## JOURNAL

## OF THE OIL AND COLOUR CHEMISTS' ASSOCIATION



#### / Vol. 47 No. 3

March 1964

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#### TRANSACTIONS AND COMMUNICATIONS

### The Scientific Evaluation of Unfamiliar Vegetable Oils\*

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#### Summary

Recent advances in the analysis of the glycerides occurring naturally in oils and fats have facilitated the determination of their chemical composition and opened up the possibility of predicting the technological behaviour of unfamiliar specimens on this basis. At the same time, a number of fatty acids of unusual structure, whose occurrence was previously unknown, have been identified as major constituents of certain seed oils. They include long-chain unsaturated acids, conjugated acids and hydroxy, epoxy and cyclopropenoid acids. Although some of them are mainly of scientific interest, others may be found suitable for economic development and help to widen the field of application of vegetable oils in industry.

In order to characterise an oil completely, the nature of the fatty acids forming the glycerides and the proportions in which they are present, the composition and structure of the glycerides and the nature and amounts of non-glyceride constituents must be known. All of this information is not yet available, but the fatty acid composition can be determined with reasonable accuracy in most instances and may be used as a basis for a preliminary evaluation. The problems involved are discussed briefly with reference to a few specific examples.

#### INTRODUCTION

The total world production of vegetable oils is estimated to be in the region of 30 million tons annually, and although the number of varieties included may, at first sight, seem to be considerable, it represents but a tiny fraction of those occurring in nature. Indeed, if all but the major oils of commerce are excluded, the field is restricted still further and only a few varieties remain. These are familiar as foodstuffs, or as raw materials for the soap, paint, linoleum, printing ink and other industries. Their technological properties have been known for many years—long before their true chemical nature could be established—and many methods of modifying them for particular purposes have been developed. In addition, a large number of other types are produced in smaller quantities, some of which find their way into the markets of the world. These, also, have been extensively studied and their value assessed technologically.

<sup>\*</sup>Presented to London Section on 26 September 1963, London Section—Thames Valley Branch on 3 December 1963 and Scottish Section—Eastern Branch on 12 February 1964.

The expression "unfamiliar vegetable oils" is taken here to represent any of the vast numbers that have not been produced in sufficient quantity for their commercial value to be assessed. All that is known of them is contained in the analytical data that have been published in the literature and, although this would fill a substantial volume, many varieties have still to be investigated. Unless some means is at hand to enable an accurate forecast to be made of their technological potentialities there is little chance of any of them attaining commercial importance. In 1948, Hilditch<sup>1</sup> advocated the assessment of drying oils on the basis of their chemical composition, but at that time sufficient reliable information regarding fatty acid composition was not available and knowledge of glyceride structure was practically non-existent. Much progress has been made since that time and new developments in analytical techniques have enabled such information to be obtained more rapidly as well as more accurately. The possibility of selecting varieties of oilseeds for cultivation on the basis of an analysis which includes the determination of the chemical composition of the oil is now becoming a practical proposition and it is the purpose of this article to discuss the problems involved.

The necessity for developing new sources of vegetable oils may be questioned. It is not suggested that there is a need at the present time for substitutes to supplement the supplies of those varieties already in use, although this is sometimes desirable—as for example with cocoa butter or tung oil. During the past few years it has become clear that our knowledge of the structure of fatty acids occurring in natural oils is still rather limited and a number of new ones have been characterised. These include conjugated acids with or without free hydroxyl groups, epoxy acids, cyclopropenoid acids, etc., some of which are present in quantities large enough to give promise of unusual technological properties of great potential value.

#### FATTY ACID COMPOSITION

The methods available for the determination of the composition of the fatty acid mixtures derived from oils and fats have undergone a gradual evolution during the past 50 years. Prior to 1926, when Kaufmann developed his thiocyanogen method<sup>2</sup> reasonable results could be obtained with oils containing only saturated, oleic and linoleic acids, but not if linolenic or other unsaturated acids were also present. The thiocyanogen technique enabled linolenic acid to be determined with greater accuracy than hitherto and it was widely used by analysts during the following decade. Unfortunately it was sometimes applied to oils containing other unsaturated acids to give erroneous results and much data of this kind are to be found in the literature of the period. It was also suspected that the theoretical equations of Kaufmann were not quite accurate and that they tended to underestimate the oleic and linolenic contents and to overestimate the linoleic. This was confirmed by a number of workers<sup>3</sup> in 1940-43 and new equations based upon the experimental thiocyanogen values of linoleic and linolenic acids obtained under carefully standardised conditions were proposed. These gave more accurate information soon to be confirmed by the UV spectrographical technique first proposed by Mitchell, Kraybill and Zecheile<sup>4</sup> in 1943. In order to illustrate the effect of these developments, some of the published compositions given for linseed oil since 1917 are shown in Table I.
			Reference				
		-	5	6	7	8	
Date		 	1917	1929	1951	1963	
Method		 	Bromination	Thiocyanogen	Spectra	G.L.C.	
Sat. acids		 	10.4	11	11.8	11.5	
Dleic		 	5.2	14	17.1	20.2	
inoleic			62.1	29	13.8	14.7	
inolenic		 	22.3	45	57.3	53.6	
Est. polyu	nsat.	 	84	74	71	68	

TABLE IAnalysis of Linseed Oils (I.V. About 180)

The data for oils of about 180 iodine value have been adjusted where necessary to make them strictly comparable. It will be noted that the estimated total polyunsaturated acid content, whose significance in film formation will be discussed later, has decreased by roughly 16 per cent as a result of the introduction of more precise analytical methods. In spite of the publicity given to these developments, the figures quoted in some reference books still show a composition which was disproved 20 years ago.

During the period reviewed above much progress was also being made in the analysis of the saturated acid fraction, and the ester fractionation technique was used with good effect by Hilditch and his associates<sup>9</sup> to estimate components of different chain lengths. The structures of a number of characteristic acids were also established—ricinoleic by Goldsobel<sup>10</sup> in 1894, elaeostearic by Boeseken and Ravenswaay<sup>11</sup> in 1925, licanic by Brown and Farmer<sup>12</sup> in 1935, parinaric by Farmer and Sunderland<sup>13</sup> in 1935, isanic by Steger and van Loon<sup>14</sup> in 1940, to mention just a few.

By 1945 the means were at hand to determine the fatty acid composition of oils and fats and reliable analyses of most of those produced commercially had been published. The methods were somewhat tedious, however, and did not permit a systematic examination of the unfamiliar oils to be undertaken. The development of gas-liquid chromatography by James and Martin<sup>15</sup> in 1952 was a notable advance in this direction and its application to the analysis of fatty acid mixtures in the form of methyl esters has now become the standard practice in most laboratories dealing with vegetable oils. When used with fatty acid mixtures whose constituents are known, an estimate of the proportions in which they are present can be obtained in a few hours. It should be noted, however, that the accuracy with which a particular acid can be determined is somewhat variable according to the amount present and the results cannot be reproduced exactly even when the analysis is repeated with the same sample under the same conditions. The practice of expressing them to the first place of decimals is necessitated by the fact that most oils contain minor components in amounts under 1 per cent, and it should not be taken as an indication of the overall accuracy. The reliability of the results depends upon the linearity of the response of the detector and the assumption that all of the components of the mixture have been recorded as peaks on the chromatogram. This should always be checked by an independent method. With oils whose major constituent acids

are in the  $C_{16}$ — $C_{18}$  range and have a relatively high level of unsaturation this is best done by comparing the iodine value calculated from the analysis with that determined on the original acids. At low levels of unsaturation this can be supplemented by determining the total saturated acid content by the Bertram method.<sup>16</sup> Oils containing acids in a wide range of chain lengths frequently have low iodine values and the most reliable check is made by calculating the saponification value. If the results of any of these calculations are wide of the mark a further examination is necessary.

When examining an unfamiliar oil whose constituent acids are not known with certainty it may still be possible to obtain an estimate of the composition by gas-liquid chromatography. Miwa *et al*<sup>17</sup> have expressed the retention times on *Apiezon* and polyester columns of a wide range of unusual fatty acids in terms of constants which depend upon the type of column packing and carrier gas but not upon the experimental conditions, and have called them "equivalent chain lengths." A similar proposal has been made independently by Woodford and van Gent<sup>18</sup>, who used the term "carbon number" for their constant. Such information may be useful as an indication of the position in which a peak is likely to occur, but when an unusual fatty acid is present the class to which it belongs should first be determined by independent tests.

The fatty acid composition of the more important vegetable oils available commercially in the United Kingdom is given in Table II. Unless otherwise

		Saturated Acids	Unsatura	ted Acie	ls*	
Oil	Source	(n in brackets)	Mono	Di	Tri	Ref.
Coconut	Solomon Is.	0.3(6)8.1(8)8.1(10)46.3(12)	O/5.5	2.2		19
Palmkernel	W. Africa	4.3(8)4.8(10)51.3(12)	P/0.6, O/11.3	1.3	_	20
Borneo tallow	Borneo	0.1(10)1.4(12)0.4(14)	O/34.0	1.2	_	
Cocoa butter	Tropics	29.2(16)33.2(18)	O/34.3	3.3	_	
Groundnut	W. Africa Nigeria	0.8(14)39.7(16)6.0(18) 0.1(10)2.4(12)1.0(14)9.8(16)	0/42.1	11.4		
oroundhui	Tugeria	3.6(18)1.6(20)2.1(22)1.1(24)	0/01.5	1.5.7		
	Uganda	0.3(12)0.2(14)12.8(16)3.3(18) 1.3(20)3.1(22)	O/46.1	31.7	-	
Olive	_	13.6(16)3.3(18)	P/1.2, O/73.5	7.4	L/1.0	21
Cottonseed	USA	0.7(14)26.8(16)0.2(18)	P/0.1, O/22.8	49.4		22
Kapok	India	0.1(12)0.2(14)21.0(16)	O/21.8, C/12.6	35.3	L/1.2	10000
Maize	USA	13 2(16)0 5(18)	0/28.2	59 1		
Sova	USA	0.2(12)0.1(14)12.0(16)	0/27.0	50.2	1/7.6	
5.5 <b>.</b>		2.9(18)	0/2/10		2,7.0	
Soya	China	10.7(16)2.8(18)	O/21.6	55.9	L/9.0	
Sunflower	Africa	0.1(12)0.1(14)7.6(16)4.3(18) 0.4(20)0.9(22)	0/23.7	60.2	L/0.8	
Tobaccoseed	India	16.8	O/10.1	71.7	L/1.4	23
Linseed	Canada	6.2(16)1.4(18)	O/19.0	14.5	L/58.9	
-	Argentine	7.0(16)5.3(18)	O/22.0	18.3	L/47.4	
Tung (Fordii)	China	3.6	O/5.8	8.4	EL/82.3	24
(Montana)	Nyasaland	4.9	O/8.7	14.8	EL/71.6	10-1210-1
Oiticica	Brazil	6.5(16)5.6(18)	O/7.0		LC/80.8	25
Mustard	India	0.1(12)0.1(14)2.7(16)0.9(18)	P/0.2, O/24.5	10.3	L/11.9	
Rapeseed	Europe	0.1(12)3.5(16)1.1(18)	P/0.3, D/16.7	16.0	L/9.6	
Castor	India	1.0(16)0.7(18)0.5(20)	O/2.9, R/89.4	4.3	L/0.6	26

TABLE II FATTY ACID COMPOSITION OF COMMERCIAL VEGETABLE OILS

\*Mono : P-Palmitoleic, O-Oleic, C-cyclopropenoid, G-gadoleic, E-Erucic, R-Ricinoleic.

Di : Linoleic. Tri : L-linolenic, EL-Elaeostearic, LC-Licanic.

stated, the results were obtained in the Authors' own laboratory and it must be noted that they represent typical commercial samples and some variations are to be expected in the composition of each type according to the origin of the parent oilseeds. With the exception of rapeseed, mustard, tung, oiticica and castor oils, the fatty acid composition of all of them follows a simple pattern in which the unsaturated acids belong to the  $C_{18}$  series oleic, linoleic, linolenic. If the iodine value is plotted against the refractive index, a straight line is obtained as shown in Fig. 1. The exceptions lie well above it and kapok oil, which con-



FIG. 1. THE RELATIONSHIP BETWEEN IDDINE VALUE AND REFRACTIVE INDEX

tains about 10 per cent of cyclopropenoid acids, only slightly above it. This provides a useful sorting test in the preliminary examination of unfamiliar oils since it draws attention to the presence cf acids causing an exaltation of refractive index at a given iodine value, the principal classes of which are described below.

# Long-chain Unsaturated Acids

Until recently, only erucic acid ( $C_{22}$  monoene) of the long-chain unsaturated acids was reported to be present as a major component of vegetable oils, although minor amounts of related acids had been recognised. It is the principal constituent of the fatty acids derived from the seed oils of the *Cruciferae* and *Tropaeolaceae*, forming from 40 to 80 per cent of the total. The most familiar examples are rapeseed and mustardseed oils. In 1958, Chisholm and Hopkins<sup>27</sup> found 42 per cent of a  $C_{20}$  monoene, gondoic acid (11:eicosenoic), in the seed oil of the Balloon Vine and two years later Smith *et al*<sup>28</sup> reported 65 per cent of the isomeric 5:eicosenoic acid in the oil of the Meadowfoam. Other long-chain unsaturated acids were also present, including a unique  $C_{22}$  diene (5:13:docosadienoic acid) which is particularly noteworthy in departing from the methyleneM. R. MILLS

interrupted system of double bonds typical of non-conjugated dienes occurring in vegetable oils. Another exception has since been reported by Bagby *et al*,<sup>29</sup> who found 35 per cent of a C<sub>18</sub> triene with double bonds in the 5, 9 and 12 positions in the seed oil from the Sierra Meadowrue. Unsaturated acids with more than 22 carbon atoms are seldom found in vegetable oils, and when present they are usually only minor constituents. An exception is the C<sub>24</sub> monoene (15:tetracosenoic acid) found to the extent of 20 per cent in the oil from the Honesty by Wilson, Smith and Wolff.<sup>30</sup>

The presence of appreciable quantities of long-chain acids is indicated by a comparatively low saponification value (under 180) provided that substituted acids are not present and the unsaponifiable content is not excessive. They may be classified by gas-liquid chromatography before and after hydrogenation, but the position of the double bonds can be determined only by classical methods. The more important members of the series are to be found in Table III.

