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Composition and fractionation of tall oil

Size analysis of organic pigments using the ICI-Joyce Loebl disc centrifuge

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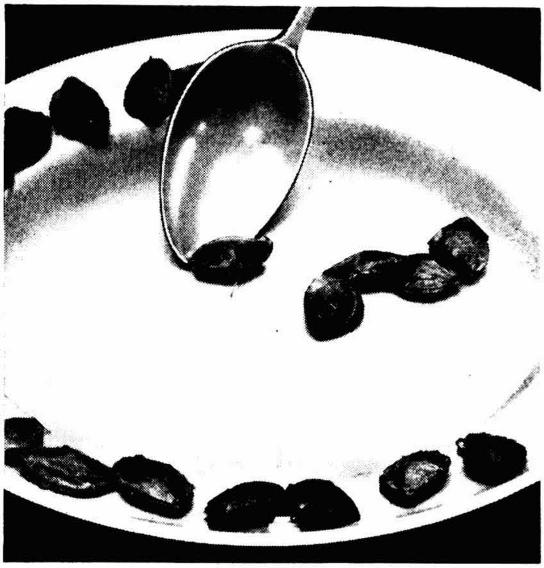

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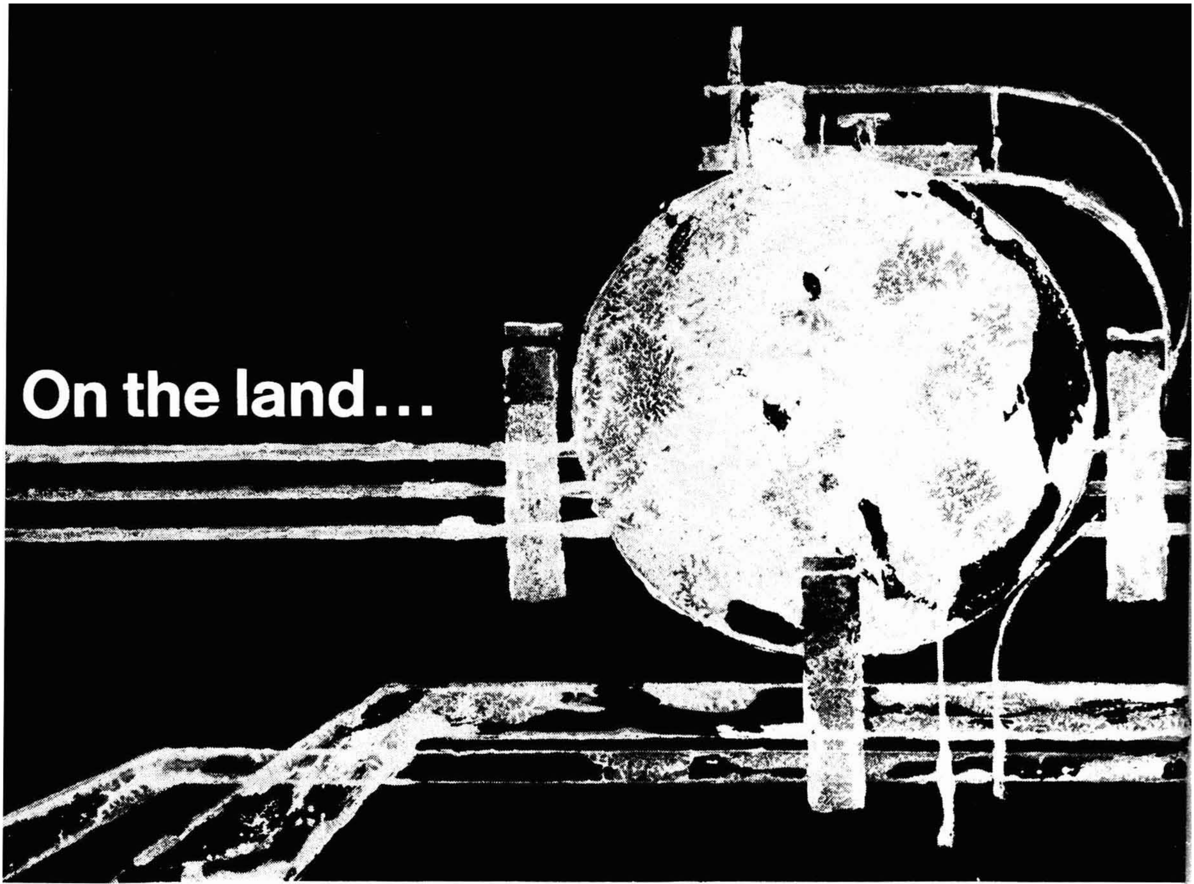
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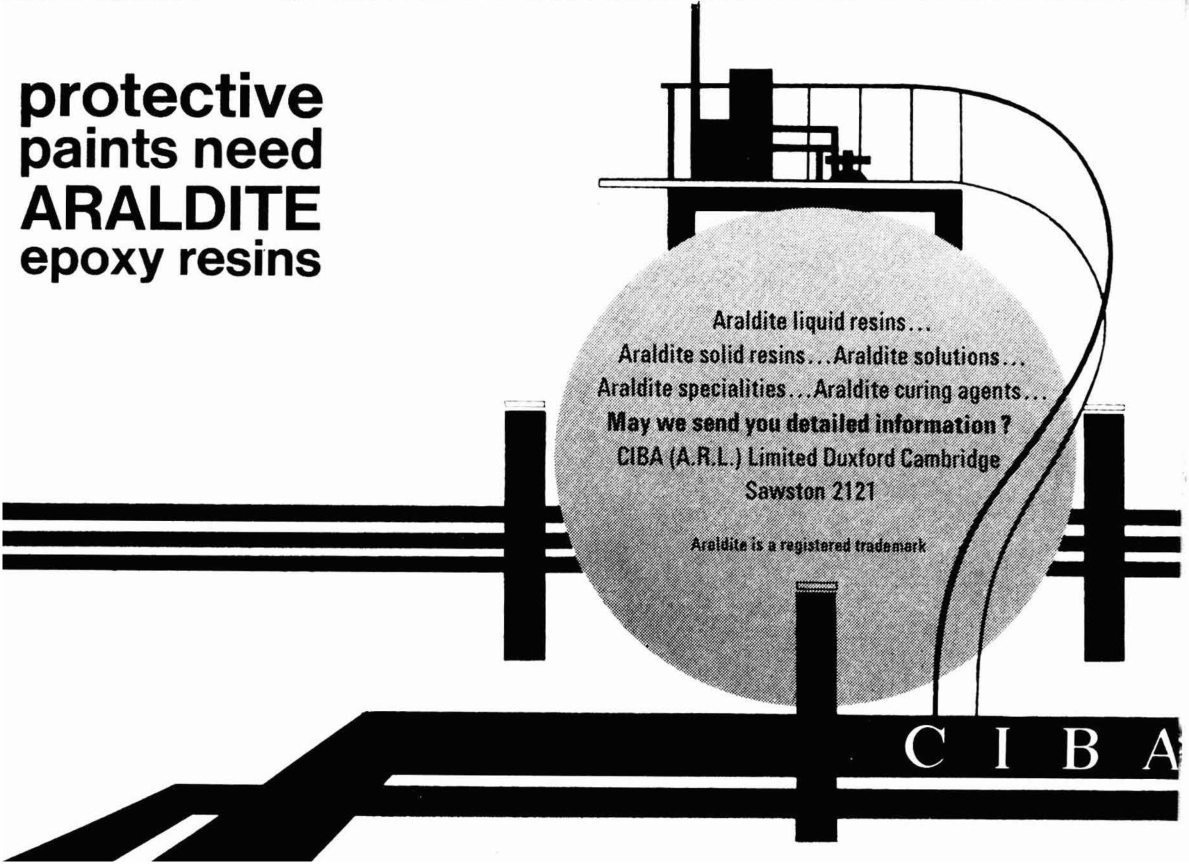

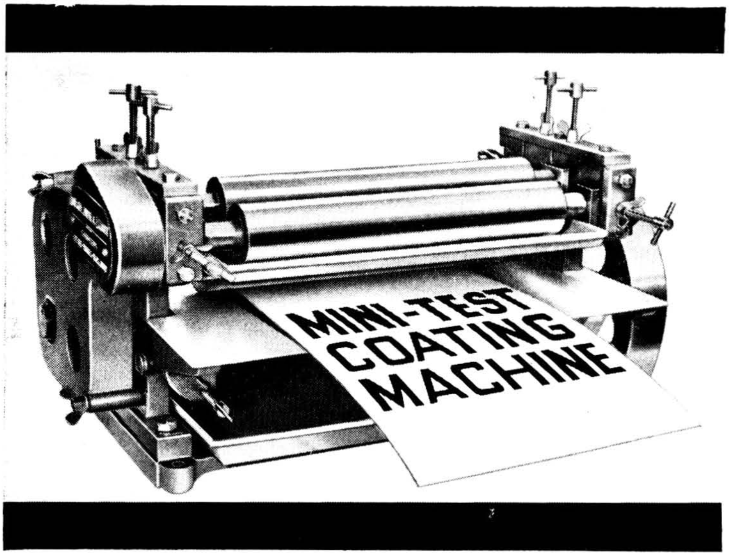

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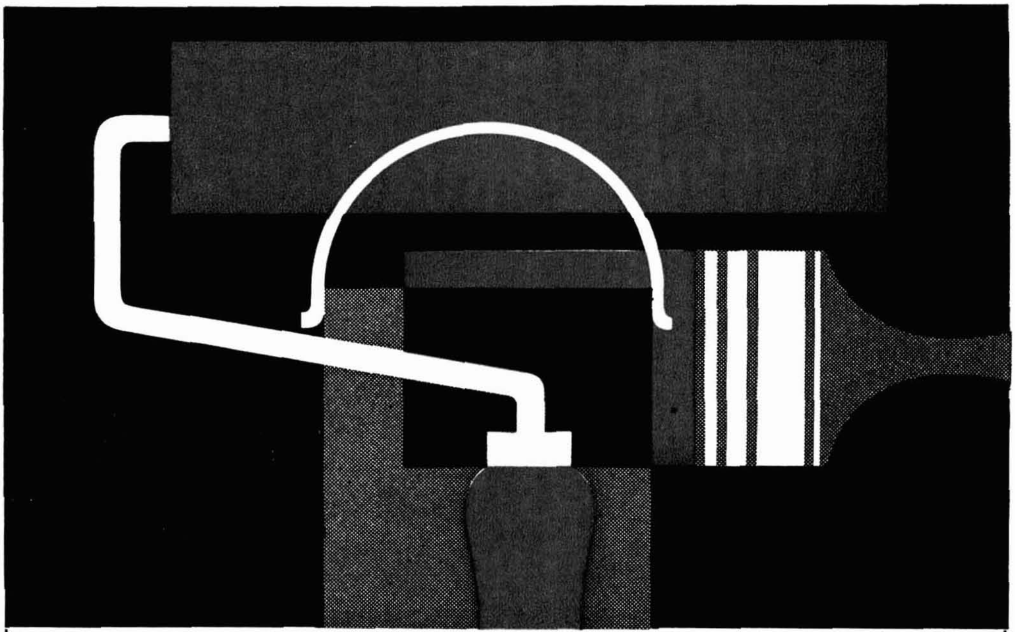

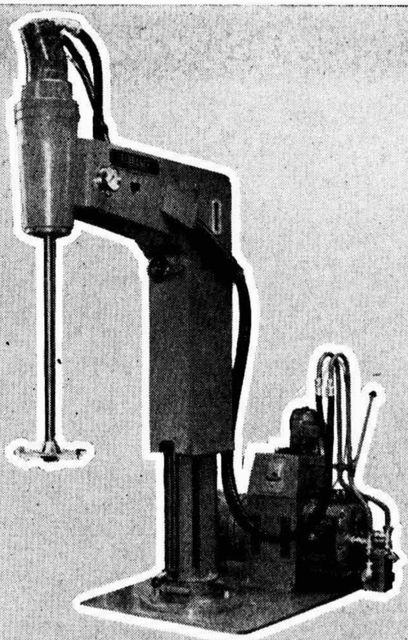

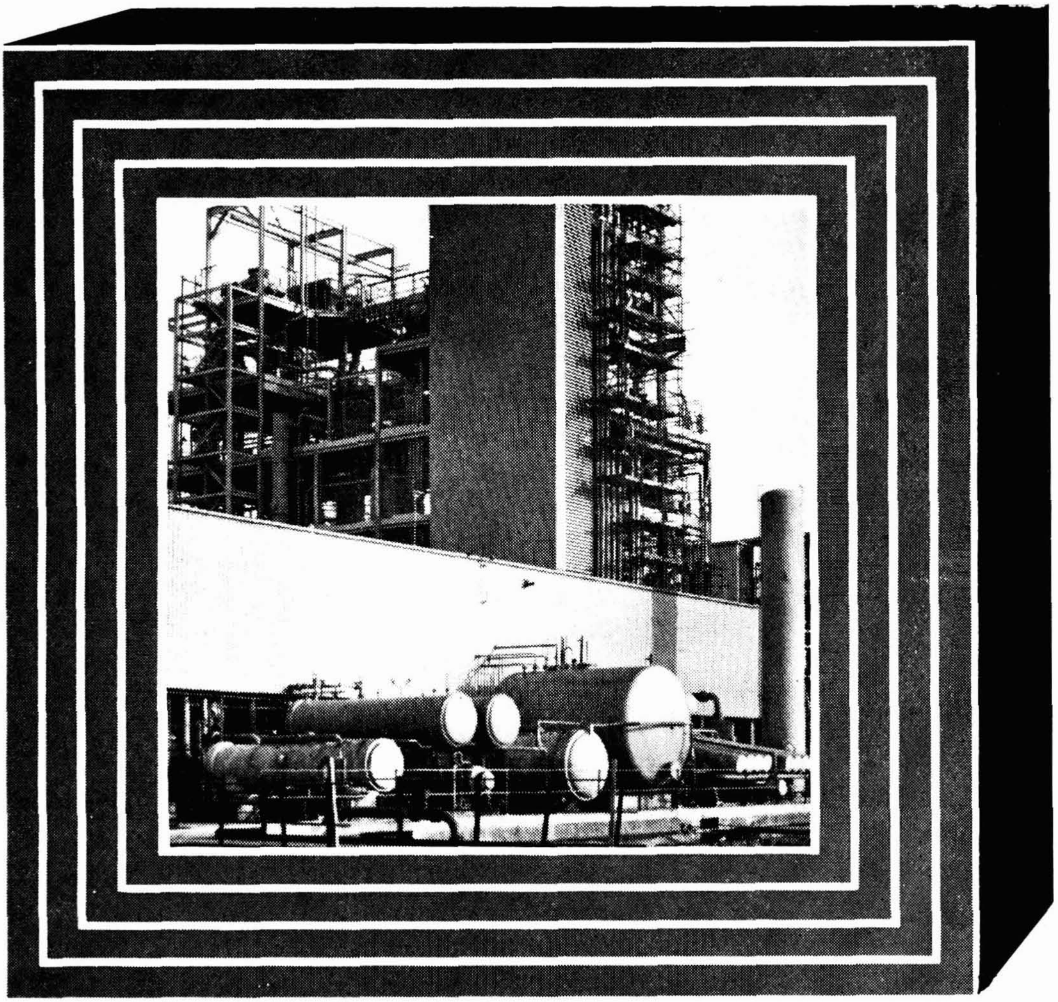

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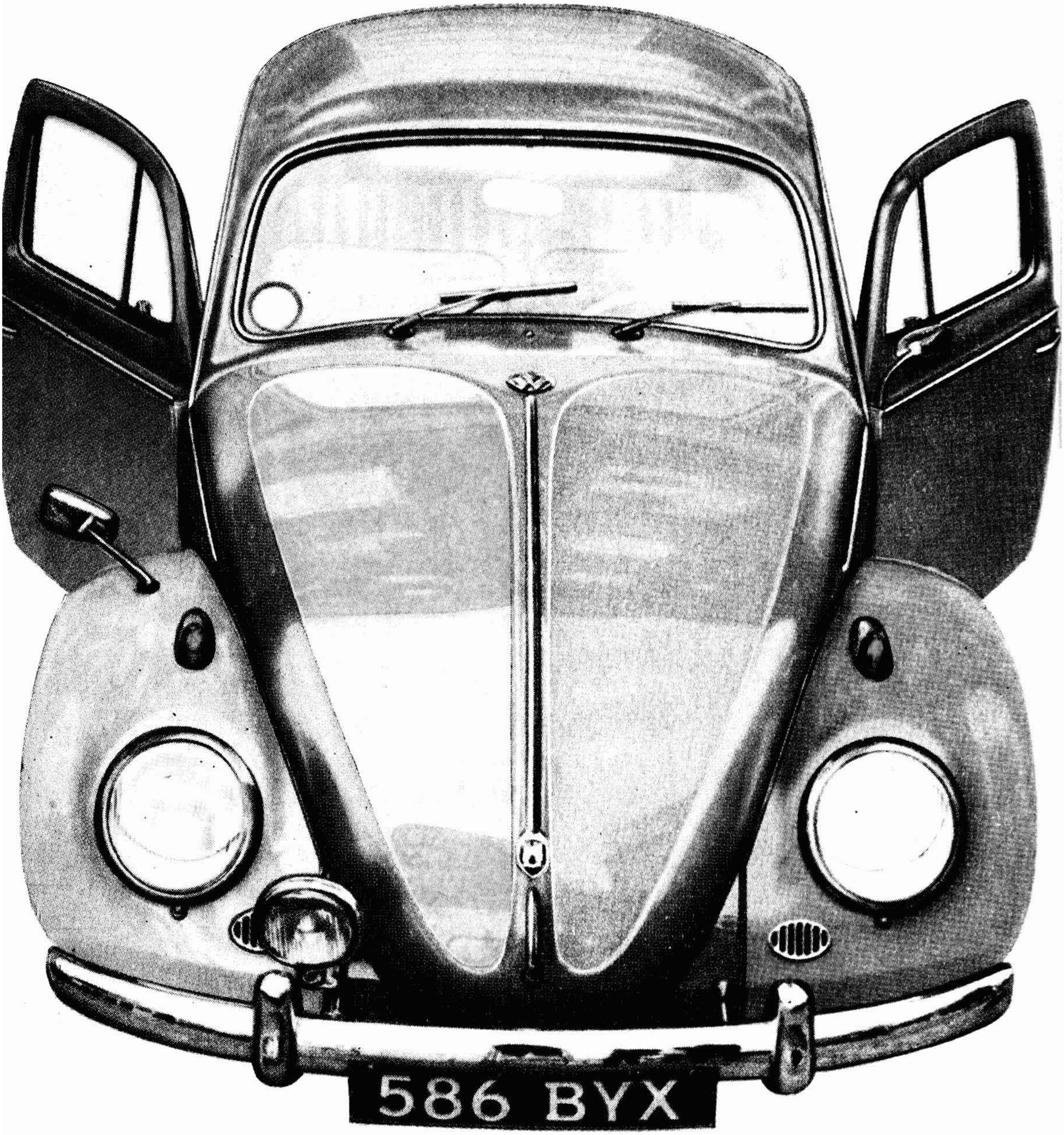

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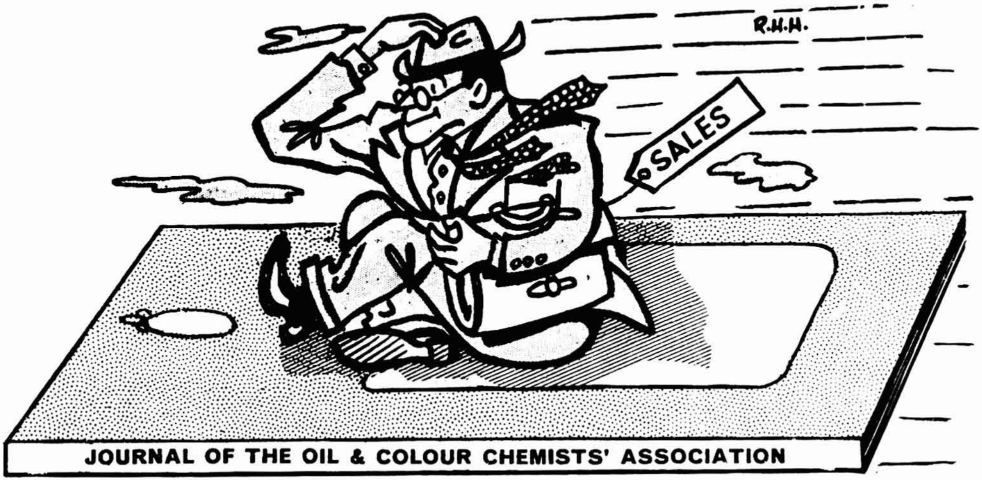

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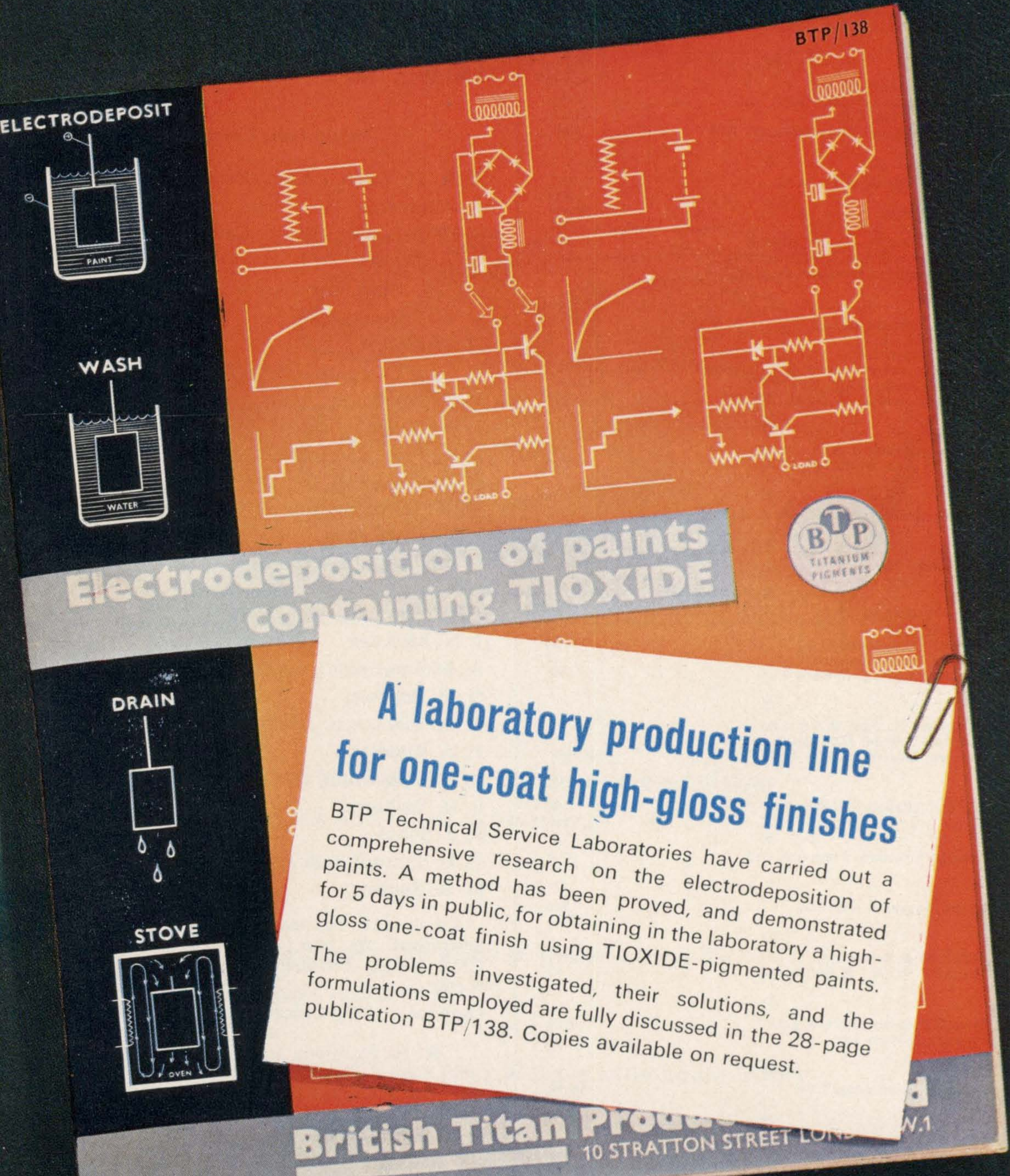
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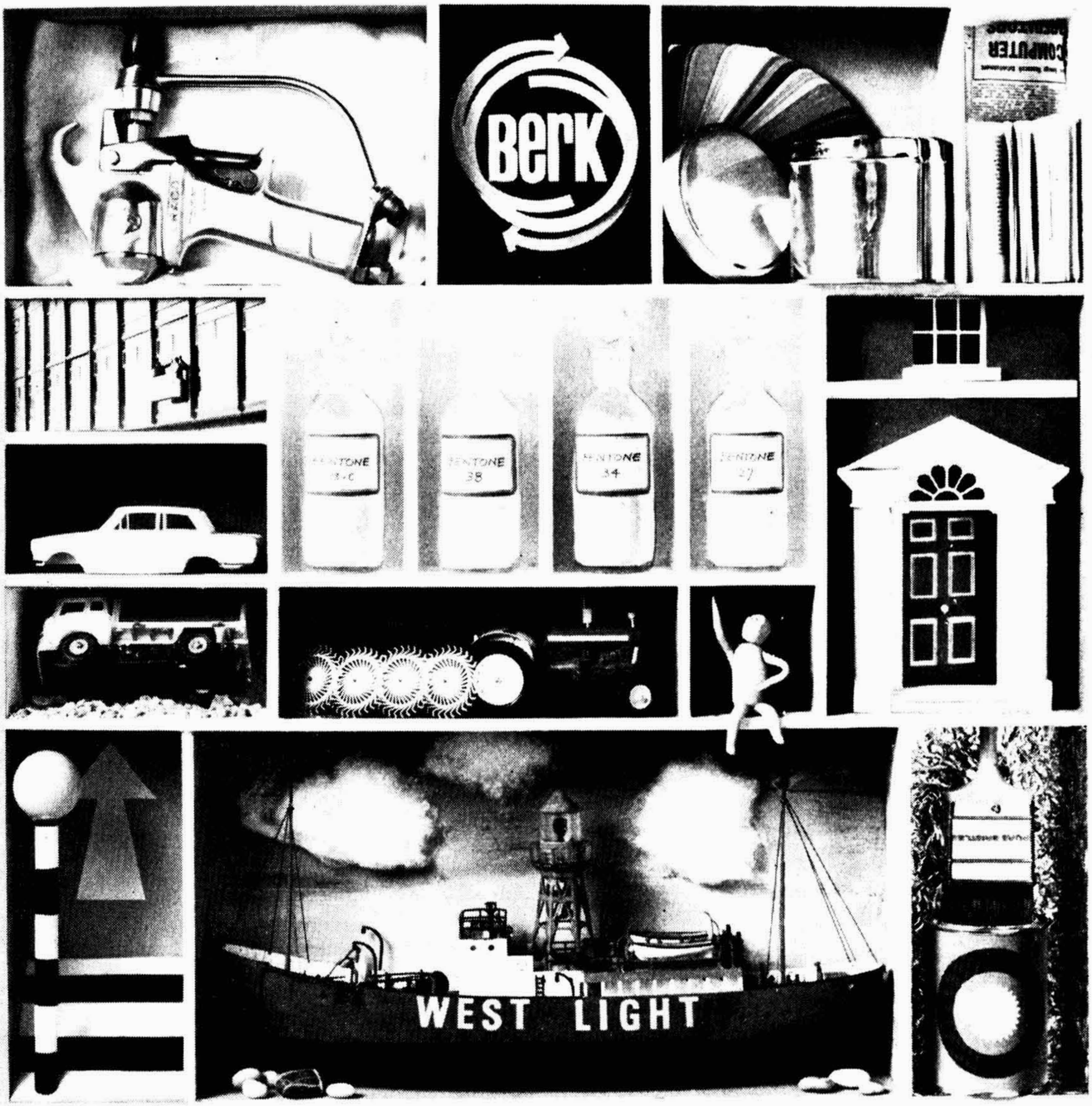
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Transactions and Communications

Composition and fractionation of tall oil*

By K. S. Ennor and J. Oxley

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

Summary

Crude tall oil, a by-product of the sulphate paper process, is fractionated into tall oil fatty acids, distilled tall oil, rosin, mixed saturated and unsaturated fatty acids, heads and pitch. The fatty acids are composed mainly of oleic and linoleic acids, whereas the rosin contains mainly abietic and dehydroabietic acids. Distilled tall oil is a mixture of fatty acids and rosin. Tall oil heads are of two types containing both saturated and unsaturated fatty acids with a large proportion of light unsaponifiables. Pitch contains mainly sterols, higher alcohols, esters and rosin.

The process employs two columns which are operated under vacuum/steam fractionation conditions using a three-pass blocked system. Each pass produces a number of finished products, and intermediates from each pass become feeds for subsequent passes. An outline of the process is given together with a discussion of the function of the two columns.

Composition et fractionnement de tall oil

Résumé

Tall oil brut, un sous-produit de la fabrication de papier par le procédé-sulfate, se fractionne vers les acides gras de tall oil, tall oil distillé, colophane, des acides gras mixtes saturés et non saturés, des têtes et du brai. Les acides gras sont composés largement des acides oléique et linoléique, tandis que la colophane contient principalement les acides abiétique et déshydroabiétique. Tall oil distillé est un mélange des acides gras et du colophane. Les têtes de tall oil sont de deux types contenant à la fois des acides gras saturés et non saturés avec une teneur importante de matière légère insaponifiable. Le brai contient notamment des stérols, alcools supérieurs, esters et colophane.

Dans le procédé on emploi deux colonnes de fractionnement sous des conditions de vide/vapeur pour effectuer une cycle de trois passes autour d'un système fermé. Pendant chaque passe un certain nombre de produits commerciaux sont formés, et les intermédiares à partir de chaque passe deviennent les matières alimentaires pour les passes suivantes. On trace les grandes lignes du procédé et également on discute la mode d'action des deux colonnes.

Zusammensetzung und Fraktionierung von Tallöl

Zusammenfassung

Rohes Tallöl, ein Beiprodukt der Sulfitzellulosefabrikation, wird fraktioniert, sodass es in Tallölfettsäuren, destilliertes Tallöl, Harz, gemischte, gesättigte und ungesättigte Fettsäuren, Vorlauf und Pech aufgespalten wird. Die Fettsäuren bestehen hauptsächlich aus Ölsäuren und Linolsäure, während Kolophonium hauptsächlich Abietin- und Hydroabietinsäure enthält. Destilliertes Tallöl ist eine Mischung von Fettsäuren und Harz. Der Tallölvorlauf besteht aus zwei Arten, die beide gesättigte und ungesättigte Fettsäuren mit einem hohen Prozentsatz von leichten, unverseifbaren Stoffen enthalten. Das Pech besteht vor allem aus Sterol, höheren Alkoholen, Estern und Harz.

Das Verfahren arbeitet mit zwei Destillationskolonnen mit reduziertem Dampfdruck (Vacuum) unter den üblichen Arbeitsbedingungen. Man benutzt ein 3 Wege- (blocked)

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*Presented to the Eastern Branch, Scottish Section, on 26 October 1966 and to the Hull Section on 5 December 1966.

System. Mit jedem Rektifikationsgang wird eine Anzahl von Endprodukten gewonnen, und Zwischenprodukte aus jedem Durchgang dienen als Charge für die folgenden Operationen. Es wird ein Umriss des Herstellungsverfahrens gegeben, und die Rolle der beiden Destillierkolonnen besprochen.

Состав и фракционирование таллового масла.

Резюме.

Сырое талловое масло, которое является побочным продуктом сульфатно-бумажного процесса, фракционируется в жирные кислоты таллового масла, дистиллированное талловое масло, канифоль, смешанные насыщенные и ненасыщенные жирные кислоты, концентраты и деготь. Жирные кислоты состоят главным образом из олеиновой и линолевой кислот, тогда как канифоль содержит преимущественно абиетиновую и дегидроабиетиновую кислоты. Дистиллированное талловое масло является смесью жирных кислот и канифоли. Существует два типа концентратов таллового масла, которые содержат насыщенные и ненасыщенные жирные кислоты с большой пропорцией легких неомыляемых веществ. Деготь содержит главным образом стерины, высшие спирты, эфиры и канифоль.

В процессе применяются две колонны, которые употребляются в условиях вакуумно-парового фракционирования, применяя трех-проходную блокировочную систему. Каждый проход производит ряд конечных продуктов, а промежуточные продукты каждого прохода служат питанием для последующих проходов. Дается краткое описание процесса с обсуждением действия обеих колонн.

Introduction

Crude tall oil, composed mainly of fatty acids and rosin, is the world's cheapest source of organic acids. It is obtained as a by-product in the manufacture of pulp by the sulphate or kraft process which was introduced a century ago. In 1905 crude tall oil was isolated in Sweden where it was named " tallolja" which means pine oil. The term tall oil was introduced to avoid confusion with pine oil which is composed chiefly of alpha-terpineol. Soon after 1930 partially purified tall oil became available on a commercial scale. The product was distilled tall oil, that is a mixture of fatty acids and rosin, and the rosin content was 20 to 35 per cent. This type of product was in demand as a substitute for linseed oil during World War II. Since that time tremendous improvements have been achieved in fractionating methods. The first effective separation of tall oil fatty acids and rosin was made in 1949 by the Arizona Chemical Company, a joint venture of American Cyanamid and International Paper. The tall oil fatty acids contained less than 2 per cent of rosin, and the rosin contained less than 3 per cent of fatty acids. At present, tall oil fatty acids can be manufactured with rosin contents as low as 0.3 per cent, but for most applications it is unnecessary to reduce the rosin below 1 to 1.5 per cent.

The shortage of drying oils during World War II encouraged the development of the tall oil industry, especially in the United States. The world production of crude tall oil now amounts to about 750,000 tons per annum and most of this is purified in the United States. Tall oil enjoys a much more stable source of supply than vegetable oils which depend upon agricultural conditions and varying crop yields. Thus tall oil products show more consistent prices than crop oils.

Source of tall oil

The sulphate process is the principal method employed to separate the cellulose fibres in wood. In this process wood chips, generally from pine wood, are digested under pressure with aqueous sodium hydroxide and sodium sulphide. Fatty acids, rosin acids and lignin are dissolved as sodium salts and the fats are saponified, which liberates the cellulose for making pulp.

The alkaline washings from the pulp are termed "black liquor" which is partially evaporated so that the sodium salts of tall oil fatty acids and rosin separate as a brown curd called " black liquor soap." This product is skimmed off and treated with sulphuric acid to liberate the crude tall oil which floats to the top.

The composition of crude tall oil varies widely and depends upon the species of pine wood, the climatic conditions experienced in different localities, and the treatment of the logs before being pulped[1]. In Scandinavia and Finland, Scots pine is mostly used in the pulp industry, whereas in the United States a much larger number of pine wood species are employed. During seasoning of the wood, the yield of recoverable tall oil is reduced and the fatty acid content in the tall oil is lowered. Trees other than pine give reduced yields of tall oil with a high proportion of unsaponifiables (neutral material). Some typical properties of a crude tall oil from Northern Finland are as follows :

Fatty acids (as oleic)	46 per cent
Rosin acids	34 per cent
Unsaponifiables	12 per cent
Acid value	155 mg KOH/g
Saponification value	165 mg KOH/g
Ash value	0.03 per cent
Moisture	1.4 per cent

The ash arises from sodium sulphate and undecomposed soaps. Most of the dark coloured material in crude tall oil is insoluble in light petroleum, and this fraction is believed to be composed of oxy acids formed by autoxidation of fatty and rosin acids during seasoning of the wood and handling of the tall oil.

In crude tall oil the saponification value is always higher than the acid value. This difference is due to the presence of esters, lactones and estolides (esters of fatty acids with the hydroxy groups in oxidised fatty acids).

Composition of fractionated tall oil products

Vacuum fractionation is the most important way to purify tall oil, although in the United States sulphuric acid refined and solvent extracted tall oils are also produced.

The most valuable products of fractionated tall oil are tall oil fatty acids and rosin. The other products are distilled tall oil, intermediate heads, final heads, a mixture of saturated and unsaturated fatty acids, and pitch. The chemical compositions of these products will be considered first and then their isolation in the fractionation process will be discussed.

Tall oil fatty acids

Two of the commonest grades of tall oil fatty acids have rosin contents of approximately 1 per cent and 4 per cent and typical properties are shown in Table 1.

Table 1

Typical properties of tall oil fatty acids

	Type A	Type B
Fatty acids (as oleic), %	98.7	93.8
Rosin acids, %	0.8	3.6
Unsaponifiables, %	1.4	2.4
Acid value, mg KOH/g	198	193
Saponification value, mg KOH/g	199	194
Gardner colour	4+	5+
Titre, °C	−8	−9

The fatty acid content is calculated from the acid value, assuming that the average molecular weight is the same as that of oleic acid. The exact chemical composition of tall oil fatty acids is best revealed by gas-liquid chromatography of the methyl esters. Some results of this technique applied to tall oil fatty acids of Scandinavian and American origin are shown in Table 2, in comparison with soya fatty acids.

The main components of tall oil fatty acids are oleic acid and linoleic acid. The assignment of peaks to cis-5, 9-octadecadienoic acid[2] and to cis-5,9,12-octadecatrienoic acid[3] is based on the identification of these constituents in Finnish tall oil fatty acids. Both of these acids react like linoleic acid. Unlike soya fatty acids, tall oil fatty acids contain no linolenic acid. Alkyds based on tall oil fatty acids or soya bean oil show equivalent excellent durability and resistance to yellowing on outside exposure. Tall oil alkyds show less yellowing in the dark than comparable formulations based either on soya fatty acids or soya bean oil. Table 2 shows that tall oil fatty acids of Scandinavian origin contain about 54 per cent of acids with two or more carbon-carbon double bonds, whereas the American tall oil fatty acids contain about 40 per cent, and this is reflected in the higher iodine value of the Scandinavian acids. Alkyds based on Scandinavian tall oil fatty acids air dry significantly faster than similar formulations using American tall oil fatty acids.

Gas-liquid chromatography of the methyl esters indicates that in tall oil fatty acids containing less than about 4 per cent of rosin, the residual rosin has a composition different from that of fractionated tall oil rosin.

Tall oil fatty acids are used mainly in surface coatings, detergents, emulsifiers, ore flotation and in the manufacture of epoxidised esters used as plasticiser stabilisers for pvc.

Distilled tall oil

Mixtures of tall oil fatty acids and rosin containing less than 90 per cent of fatty acids are known as distilled tall oils (DTO). These are distinguished by

Table 2

Chemical compositions of fatty acids from tall oil and soya bean oil

Acid	Formula	Scan-dinavian tall oil fatty acids	American tall oil fatty acids	Soya fatty acids
Palmitic	$CH_3(CH_2)_{14}COOH$	0	2	11
Palmitoleic	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$	0.2	0	0
C 17 Monounsaturated		0.2	0	0
Stearic	$CH_3(CH_2)_{16}COOH$	1	2	4
Oleic	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	33	45	23
cis-5, 9-Octadecadienoic	$CH_3(CH_2)_7CH{=}CH(CH_2)_2CH{=}CH(CH_2)_3COOH$	1	3	0
Linoleic	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$	41	34	51
cis-5, 9, 12-Octadecatrienoic	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_2CH{=}CH(CH_2)_3COOH$	12	3	0
Linolenic	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$	0	0	10
Higher fatty acids	C 19, C 20, etc., saturated and unsaturated	11.6	11	1
		100%	100%	100%
Rosin acids, %		1.3	1.3	0
Iodine value, g I/g		155	130	140

their rosin contents which range from 10 to about 60 per cent and some typical properties are shown in Table 3.

Table 3

Typical properties of distilled tall oils

	D.30	D.45	D.55
Fatty acids (as oleic), %	62	46	36
Rosin acids, %	29	42	55
Unsaponifiables, %	3.9	3.6	3.0
Acid value, mg KOH/g	176	168	173
Saponification value, mg KOH/g ..	182	175	174
Gardner colour	11−	12+	11−

Distilled tall oil finds similar outlets to tall oil fatty acids, especially in those applications where rosin is required, for example, in certain urethane oils, and also in foundry core oils.

Rosin

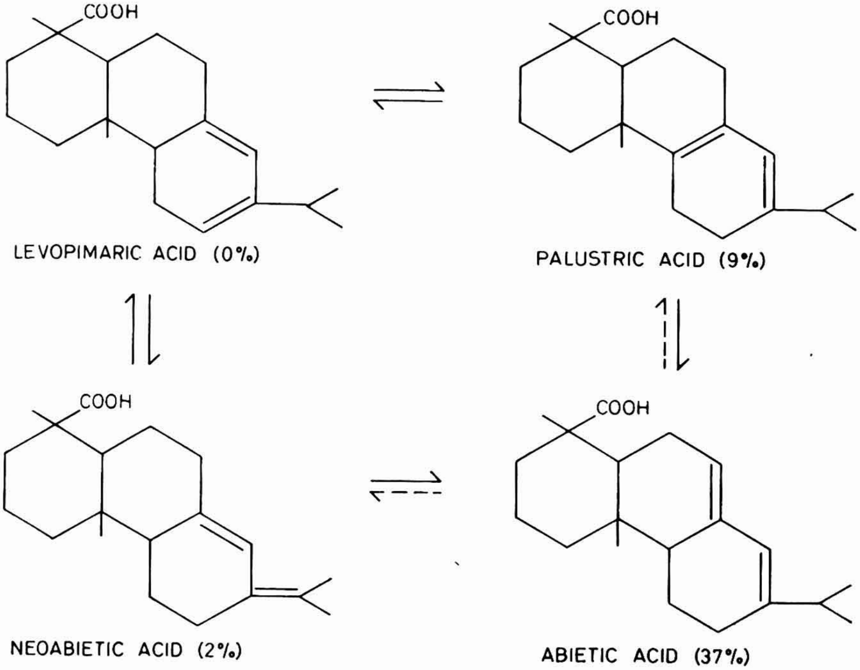
Tall oil rosin is a very pale straw coloured brittle solid with the following typical properties.

