Dr. R. H. Ottewill of Bristol University for his interest and advice ; the laboratory and workshop staff of the Development Department of British Titan Products Company Limited for their painstaking efforts, and the Directors of the Company for permission to publish this paper.

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Next month's issue

The Honorary Editor has accepted the following papers and these are expected to appear in the July issue :

- " **An investigation of the reaction between linseed oil and pentaerythritol,**" *by T. A. Cordwell.*
- " **The importance of physical effects on the action of catalytic surfaces in vinyl polymerisation,**" *by P. E. M. Allen.*
- " **Composition and fractionation of tall oils,**" *by K. S. Ennor and J. Oxley.*
- " **Size analysis of organic pigments using the ICI-Joyce Loebl disc centrifuge,**" *by J. Beresford.*

Hilditch Memorial Lecture

The Hilditch Memorial Lecture is to be held on 13th July 1967, and not 18th as published in the May issue. The lecture is open to all members of OCCA.

Editorial

Reviews of reviews of . . .

" *One of the real problems facing the scientist today is that of searching out and assessing published work relevant to his interests. This is true of any field of interest, but is particularly acute in the case of high polymer chemistry and physics.*"—Robb and Peaker in their preface to *Progress in High Polymers*, Volume 1, 1961 (Heywood & Company Ltd.).

" *The ' literature explosion ' during the last few years has brought with it a proliferation of new journals. The field of polymer science has perhaps been affected by this more than most other areas of chemistry and physics. . . . One cannot read the numerous articles of interest, very often one cannot even check the abstracts. . . . As a consequence of this situation the review article is becoming the primary source of information to a large majority of scientists.*"—from the introduction to the series *Macromolecular Reviews* (John Wiley & Sons Inc.), Volume 1 of which, edited by Peterlin, Goodman, Okamura, Zimm and Mark, has just made its appearance.

It is hardly necessary to paraphrase these remarks or to comment on their patent truth. Twenty years ago one could regularly scan the relevant sections of *Chem. Abs.* and pick up most of what was going on in the polymer world with some prospect of selecting and absorbing that which was truly significant. That is no longer possible ; *Chem. Abs.* is part of the information retrieval system which, however necessary, is a very different thing from a current awareness service. " Big brother " computerised systems are claimed capable of doing both, eventually, but all that is in sight at the moment is an opportunity of finding out quickly what is known or claimed to be known about a topic which one is able to define in some detail at the outset. The sponsors of review series, on the other hand, seek to provide regular *critical appraisals* of progress in more or less specialised topics, in advance of, and generally at a higher level than, those provided by the text books. This has been done very successfully for a number of years in *Fortschritte der Hochpolymeren-Forschung* (Springer-Verlag), which is the polymer science analogue of such " pure " chemistry publications as the Chemical Society's *Quarterly Reviews*. The *Fortschritte* is not cheap at around DM 40 per issue, but it is cheaper than most bound volumes of review papers and has the unique merit of appearing at regular intervals. The papers it contains are long enough to provide a well balanced picture of the topic under consideration, whilst they are not too long to be read at a sitting or two. This is in sharp contrast with some other series, such as Wiley's *Polymer Reviews*, which are really advanced text books, each dealing at length with a single topic. Of course, collations of review papers are liable to contain much that is not of immediate concern to the reader, but that is perhaps their greatest attraction.

The Heywood enterprise seems to have been stillborn ; at least, no second volume has appeared in six years notwithstanding the high quality of Volume 1. We wish *Macromolecular Reviews* a brighter future, for Volume 1 at least is equally authoritative. It contains accounts of optically active polymers, electrolytically controlled polymerisations, poly-9-vinylanthracene, catalysts for alpha-olefine polymerisation, the structure of crystalline polyethers and dynamic thermogravimetric analysis in polymer degradation. All are written, as they should be, close to the frontiers of knowledge. Their liberal embellishment with recent references makes them useful starting points in information retrieval, but we are firmly of the opinion that this is a secondary function. Awareness, cross-fertilisation, " fall out " and inspiration are the things of real value coming from such publications. These are what one has lost under the weight of scientific documentation ; and we submit that they cannot be put back by an indexing system, computerised or not. But how long will it be before reviews of reviews have to save us from intellectual suffocation by reviews ?

Correspondence

Sir,—Is it not time that the paint industry swept the misconceived term " anti-fungicidal " from its trade literature and labels ? For many years, while working with fungicides and fungus-resistant paints, I have frequently been mystified by the possible applications of products with reputed " anti-fungicidal " properties. Enlightenment has recently been provided by a trade pamphlet which recommends one such product for use where " fungicidal growths " are present.

One has hoped that the word has emanated from non-scientific sources, such as sales departments (and presumably not from the " other culture "), but it has now regrettably appeared in the 1965 Report of Progress in Resins, Drying Oils, Varnishes and Paints, for which this Association assumes responsibility ; dare one now hope that publicity will defeat its further spread ? Even then, there remains some doubt if " fungicidal " is permissible, in respect of paints which would be better described only as " fungus-resistant," or possibly " anti-fungal " as in the original paper to which the Report refers.

Yours truly,

P. Whiteley.

Building Research Station,
Garston, Watford.

The Honorary Editor apologises to Mr. Whiteley for the delay in publishing this letter, which was unfortunately mislaid for almost six months.

Information Received

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

Bush Beach and Segner Bayley Ltd. announce that sales of carbon blacks LT-OG and LT-DS in the UK are now exclusively handled by them. These sales were formerly handled by J. H. Little & Co. Ltd.