Acid	Carbon Atoms	Common Name	Mol. Wt.	Neut. Val.	I.V.	Source	%
Monoene 5:eicosenoic	20		310	180	80.2	Limnanthes douglasii	65
11:eicosenoic		Gondoic				(Meadowfoam) Cardiospermum halicacabum (Palloon vino)	42
5:docosenoic 13:docosenoic	22	Erucic	338	165.7	76.3	L.douglasii Brassica campestris	20 50
15:tetracosenoic	24	—	366	153	69.4	(Rapeseed) Lunaria biennis (Honesty)	21
Diene 5:13:docosadienoic	22		336	166.7	150.8	L.douglasii	10

TABLE III Long-Chain Unsaturated Acids

# **Conjugated Acids**

Prior to 1950, only three unsubstituted conjugated acids were known to occur in vegetable oils—the isomeric  $C_{18}$  trienes elaeostearic<sup>31</sup> and punicic acids<sup>32</sup> and the  $C_{18}$  tetraene parinaric acid<sup>33</sup>. In that year, Devine<sup>34</sup> showed that stillingia oil contained about 5 per cent of 2:4:decadienoic acid and shortly afterwards Hanks and Potts<sup>35</sup> reported a 2:4:dodecadienoic acid in sebastiana oil. No other sources of these acids have been found and the most recent progress has been made in identifying new isomers of elaeostearic acid. In an extensive study of various oils containing conjugated trienes, Chisholm and Hopkins showed that catalpa oil contained the *trans* 9, *trans* 11, *cis* 12 geometrical isomer<sup>36</sup> and that the seed oil from the Pot Marigold contained 43 per cent of the *trans* 8, *trans* 10, *cis* 12 positional isomer. A number of fresh sources of elaeostearic (*cis* 9, *trans* 11, *trans* 13) and punicic (*cis* 9, *cis* 11, *trans* 13) acids have also been found by these and other workers<sup>37</sup>.

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The presence of conjugated acids is indicated by UV spectroscopy, which can be used quantitatively if suitable standards are available. Infrared absorption spectra give an indication of the geometrical configuration<sup>38</sup>. As is well known, the iodine value of oils containing acids of this type cannot be determined by the Wijs method and the true value is best found by hydrogenation. This can be used to detect the presence of conjugated structures, which may also occur in substituted acids, to be described later. Table IV gives details of the acids mentioned in this section.

Bond Positions and Isomeric Form	Common Name	Melting Pt. °C.	Source	%
8-10-12 trans-trans-cis.	_		Calendula officinlais (Pot Marigold)	43
9-11-13		1	(I of Mangold)	1
trans-trans-cis.		32	Catalpa ovata	
cis-cis-trans.	Punicic	44	Punica granatum (Pomegranate)	72
cis-trans-trans	∝ Elaeostearic	48	Aleurites fordii	80
trans-trans-trans	$\beta$ Elaeostearic	71.5		-

C			-	- <b>x</b>	~		~
CONJUGATED	ISOMERS	OF	ELAEOSTEARIC	ACID.	C18	$H_{30}$	0,

#### Hydroxy Acids

Although a number of saturated hydroxy acids have been isolated from vegetable oils they never form more than a minor portion of the constituents. The main interest is in unsaturated hydroxy acids which are capable of being modified in a variety of ways to make them suitable for technical purposes. Until 1952, ricinoleic acid (12:hydroxy:9:octadecenoic) was the only member of the series known with certainty to occur as a constituent of natural fats. In that year Gunstone<sup>39</sup> found the 9:hvdroxy:12:isomer in a number of oils obtained from plants of the genus Strophantus, the amounts varying from 6.5 to 13.5 per cent in different species. The characteristic acid of Kamala oil was also shown by Gupta, Sharma and Aggarwal<sup>40</sup> to be a 18:hvdroxy conjugated triene with a structure resembling elaeostearic acid. More recently, a number of discoveries have been made which hold the promise of future commercial developments. The oil from the Cape Marigold has been found to contain 48 per cent of dimorphecolic acid<sup>41</sup>, shown by Smith et al to be 9:hydroxy:10:12:octadecadienoic acid. This can be dehydrated by boiling with glacial acetic acid to give a conjugated triene.<sup>42</sup> A non-conjugated isomer called densipolic acid (12:hydroxy:9:15: octadecadienoic) has also been found to be a major constituent of the oil from the seeds of *Lesquerella densipilia* and a few other species of the same genus<sup>43</sup>. The majority, however, contain a  $C_{20}$  hydroxy acid, lesquerolic acid, in quantities ranging from 50-74 per cent.<sup>44</sup> It was shown by Smith *et al*<sup>45</sup> to be 14:hydroxy: 11:eicosenoic acid.

In the absence of epoxy groups, it is a simple matter to estimate free hydroxyl groups, by means of the acetyl value. Morris, Holman and Fontell<sup>46</sup> in a study of the oils from the Cape Marigold, Wormwood, Fairy Dusters, Labob, Cosmos

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and Sunflower showed that these groups could be differentiated by the measurement of the absorption at  $2.795\mu$  in the near infrared region, before and after treatment with anhydrous ethereal hydrogen chloride. The increase in associated hydroxyl absorption due to chlorhydrins, produced from epoxides, is measured and there is no interference by other functional groups. The principal hydroxy acids which have so far been identified are given in Table V.

TA	BL	E	V	

Name	M.Wt.	No. of C atoms	Double Bonds	OH Group	Source	%
Ricinoleic	298	18	Δ9	Δ12	Ricinus communis (castor)	89
	298	18	12	9	Strophantus courmontii	13.5
Lesquerolic	326	20	11	14	Lesquerella lasiocarpa	45
Densipolic	296	18	9, 15	12	L. densipola	50
Dimorphecolic	296	18	10, 12	9	Dimorphotheca aurantiaca	48
Kamlolenic	294	18	9, 11, 13	18	Mallotus philippinensis	58
Isanolic	291	18	17*	8	Onguekoa gore	44

Тне	PRINCIPAL	UNSATURATED	HYDROXY	ACIDS
		0		

\*Triple bonds  $\Delta 9$ , 11.

#### **Epoxy Acids**

The first recorded evidence for the presence of epoxy acids in natural fats was provided by Gunstone<sup>47</sup> in 1954, when he showed that vernolic acid, which is present to the extent of 70-75 per cent in the seed oil of the Purple Fleabane or Indian Ironweed (*Vernonia anthelmintica*), was an epoxy oleic acid (12:13 epoxy:9:octadecenoic). Since then, three other naturally occurring epoxy acids have been discovered in seed oils : 9:10:epoxystearic acid found in *Tragopogon porrifolius* oil<sup>48</sup>, 9:10:epoxy:12:octadecenoic acid in the oil from the Garland Chrysanthemum<sup>49</sup> and 15:16:epoxylinoleic acid in *Camelina sativa* oil.<sup>50</sup> Small quantities of epoxy acids have been reported in oils from a variety of seeds and it appears that they are much more widespread than was originally supposed.

It must, however, be pointed out that the presence of small quantities of epoxy acids is not easy to establish with certainty since epoxy groups may arise as a result of autoxidation and the simpler methods of detection are not entirely specific. The Durbetaki procedure<sup>51</sup>, in which the oil is titrated with anhydrous hydrogen bromide in glacial acetic acid using crystal violet as an indicator. has been widely used by American workers, but it has been shown to give spurious results in the presence of certain unsaturated hydroxy acids (e.g. dimorphecolic) and cyclopropenoid acids. Smith et  $al^{52}$  have proposed a method for identifying epoxy acids by titrating with hydrogen bromide before and after reduction with lithium aluminium hydride, which depends upon the observation that only epoxy groups are attacked by this reagent. This is of importance, because it has definitely been established that epoxy acids do sometimes occur in oils containing the other acids reacting with hydrogen bromide. Thus Hopkins and Chisholm<sup>53</sup> isolated 12:13:epoxyoleic acid from Kenaf seed oil (which also contains cyclopropenoid acids), and estimated the amount present in the Cuban variety to be about 5 per cent. Smith et al<sup>52</sup> found both epoxy and dimorphecolic type acids in the oil from Wormwood (Artemisia absinthium).

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#### **Cyclopropenoid Acids**

The Halphen reaction, in which a red colour is developed when an oil is heated with carbon disulphide and sulphur in amyl alcohol, has long been used as a means of detecting cottonseed oil. Although originally regarded as being specific, it was later found that Kapok oil and a number of seed oils derived from plants belonging to the *Malvaceae*, *Tiliaceae* and *Bombacaceae* families gave an even stronger reaction. In 1956, Shenstone and Vickery<sup>54</sup> reported the isolation of a fatty acid from the lipid fraction of a malvaceous plant which promoted the development of " pink " whites in the eggs from hens receiving such plants as part of the diet. A year later McFarlane, Shenstone and Vickery<sup>55</sup> isolated the same acid from the seed oil of two species of the genus *Malva* and showed that it had a cyclopropene ring structure. The first evidence of the occurrence of such compounds in natural fats had been provided by Nunn<sup>56</sup> in 1952, in his work on sterculic acid which comprises more than 70 per cent of the total fatty acids of the seed fat of the Java olive (*Sterculia foetida*). The two cyclopropenoic acids have the following structures.

$$\begin{array}{c} CH_3 \left( CH_2 \right)_7 C = C \left( CH_2 \right)_6 COOH & CH_3 \left( CH_2 \right)_7 C = C \left( CH_2 \right)_7 COOH \\ CH_2 & CH_2 \\ Malvalic acid & Sterculic acid \end{array}$$

These acids are readily detected by the strong Halphen reaction and Deutschman and Klaus<sup>57</sup> have developed a spectrophotometric method of determination on this basis. They can also be estimated by titration with hydrogen bromide or treatment with hydrochloric acid<sup>58</sup>. By the application of gas-liquid chromatography, Wilson, Smith and Mikolajczak<sup>59</sup> have shown that a number of oils contain both malvalic and sterculic acids.

A characteristic feature of cyclopropenoid acids is that they polymerise when heated to 250°C without loss of unsaturation. This has been used in the author's laboratory during an investigation of a number of oils giving the Halphen reaction, and the results are given in Table VI. The fat from *Pachira aquatica* 

Characteristics		Cotton- seed	Kenaf (Cuban)	Kapok	Bombax Oleagineum	Pachira Aquatica
Iodine value : before after		107.3	110.5	98.7 <sup>.</sup> 99.2	50.4 51.0	45.8 46.6
Refractive index (25°C) :	before after increase	1.4698 1.4702 .0004	1.4700 1.4708 .0008	1.4690 1.4717 .0027	1.4635 1.4696 .0061	1.4696 1.4720 .0024
Viscosity	before	61	52	68	99	250
(Centipoises, 25°C)	after increase	68 7	77 25	123 55	370 271	800 550
Cyclopropenoid acids %		0.5	1.7	12.6	31.9	26.5

TABLE VI							
RESULTS OF	HEATING	OILS	AT	$250^{\circ}C$	FOR	15	MINS

is of particular interest since it has a high refractive index and the suggestion has been made that a hydroxycyclopropenoid acid may be present<sup>60</sup>. Further work has shown, however, that the high acetyl value is more probably due to



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reaction of acetic anhydride with the cyclopropene structure and does not necessarily indicate the presence of hydroxyl groups.

## **Miscellaneous** Acids

In addition to those mentioned in previous sections, a number of acids of unusual structure are known to occur in vegetable oils, but they are believed to be less widespread. Although evidence has been obtained recently for the presence of small quantities of keto-acids in a number of specimens<sup>61</sup> the only one to have been found as a major constituent is licanic acid (4-keto-9:11:13 octadecatrienoic). This is well known as the characteristic acid of oiticica oil, which is available commercially. Another oil that has received a considerable amount of attention on account of its unusual properties is isano (or boleko) oil. This contains two acids with both double and triple bonds—isanic (17-octadecen-9:11-diynoic) and isanolic (8-hydroxy:17-octadecen-9:11-diynoic). Isano oil has been produced in small quantities from time to time and found several industrial uses. It is not the only known example to contain acids with triple bonds, a 11-octadecen-9-ynoic acid having been found to occur in the seed oils of several species of the genera Ximenia and Santalum during the past ten years.<sup>62</sup>

Finally, there is the group known collectively as chaulmoogra oils which have been used for centuries for the treatment of human leprosy and other skin disorders. They all contain acids which are characterised by the presence of a cyclopentenyl ring and may be represented by the following general structure.

 $\begin{array}{c} \operatorname{CH}_2 \operatorname{CH}_2 \operatorname{CH}_2 \operatorname{CH}-\operatorname{R}\\ | & |\\ \operatorname{CH} = & \operatorname{CH} \end{array}$ 

where R is a normal saturated or unsaturated chain having 1-13 carbon atoms.

#### EVALUATION ON THE BASIS OF CHEMICAL COMPOSITION

It will be seen from the references cited above that considerable progress has been made during the past few years in the identification of the fatty acids occurring in glyceride oils and the determination of the proportions in which they are present in a particular specimen. This is essential before any prediction of technological properties can be made. On the other hand, it will be appreciated that knowledge of the fatty acid composition does not permit a complete evaluation. The properties of an oil or fat are also dependent upon the distribution of the fatty acids amongst the glyceride molecules, the structure of the glycerides and the geometrical isomeric form of the acids. The presence and effects of non-glyceride constituents have also to be taken into consideration. Much progress is being made in the investigation of these aspects, but there is still a long way to go and they will not be considered in detail here. On the basis of fatty acid composition alone it is possible to select oils worth producing on a scale large enough for technological appraisal, especially when they are to be used in applications other than in the form of glycerides.

Numerous optimistic claims have been made in the past concerning possible substitutes for the vegetable oils of commerce, presumably because of insufficient knowledge of the technological factors involved. This is just as important as the accuracy of the analysis when judging an oil on the basis of composition and some of the factors will now be discussed with reference to a few specific examples.