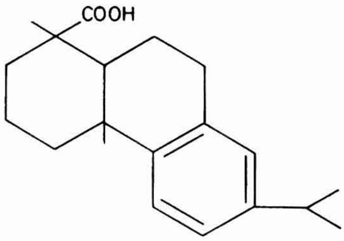
Fatty acids (as oleic)	3.0 per cent
Unsaponifiables	3.0 per cent
Acid value	163 mg KOH/g
Saponification value	172 mg KOH/g
USDA colour	WW
Ring and ball softening point	80°C

In addition to some fatty acids and unsaponifiables, tall oil rosin also contains anhydrides and esters, etc. Analysis of the methyl ester of rosin by a mass spectrometer[4] indicates abietic acid and dehydroabietic acid as the main components, as shown in Table 4. Among the components are palustric and neoabietic acids which both contain conjugated double bonds, but levopimaric acid is generally absent. When these individual acids, classed as abietic-type acids, are heated, their carboxyl groups effect an acid-catalysed isomerisation which gives an equilibrium mixture containing 95 per cent of abietic acid[5]. Pine wood contains significant proportions of each of the four abietic-type acids, but these are mainly converted into abietic acid during acidification of the " black liquor soap " and, again, during the high temperatures experienced in fractionation.

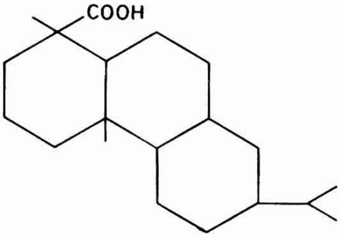
During this process, some disproportionation takes place to give dehydroabietic acid and small amounts of dihydro acids and tetrahydro acids as shown in Table 4. These acids and the pimaric type acids cannot interconvert and are much less easily oxidised than the abietic type acids.

Table 4
Chemical composition of tall oil rosin

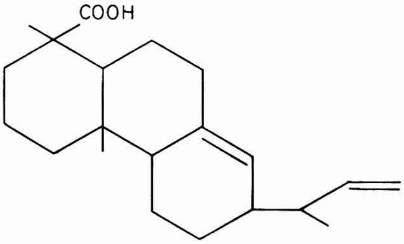




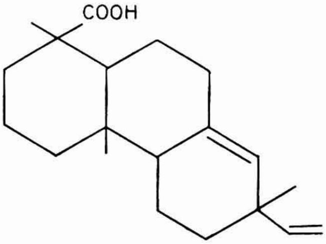
DEHYDROABIETIC ACID (23%)



TETRAHYDROABIETIC ACID (<1%)



PIMARIC ACID (3%)



ISOPIMARIC ACID (11%)

Other minor constituents are : Dihydroabietic acid (2%) Tetrahydropimaric acid (<1%) Dihydropimaric acid (<1%) Dihydroisopimaric acid (<1%) Dihydropalustric acid (2%)

Tall oil rosin, gum rosin and wood rosin are used in paper sizes, but consumption of tall oil rosin shows the most rapid growth. In the United States, 56,000 tons per annum of tall oil rosin are used in paper size which accounts for 44 per cent of the size market[6]. Tall oil rosin is also used in surface coatings and printing inks, linoleum, and as a tackifier in rubber and adhesives.

Tall oil heads and mixed saturated and unsaturated fatty acids

Two types of heads products are obtained—intermediate heads, and final heads, as well as a mixture of saturated and unsaturated fatty acids (SUFA). These more volatile components of tall oil have low rosin and high unsaponifiable contents as shown in Table 5.

Table 5

Typical properties of tall oil heads and SUFA

	Intermediate heads	Final heads	SUFA
Fatty acids (as oleic), %	68	20	74
Rosin acids, %	1.7	2.4	0.2
Unsaponifiables, %	32	72	27
Acid value, mg KOH/g	138	45	147
Saponification value, mg KOH/g ..	140	52	148
Gardner colour	15	16	12
Titre, °C	−1	−12	+23

Intermediate heads and SUFA are rich in fatty acids, but final heads are composed mainly of unsaponifiables. The neutral portion is mainly decarboxylated resin acids with some phenolic compounds[7]. The chemical compositions of the fatty acids in the heads products, determined by gas-liquid chromatography of the methyl esters, are shown in Table 6.

Table 6

Chemical compositions of the fatty acids in tall oil heads and mixed saturated and unsaturated fatty acids

Acid	Intermediate heads	Final heads	SUFA
Lower saturated	12	27	0.3
Palmitic	9	12	12
Palmitoleic	10	12	9
C 17 Saturated	0.1	0.1	4
C 17 Monounsaturated	0.1	0.1	5
Stearic	0.1	0.1	2
Oleic	26	15	19
cis-5, 9-Octadecadienoic	0.1	0.1	0.1
Linoleic	21	19	20
cis-5, 9, 12-Octadecatrienoic	8	8	8
Higher fatty acids	13.6	6.6	20.6
Total	100%	100%	100%

The fatty acids contain saturated fatty acids, notably palmitic acid, but the majority are unsaturated, with a similar distribution of acids as in the fractionated tall oil fatty acids shown in Table 2. Thus intermediate heads and SUFA are used in surface coatings, for example in non-drying alkyds, in emulsifiers, wetting agents and ore flotation. Final heads are used as a rubber processing aid.

Tall oil pitch

The pitch is the residue from tall oil fractionation and is a dark brown fluid with the following properties.

Fatty acids (as oleic)	7 per cent
Rosin acids	22 per cent
Unsaponifiables	33 per cent
Acid value	55 mg KOH/g
Saponification value	102 mg KOH/g
Hydroxyl value	36 mg KOH/g

The unsaponifiables, unlike the neutral fractions in tall oil heads, are composed of sterols and higher alcohols, especially beta-sitosterol and lignoceryl alcohol $C_{24}H_{49}OH$. A large proportion of pitch is composed of esters of either beta-sitosterol or lignoceryl alcohol with fatty acids or rosin acids. Other products are oxidised fatty and rosin acids, sulphur lignin, rosin and fatty acids. The rosin enables pitch to react with slaked lime to give hardened pitches used in floor tiles and in automobile undersealing. Unmodified pitch is used in rubber reclaiming and as a processing aid in rubber compounding.

Tall oil fractionation in the United Kingdom

In Europe, fractionation is the only technique of commercial importance for separating the constituents of crude tall oil. The first fractionation unit in the United Kingdom was designed by Foster Wheeler and constructed at Chester-le-Street, Co. Durham, during 1965.

The main physical properties which have to be catered for are :

(1) Crude tall oil is a semi-solid at room temperature so that it must be handled at 50-70°C in order to keep it liquid.

(2) Crude tall oil is corrosive due to :

  (a) traces of residual sulphuric acid from the crude tall oil (CTO) production process, and

  (b) the fatty acid and rosin.

Construction materials are stainless steel or aluminium.

(3) The unsaturated fatty acids in tall oil start to decompose above 260°C. At this temperature the average vapour pressure is about 25 mm Hg. This means that the separations are best performed under vacuum/steam distillation conditions.

Volatility of tall oil constituents

The constituents of crude tall oil in order of decreasing volatility are as follows :—

light unsaponifiables ; saturated fatty acids ; unsaturated fatty acids ;
rosin ; esters ; heavy unsaponifiables.

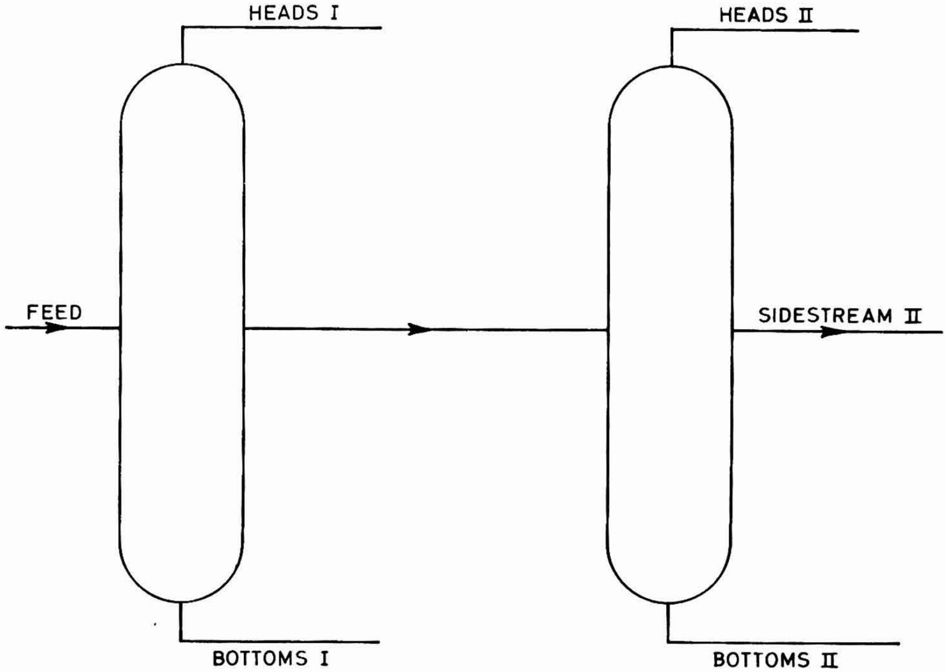
The light unsaponifiables are extracted as a final heads fraction. Saturated fatty acids are extracted as a fraction in which their concentration is about

10-40 per cent. Unsaturated fatty acids and rosin are extracted in separate named fractions while esters and heavy unsaponifiables are extracted together in the form of pitch.

Each fraction is contaminated by those above and below it on the volatility scale and it is normal to process to specification limits of contaminants in most fractions.

3 Pass blocked system

The fractionation unit has a capacity of 12,000 tons per annum of crude tall oil and is operated on a 3 pass blocked system. The reason for this is that a continuous plant would require six fractionating columns of expensive con-



Stream	Pass I	Pass II	Pass III
Feed	CTO	3rd pass UFA+ crude fatty acid	Intermediate heads
Heads I	Intermediate heads	Intermediate heads	Final heads
Heads II	Intermediate heads	Intermediate heads	Intermediate heads
Sidestream II	Crude fatty acid	UFA	SUFA
Bottoms I	Pitch	Pitch	Pitch
Bottoms II	Rosin	DTO	3rd pass UFA

Fig. 1. Three pass blocked system used for tall oil fractionation

structional materials resulting in high capital costs. The blocked system has been introduced to give the benefits of multicolumn fractionation whilst only installing two columns. Six column fractionation is achieved by operating three passes. Fig. 1 shows an outline of the 3 pass system.

In pass 1, CTO is the feed to the plant. The two finished products are pitch and rosin from the bottom of columns I and II respectively. The heads from both columns are the intermediate heads. The sidestream from column II is crude fatty acid (CFA) which is the main source of the unsaturated fatty acid (UFA) production in the second pass.

In pass II, CFA from pass I and a crude unsaturated fatty acid from a previous pass III are the feed. The finished products are distilled tall oil (DTO) and the main UFA product, which come from the base and sidestream of column II respectively.

The very small pitch cut from column I is recycled with CTO in pass I. Both heads streams are combined with the heads from pass I and a previous pass III to become the feed for the third pass. This pass produces the following two finished products.

(1) Final heads which contain most of the light unsaponifiables and

(2) Mixed saturated and unsaturated fatty acids (SUFA) which contain most of the saturated fatty acids.

Final heads are taken from the top of column I and SUFA is the column II sidestream. Once again, the pitch is recycled to pass I with CTO. Column II bottoms, that is third pass UFA, is worked up for its yield of UFA on the next pass II with the CFA from pass I.

Column functions

Each column is designed to perform specific tasks on each pass. On pass I with CTO as the feed the function of column I is to concentrate esters and heavy unsaponifiables at the base of column I into a pitch fraction. In addition to removing esters and unsaponifiables some fatty acid and rosin are automatically lost in the pitch.

The second function of column I is to remove some of the light unsaponifiables, saturated fatty acids, and coloured materials as an intermediate heads fraction.

Fig. 2 shows that liquid from the top section of column I is either recycled through a cooler to the top of the column, or passed to storage. Excess liquid which builds up in the top section of the column is pumped as reflux to the main body of the column. This design has two effects :

(1) The top section of the column remains cool, limiting the amount of vapour which carries over into the vacuum and effluent system.

(2) The reflux has an enriching effect on the heads material causing it to become richer in the more volatile components, that is, light unsaponifiables and saturated fatty acids.

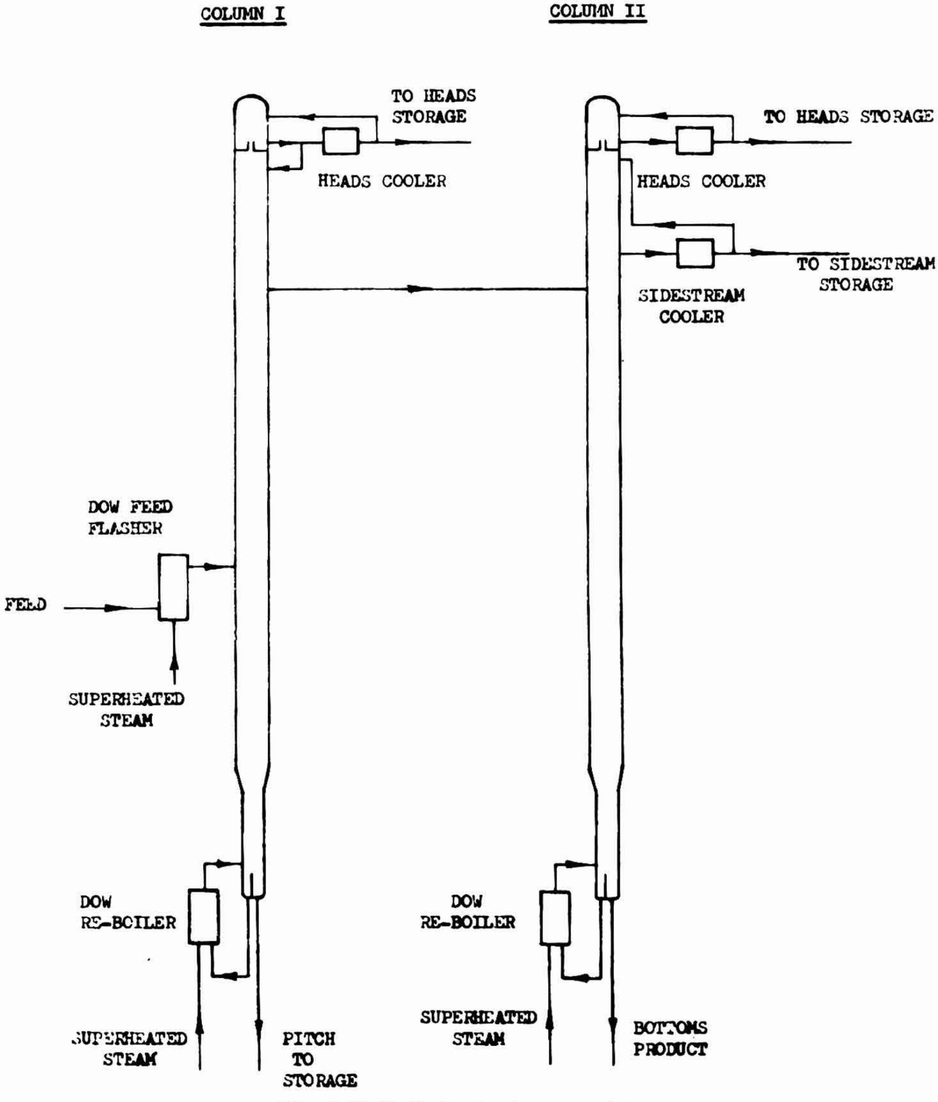


Fig. 2. Tall oil plant columns and streams

The sidestream from column I is the feed for column II and consists mainly of rosin and unsaturated fatty acids.

The function of column II is to produce rosin as a product with limited amounts of fatty acid, unsaponifiables and esters. The fatty acid is removed mainly as a sidestream which also provides its own reflux to increase its purity.

The top section of the column is kept cool in a similar fashion to column I but all build-up is passed to storage. Light unsaponifiables and saturated fatty acids concentrate in this top section.

The usual problem which occurs on this pass is a slight change of feed composition which has the effect of increasing or decreasing the fatty acid content of the rosin. If the fatty acid content becomes too high the rosin offtake rate is reduced by increasing the sidestream offtake rate. The fatty acid is preferentially drawn up the column to the sidestream since the vapour pressure of fatty acids is higher than that of rosin acids. The fatty acid content would therefore be reduced.

The composition of the sidestream would obviously change and in fact the extra rosin which would be drawn into the sidestream would cause the rosin acid content of the sidestream to increase. The over-all effect would be to reduce the rosin yield and increase the yield of reduced purity crude fatty acid.

The main function of the second pass is to produce an unsaturated fatty acid product UFA with limited amounts of rosin acids and unsaponifiables and with good colour. There are other limits but these normally do not impose serious restrictions if the three mentioned parameters are satisfactory.

Crude fatty acid (column II sidestream pass I) has a higher rosin and unsaponifiable content than the UFA product (column II sidestream pass II). In addition the colour is much darker than required. The same can be said for the smaller proportion of the third pass UFA which is recycled from the bottom of column II pass III, except that the rosin acid level is much lower.

The main function of column I is to remove most of the excess unsaponifiable material, most of the remaining saturated fatty acids and to improve the colour of the feed to column II. The small quantity of bottoms is recycled to pass I with the crude tall oil.

The function of column II is to separate the bulk of the rosin acids in the feed into a separate product at the bottom of the column, that is, DTO. This contains approximately 60 per cent fatty acids and almost all of the remaining heavy unsaponifiables.

The heads stream reduces the light unsaponifiable content and saturated fatty acid content of the UFA to the desired limits.

The objective of pass III is to separate the combined intermediate heads from passes I, II and III into fractions containing :

(1) predominantly light unsaponifiables
(2) most of the saturated fatty acids
(3) predominantly unsaturated fatty acids.

Column I separates the unsaponifiables as a concentrated material (final heads) containing some saturated and unsaturated fatty acids. The bottoms are recycled with CTO to pass I.

In column II the objective is to concentrate the saturated fatty acids in a sidestream product and produce a bottom product of unsaturated fatty acids with a low content of saturated fatty acids for recycling in pass II. The main control parameters are :

(1) The acid value of final heads
(2) The cloud point of UFA.

Acid value, a measure of the amount of fatty acids present in final heads, can be decreased by decreasing the offtake rate of the final heads.

Cloud point increases with increasing saturated fatty acid content. If the cloud point of the 3rd pass UFA is too high the offtake rate is reduced by increasing the sidestream offtake rate. The over-all effect is :

(1) To reduce the cloud point of the 3rd pass UFA and also the yield.
(2) To increase the yield of SUFA product but reduce the concentration of saturated fatty acids.

Influence of purity on yield

In the case of rosin and unsaturated fatty acids, an increase in purity leads to substantially reduced yields.

Operation

As shown in Fig. 3, warm CTO is pumped via a heat exchanger to a dehydrator held under vacuum. The temperature in the dehydrator is maintained at over 100°C by recirculation through a further heater. Apart from removing water this prevents a scale of sodium sulphate forming in the ensuing heat exchangers.

The feed heat exchanges with the bottom product from column II and is then heated in a Dow feed heater which is prior to a Dow heated feed flasher where live superheated steam at 270/300°C is injected into the feed.

Most of the feed vapourises and then passes into the first column. The flow rates on column I are controlled by flow rate controllers except for (1) the bottom offtake which is controlled by a level controller and (2) reflux to the main section of the column which is controlled by a level controller in the cooling section at the top.

The sidestream rate from column II is controlled by a flow rate controller and the cool reflux returns to the column at a rate which maintains the top of the main section at a selected temperature. The selected temperature also affects the amount of vapour passing into the cooling zone at the top of the column. The cooling zone is controlled at a constant level, excess material being pumped to storage. The bottom offtake is also controlled by a level controller.

A Dow heated reboiler at the base of each column provides sources of heat and live steam injection.

Passes II and III are operated similarly. The dehydrator is not used as such and the feed and offtake points on each column are changed to suit the pass and composition of the feed and sidestreams. The other main difference on passes II and III is that the feed flasher is used as a reboiler and the feed enters column I as a liquid.

Storage tanks are constructed mainly of either stainless steel or aluminium with inert gas blankets to prevent degradation. Mixing and heating facilities are provided.

Products are shipped out in tankers although a limited proportion is sold in drums.

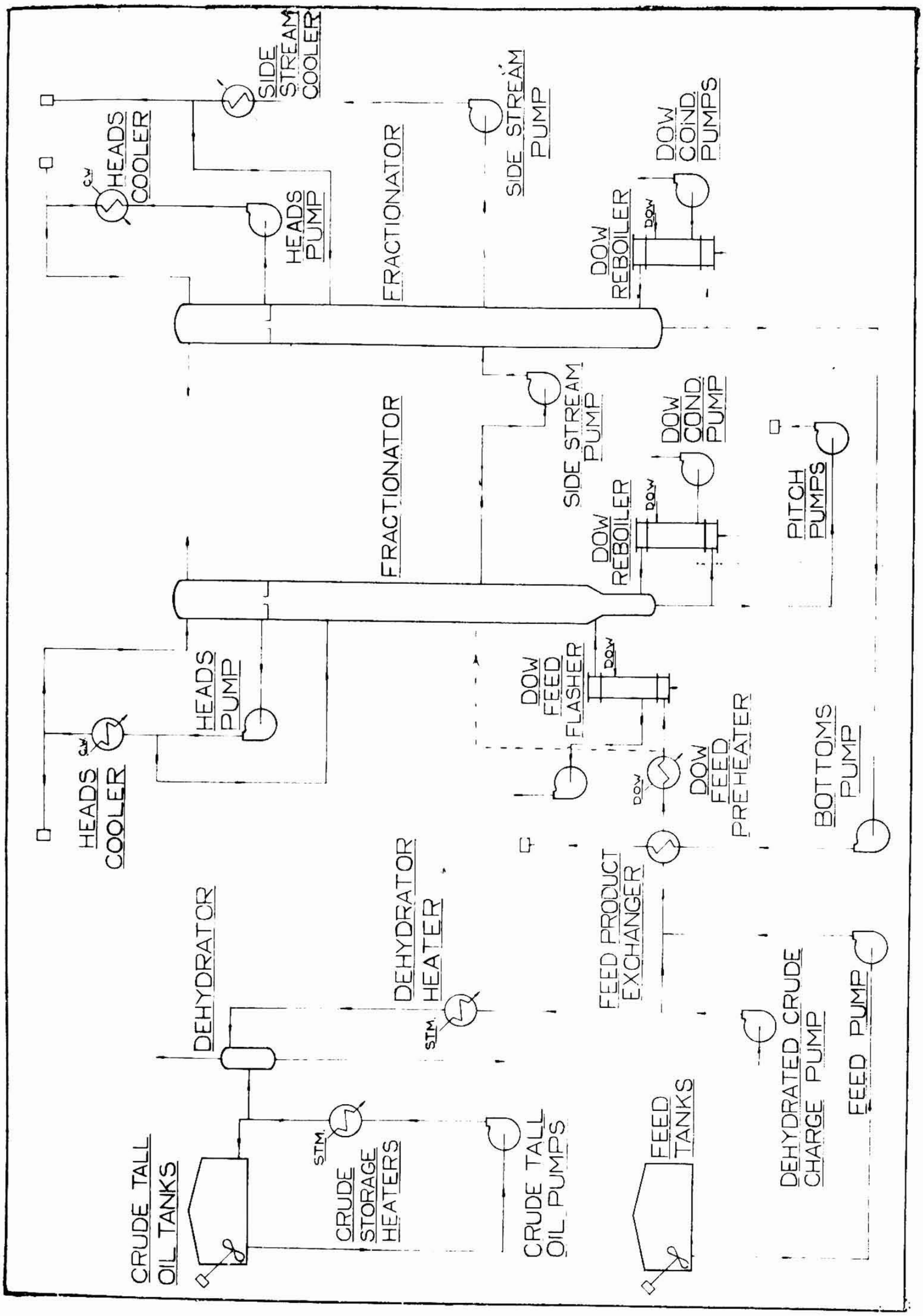

CRUDE TALL OIL TANKS
CRUDE STORAGE HEATERS
STM.
CRUDE TALL OIL PUMPS
FEED TANKS
DEHYDRATED CRUDE CHARGE PUMP
FEED PUMP
DEHYDRATOR
DEHYDRATOR HEATER
STM.
FEED PRODUCT EXCHANGER
BOTTOMS PUMP
HEADS COOLER
C.W.
HEADS PUMP
DOW FEED FLASHER
DOW
DOW FEED PREHEATER
DOW
FRACTIONATOR
SIDE STREAM PUMP
DOW REBOILER
DOW
DOW COND PUMP
PITCH PUMPS
HEADS COOLER
C.W.
HEADS PUMP
FRACTIONATOR
SIDE STREAM COOLER
SIDE STREAM PUMP
DOW REBOILER
DOW
DOW COND PUMPS

Fig. 3

Acknowledgments

The authors wish to express their thanks to the Chief Executive, Chemicals Division, British Oxygen Company Ltd., for permission to publish.

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Discussion at Eastern Branch, Scottish Section

MR. G. H. HUTCHINSON asked if cis-5,9,12-octadecatrienoic acid gave faster air drying than linoleic acid in alkyds.

DR. ENNOR said that cis-5,9,12-octadecatrienoic acid behaved more like linoleic than a trienoic acid. The double bond at C 5 was relatively difficult to conjugate and, after being treated with alkali, the cis-5,9,12-acid appeared as linoleic acid in the UV spectrum.

MR. P. A. GOWER asked how tall oil rosin differed from gum rosin. He noted that maleic resins prepared from tall oil rosin had lower melting points than those from gum rosin.

DR. ENNOR said that tall oil rosin was cheaper than gum rosin. The main difference was that tall oil rosin crystallised much more readily than gum rosin.

DR. D. R. ATHERTON asked what were the uses of tall oil pitch and heads.

DR. ENNOR said the UK offered a highly developed market for tall oil pitch especially in the rubber industry. Other uses were in thermoplastic floor tiles, foundry core binders, printing inks, wetting agents, bitumen additives and in cheap emulsifiers. Tall oil heads were used in rubber processing.

Discussion at the Hull Section

DR. JASPERSON asked if distilled tall oil with a low rosin content (0.05 per cent) could be used in the food industry.

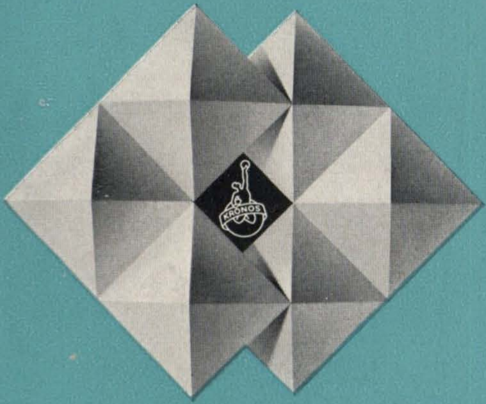
DR. ENNOR replied that he had seen a patent for the hydrogenation of tall oil glycerides for use in margarine, but he doubted if this product would be acceptable in the UK.

MR. K. B. GILKES remarked that alkyd based paints made from similar tall oil fatty acids from different sources often had very different drying characteristics.

DR. ENNOR thought that too much emphasis was often placed on the oleic : linoleic ratio ; the small variable content of cis-5,9,12-octadecatrienoic acid may be important. Drying inhibitors were unlikely to survive the process, but the products of tall oil fractionation were chemically complex.

MR. D. J. CRIMLISK endorsed Mr. Gilkes' experience and said that although a low rosin content gave superior drying properties, drying depended ultimately on the fatty acid composition.

MR. L. W. WYNN asked why there had been a resurgence in the use of tall oil products.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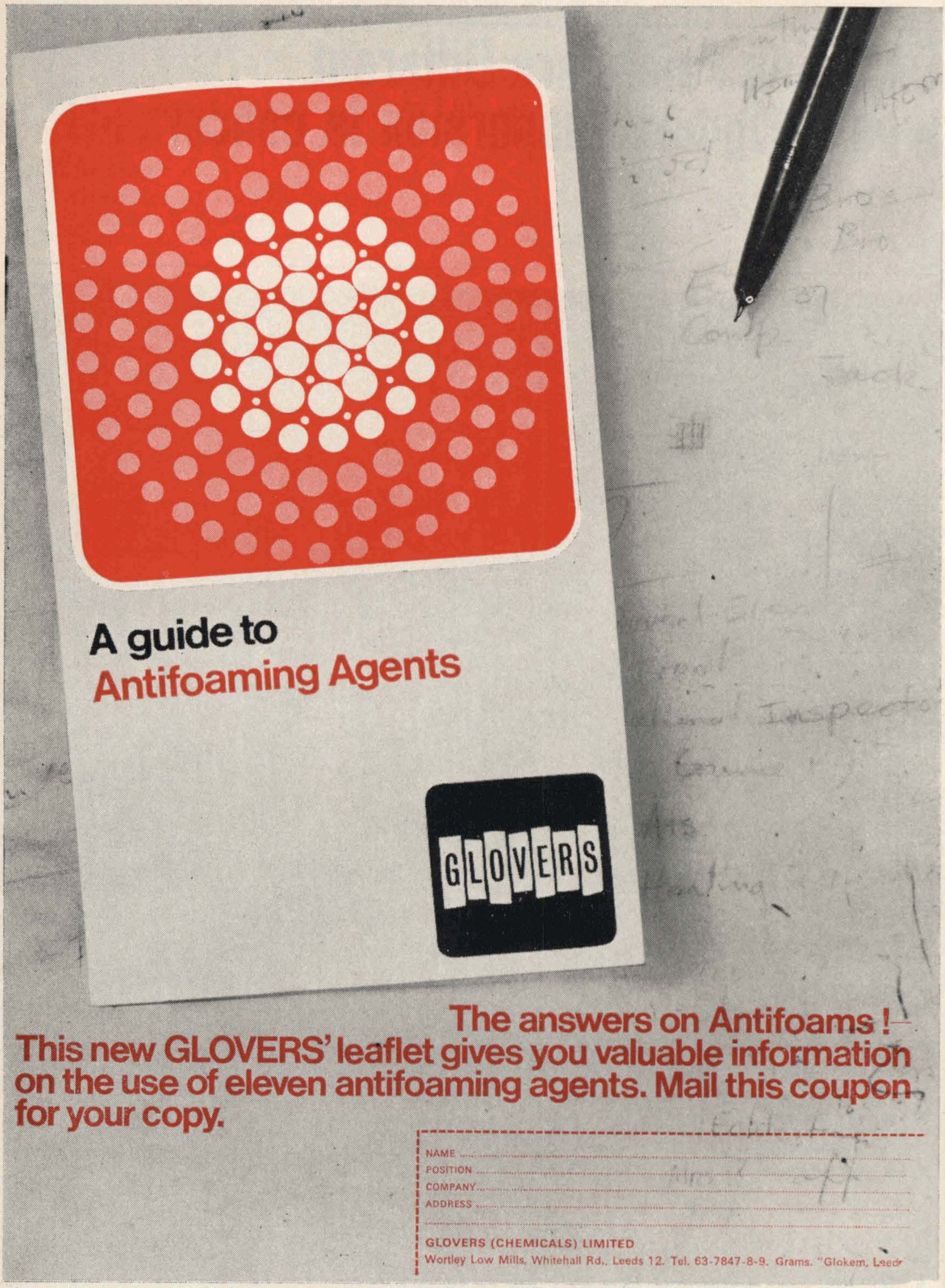
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DR. ENNOR said that large-scale development in tall oil fractionation, particularly in the United States, had greatly altered the situation between 1950 and 1960. Fractionated tall oil is now an economical source of unsaturated fatty acids competing mainly with soya rather than linseed oil.

MR. A. J. FORD said that rosin-modified alkyds from tall oil fractions showed drying inhibition compared with those from gum or wood rosin.

DR. ENNOR replied that tall oil rosin was chemically different from, and polymerised less readily than, other rosins.

DR. JASPERSON asked if conjugated linoleic acid was present in tall oil fatty acids.

DR. ENNOR said that some 6 per cent of the linoleic acid was conjugated and this was likely to improve the drying properties of alkyds.

MR. T. A. FILLINGHAM said that he had noticed differences in behaviour of tall oil from North and South Finland.

DR. ENNOR thought that the type of wood used had more effect on the crude tall oil than the climate. For instance, birch wood gave a lower yield of a poor quality crude tall oil. The UK imported a large tonnage of fractionated tall oil products mainly from the USA, Sweden and Finland.

MR. D. J. CRIMLISK asked about the yellowing of tall oil alkyds.

DR. ENNOR said that the mechanism of yellowing was not fully understood, but most suppliers claimed that alkyd paints based on tall oil fatty acids were equal or superior in yellowing resistance to those based on soya bean oil.

MR. ROBINSON added that conditions of exposure had a pronounced effect on yellowing properties.

MR. S. L. REDFEARN said that, in general, ASTM methods of analysis were used for plant control purposes. Molten rosin was sampled at high temperatures and immediately cast into cubes. Refractive index was a good guide to the content of rosin acids in certain distillate streams. It has been suggested that BSI should consider whether ASTM or Scandinavian methods were best for rosin determination.

MR. T. A. FILLINGHAM, in proposing a vote of thanks, said that the establishment of improved products from tall oil had been a common aim of many people for a good many years. Mr. Fillingham was impressed by the chemical engineering information given so freely and by the versatility of the plant.

Next month's issue

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

From the London Section Symposium on operational research methods.

- **"The purpose and scope of operational research,"** *by H. R. Watkins.*
- **"Short-term sales forecasting,"** *by P. J. Harrison.*
- **"A case study in the field of stock control/production planning in the chemical industry,"** *by A. Kemp.*

"Copolymers with vinyl esters of branched carboxylic acids in thermosetting systems," *by W. H. M. Nieuwenhuis and H. A. Oosterhof.*

"The next ten years—an analysis of current trends and future outlook for emulsion paints," *by P. O. Miles and G. R. Harrison.*

J. Oil Col. Chem. Assoc. 1967, 50, 594-614

Size analysis of organic pigments using the ICI-Joyce Loebl disc centrifuge

By J. Beresford

Geigy (UK) Limited, Simonsway, Manchester, 22

Summary

The ICI/Joyce Loebl disc centrifuge, a commercially available apparatus for particle size measurement, is described. Several techniques for using the apparatus are examined. The " buffered line start " method is shown to be the only stable one avoiding streaming and is studied in detail. Results from size determinations on aqueous organic pigment pastes show there is no effect of buffer layer volume, disc speed or paste concentration, but there appears to be a reduction of probe collection efficiency at combinations of high disc speed and high spin fluid viscosity. The experimental repeatability is good, the scatter being less than 10 per cent for a size range 0.04 to 1.0 microns.

L'analyse granulométrique des pigments organiques à l'aide du centrifugueur à disque ICI-Joyce Loebl

Résumé

On décrit le centrifugueur à disque ICI-Joyce Loebl, un appareil destiné à la granulométrie qui est déjà sur la marché. On considère plusieurs techniques pour l'utilisation de l'appareil. La méthode de la ligne de couche tampon est démontrée la seule qui évite le phénomène de ruissellement et l'on l'étudie en détail. Les résultats des déterminations granulométriques sur des pâtes aqueuses de pigments organiques révèlent que la volume de couche de tampon, la vitesse de rotation du disque, et la concentration de pâte n'exercent pas d'influence, mais il paraît que l'éfficacité du ramassage par la lance se diminue où la vitesse de rotation du disque et la viscosité sont à la fois élevée. L'appareil donne des résultats bien reproductibles, d'un écartement moins de 10% dans la gamme de 0.04 à 1.0 microns.

Grössenanalyse Organischer Pigmente mittels der ICI-Joyce Loebl Scheibenzentrifuge

Zusammenfassung

Die ICI—Joyce Loebl—Scheibenzentrifuge, ein im Handel erhältlicher Apparat, wird beschrieben. Eine Anzahl von Anwendungsmethoden dafür werden geprüft. Die " Pufferschichten-Startlinien " Methode erweist sich als die einzige, die stabil ist und Strömen vermeidet ; Sie wird gründlich unter die Lupe genommen. Aus den Resultaten der Grössenbestimmungen von organischen Pigmenten in wässrigen Pasten ergibt sich, dass das Volumen der Pufferschicht, die Scheibengeschwindigkeit oder die Pastenkonzentration keinen Einfluss ausüben, dass aber bei Kombinationen von hoher Scheibengeschwindigkeit mit hoher Viskosität der Spinflüssigkeit das Probeziehen weniger erfolgreich ist. Die experimentelle Reproduzierbarkeit ist gut, die Streuung liegt bei einem Grössenbereich von 0.04 bis 1.0 Mikron unter 10%.

Анализ величины органических пигментов применяя дисковую центрифугу I.C.I.-Джойс Лоебля.

Резюме.

Описывается дисковая центрифуга I.C.I.-Джойс Лоебля, которая является промышленно доступным прибором для измерения величины частиц. Исследуется несколько методов применения прибора. Дается подробное описание метода «стартовой буферной линии» и показано, что последний является единственным надежным методом предотвращающим размывку. Результаты измерения величины водных органических пигментных паст показывают отсутствие влияния объема буферного слоя, скорости диска или концентрации пасты, но замечается понижение в эффективности скопления проб при повышенной скорости диска совместно с высокой ротационной скоростью вязкой жидкости. Экспериментальная повторяемость удовлетворительна, с разбрасыванием менее 10% при диапазонах величины от 0,04 до 1,0 микрон.

Introduction

In recent years, increasing importance has been placed on the physical properties of organic pigments and their relation to the application behaviour of pigmented systems. One of the more obvious measurements to make is size analysis ; this is a simple statement but the realisation of these aims is not so straightforward. In application, organic pigments are present as extremely fine particles, and their size range eliminates most standard sizing methods such as sieving, optical microscopy, gravitational sedimentation, and the Coulter Counter. At the moment there appear to be only two techniques for sizing such particles : centrifugal sedimentation and electron microscopy.

The resolution limit of the electron microscope is much better than that required for pigment analysis, but, in some respects, it is too good, in so far as the operator, counting particles, must decide, if particles have coalesced, whether they are to be counted separately or together ; this decision is not always easy and not without ambiguity. The equipment and operator costs are high, and specialist personnel are required to operate it. Examples of electron micrographs are given in Figs. 1 and 2. As can be seen, problems of coalesced particles can be serious.

Recently, centrifugal sedimentation techniques have been elaborated to use disc rotors specially designed for the job[1–5]. Disc centrifuges have been designed to operate using both homogeneous and " line start " techniques and to detect amounts of particles either by collection and subsequently appropriate analysis, by photo-extinction or by deposition on plates and weighing. Each disc centrifuge seems to have its own size and speed range, and the instrument best suited to the needs of the particular system of interest is chosen. The centrifuge developed by Joyce Loebl Ltd. from the Atherton and Cooper prototype[3] was considered most suitable for organic pigments.

Before considering this instrument in detail, it might be worth indicating the reasons for rejecting other instruments. The Bostock and Donoghue and Simcar instruments only operate at relatively low speeds—one suspects that the instrument design would not allow major speed increases—and consequently the quoted lower size limits are too high. The Coulter development of the UKAEA centrifuge uses photoelectric extinction of white light as a detector whereas theoretical studies by Felder[6] and Brockes[7] have shown that extinction

Fig. 1. Electron micrograph of CI Pigment Red 3. Replica shadowed at 30°.
(By courtesy of P.R.S.)

**Fig. 2. Electron micrograph of CI Pigment Yellow 1. Replica shadowed at 30°.
(By courtesy of P.R.S.)**

coefficients of suspensions (both absorption and scattering) depend on particle size as well as concentration. Again the quoted size range, 0.4 to 30 microns (approximately) is too high for the examination of organic pigments.

The ICI/Joyce Loebl disc centrifuge

The disc centrifuge consists of three component parts ; the centrifuge unit, the collection unit and the electronic control unit.