The full range of machinery paints (BS 2660 shade) manufactured by **Gaymel Paints,** a division of Pinchin Johnston and Associates Ltd., is now contained in a colour card published by the manufacturers. The card gives application details and describes alternative machinery finishes for special environments.

Prices (Bromborough) Limited, a Unilever chemical company, have recently obtained a £175,000 order from Russia for specialised products for use in the Soviet chemical industry. The order was obtained in the face of strong competition from America, West Germany and Scandinavia, and is claimed to be one of the largest individual orders received by the company, who last year exported more than £1 million worth of their specialised chemical products.

A new portable humidity meter suitable for quickly checking the moisture content of timber and plaster is now available from **Hird-Brown Limited.** The meter, which is supplied with probes suitable for wood, is claimed to weigh only 1 lb, and is 6 in × 4 in × 3 in in size. Power is supplied by self-contained batteries, intended to be changed annually.

" Elvax " vinyl resins are the subject of the latest brochure issued by **Du Pont de Nemours International SA.**

The brochures present a brief summary of the uses of this ethylene-vinyl acetate copolymer, together with recommendations as to equipment and blend compositions.

Blundell-Permoglaze Ltd. announce the transfer of their south eastern region decorative division sales offices and depot from 9 Upper Thomas Street, London, E.C.4, to Slough, Bucks.

A revolutionary design is claimed by **The Felvic Industrial Sales Co.** for their new Air Dehumidifier. The unit, which is fully automatic for operation between 32 and 104°F, operates on a refrigeration principle, and, it is claimed, can extract up to 50 gallons of moisture in 24 hours in spaces of up to 100,000 cu ft.

Radical improvements in manufacturing techniques for paints and viscous printing inks are expected to result from the introduction of the new " ED " pigments, claim **ICI.** Said to be a major advance in pigment technology, these pigments are claimed to be rapidly and easily dispersable in any of the mixing equipment available to the paint and printing ink industries, without any loss in fastness properties.

Two ranges of ED pigments will be available : the ED-P pigments, for use in paint media, and ED-I pigments, for use in viscous printing inks. Three ED-P and six ED-I pigments are now available in development quantities, and others will be on the market in the near future.

An accelerated climatic chamber, the Frigistor Climatest, has been introduced by **De La Rue Frigistor Ltd.** The Climatest is intended for testing the weathering of plastics, paints, fabrics, etc., and, it is claimed, will produce in one year sunshine and weathering conditions equivalent to up to ten years' outdoor testing.

The samples are mounted in a chamber around a drum on which are mounted 32 ultra violet fluorescent lamps. These lamps are claimed to give excellent reproduction of daylight conditions within the range 3,000-3,600 Å, and lamps can be altered to investigate any other specific region of the spectrum. The samples are rotated around the drum, which is fitted with water sprays. Temperature, humidity and water conditions can all be precisely controlled.

A range of selective true solvents for polyurethanes is announced by **Urethaanchemie NV.** Marketed under the trade name Uresolve, the solvents are claimed to dissolve a wide range of fully cured polyurethanes, and to have a high degree of selectivity towards other plastics materials and metals. Uresolves are manufactured by the Amicon/Dynaloy Group, for whom Urethaanchemie are sole distributors.

The Printing, Packaging and Allied Trades Research Association have recently issued a report on new synthetic materials for litho platemaking. Under development at PATRA is an optical film thickness device which may be a useful tool as part of a colour control system on a letterpress machine.

A new specialist paint, Polyurethane Liquid Lino, has recently been introduced by **Colthurst and Harding Limited.** The product is said to provide floors with an exceptionally tough coating, and to be the ideal protective finish for concrete, cement, stoves, brickwork, tiles, wood and linoleum.

The Illumination Industry Standards Committee of the **British Standards Institution** has recently issued BS 950, Pt. 1, 1967, Artificial Daylight for the assessment of Colour-Illuminant for colour matching and colour approval.

Joyce Loebl & Co. Ltd. and **International Paints (Holdings) Ltd.** have been approved for the Queen's Award for Industry for 1967. The latter are claimed to be the only producing firm in the paint and allied industries to gain the award for export achievement.

Price reductions for PTFE extruded rod $\frac{5}{32}$ in to $\frac{7}{8}$ in diameter, and all sizes of extruded tube, are announced by **Polypenco Limited.**

Also by Polypenco is new High Impact Polyethylene, ultra-high molecular weight polyethylene with chemical and electrical properties superior to nylon, exceptional impact resistance, and good abrasion resistance. The price is slightly lower than that of Polypenco nylon.

Sericol Group announce the introduction of a new screen printing machine, the Sericol Sprinter, claimed to incorporate a number of new design principles giving greatly increased output, accuracy and versatility.

Tributoxyethylphosphate, a defoamer for paint, textile and paper, and a plasticiser for plastics, etc., has recently been put on the market by **Societe Protex.**

The Oleochemical Division of **J. Bibby and Sons Limited** has negotiated an agreement with **Stepan Chemical Company,** a prominent American chemical manufacturing concern, under which Bibby oleochemical products will be manufactured under licence in America for sale in the North American continent.

An increase of production of 15,000 tons of iron oxide black pigments per year is expected by **Farbenfabriken Bayer AG** following opening of the additional production facilities. This will mean that Bayer will have an overall capacity of synthetic iron oxide pigments of 170,000 tons per year.

Information Sheet No. E.152 issued by **British Resin Products Limited** describes Epok U.9193, a new, high solids low viscosity etherified melamine-formaldehyde resin supplied in n-butanol. The resin is claimed to have a very rapid rate of cure, excellent tolerance to cissing caused by overspray contaminants, and excellent compatibility with plasticising alkyds and hydroxy acrylic resins.