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# **Drying Oils**

In his "rational" evaluation of drying oils, Hilditch<sup>1</sup> formulated two criteria for the recognition of possible substitutes for linseed oil. The first was the total polyunsaturated acid content, P, and the second was defined as  $P \times$  linolenic acid content  $\times 10^{-2}$ . A good drying oil was one in which P was at least 65 per cent and the second, on "quick-drying index," about 25. These proposals were not generally accepted and some further extension is necessary if drying oils are to be assessed on a scientific basis.

Oils of the common pattern, containing saturated, oleic, linoleic and linolenic acids will have good drying properties only when the total polyunsaturated acid content is high enough to provide a certain proportion of trifunctional glycerides in addition to the difunctional glycerides, which are capable of forming linear polymers through autoxidation but cannot introduce cross-linking. There is reason to believe that linoleic and linolenic acids have a functionality of one, but oleic acid does not take part in the reactions leading to film-formation and can be classed with the saturated acids as having zero functionality. It is necessary, therefore, to consider the distribution of these two groups amongst the glyceride molecules. Precise knowledge of this is not yet available, neither has it been established that all oils follow the same pattern. Nevertheless, it appears to be reasonably certain that they lie between limits represented by the rules of even<sup>63</sup> and random distribution.

The assessment of drying oils on this basis is illustrated in Fig. 2. Molar percentages of non-drying glycerides (functionality 0 or 1) and trifunctional glycerides are plotted separately against the total polyunsaturated acid content



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using figures representing the two limits. For even distribution, the data of Barker and Hilditch<sup>64</sup> for sunflower oil have been taken and the corresponding figures for random distribution calculated from the equations of Feuge, Kramer and Bailey<sup>65</sup>. It will be seen that both pairs of curves intersect on a line representing 65 per cent of polyunsaturated acids, which was the amount stated by Hilditch to be the minimum for a drving oil. Blocks A and B represent sova bean oils (IV 128-142) and linseed oils (IV 175-190) respectively, whose polyunsaturated acid contents were determined by gas-liquid chromatography in the Author's laboratory. Line C represents a specimen of stillingia oil (IV 170) and line D segregated pilchard oil (IV 200). These have been inserted to indicate the influence of the mean number of double bonds present in the polyunsaturated acids on drying properties. Stillingia oil is probably the nearest approach to linseed oil in technological properties that has been produced commercially, and would be an even better drying oil if the polyunsaturated acid content were the only factor involved. The fact that the total linolenic acid content is only 30 per cent as against a minimum of 50 per cent for linseed must be taken into consideration. Segregated pilchard oil has a high content of undesirable glycerides, but the fact that its polyunsaturated acids have an average of about five double bonds gives it some drying properties. This is an extreme case outside the field of vegetable oils and single functionality for the polyunsaturated acids cannot be assumed.

The influence of the linolenic content on the value of a drying oil may be illustrated by a diagram (Fig. 3) in which the iodine value of the polyunsaturated acids is plotted against the total amount present. A line is drawn through the



FIG. 3. ASSESSMENT BY IODINE VALUE OF POLYUNSATURATES

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points representing linseed and stillingia oils and any oils on or above the line can be regarded as drying oils of the linseed type. Oils lying below the line are less useful in the form of glycerides but can be used in air-drying alkyds provided that the total polyunsaturated acid content is high enough (preferably over 65 per cent). It is clear from the diagram that segregated soya bean oil and familiar oils of the linoleic type cannot be regarded as linseed oil equivalents and this is in accord with technological experience.

Numerous attempts have been made in the past to extend the sources of supply of tung oil by cultivation in various parts of the world, and the possibility of finding substitutes has also received considerable attention. Only partial success has been achieved and shortages still occur from time to time even although the total demand has probably declined during recent years. One of the main obstacles to the success of attempts to find a substitute has been the very high elaeostearate content of the oil from *Aleurites fordii*, which is the preferred variety. Unless this feature can be duplicated, the technological properties will be judged to be inferior.

The possibility of producing a new tung oil substitute has arisen quite recently as a result of the discovery that the oil from the seeds of the Cape Marigold contains about 50 per cent of dimorphecolic acid (Table V) which gives rise to a conjugated triene on dehydration. A preliminary study of the film-forming properties of this oil has been made by Rheineck and Sobol<sup>66</sup> who found that dehydration occurred spontaneously on heating. The raw oil dried badly, as would be expected from its composition, but gelled when heated at 200°C for 13 hours and at 282°C for 38 minutes. Varnishes prepared with non-reactive phenolic resins were compared with standards based upon tung oil and it was stated that evaluation studies indicated that they were essentially equivalent. This appears to be rather an optimistic conclusion to draw from the evidence presented, but there is no doubt that the oil is of considerable interest and should be examined outside the narrow field of tung oil substitution.

# **Technical Oils**

Unfamiliar vegetable oils that are found to contain major quantities (generally over 70 per cent) of an unusual acid should be considered as possible raw materials for industrial processes and technical applications rather than as drying oils. The presence of monoenes of unusual chain-length, as for example the  $C_{20}$  acid occurring to the extent of 65 per cent of the acids from the oil of the Meadowfoam (Table III) offers the possibility of producing new dibasic acids by oxidative cleavage with ozone. This is unlikely to become of sufficient importance to justify large-scale cultivation, however. There is as yet no known industrial use for oils containing major quantities of cyclopropenoid acids, although their high reactivity is of interest and might lead to useful developments in the future. It is not very long since their nature was recognised and further study would appear to be worth while.

Oils containing major amounts of hydroxy or epoxy acids probably offer the greatest promise of reward for future development. The versatility of castor oil is well known and the novel structure of the acids listed in Table V will suggest a number of possible uses. An important feature of castor oil, viz. the

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high proportion of ricinoleic acid present in its glycerides, has not yet been duplicated in any of the oils in which the new hydroxy acids have been found and this may be a decisive factor in determining their commercial value. With regard to oils containing epoxy acids, some attempts have already been made to compare their properties with those of artificially epoxidised oils. Riser *et al*<sup>67</sup> studied the use of vernonia oil (oxirane oxygen 4 per cent), trivernolin and barium and cadmium vernolates as heat and light stabilisers for plasticised polyvinyl chloride. The activity of the compounds increased in the order in which they are named and was greatest with a mixture of cadmium and barium, vernolates. The results obtained either equalled or surpassed those given by the commercial controls. The number of possible outlets for epoxidised oils is increasing and this may encourage the commercial development of seed oils with a sufficiently high oxirane oxygen content.

#### **Edible Oils**

In assessing the value of an oil for edible purposes, particular attention must be given to the presence of even small amounts of biologically active constituents such as hydroxy or cyclopropenoid acids. The effects produced by epoxy acids are less well known, but any oil containing appreciable amounts should also be submitted to a proper biological examination before recommending its use for edible purposes. The possible dangers of basing an evaluation merely upon the amounts of the major constituent acids present may be illustrated by referring to some of the various species that have been suggested from time to time as substitutes for cottonseed oil. The more important of these are kapok seed oil, which is sometimes available commercially, and okra and kenaf seed oils, which have been considered to be suitable for extended cultivation. Kapok oil contains about 10 per cent of cyclopropenoid acids, as against a maximum of about 2 per cent in cottonseed oil, and has been shown to be harmful in feeding trials with rats<sup>68</sup>. Heating at temperatures above 200°C causes cottonseed oil to lose its ability to give a positive Halphen reaction and at the same time physiological activity (e.g. the production of pink egg whites and enlarged yolks when fed to hens) disappears<sup>69</sup>. However, the thermal polymers produced are equally objectionable<sup>70</sup> and a method of removing cyclopropenoid acids without their formation, involving the use of sulphurous acid-activated alumina, has been claimed by Pons, Kuck and Frampton<sup>71</sup>.

Hopkins and Chisholm<sup>53</sup> have shown the presence of epoxyoleic acid in both okra and kenaf seed oils, the highest quantity found being in the region of 5 per cent. They did not attempt to estimate cyclopropenoid acids, but recorded a positive Halphen reaction. In a sample of kenaf seed oil of the Cuban variety which the Author examined, slightly less than 2 per cent of epoxyoleic acid was found together with a similar amount of cyclopropenoid acids (as sterculic). The results of heating recorded in Table VI show it to have a greater tendency for polymerisation than cottonseed oil and it should not be assumed to be completely harmless without further study.

No information is available concerning the relative food value of the different oils and fats consumed by humans and it is generally assumed that they are equivalent. A considerable amount of attention has, however, been devoted

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to the so-called "essential fatty acids," without which complete health cannot be maintained, and especially in connection with such conditions as atheroma, or thickening of the inner coat of the arteries. Linoleic and arachidonic acids are generally considered to be the most important, since they occur to the greatest extent of any in the plasma and depot fats of man, but it is possible that other polyunsaturated acids may have a similar function<sup>72</sup>. It is known, for example, that linolenic acid and the long-chain polyunsaturated acids occurring in fish oils are equally effective in reducing the plasma cholesterol level of humans, but they do not prevent the formation of skin lesions in rats. In spite of the wide interest in this subject, stimulated by the sharp increase in the number of deaths from coronary thrombosis which has taken place during recent years, there is still no direct evidence that the adult man must receive a certain amount of essential fatty acids in his diet. However, Hansen et al<sup>73</sup> have shown this to be necessary for children, at least 1 per cent dietary calories as linoleic acid being required to prevent the development of skin lesions and 4-5 per cent for optimal nutrition. If adults are to be treated on the same basis, the optimum would be about 15 g of linoleic acid per day on a 3,000-3,500 calorie diet, as compared with an estimated national average of 6.5 g per day in the United Kingdom<sup>74</sup>.

Such characteristics as palatability, stability and consistency which are of particular importance in edible oils can all be modified by refining and hardening processes and are not necessarily related to the fatty acid composition of the raw material. The question of glyceride structure assumes a considerable importance in connection with fats that are solid or semi-solid at ordinary temperatures, however, and especially in the case of cocoa butter, whose peculiar melting and solidifying characteristics are of value in the manufacture of chocolate and determine the physical properties of the final product. If it were simply a matter of producing a fat that remains fairly hard and solid at temperatures, the problem of making a substitute for cocoa butter would not be a very difficult one. In order to obtain a product of good flavour, however, some cocoa butter must be present and the question of compatibility then arises.

A common method of assessing the quality of cocoa butter is by the determination of the cooling curve as described by Jensen<sup>75</sup>, in which a standard quantity of molten fat is allowed to cool under precisely defined conditions (of agitation, etc.) and the temperature measured at regular intervals. Cocoa butter gives a curve with a characteristic shape (Fig. 4) which is very sensitive to the addition of fats that are not compatible with it. It was shown by Chapman, Crossley and Davies<sup>76</sup> that this was due to a regularity of glyceride structure in which unsaturated acids (oleic, linoleic) occupied the central or beta positions. Of the three pure triglycerides-2-oleopalmitostearin (POS), 2-stearo-oleopalmitin (OSP) and 2-palmito-oleostearin (OPS)-which they synthesised, only the first was compatible with cocoa butter. It is now known that this structure is essential for compatibility and that the melting point of the mixture depends upon the relative proportions of palmitic and stearic acids present in the glycerides. Borneo tallow, for example, resembles cocoa butter in many respects, but has a higher melting point because of the higher stearic acid content (see Table II).

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FIG. 4. COOLING CURVES OF COCOA BUTTER AND ITS MIXTURES WITH SYNTHETIC GLYCERIDES

Although the accuracy of known methods of glyceride analysis is questionable, it is possible to determine which acids are attached to the *beta* position by analysis of the monoglycerides formed by enzymic hydrolysis, which attacks only the alpha positions under suitable conditions<sup>77</sup>. By applying the technique to pure synthetic triglycerides, Crossley and Padley<sup>78</sup> have shown it to be at least 98 per cent specific for the 1:3 positions. The theory that the fatty acids split from these positions were originally distributed amongst them in a random manner is not so well established experimentally, however. If true, cocoa butter would contain about 3 per cent of fully saturated glycerides, which might be expected to have an adverse effect upon the cooling curve. It is interesting to note that Barrett et al<sup>79</sup> were not able to detect any by thin layer chromatography on silica impregnated with silver nitrate, which is one of the most sensitive methods now available for the identification of glyceride types. Much still remains to be learned about glyceride structure and its effects upon the physical nature and technological behaviour of fats and without such knowledge a complete scientific assessment is not possible. Nevertheless, the progress made during the last few years has been rapid enough to suggest that this goal will be attained in the not too far distant future.

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#### REFERENCES

- 1. Hilditch, T. P., JOCCA, 1948, 31, 1.
- 2. Kaufmann, H. P. Z. Untersuch, Lebensm., 1926, 51, 15.
- 3. Matthews, N. L., Brode, W. R. and Brown, J. B., Oil and Soap, 1941, 18, 182; Riemenschneider, R. W., Swift, C. E. and Sando, C. E., ibid., 1941, 18, 203; Rose, W. G. and Jamieson, G. S., ibid., 1941, 18, 173; Walker, F. T. and Mills, M. R., J. Soc. Chem. Ind., 1943, 62T, 106.
- 4. Mitchell, J. H., Kraybill, H. R. and Zecheile, F. P., Ind. Eng. Chem. (Anal.), 1943, 15, 1.
- 5. Newton Friend, J., " Chemistry of Linseed Oil," 1917, p. 64.
- Kaufmann, H. P. and Keller, M., Z. Angew. Chem., 1929, 42, 76.
   Hilditch, T. P. and Riley, J. P., J. Sci. Food Agric., 1951, 2, 543.
- 8. Author's unpublished results 1963.
- 9. Hilditch, T. P., "The Chemical Constitution of Natural Fats," 3rd Ed. 1956, p. 581. 10. Goldsobel, A.G., *Berichte*, 1894, **27**, 3121.
- 11. Boeseken, J. and Ravenswaay, H. J., *Rec. Trav. Chim.*, 1925, **44**, 241. 12. Brown, W. B. and Farmer, E. H., *J. Chem. Soc.*, 1935, 1632.
- 13. Farmer, E. H. and Sunderland, E., ibid., 1935, 759.
- 14. Steger, A. and van Loon, J., Rec. Trav. Chim. 1940, 59, 1156; 1941, 60, 342.
- 15. James, A. T. and Martin, A. J. P., *Biochem. J.*, 1952, **50**, 679. 16. Pelikan, K. A. and von Mikusch, J. D., *Oil and Soap*, 1938, **15**, 149.
- 17. Miwa, T. K., Mikolajczak, K. L., Earle, F. R. and Wolff, I. A., Anal. Chem., 1960, 32, 1739.
- 18. Woodford, F. P. and van Gent, C. M., J. Lipid Res., 1960, 1, 188.
- Dale, A. P. and Meara, M. L. J. Sci. Food and Agric., 1955, 6, 162.
   Carsten, H. A., Hilditch, T. P. and Meara, M. L., J. Soc. Chem. Ind., 1945, 64, 207.
   Craig, B. M. and Murty, N. L., J. Amer. Oil Chem. Soc., 1959, 36, 549.