The centrifuge unit

The rotor, manufactured from solid perspex, accurately machined with a 360° cavity, is fixed directly to a horizontal shaft and can rotate at stepped speeds up to 8,000 rpm. An annular depression (cusp) is machined in the rear face of the disc to aid in forming a stable layer of dispersion on the spin fluid surface (see Fig. 3). A motor stabilising feed-back loop is obtained by chopping a beam of light, incident on a photocell, with a slotted plate attached to the other end of the motor shaft. The chopped signal is compared against a crystal oscillator to control the motor current. The sampling head, an integral part of the centrifuge unit, allows an undersize fraction to be extracted whilst the disc continues to rotate ; the technique is analogous to inside turning on a lathe. A sharp-angled, thin-walled, metal probe is inserted in the rotor cavity

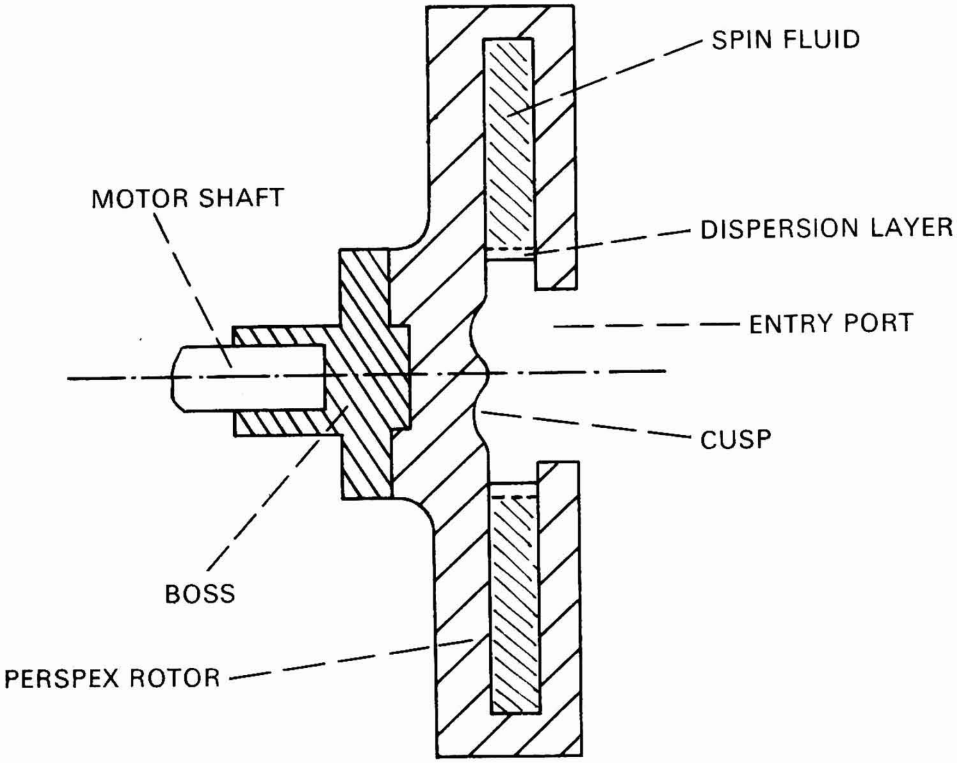


Fig. 3. Plan view of disc profile

and offset from the disc centre. The probe is driven at 1 rpm and cuts into the liquid to increasing depth ; at the same time, suction is applied to the probe so that the liquid is removed to the collection unit as a foam. After half a revolution the probe has cut to its maximum depth and this is set to leave 5 ml of liquid in the disc, so giving a final collection radius as an apparatus constant (see Fig. 4). As the probe returns to its rest position the disc motor is automatically stopped. The timing of the sequence can be started by using the injection to initiate the timing clocks and on reaching completion time these automatically start the probe sampling cycle. The probe takes 30 seconds to reach the final collection radius and this is deducted from the sequence time for a particle of selected diameter to reach this radius. The probe speed is chosen so that the probe lags behind such a particle until the final collection radius[3].

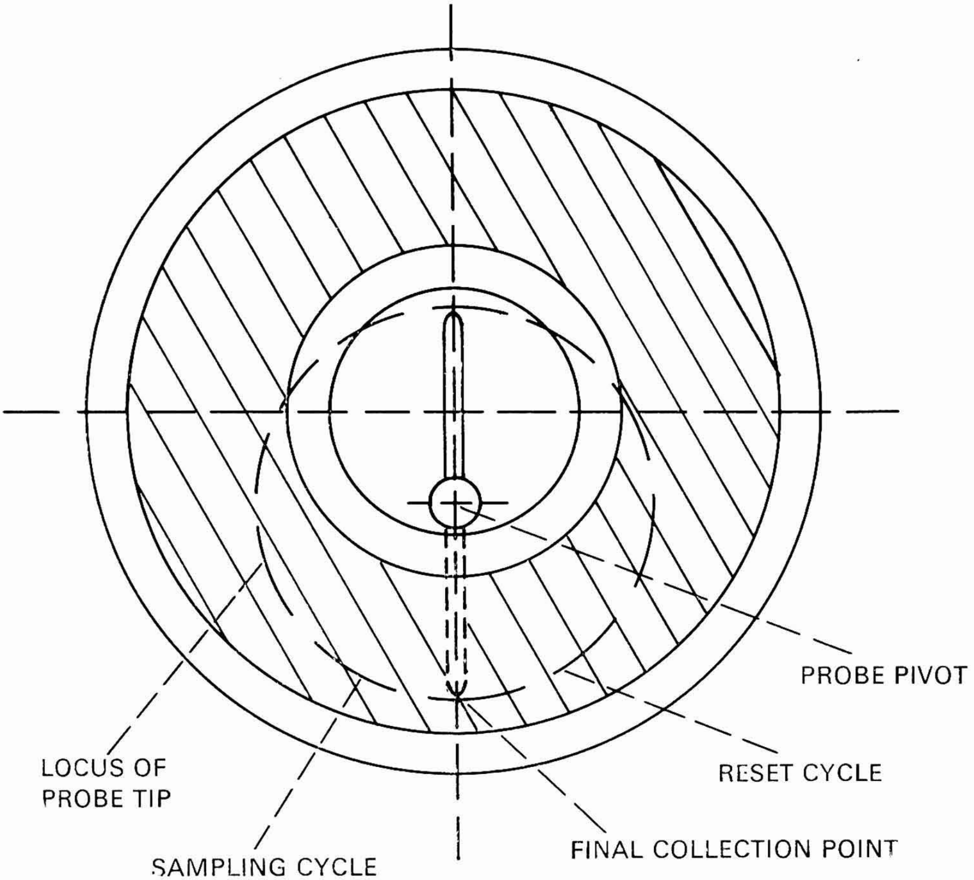


Fig. 4. Disc and probe relationship during sampling

The collection unit

This comprises a vacuum pump attached to the probe to create the suction, together with volumetric flasks into which the fractions are collected.

The electronic control unit consists of the sequential switching system, motor speed control servomechanism, the supply transformer, power amplifier and three centrifuge timers.

Modes of operation

1. *Two layer or line start techniques.* Originally it was suggested that a simple line start technique could be used. So long as the spin fluid is of lower density than the particles but higher than the mean density of the dispersion, it should be possible to form a stable dispersion layer at the surface of the spin fluid and the particles should sediment in an acceptable way. This method has been described in detail by Atherton, Cooper and Fox[8]. Following their method of obtaining the size fractions it was not possible to obtain a reasonable sedimentation pattern when observed under stroboscopic illumination. The sort of pattern seen with the author's systems is shown in Fig. 5 and the phenomenon

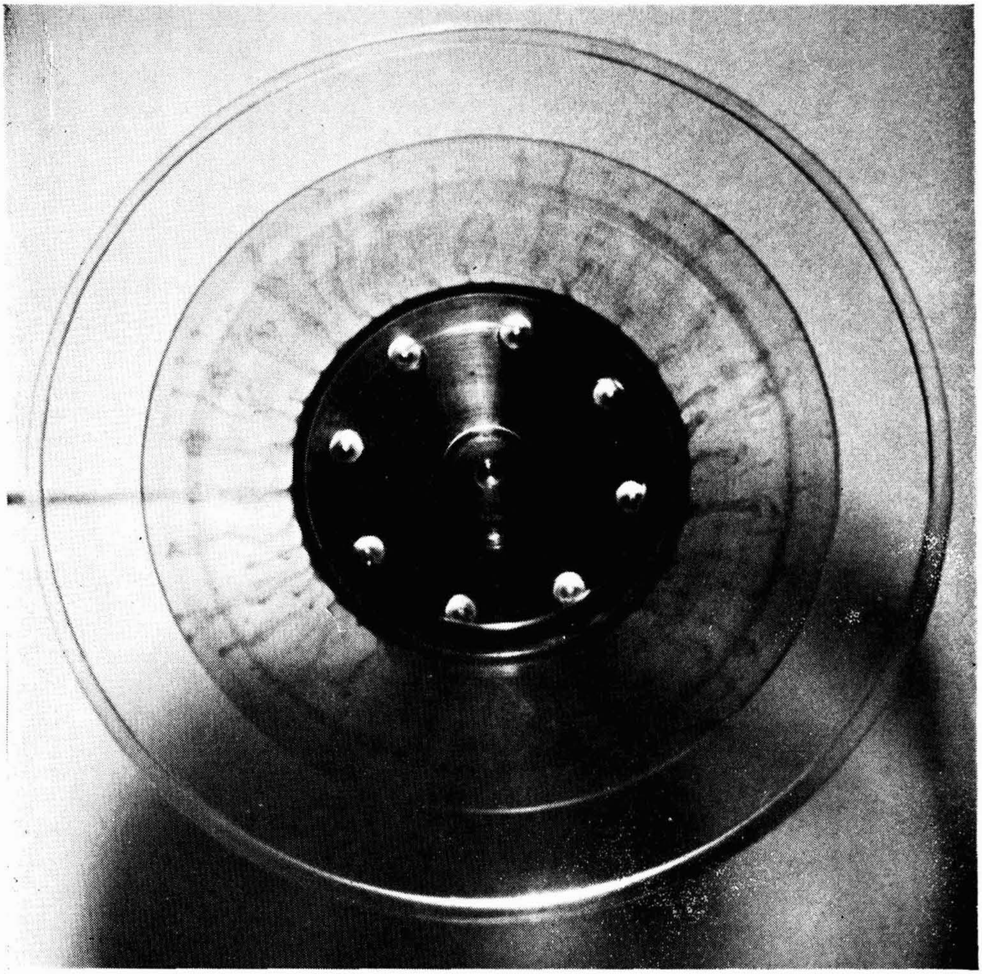


Fig. 5. Line start technique (Atherton)

of " streaming " is very evident. Using this simple method, streaming was unavoidable. Since several workers (e.g. Scarlett, *et al*[9], Burt[10]) have suggested that results from streaming systems are meaningless, it became necessary to search for another method.

Initially attempts were made to alter the viscosity/density relations between the spin fluid and the dispersion. The only successful method of preventing streaming in the " two layer " technique required thickening the dispersion layer, for example with Callosec MAH (ICI), but, often, the particle residence time in this layer was greater than the sedimentation time. Other problems arose with collection of this high viscosity layer.

Burt[10] has suggested there is a critical concentration below which streaming does not occur. This conclusion appears to be derived from the recorder trace and the final size distribution from a photo-extinction detection method ; there does not appear to have been any direct viewing of the rotating disc and from the present studies this is essential. By viewing the rotating disc with the stroboscope, streaming was observed when the pigment concentration was as low as 0.004 per cent w/w. There was no point in using concentrations much below this, as analysis of the fractions would have been almost impossible.

2. *A homogeneous technique*. As it had not proved possible to use the two layer technique successfully, attention was turned to the less convenient methods of homogeneous suspensions. Murley[11] has described a method of calculation using a homogeneous suspension in which the inner surface radius (S) is used as a variable. It is necessary to plot the weight collected (W) against S, and the tangents at a series of S yield the cumulative weight percentage against diameter. All other variables in the equation, time, density difference, angular velocity, etc., are kept constant. In the author's experiments it was necessary to perform two or three experiments at different disc speeds to cover satisfactorily the size range of interest. The resultant curves did not overlap as well as expected (Fig. 8). It is felt that the large scatter on the results is an effect of having to draw tangents, that is, to differentiate, a process which tends to increase inaccuracies.

3. *The " buffered line start " technique*. The previous suggestion was not pursued at length because of private discussions with Joyce Loebl Ltd., and a subsequent lecture by M. H. Jones[12] suggesting another technique which was certainly more convenient and seemed interesting. Joyce Loebl Ltd. have called it the " buffered line start " technique. A thin layer of a liquid, miscible with the spin fluid and dispersion layers, is interposed between them, so buffering any interfacial effects. This is similar to a technique suggested by Scarlett[9] but there is an important difference between the two. Scarlett suggests using the simple method described above ; for example, 10 per cent aqeous sucrose spin fluid, add 1 ml of water to the inner surface whilst the disc is in uniform motion and then place the aqueous dispersion on to this ; whenever this was tried in the author's centrifuge streaming resulted, as can be seen in Fig. 6. Using the above example, the Joyce Loebl technique is the same, except that after introducing the water buffer layer, a transient acceleration is applied to the disc so that the water layer is surface mixed with the sucrose ; the dispersion is injected on to this. The resultant effect is shown in Fig. 7. There is no evidence of streaming. Dispersions have been run, using this technique, for up to four hours and at no time has streaming been observed. Scarlett concluded that streaming

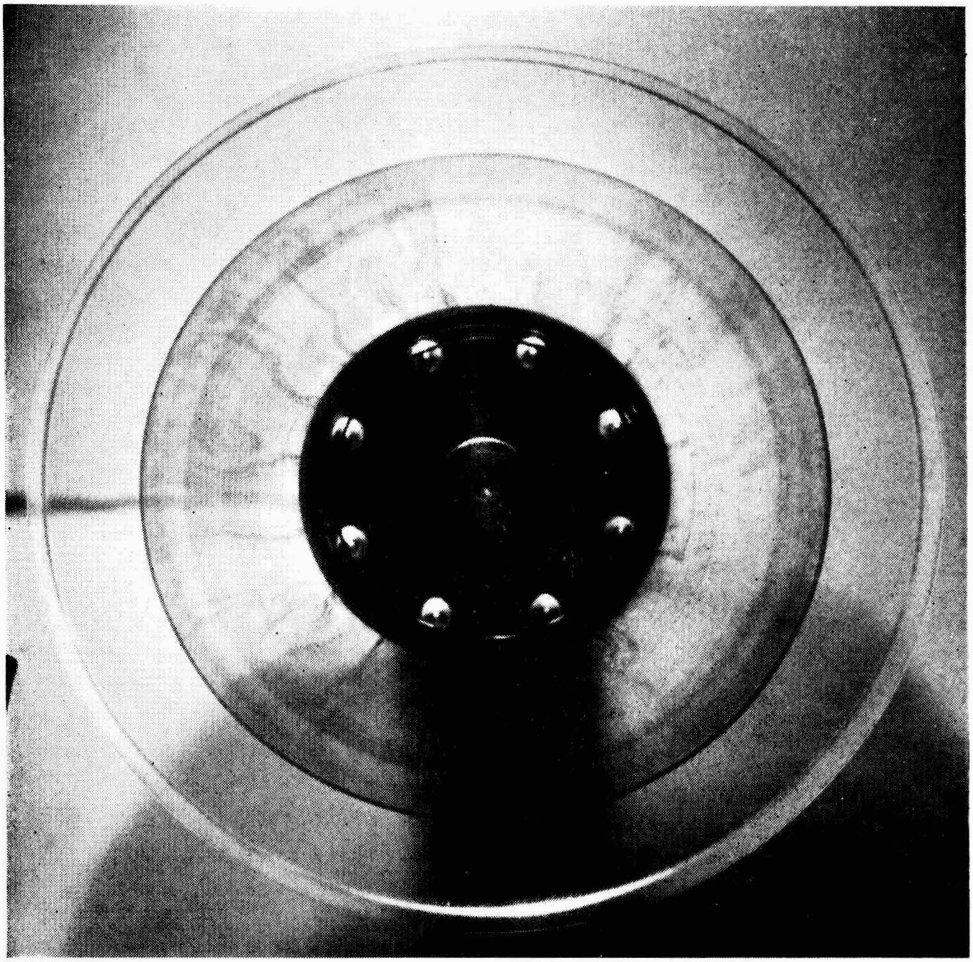


Fig. 6. Three-layer technique (Scarlett)

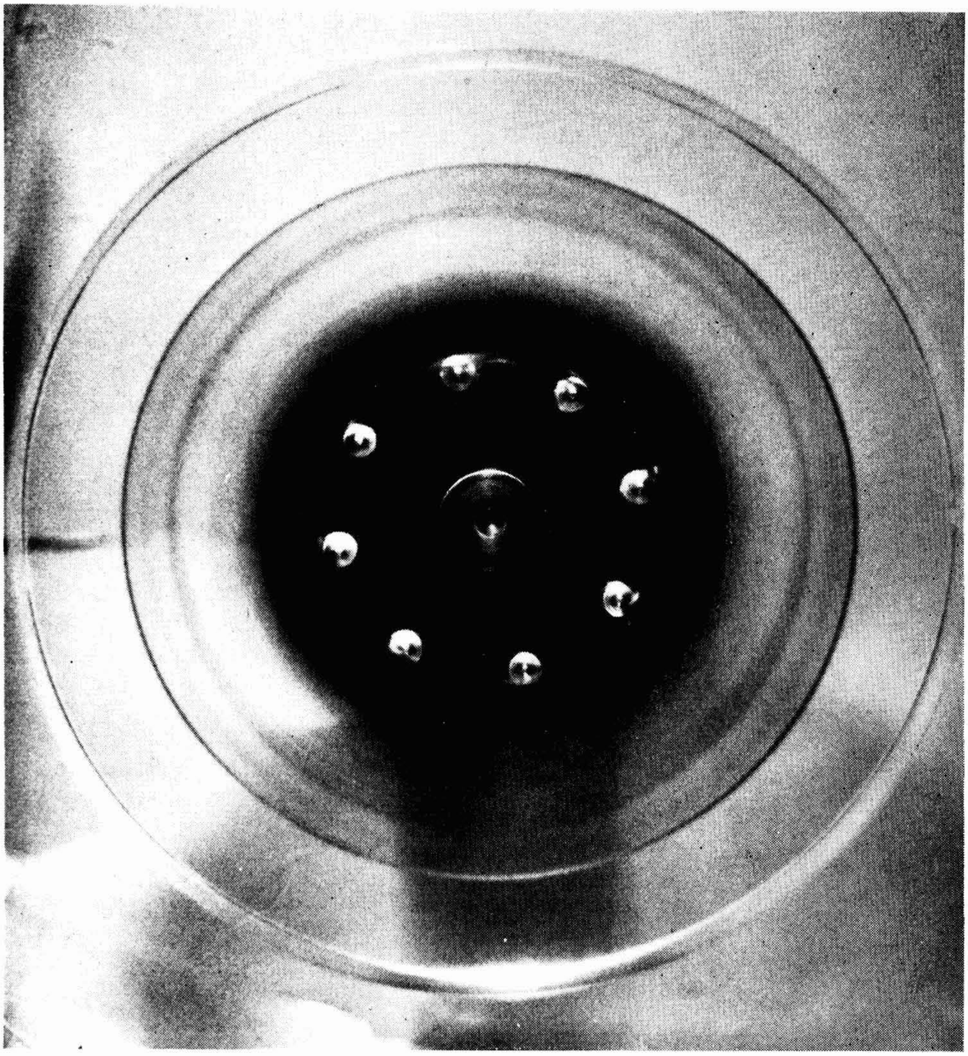


Fig. 7. Buffer layer technique (Jones)

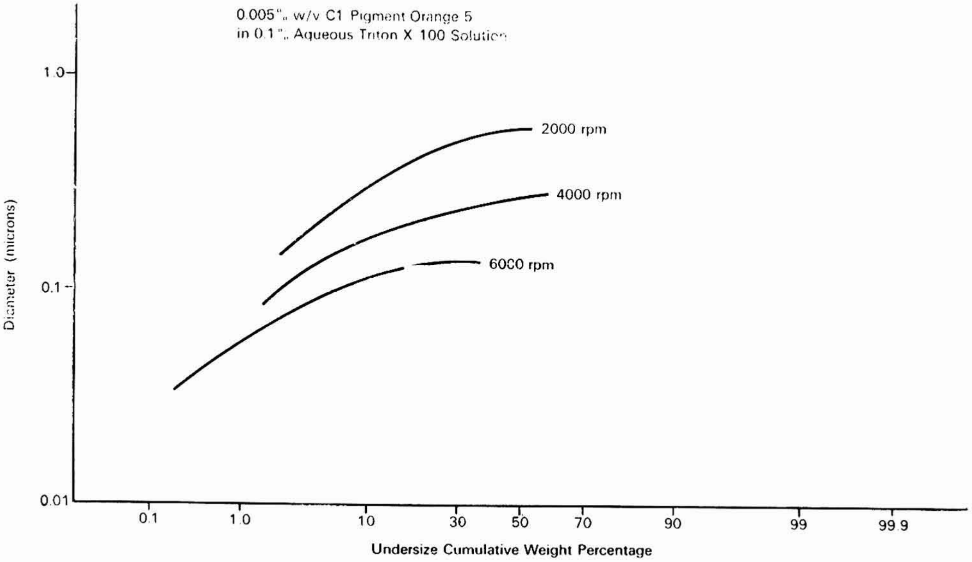


Fig. 8. Homogeneous technique

was caused by disturbances, created by the injected dispersion, in the liquid rotating in equilibrium with the centrifuge. This cannot be the complete reason or the suggestion for confining the disturbance to the surface would be successful. Jones suggested the existence of a skin effect, caused by interfacial forces, in the two layer technique, which creates a rapid particle concentration increase at the interface between the two layers, leading to the unstable condition of a layer of high density above one of lower density. If the interfacial boundaries are removed this increase cannot happen and streaming is avoided. In effect, the mixing of the buffer layer creates a region of smoothly increasing sucrose concentration and interfacial forces are eliminated. Figs. 9a and 9b show the suggested density profiles with time, for the two layer and the buffered line start techniques.

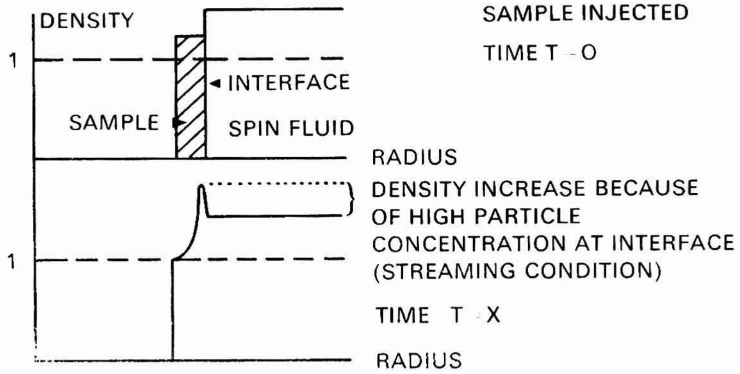


Fig. 9a. Density profiles for line start

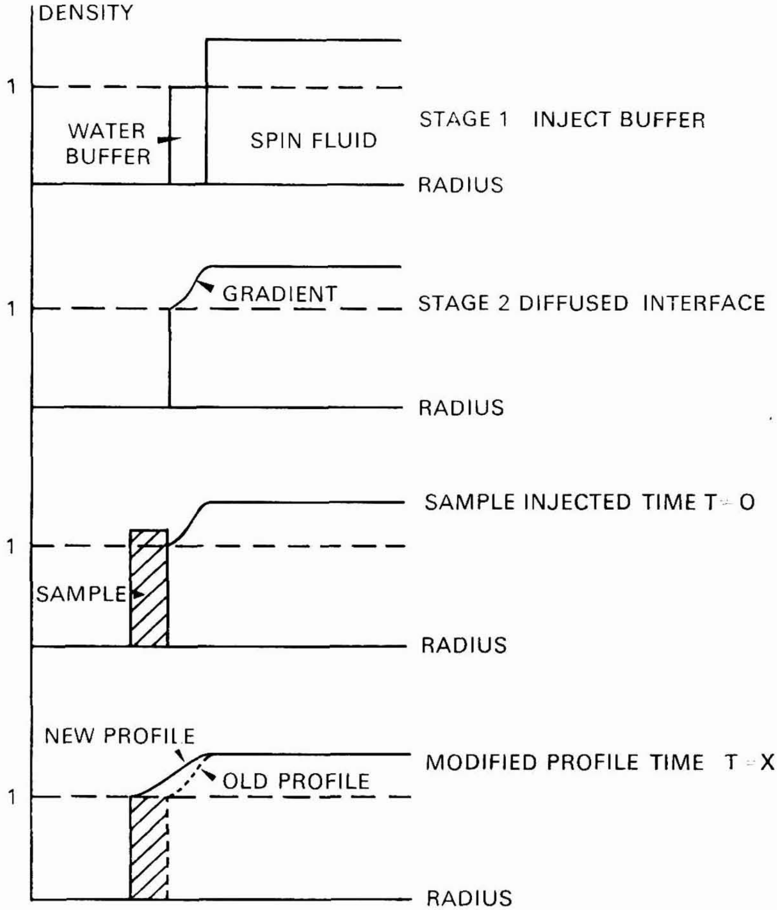


Fig. 9b. Density profiles for buffered line start

Limits of the techniques

A technique having been found which appeared sufficiently stable, it was logical to examine the operating conditions. Samples of commercially available aqueous pigment pastes were used to avoid problems associated with the poor reproducibility of laboratory scale grinding techniques. The variable parameters of the system can be listed as :—

(1) disc speed
(2) particle/liquid density difference
(3) spin fluid viscosity
(4) start radius
(5) buffer layer volume
(6) dispersion layer volume
(7) particle concentration in the dispersion
(8) time of centrifugation
(9) collection radius.

The time of centrifugation is fixed, usually by choosing the other parameters to give a convenient time, and the collection radius has been set as an apparatus constant (for design convenience). Thus the effects of speed, viscosity and buffer layer volume have been examined. A completely separate study was made of the concentration effect because of the importance attached to it by Scarlett[9] and Burt[10].

Materials

Two pigment pastes have been used throughout this work, aqueous dispersions of C.I. Pigment Red 112 (Irgalite Red CPV3) and C.I. Pigment Orange 5 (Irgalite Red CPV8). Spin fluids used were 10 and 20 per cent w/v aqueous sucrose solutions plus 0.01 per cent w/v aqueous Triton X-100 (Rohm and Haas), a non-ionic surfactant. A 0.01 per cent aqueous Triton X-100 solution was used to dilute the pigment pastes to the required concentrations and also formed the buffer layer.

Disc speeds and spin fluid viscosity effects

Two parameters which could affect the results are disc speed and spin fluid viscosity. To investigate disc speed effects, trials were carried out in which each diameter was measured using 4,000 rpm and also using the speeds between 2,000 and 8,000 rpm most convenient to that diameter, that is 8,000 rpm for 0.05 microns, 6,000 rpm for 0.1 microns, and so on. These trials were made at two different sucrose concentrations in the spin fluid to study the effect of viscosity. A summary of the trials is given below :—

Sucrose concentration (% w/w)	*Disc speed (rpm)*	*Number of trials*
20	4,000	5
20	2-8,000	5
10	2-8,000	3
10	4,000	1
10	6,000	1

Calculation of the time to achieve a certain cut-off diameter has been given by Atherton[8], but the particular fraction concentration analysis should be described. The fractions are collected into 100 or 50 ml volumetric flasks and, if the pigment content is sufficiently high, are made up to volume with water. A 10 ml aliquot is removed and made up to 100 ml with a 1 : 5 mixture of methyl ethyl ketone (MEK) and isopropyl alcohol (IPA). If the pigment content is low, the fractions are made up to 100 mls directly with the MEK/IPA mixture. The optical densities of the solutions are measured and the cumulative weight percentages (W) obtained by comparing the optical density of the undersize fraction (Du) with that of the oversize fraction (Do) (at the same dilution) plus that of the undersize fraction, i.e.

$$W = \frac{Du}{Do + Du} \times 100\%$$

Size distribution curves can be plotted and the diameters at which certain undersize percentages occur are given in Tables I and II. The means, standard deviations about means (σ) and 95 per cent confidence limits (1.98σ) are also given.

Table 1

C.I. Red 112 in 20% sucrose using 4,000 rpm

Undersize percentage	Diameters (microns)					Mean (microns)	Standard deviation (σ)	95% Conf. limits (1.98σ)
	Run 1	Run 2	Run 3	Run 4	Run 5			
10	0.041	0.041	0.038	0.042	0.045	0.0416	0.0019	0.0038
25	0.061	0.060	0.057	0.058	0.059	0.0590	0.0016	0.0032
50	0.094	0.094	0.091	0.093	0.094	0.0932	0.0013	0.0026
75	0.145	0.150	0.145	0.147	0.152	0.1478	0.0031	0.0062
90	0.232	0.230	0.218	0.210	0.225	0.2230	0.0090	0.0180

Buffer layer volume = 1 ml. Dispersion volume = 1 ml.

Table 2

C.I. Red 112 in 20% sucrose using 2,000-8,000 rpm

Undersize percentage	Diameters (microns)					Mean (microns)	Standard deviation (σ)	95% Conf. limits (1.98σ)
	Run 6	Run 7	Run 8	Run 9	Run 10			
10	0.051	0.049	0.050	0.050	0.049	0.0498	0.0009	0.0018
25	0.068	0.066	0.065	0.066	0.064	0.0658	0.0015	0.0030
50	0.099	0.102	0.108	0.102	0.098	0.1002	0.0018	0.0036
75	0.155	0.160	0.175	0.175	0.170	0.1670	0.0091	0.0182
90	0.225	0.250	0.270	0.260	0.245	0.2460	0.0192	0.0384

Buffer layer volume = 1 ml. Dispersion volume = 1 ml.

Table 3 gives the significances of difference at each undersize percentage between the two sets of results. As can be seen, the differences are highly significant at all levels and extremely so at the lower diameters. From Tables 1 and 2 it is possible to plot control charts for the two different sets of results using the 1.98σ (95% confidence) limits. These are given in Figures 10 and 11. The other results of this series are given in Table 4.

Table 3

Significance of difference tests. Tables 1 and 2

Undersize percentage	Standard deviation (σ)	Students "t"	Degrees of freedom	Significance level
10	0.00150	8.64	8	<0.1%
25	0.00154	6.98	8	0.1%
50	0.00158	7.00	8	0.1%
75	0.00679	4.47	8	<0.5%
90	0.01500	2.42	8	3%

Table 4

C.I. Red 112 in 10% sucrose

Undersize percentage	Diameters (microns)				
	Run 11	Run 12	Run 13	Run 14	Run 15
10	0.042	0.044	0.041	0.044	0.044
25	0.059	0.059	0.058	0.057	0.059
50	0.096	0.092	0.093	0.087	0.091
75	0.155	0.162	0.155	0.133	0.148
90	0.230	0.245	0.238	0.213	0.232
Speeds (rpm)	4,000	6,000	various between 2-8,000		

Buffer layer volume = 1 ml. Dispersion volume = 1 ml.

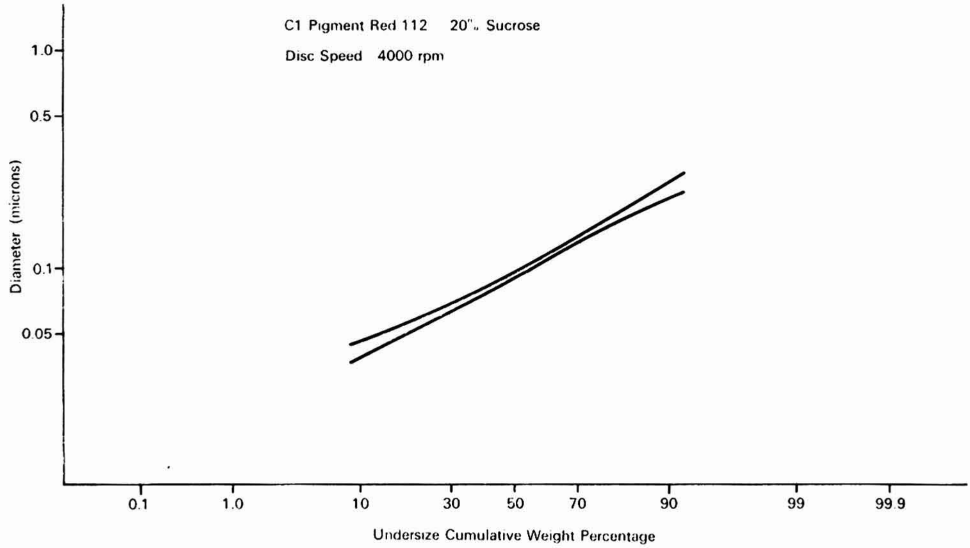
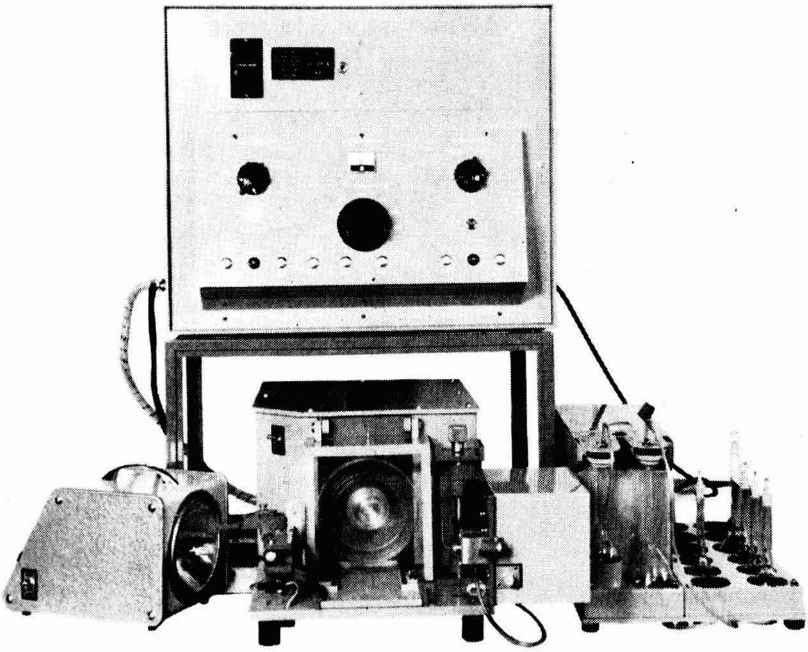
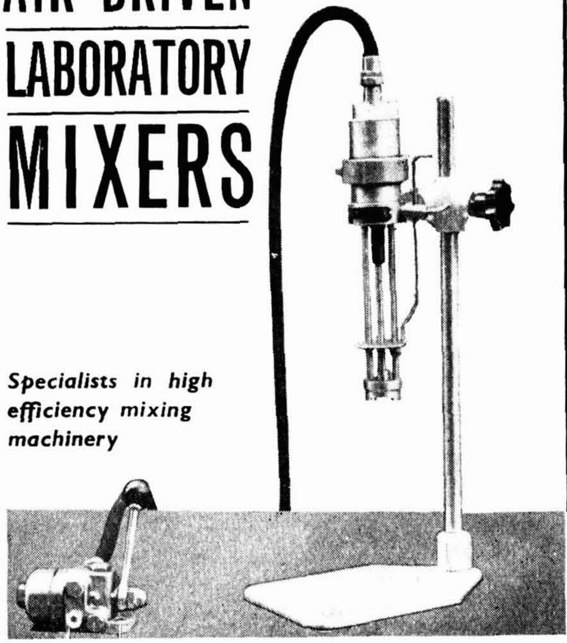


Fig. 10. 95 per cent Confidence limits

It can be seen from the above tests that the various speed results using 10 per cent sucrose are significantly the same as those using 4,000 rpm and 20 per cent sucrose (Table 5) but highly significantly different from the various speed results using 20 per cent sucrose (Table 6). The results of runs 11 and 12 lie within the 4,000 rpm/20 per cent sucrose control limits and therefore can be considered as not different. In other words, therefore, when the spin fluid viscosity is high there are significant differences between different disc speeds, but if the viscosity is kept low enough disc speed has no effect. It is believed that this effect is caused by a reduction of probe collection efficiency when high disc speeds are combined with relatively high viscosity spin fluids.





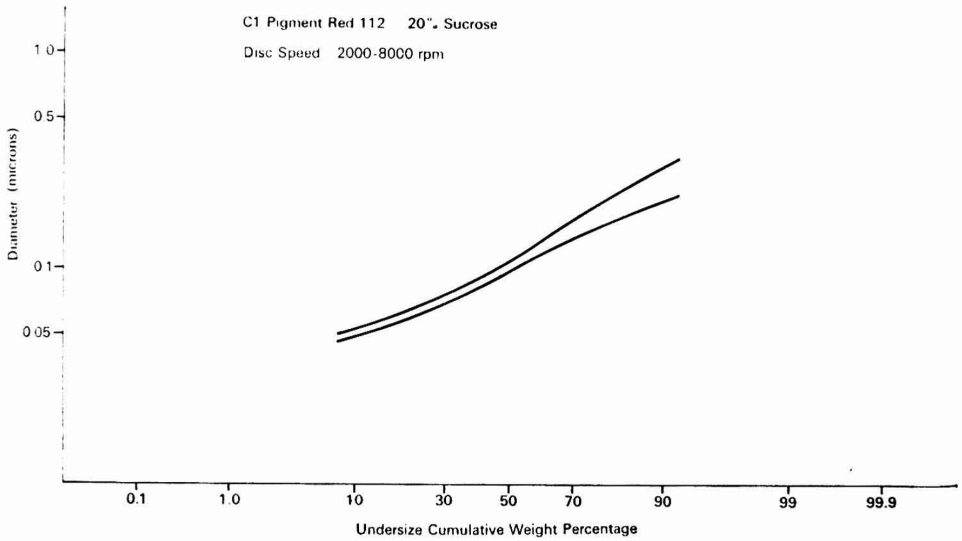


Fig. 11. 95 per cent Confidence limits

Table 5

Significance of difference tests. Tables 1 and 4 (Runs 13, 14, 15)

Undersize percentage	Standard deviation (σ)	Students "t"	Degrees of freedom	Significance level
10	0.00187	1.026	6	>15%
25	0.00141	0.972	6	15%
50	0.00208	1.904	6	5%
75	0.00698	0.491	6	>30%
90	0.01055	0.610	6	25%

Table 6

Significance of difference tests. Tables 2 and 4 (Runs 13, 14, 15)

Undersize percentage	Standard deviation (σ)	Students "t"	Degrees of freedom	Significance level
10	0.00123	7.573	6	<0.5%
25	0.00135	7.916	6	<0.5%
50	0.00238	5.699	6	<0.5%
75	0.00986	3.015	6	0.5-1.0%
90	0.01740	1.441	6	10%

Buffer layer volume effect

Although Atherton and Tough[13] have shown that the extra volume of 1 ml of dispersion does not create a significant error on the calculated diameter, the effect of buffer layer volume on the stability of the system has been studied with the intention of finding the lowest useful volume. C.I. Pigment Red 112 was measured at 0.5 per cent w/w paste concentration using 10 per cent sucrose and a 0.5 ml dispersion volume. Three repeat determinations of size were carried out at three 0.01 per cent w/v aqueous Triton X-100 buffer layer volumes (1, 0.5 and 0.25 ml). Results are given in Table 7.

Table 7

Effect of buffer layer volume

Run number	Diameters at undersize % (microns)					Buffer layer volume (ml)
	10	25	50	75	90	
13	0.041	0.058	0.093	0.155	0.238	1.00
14	0.044	0.057	0.087	0.133	0.213	
15	0.044	0.059	0.091	0.148	0.232	
16	0.043	0.058	0.093	0.149	0.213	0.50
17	0.045	0.059	0.092	0.144	0.200	
18	0.047	0.062	0.095	0.143	0.220	
19	0.046	0.064	0.094	0.141	0.220	0.25
20	0.045	0.065	0.100	0.155	0.230	
21	0.046	0.062	0.094	0.150	0.230	

Table 8

Analysis of variance. Buffer volume effect

Source of variation	Sum of squares	Degrees of freedom	Mean sum of squares	Variance ratio (F)	Significance of variance
Diameter (D) ..	0.18709747	2	0.09354874	2636.0	$\leqslant$1.0%
Buffer volume (B)	0.00021205	4	0.00005301	1.494	>10%
B and D Interaction	0.00044506	8	0.00005563	1.568	>10%
Residual	0.00106467	30	0.00003549		
Total	0.18881925	44			

Results of an analysis of variance on the effects of buffer volume and diameter are given in Table 8. The high significance of the D effect is to be expected, obviously ; also there is no effect of buffer layer volume. Because of this insignificance it is possible to obtain an indication of the repeatability of the technique from the fourteen size distribution runs, numbers 1—5 and 13—21. This is given in Table 9 and the control chart shown in Fig. 12.

Table 9

Repeatability of technique C.I. Red 112

Undersize percentage	Mean (microns)	Standard deviation (σ)	Relative standard deviation (%)	95% limits (1.98σ)
10	0.0434	0.00253	5.83	0.0050
25	0.0599	0.00253	4.22	0.0050
50	0.0932	0.00281	3.02	0.0056
75	0.1469	0.00582	7.84	0.0115
90	0.2222	0.01065	9.50	0.0211

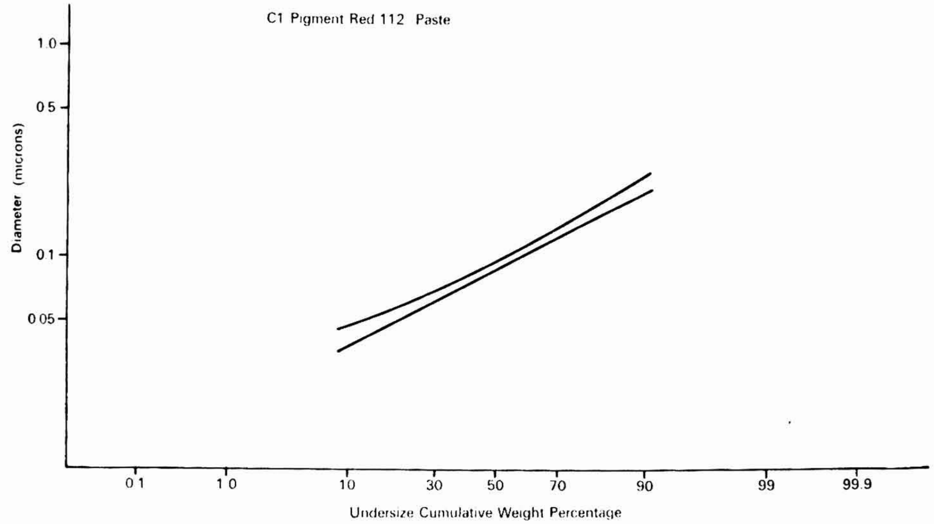


Fig. 12. 95 per cent Confidence limits

Critical concentration effect

As mentioned earlier, Burt[10] and Scarlett[9] suggested a critical concentration exists above which stable conditions can not be achieved with the two layer technique. If this were true for the buffered layer technique it should be shown by a significant concentration effect in an analysis of variance for results from several concentrations. Three repeat determinations of size were made on each of five concentrations of C.I. Pigment Orange 5 paste in 0.01 per cent w/v aqueous Triton X-100 using 10 per cent w/v aqueous sucrose as spin fluid and 0.01 per cent w/v aqueous Triton X-100 as buffer layer. The buffer layer and dispersion volumes were kept at 1.0 ml except for the highest pigment concentration when 2 ml buffer layer and 0.5 ml dispersion volumes were necessary to create repeatably stable conditions. The pigment was solubilised with acetone for the colorimetric analysis. The paste concentrations used were 5, 1, 0.5, 0.1 and 0.01 per cent w/w. A slightly more elaborate technique was needed to obtain sufficiently strong solutions for analysis of fractions from the 0.01 per cent paste concentration. The fractions were collected into volumetric flasks, as usual ; a small amount of MEK was added and the mixture transferred to a separating funnel. Sufficient MEK was added to give two immiscible layers, the lower being aqueous sucrose, the upper a pigment solution in MEK. The aqueous phase was transferred into the original flask and the solvent phase into a 50 ml flask. This aqueous phase separation was repeated twice. Finally a few drops of acetone were added to the combined solvent phases to solubilise any trace water and the solution was made up to 50 ml. Colorimetric analysis was carried out in the usual way. Results are given in Table 10 and the variance analysis in Table 11

There is no significant concentration effect over a 500 fold range. It was considered neither possible nor necessary to extend the range below the lowest pigment concentration used, that is approximately 0.004 per cent w/w. The overall standard deviations about the means for each undersize percentage, and the 95 per cent confidence limits are given in Table 12 and a control chart in Fig. 13.