Reviews

TECHNIQUES OF POLYMER EVALUATION. VOL. I. THERMAL ANALYSIS

By P. E. SLADE JR. and L. T. JENKINS (Editors). London : Edward Arnold (Publishers) Ltd. New York : Marcel Dekker Inc. 1966. pp. x + 253. Price 85s.

This may be considered a source book concerned, as its title implies, mainly with practical aspects of the thermal analysis of polymers. Three basic techniques are covered : differential thermal analysis (86 pp.), thermogravimetry (129 pp.) and the analysis of gaseous pyrolysis products, here entitled " effluent gas analysis " (17 pp.).

Differential thermal analysis (DTA) was introduced into inorganic chemistry by Le Chatelier in 1887, some 30 years before the apparently simpler technique of thermogravimetry was used. The past 15 years have seen extensive application of both in the study of polymers, and the present collation of the literature is timely.

DTA is treated in an entirely practical manner, with an analysis of instrumentation, details of experimental techniques and a description of commercial instruments in the first chapter, followed in the second by a detailed discussion of application in the study of first and second order transitions, crystallinity, cross-linking and decomposition. Chapter 3 introduces thermogravimetry with similar emphasis on experimental procedures. This is followed by 100 pages on quantitative calculations, which are largely concerned with an extension of the principles of reaction kinetics to thermogravimetric data. A similar treatment of DTA would have been useful. The final chapter on effluent gas analysis is again essentially practical in its approach, and describes the analysis of volatile pyrolysis products by such techniques as gas-liquid chromatography, infra-red and mass spectrometry. Although furnishing a useful review, it is perhaps too brief to cover the subject adequately.

The book is commendably free from errors and the 458 references cover the literature to 1964. The price must be considered high for a publication of this size notwithstanding its highly specialised nature. This is the more relevant in view of the speed with which the subject is developing and the fact that the pages devoted to commercial instruments are inevitably obsolescent already. Any polymer science library with pretensions to good coverage will place this book and, no doubt, its successors, on its acquisitions list, but we suspect that private purchasers will be few in number.

A. R. H. TAWN.

INTRODUCTION TO PAINT CHEMISTRY

By G. P. A. TURNER. London. Chapman and Hall. 1967. Science Paperback. Pp. 244. Price 25s.

This book, which is intended for use by the trainee paint technologist, consists of two main parts. The first chapters give a summary of inorganic and organic chemistry, starting from first principles and finishing with the elementary principles of polymerisation. The second part of the book deals with the elementary principles of paint and pigmentation, and then goes on in more detail with chapters on solvents, additives, and the various types of polymers and paints. These are covered in some detail in an up-to-date manner.

The book is clearly written and presents a considerable amount of material which would be useful to the student. Certain omissions are rather unexpected ; colour and other optical properties are rather briefly treated, and there is no indication that instrumental methods of measurement may be used. A more surprising omission is any treatment of pigment chemistry. In two pages the reader is informed that pigments may be natural or synthetic, or inorganic or organic, and the relative merits of these classes are given. The general properties required of pigments are covered in greater detail.

Although the book is a little incomplete in its scope, it has much to offer in its clear exposition of those topics which are covered, and would be of considerable value to the student.

V. T. CROWL.

Bristol

Solvents : some topics for discussion

The one hundred and fifty-fourth meeting of the Bristol Section took place at the Royal Hotel, Bristol, on 24 February 1967, under the chairmanship of Mr. R. J. Woodbridge, when a paper entitled " Solvents : some topics for discussion " was given by Mr. L. A. Tysall, of Shell Research Limited.

Mr. Tysall's paper consisted broadly of three parts :

(1) Solvent parameters, a general survey of their status and an assessment of their significance.

(2) Methods and techniques of measuring solvent retention in paint films.

(3) The effects of various solvents on the properties of electrodeposited paint films.

Mr. Tysall commenced by describing how it was possible to arrange and tabulate the solubility characteristics of certain common resins with solvents of similar polarity. Such a basis had, however, certain discrepancies and attempts had been made to produce a more refined criterion of resin solubility on a basis of some theoretical significance.

Much of the work involved the solubility parameter

$$\delta = \sqrt{\frac{\Delta E}{V}}$$

where $\frac{\Delta E}{V}$ is the energy of vaporisation per c.c.

(Δ E being the molar energy of vaporisation (calories) and V = molar volume in c.c.)

This parameter was associated with the energy required to separate the molecules of solvent (or resin) from each other, but as it stood it did not satisfactorily account for all solubilities or insolubilities of nitro-cellulose.

Mr. Tysall then referred to the work of Burrell, in which attempts were made to improve solubility prediction by dividing solvents into three groups, consisting of " high, medium and low " degrees of hydrogen bonding. Further efforts had been made to arrange three groupings into a numerical basis. Work by Gardon was interesting since it defined a fractional polarity " P " with values ranging from 0-1 and which corresponded approximately to Burrell's " high, medium and low " groupings.

By the introduction of a third parameter, i.e. " dipole moment," it was suggested that any remaining anomalies of solubility could be rectified, and the work of Crawley, Teague and Lowe demonstrated how a three-dimensional map could be produced. Whilst the combined techniques were of increased complexity, it was possible to account for a high percentage of known solubilities.

It was well known that many paint films which are normally considered " dry " contain appreciable quantities of solvents. Such solvents can act as plasticisers and therefore influence film hardness. In some cases the presence of such solvents had been shown to reduce the water resistance of a film. There were also potential hazards in that they might contaminate the contents of containers where the films were used as protective linings.