- Chakrabarty, S. R. and M. M., *Indian Sci. J.*, 1954, **19**, 165.
   Chakrabarty, S. R. and M. M., *Indian Sci. J.*, 1954, **19**, 165.
   Hilditch, T. P., and Mendelowitz, A., *J. Sci. Food Agric.*, 1951, **2**, 548.
- 25. Machado, A., Rev. Soc. Brasil Quim., 1938, 7, 73.
- 26. Binder, R. G., Applewhite, T. H., Kohler, G. O. and Goldblatt, L. A., J. Amer. Oil Chem. Soc., 1962, 39, 513.
- Chisholm, M. J. and Hopkins, C. Y., Can. J. Chem., 1958, 36, 1537.
   Smith, C. R., Bagby, M. O., Miwa, T. K., Lohmar, R. L. and Wolff, I. A., J. Org. Chem., 1960, 25, 1770; 1961, 26, 1261.
   Bagby, M. O., Smith, C. R., Mikolajczak, K. L. and Wolff, I. A., Biochem., 1962, 1, 632.
   Wilson, T. L., Smith, C. R. and Wolff, I. A., J. Amer. Oil Chem. Soc., 1962, 39, 104.

- 31. van Loon, J., Rec. Trav. Chim., 1931, 50, 32.
- 32. Farmer, E. H. and van den Heuvel, F. A., J. Chem. Soc., 1936, 1809. 33. Tsujimoto, M. and Koyanagi, H., J. Soc. Chem. Ind. Japan, 1933, **36**, 110.
- 34. Devine, J., J. Sci. Food Agric., 1950, 1, 88. 35. Hanks, D. P. and Potts, W. M., J. Amer. Oil Chem. Soc., 1951, 28, 292.
- Hopkins, C. Y. and Chisholm, M. J., communications to 6th ISF Congress, London, 1962.
   Ahlers, N. H. E. and McTaggart, N. G., J. Sci. Food Agric., 1954, 5, 75.
   Ahlers, N. H. E., JOCCA, 1950, 33, 421.

- Gunstone, F. D., J. Chem. Soc., 1952, 1274; J. Sci. Food Agric., 1952, 3, 185: 1953, 4, 192: Barucha, K. E. and Gunstone, F. D., *ibid.*, 1955, 6, 373.

- 40. Gupta, S. C., Sharma, V. N. and Aggarwal, J. S., *J. Soc. Ind. Res. India*, 1952, **11B**, 463.
   41. Earle, F. R., Wolff, I. A. and Jones, Q., *J. Amer. Oil Chem. Soc.*, 1960, **37**, 254.
   42. Smith, C. R., Wilson, T. L., Melvin, E. H. and Wolff, I. A., *JACS*, 1960, **82**, 1417.
   43. Smith, C. R., Wilson, T. L., Bates, R. B. and Scholfield, C. R., *J. Org. Chem.*, 1962, **27**, 3112.
- 44. Mikolajczak, K. L., Earle, F. R. and Wolff, I. A., J. Amer. Oil Chem. Soc., 1962, 39, 78. 45. Smith, C. R., Wilson, T. L., Miwa, T. K., Zobel, H., Lohmar, R. L. and Wolff, I. A.,
- J. Org. Chem., 1961, 26, 2903.
  46. Morris, L. J., Holman, R. T. and Fontell, K., J. Amer. Oil Chem. Soc., 1960, 37, 323.
  47. Gunstone, F. D., J. Chem. Soc., 1954, 1611.
- 48. Chisholm, M. J. and Hopkins, C. Y., Chem. & Ind., 1959, 1154.
- 49. Smith, C. R., Bagby, M. O., Lohmar, R. L., Glass, C. A. and Wolff, I. A., J. Org. Chem., 1960, 25, 218.
- 50. Gunstone, F. D. and Morris, L. J., J. Chem. Soc., 1959, 2527.
- 51. Durbetaki, A. J., Anal. Chem., 1956, 28, 2000.

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- 52. Smith, C. R., Burnett, M. C., Wilson, T. L., Lohmar, R. L. and Wolff, I. A., J. Amer. Oil Chem. Soc., 1960, 37, 320.

- Chem. Soc., 1900, 37, 520.
   Hopkins, C. Y. and Chisholm, M. J., *ibid.*, 1959, 36, 95.
   Shenstone, F. S. and Vickery, J. R., *Nature*, 1956, 177, 94.
   McFarlane, J. J., Shenstone, F. S. and Vickery, J. R., *ibid.*, 1957, 179, 830.
   Nunn, J. R., J. Chem. Soc., 1952, 313.
   Deutschman, A. J. and Klaus, I. S., Anal. Chem., 1960, 32, 1809.

- 58. Bailey, A. V., Magne, F. C., Boudreaux, G. J. and Skau, E. L., J. Amer. Oil Chem. Soc. 1963, 40, 69.
- 59. Wilson, T. L., Smith, C. R. and Mikolajczak, K. L., ibid., 1961. 38, 696.

- de Bruin, A., Heesterman, J. E. and Mills, M. R., J. Sci. Food Agric., 1963. 14, 758.
   Earle, F. R., Wolff, I. A. and Glass, C. A., J. Amer. Oil Chem. Soc., 1962, 39, 381.
   Grigor, J., MacInnes, D. and McLean, J., Chem. & Ind., 1954, 1112; J. Chem. Soc., 1955, 1069.

- (1955, 1069.)
   Hilditch, T. P., "The Chemical Constitution of Natural Fats," 3rd Ed., 1956, p. 306.
   Barker, C. and Hilditch, T. P., *JOCCA*, 1950, 33, 6.
   Feuge, R. O., Kramer, E. A. and Bailey, A. E., *Oil and Soap*, 1945, 22, 202.
   Rheineck, A. E. and Sobol, H., *Paint Tech.*, 1963, 27, 5 518.
   Riser, G. R., Hunter, J. J., Ard, J. S. and Witnauer, L. P., *J. Amer. Oil Chem. Soc.*, 1962, 202. 39, 266.
- Dijkstra, G. and Duin, H., *Nature*, 1955, **176**, 71.
   Evans, R. J., Bandemer, S. L. and Davidson, J. A., *Poultry Science*, 1960, **39**, 1478.
- 70. Perkins, E. G., Food Tech., 1960, 14, 508.

- Perkins, E. G., Food Tech., 1960, 14, 508.
   Pons, W. A., Kuck, J. C. and Frampton, V. L., US Patent 3,087,946 (1963).
   Kingsbury, K. J., Morgan, D. M., Aylott, C. and Emerson, R., Lancet, 1961, (ii), 739.
   Hansen, A. E., Haggard, M. E., Boelsche, A. N., Adam, D. J. D. and Wiese, N. F., J. Nutrit, 1958, 66, 565 : Adam, D. J. D., Hansen, A. E. and Wiese, H. F., *ibid.*, 555.
   Kingsbury, K. J., Morgan, D. M., Gundrie, M., Shervington, P. and Heyes, T. D. in press.
   Jensen, "The Chemistry, Flavouring and Manufacture of Chocolate Confectionery and Cocca," 1931, p. 172.
   Chapman, D. Crossley, A. and Davies, A. C. J. Cham. Soc. 1957, 1952.

- Cocoa, 1991, p. 112.
  Chapman, D., Crossley, A. and Davies, A. C., J. Chem. Soc., 1957, 1052.
  Coleman, M. H., J. Amer. Oil Chem. Soc., 1961, 38, 685.
  Crossley, A. and Padley, F. B., communications to 6th ISF Congress, London, 1962.
  Barrett, C. B., Dallas, M. S. J. and Padley, F. B., J. Amer. Oil Chem. Soc., 1963, 40, 580.

#### DISCUSSION AT LONDON SECTION

MR. W. O. NUTT asked whether any work had been done on the relationship between the molecular configuration of fatty acids and the cell biology of plants and whether electron bombardment would affect the genes/chromosomes balance and thus enable fatty acids of a predetermined configuration to be produced.

MR. M. R. MILLS replied that this was a little beyond his scope. Although it had been stated to be a biological fact that plants always produced fatty acids with an even number of carbon atoms, the cyclopropenoid acids provided an exception. Malvalic acid had 18 carbon atoms with 17 in the chain and sterculic acid had 19 carbon atoms with 18 in the chain. Whichever way this was viewed, one of these must be regarded as having an odd number of carbon atoms. Recent reports from American workers had suggested that both were present in some oils and this posed a biological problem. Much remained to be learned about these processes before the possibility of changing the configuration of fatty acids could be contemplated.

DR. C. T. COWAN asked whether the presence of a cyclopropenoid group in a vegetable oil could have a marked influence on the taste or flavour.

MR. MILLS said that he had not tasted any of the oils which contained major quantities. Many of the seeds that he had examined had a musty smell, but this may have been due to the fact that they had been grown in damp, swampy conditions. Flavour was usually dependent to a greater extent upon trace constituents than upon glyceride composition.

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MR. N. R. FISK said that the Russians appeared to be the only people to use linseed oil for frying and asked Mr. Mills if he had any comments to make about the flavour of familiar things fried in linseed oil.

MR. MILLS replied that linseed oil was said to have a fishy flavour which tended to revert after partial hydrogenation and deodorisation. He thought that small quantities may have been used in wartime and more recently its biological effects had been studied in connection with atheroma research. Even tung oil had been tried, but the results had been startling and the tests had soon been discontinued.

DR. H. G. RAINS, after commenting that although there might still be some doubt as to the structure of the fatty acids mentioned towards the end of the lecture, those mentioned earlier seemed to have been characterised with reasonable certainty, asked whether the constitution had been determined by reaction with ozone and the subsequent examination of the scission products.

MR. MILLS replied that a number of oxidative cleavage techniques had been developed for use in the laboratory and these were commonly employed for determining the position of double bonds. It was also important to know the *cis/trans* configuration and the glyceride structure. In the absence of complete knowledge of this kind no prediction could be made of the physical properties of an oil or fat.

MR. D. N. GRINDLEY asked for further information on the method of determination of epoxy acids by titration with hydrobromic and acetic acids.

MR. MILLS said that the method was due to Durbetaki and was quite commonly used in America. (Now published by ASTM as D1652-62T quoted in *Off. Dig.*, **35**, 464, 943, September 1963.) It involved titration in an enclosed system, using a magnetic stirrer, with anhydrous hydrobromic acid in glacial acetic acid using crystal violet as an indicator. The end point was precise, but some patience was required to attain it as the reaction was rather slow, especially when reactive groups other than epoxides were present.

MR. C. R. MALYAN asked whether Mr. Mills could confirm that the erucic content of rape seed oil had been diminishing over the years.

MR. MILLS replied that he was not aware of the publication of reliable analytical data over a long enough period to give colour to this suggestion.

MR. MALYAN said that the question arose not only as a result of GLC analysis, but he believed that there had been a tendency for the iodine value to rise. A recent figure of 110 (BSS limits 93-107) suggested that the reduction in erucic acid might have been compensated by an increase in linoleic acid which might eventually lead to the possibility of using rapeseed oil in air-drying alkyds.

MR. MILLS replied that "rapeseed oil" could be obtained from a number of related seeds other than genuine rape and it was not infrequent for such small seeds to be mixed.

MR. R. G. KINSMAN asked whether anything was known about the effects of the diet of plants, e.g. fertilisers, on the fatty acids which could be obtained from them.

MR. MILLS replied that he had no knowledge on this point, but the effects of climate were well known, viz. a given species grown under cold conditions would produce an oil of higher iodine value than in warmer surroundings.

MR. NUTT asked whether the genes/chromosomes balance control by, e.g. gibberellic acid, would affect the molecular constitution of fatty acids.

MR. MILLS replied that he had not heard of any work on this subject.

DR. M. L. ELLINGER commented on the variation of drying properties of linseed oil from different climatic sources. She asked whether the enzyme splitting method for determination of glyceride structure was a new technique as it was reminiscent of the classical method for the determination of asymmetric substitution of carbon atoms in simple organic compounds.

MR. MILLS replied that it had only recently been applied to the analysis of glycerides. The observation that the *alpha* positions were preferentially attacked explained the well-known fact that free fatty acids occurring naturally in an oil as a result of the action of lipolytic enzymes differed in composition from those present as glycerides.

MR. G. F. JONES referred to the biological effects produced by linseed oil and recalled that a septuagenarian varnish maker used to attribute his longevity to the daily ingestion of  $\frac{1}{2}$  pint of best tanked linseed oil.

MR. MILLS remarked that a friend had taken soya bean oil regularly since an attack of thrombosis and was now in excellent health. There was evidence that polyunsaturated acids were beneficial under certain circumstances, but not if they were conjugated, as in tung oil.

MR. N. R. FISK referred to a previous question and said that he thought much more would have to be learned about genetics and the effects of irradiation before it would be possible to secure controlled changes in the nature of fatty acids or group composition. The effect of gibberellic acid was merely to multiply the number of chromosomes, thereby making a bigger plant with more of the same oil in bigger seeds. When irradiation was used the aim was at one particular gene out of the many in a chromosome and there were many chromosomes. He thought that it was an interesting reflection on the rate of development of industrial chemistry that Nature in producing oils containing epoxy fatty acids, appeared to be holding a mirror to it.

MR. C. R. MALYAN stated that supplies of linseed oil originating in Canada and of iodine value nearly 200 had been seen recently in this country. He asked whether this was likely to spread and suggested that lack of uniformity in alkyd processing might necessitate the blending of oils from different sources.

MR. MILLS commented that the use of GLC analysis made the production of blends of uniform composition at least a possibility, but the cost of doing this in the average factory might prove to be prohibitive.