Table 10

C.I. Pigment Orange 5. Concentration effect

Paste concentration	Run number	Diameter (microns) at undersize percentage				
		10	25	50	75	90
5%	22	0.112	0.145	0.191	0.315	0.55
	23	0.110	0.145	0.185	0.310	0.54
	24	0.112	0.150	0.195	0.310	0.53
1%	25	0.102	0.135	0.180	0.290	0.54
	26	0.105	0.140	0.183	0.290	0.52
	27	0.108	0.140	0.180	0.300	0.56
0.5%	28	0.098	0.130	0.182	0.285	0.50
	29	0.110	0.132	0.181	0.285	0.56
	30	0.100	0.128	0.180	0.290	0.51
0.1%	31	0.108	0.138	0.172	0.280	0.50
	32	0.102	0.131	0.175	0.280	0.53
	33	0.102	0.135	0.178	0.285	0.54
0.01%	34	0.103	0.130	0.172	0.290	0.56
	35	0.102	0.135	0.182	0.290	0.62
	36	0.100	0.134	0.172	0.285	0.66

Table 11

Concentration effect. Analysis of variance

Source of variation	Sum of squares	Degrees of freedom	Mean sum of squares	Variance ratio (F)	Significance of variance
Concentration (C)	0.004366	4	0.001092	1.148	>10%
Diameter (D) ..	1.939651	4	0.484913	509.9	⩽1%
C and D Interaction	0.015217	16	0.000951	5.011	<1%
Residual	0.009489	50	0.0001898		
Total	1.968723	74			

Table 12

Standard deviations about means. C.I. Orange 5

Undersize percentage	Mean (microns)	Standard deviation (σ)	Relative standard deviation (%)	95% Conf. limits (1.98σ)
10	0.1049	0.00467	4.45	0.0093
25	0.1365	0.00961	7.04	0.0190
50	0.1805	0.00658	3.65	0.0130
75	0.2923	0.01120	3.83	0.0222
90	0.548	0.0429	7.83	0.0849

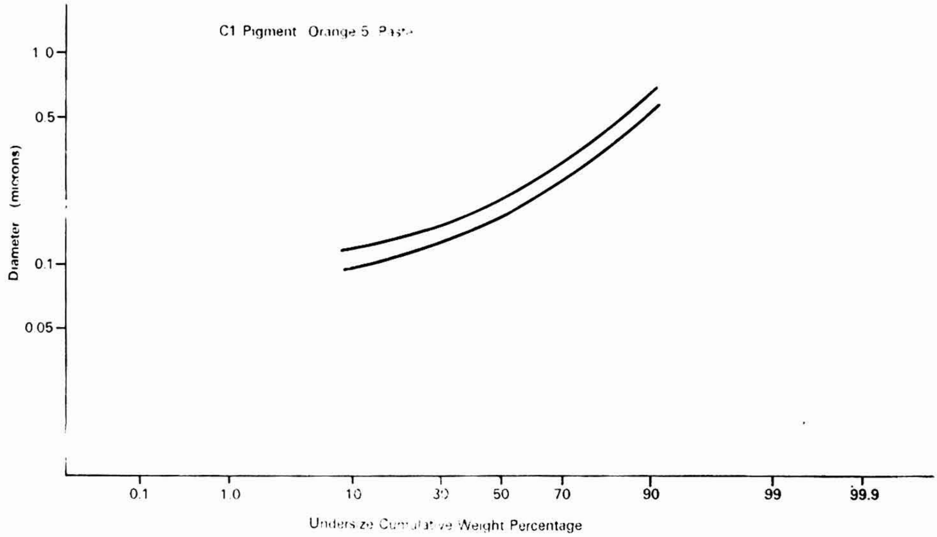


Fig. 13. 95 per cent Confidence limits

Discussion

The buffered layer technique is a convenient method of obtaining stable sedimentation conditions. There are significant differences when high speeds are used at relatively high spin fluid viscosities. Since using high speeds at lower spin fluid viscosities gave significantly the same results as 4,000 rpm with 20 per cent sucrose, it is suggested that the differences are caused by inefficient probe collection at the high speed, low spin fluid volume, higher viscosity end. It is only fair to point out that the manufacturers of the centrifuge have amended the probe design to avoid loss in collection efficiency such as was observed in this work. Not having used the new system, the author is unable to comment.

The trials on buffer layer volume have shown no significant effect but, in practice, the 0.25 ml volume is much more difficult to handle and care is needed to avoid over or under boosting the system. This volume was taken as a practical lower limit of buffer layer volume for this reason.

There is no significant effect over a five-hundred fold variation of pigment concentration and this was considered sufficiently wide to conclude that no critical concentration exists with this technique. From practical considerations, 5 per cent w/w paste concentration was prone to instability, hence the use of a 2 ml buffer layer. Although buffer layer volume has been shown to have no significant effect a 2 ml buffer layer will lead to inaccuracies in the calculated diameters. This is why the 5 per cent concentration results appear somewhat higher than the rest.

Tables 9 and 12 show that relative standard deviations about mean diameters vary between 3 and 10 per cent. It should be remembered that the diameters quoted are all equivalent spherical diameters, based on particles having the same hydrodynamic properties as the spheres. A variation below 10 per cent can therefore be considered reasonable.

Conclusions

Several techniques for using the ICI/Joyce Loebl disc centrifuge to analyse the size distributions of aqueous organic pigment pastes have been investigated. The only method which gives sufficiently stable conditions is the buffered line start technique. It has been shown that there is no critical concentration even over a 500 fold variation and volume effects of the buffer layer have no significance. The viscosity of the spin fluid can have an adverse effect on the collection efficiency of the probe at high speeds, but an alternative, improved, version is now available. The repeatability, on mean diameters as low as 0.04 microns, has been shown to be good, the scatter on the results being less than 10 per cent.

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An investigation of the reaction between linseed oil and pentaerythritol

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Summary

The investigation entails the quantitative analysis by a thin layer chromatographic method of samples from the reaction of linseed oil with pentaerythritol. It shows that optical density readings for separated and visualised components can be taken directly from the chromatoplate and indicates the most economical reaction time for the system examined.

Une investigation sur la réaction d'huile de lin avec pentaérithritol

Résumé

L'investigation s'agit de l'analyse quantitative par chromatographie en couche mince des échantillons en provenance de la réaction d'huile de lin avec pentaérithritol. Elle démontre que les lecteurs de densité optique à partir des constituants séparés et révélés peuvent s'effectuer directement sur la chromatoplaque et également elle indique la durée de réaction la plus économique à l'égard du système examiné.

Die Reaktion Zwischen Leinöl und Pentaerythritol—Eine Untersuchung

Zusammenfassung

Die Untersuchung besteht aus der quantitativen Analyse von Proben aus Reaktionsprodukten von Leinöl mit Pentaerythritol mittels Dünnschicht-Chromatografie. Sie erweist, dass Ablesungen der optischen Dichte abgetrennter und sichtbar gemachter Komponenten direkt von der Chromatoplatte erfolgen können und zeigt die sparsamste Reaktionszeit für das geprüfte System auf.

Исследование реакции между льняным маслом и пентаэритритом

Резюме

Исследование состоит из количественного анализа тонкослойным хроматографическим методом образцов реакции льняного масла с пентаэритритом. Исследование показывает что показания оптической плотности для разделенных и видимых составных частей могут быть взяты непосредственно из хроматографической съемки и дает самое экономное время протекания реакции для исследуемой системы.

Introduction

The separation of glyceride mixtures on thin layers of silicic acid depends upon the hydroxyl content of the components. The more free hydroxyl groups there are in the molecule the more strongly it will be adsorbed on the silicic acid. The two types of diglycerides (1, 2 and 1, 3) can be separated because the hydroxyl group in the 2 position is screened by other groups and is therefore less available for adsorption than those in the 1, 3 positions.

Workers at the Paint Research Station, Teddington, Middlesex, have successfully used thin layer chromatography for the separation and quantitative determination of glyceride mixtures using a concentration gradient technique of development[1]. The separated components can be visualised by charring with sulphuric acid to produce dark coloured spots[2]. It has been found that, for glycerides, an integrated function of the size of the spot and its optical density (as produced by sulphuric acid) is directly proportional to the weight of the compound in the spot[3,4]. The integrated function is obtained by measuring the area under the peaks given by plotting the optical density against distance travelled along the plate.

Experimental

The reaction charge used in the present work was as follows :—

Alkali refined linseed oil : 878 g.
Pentaerythritol : 272 g.
i.e. 1 : 2 molecular ratio.

The catalyst, litharge, was used at 0.05 per cent by weight on the oil. The reaction was carried out in a 1 litre glass reaction vessel with ground glass joints, fitted with a mechanical stirrer and heated by an electric mantle. The temperature was maintained within ± 2°C. of 200°C. throughout the reaction.

The samples were taken out of the reaction mixture at definite intervals, close at first then lengthening later. They were quickly cooled to prevent any reverse reaction occurring. 5 per cent solutions of the samples were prepared in 1 : 1 acetone : ethyl alcohol.

For optical density determinations, an " Elphor " Photometer (Dr. Bender and Dr. Hobein) was obtained. This apparatus takes manual readings at 1 mm steps along a distance of 16 cms. The film holder is moved by a rack and pinion device in 1 mm intervals. It has a fixed slit of 1 mm width and 3½ cms length. This was reduced to 5 mm length by fitting a metal mask, so that, when later the optical density of the spots was measured, the light passed through the centre of the spots only. The film holder was fitted with two thin glasses of 16 cms × 4 cms which are made to sandwich films being measured. These were removed and more substantial glasses of the same width and length were prepared ; these were to be used as the chromatographic plates themselves.

No proprietary apparatus was available for application of thin layers of silica gel to this size of plate, so an applicator was made which gave a wet film thickness dependent upon two metal shims placed on the plate. The silica gel slurry was drawn down the plate by a doctor blade. After some experimentation, it was found that the best films were those of around 230 microns dry film thickness. At 450 microns the separation of the spots was poor and overlapping occurred. The slurry mixture used was as follows :—

Kieselgel G (Merck)	1.5 g.
Distilled Water	2.6 ml.

The coated plates were allowed to stand overnight ; they were then activated by heating at 120°C for 15 minutes ; after cooling, 0.01 ml spots of the 5 per cent solutions of the samples in 1, 1 acetone : ethyl alcohol were applied by micropipette (using a " Vadosa " filling device) in the centre of a base line 1½ cm from the end of the plate. The plates were then replaced in the oven for two minutes to remove the solvent.

The concentration gradient technique as developed at the Paint Research Station was used, and the solvent used in their work on glyceride mixtures tried, i.e. 20 per cent diethyl ether in petroleum ether increasing to 60 per cent diethyl ether in petroleum ether.

50 ml of 20 per cent diethyl ether in petroleum ether was poured into a " Shandon " circular developing tank, and filter paper strips were placed in the tank so as to dip into the solvent. A lid was fitted and the tank was then placed on a magnetic stirrer and allowed to become saturated with vapour for an hour.

The plates were placed in the tank in as near a vertical position as possible and the lid quickly replaced. A burette was fitted, with its jet passing through a tight fitting hole in the lid. In this way 50 ml of diethyl ether were titrated into the tank during development whilst still maintaining a saturated atmosphere. The diethyl ether was added at a constant rate over the first 20 minutes of the 25 minute development time, for a 14 cm travel along the plate. It was found that the magnetic stirrer tended to throw droplets of solvent about the tank, some of which landed on the plates. To prevent this a half-pint plain tinplate can was treated as follows :—

The bottom was cut out to produce an open ended cylinder, and V shaped cuts were made in the walls at one end. The cylinder was then placed in the tank and held in place by a glass rod across the tank. With the stirrer magnet then placed inside the cylinder a good stirring rate could be achieved without any droplets escaping. The burette was fixed so that the added solvent dropped into the cylinder and was thus well dispersed.

After removal from the tank the plates were heated for 1 minute at 120°C to remove solvent and, after cooling, were sprayed with 50 per cent aq. sulphuric acid. This was done using a " Shandon " aerosol spray with a glass jar and spray nozzle, the whole being enclosed in a polythene bag. Care was taken to spray enough acid to char the spots without soaking the adsorbent. This was important, as will appear later. The sprayed panels were heated for two hours in a covered litre beaker in an oven at 120°C to char the spots.

The separation of the spots was rather poor ; they were not spread sufficiently along the length of the plate. Some spots were obtained however, and the plates were used to investigate the next stage of the process.

At this stage it is usual to photograph the plate and measure the optical density of the spots from the negative. As no apparatus was available for this, it was necessary to devise a method of taking optical density readings directly from the plates. This was done by spraying the dried plates with a 25 per cent solution of silicone oil (MS.200/20. Midland Silicones Ltd.) in petroleum ether until the plate showed a uniform translucency on the uncharred parts of the plate. The silicone oil was found to be completely unaffected by the residual sulphuric acid.

It was found, however, that, if excess acid had been sprayed on the plate, the residue after heating was sweated out on spraying with silicone oil and could disrupt the spots. The translucent plates were then fitted into the film holder of the " Elphor " photometer and the output of the lamp adjusted so as to give a near zero reading on the uncharred parts of the plate. The instrument gives readings for optical density from 0.0 to 2.0, the full scale deflection being 20 microamps. Starting with the slit a few mm before the base line, the readings were taken at 1 mm steps along the plate. The instrument proved to be quite sensitive, as good response was given even for faint spots.

It was decided that the composition of the developing solvent be varied to see if better separation could be achieved. Various proportions of diethyl ether in petroleum ether were tried, and it was found that, by starting with 40 per cent diethyl ether in petroleum ether (60-80°C), and increasing the concentration of the diethyl ether to 70 per cent during the development, a much better separation was obtained.

The diethyl ether was added over the first 20 minutes of development time, the total development time being 30 minutes.

Readings of optical density were taken directly from the plates, as previously described. The values of optical density were plotted against distance travelled along the plate, and, from the curves obtained, the areas under the peaks were determined. Six peaks were obtained having the following mean Rf values :

0.0, 0.1, 0.25, 0.32, 0.4, 0.6.

The Paint Research Station investigators found, in their separations of partial ester mixtures of the linseed oil/pentaerythritol reaction by thin layer chromatography, that the components gave the following Rf values. Silica gel films were used, and a solvent changing from 20 per cent diethyl ether in petroleum ether to 60 per cent diethyl ether during development.

0.0	Glycerol
0.08	Pentaerythritol monoester
0.18	Monoglycerides
0.28	Pentaerythritol diesters
0.37	1, 2 Diglycerides
0.46	Pentaerythritol triesters and 1, 3 diglycerides
0.81	Triglycerides and pentaerythritol tetraesters

The glycerol used in the experiments described in this paper produced a peak at the origin when spotted on a plate and treated according to the method described. Pentaerythritol produced a very small peak, also at the origin.

However, the effect of free glycerol on the very intense spot at the origin of the plates was thought to be negligible, as if all the glycerol in the linseed oil became free, the amount present would be so small as to produce hardly any peak at all. (This was deduced from the size of the peak given for the weight of glycerol taken in the above experiment.) Likewise, the effect of free pentaerythritol can be discounted.

To check the position of the triglycerides a spot of linseed oil was developed, and was found to give a dense spot at 0.6 Rf value. Very faint spots were given which corresponded to those at 0.32 and 0.4 on the plates of the partial ester mixtures. This confirms that the component at 0.6 Rf value is the triglyceride and the faint spots given by the linseed oil are traces of 1, 2 and 1, 3 diglycerides in the oil.

Although the Rf values obtained are lower than those recorded at the Paint Research Station, the components will be separated in the same order, as the developing solvents are the same.

The components may therefore be identified as follows :—

Rf value	
0.0	Pentaerythritol monoester
0.1	Monoglycerides
0.25	Pentaerythritol diesters
0.32	1, 2 Diglycerides
0.40	Pentaerythritol triesters and 1, 3 diglycerides
0.60	Triglycerides and pentaerythritol tetraesters

It has been suggested in some literature that the response to charring by sulphuric acid may vary from triglyceride to monoglyceride, but this applied to saturated fatty acid esters. Unsaturated compounds give greater response to charring than saturated ones.

It will be observed from the areas under the curves that, at the times when there is most variation in concentration of the components, i.e. in samples 1, 2, 3 and 4, the area under the total curve remains almost constant.

Results : (0.01 ml. of 5% solution = 5×10^{-4} g. of sample)

Sample 1 15 min. @ 200°C.

Peak 1	3.967 in.^{2}	= 1.59×10^{-4} g.	31.8% Pentaerythritol monoesters
Peak 2	2.815 in.^{2}	= 1.13×10^{-4} g.	22.6% Monoglycerides
Peak 3	0.796 in.^{2}	= 3.19×10^{-5} g.	6.4% Pentaerythritol diesters
Peak 4	1.420 in.^{2}	= 5.70×10^{-5} g.	11.4% 1, 2 Diglycerides
Peak 5	1.273 in.^{2}	= 5.10×10^{-5} g.	10.2% Pentaerythritol triesters and 1, 3 diglycerides
Peak 6	2.186 in.^{2}	= 8.77×10^{-5} g.	17.6% Triglycerides and pentaerythritol tetraesters
	12.457 in.^{2}	= 5.0×10^{-4} g.	of sample

Sample 2 30 min. @ 200°C.

Peak 1	4.835 in.^{2}	= 1.93×10^{-4} g.	38.6% Pentaerythritol monoesters
Peak 2	3.604 in.^{2}	= 1.44×10^{-4} g.	28.8% Monoglycerides
Peak 3	0.732 in.^{2}	= 2.90×10^{-5} g.	5.8% Pentaerythritol diesters
Peak 4	1.102 in.^{2}	= 4.40×10^{-5} g.	8.8% 1, 2 Diglycerides
Peak 5	1.473 in.^{2}	= 5.88×10^{-5} g.	11.8% Pentaerythritol triesters and 1, 3 diglycerides
Peak 6	0.779 in.^{2}	= 3.11×10^{-5} g.	6.2% Triglycerides and pentaerythritol tetraesters
	12.525 in.^{2}	= 5.0×10^{-4} g.	of sample

Sample 3 45 min. @ 200°C.

Peak 1	4.900 in.^{2}	$= 1.90 \times 10^{-4}$ g.	38.0% Pentaerythritol monoesters
Peak 2	3.745 in.^{2}	$= 1.45 \times 10^{-4}$ g.	29.0% Monoglycerides
Peak 3	0.330 in.^{2}	$= 1.28 \times 10^{-5}$ g.	2.6% Pentaerythritol diesters
Peak 4	0.805 in.^{2}	$= 3.13 \times 10^{-5}$ g.	6.2% 1, 2 Diglycerides
Peak 5	1.897 in.^{2}	$= 7.37 \times 10^{-5}$ g.	14.7% Pentaerythritol triesters and 1, 3 diglycerides
Peak 6	1.200 in.^{2}	$= 4.66 \times 10^{-5}$ g.	9.3% Triglycerides and pentaerythritol tetraesters
	12.877 in.^{2}	$= 5.0 \times 10^{-4}$ g.	of sample

Sample 4 1 hour @ 200°C.

Peak 1	5.185 in.^{2}	$= 2.10 \times 10^{-4}$ g.	42% Pentaerythritol monoesters
Peak 2	3.730 in.^{2}	$= 1.51 \times 10^{-4}$ g.	30% Monoglycerides
Peak 3	0.526 in.^{2}	$= 2.13 \times 10^{-5}$ g.	4.2% Pentaerythritol diesters
Peak 4	0.720 in.^{2}	$= 2.91 \times 10^{-5}$ g.	5.8% 1, 2 Diglycerides
Peak 5	1.528 in.^{2}	$= 6.18 \times 10^{-5}$ g.	12.4% Pentaerythritol triesters and 1, 3 diglycerides
Peak 6	0.660 in.^{2}	$= 2.67 \times 10^{-5}$ g.	5.4% Triglycerides and pentaerythritol tetraesters
	12.349 in.^{2}	$= 5.0 \times 10^{-4}$ g.	of sample

Full results can be seen in Table 1

If it were the case that the degree of blackening varied greatly for the components under examination, then, as one component decreased in concentration, say the triglycerides, the decrease in area under its peak would not be balanced by the increase in area under the other peaks. As it is, the decrease in area under the triglyceride peak is balanced by an increase in area under the monoester peaks. It has been taken, therefore, that the response to blackening is virtually equal for all the components, and that the total area under the curves is equivalent to the weight of sample spotted on the plate. The various percentages of components have then been calculated from their separate areas. The object of the reaction is, of course, to obtain a high yield of monoesters. Fig. 1 shows that, at the reaction temperature of 200°C, there is little increase in yield of monoesters after the first two hours. The curves for the other components also show little change in concentration.

Table 1 shows the percentage composition of the reaction mixture at the intervals at which the samples were taken.

Table 2 shows the change in concentration of the combined monoesters with time. Fig. 2, plotted from these figures, clearly indicates the time at which it is no longer economical to proceed with the reaction, as the gain in monoester is very small for large increase in time.

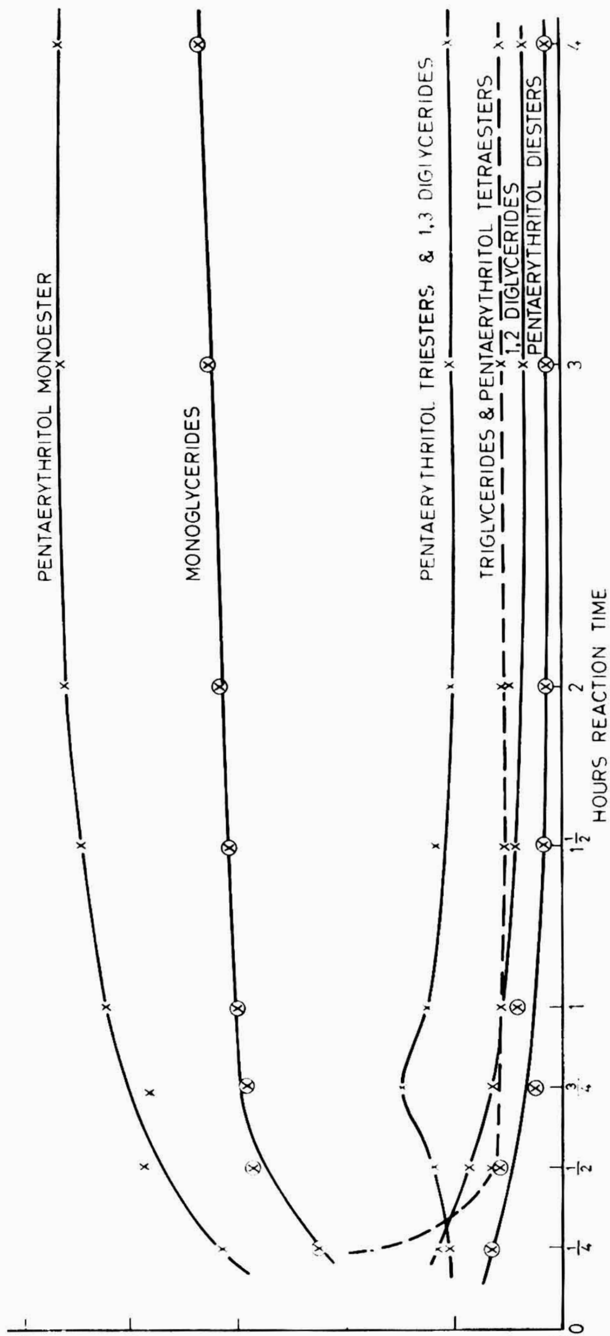

Fig. 1. Percentage composition of reaction mixture v reaction time

Table 1

Component	15 min.	30 min.	45 min.	1 hour	1½ hours	2 hours	3 hours	4 hours
Pentaerythritol monoesters	31.8%	38.6%	38.0%	42.0%	44.5%	46.0%	46.2%	46.4%
Monoglycerides	22.6%	28.8%	29.0%	30.0%	30.7%	31.8%	32.6%	33.2%
Pentaerythritol diesters	6.4%	5.8%	2.6%	4.2%	1.5%	1.2%	1.3%	1.2%
1, 2 Diglycerides	11.4%	8.8%	6.2%	5.8%	4.3%	5.0%	3.4%	3.4%
Pentaerythritol triesters and 1, 3 diglycerides	10.2%	11.8%	14.7%	12.4%	11.7%	10.2%	10.6%	10.2%
Triglycerides and pentaerythritol tetraesters	17.6%	6.2%	9.3%	5.4%	7.1%	5.8%	5.8%	5.7%

Table 2

Time 'T' hours	% Pentaerythritol monoester	% Monoglyceride	% Combined monoesters "C"	Increase in "C" per ¼ hour "Δ C"	$\frac{\Delta C}{\Delta T}$	Time 'T' hours
¼	32.0	22.5	54.5	—	—	—
½	35.5	28.0	63.5	9.0	36.0	½
¾	40.0	29.8	69.8	6.3	25.2	¾
1	42.4	30.1	72.5	2.7	10.8	1
1¼	44.0	30.5	74.5	2.0	8.0	1¼
1½	44.6	31.0	75.6	1.1	4.4	1½
1¾	45.3	31.3	76.6	1.0	4.0	1¾
2	45.9	31.7	77.6	1.0	4.0	2
2¼	46.0	32.0	78.0	0.4	1.6	2¼
2½	46.0	32.2	78.2	0.2	0.8	2½
2¾	46.0	32.4	78.4	0.2	0.8	2¾
3	46.0	32.6	78.6	0.2	0.8	3
3¼	46.1	32.8	78.9	0.3	1.2	3¼
3½	46.1	33.0	79.1	0.2	0.8	3½
3¾	46.2	33.0	79.2	0.1	0.4	3¾
4	46.3	33.0	79.3	0.1	0.4	4

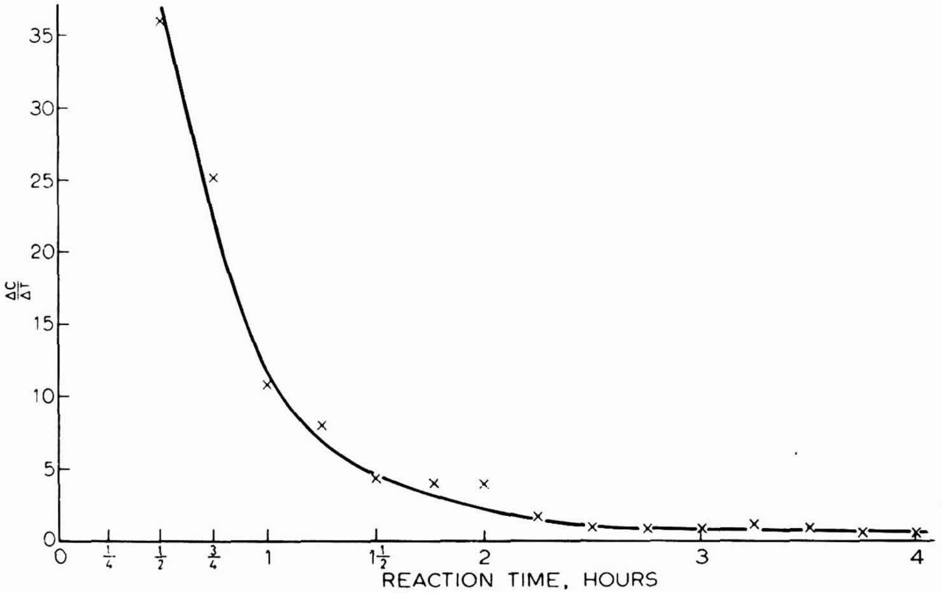

Fig. 2. Change in concentration of combined monoesters v reaction time

Conclusions

The optimum time for the production of monoesters from linseed oil and pentaerythritol at a reaction temperature of 200°C is two hours when using litharge as catalyst to the extent of 0.05 per cent on the oil. The combined yield of monoesters is about 78 per cent.

Thin layer chromatography has proved to be a useful means of following the reaction. The weakness of the technique is the method of making the spots visible. Too little or too much acid can give trouble.

The " Elphor " photometer for taking the absorbance readings is easy to use and has given good results.

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The importance of physical effects on the action of catalytic surfaces in vinyl polymerisation*

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Summary

The importance of steric considerations in polymerisation, and the effects of catalysis on the steric control of addition polymerisation are discussed.

Several theories of catalytic action in vinylic polymerisations are outlined, and the strengths and weaknesses of each discussed in relation to current work.

L'importance des effets physiques sur la mode d'action des surfaces catalytiques dans le domaine de polymérisation vinylique

Résumé

On discute l'importance des considérations stériques dans le domaine de polymérisation et également les effets qu'exercent des catalyseurs sur la configuration stérique des polymères d'addition.

On trace les grandes lignes de plusieurs théories de l'action catalytique en ce qui concerne la polymérisation vinylique, et l'on discute également les pours et les contres de chaque théorie au point de vue des expériences courantes.

Die Wichtigkeit Physikalischer Funktionen für das Verhalten Katalytischer Oberflächen bei der Vinylpolymerisation

Zusammenfassung

Die Bedeutung sterischer Gesichtspunkte bei Polymerisierung, und die Auswirkungen, welche Katalyse auf die sterische Kontrolle von Additionspolymerisation hat, wird besprochen.

Es werden verschiedene Theorien für katalytische Wirkung bei der Polymerisation vinylartiger Verbindungen skizziert, und Vorteile oder Schwächen jeder einzelnen Theorie im Lichte der zur Zeit schwebenden Arbeiten besprochen.

Значение влияния физических эффектов на действие каталитических поверхностей в виниловой полимеризации

Резюме

Обсуждается значение структурных соображений в полимеризации и влияние катализа на структурный контроль добавочной полимеризации. Предлагается несколько теорий каталитического действия в виниловой полимеризации и обсуждаются их преимущества и недостатки по отношению к текущей работе.

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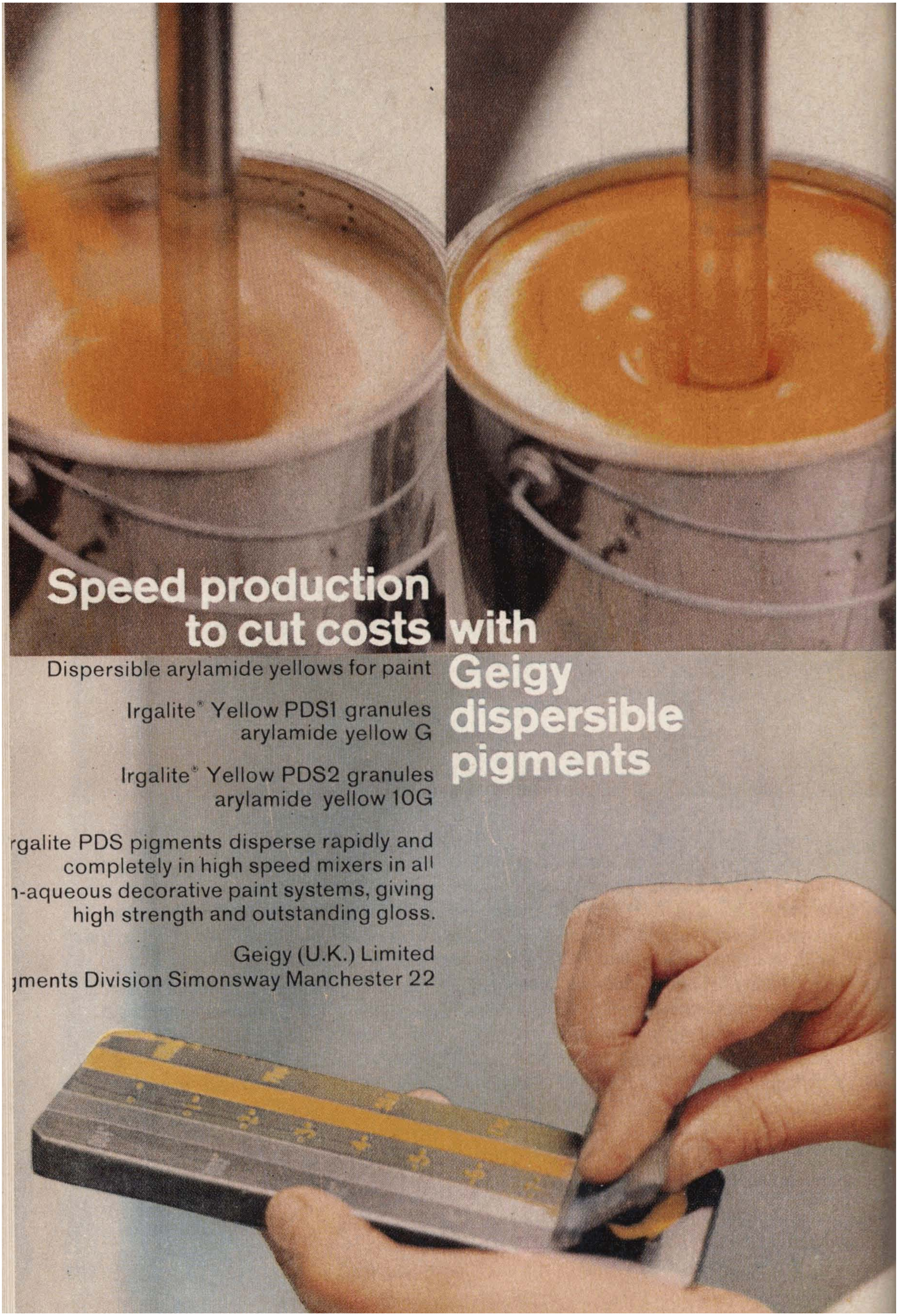

Introduction

Solid catalysts are important in polymerisation because they are among the best means of controlling the growth of the polymer molecules and, in particular, the *steric* control of the addition of each monomer unit. Fig. 1 shows what happens if a vinyl monomer ($CH_2=CHX$) is allowed to polymerise without steric control. In the chain of a vinyl polymer, alternate carbon atoms are asymmetric. There are two ways of disposing the tetrahedral substituents at every alternate carbon atom. If no steric control is exerted as the chain grows, the configuration of these asymmetric carbon atoms is randomly disposed. This is the *atactic* or stereorandom configuration. The consequence is that the chain cannot take a regular conformation. The size of the substituent group (X) in Fig. 1 has been reduced for the sake of clarity. In most vinyl polymer chains there will be strong steric interference between adjacent substituent groups. The planar zig-zag conformation shown in Fig. 1 is normally prohibited and the chain will take the so-called *random coil* conformation shown in Fig. 2. Since a regular conformation of the chain is not possible, the solid state must be amorphous and have properties typical of amorphous polymers. The material will be isotropic and optically homogeneous. There will be no fibre-forming tendency since the strength of the material is the same in all directions. If the material does not absorb visible light, it will be transparent.

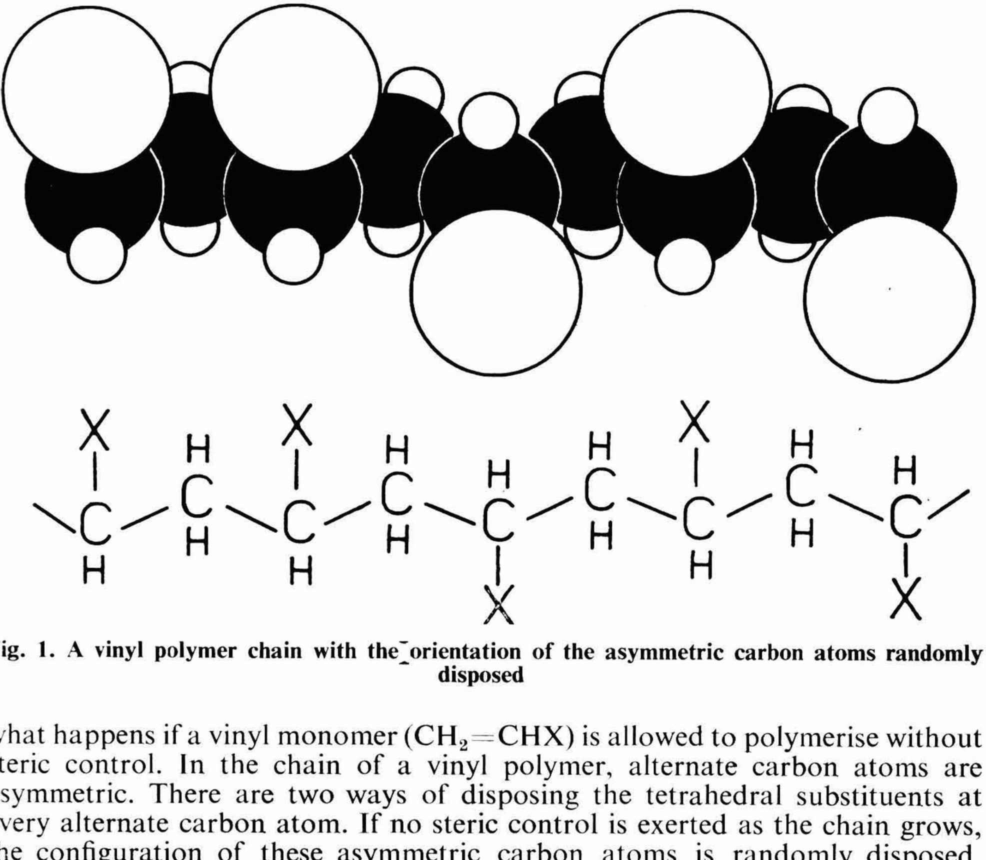

Fig. 1. A vinyl polymer chain with the orientation of the asymmetric carbon atoms randomly disposed

If the addition of the monomer units can be controlled sterically then an entirely different situation arises. Fig. 3 shows the chain configuration of the two most perfect stereoregulated forms of a vinyl polymer chain—the *isotactic* and

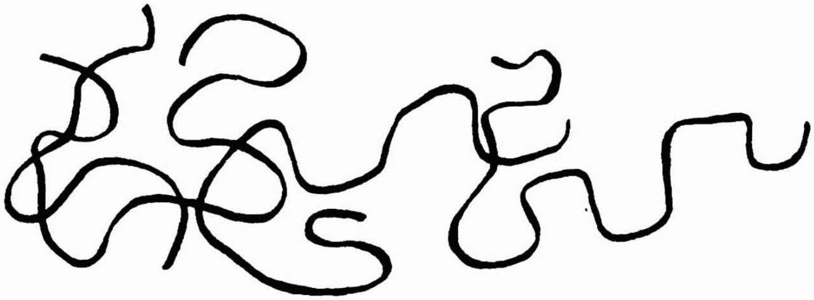

Fig. 2. Amorphous polymeric material with the polymer molecules taking a random coil conformation

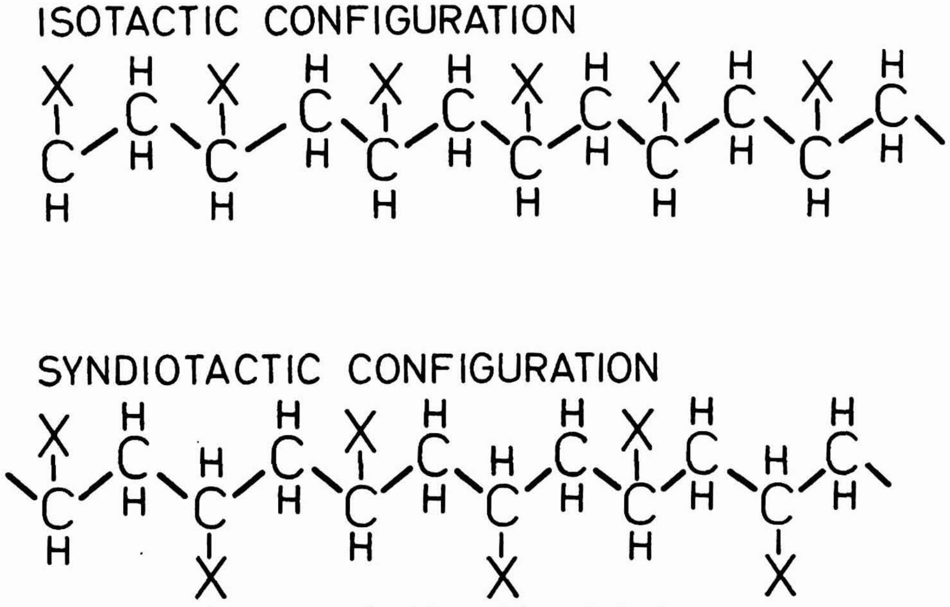

Fig. 3. Some stereoregulated forms of linear vinyl polymer molecules

the *syndiotactic*. In the former the same orientation of the asymmetric C-atoms is maintained along the chain. In the latter there is a regular alternation of configuration. The regular configuration means that the chains may take a regular conformation. In the syndiotactic configuration, the bulky side groups are as far apart as possible and planar zig-zag configurations are sometimes possible. In an isotactic configuration the bulk of the side groups forces the chain into a helical conformation (Fig. 4). Chains of regular conformation may be stacked in a regular lattice to form a crystalline polymer, as shown in Fig. 5[1].