PURE ISTLES

Simple weight-loss measurements did not give reliable estimates of the quantities of solvents retained, but the more recent techniques of utilising gas chromatography (GLC) and radioactive tracers were highly effective in this respect.

GLC techniques had been greatly refined in recent years and were now able to measure small quantities of solvent with good precision, even with fairly complex solvent mixtures.

The most useful technique was to release the solvents present, from a small area of a suitable film, by a combination of high temperature and low pressure, the volatile material being collected in a cold trap ; the contents of the trap were then injected and analysed. The weight of solvent released would vary with the chosen temperature and pressure, but if the conditions were fairly severe (e.g. 100°C and 1 mm Hg pressure) it was reasonable to assume that any solvent still retained would be unlikely to be released in practice.

By taking the condition of the film as a zero level, it was possible to estimate the solvent retained under practical conditions.

By the use of suitable isotopes giving low energy β particles, namely C^{14} or H^3, it was possible to tag the chosen solvent and thus measure its concentration in a film under given conditions. A suitable technique was to prepare a small quantity of test lacquer containing a proportion of the chosen solvent in the tagged form, as required to measure the expected quantities.

Films were applied by doctor blade, initially dried to release the bulk of solvent under safe conditions, and then cut into suitable pieces (2 in × 3 in), each piece being finally dried as desired. The piece could then be dropped into a suitable scintillation solvent which dissolved the film and also absorbed the energy from the β particles, and, in conjunction with a suitable phosphor, emitted photons which could be counted. (In practice an aliquot portion of the solution was used.) There were certain difficulties in finding a scintillation solvent which would dissolve the film-former, but for most non-convertible binders, mixtures of toluene and tetrahydrofuran worked satisfactorily.

There were some practical difficulties in using these tracer techniques. Regulations covering the use or disposal of radioactive materials involved medical checks on personnel and the use of special premises and precautions (even when the level of radioactivity was very low). Also a number of possible lacquer components acted as " quenchers " for the scintillation process and gave anomalous values ; modern equipment was often able to apply corrections for this, but added further complications to the operation.

Electrodeposition paints normally contained a proportion of solvents which were incorporated to improve the dilution and stability of the resin, aid paint manufacture, reduce the tendency of foaming and improve flow properties of the deposited film. Much of the technical effort in this field had been directed towards the development of suitable resins, pigmentation aspects and process control, and until recently little investigation work had been carried out in respect to solvent addition.

Mr. Tysall went on to describe an investigation into the effects of additions of various types of solvents. The work had involved the use of several alcohols and glycol ethers in paint systems based on Epikote resin DX16. It was shown that not only the type of solvent, but also the quantity involved, greatly affected the maximum operating voltage and throwing power of the system ; paints which were easy to dilute tended to give low throwing power.

All systems gave approximately the same film thickness at their maximum operating voltage, but at a given fixed voltage there were considerable differences.

In comparison with systems formulated with solvents, those without solvents produced films of poor appearance, were difficult to handle and produced inconsistent film weights from one deposition to another.

There followed a most interesting discussion, opened by Mr. J. Atkins, in which Mr. Tysall dealt with a wide range of solvent topics.

A vote of thanks, proposed by Mr. F. E. Ruddick, was warmly supported by the members and guests present.

F. E. R.

London

Southern Branch

Polyesters

On 13 March in the Keppels Head Hotel, Portsmouth, Mr. C. A. J. Benfield gave the last technical lecture of the current session on " Polyesters." The Chairman of the Southern Branch, Mr. J. C. Kingcome, introduced the speaker, who had been a naval architect at one time. It was not surprising, therefore, that the main content of the lecture concerned the use of glass fibre reinforced polyesters in boat building.

The history of reinforced plastic boat building was outlined from the first seaplane floats moulded in 1947 to the present day construction of 80 ft fishing trawlers.

Contact moulding was explained in some detail and the uses of steel, wood, plaster and reinforced plastic moulds were discussed. Glass reinforcements of various types, such as chopped strand mat, roving, scrim, could be used to achieve specific physical properties. Ultimate tensile strengths from 10,000 lb/sq in to 120,000 lb/sq in were possible. Weathering and water resistant properties of the reinforced plastic laminates were stated to be satisfactory provided suitable resins were used and fully cured.

Advantages of reinforced plastics for boat construction included :

(1) High strength/weight ratio ;

(2) Fabrication of large structures in one piece ;

(3) Design freedom because of the wide range of strength properties possible using various glass reinforcements ;

(4) Good resistance to corrosion and any form of biological attack, though anti-fouling paints were still necessary ;

(5) Ease of maintenance and repair ;

(6) Economy of producing a number off the same mould. Also this was one industry where raw material costs had fallen over the past few years.

The speaker referred to the low modulus of reinforced plastics as a disadvantage and also the difficulties of inspection and quality control. The latter made strict supervision essential.

Sandwich construction of boats, where a thin polyester laminate was used with a foamed plastic core, was discussed. The speaker also mentioned the use of polyester/glass fibre as a protection on new plywood boats.

This interesting lecture was illustrated with slides and a number of exhibits. A useful discussion followed the lecture and many questions were posed. The speaker agreed that reinforced plastic sheathing of wooden hulls was now a widely accepted technique which resulted in good performance especially if applied at the time of building. In answer to another question, the speaker explained that it would probably not be possible for many years to avoid removing large hulls from the water to clean off fouling, for it was not yet possible to incorporate suitable anti-fouling poisons in the resin system. To paint reinforced plastics, the recommended preparation was mechanical abrasion of the surface plus removal of release agents. Special polyurethane or epoxy finishes were reported to give good results, but little was known of the adhesion of conventional paints, e.g. anti-fouling paints.