MR. J. R. GROOM asked what were the geographical or climatic factors which affected the structure and composition of a vegetable oil.

MR. MILLS replied that it was a general rule that a particular variety of seed produced an oil with a higher unsaturation when grown in a cooler climate. It did not follow, however, that seeds indigenous to warm climates always produced oils of lower unsaturation than other varieties growing in colder conditions. The type of fatty acids found appeared to be dependent upon the botanical identity of the plant.

DR. S. H. BELL said that running through the discussion there was a thread of considerable interest in the biological side. There seemed to be three stages controlling the type of oil produced by a plant. First the chromosomes and genes which told the plant what it was to produce, and the possibility of modifying them had been mentioned. Then there was the actual mechanism of production within the plant and finally the effects of environment. The fact that plants would produce quite complicated chemical compounds with very little fuss and bother compared with our own industrial methods for producing chemicals was deeply interesting. Presumably biological catalysts were involved. An enzyme splitting process had been mentioned as an analytical technique and he wondered whether any work had been done in using biological methods industrially for splitting or otherwise manipulating oils to make desired modifications or to give new products.

MR. MILLS said that although he was aware of some such work having been attempted, it had not been published and so he could not make any useful comments.

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MR. H. A. NEWNHAM reproached Mr. Mills for omitting to mention cashew nut shell oil.

MR. MILLS replied that his remarks had been confined to glyceride oils and this was a phenolic liquid.

DR. M. L. MEARA asked Mr. Mills to comment upon the fact that stillingia oil was reported to have a very high optical rotation—16.9°—although the component fatty acids did not appear to contain any asymmetric carbon atoms.

MR. MILLS replied that stillingia oil had been available in this country for only a short time and his interest in it had been mainly of a technological nature. Many of the lesser known oils had features which had not been explained satisfactorily, as for example the inability of raw perilla oil to form a continuous film. He agreed that the optical rotation shown by stillingia oil would not have been predicted from what was known of the fatty acid composition.

MR. MALYAN suggested that it had been thought to be associated with the  $C_{10}$  conjugated dienoic acid.

DR. MEARA also commented upon a sample of oleic acid seen in America which was said to contain 50 per cent of *trans* acids.

MR. MILLS suggested that this may have been derived from a processed fat.

MR. J. D. LEWIS asked what was the smallest quantity of oil on which a worthwhile evaluation could be made.

MR. MILLS replied that it depended upon what was required. By the application of modern techniques much could be learned of the fatty acid composition and complexity of the glyceride mixture with only a few grammes. At any rate this would be sufficient to decide whether or not the material was of sufficient potential interest to warrant efforts being made to obtain a larger quantity. Small samples should be obtained in the form of seeds which could be botanically identified.

MR. C. R. PYE (*in a written contribution*) commented that reverting to the unexplained peculiarities in the behaviour of oils, the direct replacement of stillingia for linseed in combination with oiticica oil in varnishes always produced a darker colour than expected, whereas perilla in place of linseed in a similar oil combination gave unexpectedly pale varnishes. Furthermore the after-yellowing of the perilla/oiticica combination was considerably less than would have been expected from the known fatty acid compositions of the individual oils.

MR. MILLS pointed out that two different effects were involved in Mr. Pye's observation. The colour of varnishes was mainly dependent upon the non-glyceride constituents of the oils used and the nature of any refining treatment they had received. Although after-yellowing was dependent upon fatty acid composition amongst other factors, he would not agree that sufficient knowledge had been accumulated to make an accurate prediction possible. Attempts to relate the yellowing of soya alkyds to the linolenic acid content had been abortive.

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# Some Investigations on the Compatibility of Inorganic Pigments with Polyvinyl Acetate Dispersions

## By H. J. LEUGERING

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### INTRODUCTION

In recent years, polyvinyl acetate dispersions (pva dispersions) have become widely established as pigment binders for emulsion paints. Dispersions differ considerably from homogenous solutions in their physical and chemical properties, for example, film formation in dispersions obeys entirely different laws as compared to film formation from a solution. Characteristic effects are observed when the interaction between pigments and pva dispersions is studied. A number of questions appear to remain unexplained.

In the manufacture of emulsion paints the compatibility of the polymer dispersion with the pigment is of high importance. This paper deals with a special marginal case of pigment compatibility—the compatibility of pva dispersions with dry inorganic pigment.

In practice, inorganic pigments are first pre-wetted with water before being mixed with the dispersion. This is done in any case to obtain the finest possible distribution of the pigment particles in the dispersion. Nevertheless, the question how dry pigment powder behaves when it is mixed with pva dispersions is of general interest. Certain types of dispersions can be mixed together with dry inorganic pigments in order to obtain nearly homogenous paints without a high expenditure in mechanical energy. With certain other dispersions, however, this is not possible.

What, then, are the causes of this difference in behaviour? As will be seen later, there is a certain relationship between pigment compatibility and the strength of films from the pure pva dispersion in the phase of incipient consolidation.

# PIGMENTATION EXPERIMENTS

First, consider a pva dispersion, which is polymerised in the presence of polyvinyl alcohol as protective colloid. Such a dispersion has a particle size distribution of about  $0.5-5\mu$ . When a dispersion of this type is mixed with TiO<sub>2</sub>-pigment in the weight ratio 1 : 1 after a few seconds an almost solid mass is formed, which, however, after the addition of a small amount of water, yields a smooth paste. This can be spread on a glass plate with a glass rod. After drying, a uniform and smooth film is obtained.

If the same experiment is carried out with a pva dispersion, which is obtained by polymerisation in the presence of an emulsifier of the soap type (for instance dodecylphenylsulfonate) and which consists of very fine particles

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of less than 0.5 microns, an entirely different behaviour is observed. Immediately after the pigment has been added a nonhomogeneous granular mass containing clear liquid is formed. This cannot be homogenised either by further stirring or by dilution with water and therefore cannot be spread as a smooth film on a glass plate.

The strange incompatibility of this dispersion with the pigment might at first glance be attributed to a deficiency in the emulsifier. That this assumption is incorrect is demonstrated by comparison of the two following charges :

#### Charge I

Ten parts of a pva dispersion of small particle size (below 0.5 micron in diameter) are at first diluted with five parts of water. To the diluted dispersion ten parts of a pigment-mixture are added.\*

#### Charge II

Ten parts of the pigment mixture are wetted with five parts of water. The wetted pigment is mixed together with ten parts of dispersion.

Charge II, in which the dispersion is stirred into the pre-wetted pigment, always yields a more homogenous paint than Charge I.

The two charges, however, contain the same amount of emulsifier, and therefore we come to the conclusion that the difference between the two charges is not caused by the emulsifier.

The same result is obtained when the surface tension of dilute dispersion is measured before and after the addition of pigment powder.

Dispersion**		S	urface tension	σ (dyn cm <sup>-1</sup> )	
	Dilution:	1:5	1:10	1:20	1:20 + pigment*
A B C D		34, 4 35, 9 35, 7 33, 5	35, 2 37, 7 38, 0 36, 3	37, 4 37, 6 38, 0 36, 8	31, 3 33, 3 33, 3 31, 2

TABLE I

EFFECT OF PIGMENT ADDITIONS ON THE SURFACE TENSION OF DILUTE DISPERSIONS

\*1 g dispersion was diluted with 20 ml  $H_2O$ . 1 g  $TiO_2$  (rutile) was added and thoroughly mixed in. After a period of 2 minutes the surface tension was determined with a DuNouy tensometer.

\*\*Dispersions A, B, C, and D are laboratory samples of small particle size.

Table I shows the results. As can be seen, the incorporation of pigment does not raise the surface tension. The very slight reduction in surface tension is presumably due to selective adsorption of certain components of the liquid phase by the pigment powder. The test shows that a deficiency in the emulsifier

\*The pigment mixture used in these experiments has the following composition :

40 parts by weight TiO<sub>2</sub> (rutile)

- 52 parts by weight barytes
- 5 parts by weight talc

3 parts by weight chalk

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cannot in general be assumed to be the cause of the incompatibility of the mixture of the pigment and the dispersion.

#### MICROSCOPIC STUDY OF THE INTERACTION OF DISPERSION AND PIGMENT

Titanium dioxide (rutile), which was used in the microscopic investigation, consists mainly of secondary aggregates of varying size of about 100 - 500 microns in diameter while the primary particles are only 0.2 - 0.5 microns in size. If some TiO<sub>2</sub>-pigment and a drop of dispersion with poor pigment compatibility are placed on a slide and quickly covered with a cover slide, observation under the phase contrast microscope will show the formation of a light, sharply defined layer of constantly increasing diameter around each secondary particle<sup>\*</sup>.

Fig. 1 shows the development of a layer of this kind one to two minutes after the preparation of the specimen. If pressure is applied to the specimen under the microscope by means of a spatula or a similar instrument the layer surrounding the pigment aggregate will be seen to consist of a film that cannot



FIG. 1 Magnification  $\times$  47

be re-emulsified even by repeated pressure on the cover slide (Fig. 2). The film envelops the pigment aggregate and delays or prevents its complete impregnation with the liquid phase of the dispersion.

A similar film formation can be observed at the rim of the cover slide. It is visible as a sharply defined line that can be particularly clearly detected under the phase contrast microscope. This line shifts parallel to the rim of the cover slide as a function of time (Fig. 3).

\*The same observation can be made with other inorganic pigments such as lithopone, barytes, gypsum, etc.



FIG. 2 Magnification  $\times$  47



FIG. 3 Magnification  $\times$  47

Close scrutiny reveals this line to be the boundary where the Brownian movement ceases. If a light pressure is applied to the cover slide, it can be seen to what extent the individual pva particles have coalesced. With most dispersions that exhibit inferior or average pigment compatibility the irreversible consolidation of the individual dispersion particles occurs immediately the particles have approached each other so closely that Brownian movement is suppressed. In the case of dispersions with good pigmentability, the film can be easily deformed and disintegrated under these conditions although even in these dispersions complete disintegration into individual particles does not usually occur.

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Fig. 4 shows the thickness of the film zone at the edge of the cover slide and at the edge of a pigment particle as a function of  $\sqrt{t}$ , t being the observation time in minutes. One can see that, at first, the film formation rate is about the same in both cases—at least at the beginning of film formation. Eventually, however, the film formation around the pigment particle comes to a halt; this may be due to the saturation of the pigment particle with the liquid phase. At the edge of the cover slide, however, the water vapour has a constant partial pressure so that liquid continuously diffuses from the dispersion and, therefore, the film growth continues. It may be concluded that the mechanism of film formation is the same in both cases. Accordingly, the problem to be dealt with is not a migration of emulsifier into the pigment particle—with subsequent coagulation of the dispersion—but with the loss of liquid phase in the polymer dispersion.



FIG. 4. SMALL PARTICLE SIZE DISPERSION (Calibration of the scale : 10 graduations = 0.032 in.

If pigmentation tests are carried out with pva dispersions with different pigment compatibility and a drop of the mixture is spread on a slide by means of a cover slide to form a very thin layer, light fragments of film free from pigment can be easily discerned by the phase contrast microscope by using the dark field illumination. Compact pigment aggregates are to be found as well. The poorer the pigment compatibility the larger and more frequent are these gellike fragments and pigment aggregates. These are obviously to blame for the poor brushing properties. Figs. 5 and 6 show examples of two dispersions with good and inferior pigmentability (magnification  $\times 110$ ). The transparent, pigment-free components seem to consist of fragments of film formed by the mechanism already described.



FIG. 5 Magnification  $\times$  110



FIG. 6 Magnification  $\times$  110

# QUANTITATIVE EXPERIMENTS

From the above observations it may be concluded that the rate of film formation from the pure pva dispersion and the film strength in the phase of incipient consolidation are of special importance for the behaviour of the dispersion during the dry pigmentation.

## **Determination of Film Formation Rate**

The film formation rate can be determined microscopically. A drop of the dispersion to be investigated is put on a slide and covered with a cover slide. Under the weight of the cover slide the droplet is spread outwards until it reaches the edge of the cover slide. At this moment a stop-watch is started, the zero-point of the scale of the eyepiece micrometer is lined up with the edge of the cover slide and the displacement of the zone is observed as a function of time. The results seem to be independent of the thickness of the dispersion layer within the limits of experimental error. Reproducibility is better than  $\pm$  ten per cent.

If the film thickness which is measured parallel to the edge of the slide is plotted as a function of  $\sqrt{t}$ , curves slightly arched to the  $\sqrt{t}$  axis are obtained. The difference between readings after one and ten minutes was used as a relative measure of the film formation rate. The uncertainty of the determination of the zero-point on the scale was thus excluded. As absolute values of the film formation rate are beyond the scope of this investigation, a conversion in absolute units was not carried out.

## **Measurement of Initial Film Strength**

The mechanical strength of a film formed from a pva dispersion in the phase of incipient consolidation cannot be determined experimentally without elaborate apparatus. This problem has not, to the best of our knowledge, been dealt with in the literature. A semi-quantitative method for the determination of this important property has, however, been developed. This employs the plate-cone device of the Haake rotary viscometer.

This device consists of a stationary face-ground base plate that can be pressed with a given force against a very shallow cone with an aperture angle of approximately  $0.3^{\circ}$ .\* The cone can be rotated by a motor through a torsion dynamometer. With the cone held and the drive motor switched on, the torsion dynamometer is stressed and the torque acting on the cone rises continuously. The torque can be read off a scale. If a drop of pva dispersion is placed in the centre of the base plate and the cone mounted, with the motor switched off, the drop spreads outwards up to the edge of the cone. The drop must be of such a size that no unduly large amount is squeezed out beyond the edge. Any excess should be rapidly wiped away with filter paper. When the cone is stationary, a film starts to form immediately at the outer boundary edge. If, after a certain interval—three minutes throughout the present tests—the motor is switched on, a constantly rising shear stress builds up in the circular film layer and can be directly read off the scale. Once the maximum shear strength of the film is reached, the cone starts to move jerkily and the pointer begins to fall. The maximum scale reading (PC value) is a relative measure of the shear strength of the film whose rate of formation under comparable conditions was measured microscopically as already described. The PC value is a measure of the strength of the film in the state of incipient consolidation. The PC measurements have a limit of error of +30 per cent. In every case, the mean value of five to seven measurements was determined. Conversion into absolute units was again dispensed with.