Crystalline, or partly crystalline, polymeric material has characteristic properties which differ considerably from those of its amorphous counterpart. This is so even if the two materials have the same chemical composition and molecular weight. Single crystals or crystalline regions are anisotropic. As

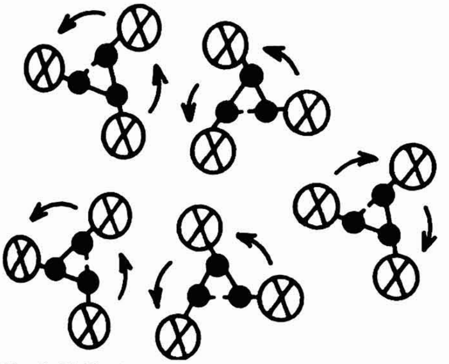

Fig. 5. Helical polymer chains (e.g. that shown in Fig. 4) stacked on a regular lattice in a crystalline region (see Ref. 1)

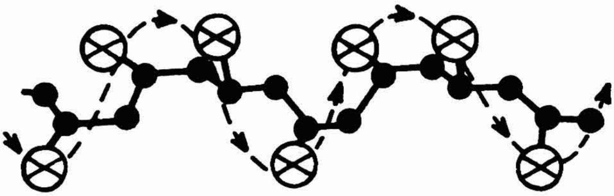

Fig. 4. A helical conformation of a stereo-regular vinyl polymer chain ● represents C-atom in the backbone, ⊗ the substituent group (see Ref. 1)

normally prepared, the crystalline regions will be randomly oriented and so the bulk will be isotropic. However, the crystalline regions may be drawn into line by stretching the material. If the raw product is in the form of a filament, cold drawing will pull the axes of the crystalline zones into line (Fig. 6). The material

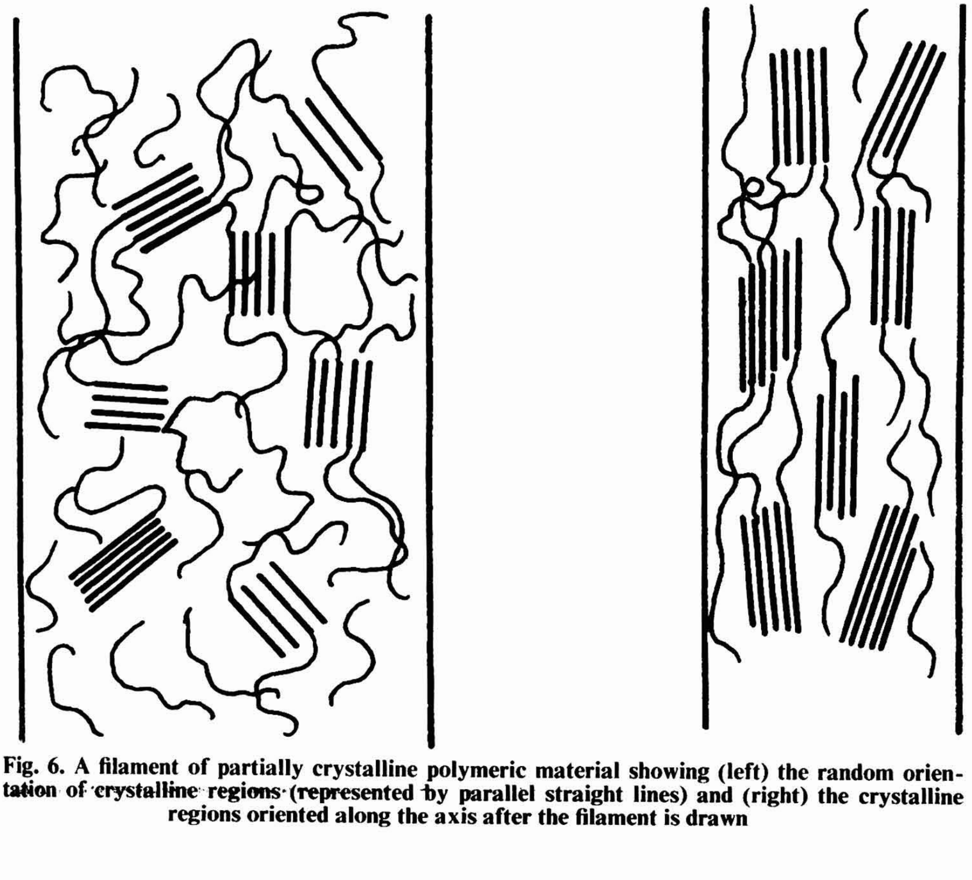

Fig. 6. A filament of partially crystalline polymeric material showing (left) the random orientation of crystalline regions (represented by parallel straight lines) and (right) the crystalline regions oriented along the axis after the filament is drawn

is now anisotropic. The molecular helices or zig-zags are aligned along the filament so that the cohesive strength is greatest in this direction. In other words the material has typical fibre-forming properties. The moulded material will also differ from the corresponding amorphous product : if not coloured, it will be opalescent due to the difference in refractive indices of the crystalline and amorphous regions. It will have a true melting point which is higher, often many degrees higher, than the softening temperature of the amorphous material. The density will be higher. Impact and tensile strength, Young's modulus, hardness and heat distortion temperature may be significantly increased.

There are very good reasons to stereoregulate the growing chains of a vinyl polymer.

The requirements for steric control

It is necessary to distinguish between two types of growing polymer chain. A vinyl monomer polymerises by a chain reaction. Chain growth occurs by successive additions of monomer units to a reactive chain end which reproduces itself after each addition. This is known as the *propagation* reaction. If steric control is to be exerted at each addition two cases have to be distinguished : *free* propagating species : *free radicals*, e.g.*

$$\sim CH_2\cdot CHX + CH_2{:}CHX \rightarrow \sim CH_2\cdot CHX\cdot CH_2CHX\cdot \qquad (1)$$

or *free ions*, e.g.

$$\sim CH_2\cdot CHX{:}^- + CH_2{:}CHX \rightarrow \sim CH_2\cdot CHX\cdot CH_2\cdot CHX{:}^- \qquad (2)$$

$$\sim CH_2\cdot CHX^+ + CH_2{:}CHX \rightarrow \sim CH_2\cdot CHX\cdot CH_2\cdot CHX^+ \qquad (3)$$

or *bound* propagating species. This case at one time appeared to be confined to metal-organic compounds. Propagation is the result of successive insertions of monomer in the bond joining the growing polymer chain to a metal atom. Two types of bound propagating species are known : polar, but essentially covalent, bonds :

$$\sim CH_2\overset{\delta-}{C}HX - \overset{\delta+}{Mt} + CH_2{:}CHX \rightarrow \sim CH_2\cdot CHX\cdot CH_2\cdot\overset{\delta-}{C}HX - \overset{\delta+}{Mt} \qquad (4)$$

and ion-pairs :

$$\sim CH_2\cdot CHX{:}^-, Mt^+ + CH_2{:}CHX \rightarrow \sim CH_2\cdot CHX\cdot CH_2\cdot CHX{:}^-, Mt^+. \qquad (5)$$

There is increasing evidence that some polymerisations previously thought to involve free cations do not do so[2] and so we ought to add

$$\sim CH_2\cdot CHX^+, Y^- + CH_2{:}CHX \rightarrow \sim CH_2\cdot CHX\cdot CH_2CHX^+, Y^- \qquad (6)$$

where Y^- is the appropriate gegen ion.

If a regular chain conformation is required all monomer units must add in a reproducible manner, e.g. the head-to-tail addition shown in the equations above. This is essential : one unit the wrong way round will disrupt a regular conformation for many units. This, fortunately, normally takes care of itself. There is sufficient difference in reactivity between the two ends of most monomer molecules to ensure that they add almost exclusively in one way. It may not

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*$\sim$Signifies the polymer chain attached to the propagating chain end

necessarily add the way shown in Equations 1-6, but whichever way it adds, the manner of addition is likely to persist for the length of the molecule.

This is the only prerequisite of steric control which is self-regulating. In every other case external orientating influences must be imposed on the propagating chain ends. For each type of propagating species, further categories have to be distinguished—the configuration of the reactive site. With carbon sites there are two possibilities—the planar trigonal sp^2 and the tetrahedral sp^3.

For a planar growth site the steric configuration of the carbon atom in the growing polymer chain is only fixed once the *next* monomer unit is added. In a free propagating species (Fig. 7), steric control of addition means that the rotation of the growth site must be restricted and the monomer can only be allowed to approach from one side of the plane of the site. At a given temperature one or other placement will be thermodynamically preferred, but, unless there are strong repulsive forces between substituents on the growth site and on the monomer, the free energy changes associated with the two modes of reaction will not be sufficiently different for one mode to overwhelm the other. The chain configuration will consist of units of the two steric configurations randomly disposed in the proportions prescribed by the relative free energy changes. In general, then, there is little chance of steric regulation. Adsorption of monomer on a surface is unlikely to help unless the rotation of the growth site can also be restricted. It is reasonably well established by electron-spin-resonance spectroscopy that most carbon free radicals have a planar trigonal structure. Free carbonium ions are believed to be planar and carbanions are probably either planar or else tetrahedral, but rapidly inverting. The geometrical requirements for steric control at a rapidly inverting tetrahedral site are the same as if it were planar.

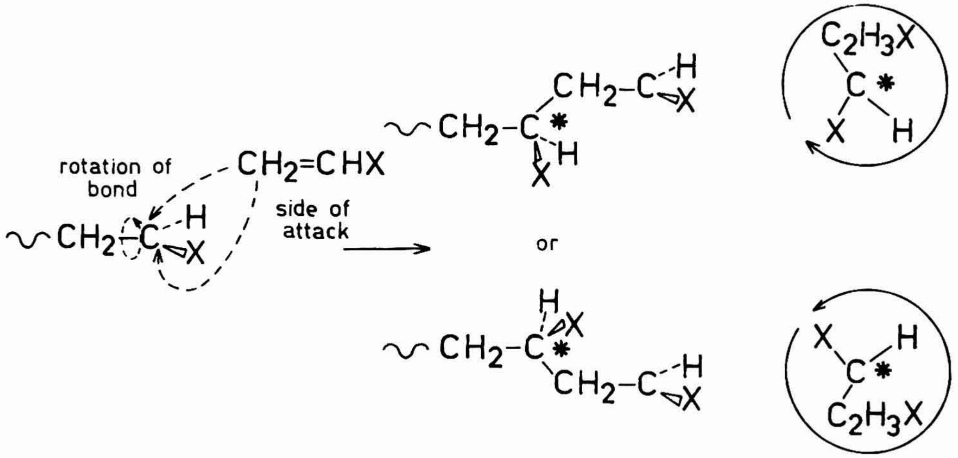


Fig. 7. Requirements for steric control at a free propagating species where the chain end has a planar configuration. The insets show the disposition of the substituents on the starred C-atom as viewed from the right of the diagram

At a non-invertible tetrahedral site the steric configuration of a C-atom is fixed as the monomer bearing it adds to the growth site. The problem of steric control then is a question as to whether the configuration of growth site is maintained or changed on addition of each monomer. The requirements are shown in Fig. 8. It is necessary to control the rotation of the monomer molecule, the side from which it is attacked, and the manner in which the double bond opens—cis or trans. The probability of effective steric control is not very great.

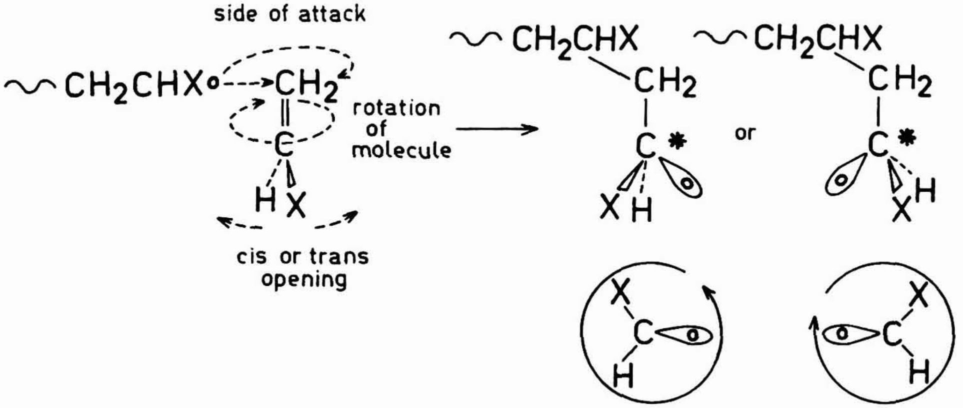


Fig. 8. Requirements for steric control at a free propagating species where the chain end has a tetrahedral configuration. The insets show the dispositions of the substituents on the starred C-atom, as viewed from the bottom of the diagram. O could represent the unpaired electron of a free radical, the non-bonding electron pair of an anion or the vacant orbital of a cation

One possibility would be preorientation of monomer molecules on a surface. If they were all suitably lined up by chemisorption, stereoregular polymers would be formed (Fig. 9). A mechanism of this type was suggested nine years ago by Friedlander[3]. It is pure speculation ; there has been no attempt to correlate bond distances with the lattice dimensions of the catalyst. On the whole it seems rather improbable—though there is no evidence for or against it.

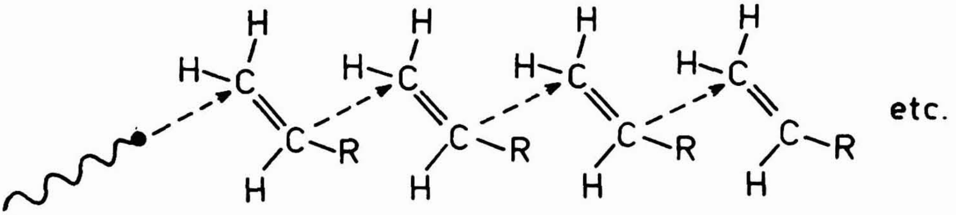


Fig. 9. A possible mechanism for the stereoregulated polymerisation of monomer molecules suitably preoriented on a catalyst surface (see Friedlander and Oita[3])

With bound propagating species, the requirements for steric control are considerably less stringent. If the growth site is a C-atom, it is tetrahedral and non-invertible. A bound tetrahedral site has relatively few degrees of freedom (Fig. 10). Since the reaction is now an insertion reaction, cis-opening of the double bond is assured. It is necessary to control the aspect in which the monomer presents itself and the side from which it approaches. These must either be the same at each addition of a monomer molecule, alternate, or occur in some more elaborate but regular pattern.

This is a much more controllable situation. Monomer molecules can be reproducibly oriented by *steric blocking* (the clash of bulky side groups on monomer and chain), *intermolecular forces* (electrostatic forces operate at long range so the monomer could be preoriented before the orbitals had over-

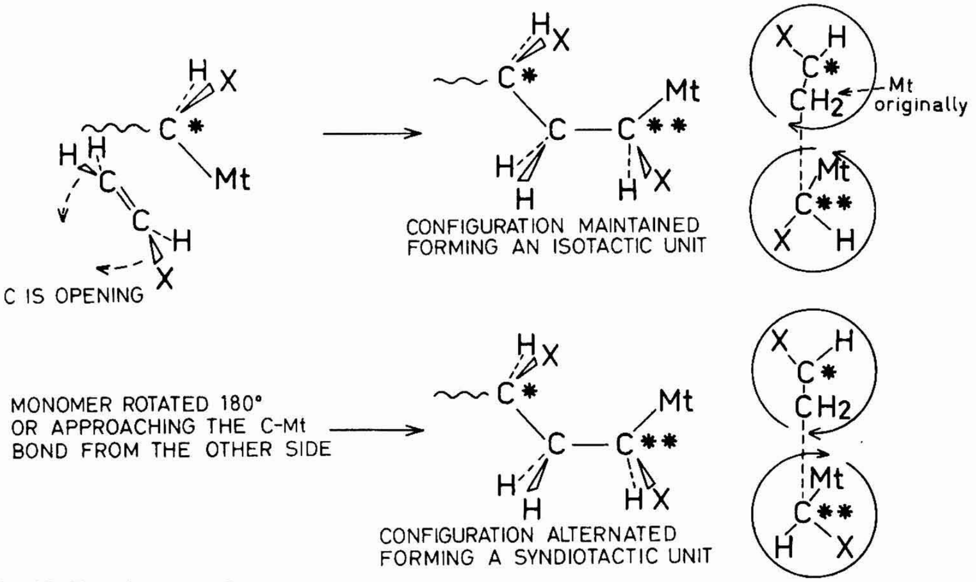
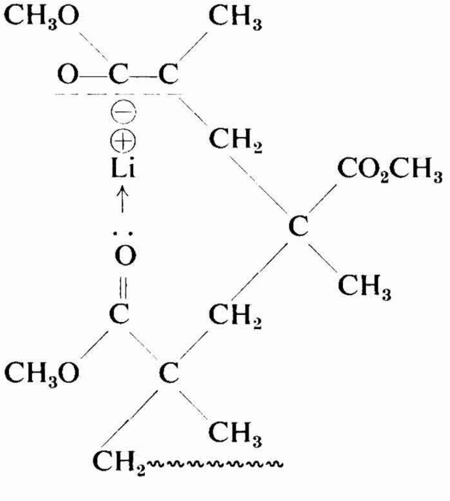


Fig. 10. Requirements for steric control at a bound propagating species. In the insets, the disposition of the substituents on the end and penultimate asymmetric carbon atoms (C* and C) are compared**

lapped sufficiently to form the new bond) and *preorientation on an adjacent site* (in homogeneous systems—co-ordination of the monomer to an adjacent atom in a particular orientation ; in heterogeneous systems—preadsorption of the monomer on an adjacent site on the catalyst). Steric or polar interactions may also control the side from which the monomer approaches the reaction site. This effect is likely to be enhanced if part of the reaction site is attached to a catalyst surface, or, in a homogeneous system, if the site is co-ordinated to monomer, solvent, or even to units of its own polymer chain as has been postulated by Glusker[4] for the polymerisation of methyl methacrylate with organolithium compounds.



I

Ziegler-Natta catalysts

In view of what has been discussed above, it is not surprising that most recipes for stereospecific polymerisation involve solid catalysts. These can be classified very roughly into two groups—metal oxide catalysts and those based on reactive organo-metallic compounds. The latter are most studied (at least as far as the open literature is concerned). The archetype is the Ziegler-Natta catalyst which is essentially a crystalline transition metal salt (usually a halide) activated by an organo-metallic compound (most commonly an alkyl aluminium compound). They are prepared in two ways. The covalent compounds of the highest oxidation state of the transition element (e.g. the liquid $TiCl_4$) may be reduced with organo-metallic compound (e.g. $Al(C_2H_5)_3$). The precipitate, consisting predominantly of lower oxidation-state compounds, is the catalyst. Cleaner and more chemically defined catalysts are prepared by treating the crystalline compounds of lower oxidation states (e.g. $TiCl_3$) with the organo-metallic compound (e.g. $(C_2H_5)_2AlCl$). There is, of course, more to it than this—additives, impurities, particle-size, age-curing, heat-curing, addition of monomer before or after the formation of the catalyst can all influence the action of the catalyst. Some of the particulars may be found elsewhere[5], but not everything is public knowledge.

Identification of the catalytic site

The catalyst contains both metals. There is reasonably conclusive evidence that the polymerisation mechanism involves a repeated insertion reaction (Eqn. 4) at a metal-carbon bond. The incorporation of alkyl groups from the catalyst as end-groups of the polymer chain is well established[6]. This does not in itself prove that the reaction occurs at a metal atom originally in the organo-metallic compound, because there is considerable exchange of alkyl and halide groups between the two metals during the catalyst-forming reactions. Carrick[7] has suggested the contrary. He found that, in the copolymerisation of ethylene and propene, the composition of polymer was independent of whether the organo-metallic substance used was $(i\text{-}C_4H_9)_3Al$, CH_3TiCl_3, $(C_6H_5)_2Zn$ or $(n\text{-}C_4H_9)_2Zn$, but strongly dependent on whether the transition metal compound was VCl_4, $VOCl_3$, $TiCl_4$, $ZrCl_4$ or $HfCl_4$. The composition of a copolymer depends on reactivity ratios which are characteristic of the mechanism of the growth reaction. Carrick interpreted his results as evidence that the growth reaction occurs at a transition-metal centre. This would be conclusive if the growth reaction were the rate-controlling process, i.e. if the polymerisation were *chemically controlled.* This is not proven. A number of purely physical processes could be rate controlling.

The sequence of events during the course of a polymerisation at a catalytic surface may be itemised as follows : (i) diffusion of monomer to the surface, (ii) (a step probable but not essential) adsorption of monomer on the surface, (iii) addition of the monomer to the growing chain, (iv) desorption of the polymer, (v) diffusion of the polymer away from the surface. Any of these steps could be the slowest. If step (iii) is the rate-controlling process, Carrick's hypothesis and conclusions are valid. If it is not, the hypothesis may fail.

The influence of physical effects on the rate of polymerisation has been demonstrated in a number of cases. In one system which has been studied at the University of Birmingham, styrene polymerised by a heat-cured, Grignard-reagent-$TiCl_4$ catalyst, the rate continually decelerated (Curve A, Fig. 11). During the process the catalyst particles became encased in polymer gel which was visible evidence that step (v) was the slow one. It controls the rate of polymerisation, because the accumulation of gel restricts the supply of monomer to the catalyst surface[8]. In other systems acceleration is observed (Curve B, Fig. 11) which is associated with a cleavage of the catalyst particles during the polymerisation[9]. These two effects may be related. One of the problems in Gill's work was the formation and persistence of a gel phase, since polystyrene is soluble in the monomer and solvents used. In fact the gel capsules could only be dissolved off the catalyst particles by prolonged and drastic treatment (e.g. boiling xylene). If, however, the catalyst was destroyed with HCl in ethanol, the polymer could be readily dissolved which led to the conclusion that the

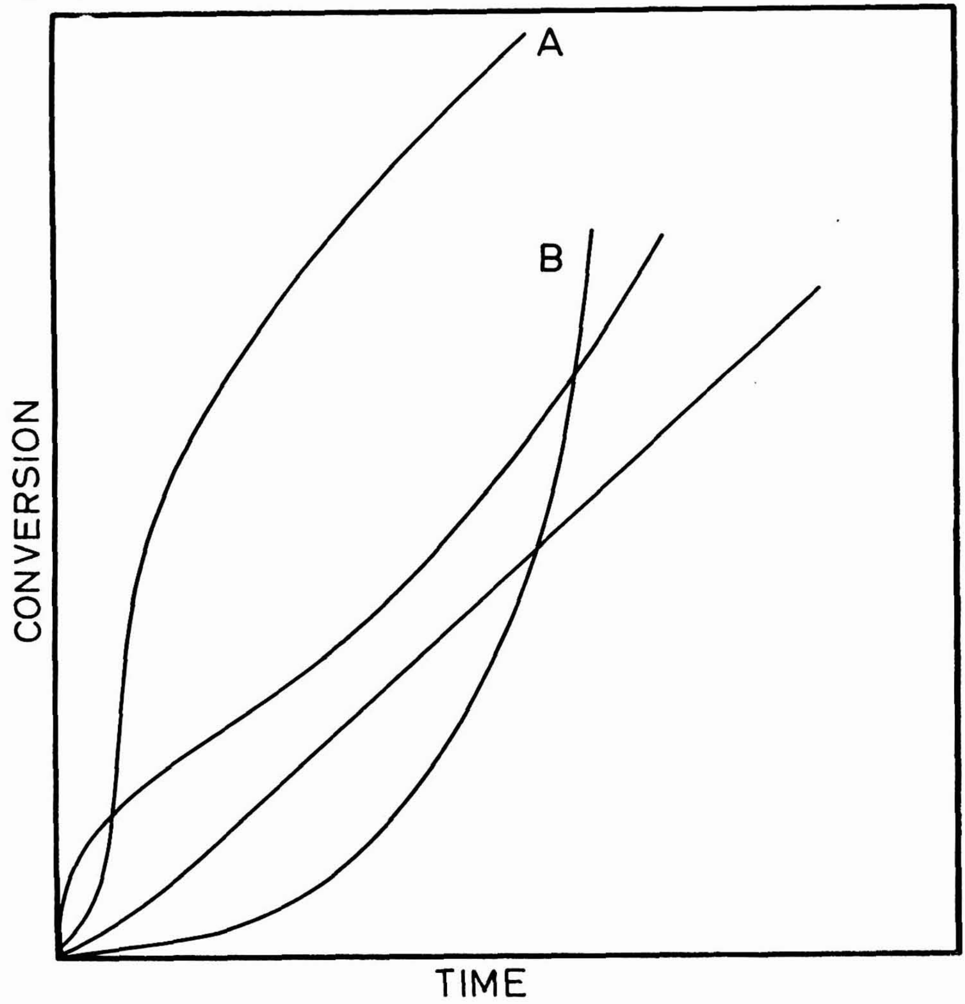


Fig. 11. Typical conversion curves for Ziegler-Natta type polymerisations

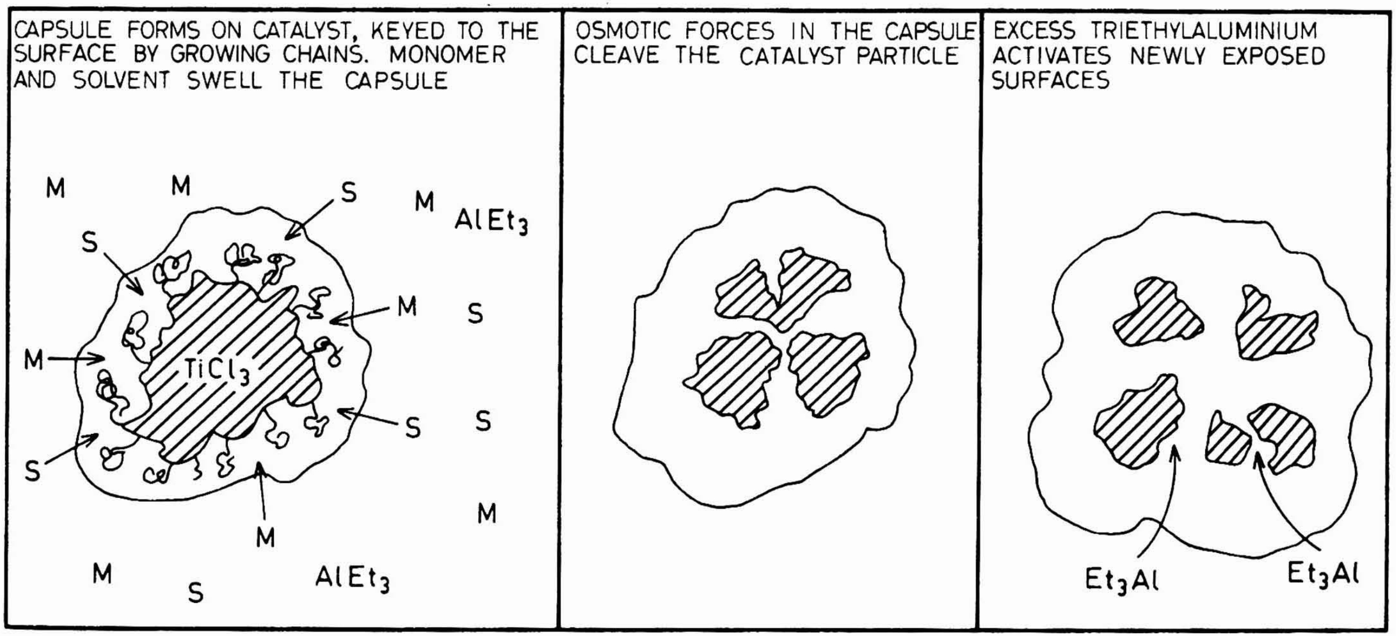


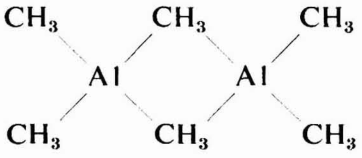
Fig. 12. A possible explanation of accelerating polymerisations (curve B, Fig. 11)—osmotic disruption of the catalyst by the swelling of encapsulating (or adsorbed) polymer

reason for the " stability " of the gel phase was that it was keyed to the catalyst by the growing polymer chains which are bonded to metal atoms on the surface of the catalyst. If the monomer and diluent are soluble in the polymer, the capsule will swell. The swelling of the capsule will exert considerable force on those polymer molecules keyed to the catalyst and something must give. If the conditions are such that the polymer molecules are flexible and have a reasonable amount of freedom of movement, the keyed molecules will probably release the tension by slipping out of their entanglement with molecules not bonded to the catalyst. If this is not possible, the catalyst will be torn to pieces (Fig. 12)—the bonds joining the polymer molecule to the catalyst are strong, stronger than those holding the crystallites of the catalyst together. In some systems the original catalyst particles are totally disrupted and distributed uniformly throughout the gel[10].

Except in extreme cases where the solubility of the two monomers in the polymer differed considerably, gel capsule formation would probably not have a great effect on copolymer composition. If, however, the adsorption or desorption steps were controlling, then Carrick's conclusions may be disregarded. The copolymer composition would be determined by the relative extent of adsorption of the two monomers. The dependence of the copolymer composition on the transition metal compound would be merely a reflection of the different relative adsorption of the monomers on the different lattices, and nothing can be inferred about the identity of the growth site. Schindler has proposed just this and has recently produced some evidence favouring a growth site involving either the metal from the organometallic compound or both metals[11]. If he is right, this is a case where an interpretation based on purely chemical reasoning leads to a false conclusion.

Theories based on a bimetallic centre

The theory that the growth site involves both metals is quite old. Authors have been fascinated by the fact that most organometallic substances involved in these reactions are polymeric, with the metal atoms joined together by electron deficient three-centre bonds $Mt\cdots C\cdots Mt$, e.g.



II

Mechanisms typical of this type are those of Patat and Sinn[12] and Natta and Mazzanti[13]. The type of transition state structure suggested is shown in Fig. 13. The growth site is a bridge alkyl group. Although cis opening of the monomer double bond is ensured, the model is insufficient to explain stereospecificity. It is suggested that the monomer is first co-ordinated to monomer, but the exact manner in which this controls the stereochemistry of the insertion reaction is unspecified.

If dicyclopentadienyl titanium dichloride is reacted with alkyl aluminiums, soluble complexes are formed which have some initiating power. These com-

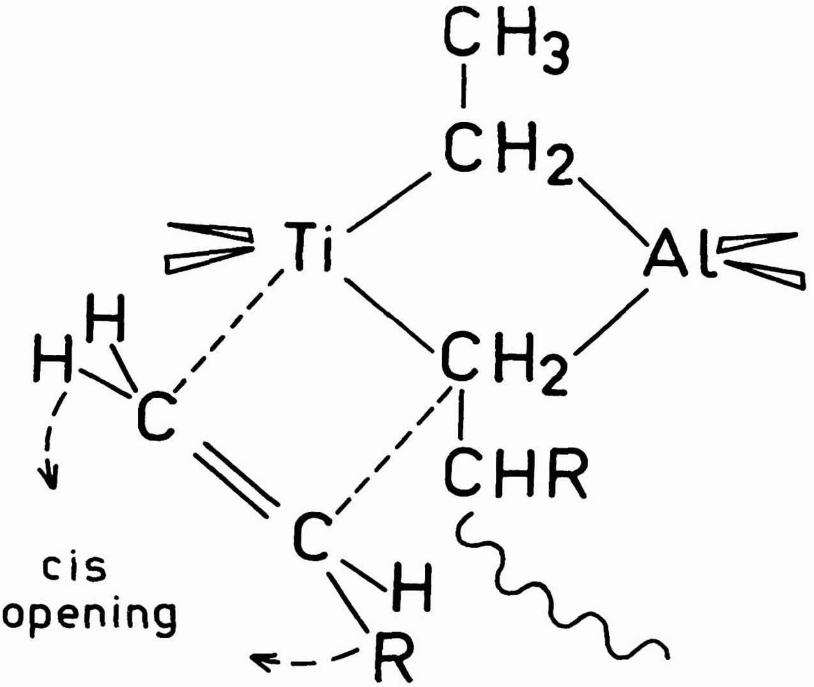
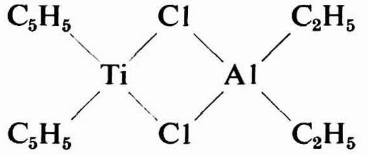


Fig. 13. The Patat-Sinn mechanism—typical of bimetallic theories incorporating bridged structure and co-ordination of the monomer

plexes have been called " soluble Ziegler catalysts "[14] and have given great impetus to the bimetallic hypothesis. Some of them are definitely bimetallic bridged structures, e.g.

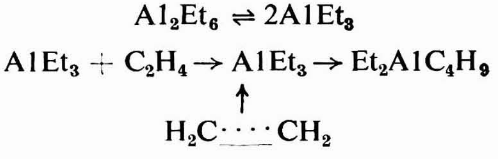


III

which has been definitely established by crystallographic methods[15]. Analogous hydrogen-bridged and hydrogen and chlorine-bridged structures have been demonstrated in reaction mixtures[16] and isolated complexes[17] by electron spin resonance measurements. However, there is no definite evidence for the existence of carbon-bridged complexes, which is really required if these complexes are to lend support to the Patat-Sinn type of mechanism. Furthermore there is considerable doubt whether the actual initiating species in these systems have yet been identified[18].

The co-ordination mechanism

Ziegler has never subscribed to the bimetallic mechanism[19]. He favours a pure co-ordination mechanism in which the monomer is first co-ordinated to a metal atom. The Patat-Sinn and the Natta-Mazzanti mechanisms involve just such a co-ordination, but Ziegler claims that this is unlikely to occur at a metal involved in a bridged complex. He contends that the vacant orbital available for overlapping with the π-system of the monomer would, in a bridged complex, be involved in the multicentre bridge-bonds. In support of his contention, he quotes his kinetic results on the reaction of triethyl aluminium with ethylene, which indicates that only the monomeric form of triethyl aluminium is reactive



$$Al_2Et_6 \rightleftharpoons 2AlEt_3$$

$$AlEt_3 + C_2H_4 \rightarrow \underset{\underset{H_2C\cdots CH_2}{\uparrow}}{AlEt_3} \rightarrow Et_2AlC_4H_9 \qquad (7)$$

It is interesting that the role of co-ordination has only recently been demonstrated directly—and this, unfortunately, in a system where the polymerisation mechanism is atypical. Casey, working at the University of Adelaide, has shown that when triethyl aluminium is mixed with acrylates, methacrylates, methacrylonitrile, acrylonitrile, acetophenone, acetaldehyde, benzaldehyde, methyl vinyl ketone and many non-polymerisable substances, yellow complexes are formed. In the case of acrylates and methacrylates the n.m.r. lines associated with the vinyl hydrogens of the monomer are completely transformed in the complex. They are still, however, in the vinyl region of the field. It is only after polymerisation has begun that the vinyl lines disappear and new lines appear in the part of the field corresponding to the hydrogens on saturated C-atoms. However, some, at least, of these polymerisation mechanisms are atypical in that they are photochemical and sensitised by visible light[20].

The Cossee mechanism

It will be noted that in all the mechanisms discussed so far, only Friedlander takes significant account of that important physical effect—the presence of the surface. All the other mechanisms are based essentially on observations of homogeneous reactions. Furthermore very few give a detailed explanation of the stereoregulation. There are some in the literature that claim to do this. There are even some that work in two-dimensional projection. With the exception of the Bawn-Ledwith mechanism demonstrating how steric blocking induces stereoregularity in the *homogeneous* polymerisation of isobutyl vinyl ether,[5b] none works in a three-dimensional model—at least as far as the author's knowledge and manipulative skill is concerned.

Instead of attempting to build a theory by induction from the reactivity and mechanistic data so abundantly available from the study of analogous homogeneous reactions, Cossee bases his theory on the facts that the Ziegler polymerisation is a surface reaction and the surface is highly specific. The obvious physical factors involved are the dimensions of the lattice of the catalyst and the dimensions of the monomer. The mechanism is a detailed explanation, in these terms, of the stereoregulation of propene polymerisation to the isotactic form on the surface of a catalyst based on α-$TiCl_3$ This is shown in Figs. 14-22. The models are not to scale. However, the mechanism works in true scale as may be seen in the diagrams of Cossee's paper[21].