A question outside the marine field concerned car bodies. The speaker said that reinforced plastics were not used for the mass production family car, but were of interest for limited production, as of sports cars. Contact moulding for this purpose was used in the UK, but hot moulding techniques were used in the USA. However, glass fibre reinforced nylon and similar materials were finding increasing use in car construction. On the other hand, commercial vehicles provided a better outlet now and probably in the future in, e.g., hovercraft.

Shrinkage of polyesters need not be a problem if taken account of in design and formulation. Shrinkage in the plane of the laminate was insignificant, but across the thickness of the laminate it might cause distortion of flanges, etc.

The 23 people present had obviously found the lecture most stimulating and on behalf of those present Mr. R. A. Brown proposed a vote of thanks.

J. K. B. B.

OCCA 19

The technical review of OCCA 19, collated from reports by members, appeared in the May issue. In addition, the reporters were asked to state their general impressions of the technical advances shown at the exhibition, and the following article, giving a summary of these reports, has been prepared by Dr. V. T. Crowl and Mr. R. A. Brett.

This year's exhibition at Alexandra Palace attracted wide interest, especially from overseas, as shown by the larger number of overseas exhibitors, and the increasing number of visitors from abroad. Indeed, so international has the Exhibition become that at least one company was demonstrating the properties of resins which would only be available on Scandinavian markets. No single main theme was dominant this year, such as electrodeposition or thermosetting acrylics had been at previous Exhibitions. There were, however, a number of very interesting products on show, which may well indicate the path of future trends.

In the resin field, this was the first year that commercially available oil free alkyds were shown, and there was evidence that this type of material, used in conjunction with a methylated melamine resin, may become of major importance, particularly for coil coating. It was noted that only overseas resin manufacturers featured these materials but one assumes that UK producers are well aware of developments in this field.

Although a number of modified versions of polymer emulsions were on show, the most interesting development was the production of vinyl acetate-ethylene copolymer emulsions by a new technique in which the ethylene was introduced as grafted side chains. The resulting improvement in scrub resistance was most impressive, particularly at high pigment volume concentrations.

In contrast to recent years, resin manufacturers did not place the same importance on the technicalities of electrodeposition application with the exception of one exhibitor who demonstrated a continuous strip apparatus for assessing tank stability. The growing acceptance of the electrodeposition technique was, however, emphasised by the increasing number of water dispersible resins declared suitable for this type of application, including many designed specifically for this purpose. Of particular interest were resins capable of withstanding high voltage application.

Thermosetting acrylics did not appear to achieve the prominence shown in recent years at the exhibition although many resin manufacturers are now entering this field for the first time. One important point, however, was the suggestion that the problem of repairing car bodies coated with acrylic finishes had now been overcome by the use of acid catalysed systems.

In the conventional alkyd field, emphasis was placed on products having improved colour retention for decorative finishes, special consideration being given to the coating of radiators with white or pale coloured paints. New products shown included a range of acrylated types, urethane modified alkyds and a variety of very short oil alkyds suitable for fast air drying industrial finishes. Further developments in the use of alkyds as components of powder coatings were noted.

There were many developments in pigments. Several new grades of titanium dioxides were on show, including some developed especially for water based emulsion paints. The continuing developments in this particular field are to be commended, even though the task of the user in selecting from the many competitive grades is made more difficult.

Improved dispersibility was in fact the main theme of the pigment exhibits, and, following the example of one exhibitor at the previous exhibition, there were several more new easily dispersible grades of organic pigments, designed for either paint or printing ink applications. This appears to be a main development in the gradual progress towards high speed methods of paint and ink manufacture.

Several new types or improved grades of organic pigments were on show, including a new dioxazine violet, a dibromoanthranone vat red, new arylamide yellow pigments, a new perylene red pigment, and several new grades of phthalocyanine blue, including one of the *epsilon* crystal form, now available commercially for the first time. In addition, there were several new pigments especially developed for printing inks. It is perhaps in this somewhat less spectacular way, of the development of a new grade of a particular pigment for a special purpose, that steady progress is maintained in the pigment field from year to year. Also of interest was the emphasis on the use of various pigments for polychromatic car body coatings, and of transparent hydrated iron oxide pigments as "gold pastes" for foil coatings.

In the protective coatings field, a very interesting technical display showed the use of electrodeposited zinc flake primers over which conventional top coats could be electrodeposited. The use of such pigments in heat resistant paints, and the development of zinc dust primers suitable for spot welding were also shown. Several displays featured technical information about the uses of extenders in paint formulations, and the development of water based primers pigmented with lithopone and anti-corrosive pigments was shown by one exhibitor. Another item was a display of results obtained in the use of zinc orthophosphate in anti-corrosive primers.

Another feature of this year's Exhibition was the prominence given to additives, such as wetting agents, dispersing agents, flotation control agents, anti-settling agents, bodying agents, anti-gelling agents, anti-foaming agents and the like, many of them designed for specific types of system. In fact, you name it, we've got it. Among the more unusual products of this type were various combinations of light-fast coloured pigments designed to increase the effective hiding power or to mask the yellowing of white gloss paints, and the use of a molecular sieve to adsorb water in zinc rich primers and prevent gas build up.

Perhaps one of the most interesting features this year was the spread of the coatings industry into the traditional building materials field, as shown by the development of polyurethane and emulsion based flooring compositions, resin-bonded plasters, and textured masonry finishes. An interesting suggestion was the use of acrylic fibres for texturing and reinforcing surface coatings and plasters. The break-through of paint-like products as textured and multicoloured finishes is probably essential if really long-life decorative treatments are to be acceptable.