<sup>\*</sup>The measurements were carried out with the cone PK 306 and dynamometer No. 500. The temperature was maintained at  $20^{\circ}$ C.

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## DRY PIGMENTATION PROPERTIES, PC VALUE AND FILM FORMATION RATE

Thirty-two pva dispersions were investigated. All dispersions were plasticised by addition of 15 per cent dibutyl phthalate. The polymerisation was carried out in the presence of soap-type emulsifiers. The dispersions fell into six different groups. To some, emulsifiers and polyethylene glycol were subsequently added and to others varying amounts of ethylene oxide-propylene oxide blockcopolymers after or during polymerization. The film formation rate (FF) and the initial film strength (PC value) of these dispersions were determined. At the same time, the dispersions were dry pigmented with the pigment mixture mentioned above in a 1 : 1 weight ratio. The resulting pastes were spread out on glass plates by means of a glass rod and left to dry. Finally, the plates were numbered on the basis of the coating quality, 1 being the poorest rating. Microscope specimens were also produced from most of the pigment charges. These were also arranged in order of quality; specimens that appeared to be largely homogeneous under the microscope (dark field illumination) being rated as good and those that contained unresolved pigment aggregate and fragments of film being allotted the lowest ratings. Careful scrutiny reveals even finer differences between individual charges. These two methods gave about the same order of quality. Fig. 7 shows the PC value of the dispersion plotted



FIG. 7. DRY PIGMENTABILITY AND FILM STRENGTH

against the dry pigmentation properties determined on coatings on glass (number of coating quality). The tendency of pigmentation properties to improve with a decrease in PC value, that is, with a decrease in initial film strength, can be clearly seen. When the considerable limit of error involved in the subjective assessment of the quality of the coatings, and the wide scatter of the PC values are taken into account, the correlation between the PC value of the dispersion and dry-pigmentation properties appears to be fully satisfactory.

A general relation between film formation rate and dry-pigment compatibility need not necessarily exist since it is a question not merely of the thickness of the film formed around the pigment aggregates but also of its strength. Only with dispersions of essentially similar composition can it be assumed that pigmentation properties improve with a decrease in the film formation rate. That this is true as a first approximation is indicated by Fig. 8 in which the film formation rate is plotted against the dry-pigmentation rating, but only for dispersions of one group which are all prepared under comparable conditions.

The variation in the initial strength of a film is seen most clearly when the film strength (expressed by the PC value) is calculated on a unit of film thickness.



Table II shows the quotient when the PC value is divided by the FF value as a measure of the relative film strength. It can be clearly seen that the addition of 2-3 per cent polyethyleneoxide-polypropyleneoxide-blockcopolymer (75 per cent polyethyleneoxide reduces relative strength by about half. Relative film strength is reduced to about a third if five per cent of such a copolymer is added

Group	Formulation	Relative film strength PC/FF	Dry-pigmenta- tion compatibil- ity (mean rating)
I	Standard Formulation*	10, 3	
	henylsulphonate and polyethyleneglycol (1 per cent)**	13, 2	11
m	cent polyethyleneoxide-polypropylene- oxide-blockcopolymer (P)***	13, 3	4
VI	as I but with addition of 2 per cent P during polymerisation	6, 6	19
V	as I but with addition of 3 per cent P during polymerisation	6, 1	25
VI	as I but with addition of 5 per cent P during polymerisation	3, 9	27

#### TABLE II

\*Formulation for small particle size (Mowilith DV-grade) (compare DRP 744 318 of 27. 7. 1940).

\*\*Molecular weight (Mn) about 4000.

\*\*\*75 per cent of polyethyleneoxide ; Mn ca. 4500.

during polymerisation. The dry-pigmentation properties are indicated in the fourth column of table II by the mean rating of the relevant group. A clear correlation is found to exist between the mechanical properties of the film in the phase of incipient consolidation and dry-pigmentation properties.

#### CONCLUSIONS

Surprisingly, the tests show that the dry-pigmentation properties of a pva dispersion are closely related to film formation. When inorganic pigments, which are present mainly in the form of secondary aggregates, are stirred into the dispersion, the dispersion is initially deprived of part of the aqueous phase so that particles in the vicinity of the pigment aggregate approach each other until they are almost in contact. At this stage, the dispersion particles begin to coalesce (start of film consolidation). The ease with which the pigment aggregate is resolved into primary particles and mixed homogeneously with the dispersion particles is inversely related to the rate of coalescence. The results clearly show that the addition of emulsifiers and other additives to the dispersion after the polymerisation improves dry-pigmentation properties only to a limited extent. A substantial improvement cannot be achieved by subsequent additions. This phenomenon can be explained as follows: If the dispersion particles are brought within a certain interval of each other through the withdrawal of the liquid phase, the molecules of the emulsifier or of the protective colloid reversibly adsorbed on the particle surface are displaced from that surface and cannot, therefore, significantly retard the consolidation process. If, however, relatively hydrophilic molecules are firmly combined to the surface of the polyvinylacetate particles, for example by grafting, they cannot be displaced when the dispersion particles come into contact with each other. This accounts for the striking effects on dry-pigmentation properties when polyethyleneoxide-polypropyleneoxide-blockcopolymers are added during polymerisation. Subsequent additions. however, have relatively little effect.

In the case of pure pva dispersions, the rate of film consolidation is in inverse ratio to the particle size.<sup>1</sup> Moreover, excessive particle size impairs important properties such as gloss so that the optimum size should not be exceeded. In dispersions to which, for instance, the above mentioned polyethyleneoxidepolypropyleneoxide-copolymers have been added during polymerisation, particle size plays a far less important role so that very fine dispersions with good pigment compatibility can be prepared. A discussion of the extent to which other important properties can be modified by the addition of such compounds is beyond the scope of this investigation. All experiments described here show that a reduction in initial film strength and, if possible, a reduction in film formation rate, is essential for the production of dispersions with good pigment compatibility.

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#### REFERENCES

1. Talen, H. W., *JOCCA*, 1962, **45**, 387, also : J. Hengstenberg and W. Sliwka ; lecture "Dispersionen" in "Struktur und physikalisches Verhalten der Kunststoffe" ; published by K. A. Wolf, Springer-Verlag 1962, p. 812.

# The Electrodeposition of Paint\*

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#### Summary

The paper is presented in two parts. The first part consists of a general review of the conditions arising when charged electrodes, one of which is a metallic article to be coated, are immersed in a resin solution or emulsion. It is suggested that the usually accepted views of electrolysis and electrophoresis may not be entirely true for these systems and it is believed that local ionic precipitation or coagulation may be an important factor. The advantages and disadvantages of the process as a means of coating are briefly discussed. The second part of the paper deals in more detail with the experimental findings on various aspects of the process.

#### INTRODUCTION

The deposition of metals from solutions of their salts, as in electroplating, has been practised industrially for many years. Normally these processes involve the electrolysis of true solutions of simple or complex metallic salts. The general principles are well known and can be found in any text-book on physical chemistry. It is sufficient to say that in aqueous solution, salts of electrolytes separate into "ions," the cations carrying a positive electric charge and the anions a negative charge. This separation into ions needs no external source of electric potential and no electrical energy is expended in causing the ionisation. When two electrodes are immersed in the solution and connected to a source of DC potential, a potential gradient exists in the solution between them. Under its influence ions in the immediate vicinity of the electrodes are discharged and there is therefore a net overall movement of the cations and anions through the solution towards the negative and positive electrodes respectively. On discharge of the ions a variety of events may occur, according to the natures of the ion concerned and of the electrode. In electroplating, for the moment, simply consider that the metallic ion is discharged and an atom of the metal is deposited on the surface of the electrode. It should be remembered that in electrolysis the solution itself must remain electrically neutral, so that for every ion deposited at one electrode its equivalent of opposite sign must be deposited at the other electrode. Further, that a discharged ion is a highly reactive entity which may react with the metal of the electrode to form soluble or insoluble products, with the water of the solution evolving hydrogen at the cathode and causing local alkaline conditions or oxygen at the anode and local acid conditions. The importance of these factors will become evident later.

Suppose that instead of a simple metallic salt as electrolyte there is in solution the sodium or ammonium salt of an alkyd resin such as can be obtained by dissolving an alkyd resin of sufficiently high acid value in sodium or ammonium hydroxide.

<sup>\*</sup>Read before the Hull Section on 16 December 1963.

Ionisation will occur in solution to a greater or lesser extent and upon electrolysis the positive sodium ions will migrate towards and be deposited at the cathode with the evolution of hydrogen and the formation of caustic soda. The negative "alkyd" anions will correspondingly migrate towards and be discharged in equivalent amounts at the anode. Upon discharge, the ion may react with water to form the water insoluble "alkyd acid" and so be deposited, or alternatively it may react with the metal of the anode to form metallic salts which if insoluble in water will be deposited.

Up to this point, only substances which are in solution have been dealt with, but analogous circumstances may arise with emulsions or dispersions. It is well known that most emulsion particles carry a surface charge, either on account of ionisable surfactant molecules which are adsorbed upon the surface of the particle or because the dispersed substance itself contains certain polar groups, some of which are located at the liquid/particle interface and are thus able to ionise. In either case the particle acquires a net electrical surface charge and has its associated cloud of counterions; this net charge is one of the reasons for the stability of the dispersion, since the mutual repulsion of these charges tends to prevent the particles from colliding and coalescing.

If such an emulsion or dispersion is subjected to a potential gradient between two electrodes the particles will move under its influence towards the appropriate electrode and there be discharged to a greater or lesser extent and deposited. In many respects a charged particle of this type may be regarded as an enormous ion carrying a large number of unit charges upon its surface. This phenomenon is known as electrophoresis. If it is supposed that the particles carry charges on account of the surfactant present, then counterions must exist which will move towards and be discharged in an analogous way at the other electrode, thus as deposition occurs at one electrode the equivalent of counterions will be discharged at the other electrode, where any of the secondary reactions possible in electrolysis may occur.

The mechanism just described is not the only way in which a resin can be deposited. Two other mechanisms should be considered. First, depletion of the surfactant in solution by electrolysis can cause desorption of surfactant from the surface of the emulsion particle resulting in destabilisation and coagulation. Secondly, electrolysis of electrolyte or surfactant will produce anions which on discharge will produce dissolution of the metal anode ; where this metallic ion can form insoluble salts with either the polymeric substance or its surfactant, precipitation will occur.

The industrial applications of electrolysis are numerous and well known and need no further description. The possible industrial use of electrodeposition of organic materials seems to have been realised at least as long ago as the 1920s in connection with the deposition of rubber from latex and was extended to emulsions of other polymeric substances<sup>7</sup>. Its use has been extended to the deposition of oxides, etc., for coating filaments of radio valves<sup>3</sup>. Crosse and Blackwell<sup>1</sup> patented a process for the interior coating of cans with an oleoresinous lacquer by electrodeposition in 1936, although a paper by Sumner<sup>2</sup> describing the process refers to the electrolysis of the salts of resin and other acids rather than electrophoresis. There are wide analytical uses of electrophoresis for the separation of complex molecules in a mixture, such as proteins. There is therefore a considerable background of knowledge and prior disclosure which makes it impossible at this stage to obtain "master" patents, so that no one company can now monopolise the field.

The ability of an electrolyte to ionise in solution is largely a function of the dielectric constant of the solvent concerned, so that to all intents and purposes these processes are limited to water-borne paint systems. Electrophoretic processes have been described in non-aqueous solvents<sup>8</sup>, but because the charges involved are much smaller, the voltages required are much higher. It will be assumed, therefore, that in what follows only water-based systems are concerned. That such a long time has elapsed since the Crosse and Blackwell patent was published before any real practical development occurred is largely because until recently few suitable water-based media existed upon which paints could be formulated<sup>6, 9</sup>.

# FACTORS INFLUENCING THE PROCESS

So far only simple solutions or dispersions of resinous substances have been considered. Practical paints must contain pigments, possibly extenders, various additives, and may well be based upon a mixture of resins. If a paint is to be deposited electrically, then not only the resin but all the other required constituents, other than water, must undergo simultaneous deposition at the same electrode. Further than that, they must all be deposited at the correct relative rates, otherwise the composition of the bath in which the process is carried out will gradually change and so the composition of the coating deposited. It would be hopeless to attempt to maintain the composition by continual analysis and appropriate additions. It is fortunate that approximately the required relative rates can be achieved by correct formulation. Another problem that arises is the build up of by-products in the tank ; it was mentioned earlier that no action can occur at one electrode without a corresponding one at the other electrode. This may lead to a gradual build up of acids, alkalis, metallic salts from the dissolution of the electrodes, all of which are objectionable and which will alter the electrical characteristics of the paint in the bath and so affect the rate of deposition and the nature of the deposit. It will therefore be realised that although demonstration of the process is simple, the many complicated factors involved make the provision of a system which will run constantly for long periods very exacting.

Two extreme types of deposit can arise, although almost any intermediate is possible. One is a deposit which rapidly acquires a high electrical resistance as it is formed, where the current rapidly falls to near zero and coating virtually ceases. The other is a deposit whose conductivity remains almost equal to that of the paint from which it was formed; here the current remains almost constant and coating continues at a nearly constant rate for as long as desired. Both types have their advantages and disadvantages.

When an article to be coated is made an electrode in a bath the flux of current between it and the other electrode will be concentrated in the shortest path between them. When the resistance of the film deposited increases, so the flux of current will be diverted to other parts of the electrode of lower film resistance; the continuation of this process will eventually result in the formation of a uniform deposit over the whole surface of the article, however

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irregular its shape. It means also that sharp corners and angles where the current density is greatest will receive the first deposit and will tend to be as well coated as the remainder. A possible disadvantage of this type of deposit can be the existence of a definite limit to the thickness of coat that can be applied, which in some cases may be well under 0.001 in.

The other type of deposit can be built up almost indefinitely to any thickness that is desired, but since the current tends to take the shortest path, i.e. the one of least resistance and no substantial increase of resistance occurs, the deposit tends to concentrate on one side of the article. Thus whilst one type is almost independent of the geometry of the electrodes, the other type is highly dependent upon it. Evidently both extremes are in some way undesirable and a compromise must be made to achieve acceptable levels of film thickness and uniformity of coating.