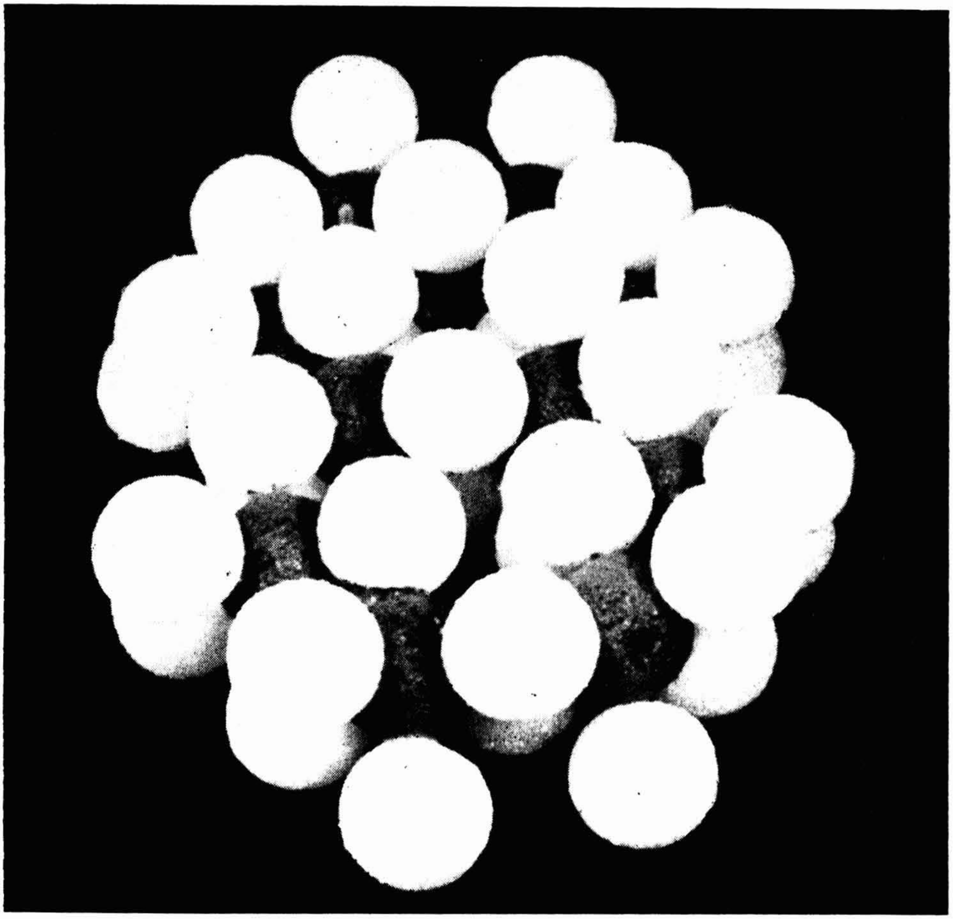


Fig. 14. 001 face of 1-$TiCl_3$ crystal. Cl atoms are white, Ti dark. The model is not to scale—the actual diameters are Ti: ca. 0.7Å; Cl: ca. 1.8Å. Note: the surface consists of a layer of chlorine atoms, the Ti atoms in the layer beneath are in six membered rings with a vacancy in the middle

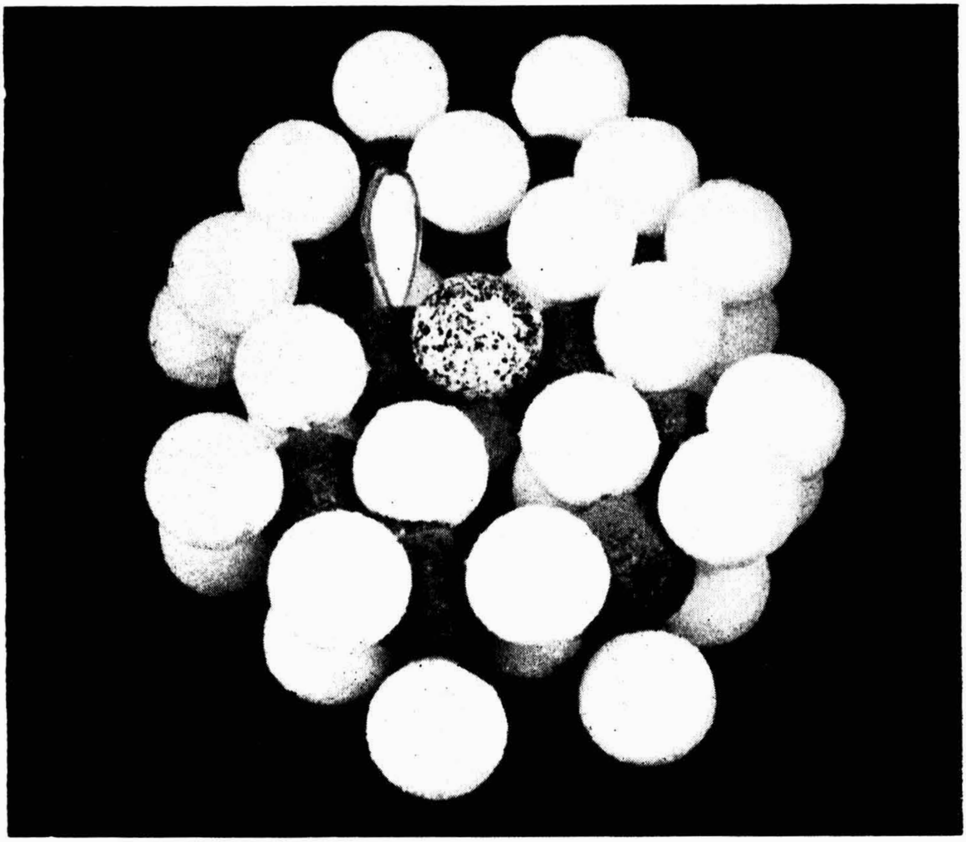


Fig. 15. The attack of $(C_2H_5)_3Al$ has removed two Cl atoms replacing one by an ethyl group. The speckled ball represents the CH_2 of this ethyl group. Note the hole left by the vacant Cl site and the vacant orbital on the Ti of the active centre

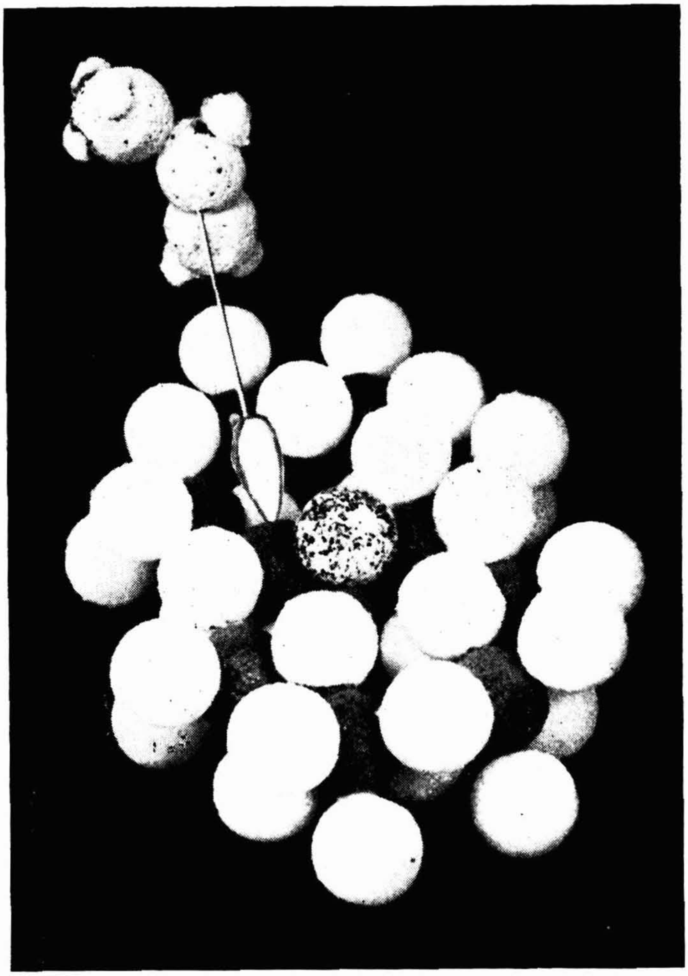


Fig. 16. For reaction, propene must co-ordinate with the Ti of the active centre. Its π-orbital must overlap the vacant orbital on the Ti with the vacant orbital perpendicular to the plane of the propene molecule. The propene must be co-ordinated with its $CH_2=$ down. The $CH_3CH=$ end will not fit in the hole left by the Cl vacancy. The mode of attack shown is *not* permitted because of a steric clash of the $-CH_3$ with the Cl atom to the left of the hole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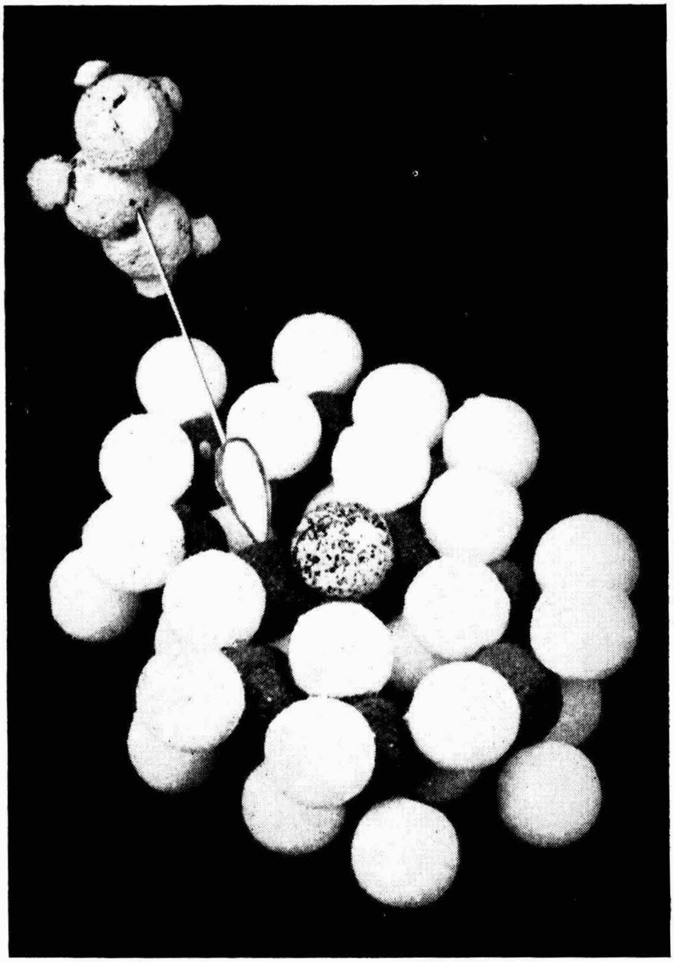

Fig. 17. The permitted mode of attack

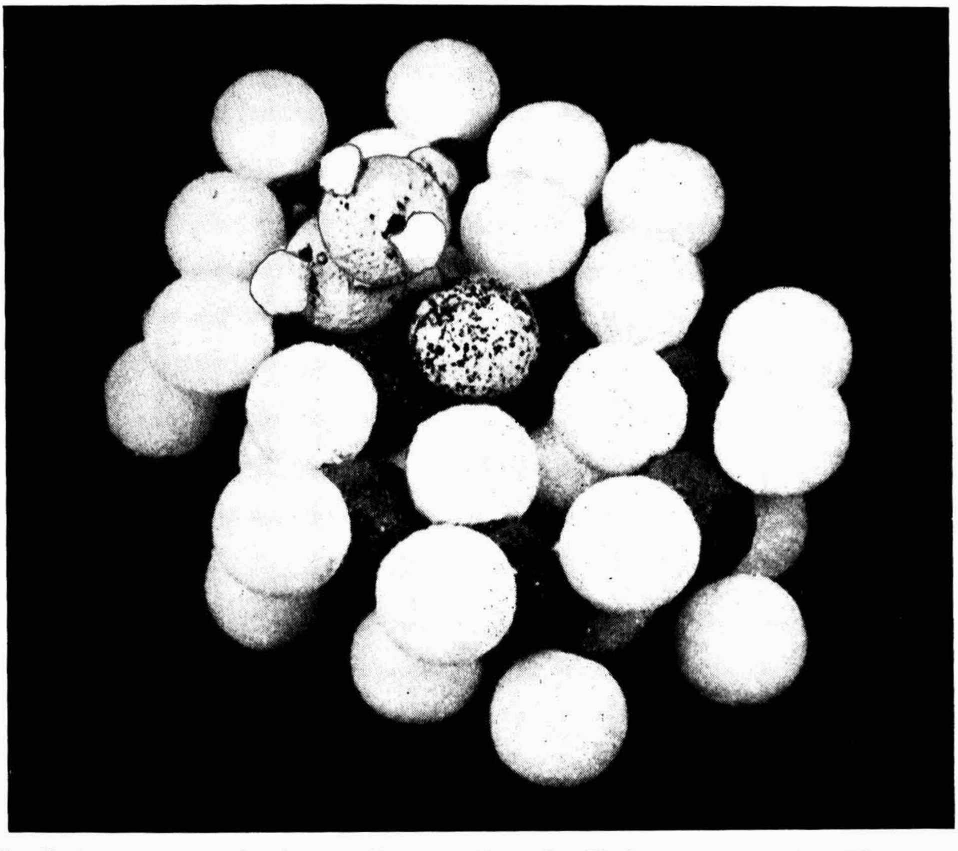

Fig. 18. The propene molecule, co-ordinated to the active Ti, through its π-system. The $CH_2=$ is eclipsed by the $=CH.CH_3$ end of the molecule

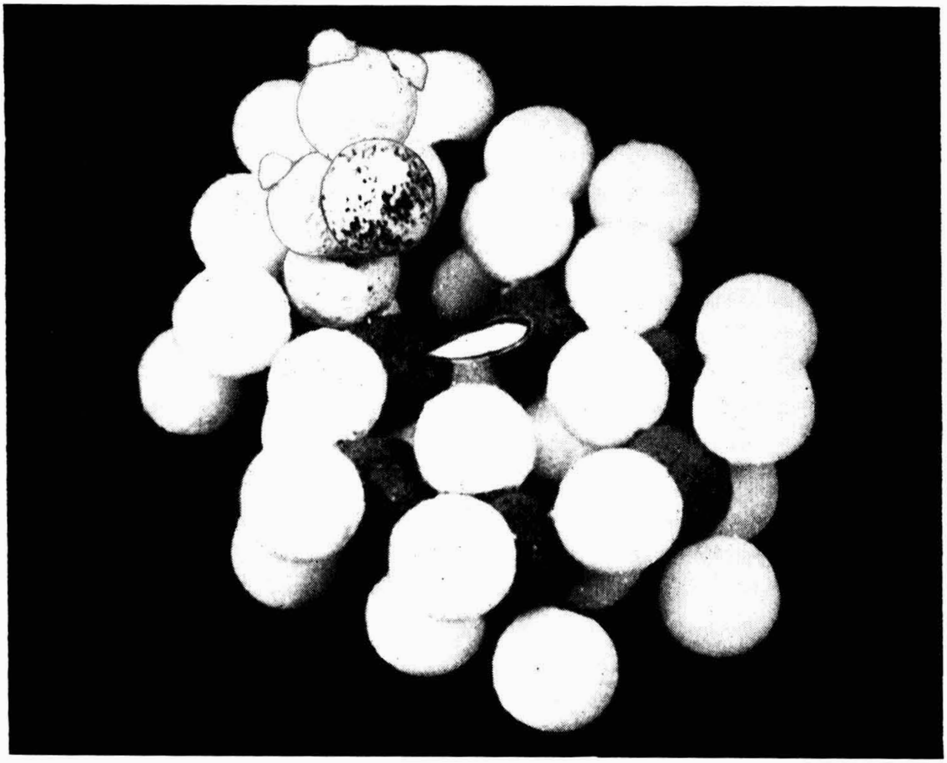

Fig. 19. Reaction: the double bond has opened, the $CH_2=$ of the propene is σ-bonded to Ti and the $-CH_2-$ of the ethyl group (speckled) is bonded to the propene $=CH.CH_3$. Note the orientation of the asymmetric C atom: a clockwise tour, from an end-on viewpoint, encounters substituents in the order $-H$, $-CH_3$, speckled $-CH_2-$. Note also the new hole and vacant orbital which are symmetrically identical with the original ones

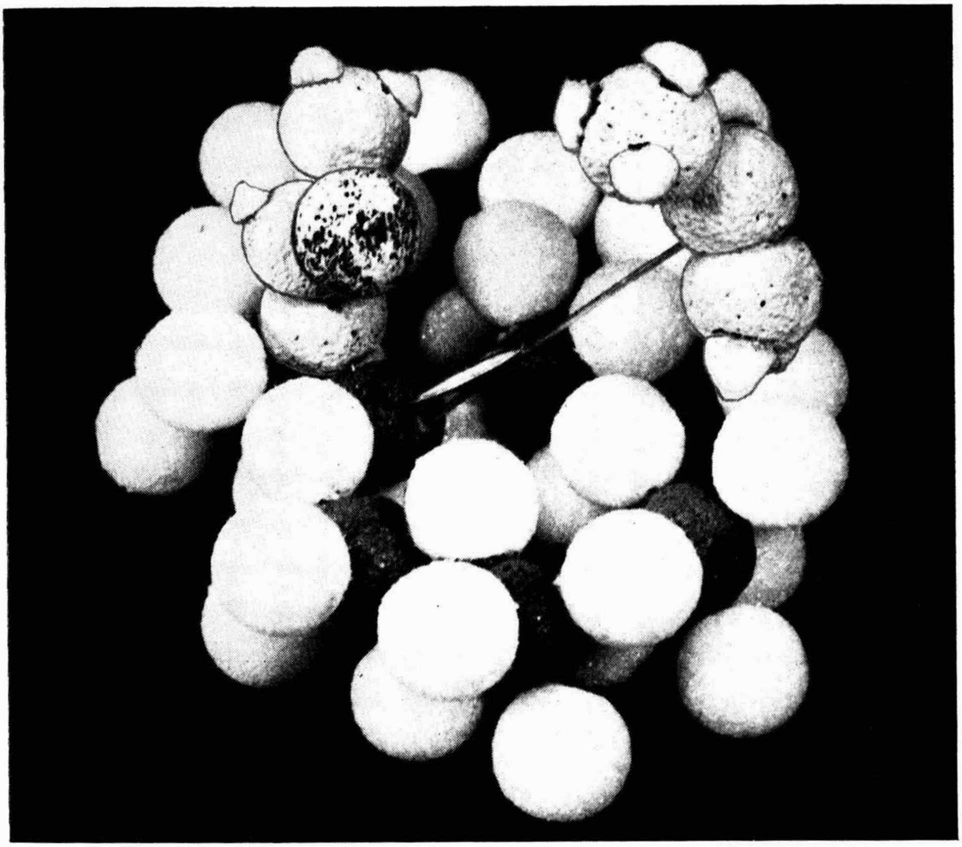

Fig. 20. Attack of second propene molecule in the only permitted orientation

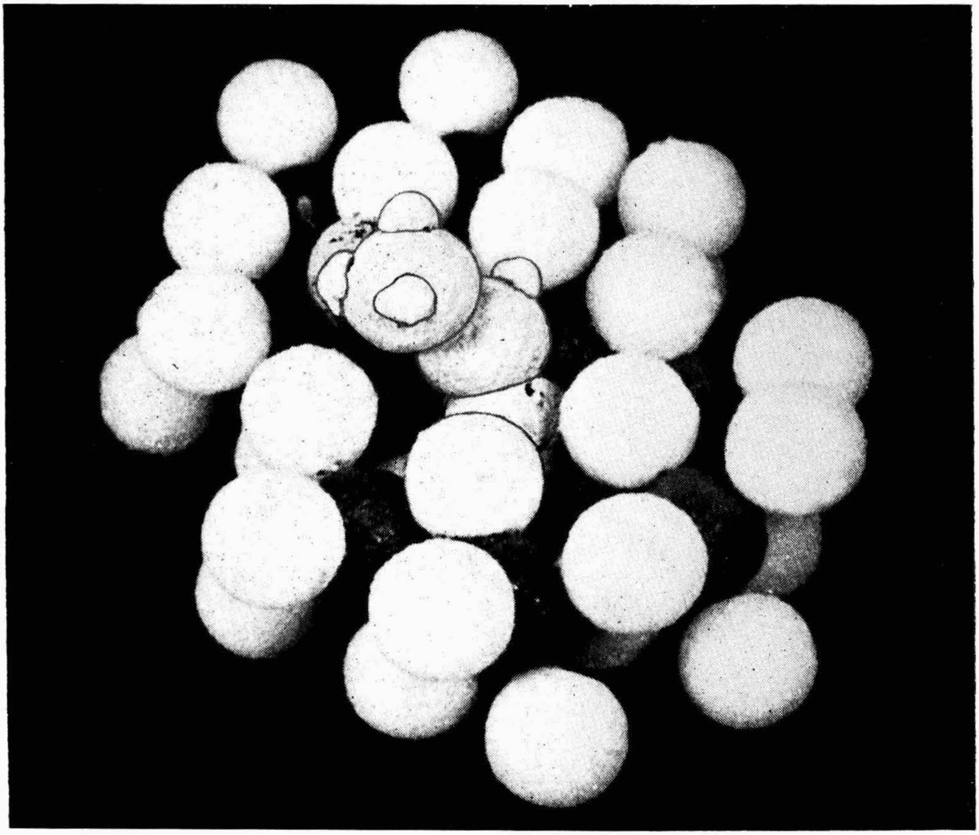

Fig. 21. Co-ordination of the second propene molecule. Note the incipient polymer chain has been reduced to one speckled $-CH_2-$ group, in the interests of clarity

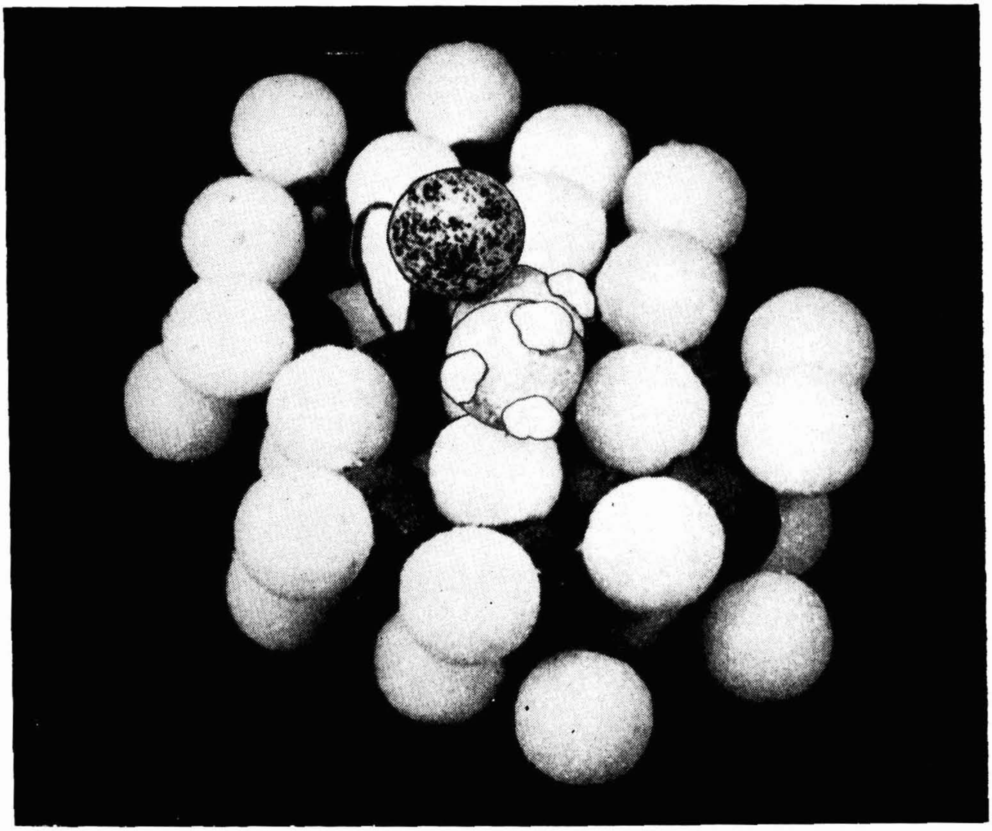

Fig. 22. Addition of second monomer. Note a clockwise tour round the new asymmetric C encounters substituents in the same order as before, though the speckled ball is now the $-CH_2-$ of the incipient polymer chain. Note also that the original hole and vacant orbital have been regenerated ready to accept a third propene molecule and reproduce the symmetry of the addition reaction and continue the growth of a stereoregulated isotactic polymer chain

Chemically, the reaction is a simple co-ordination mechanism involving the transition metal only. The sole purpose of the alkyl metal compound is to generate active centres on the crystal surface. So we have a model which is chemically acceptable and which, by paying due regard to the physical aspects of the system, is able to explain the stereoregulation of the addition. However, this is probably not the last word. There are some doubts, and one piece of contradictory evidence. The main doubt is about the postulated nature of the surface—whether the holes would persist or whether the adjacent atoms would accommodate to spread the defect. The author has been unable to extract a definite opinion on this point from any solid-state chemist of his acquaintance. The piece of evidence that is difficult to accommodate on the Cossee theory is a physical observation. Rodriguez and Grabant[22] have published some beautiful electron-micrographs of polypropene growing on α-$TiCl_3$ crystals activated by $(CH_3)_3Al$. These show that the main centres of polymer production lie on a line originating in the centre of the face of the crystal spiralling out to the edges. The locus of these centres is, without doubt, a growth spiral (Fig. 23).

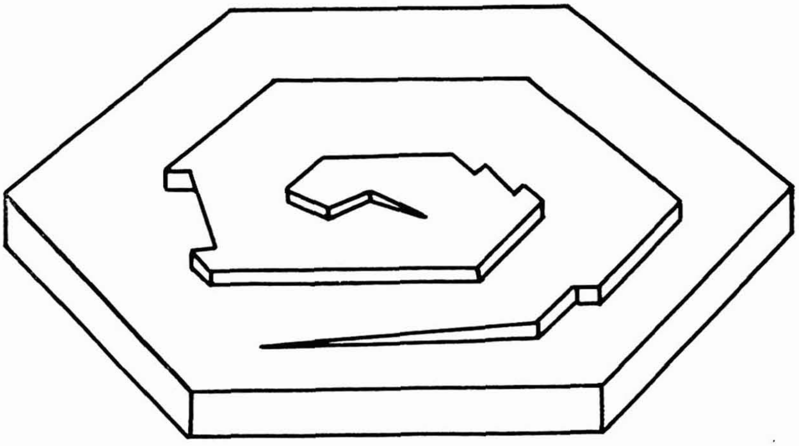

Fig. 23. Growth spirals on the surface of crystal face

Growth spirals arise because of screw dislocations (Fig. 24) in a growing crystal. Atoms at the emergent dislocation are more reactive and so the crystal grows preferentially at the dislocation and a spiral step develops on the surface, as shown in Fig. 23. The significance of these growth spirals in a Ziegler-Natta polymerisation is that the spiral step exposes the Ti atoms in the layer below the chlorine layer which forms the surface of a perfect crystal. The difficulty about this from the point of view of the Cossee mechanism is that a Ti atom

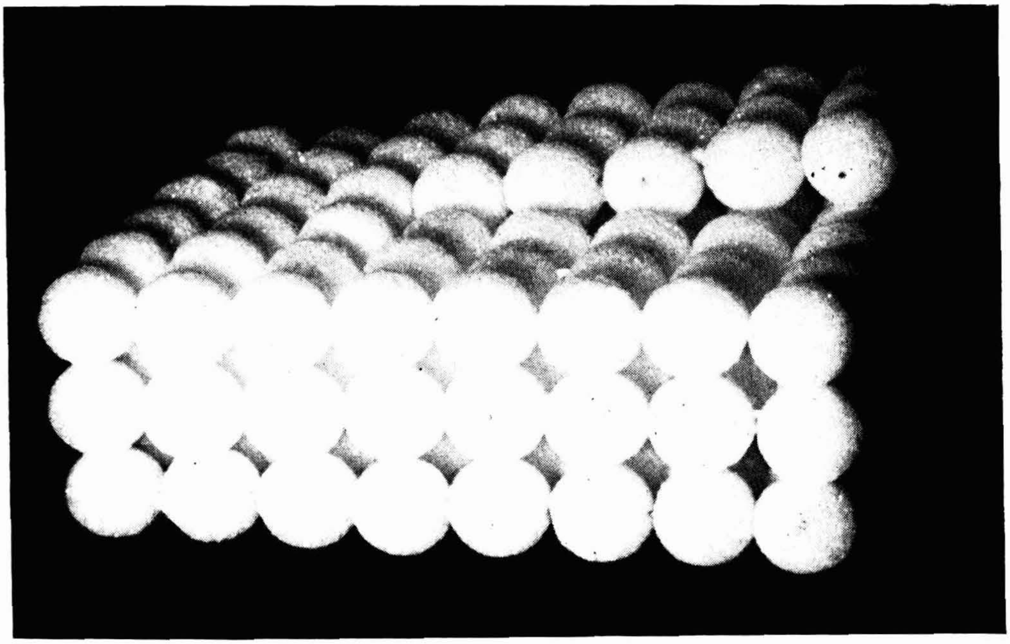

Fig. 24. A formalised model of a screw dislocation emergent at a crystal face. In a $TiCl_3$ lattice in which the perfect surface consists of Cl atoms, a screw dislocation would expose Ti atoms from the layer beneath

exposed at a step is unlikely to be a stereospecific site. The ring of chlorine atoms which ensure that the propene molecule can present itself only in the correct orientation (Figs. 16, 17, 20) will be incomplete. One possible explanation, that the isotactic polymer arises from Cossee sites uniformly distributed over the surface of the crystal so that they escape detection on the electron micrograph, is not satisfactory. Most of these catalysts are highly stereospecific. The yield of atactic polymer is often very low and it seems that a mechanism will have to be developed to account for stereoregulation at the growth spiral.

The problem is undoubtedly still an open one. The last word is yet to be spoken. However, we can be certain that whoever speaks it will have paid proper attention to the physical factors involved. The time is past when authors can expect to catch the attention of an informed audience with ingenious adaptations of theories and mechanisms appropriate to homogeneous reactions.

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NOTE.—Since this was written Rodriguez[23] has published accounts of an extensive chemical and physical investigation of these catalysts. He postulates an additional active centre of the Patat-Sinn type, which operates stereospecifically through steric clashes between the propene methyl and chlorine and alkyl groups on the catalyst. Attention must also be drawn to the modified Cossee mechanism which is compatible with Rodriguez's electron micrograph[24].

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Correspondence

The potential distribution technique of assessing the action of pigments in corrosion protection

SIR,—Bharucha[1, 2] has described a technique in which an examination of the potential distribution plot, obtained by scanning with an electrode over the contact couple formed at the boundary of a painted area on a metal panel immersed in a high resistance electrolyte, was claimed to give information on the mechanism of protection by the paint film.

Experimentally, the technique consisted of coating prepared samples of metal sheet, of dimensions 7.5 × 2.4 cm, over one half of their length with the paint. After a suitable curing period the painted samples were placed flat, painted side up, in an electrolyte consisting of triacetin containing approximately 3 per cent water and having an electrical conductivity of 1.1180×10^{-8} mho/cm^3 at 25°C. A fixed reference electrode was mounted with the tip immersed in the electrolyte a standard distance from the sample and a similar electrode used to scan along the length of the sample a small distance above it. The potentials were recorded using a suitable electrometer. Readings were taken at intervals until a steady state was reached and the potentials remained constant for 30 minutes. The potentials recorded were those in the electrolyte very near to the surface of the sample, reversal of the sign of these potentials gave the potentials of the samples at the various points.

It was shown that the theoretical potential distribution in the case of a system affording resistance inhibition was S shaped, Fig. 1. Deviations from this were interpreted in terms of chemical inhibition, Fig. 2. Variations in the

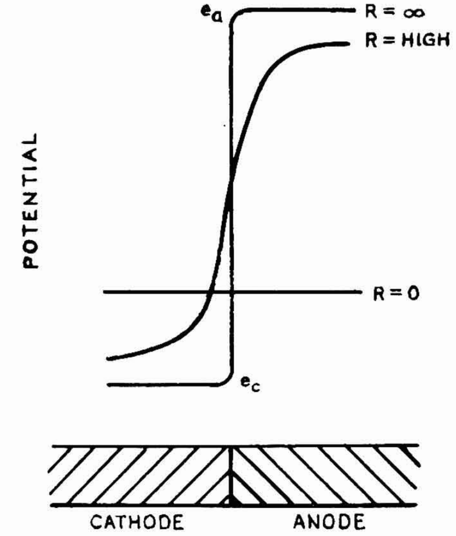

Fig. 1. Theoretical potential distribution curves for the area near the painted/unpainted boundary of a contact couple

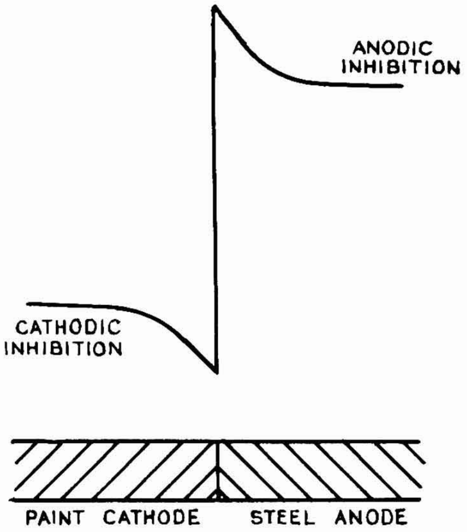

Fig. 2. Deviations from the ideal potential distribution curve produced by anodic and cathodic inhibition

dimensions of the S curve were correlated with differing degrees of resistance inhibition, a compressed curve indicating a higher degree of inhibition.

Recently an attempt was made to assess, by this technique, the protection given by some chromate pigmented epoxy/polyamide compositions to samples of an aluminium alloy sheet, L71, and also to an alloy sheet clad with pure aluminium, L73. The sheet was used both degreased and pretreated in a chromate/sulphuric acid etching bath, DTD 915 A.

The paints were formulated with either zinc potassium chromate or strontium chromate to contain a common CrO_3 content of 20 per cent on the resin solids. Some initial experiments were also carried out using zinc tetroxy chromate at the 15 per cent pigmentation level.

The results were all essentially of S form, that is, they did not show the deviation previously ascribed to chemical inhibition, but, unexpectedly most showed a reversed potential distribution. Bharucha had shown that a reversed potential distribution could occur in cases where sacrificial protection was expected, such as with a zinc rich composition ; but, there was no component in the present system known to act as a sacrificial anode. It was suspected that this reversed result was in some way associated with the nature of the substrate and to examine this further the unpigmented systems shown in the Table 1 were examined.

It can be seen from Table 1 that the normal distribution was obtained only with mild steel and the pretreated L73.

It had been shown that triacetin, containing 3 per cent water, slowly attacked mild steel ; consequently, the uncoated portion of the specimen became anodic to the coated portion and current flowed in the liquid path of the circuit from the uncoated portion to the coated. It is unfortunate that the nature of the conducting ions was not established, but it seems probable that conduction was due to traces of acetic acid, either originally present in the triacetin, or formed by hydrolysis owing to the presence of water. It is known that acetate ions at low concentration or low pH are corrosive to iron.

Table 1

Metal	Paint composition	Direction of potential distribution
L71	Epoxy/polyamide	reversed
L73	,,	reversed
$L73_p$	,,	normal
Mild steel	Epoxy/polyamide	normal
L71	Alkyd	reversed
Mild steel	,,	normal
Magnesium	Epoxy/polyamide	reversed
Magnesium_p	,,	reversed
Magnesium	Alkyd	reversed

($L73_p$—DTD915A, Magnesium_p—DTD626)

In the experiments where sacrificial protection cannot be the case and where the direction of the current was reversed it seems that the triacetin solution was inhibitive and attack took place at the metal surface underneath the coating, probably owing to the fact that the coating was more permeable to water and oxygen than to charged ions. A similar type of attack has been observed on mild steel, coated with polystyrene and immersed in 0.1 N. sodium hydroxide[3].

It appears that triacetin, containing 3 per cent water, attacks some materials more rapidly than others and that it is the rate of initial attack which controls the direction of flow of the current.

It was suggested[2] that it was possible from the shape of the curves, Fig. 2, to obtain information regarding chemical inhibition, and almost all of the initial work was carried out with mild steel.

The author claimed that " The choice of triacetin was made on account of its low electrical conductivity, stability, and non-reactivity with the paint film for the duration of the experiment." Experiments have been carried out to check this point and it has been found that, provided the triacetin mixture was not too old, attack on paint films was negligible, even when they contained large quantities of soluble material such as lead soaps.

In view of this, it was very difficult to see how the polarisation of the uncoated metal could have been affected by anything in the paint coating and it followed that it was necessary to look elsewhere for an explanation of the shape of the curves obtained with certain lead pigments. The present authors, however, after examining a very large number of curves obtained from the steel/red lead system, were not able to satisfy themselves that the distorted S curves obtained for that system by Bharucha were typical of the system.

If the pigment were an anodic inhibitor, then the air-formed oxide film would be reinforced until it became impermeable to iron ions ; if it were a cathodic inhibitor, then the surface of the iron, underneath the paint coating, would become covered with a layer, impermeable to electrons. In both cases an additional resistance would be inserted into the circuit, but the value of the resistance would be very small compared with the resistance of the paint film and the effect it might have on the S shaped potential distribution curve would be very slight. It was claimed that " Variations in the dimensions of the S shaped curve may be correlated with the different degrees of resistance inhibition, a curve that is small and compressed indicating better resistance inhibition than one that is large and elongated." This seems very reasonable.

The extent of the potential drop from the maximum in the curve to the minimum has been estimated and found to be :—

Iron oxide	200-275 millivolts
Red Lead	33-61 millivolts
Calcium plumbate	26 millivolts

from the published curves[2] for iron oxide, 100 microns ; red lead, 112 microns ; calcium plumbate, 112 microns. These curves have been replotted on the same scale in Fig. 3, from which it can be seen that the curves became progressively flatter.

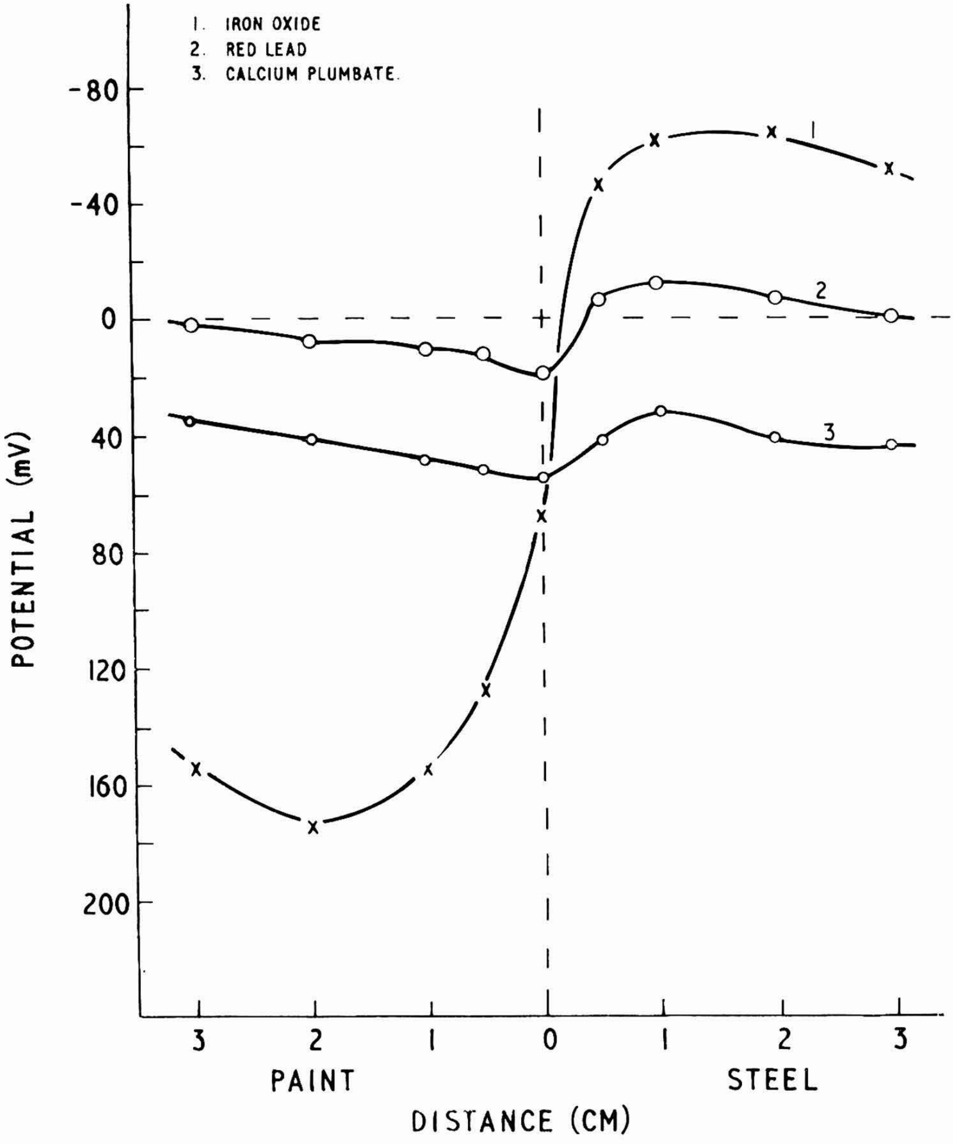

Fig. 3. Published curves plotted on the same scale

In the present examination it was also observed that the curves obtained for the high resistance epoxy/polyamide films were more compressed than those obtained for the lower resistance alkyd films.

Kittleberger and Elm[4] measured the rates of diffusion of sodium chloride through paint films and found that they were proportional to the film resistances, films of red lead/linseed oil were found to be several hundred times less permeable than films of iron oxide/linseed oil and consequently had much higher resistances. This observation provides an explanation of the curves in Fig. 3, since the higher the resistance of the coating, the more the potential drop will take place in that part of the circuit and the less in the triacetin-water mixture.

Conclusion

The method developed by Bharucha for examining the properties of paint films does not provide information regarding chemical inhibition. It does provide information with respect to the electrolytic resistance of the coating, but only under conditions of low water activity and these are very far removed from practice.

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Review

THE CONDENSED CHEMICAL DICTIONARY

Edited by ARTHUR and ELIZABETH ROSE. New York : Reinhold Publishing Corporation, 1967, Pp. xxi+1044. Price £7.

This new edition of a well known volume is published five years after its predecessor. It is obvious that in this space of time there have been many new materials and processes developed and an equally large number have become obsolete or of decreased importance. It says much for the care and energy exhibited by its editors that this dictionary is so up to the minute in its information. The problem of remaining up to date is a major one in producing a dictionary. It must be realised that there are limitations to a one volume scientific dictionary in that it is not possible to cover all the materials and processes. It is here that the skill of the editors becomes apparent and in this book it can be said that an excellent job has been done in deciding what should be included and, to a lesser degree, what must be left out of what is after all a " Condensed " dictionary. Many text books contain masses of tables of chemical and physical constants which often are seldom consulted. However, in a book of this nature it is felt that the inclusion of a number of such tables would have been a welcome addition.

The book, as is usual with most American publications, is well bound and clearly set out. Compounds are easily found and a particularly pleasing aspect is the manner in which short, interesting articles have been compiled in connection with many definitions. Here again credit must be given to the manner in which the difficulty of conveying as much as possible in a small space has been overcome. If fault must be found, it is in the unusually large number of references to American trade names, which cannot be of interest to users in other countries. It is felt also that more information could have been given under the sub-heading "Uses." Here the information is extremely brief and in many cases is limited to one word, e.g. "Medicine." There are included two lists of manufacturers and an article on shipping regulations, both unfortunately referring only to America, and one page explaining to those unused to the complexities of a chemical dictionary how to find the particular compound of their interest.

It is often a dull job reviewing a dictionary and one normally takes extracted examples for examination, but this is a book which surprisingly enough is interesting and pleasing to browse through, particularly because of the manner in which the definitions are reported. It becomes at once informative and to the reviewer at least, not a little nostalgic. However, the purpose of this book is as a work of reference and in this respect it is a worthy successor to the sixth edition.

G. ANDERSON

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.)*

A new, improved *Viton* fluoroelastomer is announced by **Du Pont.** The new material, *Viton A-35*, is claimed to facilitate processing with no sacrifice in the polymer's heat and fluid resistance. It is claimed to have excellent mould flow characteristics, and low viscosity, providing for easier mixing and faster, smoother extrusion.

Lewis Berger (Great Britain) Ltd. have recently acquired the premises of S. E. Norris Ltd., Chadwell Heath, and will be converting the buildings for emulsion production.

Lewis Berger expect the new plant to produce 1,000,000 gallons of emulsion per year initially.

A six-page leaflet describing the *Ransburg* range of electrostatic spraying equipment has been produced by **Henry W. Peabody (Industrial) Ltd.**

Albright & Wilson have announced that, as from 1 July 1967, the main wholly-owned subsidiary companies in the United Kingdom will become, for management purposes, operating divisions of the parent company.

The new *CLT5 Gloss* range of gloss offset inks is the subject of **Coates Brothers Inks Limited** Technical Information Leaflet No. 120. The new range is based on the same high-body, low-tack principle as the *CLT5* range, and is claimed to have qualities of fast setting and excellent water tolerance, press stability, distribution and transference, together with a finish equal to the best of modern full gloss litho inks.

Two new pigments have recently been introduced by **Geigy (UK) Limited.** *Irgalite Red PDS3* is the third member of Geigy's new range of easily dispersible organic pigments for paints. A toluidine red, *Irgalite Red PDS3* is claimed to disperse efficiently in cavitation mixers to give a brighter shade and higher gloss than conventional toluidine reds dispersed by ball mixing.

Irgazin Violet 6RLT is an addition to the *Irgazin* range, a red shade dioxazine violet with excellent tinting strength. It is claimed to have excellent fastness to light and very good fastness to weathering and overpainting.

Polypenco Limited have reduced the prices of *Nylatron GS* and *Nylon 66* Extruded Round Rod and Plate in all their standard list sizes. New price lists are now available.

A fast-drying and durable road marking material containing glass beads to give a high degree of reflection from vehicle lights has been developed by the **Storry Smithson Group.**

The material, *Stradaline*, is a thick plastic resin coating and is available in two types, cold (suitable for application by brush, spray or marking machine) and hot (solid, applied by stencil while molten), both types setting almost immediately. Advantages claimed are water resistance, ease of application to damp surfaces, and good abrasion resistance.

A slide rule for analysing the direction of a colour difference in terms of hue, saturation and luminosity has been designed by **Instrument Development Laboratories,** and is being marketed by **Livingston Electronics Limited.** Known as the *Color-Eye XYZ Ratio Analyser*, it is used in conjunction with the X, Y and Z ratio values obtained directly from a tristimulus colorimeter.

Ault and Wiborg (Export) Limited is the name of the new subsidiary formed by the Ault and Wiborg Group of Companies. As from 1 May the new company will control the overseas business of the group, including export of group products to 78 countries throughout the world.

The object of the reorganisation is to co-ordinate and rationalise the overseas marketing activities of the various companies in the Ault and Wiborg Group, and to strengthen the overall selling operations by a concentration of effort by products and markets.

A new organic pigment, *Permanent Red HF3S*, is announced by **Farbwerke Hoechst AG.** The pigment, which has a bright, yellowish red shade, is claimed to have good light, weathering, over-lacquering, and organic solvent fastness, and heat resistance.

British Titan Products Co. Ltd., have recently published four new publications for the paint industry. Three of these describe a new grade of *Tioxide* TiO_2 pigment, and its formulation and manufacture. The fourth gives the results of new work on catalysis in the field of acrylates carried out by **Titanium Intermediates Limited.**

The two biggest producers of wood preservatives in Germany, **Desowag-Chemie GMBH** and **Farbenfabriken Bayer AG,** announce that they will co-operate in the future in the field of wood protection. The co-operation will take place through Desowag-Bayer Holzschutz GMBH, under the management of the present manager of Desowag-Chemie.