Improved versions of various laboratory instruments were shown, together with some new developments or production models of apparatus previously announced. The display of manufacturing equipment included several new types of dispersion mills, including a continuous vibro-energy mill, and a new type of rotary mill designed for gravure and flexographic ink production. Many of the pieces of equipment from the continent were equipped with labour saving devices such as hydraulic lifts, and were well instrumented. Several items of filling equipment were on show, including an automatic rotary aerosol pack filler.

The President, Dr. S. H. Bell, with Mr. H. Meyer (left) President of the SLF, during Dr. Bell's Scandinavian tour

President visits Scandinavia

In April, at the invitation of the Federation of Scandinavian Paint and Varnish Technicians (SLF), the President, Dr. S. H. Bell, made a tour of the Scandinavian countries, when he lectured on the work of the Paint Research Station of which he is Deputy Director. The SLF was particularly pleased that Dr. Bell was able to make this tour during his term of office as President of the Association.

Lectures were delivered to all groups of the Federation, at centres in Bergen, Oslo, Gothenberg, Copenhagen, Malmo, Stockholm and Helsinki, and were very well received.

In the course of the tour Dr. Bell was able to discuss OCCA activities and other matters of mutual interest with Officers of the Scandinavian Federation.

Newcastle Section

The annual Ladies' Night of the Newcastle Section was held at the Five Bridges Hotel, Gateshead, on Friday, 24 February. Guests of honour were the President, Dr. S. H. Bell, and Dr. and Mrs. A. I. Escolme. Dr. Escolme has been a very active member of the Section since its foundation, was Chairman in 1953 and 1954, and has been a Vice-President of the Association. He retires this year. Other principal guests included Mr. N. Cochrane (Chairman, West Riding), Mr. C. H. Morris (Chairman, Midlands), Mr. R. J. Woodbridge (Chairman, Bristol), and Mr. D. Findlay (Chairman, National Federation of Master Painters and Decorators—Newcastle Section) with their ladies.

A group from the Newcastle Section Ladies' Night. (Left to right): Mrs. Escolme, Dr. A. I. Escolme, Dr. S. H. Bell (President), Mrs. Farrow, Mr. E. L. Farrow (Chairman, Newcastle Section)

Scottish Section

Annual General Meeting and Smoking Concert

The Annual General Meeting of the Scottish Section was held on Friday, 7 April, in the Lorne Hotel, Sauchiehall Street, Glasgow. The Chairman, Mr. I. S. Hutchison, expressed the thanks of the section to the retiring Office Bearers and Committee Members whose efforts had done so much to make the past season a most successful one.

Office Bearers and Committee Members for 1967/68 were appointed as follows :

Chairman :
I. S. Hutchison

Immediate Past Chairman :
Dr. D. Atherton

Vice-Chairman :
J. Miller

Hon. Secretary :
E. M. Burns

Hon. Treasurer :
T. B. Hannah

Representative on Council :
A. S. Fraser

Hon. Publication Officer :
Dr. J. D. Easton

Hon. Education Officer :
A. McLean

Hon. Programme Officer :
R. G. Gardiner

Hon. Research Liaison Officer :
D. Rowley

Hon. Junior Section Liaison Officer :
P. Birrell

Committee :
Messrs. B. G. Anderson, C. S. MacLean, H. A. Munro, W. Peden, A. Pisacane, A. H. Smith.

After the meeting members and guests withdrew to the Eglinton Arms Hotel, Eaglesham, for the traditional Smoking Concert. A pleasant meal was enjoyed and with Mr. Miller as genial compère the evening ran its usual course of gaiety and good fellowship.

Entertainment with a professional touch was provided by Forbes Whitelock and Glen Arneil and by George Fleming, who is a member of Eastern Branch. Amateur, but by no means amateurish, contributions from our own members completed the bill.

West Riding Section

Annual General Meeting

At the 15th Annual General Meeting of the West Riding Section of the Oil and Colour Chemists' Association, held on Tuesday, 11 April 1967, at 7.30 p.m., in the Great Northern Hotel, Leeds, the following Officers and Committee Members for the session 1967/68 were elected :

Chairman :
L. H. Silver

Vice-Chairman and Representative on Council :
Dr. L. J. Watkinson

Hon. Secretary :
D. Morris

Hon. Treasurer :
T. R. Smith

Hon. Publications Officer :
J. N. McKean

Social Secretary :
D. Young

Hon. Auditor :
Dr. K. Hargreaves

Committee :
Mrs. K. Driver, Messrs. J. R. Groome, M. J. Cochrane, D. Gray, and D. Morris.

The retiring Chairman, Mr. N. Cochrane, in his remarks commented upon the success of the section's first symposium on Dispersion and how it had encouraged the committee to organise a more ambitious function with which to open the forthcoming session. This will be a full day Symposium on Additives—full title to be announced later—and it is hoped that this controversial subject will draw a good attendance from the many branches of the surface coatings industry.

After the formal business of the evening the members were joined by their ladies and other guests to enjoy a pleasant buffet supper.

News of members

Dr. P. M. Troll, an Ordinary Member attached to the London Section, has returned to Frankfurt to take up a senior appointment in the Application Department of Farbwerke Hoechst AG. Dr. Troll was previously a member of the board of Hoechst Chemicals Limited and of Harlow Chemical Co. Ltd.

Mr. R. L. Gironimo, an Ordinary Member attached to the Midlands Section, and Chairman of the Midlands Section of the Paintmakers Association, has become Managing Director of A. Learner and Co. Ltd., while remaining on the board of Ault and Wiborg Limited, of whom A. Learner is a subsidiary.