As a very broad generalisation it is perhaps fair to say that usually solutions of polymers, such as alkali salts of alkyd resins, give the electrically resistant type of film upon electrodeposition, whilst emulsions are usually deposited as the more conductive type. There are, however, exceptions in both directions and many cases of intermediate behaviour.

## THE MECHANISM OF DEPOSITION

The usual theory of electrolysis assumes that when an ion becomes discharged at one of the electrodes, its whole charge is almost instantaneously lost, for example an  $SO_4^{\gamma-}$  ion is discharged to become a  $>SO_4$  radical, which rapidly reacts, according to its environment, resulting ultimately in the formation and release of an oxygen molecule or the dissolution of the electrode and the formation of the equivalent of the metallic ion. The authors' work has led to the conclusion that this may not be the case where a large, complex poly-acidic ion is involved and this applies still more forcibly when an emulsion particle carrying a very large number of ionised polar groups upon its surface is involved.

It is not regarded as valid to consider either of these as a form of charged conductor, which would immediately lose all its charge upon approaching sufficiently close to an oppositely charged electrode. It is suggested that, in these instances, it is possible to discharge these large molecules or emulsion particles gradually, either as they come into near approach to the electrode by re-orientation or, alternatively, oppositely charged ions approach them and are able to form an insoluble, non-ionised product. Since the majority of the complex molecules and surfactants concerned in the electrodeposition are anionic, it is proposed to confine the discussion to the phenomena occurring at the anode.

It is possible to divide the anionic substances present in a paint and dischargeable at the anode into a number of different types, which may be listed as :

(i) Simple inorganic anions, arising from extraneous electrolytes which are present as impurities, catalyst residues, etc.

(*ii*) Organic anions arising from surfactants present in the aqueous phase and which are not adsorbed on to the surface of an emulsion droplet or pigment particle.

(*iii*) Anions arising from unreacted products, for example phthalic acid anions, arising from unreacted phthalic anhydride in alkali soluble alkyds.

(*iv*) Complex polybasic anions due to the water soluble resin to be deposited, which may show a wide variation in molecular weight, although having nearly uniform equivalent weights.

(v) Emulsion droplets and pigment particles carrying adsorbed layers of ionised anionic surfactant.

(vi) Emulsion particles carrying ionisable, anionic groupings as part of the polymer chain. Some of these groups will be situated at the surface of the droplet and therefore able to ionise in the aqueous phase and give the droplet a net negative charge.

The distinction that must be made between cases (v) and (vi) is that in (v) the surfactant is in equilibrium with the surfactant in solution. The relative amounts adsorbed and in solution depend upon the strength of the adsorption, the area available for adsorption and the water solubility of the surfactant. Although this equilibrium exists, it is a dynamic one and there is a constant interchange between the adsorbed and dissolved surfactant. In (vi) the anionic groupings may be regarded as being more firmly attached to the surface of the emulsion droplet by entanglement of its polymer chain and the equilibrium between solution and "adsorption" is near to total "adsorption."

There are a number of experimental observations which are not readily explained, if it is assumed that a complex ion or emulsion droplet is immediately and totally discharged when it approaches sufficiently closely to the anode. Amongst these are :

(a) The initially formed coagulum becomes more difficult to re-disperse as current continues to be passed through it. If it were initially completely discharged, the only further charge that could occur is dehydration by electroendosmosis, and since in many cases the water content of the coagulum does not greatly decrease, this cannot be regarded as a satisfactory explanation. If it is accepted that the initial coagulum can be formed by only a partial discharge, the decreasing dispersibility, on passage of further current, can be explained, whether or not electro-endosmosis also takes place.

(b) Many systems which deposit as a compact film of considerable electrical resistance continue to pass a residual current, even when the content of extraneous electrolytes in the continuous phase is at a minimum.

(c) If the polymeric ion or emulsion particle were instantaneously discharged, then as with simple electrolytes there would be a fixed relationship between the dry weight of the deposit and the number of coulombs of electricity passed. Whilst in general such a relationship does exist to a rough approximation, when a substantial deposit is formed, it certainly does not hold good for the initial coagulum.

(d) It is easy to see how the first layer of polymer may be formed upon the surface of the electrode, but how are the next and subsequent layers to be discharged? This is particularly relevant in the case of an emulsion, where, although the aqueous phase in the interstices between deposited droplets may

be conductive, an emulsion particle near the deposited layer cannot approach more closely than 2 or  $3\mu$  or more to the electrode.

It is believed that the above considerations invalidate the immediate discharge hypothesis, but that once the possibility of a gradual discharge is admitted the facts become capable of rational explanation. It is suggested that as far as the actual deposition is concerned, both direct electrolysis and electrophoresis are relatively unimportant, and that it arises from the ionic precipitation or coagulation by metallic or other ions, which are themselves produced by associated electrolytic processes. This point of view is not entirely new and was put forward by Fink and Feinleib<sup> $\frac{1}{4}$ </sup> in the case of synthetic latices. Much of the work on the anodic deposition of rubber was carried out with zinc anodes, whose electrolytic dissolution produced a local high concentration of zinc ions which coagulated the latex around the anode. In this case it was the rubber film that was desired, so that adhesion of the coagulum to the anode was not required. The mechanism suggested, therefore, depends upon the electrolysis of electrolytes, surfactants, etc., to produce the necessary ions in the locality of the anode. Electrolysis and electrophoresis of the resinous material are only relevant in so far as they aid the transport of the complex molecules or particles towards the electrode.

It would be laborious to describe all the various ways in which the processes can operate in a representative number of different systems since several of them may operate simultaneously in any given system. It is, therefore, proposed to outline a number of means by which it can occur; the reader should then readily be able to judge which are likely to be operative in any individual example.

(i) Suppose that an emulsion particle is stabilised with an anionic surfactant and that some equilibrium exists between the adsorbed surfactant upon its surface and that in solution in the aqueous phase. Further suppose that the surfactant, for instance the sodium salt of a carboxylic acid, in solution is undergoing simultaneous electrolysis, then in the region of the anode its concentration in solution will be reduced, and hence in order to maintain the equilibrium between adsorbed and dissolved surfactant, desorption from the emulsion particle occurs. In this way the emulsion particle gradually becomes destabilised and finally coagulation of the emulsion particles in the region of the anode takes place. It should be noted that this process does not need the presence of any extraneous electrolyte and it is certainly involved in the electrolytic deposition of pigments from aqueous dispersions. If it is assumed, as seems reasonable, that the surfactant anions can reach the electrode through the interstices in the coagulum, then the process can continue and no difficulty arises in explaining how particles can be coagulated at relatively great distances from the electrode.

(*ii*) Consider an emulsion of a polymer which contains carboxyl groups along the polymer chain, and that the chains at the surface are so entangled that they cannot pass into the aqueous solution. The emulsion droplets are stabilised by the surface carboxyl groups which protrude into the aqueous phase and whose ionisation results in a net negative charge on the surface of the particle. Suppose that the deposition is to be carried out upon a steel anode and that some extraneous electrolyte is present in the solution, which is assumed to
yield chloride ions. Electrolysis of the electrolyte results in the discharge of  $C1^-$  ions at the anode, the dissolution of iron and the formation of ferrous ion, which under the influence of the existing potential gradient will migrate away from the anode. It is highly probable that the ferrous salts of such a polymeric acid will be insoluble in water and only weakly ionising, ion exchange between a projecting -COOH and Fe<sup>2+</sup> will occur with the formation of the insoluble iron salt and the loss of a negative charge. The emulsion particle is therefore gradually destabilised and ultimately coagulated, the migration of Fe<sup>2+</sup> through the coagulated film allowing further deposition to continue at distances relatively remote from the anode. This example has been given for the case of iron but is equally applicable to any other metal which will provide suitable coagulating cations.

(*iii*) The mechanism described under (*ii*) is applicable to the case of an emulsion carrying a labile surfactant, since the presence of the cation can render the surfactant in solution insoluble and so disturb the adsorbed-solution ratio and gradually strip the emulsion of surfactant as in (*i*). Alternatively, the adsorbed surfactant can be rendered non-ionising by the formulation of insoluble salts without desorption.

(*iv*) Now consider a soluble polymer in solution as the ammonium salt of a complex polycarboxylic acid. This resin would doubtless precipitate at the anode, due to a local concentration of suitable cations. In this case it is not essential to postulate the formation of cations by electrolysis, because, even if no extraneous electrolyte or surfactant is present, acidic conditions will arise in the vicinity of the anode and which would precipitate the polymer in the form of the acid. Such a condition can of course arise due to the disturbance of the hydrolytic equilibrium by removal of ammonium ions from the locality of the anode by electrolysis.

Obviously these examples can be extended to other cases. It would not be reasonable to suggest that these ionic mechanisms are the only ones that operate and indeed there may well be instances in which they are not principally involved. It is believed, however, that they do offer an explanation of the discrepancies listed under (a)-(d).

There is a certain amount of additional experimental evidence in favour of the ionic mechanism, for example, if an acrylic acid copolymer of a certain type is electro-deposited on to a zinc anode, the water resistance of the stoved film is markedly better than that of a film applied to steel by spraying. Evidently the zinc introduced into the polymer in this way has a cross-linking effect.

Experiments with unpigmented films formed from both emulsion and solution systems have shown that the initially formed coagulum may contain almost as much water as the bath from which it was deposited and that such a coagulum may appear to be reasonably dry and rigid even although water in the region of 70 per cent may be present. This is regarded as further evidence that the deposits are, at least initially, loose partially discharged, ionically formed coagula.

Whether or not the ionic mechanism is operative, deposition upon an iron anode will result in the dissolution of iron and it is unfortunate that ferric salts are highly coloured and that the original greenish ferrous ion are soon oxidised

to the brown ferric state upon exposure. This effect is very easily seen, the deposit when first formed upon iron electrode has a pale greenish colour but upon exposure to the air or when a film is stoved becomes brownish. Staining is almost always apparent with either emulsion or solution systems when electrodeposited upon an iron or steel electrode. The effect is demonstrably more apparent the higher the content of electrolytes in the aqueous phase. If the deposition can be carried out at the cathode, then since there is little tendency for the electrode to dissolve, the problem can be overcome. Such a solution of the problem unfortunately introduces other difficulties.

Reference has been made earlier to the varying ways in which the electrical resistance of the deposited film can build up as deposition continues. The impression may have been given that this is solely a function of the type of solution or emulsion in use, and perhaps also of its content of extraneous electrolytes, but there are other factors involved which may have a profound influence upon the way in which the film is laid down. The applied voltage is perhaps the most significant of these, but before discussing this effect, another phenomenon must be briefly described.

#### **Electro-Endosmosis**

If a bath is divided into two compartments by means of a suitable porous plate, each side filled with a solution of electrolyte, electrodes placed in each compartment and connected to a source of DC potential, an electric current will flow across the plate ; then if the plate is free to move, it will do so because of electrophoretic forces due to surface charges on the plate. As the plate moves the solution will move through it, so as to maintain an equal hydrostatic pressure on each side.

Conversely, if the plate is unable to move, the solution moves through the plate increasing the level of liquid one side and diminishing it on the other until an equilibrium is reached when the hydrostatic pressure is equal to and counterbalances the electrical forces. This phenomenon is known as "electroendosmosis."

The explanation of the effect is that the surface of the capillary passages through the plate carry ionisable polar groups, one ion being firmly attached to the surface of the capillary but the counter ion is free to move under the electric potential gradient present. Each counter ion that leaves the capillary carries with it a hydration layer of water, but in order to maintain electrical neutrality another counter ion must enter the capillary from the other side carrying its hydration layer, thus as the counter ions move along the capillary from one site to the next, they carry water with them, thus producing the endosmotic effect. Since electrolysis of the electrolyte is proceeding it might be thought that ions of the same sign as those on the surface of the capillary would also pass through carrying water in the opposite direction, the absence or diminution of this movement may be attributed to some reluctance of ions to enter a capillary whose walls are lined with a similar charge.

A porous deposit of polymer on a metallic electrode could undergo a restricted kind of electro-endosmosis, because the water leaving one side of the film cannot be replaced by water entering from the other. Therefore, if the effect does occur it will have the effect of dehydrating the film and since its removal would tend to create a "vacuum," the film would be expected to be compacted by the hydrostatic pressure on its surface.

Suppose that a porous film has been deposited upon the anode from an emulsion carrying an anionic surfactant consisting of the sodium salt of a carboxylic acid; this may be regarded as a porous plate, whose capillaries are lined with surfactant anions, so that under the potential gradient existing across the film, sodium ions will tend to move out of it carrying with them their hydration layer of water, surfactant anions in equivalent amount will be deposited at the anode, and desorption of the surfactant from the polymer will occur to maintain the adsorption-solution equilibrium. Under these conditions, not only will the film become less conductive because of its dehydration, but also because what electrolyte remains is becoming diluted owing to the electrolysis of the surfactant. It is therefore not surprising that the electrical resistance of a film may increase rapidly. It is evident that the extent to which the effect takes place will depend upon the voltage gradient across the film and not upon the voltage applied.

If the electro-endosmosis effect is to take place, the film must be able to provide conditions akin to those of a "charged capillary," therefore, if such an effect does occur, it may be regarded as some evidence of the validity of the suggestion that partial discharge of polymer molecules and emulsion droplets is possible and for the general picture of an ionic mechanism. It is difficult to see how otherwise the condition of a "charged capillary" could arise.

The number of molecules of water associated with an ion depends upon its size and intensity of charge. Figures of the order H<sup>+</sup> 7, Na<sup>+</sup> 11, K<sup>+</sup> 7 have been found<sup>5</sup>. It has been indicated above that the initial coagulum from a dilute solution or dispersion may contain water in the region of 70 per cent. Calculations based upon an alkaline solution of a polymer having a molecular weight of 1000 and carrying three carboxyl groups upon each chain, show that the quantity of electricity required to convert all the carboxyl groups to the iron salt would simultaneously reduce the water content of the film from 70 to 64 per cent, if electro-endosmosis were operative to its maximum possible extent.

# **Non-Ionic Mechanism**

It has previously been shown that there is considerable evidence for an ionic mechanism. An experiment which strongly supports this opinion and also indicates its effects upon electro-endosmosis may be quoted.