The British Paper and Board Industry Research Association and the **Printing, Packaging and Allied Trades Research Association** are to merge to become one organisation, if members of both associations agree. The councils of both organisations have studied a report on the advantages and disadvantages of merging, and agreed on the merger unanimously.

Under the scheme proposed the two associations will combine at PATRA's site at Leatherhead, while the BPBIRA site at Kenley will be sold and the money added to the liquid resources of the proposed new organisation, out of which the costs of new accommodation will be met.

BP Chemicals (UK) Limited, Industrial Solvents Division, have published a new *Bisol* Data Book, giving comprehensive data about BP's range of solvents, plasticisers, acids, intermediates and monomers.

The book is in an " easy reference " format, being divided into three major sections : solvents ; plasticisers ; and acids, intermediates and monomers.

Pneumatic Plant Services Ltd. have recently been appointed sole agents for the *Handy I* and *Handy II* range of oil-free diaphragm compressors and vacuum pumps. These are claimed to be easily portable and capable of being used anywhere, do not require suppression, and can be built into machines and special equipment.

The *Handy I* has a capacity of 4.5 cfm, is driven by a ½ hp electric motor and weighs 32 lb, while the *Handy II* has a capacity of 7.5 cfm, a ¾ hp electric motor and weighs 42 lb.

Laporte-Synres, who are shortly to begin production of synthetic resins in the new plant which is nearing completion at Stallingborough, Lincolnshire, have introduced three new information booklets. These contain up-to-date information about test methods and selection of resins for use in inks suitable for various printing methods.

Section Proceedings

Bristol

Industrialised building

The 155th meeting of the Bristol Section took place on 31 March 1967 at the Royal Hotel, Bristol, with Mr. R. J. Woodbridge as Chairman, 33 members and guests being present.

The speaker on this occasion was Mr. K. F. J. Humphries, of the Ministry of Housing and Local Government Industrialised Building and Consortia Group, who presented a paper entitled " Industrialised building."

The nature of the lecture was a little out of the ordinary since Mr. Humphries presented some 80 slides and invited discussion at any time should a point of interest be noted.

Mr. Humphries defined the expression of " industrialised or system building " as any method of construction which could substantially increase productivity, in comparison to the average levels obtained by traditional building methods.

The historical aspect of industrialised building was reviewed and it was evident that availability of raw materials had influenced design and building techniques. The now demolished Crystal Palace structure, which was built in 1879 from prefabricated glass and cast-iron components, was cited as a typical example of 19th century development.

Present day building systems demanded greater flexibility in design and planning and many new types were based on Parker Morris Standards. This involved improved standards of thermal and sound insulation, fire resistance and durability, and called for a greater understanding of newer raw materials—such as plastics and light alloys.

During the showing of the slides, Mr. Humphries described the progress of concrete building systems as developed in this country since the war. The advantages and disadvantages were compared against similar systems developed in Scandinavia and Russia, where, due to the short building season, prefabrication methods using factory constructed units were well established.

A lively discussion was opened by Mr. T. Jones, during which Mr. Humphries gave his personal views on interior decoration. He thought that painting systems, as now used for interior decoration, would be replaced by coatings which could be applied by pressure adhesive techniques, either with or without removable backing paper.

In proposing a vote of thanks, Mr. L. J. Brooke commented on the immense interest which Mr. Humphries had sustained during the presentation of his paper, and this was heartily confirmed and endorsed by all those present.

F. E. R.

London

Artists vis-à-vis the paint industry

The following is an abridged version of the talk by Gluck at the London Section AGM on 20 April 1967. (See Notes and News.)

My theme deals with Art and Science as befits the great artist and experimenter Leonardo da Vinci, whose image is your official emblem ; but the title I have chosen for my talk will already have given you some inkling that the aims of my profession in the use of paints and media are not identical with yours as suppliers—in the main—for industry. In fact our aims are diametrically opposed. The difference between an artist's use of paint and that of the industrial painter is so fundamental that it is important that, from the outset, I should make the difference very clear. An industrial painter's method of laying on paint by hand, roller or spray is such as to *eliminate identity*, whereas the complete reverse is the aim of the artist, whose identity must not only have free expression, but be as recognisably personal as his handwriting. His brush is his pen. It is therefore clear that the paints and media available to an artist must be capable of responding to the direction of his brushstroke without any distortion of his intention.

It is also clear that should an industrial painter attempt to indulge in a highly individualistic application of his materials, he would not only be mis-using his paints for the purpose for which they were made and for which he is applying them, but he would soon find himself out of a job. Industrial paints do not envisage impastoed application. Yet, throughout the centuries, paints and media have had to fulfil these two disparate functions ; on the one hand to permit the exploitation of the personality of the artist, on the other the elimination of the identity of the artisan.

In earlier ages, paints and media used for art and industry shared the same nomenclature and, except, perhaps, for a higher quality for special uses, the same nature, but all this has been changing fast, and as you all well know the demands of industry are now so predominant and vast all over the world that the special needs of small bodies outside industry stand little chance of being supplied with material suited to their individualistic requirements. This is the position of the artist today. It is therefore necessary for me to give you some idea of the process of picture making, and of how the artist is affected by the unceasing changes in industrial paint making, changes which accelerate at such a pace that it is clear not much time can have been given to really long term tests. For years I have been a subscriber to leading journals on the technology of paints and media, and I find a new vocabulary regarding paints and media has grown up which is well-nigh unintelligible to the artist, as bearing no relation to that used until very recently by all artists, and to be found in artists' text books. All these changes have had a profound and disastrous influence on the painting of pictures.

In order to prove my statement that the artist's purpose in applying paint is diametrically opposed to that of the industrial painter, it will be necessary to analyse what constitutes " a picture." A picture is a painting within chosen physical limits which should be appropriate to its subject. By that I mean that the artist will choose to express his subject on an appropriate substrate which will have to exist within a frame, the whole being transportable. Industrial painting, on the other hand, is done for practical purposes and any aesthetic considerations would lie only in the field of decoration, even if the colour of such decoration could be argued to have a subjective influence on the beholder. When, as decoration, industrial paint is used to produce certain emotional responses, it can only do so by juxtaposition of colour and mechanical methods of application. I have yet to see any industrial application of paint that expresses the handwriting of the executant. The artist in painting a picture is a visionary, expressing his vision through skills appropriate to architects, engineers, builders, decorators and chemist-physicists. By this I do not mean that to practice as an artist he has to be qualified in any of the above professions and trades, what I mean is that, in the carrying out of his vision, he will, if he is a good artist, have combined all these approaches to his vision in order to create the composition of his picture. A picture to be comprehensible must be able to operate for the observer. Its parts must carry out a function as closely knit to the whole as the organs of our bodies, or the parts of an engine, or the ingredients of a prescription. Yet, for a picture to live and function and speak to us of the artist's intention, the artist has to use matter physically to express his insubstantial thought. This he does by a process of illusion.

It is conceded that the greatest art conceals art, meaning by this that the transference of the artist's vision should not be vitiated by any self-assertive irrelevance which can destroy the effect of the whole and therefore the illusion he wishes to create. We must all, at some time, have been transported into higher spheres than that on which we live, by a supreme performance on the violin, when a fractional slip by the performer will have suddenly broken the spell by reminding us that the heavenly sounds we have heard were produced by cat-gut. It is as if the organs, mercifully hidden within our miraculously co-ordinated bodies, were to obtrude, thus destroying the unified beauty of the flesh concealing them and their functions.

All great works of art through the ages have conformed to this principle of wholeness, even those considered revolutionary at the time of their creation. We, their heirs, undisturbed by their break with contemporary practices, owe our heritage to the survival value of this fundamental attribute. It is the only touchstone we have by which to judge the merit of a work of art, because this unity of conception and execution is, irrespective of date or subject matter, the only way in which a picture can communicate intelligibly without distracting the observer with irrelevancies.

No artist, however original or before his time, can escape the imponderable influences of the period in which he lives. If he tries to dissemble, he does so at the peril of anaemia. He can only succeed as an avowed dissenter, and even then the spirit of his time will impress itself insidiously. This is seen most vividly in the graphic work of Blake, where his unique and symbolic approach to eternal themes is nevertheless imbued with an unmistakeable 18th century visual interpretation.

Not long before the outbreak of the last war, an old lady, very disturbed by the work of Picasso, asked me to explain him to her. I replied that if she was able to understand her daily newspaper she could understand Picasso. Picasso has chosen as his theme the fragmentation of human life today. Can we deny that our daily newspapers give us nothing else? Francis Bacon's paintings give us the same traumatic experience we would suffer on seeing the result of a murderous raid perpetrated by maniacs. Again, only an illustration of what we read in our daily papers, or endure on fictional or documentary television. At least Picasso's fragmentary approach will occasionally betray compassion for the present lot of mankind. Francis Bacon's—none. The more blood and viscera, the more the merry chink of money at the turnstiles. To find the touchstone against which to evaluate these two obsessional painters we have to search history for a period comparable to our own when war created social disorder and cruelty. The Thirty Years War, like our two world wars, generated a taste for the horrible in the arts, but humanity has only preserved those paintings in which the artist's representation reveals his compassionate attitude to the horror and suffering he depicts. Great artists like Rembrandt and Goya did not paint to *épater le bourgeois*, or to create detached documentaries. They give us their comment on man's inhumanity to man, therefore their exercises in the horrific do not disgust us, nor does their compassion weaken the force of the horror they illustrate factually. On the contrary, their compassion serves to emphasise the depths of the horrors they depict. Great tragedy seen through the eyes of great artists purges, but our last two wars have only produced artists capable of feeble obsessional yelps, not roars of protest ; artists with only an apparent desire to perpetuate horror and mental unbalance without the virility or moral toughness to exploit their, and humanity's, powers of rejection and rejuvenation.

Rembrandt's " Slaughtered Ox " appears at a casual glance merely a factual representation of a disembowelled carcass in a butcher's cellar. This commonplace subject has, nevertheless, had the power since painted to shock those willing to eat beef, but unwilling to face reality. Yet, the more one studies this great painting, the more one becomes aware of the profound implication it holds of man's relationship with animals. and the basic facts of our life on earth. Rembrandt teaches us through this powerful picture that beauty is to be found anywhere, but that it cannot be communicated unless a single-minded loving and understanding interest has guided the choice of subject. The further preservative that has ensured the survival of great and savage paintings, lies in the quality of the painting itself. This last and basic preservative is ignored by our present purveyors of shock art.

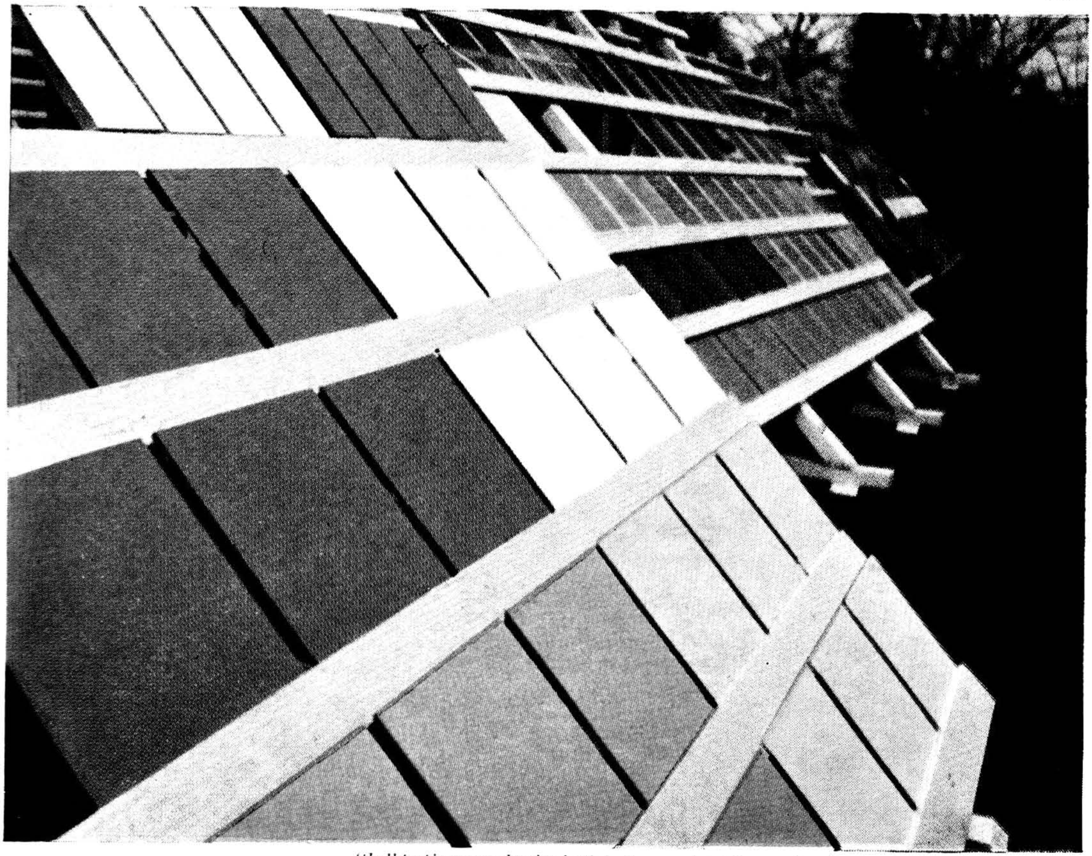
There are those who think that the composition of a picture can be taught. I, on the contrary, believe the artist's vision of his subject should dictate not only the design of his picture, but its size and every detail it contains. An artist's vision, is, in a sense, a triggered snapshot which has to be developed, and in the medium appropriate to the artist's conception. This is why all rules which are, by definition didactic, are so often broken and, most effectively, by great and original artists.

Many years ago, a young man sought to prove in a book entitled "*Canon Tiburtius de Composition*" that the great Masters worked out their compositions on mathematical lines, illustrating his thesis with reproductions of great masterpieces criss-crossed with lines looking like scaffolding on a building. But if the using of such mechanical props was a truth, how easy it would have been for the number of masterpieces to have been increased a thousandfold by any adept mechanician merely following these precepts; like painting by numbers. But, of course, it is not a truth that immutable mathematical proportions guided the Masters in setting out their compositions; it is only one more proof that any masterpiece will contain in itself many parts harmonising to create a whole. This is why it is fallacious to subscribe to the present cult that detail is detrimental to a picture, and will destroy its breadth.

The avoidance of detail in pictures nowadays is only due to the incompetence of painters unable to control the parts of their pictures. They attempt to cover this incompetence by jargon indicating that the grandeur and breadth of their conception would be destroyed if the parts of their pictures were recognisably detailed. So we are treated to meaningless abstract empty shapes, mere decoration without specific meaning, and therefore incapable of making intelligible communication other than mouthing at the viewer. Breadth is not emptiness, any more than breadth of mind indicates vacuity. Pythagoras defined Beauty as "The Reduction of Many to One." Mozart, when asked if he had finished a commissioned work, replied :—"Yes, it is finished, I only have to write it down." Like the instruments in an orchestra, detail is only destructive if assertively out of harmony with the whole.

When I am painting a picture I always feel that I am rehearsing an orchestra for an already composed piece, and many times have said to people viewing an unfinished picture (which one always deplores) "You see that unfinished bit is like the drums being too loud. I still have to see that none of the instruments are heard individually unless needed for the effect of the whole." I point out that the smallest distraction from the original complete vision will destroy the unity and force of an artist's intention.

A slight emotional response to a subject cannot stand up to inflation out of scale. For years controversy has raged as to whether Constable's sketch for "The Leaping Horse" is a better picture than the larger work he painted from it. In my opinion there is no comparison. Some years ago they were shown side by side at the Tate Gallery, making evident that, when Constable painted the sketch he had the larger painting in mind. The sketch has all the dash, immediacy and brilliance of a Master's summary of his vision; whereas the final picture contains not only all the qualities of light and sparkle of the sketch, but has expanded into a great orchestral work where the artist has had full scope and opportunity to exploit his vision to the limit of his capacity. Only amateurs without intensity need fear diminution of power during carrying to conclusion a work that takes a long time to create. The vision once seen must be adhered to through thick and thin, and many sacrifices of pleasant by-ways and second thoughts must be sternly made if the purity and power of the original purpose of the work is to be preserved through the long and often exhausting processes of bringing to birth a finished work of art. A work is only finished when all that the artist set out to do is accomplished. Finish is not finick, and the greater the artist's vision, the more likely his dissatisfaction with the final result. There are only rare moments when he can feel



Shell testing panels give both indoor and outdoor paint the toughest test of all – nature!


PURE
ISTLES

he has produced his best, and that feeling, however humble the result, is the greatest reward he can receive.

There is, in England, complete non-comprehension of the difference between an artist and an artisan. It is to be regretted that the best elements of the Guilds have not been preserved. There was a beneficient aspect to a brotherhood that, whatever the object of their brushwork, could rely on certain standards of worthiness in their materials. The present plight of the artist is due to the complete breakdown of the machinery that ensured, by penalties for infringement, that unworthy or adulterated materials must not be used by a member of the fraternity. Was not this rule as protective to the practitioner as to his client ? Would to God it applied today to protect the artist. The activities of the Painters' Company have been partly assumed by other bodies of modern growth, but these do not provide the beneficient control exercised by the Company in the comparatively simple conditions of the 16th and 17th centuries.

What protection is now available for the artist ? The answer is none. With the single exception that one firm now retails and exports cold-pressed linseed oil as a medium, not one effort has been made by firms professing specialisation in artists' materials to alleviate the universally deplored troubles, anxieties and frustrations of serious professional artists. As I have already pointed out, these firms are small, and depend on what is produced by industry, and, as I see it, there will not be any solution to the problems against which artists struggle vainly until the Paint Industry as a whole, in the spirit of the ancient Painters' Company, shows a civilised interest in the Fine Arts. The paint industry must realise that paint made for industrial purposes, to stand up to industrial wear and tear, and to solve all the increasingly complex problems set by the unceasing and rapid changes made in the technology of all material objects demanded by mankind all over the world, is not suitable for painting pictures.

It is not only I who am crying in the wilderness. Ralph Mayer, internationally known as paint chemist and an authority on artists' materials and techniques, and lecturer on Art at Columbia University, repeats, in the latest edition of his manual " The Artist's Handbook " :—" A good deal of the best work on the chemistry of natural raw materials which are used for painting has been done either in industrial laboratories or by men who have approached the problems from the viewpoint of Industry. This has directed research into channels not directly in line with the application of results to artistic painting, because the commercial or industrial value of these products as artists' materials is insignificant as compared with their commercial value in other uses."

In order that you may appreciate the contrast between the industrial use of paint and that of artists, I ask you to examine the brushwork and effects achieved by those great impressionists, Velazquez, Rembrandt, Franz Hals and others whose handling of paint is discernible and individual, and to query how they and their effects would have fared if all that had been available to them had been a medium-oil-length soya pentaerythritol alkyd, applied, as it would have to be, mechanically. If you study the Masters I have mentioned you will surely realise that the paints they used were capable of the effects their brushes produced, without the distortion of suede-effect dichroism. This is because the two basic raw materials of their oil paints were fundamentally different from those produced today. Their oils were pressed cold, their pigments were hand ground, thus producing irregularly shaped pigment particles of varied size which, when ground with the oil, produced a stronger paint film capable of inimitable personal effects.

Lewkowitsch and Warburton state that :—" . . . for the best and finest kinds of linseed oil (artists oil) the seed is pressed cold . . .." Hilditch states that " poppy seed oil for artists' paints is obtained only from the first cold pressings of the seed," and that this oil and walnut oil have been " the favourite medium of artists since their employment by the great medieval and renaissance painters." I have not been able to trace any manufacture in this country of walnut oil, and poppy oil, though available, is not cold pressed, though at last the means to obtain it cold pressed do exist.

Brace, in his book on " The History of Seed Crushing in Great Britain," describing 18th century methods says :—" Evidently at this early period, the superior quality of the oil produced by expression in the cold had been appreciated, coupled with the fact that moisture and heat would enable higher yields to be obtained though at a sacrifice of quality." The artist has still to endure this sacrifice of quality in his paints. When Hilditch made his pronouncement no genuine cold pressed linseed oil was obtainable anywhere. It is only within the last years six that, owing to the enterprise of Messrs. Wilson & Sons (Dundee) Ltd., genuine cold-pressed linseed oil had been produced by their Caledonian Oil Mills, Dundee, and is now listed in Winsor & Newton's catalogue as a medium. Unfortunately, poppy oil is still not cold pressed, and this is to be deplored now that the means to press it cold are available.

Not only have the sales of this cold pressed linseed oil increased steadily (without any advertisement until this year) but it has also a growing market in the United States. Yet still artists' oil paints are made with the proved deleterious heat expressed oils, and the artist is still unable to obtain paints made with the cold pressed oils agreed by all authoritative oil and paint chemists to be the best for artists' use.

Do you consider it reasonable that, after so many authoritative pronouncements on the superiority of cold pressed oils have been published by universally respected oil and paint chemists, that the artists' colourmen still ask for proof that cold pressed linseed and poppy oil are best ? The British Standards Institution has been able to formulate standards for heat expressed linseed oils, but so far no standard has been agreed for the cold pressed.

But it is not only the artists who suffer. Cabinet makers equally have trouble with the linseed oil they use, and there are other specialist trade users of linseed oil who, in varying degrees, have suffered since the disappearance of a linseed oil devoid of " foots." Cold pressed linseed oil is free of this trouble, and the problem it poses, and no process is needed to refine the oil in order to remove such deleterious matter.

You will remember that I said a picture consists of orchestrated parts as does a piece of music to be performed by an orchestra. What sort of orchestrated effect is possible if, when the composition is performed, all the instruments are out of tune ? Yet this is a precise illustration of the frustration suffered by every painter using artists' oil paints today, as all artists' present-day oil paints produce the suede-dichroic effect, that is, the effect produced by rubbing suede in different directions.

During the time-wasting and ruinous years I have had to spend tracking down the causes of the suede-effect, I have had the free and interested assistance, through tests, and sample manufacture, of the laboratories of many eminent firms also from friendly chemists and physicists here and in the United States, and I should like now to register my gratitude, not so much for the material help they gave me, though that was considerable, as for the confirmation that it is possible to find in industry a disinterested desire to help artists to solve their problems—help which has not been forthcoming from those who confess to serve artists exclusively. The plain truth that the suede effect is primarily caused in oil paints by too finely ground pigments and heat expressed oils made into paint mechanically, has been proved. The addition of metallic soaps will merely aggravate the effect.

The artist uses his paints as the magician weaves his spell, to conjure up his visions, and the colourmen who profess to serve him must not behave with the irresponsibility of the

The Good Hope Castle speeds majestically down the Solent en route for Cape Town.

Sorcerer's Apprentice. I therefore now appeal to you all individually, and collectively, as experts in the technology of paint, to tell me tonight whether you consider the works of artists should be " disposable " and that their materials should contain " built-in obsolescence," or that the kind of paint so admired and preserved through the centuries to this day, should be made available for those artists, the possible Masters of the future, wishing to paint with integrity and without frustration ? I ask you in the name of Leonardo da Vinci to come to the rescue of artists at this moment of crisis, when all that has been so highly valued, and still is, may be lost for ever, and to apply to our problems your splendid and apt motto—" *Et mente et manu.*"

GLUCK

Notes and News

20 OCCA Technical Exhibition

20-OCCA (the Association's Twentieth Technical Exhibition) will be held at Alexandra Palace, London on the following dates and times :

Monday 25 March	3.00 p.m.-6.30 p.m.
Tuesday 26 March	10.00 a.m.-6.00 p.m.
Wednesday 27 March	10.00 a.m.-6.00 p.m.
Thursday 28 March	10.00 a.m.-6.00 p.m.
Friday 29 March	10.00 a.m.-4.00 p.m.

The Invitation to Exhibit was despatched to companies both in the United Kingdom and overseas at the end of May and many completed application forms have already been returned. Any company intending to exhibit in 1968 must return a completed application form to the General Secretary by **4 September 1967.**

Copies of the *Official Guide* to the Exhibition will be sent individually to chemists and technologists in the paint and allied industries in Western Europe, to consuming firms in this country and to all members of the Association wherever resident. Copies can also be obtained free of charge from the Association's offices ; admission to the Exhibition is free.

Each copy of the *Official Guide* will contain a form of application for tickets for the Exhibition Luncheon, which will be held at the Savoy Hotel, London W.C.2. on Monday 25 March 1968.

Also being prepared for distribution on the Continent is a leaflet in English, French, German, Italian, Russian and Spanish, containing a map and directions on how to reach the Exhibition.

Any companies wishing to apply for stand space at 20-OCCA who have not previously exhibited should write to the General Secretary at the address given on the front cover of the *Journal.* The exhibition is believed to be unique in that it is entirely technical, and is aimed at ensuring that technical advances are passed on as quickly as possible to the technical personnel in the paint, printing ink and allied industries. The technical advances may relate to new products, new knowledge of existing products and their uses, or in suitable cases existing knowledge which has not been available to the consuming industries.

In order to show the high regard in which the Exhibition is held, some extracts from the reports of OCCA 19 in other journals are given below :

" Having run out of superlatives to describe the fine exhibition organised by the Oil & Colour Chemists' Association, it is perhaps sufficient to record what a splendid friendly show this is.

It is not too large to cover quite comfortably in one day, and it is rather like the gathering of all the members of one large family. The standholders all vie with one another in the technical excellence of their displays, in laudable contrast with the alcoholic aura that pervades many of the larger, more commercial shows "—*Rubber and Plastics Age.*

" Undoubtedly the most useful and interesting exhibition in the field of chemical industry is the annual technical display which the Oil & Colour Chemists' Association (OCCA) have organised for many years.

To sum up, a very interesting and attractive technical exhibition. OCCA well merits all the complimentary remarks made by Mr. Darling on its technological and educational activities " —*Chemistry and Industry.*

" As already reported, the 19th Technical Exhibition of the Oil & Colour Chemists' Association was a good one with a wide variety of technical items on show "—*Paint Oil & Colour Journal.*

" With an attendance at least equal to last year's and with visitors from some 30 countries attending, this year's exhibition was voted an unqualified success, and the doubts previously expressed by some members of the industry as to the wisdom of the move to Alexandra Palace would now seem to have been dispelled "—*Paint Technology.*

" The OCCA Exhibition is the only really comprehensive Exhibition in our branch of industry in Europe, and the paint technologist who has visited it without feeling that he has had some profit from it has devoted too little time to it, or else there is something wrong with him."—Helge Meyer, *Farg Och Lack.*

Germany

20 years GDCh-Fachgruppe " Anstrichstoffe und Pigmente " conference

The Section " Paints and pigments " of the Gesellschaft Deutscher Chemiker (GDCh), the German equivalent of OCCA, with similar aims, celebrated, with Dr. W. Geilenkirchen as chairman, its 20 years anniversary on 10 and 11 April 1967 in Cologne. It consisted of a business meeting, social activities and a series of 13 lectures, largely referring to pigment-binder relationships and to various aspects of weathering. The balance of the papers dealt with topical subjects. The number of registered participants was 214, many of whom came in daily from the area and the near Ruhr district, both of which are thick with paint and raw material producers' factories. There was only a small sprinkling of foreign visitors.

The session was opened by an address by E. A. Becker, the founder chairman of the Fachgruppe and a former chairman of FATIPEC (Wiesbaden), which was most interesting. From small beginnings the membership has risen to over 400, covering a turnover in pigments and dyestuffs as well as varnishes and paints (exclusive of emulsion paints) of well over two million Deutschmark, of which more than half is derived from paints. During the 20 years of its existence 31 lecture-meetings have been held, and the number of papers read by members, including those at FATIPEC conferences, has been 725. At present there is a spring and an autumn meeting, which takes place on the occasion of the AGM of the mother-association GDCh. There seems, however, to be a growing desire to condense these conferences into one.

Following Dr. Becker's talk, H. F. Sarx surveyed the " Development of media 1947-67." The post-war troubles with regard to availability of raw materials were no doubt even greater than our own!

Of the latest trends mentioned, a few stick out in the mind : Isomerised and dimerised fatty acids being increasingly used, groundnut, safflower soya oil fatty acids replacing more and more rectified tall oil fatty acid ; neopentylglycol and other newer alcohols finding application ; acrylic alkyds being particularly useful for undercoats ; oil-free polyesters gaining in importance ; the dispersion of emulsions getting finer and finer and finding use in rough castings, etc. ; on the industrial finishes side in particular : the increased importance of finishes for application by roller coating, the " bake-sand-bake " acrylic motor car finishes, PVF organosols and masked isocyanate lacquers, which only open up on stoving.

The " Development of pigment since 1947 " was surveyed by K. Heinle. In this field the developments in Germany seemed to have more or less paralleled those in this country. Amongst the newer colours, the speaker referred to chromophthals, which due to increase in molecular weight gained in solvent resistance, the improved and cleaner shades of β-phthalocyanines, the vat colours and pigments with condensed ring systems, dihydroxyazines, isoindolinone and quinacridones.

These papers, occasioned by the 20 years Jubilee of the Fachgruppe, were followed by ten conference papers, spread over two days.

Angle of contact measurements for the determination of energies of wetting related to the presence of pigments

by A. W. Neumann

Owing to the known difficulties of measuring the contact angle of powdery solids, the wettability of pigments has had little investigation. That of a group of substances, similar in respect of surface energies, i.e. the plastics, is fairly well known. Findings in the field of wetting of plastics have in the present work been transferred to organic pigments with the purpose of creating reproducible values.

Within the framework of this investigation, in which one and the same system, i.e. pigment/organic solvent, is used, the contact angle obtained depends very much on the conditions and manner of experiment. Therefore, interfacial energy criteria, learned on the investigation of wetting of plastics, were applied for establishing the equilibrium of contact, i.e. of that angle of contact which forms under the sole effect of the inter-molecular forces without being influenced by geometrical conditions.

Important interfacial energy conceptions, definitions and relationships are explained first. It was shown that the measurements of the contact angles between plastics and organic liquids supplied directly the free energy of wetting, called tension of wetting, the temperature dependence of the angles of contact and the total energy of wetting, called heat of wetting. The measurements of contact angles on polytetrafluoroethylene in different organic liquids were compared with its sedimentation performance in powder form in the same liquids ; remarkable parallels between sedimentation and wetting results.

Direct utilisation of these similarities in the technical application of organic pigments in practice was not possible, because direct measurements of contact angles on powders cannot be made. As processes described in the literature were unsatisfactory, at least, quantitatively, only two possibilities remained, as long as no large enough single crystals were available, i.e. to either compress pills from pigments or to evaporate them in high vacuo on to suitable substrates. So far no success had been achieved with pills. It was, however, possible to obtain consistent measurements in respect of interfacial energies on pigment layers, evaporated in very thin layers ; i.e. on Heliogen blue LBGN and LBGO, Hansa red B, Permanent violet RL, Permanent red BL, Indanthrene brilliant orange GR and Permanent pink E.

The surface tensions of the pigments could be calculated from the measured contact angles and the surface tension of the measuring liquid. For the pigments investigated, so far, they lie between 32 and 36 dyne/cm and, therefore, possess the expected dimension. Determination of heat of wetting from the temperature dependence of wetting required a further improvement of vaporising technique.

The possibility guiding cellular flow caused by interfacial tension in paint films

by G. Marwedel[1]

H. Jebsen-Marwedel found that in molten glass and enamel layers a cellular division of the surface could occur, if miscible areas or layers of differing surface tension were present. If a third common phase was possible, e.g. vapour-saturated air due either to penetration of a lower or inner layer of lower surface tension towards the outside, or to areas of different surface tension lying adjacent on the surface, under the influence of the so-called spreading pressure (Spreitungsdruck), shearing of the mass occured if the centres of spreading or swelling were suitably distributed statistically. These encountered the neighbouring spreading waves and were deflected downward or inward. In this way the surface became polygonally divided[2].

Jebsen-Marwedel described such phenomena as "Schlierenwirbelphaenomen (schliere vortex phenomenon) of dyne-active liquid partners." In the search for proving general validity, co-operating with Jettmar and Roesler, he turned his attention to varnishes.

Following on, Brueckner observed that the dynamics of the process could be considered as the rotation of a resulting vector, which could be constructed by geometrical addition of the involved and continuously changing, surface and interfacial tensions caused by the mixing process.

Thanks to the iris diaphragm effect a particularly clear form of the " Schlierenwirbelphaenomen," permitting almost quantitative photographical exploitation, was possible.

The spreading over a surface/time, i.e. the spreading speed V in cm^2/min of the one phase with low surface tension over another with a higher one results in :

$$V = \frac{k}{t^{1/a}} \cdot \frac{\Delta\sigma^{1/b}}{\eta c} \qquad (1)$$

in which $\Delta\sigma$, also called primary impulse, is the difference in surface tension of the liquid phases, which take part in the spreading process. ηc is the viscosity in cp provided the mixing of the phases is complete. It results from the concentration function of the viscosity. t is the duration of the experiment in minutes. a, b and k are the constants. The equation (1) can also be written :

$$\frac{V \cdot t^{1/a}}{\dfrac{\Delta\sigma^{1/b}}{\eta c}} = K \approx \text{const.} \qquad (2)$$

The product $V \cdot t^{1/a}$ results for itself in approximate constancy and proved to be proportional to the quotient $\Delta\sigma^{1/b}/\eta c$ from which it was concluded that the reduction of interfacial energy resembled the reduction of an electric field, e.g. on discharging a condenser, say by autoinduction. It was therefore possible that one interface was reduced and reconstituted at another place. On reduction of this new interface the original one was reconstituted, whereby after several repeats an oscillation, cushioned by the viscosity, originated. H. Linde, S. Pfaff, E. Schwarz and Ch. Zirkel have observed such forms of activity of free interfacial energy in many variants. Equations (1) and (2) lead to conclusions regarding film formation. It was necessary to keep $\Delta\sigma$ as low as possible in order to cushion the spreading process in a paint layer. In addition it should be attempted by the viscometric performance to put a brake to mobile processes. The changes of viscosity in time must, however, still permit a reduction of structure by diffusion.

Scheme for these interlocking processes:

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[1] The session chairman, Prof. Hamann, drew attention to the fact that the work described was carried out by the owner-chemist of a comparatively small paint works.

[2] Jebsen-Marwedel, H., *Chem. Ztg.*, 1966, **12**, 393-402.

evaporation
↓
pressure of spreading
↓
speed of spreading

impulse, depending on	cushioning, depending on
↓ course of functions in time of concentration and temperature of σ.	course of functions in time ↓ of concentration and temperature of η.

It was also possible to formulate the connection between surface tension and viscosity as a kind of state of equilibrium, to approximately calculate the disturbance of this equilibrium following the appearance of a new interface due to changes in temperature and concentration and to connect it with equation (1).

In order to keep the primary impulse as low as possible the attempt had to be made to approximate the surface tension of the evaporating solvent to that of the film former. This thought led to an estimation of the surface tension of semi-solid and solid resins. This was carried out by means of the temperature function of the surface tension in the molten state and by means of the connection between surface tension and density.

Table 1

Surface tensions of semi-solid resins

Resin type	*Surface tension dyne.cm*$^{-1}$
Soya alkyd resin	36,4
Cyclohexanone resin	44,1
Xylenol-Formaldehyde resin	43,4
Polyvinylether	37,7
Acrylic resin	44,1
Polystyrene	43,0

Reduction of structure could also occur if the viscometric performance was favourable whilst $\Delta\sigma$ is still present. This applies also to low molecular resins. By subsequent curing, cross-linked films, free of defects, could be obtained.

The proof for these observations was obtained by projecting and photographing pictures on a screen, of 25 per cent solutions of the isobutyl ester of the polymethacrylic acid in (a) petroleum solvent (140/200)—butanol, i.e. solvents of much lower surface tension than the resins as against in (b) xylol-methylglycolacetate, i.e. of higher surface tension ; (a) showed a silhouette, (b) no blemishes.

This can be summarised as an attempt to produce faultless films by reducing the transportation processes to enable the diffusion to take place more slowly under normal conditions.

Also, if film formation originated from processes of polycondensation, polyaddition and polymerisation defects due to the "Schlierenwirbelphaenomen" were possible, provided that statistically distributed, periodical changes of the surface tensions occurred during solidification.

Jettmar demonstrated the importance of these processes for the performance of pigments in binders with regard to segregation.

Pigment floating and pigment flooding by W. Jettmar

Well wetted pigments could easily be dispersed. Such dispersions were stable and offered no problems in use. The dispersion of badly wetted pigments was difficult, usually showing instability to flocculation and resulting in loss of colour strength. This strength would be reduced in the case of a flocculating coloured pigment if mixed with a non-flocculating white pigment ; if, however, the white pigment flocculated, the colour strength appeared to increase. Co-flocculation had been postulated by F. K. Daniel as the aim, because only rarely an ideal wetting of the pigment by the binder took place.

The surface characteristics of the pigments and their interaction with the binder were responsible for the cohesion of a flocculate. However, kinetic energy such as Brownian movement, which brought the particles together, was also necessary for the formation of flocculates. Due to the low energy involved, the formation of such a flocculate, e.g. in a paint or a low viscous flexographic or photogravure printing ink, required some time. The phenomena of the more energised currents in a drying paint or ink layer, which could separate out a flocculating and a less flocculating pigment within seconds to a great extent were much more dangerous.

The vortex in the Bénard cell (see also the paper by G. Marwedel) circulated the pigment during the drying process from the solvent-rich interior to the binder-rich surface, resulting from evaporation. This flowing layer had a thickness of a few microns only. During the flow the pigment was repeatedly exposed to binder and solvent shock. The various currents, and therefore also the pigment particles clashed with each other at the source and the periphery of the cells. Thus the most ideal conditions for flocculation were produced for a pigment which tends to flocculate in one of the frequently numerous constituents of a medium. A resulting flocculate solidified and resists the circulation, when it was expelled from the flowing lamina and deposited in the less turbulent centre of the vortex. In this way the flocculating pigment disappeared from the surface, whilst the non-flocculating pigment was continuously re-circulated to the surface. After gelling of the system the non-flocculated pigment was therefore concentrated in the dry film surface.

The dynamics of these movements could be made recognisable by filming. The speeds were a multiple of particle diameter per second. Pigment agglomerates of 5-10μ can still be transported, whilst the voluminous flocculates, often having the size of several hundred microns, dropped out from the current. The photographs of the films taken proved that Daniels' postulate of co-flocculation could be realised. They also demonstrated how sensitively the pigments react. Only a change in the ratio of two pigments, whilst the binder remains unchanged, could influence the pigment flocculation.

Adsorption of polymers and the stability of pigment dispersions in non-aqueous media

by V. T. Crowl

The stabilisation of dispersions of titanium dioxide and iron oxide pigments in benzene by polyesters of adipic acid and neopentyl glycol terminated with different functional groups has been studied. Adsorption of the polyesters corresponded to approximately a close-packed monolayer, being somewhat lower for the hydroxyl-terminated polyester. Stability of the pigment dispersions was high in solutions of carboxyl- and hydroxyl/carboxyl-terminated polyesters, but extremely low with hydroxyl-terminated polyesters. Interaction of the ester groups with the pigment surface, as shown by infra red spectroscopy, was found to occur at low surface concentrations, but not at higher concentrations, suggesting that at low concentrations the polyester molecules lay flat on the surface, while at higher concentrations the polyester molecules lay on the surface in random coils. The dispersed pigments were found to be uncharged, and stabilisation by an adsorbed layer mechanism was postulated.

The study of the stabilisation of pigment dispersions has been extended to practical alkyd paint systems, with phthalocyanine pigments. In a series of experiments the degree of flocculation of the phthalocyanine pigments under practical conditions was found to be related to the particle size distributions of the pigments. The pigments were found to absorb monolayers of alkyd polymer sufficient to stabilise smaller ($< 0.2\mu$) but not larger particles.

Experiences with new dispersers

by T. Doorgeest

A report of investigations over the last years at the Verfinstituut TNO, Delft, on which of the new internationally offered dispersers of pigments prove best. Out of a number the " Red Devil " mill for small batches, the "Attritor," because fast and reproducible, a ball mill "Kugelstaumuehle," in which the balls are moved against a stationary blade, though rather slow-working, were found best.

Not only the grinding aspects but also wear and tear were determined. Without reproducing a number of the slides shown no more informative abstract can be given.

Experiences on weathering of alkyd-based paints in different climates

by H. J. Freier

An attempt was made to find a relationship between observations and results over a long period on test fences with the climatic conditions of the various testing stations. In this work the effects of the various climatic actions on gloss retention have been considered in the first place. The rapid loss of gloss of paints based on alkyd resins in marine atmospheres as against their performance in inland climates was thought to be due to the frequent moist-dry-changes at simultaneous exposure to radiation from the sun. The results of weather-o-meter tests were also discussed in brief with the result that gloss retention of alkyd-based paints showed similar differentiations as on exposure tests. Apart from gloss retention, film defects such as corrosion, blistering and mould growth have also been considered. The salt content of the air three kilometers inland on the North Sea island of Sylt dropped to one-fifth compared with the immediate neighbourhood of the sea.

In view of the manifold potential aspects of observation during exposure a report like this could never claim completeness.

Investigations of the influence of various experimental conditions on the damage of surface coatings by UV-light : exemplified by ethyl cellulose

by K.-H. Reichert and R. Sattelmeyer

Previous investigations of the effect of UV-light on paint films have shown that it was possible to prove by means of IR spectroscopy the chemical structural changes in the medium and that these could be used as a measure for assessing the total damage of films regarding their stability.

In further work the influence of various atmospheric conditions was followed up, using ethyl cellulose as an example. IR-spectroscopic measurements of non-pigmented films supplied the information that UV-exposure in air caused severe changes of the medium, whilst exposure in nitrogen or in vacuo caused only slight damage of the films. In these tests the presence of humidity had only a minor effect. As on the other hand, the films hardly changed in presence of ozone and absence of light, the concerted effect of light and oxygen must be considered as responsible for the defects of ethyl cellulose films.

In addition, exposures, using suitable light filters, demonstrated that changes in the structure of the medium depended strongly on the radiated wave length. No changes worth mentioning were found above 300 mm.