Mr. J. G. Campbell, an Ordinary Member, has recently returned to the Scottish Section, following his appointment as Director Designate of Charles Tennant and Co. Ltd., in Glasgow.

Mr. P. F. Bridle, an Ordinary Member attached to the London Section, has been appointed Managing Director of

Ferguson and Menzies Ltd., relinquishing his position as Sales Manager of the Surface Coating Paint Division of Hercules Powder Company.

Mr. Bridle has been a member of OCCA since 1948, and contributed to Volume Two of the Paint Technology Manuals.

Mr. F. Sowerbutts, the President Designate, has relinquished his duties as Secretary of the Surface Coating Synthetic Resin Manufacturers Association, owing to pressure of future commitments. The position will be filled by Mr. B. Rye.

The Chemical Society is to sponsor an International Symposium on Solution Properties of Natural Polymers from 25 to 28 July 1967, to be held in the Department of Chemistry, University of Edinburgh.

The 45th Annual Meeting of the Federation of Societies for Paint Technology is to be held at the Municipal Convention Hall, Minneapolis, USA, from 15-18 October, when the Joseph J. Mattiello Memorial Lecture, entitled " Particle Size as a Paint Formulating Parameter " will be delivered by Mr. Fred B. Stieg, Jr.

Obituary

J. C. Kingcome

We are sorry to report the death on 6 May of Mr. J. C. Kingcome, Chairman of the London Section, Southern Branch.

Mr. Kingcome was educated at Farnham Grammar School and King's College, London, joining the Dockyard Laboratory in Portsmouth a year after graduating in 1933. Employed by the Navy Department until his death, he was elected a Fellow of the Royal Institute of Chemistry in 1965. He served on many Navy Department, Inter-Service and British Standards committees, with particular interest in underwater corrosion and anti-fouling problems. An Ordinary Member of the Association since 1947, Mr. Kingcome was first Honorary Treasurer of Southern Branch of the London Section, serving in 1961, 1962 and 1963, Publications Secretary 1965-66, and Chairman 1966 up to the time of his death.

Mr. Kingcome is survived by his wife and two daughters, and mourned by many friends in the paint industry and beyond.

Register of Members

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

Ordinary Members

BULLOCK, ARTHUR GEOFFREY, B.SC., 22 Fenwick Avenue, Takapuna, New Zealand. (*Auckland*)

COMPSTON, RONALD DAVID, B.SC., Balm Paints (NZ) Ltd., PO Box 1009, Auckland, New Zealand. (*Auckland*)

EDWARDS, BRIAN DOUGLAS, D.I.C., 127 Crowley Street, Zillmere, Brisbane, Queensland, Australia. (*Queensland*)

EDWARDS, DAVID THOMAS ARCHIBALD, B.SC., Ciba Ltd., A.M.P. Chambers, Featherston Street, Wellington, C.1, New Zealand. (*Wellington*)

HACKNEY, THOMAS, 73A Hamilton Road, Hataitai, Wellington, New Zealand. (*Wellington*)

MARTIN, DAVID REDPATH, B.SC., Lime & Marble Ltd., Mapua, Nelson, New Zealand. *(Wellington)*

MILLS, KENNETH L., B.SC., Balm Paints (NZ) Ltd., PO Box 1009, Auckland, New Zealand. *(Auckland)*

MOORE, WILLIAM ALEXANDER, B.SC., 224A Greenlane Road, Epsom, Auckland, S.E.3, New Zealand. *(Auckland)*

NESS, ROBERT ALEXANDER, B.SC., 122 Tinakori Road, Wellington, New Zealand. *(Wellington)*

STEYN, JAN MICHAEL, ICI (SA) Ltd., PO Box 11270, Johannesburg, South Africa. *(South African)*

USHER, ROBERT WARREN, c/o Ushers Paints, 374 Newman Road, Geebung, Australia. *(Queensland)*

Associate Members

BECKER, LOU, Worldwide Camps Pty. Ltd., Barfield Crescent, Elizabeth West, South Australia. *(South Australian)*

JOHNSON, ROBERT DAVID, 255 Mt. Smart Road, Onehunga, Auckland, New Zealand. *(Auckland)*

MAHER, MICHAEL CHARLES, 170 Daniell Street, Wellington, New Zealand. *(Wellington)*

PARSONS, ALAN GEORGE, ICI (SA) Ltd., PO Box 11270, Johannesburg, South Africa. *(South African)*

SMITH, DONALD FRASER, c/o ICI (SA) Ltd., PO Box 7796, Johannesburg, South Africa. *(South African)*

TESTI, JOHN HALTON, Gollin & Co. Ltd., 14 Stephens Place, Adelaide, South Australia. *(South Australian)*

Junior Members

GREY, COLIN ALBERT, 15 Duffy Street, Essendon, Victoria, Australia. *(Victorian)*

HOMAN, WILLIAM BARRY, Berger Paints Ltd., 938 South Road, Edwardstown, South Australia. *(South Australian)*

MARRIOTT, ROGER MITCHELL, 290 Newman Road, Geebung, Australia. *(Queensland)*

STRASSBURG, PETER JOHN, c/o G. C. Shave Ltd., 122 Bluff Road, Jacobs, Durban, South Africa. *(South African)*

TURNBULL, RODERICK BRYAN, 160 Cowey Road, Durban, South Africa. *(South African)*