According to earlier observations on ethyl cellulose films pigmented with anatase the IR-spectroscopically measured damage of the medium by UV-light was greatly repressed in presence of pigments. Using IR-spectroscopy again, these findings were confirmed for a number of other pigments. The degree of damage at 10 per cent PVC was, even at different humidities, by and large the same with the pigments used.

In contrast to the total damage to films of ethyl cellulose found by means of IR-spectroscopy, observations of the film surfaces, e.g. gloss and yellowing, showed characteristic differences regarding the influence exerted by various pigments as well as by application of differing humidities. Anatase pigmented films deviated in particular, losing gloss according to the increase in humidity, whilst the other pigments investigated lose gloss more, the drier the atmosphere.

Investigations of the lightfastness of pigments of standard depth of colour

by G. Riedel

For the determination of the lightfastness of a surface containing pigments in general the blue wool scale to DIN 54003 was used. Numerous factors affect the lightfastness of a coloured paint film. Amongst the most important were the chemical composition of the pigments, mean particle size of the dispersed pigments, the surrounding medium, the spectral composition of the source of light, atmospheric conditions, and the depth of colour of the paint film.

The effect of the depth of colour on the lightfastness of different classes of pigments was the subject of this investigation which included phthalocyanine, vat, quinacridon red pigments, lakes of azodyes, molybdenum-tungstic acid lakes of basic dyes, various metal complex dyes and iron oxide.

The colourist described the colour intensity of a colouring as depth of colour. Generally, the lightfastness diminished as the depth of colour was reduced. That was why defined colour intensities, so-called standard depths of colour or " Richttyptiefen," have been standardised by means of patterns, though this test was not yet customary with pigments.

It was shown that in the case of numerous pigments the lightfastness was depending greatly on depth of colour. Tests were not only carried out to DIN 54003 for textile colourings for standard depths of colours, but far beyond for very low depth.

Apart from the blue wool scale comparisons, changes were also determined colorimetrically. Exposures were carried out in a Xenon-fadeometer, with intermittent measurements with the Spectrophotometer " Spectronic 505 " in order to determine changes in the spectral re-emission and of the Standard Colour values.

From changes of the K/S values in the absorption maximum the declining concentration of coloured pigment was calculated and plotted against exposure in megalux hours. Medium fastness was recorded in half-life periods in megalux hours. The indication for reduction of concentration was correct only in the cases of bleaching without changes of hue. The total changes in the case of changes of hue, darkening or yellowing could only be indicated with the help of a sensitive distance ΔE, the size of which can be valid in such tests as measure of fastness to light. The coloristic significance of this distance depended, however, strongly on hue and lightness, that was why comparisons regarding the distance were only possible between pigments whose hue is very close.

For the purpose of describing lightfastness of the same hue changes of the parameter B for depth of colour (see F. and L.11 (1965), 894) were determined as additional constant. This parameter fixes the standard depth of colour by numbers, which can be calculated from colorometric data.

To summarise the results of the investigations :

The lightfastness of phthalocyanine, some vat pigments and iron oxide was independent—within the investigated range—of depth of colour. The fastness of all the other pigments tested was very dependent on depth of colour, less so with the lowering of the latter. Lakes of azo dyes in particular showed a pronounced dependence of their lightfastness on depth of colour, as did molybdenum-tungstic acid lakes of basic dyes. The lightfastness of quinacridone red pigments was also dependent on the depth of colour.

Investigations of pigmentation for electrophoretic painting

by K. Nollen and G. Handloser

The charges which inorganic and organic pigments obtained in aqueous binders were intrinsically negative, so that in principal every pigment which could be dispersed in aqueous media could be used in connection with electrophoretic application. Resistance and thickness of films as well as throwing power were affected by pigmentation (pigment loading, electrical resistance).

This influence was considerably more pronounced with low-resistance than with high-resistance media, so that by suitable choice of a pigment a low-resistance binder could acquire the properties of a high-resistance one.

Aqueous polyurethane dispersions

by D. Dieterich

Polyisocyanates already at room temperature with polyhydroxy-compounds forming polyurethanes. The coreaction of two component polyurethane lacquers was based on this process. Corresponding one-component systems contained polyurethane-polyisocyanate, which cured under the influence of atmospheric humidity. The air drying urethane alkyds were a third group of urethane lacquers. These polyurethane systems as used in the paint industry required the use of organic solvents.

So far the technically and economically desirable application of polyurethanes from an aqueous phase, as known for a long time with vinyl polymers, had not been possible.

Polyurethane dispersions of relatively coarse particle size, which formed flexible films of elastomers, could be produced by means of emulsifying agents according to a patent by Du Pont, elaborated by Wyandotte. They were, however, of no interest to the paint industry.

A process had been developed by Farbenfabriken Bayer by which polyurethanes could, by the introduction of ionic centres, be transformed into aqueous colloidal solutions, from aqueous dispersions, without the aid of emulsifying agents. This process, which was very variable, also made the production of polyurethane dispersions for the paint industry possible.

These dispersions dried at room temperature in the shortest time, forming films of high gloss with pendulum hardness values of over 180 secs. They permitted rapid repainting. Gloss, elasticity and abrasion resistance equalled those usual for solvent-based polyurethane coatings. Good adhesion, water vapour permeability, solvent- and alkali resistance were further advantages. They could be applied over damp substrates.

On the negative side, so far, there was yellowing, and unsatisfactory outdoor durability and pigment compatibility.

The standard of the papers was high, but unfortunately they were not available in print before being delivered—almost in full. They will be reproduced in the two German paint magazines.

The discussions under the chairmanships of Dr. Culemeyer, Professor Hamann, Dr. Sarx and Dr. Funke were lively and meaningful.

Only two of the speakers came from abroad, Dr. T. Dorgeest of the TNO, Delft, and Dr. V. T. Crowl of the PRS Teddington. The latter's excellent paper, delivered in well spoken English, had an excellent reception for its content as well as its crystal clear presentation.

Such conferences, beyond the scientific, technical and social content also offer opportunity for stimulating talks between colleagues. Thus it was learned that aqueous polyurethane dispersions—see the paper by D. Dieterich—are considered promising and being already tackled by a few of the leading German paint works. Large customers over there are also exerting some pressure for industrial finishes curing in seconds by radiation. Apparatus for this method of application is already on offer, but manufacturers still have formulating problems, i.e. to find the resins which respond favourably to radiation.

As regards electrophoretic application the number of active plants is still rather modest, about 64 to 70, six of which, in the motor car industry, are very big. They are kept going, in effect, by only two of the largest paint manufacturers, though a third has won a footing in one of them. The paints for the other smaller tanks are supplied by a number of companies, and these installations have been found to be economical only where large production guarantees that the tanks are never idle for any length of time, such as car accessories, covers for electrical apparatus, metal seats, etc.

The writer watched the reconstitution of a big multicoloured traffic sign with road marking paint—most likely chlorinated rubber type—on the tarmac of a busy thoroughfare near the famous Dom. In reply to my praise for their great care, one of the painters replied: " It is so and so's paint (one of the best known firms), but in eight days we shall have to do it again." In the residential quarters of beautiful, ancient, Cologne the original and re-built burgher houses of past centuries, painted neatly in pastel coloured " Dispersionsfarben " are standing high, shoulder to shoulder, each topped by a small black trilby. In large parts of the enormous shopping centre vehicle traffic is excluded. Displays of a paint shop included emulsion paints in transparent plastic bottles showing the bright colours of their contents, and half kilo round screw capped tins containing various clear varnishes. Vivid, almost fluorescent colours were in the fashion shops, notably in one where a big window was filled with the models of about 20 chic young ladies surrounding a solitary elegant male, also topped by a black trilby—and reading—*The Times* !

A very friendly atmosphere characterised the concluding social evening in which Dr. Geilenkirchen gave proof that he is not only an able chairman but also has Cologne humour in his veins.

M. HESS.

London Section

Annual General Meeting

The Twenty-Ninth Annual General Meeting of London Section was held on 20 April, 1967 at the Criterion-in-Piccadilly, London, W.1. with Mr. R. N. Wheeler in the chair. At the start of the meeting members stood for a few moments in silent memory of Mr. C. R. Pye.

After the minutes of the 28th AGM had been adopted, the Hon. Secretary Mr. V. F. Jenkins proposed the adoption of the Committee's Annual Report. Mr. A. G. Holt, in seconding the report, referred to the fact that Thames Valley Branch had now become a Section. He wished to express his thanks to the London Section Committee for their encouragement of Thames Valley activities over the last few years, which had led to eventual Section status, and expressed a strong desire that close collaboration between the two neighbouring sections should continue. Mr. Wheeler expressed the best wishes of the London Section on the formation of the new Thames Valley Section, and said that it should be possible to work out some means of ensuring full co-operation between the two Sections. Mr. J. K. Burke, speaking for Southern Branch, said that in spite of difficulties due to their limited membership spread over a wide area, the Branch would go forward into next session with confidence. The Committee's report was adopted unanimously.

The financial report, proposed by the Hon. Treasurer Mr. J. E. Pooley, and seconded by Mr. F. W. Davis, showed that some economies had been made on the costs of reporting and of refreshments provided before the meetings. Mr. Pooley expressed particular thanks to Mr. W. Campbell, who was retiring this year from his position as Hon. Auditor. The report was adopted unanimously.

Mr. R. N. Wheeler then proposed the election of the Hon. Officers, as follows. Hon. Secretary, V. F. Jenkins ; Hon. Treasurer, J. E. Pooley ; Hon. Publications Officer, Dr. V. T. Crowl ; Hon. Programmes Officer, D. E. Eddowes; and Hon. Auditor, A. H. Soane. Mr. H. A. Newnham then proposed the election of Mr. R. N. Wheeler as Chairman. In seconding the proposal, Mr. M. R. Mills, a past chairman of London Section, said that in these times of change, new ideas were needed, and he had no doubt that " Dickie " would provide the necessary lead. New members elected to the Committee were Mr. F. W. Davies, Mr. R. H. E. Munn, and Mr. R. M. W. W. Wilson.

Mr. N. Fisk and Mr. H. A. Newnham raised the question of student activities, and Mr. D. Eddowes said that a small sub-committee, consisting of Dr. H. R. Hamburg, Mr. D. Soar and himself had planned two items for the coming session, a visit to a research organisation, and a lecture, probably at East Ham.

After the dinner, the well-known artist Gluck gave an extremely interesting talk on " The Artist vis-à-vis the Paint Industry." This was followed by a stimulating discussion.

An abridged version of Gluck's talk can be found in Section Proceedings.

V. T. C.

Newcastle Section

Annual General Meeting

The AGM was held on Thursday 6 April. Thirty-three members and two visitors were present.

The Chairman (Mr. E. L. Farrow), Vice-chairman (Mr. D. M. James), Research Liaison Officer (Dr. T. A. Banfield) and Publications Officer (Mr. D. M. James) retired, and the Committee nominated new officers for these posts.

The officers elected were :

Chairman :	D. M. James
Vice-chairman :	J. A. Willey
Secretary :	B. Ridley
Treasurer :	A. W. Blenkinsop
Publications Officer :	H. D. Jefferies
Research Liaison Officer :	C. N. Finlay
Co-ordinating Officer for Technical Education :	P. C. Edbrooke
Secretary of Junior Activities Sub-committee :	K. F. Baxter
Representative on Council :	H. D. Jefferies

During the year Mr. G. L. Lewis died and Mr. P. B. Marsden left the Section, and at an Extraordinary Meeting on 3 November 1966, Messrs. R. G. Carr and D. Dixon were elected to the Committee to fill their places. At this AGM Messrs. J. G. Bell and K. V. Hodgson retired, and Mr. C. N. Finlay was elected to office. There were four vacancies to bring the Committee to strength, and after a ballot on five names the following was the composition of the Committee in addition to the Officers :

E. L. Farrow (Immediate Past Chairman)
R. G. Carr
D. Dixon
H. Fuller
F. Hellens
W. Phillips
D. H. Tate

The Junior Activities Sub-committee was constituted as before : The Vice-chairman, Mr. K. F. Baxter and Mr. P. C. Edbrooke nominated by the Committee, and Messrs. H. Fuller, D. W. Hudson and W. Phillips as elected members.

Mr. T. W. Robinson, after 12 years' service an an auditor, retired. Mr. E. G. Elphinstone was elected in his place, and Mr. F. G. Palmer remains the other auditor.

The Reports of the Committee, Treasurer, Research Liaison Officer and Junior Activities Sub-committee were presented and adopted. The Programme for 1967-68 was presented : it was noted that the March meeting would be on Tuesday 12 March 1968, and not the usual Thursday, in order to accommodate Mr. van Londen of TNO, who was addressing both Newcastle Section and the London Section Southern Branch that week. Also Ladies Night would be on 23 February 1968, at the Five Bridges Hotel, Gateshead.

The evening ended with a talk by Miss Gillian M. Service of the Milk Marketing Board, on "English Cheese," followed by the same subject in tangible form.

D.M.J.

Scottish Section

Annual golf outing

The annual golf outing of the Scottish Section took place on 29 April to Aberdour Golf Club. A large entry of members and friends participated in the two sections.

The outing was again favoured by brilliant sunshine and some excellent scoring resulted.

The winners were :

Whittaker Cup Competition
(members only)

	Net score
First Prize and Whittaker Cup : J. H. Stewart ..	61
Second Prize (joint) : A. H. Smith ; R. Harvie ..	64
Third Prize : G. Anderson ..	65
Fourth Prize : W. R. Willis..	67

Visitors' Competition

	Net score
First Prize : Jas. Scott ..	61
Second Prize : D. P. Storey..	62
Third Prize : R. Martin ..	65
Fourth Prize : F. T. McIntosh	67

Members' consolation prize was won by E. A. Bullions and the visitors' consolation prize by W.Milne.

The Plastics Institute Symposium

"Forming and facing of concrete with plastics"

Although at first sight the title of the Symposium "Forming and Facing of Concrete with Plastics" seemed to be rather too specialised for people connected with the paint and allied industries, its attention proved worthwhile and revealing. On the invitation of the Plastics Institute altogether about 350 participants had registered for the full day's session on the 18th April, 1966, in the Kensington Palace Hotel.

It was estimated that over 100 people represented large contractors, builders and civil engineering firms, about 50 building materials, merchants and fabricators, cement works and wood importers, 20 plastics fabricators, 25 architects and clerks of works from towns, counties, harbours, British Rail and large private firms. Twenty-five representatives from Ministries, research institutions, colleges, 10 consultants in various fields concerned, 25 synthetic resin and chemical manufacturers and importers, and last but not least 7 paint manufacturers. The remaining participants may belong under any of the headings or represent miscellaneous interests. The mixture was certainly very unusual, but hardly "as before," though very healthy for the purpose of the session.

As it turned out, "paints" in their many forms ; water borne, in solvents and solvent free, qualified to belong under the heading "plastics." Some of the lectures would have been an eye-opener for many a paint man. Much of what could have been his field of operation, the plastics industry, by a mixture of empiricism and scientific research somewhat comparable to the development of the paint industry, has carved out for itself. This is an area in which the possibility of the growing consumption of the products involved seems to be almost unlimited. Research institutes and the laboratories of the very large contractors play their part. To illustrate this point, Mr. Nutt of the Cement Marketing Company showed, in a discussion, slides of a ¾ mile long experimental road where the concrete had been topped with a half-inch thick layer of a polyester-cement compound, mixed on the spot in six cwt. batches. But large quantities of various paints were absorbed by mixing with or coating of concrete, the coating of wood and metal facings for forming, etc., as will be referred to below in the reports of some of the papers given.

The opening address was given by Sir Frederic Snow, the celebrated consulting engineer. He gave a historical survey of the fairly young subject, emphasising that, thanks to plastics, shuttering of concrete offered " an extra over " for structure in cement and stressed the great potentialities. Surface decorations by use of three-dimensional moulds and plastic sheets, complicated formwork and the facing of concrete, have become possible with the help of plastic materials. Thanks to new resins, surface coatings could be used to advantage. As far as the cost of plastic (e.g. polyester-glass fibre) moulds and coated shutters were concerned, these were compensated by the possibility of repetitive use, better surface and longer life of concrete facings, and the results being aesthetically more acceptable. However, a new philosophy was required from manager to the workman so that the necessary care for obtaining the better results was exercised.

The Chairmen of the two sessions were Mr. D. P. Bromley, director of one of the ten building centres, the Midland Design and Building Centre, and Mr. J. Drage, director of the National Building Agency.

" Moulds " was the subject of Dr. M. Levitt of the Research Committee for the Cast Stone and Cast Concrete Products Industry. He described amongst other things the practical principles involved in the manufacture and use of glass fibre reinforced polyester resin (GRP) and thermoplastic moulds, their usefulness for non-standard shapes, tools and chemicals, gel-coats and laying-up resins, the advantages of ortho- and isophthalic resins, reinforcements and release agents, PVC, polystyrene and rubber-molten mould production, price comparisons, etc.

" Barrier paints for formwork " was the theme of W. E. Murphy of the Cement and Concrete Association.

The purpose of painting formwork was to extend its life by sealing its face with a hard impervious coating, termed barrier paint. Concrete cast against a sealed form face is normally also of a lighter and more uniform colour than one cast against an absorbent face. Possible blemishes due to imperviousness can be inhibited by the right techniques. The choice of paints or varnishes depends not only on suitability for sealing, but also cost, ease of application and durability. The importance of correct and careful application, and the advantages of applying a separate release agent before each use, were stressed. The speaker referred almost exclusively to timber and plywood forms which needed to be protected against moisture absorption and action of alkali, though the advantages of plastic (nylon) coated metal forms against uncoated steel ones were also enumerated.

Vinyl and alkyd resin based paints were described as unsuitable, two pack epoxy and polyurethane resin based paints were recommended. The usefulness of applying separate coats of chlorinated rubber paints to edges was mentioned. Dark discolorations of the concrete and sticking have sometimes occurred with polyurethane paints.

The more impermeable types of coatings, on the debit side, cause a greater incidence of blemishes, especially blow holes in the concrete casts.

There was a greater need for paints giving with the moisture movement of the substrates, especially at the edges of wood.

" Formwork linings " by D. H. Stephens and C. J. Wilshere of John Laing Research and Development Ltd.

This paper had the purpose of justifying doing away with surface coatings for formwork by attaching a replaceable thermoplastic loose lining to the plywood formwork with a stainless steel edge and adhesive tape. The authors claimed better durability and abrasion resistance, and the saving of mould oil or release agents. A patent application was pending.

A very long paper—" The formulation of high-polymer compounds for the surfacing, repair, protection or decoration of concrete structures " by J. Rowland, was read by N. Rowland.

This was based on fifteen years' experimenting with high polymer synthetic resins in connection with concrete structures. Need for collaboration between building and cement industry, architects, etc., with resin producers, formulators and compounders (such as the author's company) was emphasised so that these expensive materials can be used effectively. Supervision on site and the presentation of the compounds suitably pre-packed and weighed was rightly postulated to minimise the possibility of error on building sites.

Compounding of concrete and cement mortars with synthetic resins was of advantage for defeating various disadvantages such as miscellaneous adhesion troubles, poor resilience and cracking, discoloration on weathering, internal cracking, poor resistance to chemicals, food, etc., and for improving the weight/strength ratio.

Mr. Rowland suggested that the choice of high polymers for compounding should not only include improvement of tensile, compressive and cross-breaking strength, but also of adhesion, cohesive strength, wetting properties, penetration of porous surfaces, resistance to chemical attack and weather resistance. Conversion of catalysed compounds should take place in the cold.

He recommended as commercially available resins, suitable for use in compounds, two-component epoxies, polyamide or polyamine cured or unsaturated polyesters, according to the degree of filling, for self-levelling and non-skid floors, grouts, adhesives ; the latter resin in particular also as concrete surface hardeners and moisture barriers.

The use of one-can polyurethanes mainly unfilled, was suggested, e.g. for surface hardening of concrete and wood block floors, curing dusting screeds, moisture barriers, for laying floor tiles, etc. Acrylic emulsions, lightly filled, were recommended for stabilising cement sand washes (" cementitious mortars "). Furane resins with fillings were suitable for tile grouting compositions or as a flooring with good acid and heat resistance, and if containing Furacrolein, for setting concrete under water. Not recorded here are the suggestions for the use of the various resins in surface coatings with which OCCA readers are familiar. Disadvantages of several resins were also reported. As an example of usefulness he cited that polyester resin mortars " formulated for application to an airfield runway will accept trafficking by a jet aircraft after a setting period of an hour and a half at normal temperature."

Of all the resins enumerated he seemed to favour polyurethanes most of all.

Of development products he enumerated " a dispersion of Portland cement in polyester resin/styrene with water soluble redox catalyst " and emulsifiable epoxy compounds as additives to sand and cement screeds for flooring—all miscible with water.

Combinations of the different classes of compounds may offer advantages, such as complementary use of acrylic mortar/polyisocyanate floor toppings for heavy duty factory and warehouse floors.

Of interest was the remark that " most formulators are now prepared to sell their materials under guarantee of free replacement " and that " these guarantees are being extended to a greater variety of work." Warning was given against using cheapened materials but stress laid on the fact that thanks to the possibility of saving a variety of materials and stages of construction or saving in labour and time, the economical aspect can take care of itself.

This interesting paper shows a great deal of pioneering spirit, information and common sense, though resin and paint chemists would not be in agreement with every pronouncement.

" Brushed and sprayed finishes " was the title of Mr. J. Branton Screenton's (of Screenton Paintmaker Ltd.) paper.

Although most readers will be familiar with the subjects discussed, a summary will be given, as the speaker appears to have long experience with concrete as a substrate.

Various emulsion paints based on homo- or copolymers were recommended for decorative, sand, stone and texture finishes of high alkali and wear resistance where moisture permeability was necessary. Their limited use in aggressive situations was emphasised.

Chlorinated rubber paints including the thixotropic version, which the speaker seemed to consider particularly suitable, were suggested for application where a high degree of water and water vapour impermeability, resistance to moulds and many corrosive influences are important. Thick, reinforced layers of tough, impervious coatings could be brushed or trowelled to a rough concrete surface.

Styrene butadiene copolymer paints were mentioned for use where resistance to alkali and many acids, animal and vegetable oils and fats as well as moisture impermeability were important.

Two-pack epoxy paints including the solvent-free versions had their place in atmospheres of high humidity, chemical aggressiveness and elevated temperature applications, where wind and waterborne sand scours the surfaces, and where taint-free protection was required on concrete water tanks and food silos. Their impermeability, toughness, high gloss and resistance to fats, oils, solvents, etc., were also mentioned. Reference too was made to the comparatively cheap coal tar epoxy paints.

Moisture cured polyurethane resins were being mainly used for poured or brushed concrete floor paints and concrete surface fillers. Attention was drawn to the necessity of incorporating the fillers on the site, due to the moisture sensitivity of this type of resin.

Two-pack polyurethane paints were recommended for their resistance to alkalis, acids, solvents and water.

Silicone resin solutions have been included because of their water repellency on exterior concrete, resulting in a decrease of water absorption, thus of frost damage and dirt collection, and because the appearance of the substrate remains unchanged. Silicone treatment of concrete was found to be still effective after approximately 14 years ; the performance on cement render too was remarkable, in so far as the moisture absorption after 12 years was very slight, whilst it was about ten per cent on untreated render.

The importance of concrete surface preparation was stressed, in particular the necessity for the removal of mould, oil residues, dirt, latence, efflorescence, loose and powdered materials. Fillers and stoppers containing the organic binders mentioned were recommended for blowholes, voids, etc. Water sensitive fillers e.g. the gypsum/cellulose type used on exterior concrete, were the cause of failures, e.g. in swimming pools. Latence and bagging cause flaking, as did an attempt to cover or fill overlaps with paints.

The following approximate cost comparisons were given for coatings on concrete, per square yard :

3 coats emulsion paint	2s. 0d.
3 ,, chlorinated rubber paint	3s. 0d.
2 ,, 9 mil thick chlorinated rubber paint	6s. 6d.
3 coats styrene butadiene paint	3s. 0d.
2 heavy (9 mil) coats two-pack epoxy paint	13s. 0d.
2 heavy (9-10 mil) epoxy/coal tar paint	6s. 0d.
4 coats polyurethane paint	6s. 0d.
1 coat silicone solution	2s. 0d.

Suitable techniques of application were also discussed. Some special coatings needed a squeegee or spreader, various rollers had their merits and demerits, the first coat should best be applied by making good use of a brush, whilst the next coats should be sprayed, preferably airless.

The following approximate yardage/time schedules were given for applications by:

brushing	9-10 sq. yds/hour
rolling	15-10 ,, ,, ,,
normal spraying	30 ,, ,, ,,
airless spraying	over 100 ,, ,, ,,

This speaker also emphasised the importance of site supervision and co-operation with applicators and makers of finishes. He modestly restricted himself to fields with which he is familiar. There are, of course, other types of coatings for concrete, such as cement paints. He also declined to answer a question regarding suitable coatings for sea defences. Mr. W. O. Nutt, however, volunteered an answer : polyester cement, three in. thick, after three hours setting time, would give protection for over three years.

Mr. W. G. Mitchel, a design consultant, and Mr. Monks, a plastic moulder, showed slides of artistic designs of concrete shapes and figures, the moulds for which had been produced with polyurethane foam, hot melt PVC and GRP. It is worth noting that from a single polyurethane foam mould, as many as 750 casts for covering a building in Croydon could be made.

Dr. Rowe of the Cement and Concrete Association summed up the papers. He said that concrete too is a plastic material. Provided it was treated as it should be, it would perform on its own as required. Formwork made a new philosophy necessary ; optimising by choosing the right materials at reasonable costs. Plastics containing materials should in the first place be used where they contributed to good designs such as those shown by Mr. Mitchel, rather than for repairs. There is a need for dissemination of information. Great advances have been made in the concept of what a concrete surface should be like by utilising the adaptable properties of plastics for the forming and facing of concrete.

The successful Symposium makes it obvious, that the potentialities for the use of synthetic resins and surface coatings in connection with the modern building techniques are enormous.

The Symposium was well organised and prepared. Early distribution of most of the papers to the participants made preliminary study possible. The time for discussion, which showed up the great interest of the listeners, was frequently too short. As this was a concentrated working session, personal contacts had to be restricted to the lunch-hour break.

M. HESS.

Obituary

Mr. W. P. Jenkins

We regret to record the death, on 22 May, of Mr. W. P. Jenkins, an Ordinary Member of the Newcastle Section. Mr. Jenkins was extremely active in the Association, and was a Founder Member of the Newcastle Section, being the first Honorary Secretary at its inception in 1942. After holding this office for four years he became Chairman of the Section in 1946-48, was elected to the position of Vice-President of the Association 1948-49, and became Research Liaison Officer in 1951.

A well-known and popular figure throughout the surface coatings industry, he served on the Council of the Paint Research Station for some years, and was still actively concerned with the affairs of British Paints Limited, with which firm he had been employed since its early days in Cardiff as J. Dampney & Co., at the time of his death, although he had officially retired three years ago.

Mr. Jenkins is survived by his wife and a married daughter, and the surface coatings industry is a little poorer for his passing.

News of Members

Mr. A. J. Gibson, an Ordinary Member attached to the London Section, and a Past President of the Association, who is the father of the late Guy Gibson, V.C., named a Lancaster bomber after his son at the Biggin Hill Air Fair on 13 May, in the presence of many past and present members of 617 Squadron (The Dam Busters). Guy Gibson lead the raid on the Ruhr dams in 1943, for which he was awarded the V.C.

N. A. Bennett, an Ordinary Member attached to the London Section, and President of the Association from 1957-59, has now left the country to take up residence in Malta.

Mr. Bennett was Chairman of London Section 1943-45, and Honorary Treasurer of the Association from 1951 to 1956, when he became President Designate. He has moved to Malta following his retirement from Griffiths Bros. after a long career in the paint industry, including service on the Council of the Paint Research Station.

The British Society of Rheology is to hold a conference entitled " Non-Newtonian flow through pipes and passages," from 18-21 September, at the Royal Military College of Science, Shrivenham.

The 5th Congress of the Federation of Scandinavian Paint and Varnish Technicians will take place in Gothenburg, Sweden, from 18-20 September 1967. A paper entitled " Electron beam curing of coatings " will be given on behalf of OCCA by Mr. A. R. H. Tawn. Registration forms and further information are available from the Congress Secretary, Box 55, Mölndal 1, Sweden.

The next symposium in the series Plastics and Polymer Technology, organised by the Borough Polytechnic, will be on " Surface technology and decoration of plastics," and will be held on 26 and 27 October 1967. Further details are available on application to the Secretary, Borough Polytechnic.

South Birmingham Technical College are to hold a short lecture course on " Colour measurement and colour control " on successive Thursdays in October and November. Further details will appear in the *Journal* within the next two months.

Register of Members

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

Ordinary Members

BARTLETT, JOHN RAYMOND, 4 Birchcroft Road, Sutton Coldfield, Warwickshire. (*Midland*)

BECK, JOSEPH, M.SC., A.R.I.C., 36 Keble Road, Maidenhead, Berks. (*Thames Valley*)

BELLAMY, GERVIAS THOMAS, 124 St. Dunstans Hill, Cheam, Surrey. (*London*)

BOASE, ALLAN SWINTON, 20 Astley Street, Montmorency, Victoria, Australia. (*Victorian*)

BOWERMAN, TERRY, 37 Palm Avenue, Footscray, Sidcup, Kent. (*London*)

BUDD, LESLIE CYRIL, 8 Howards Road, Plaistow, London, E.13. (*London*)

CAMPBELL, JAMES PORTER, M.C.I.C., The General Paint Co., PO Box 181, Beirut, Lebanon. (*Overseas*)

GIDLEY, WILFRED GORDON, " Mondello," 7 Diana Close, Alverstone, Gosport, Hants. (*London*, *Southern*)

GOODMAN, S., L.R.I.C., A.C.T.(BIRM.), 77 Kingsley Road, Kingswinford, Brierley Hill, Staffs. (*Midland*)

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Oil and Colour Chemists' Association

President: S. H. BELL, PH.D., D.I.C., A.R.C.S., F.R.I.C.

The Oil and Colour Chemists' Association was formed in 1918, to cover paint, printing inks, pigments, varnishes, drying and essential oils, resins, lacquers, soaps, linoleum and treated fabrics, and the plant, apparatus and raw materials useful in their manufacture. In 1923 it absorbed the Paint and Varnish Society. The stated purpose of the Association is to promote by discussion and scientific investigation the technology of the industries concerned with the above-mentioned products, and to afford members opportunity for the interchange of ideas. This is achieved by the regular holding of ordinary meetings at which papers are presented, and the organisation of annual technical exhibitions, biennial conferences, educational activities and practical co-operative experimental work. Details of these activities are given in the *Journal of the Oil and Colour Chemists' Association*, which is published monthly, and whose pages are open to receive communications and other pronouncements on scientific and technical matters affecting the members of the Association and the industries concerned. The Association's meetings also afford opportunities for members to meet informally and socially.

There are Sections of OCCA in Auckland, Bristol, Hull, Ireland, London, Manchester, the Midlands (with a Trent Valley Branch), Newcastle upon Tyne, New South Wales, Queensland, Scotland (with an Eastern Branch), South Africa (with Branches in the Cape, Transvaal and Natal), South Australia, Thames Valley, Victoria, Wellington, West Australia and the West Riding, and these are responsible for the conduct of their own local affairs. There is also a General Overseas Section. There is also a close alliance between the Association, the Federation of Societies for Paint Technology in the United States, and the Fédération d'Associations des Techniciens de l'Industrie des Peintures, Vernis, Emaux et Encres d'Imprimerie de l'Europe Continentale (FATIPEC). The Association also maintains cordial relations with the Scandinavian Federation of Paint and Varnish Technicians (SLF).

Ordinary Membership is granted to scientifically trained persons, and Associate Membership to others interested in the industries covered. Junior Membership, which is intended primarily for students, is open without restriction to persons under the age of 21 and to those up to 25 who are following a course of technical study. The annual subscription in each case is three guineas, except for Junior Members whose subscription is 10s. 6d. An entrance fee of 10s. is payable by all members. Applications for membership are invited from suitably qualified persons who are engaged or otherwise interested in the industries noted above. Applications, which should be supported by two members of the Association (one of whom must be an Ordinary Member), should be forwarded to the General Secretary at the address given below. Application forms and full details of membership may be obtained from the offices of the Association.

PUBLICATIONS

Journal of the Oil and Colour Chemists' Association. Published monthly. Subscription rate to non-members in UK and abroad, £7 10s. p.a. post free ; payable in advance.

An Introduction to Paint Technology (Second Edition). Pp. 187, illustrated, with index, 15s. (including postage).

Paint Technology Manuals

Part 1 : " Non-convertible Coatings," Pp. 326, 35s.
Part 2 : " Solvents, Oils, Resins and Driers," Pp. 239, 35s.
Part 3 : " Convertible Coatings," Pp. 318, 35s.
Part 4 : " The Application of Surface Coatings," Pp. 345, 35s.
Part 5 : " The Testing of Paints," Pp. 196, 35s.
Part 6 : " Pigments, Dyestuffs and Lakes," Pp. 340, 35s.

General Secretary: R. H. Hamblin, M.A., F.C.I.S., F.C.C.S., Wax Chandlers' Hall, Gresham Street, London, E.C.2.

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Because of the enormous success of the first edition (10,000 copies sold) and the rapid advances made in the technology of the Paint and Allied Industries during the past decade, the Council of the Oil and Colour Chemists' Association has authorised the complete revision of the " Introduction to Paint Technology."

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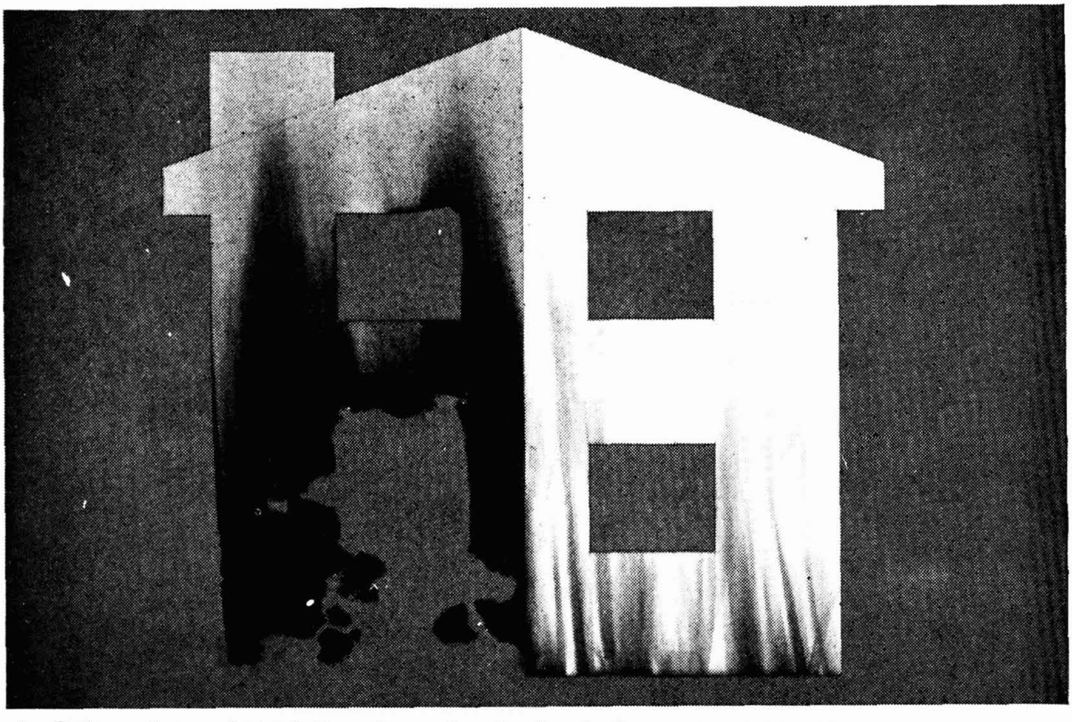

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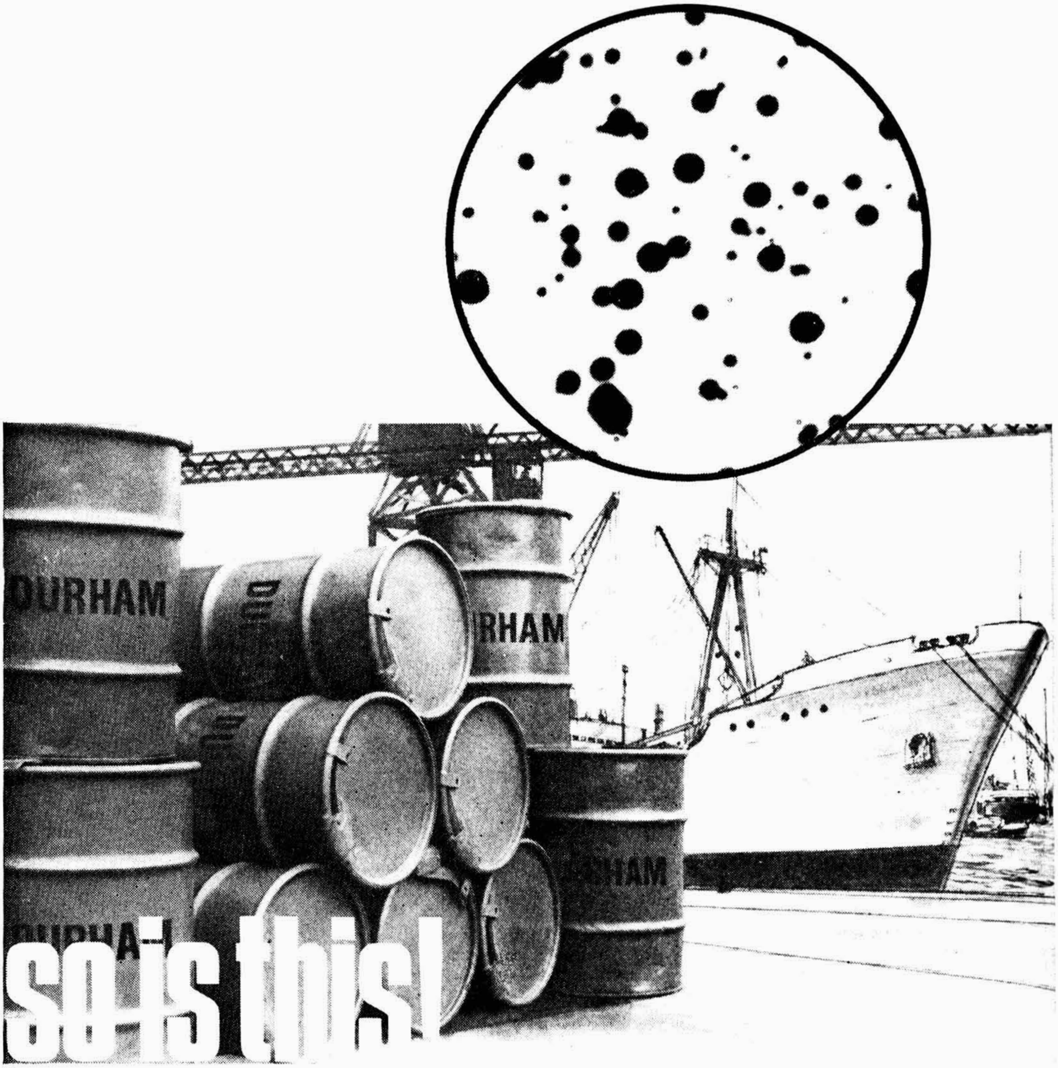
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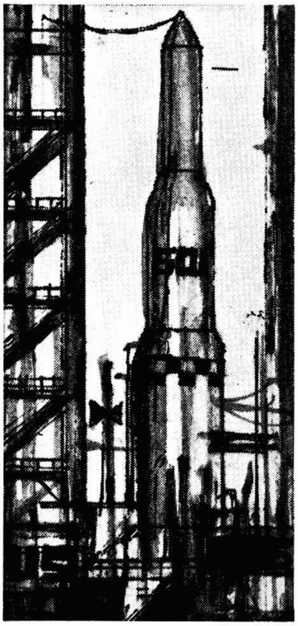

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†*The Twentieth takes place* 25-29 *March* 1968

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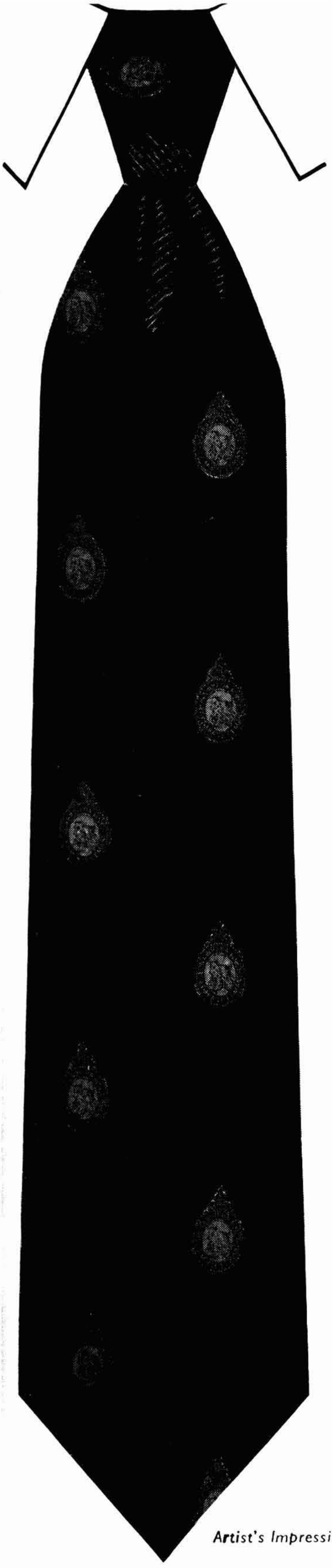

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The Council has authorised the production of an exclusive tie for Members of the Oil & Colour Chemists' Association. The Association's insignia is woven in red and gold silk on a dark blue terylene background.

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Oil and Colour
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