Forthcoming Events

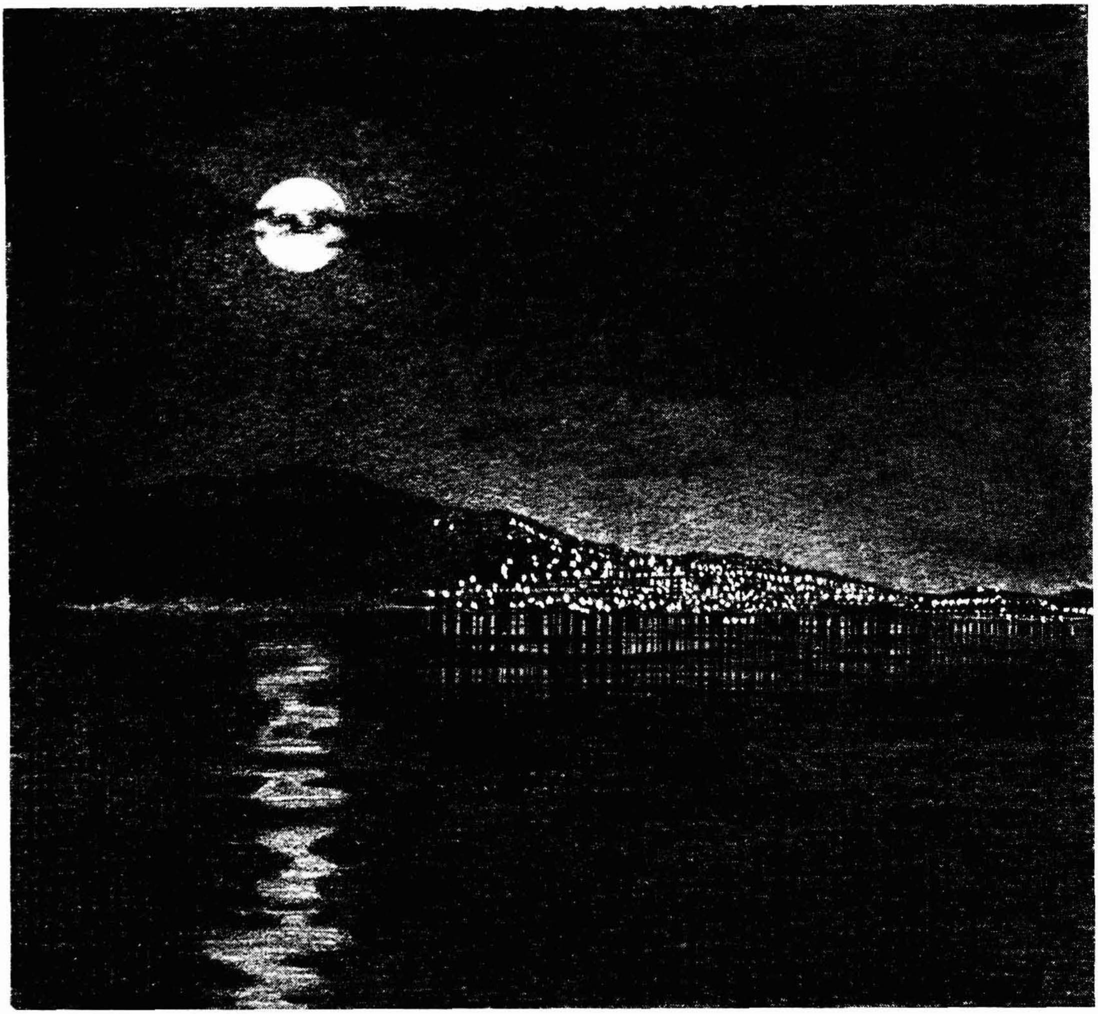
Details are given of meetings in the United Kingdom up to the end of the month following publication, and in South Africa and the Commonwealth up to the end of the second month.

Thursday 15 June

New South Wales Section. Factory Inspection—to be arranged.

Tuesday 20 to Saturday 24 June

Association Biennial Conference. To be held at Grand Hotel, Scarborough.



CLASSIFIED ADVERTISEMENTS

Classified Advertisements are charged at the rate of 9s. per line. Advertisements for Situations Wanted are charged at 2s. 6d. per line. A box number is charged at 1s. 0d. They should be sent to the General Secretary, Oil & Colour Chemists' Association, Wax Chandlers' Hall, Gresham Street, London, E.C.2. Telephone: Monarch 1439

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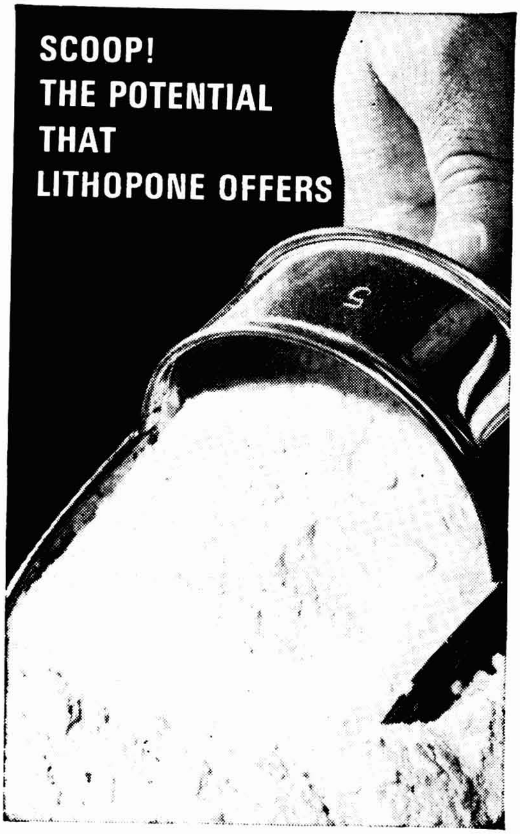

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