Comparative depositions were made upon platinum and steel electrodes, using an acrylic acid co-polymer emulsion, stabilised principally by carboxyl groups present in the polymer chain.

In both instances the initial current was the same, but the current after 90 secs had fallen on steel to 1/15th of its value on platinum.

The water contents of the wet films were 61.4 per cent on Pt and 18.2 per cent on steel, showing the different extents to which electro-endosmosis had proceeded. The dry film weights were 0.52 g on Pt and 0.109 g on steel per sq in of electrode surface.

Furthermore, the deposit on platinum was dissolved rapidly by dilute ammonium hydroxide whilst that on steel was more slowly dissolved and the film immediately adjacent to the metal was not removed.

### Gassing

The evolution of gas, for instance, when dilute sulphuric acid is electrolysed is very well known, and it can arise when aqueous paints are electrodeposited; it may occur at both the anode and the cathode, and whether emulsion or solution systems are used.

As has been stated earlier a discharged ion is an entity which cannot exist more than instantaneously and it must react with something, and gassing arises when the ions react with water. Thus we have at the cathode

$$\begin{array}{c} \mathsf{M}^{+} + e \longrightarrow \mathsf{M} \\ \mathsf{M} + \mathsf{H}_2\mathsf{O} \longrightarrow \mathsf{M} \mathsf{OH} + \mathsf{H} \\ \mathsf{2H} \longrightarrow \mathsf{H}_2 \\ \\ \mathsf{A}^{-} \longrightarrow \mathsf{H}_2 \\ \mathsf{A}^{-} \longrightarrow \mathsf{A} + e \\ \mathsf{A} + \mathsf{H}_2\mathsf{O} \longrightarrow \mathsf{A} \mathsf{H} + \mathsf{OH} \\ \mathsf{2} \mathsf{OH} \longrightarrow \mathsf{H}_2\mathsf{O} + \mathsf{O} \end{array}$$

 $2 O \longrightarrow O_{2}$ 

and at the anode

$$\begin{array}{c} \mathrm{NH_4^+} + e \longrightarrow \mathrm{NH_3} + \mathrm{H} \\ 2\mathrm{H} \longrightarrow \mathrm{H_2} \\ \mathrm{NH_3} + \mathrm{H_2O} \longrightarrow \mathrm{NH_4OH} \\ \mathrm{NH_4^+} + e \longrightarrow \mathrm{NH_4} \\ \mathrm{NH_4} + \mathrm{H_2O} \longrightarrow \mathrm{NH_4OH} + \mathrm{H} \\ 2\mathrm{H} \longrightarrow \mathrm{H_2} \end{array}$$

Gassing at the anode does not usually cause much trouble when deposition is taking place at this electrode, it is of interest, however, that under some circumstances gassing at the cathode can give rise to stable dispersion of bubbles which gradually extends through the bath and finally appears in the deposit found at the anode.

# **Deposition of Pigment**

or

Reference was made earlier to the fact that the pigments present in a paint can be co-deposited with a resin, it is evident that whatever the method by which the resin itself is deposited, electrolysis, ionic coagulation or electrophoresis, the pigment must be deposited in a manner similar to an emulsion. The direction of movement of the pigment and its rate of deposition is a function of the surfactant or other material adsorbed upon its surface. There is little doubt that when a pigment and a resin solution or emulsion are being co-deposited, there is some degree of mutual entrainment, which tends to deposit them in closer equality to the proportions in which they are present in the paint. When

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the pigment is initially dispersed in an unsuitable surfactant, it is possible to have a system in which the resin is deposited as a clear, transparent film from a pigmented dispersion.

## **Factors Influencing Paint Formulation**

The formulation of a paint for electrodeposition must take into account all the factors which have been discussed, ensure that the pigment and resin are deposited in the correct proportions and, of course, must take into account the usual principles of paint technology to form a film having the necessary durability, adhesion, flexibility, water and corrosion resistance and so forth. The situation becomes still more complicated in dual resin systems, for example alkyd-amino combinations, because now two resins and the pigment must still be made to co-deposit at the correct relative rates. Other problems which may be mentioned are the replenishment of the paint in the bath and the avoidance of change in composition as the process proceeds due to the build up of electrolytes, products from the counter ions arising from the resins and surfactants. Even this does not complete the list of factors over which some control must be exercised. Non-ionic components, pH, and temperature all play an important role in the smooth functioning of the process.

### **Advantages Gained from the Process**

Having reviewed the process and outlined some of the many factors which are involved, let us now consider what is likely to be gained by the use of the process and, to be fair, in what ways it will be inferior to other methods of paint application.

First, it is a process which is ideally suited to automatic operation, other steps such as degreasing, pre-treatment, washing and stoving can all be arranged to operate upon the same conveyor line, so that manual labour is needed only to place the articles on one end of the line and remove the pre-treated, coated and stoved parts from the other. Against this it must be admitted that technical supervision of the bath will be more exacting, viscosity and solids content control as with ordinary dip tanks is inadequate.

Secondly, because the rate of build up of electrical resistance in the film can be controlled by the formulation and selection of voltage conditions, a controlled film thickness can be applied to all parts of the article. The method is therefore ideal for box sections and the like which are relatively inaccessible to normal dipping or spraying methods. For the same reason penetration into welds and crevices is excellent.

Thirdly, it has been stated that the film deposited is dehydrated and compacted by the development of an increasing potential gradient across the film. Under the correct conditions the deposited film is so firmly coherent and adherent that it can be washed with a jet of water to remove the usual "dipped coat" that is always superimposed upon electrodeposited film. In this way drainage of the paint is avoided, so that no tears are formed, there is no blistering of thick edges and no bridging of screw or rivet holes. Usually the paint is so dilute, that even if there is no after washing, the dip applied coat is negligible ; sometimes an improved gloss can be obtained if the articles are not washed.

Fourthly, on account of the rigidity and tendency of the electrodeposited film to "cross link," no flash-off time is usually needed and when almost entirely enclosed articles are coated and stoved, "solvent washing" is completely absent. There is always a certain amount of sagging in dip applied coating, so that the top of an article is more thinly coated than the bottom, this does not occur with electrodeposited films and the film thickness remains uniform after stoving.

It has already been mentioned that corners and sharp edges are coated at least as thickly as the rest of the article. There is one slight disadvantage in this respect because if cracks and crevices exist in the metal being coated, deposition will cease when they have received their quota of paint, electrodeposited paints therefore have little filling power and the smoothness of the coating is no better than that of the original article.

The firmness of the deposit formed by electrodeposition enables the articles, after washing, to be handled more easily without marking prior to stoving than would be a similar dip or spray applied coating. The problems associated with the deposition of high gloss finishes have not yet been fully solved, but smooth, uniform priming coats may be obtained, in which there is a complete absence of "bits," runs and sags and which therefore need no flatting. Conventionally applied finishing coats applied over them have excellent appearance and gloss.

It is visualised that, at least for the immediate future, the process will be limited to water-borne paints. An added bonus is therefore freedom from fire and toxic hazards and freedom from odour. It is not usual to run the plants at high voltages, although the currents may be very large, so that there is no excessive danger from electric shock.

No mention has yet been made of the time required to coat an article: this depends upon a number of factors, such as the type of formulation, voltage applied, current available, the size and shape of the article and the distance separating the article and the other electrode. As a rough guide it is anticipated that the time will vary within the range  $\frac{1}{2}$  to 5 min., according to the factors just mentioned.

Lastly, the cost of the electricity required, when calculated back to units of mains current is negligible. Obviously, the cost of transformers and rectifiers may become very significant if large areas are to be coated, but at least ordinary unsmoothed rectified AC is entirely adequate. The cost of the mechanical parts of the plant is not appreciably greater than that of an equally automatic dip plant.

# EXPERIMENTAL RESULTS

Enough has been said above to indicate that electrodeposition is an extensive and complicated subject. It would be impossible in a paper of reasonable length to discuss in any detail all the matters which have been raised. It is, therefore, proposed to select a few of them for more detailed discussion. It should be emphasised that examples have been selected to illustrate certain points, they are not limited to any particular system, nor do they necessarily represent what would happen in a practical process.

## **Charge-Weight Relationships**

The unit of electrical current is the Ampere, which is defined as that current which will deposit silver from its solutions at a rate of 0.001118 grams/sec.

The unit of quantity is the Coulomb which is the quantity of current that passes when a current of 1 ampere flows for one second. Obviously, one coulomb will deposit 0.001118 grams of silver and this is independent both of the time taken and the voltage applied in doing so.

In electro-chemistry, the sub-unit is the Faraday, which is the quantity of electricity required to deposit one gram equivalent weight of silver or of any other metal or ion. This is equal to 96,500 coulombs.

The chloride ion has an equivalent weight of 35.5, and a gram equivalent weight will contain  $6.03 \times 10^{23}$  ions, thus each ion carrying one electronic charge will weigh  $\frac{35.5}{6.03 \times 10^{23}} = 5.89 \times 10^{-23}$  grams. If an alkyd resin, for example, is to carry sufficient acidic polar groups to render its alkali salts watersoluble it must have an acid value of about 70, which corresponds to a gram equivalent weight of  $\frac{56 \times 1000}{70} = 800$ , from which it can be calculated that the weight per electronic charge is  $132 \times 10^{-23}$  grams. That is the weight per unit charge or the weight deposited per Faraday is 22.5 times as great as for chloride. When compared to, say, zinc plating on a volume basis, the deposition of the alkyd is still more profitable in terms of deposit per unit of current passed.

Now consider an emulsion of a resin stabilised with a surfactant, we shall find that it is even more profitable in this respect. It can be calculated that in a monodisperse emulsion of droplet size  $0.2\mu$  diameter, each droplet will weigh about  $4.19 \times 10^{-15}$  grams, and that with an average amount of surfactant, if completely adsorbed and fully ionised, each droplet would carry  $2 \times 10^5$ electronic charges per particle. Hence the weight per electronic charge is  $4.19 \times 10^{-15}$ 

 $\frac{10}{2 \times 10^5}$  grams = 2.1 × 10<sup>-20</sup>, grams.

This is approximately 360 times as great as for the chloride ion and 16 times as great as for the alkyd resin. If current consumption were the only consideration then obviously an emulsion system would be highly profitable.

The conductivity of a solution of an electrolyte is proportional to the sum of the mobilities of the ions present. The mobility of a complex ion will be less than that of a small inorganic ion because of its size and complex shape and, therefore, increased viscous drag, although the presence of a number of electronic charges upon it would tend to increase its mobility. Arguing on these lines it might be thought that the mobility of an emulsion particle would be very slow, but the presence of manifold electronic charges and the relatively small surface area in relation to its bulk, increase the mobility. It has been shown that colloidal particles migrate under an electric potential at a rate of the same order as a simple ion.

# **Current-Time Relationship**

It has been stated above that with some types of resin the deposited film rapidly develops a high resistance and the current falls off rapidly, but with others there is no such change. Fig. 1 illustrates the behaviour of some typical resin solutions and emulsions in this respect, from which the wide difference in behaviour can be seen.



In order to avoid complications due to the geometry of the system, the experiments discussed in this section, were all performed using electrodes whose backs and edges were sealed, so that all the current flows in a direct path between faces which were opposite each other. The electrodes were rigidly clamped in a plastic block so as to be parallel to each other and a constant distance separated them in all these experiments.

The area under each curve represents the current integrated with respect to time which is equal to the number of coulombs passed during the experiment, from which the weight of deposit per Faraday can be calculated. This weight may be substantially lower than the true electro-chemical equivalent if there is wastage of current due to the presence of extraneous electrolytes, or less if, as has been discussed, coagulation occurs before all the ionic charges are completely neutralised.

### **Film Resistance**

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If it is supposed that during an experiment so little material is removed from the bath that no significant change occurs in its concentration, then it may 1964

be assumed that the conductivity of the bath will not alter during the course of the experiment. Under these circumstances the resistance of the film deposited can be calculated from the current passing and a knowledge of the applied voltage between the electrodes. The distribution of the potential across the film and through the liquid of the bath may also be calculated.

If V is the voltage applied to electrodes and  $C_0$  is the initial current, then the resistance R of the liquid in the cell is  $V/C_0$ ; if after a time t the current drops to a value  $C_t$ , then  $\frac{V}{C_t} = R + r$  where r is the resistance of the film deposited from which the value of r is easily found. Then if  $V_f$  and  $V_1$  are the potential differences across the film and the liquid in the cell respectively  $V = V_f + V_i$ , from which it can be shown that  $V_f = \frac{rV}{R + r}$  and hence  $V_1 = V - V_f$ .

Fig. 2 shows some examples of how the film resistance can change with time and its effect upon the potential gradient across the film and the liquid in the cell respectively. The former indicates why compaction of the film and dehydration of electro-endosmosis or other mechanism occurs, since when it is realised that the film may be of the order of 0.001 in. the potential gradient in terms of volts/cm is very high, whilst  $V_1$  becomes very low, and hence the current is very small and coating almost ceases.



FIG. 2. FILM RESISTANCE TIME GRAPH FOR AN ACRYLIC ACID CO-POLYMER SOLUTION

# **Effect of Concentration**

Fig. 3 shows the current-time relationship for various concentrations of a typical resin emulsion. It will be seen that, as would be expected, the initial current increases as the concentration rises, but that the change of current with time does not follow the same pattern at each concentration. The upright lines on the figure show the dry weight of deposit obtained at the end of each experiment. In this particular case the initial current rises steadily with increasing concentration, but this is not necessarily always the case; in some instances the current may decrease at the highest concentration. This may be attributed to (a) a decreased mobility of the ions and particles when the viscosity rises sharply with increasing concentration and (b) the repression of the ionisation of surfactants, polymeric ions, etc., at increased concentration.



FIG. 3. THE EFFECT OF CONCENTRATION ON AN ACRYLIC CO-POLYMER EMULSION

It will be apparent from the graphs that the yields of dry deposit are approximately in line with the area under each of the curves; the actual relationship obtained from these graphs is shown in Fig. 4. If the films laid down at the various concentrations were similar in structure, then some direct relationship should exist between the number of coulombs passed and the resistance of the film obtained; the curves in Fig. 4 show that this is not the case.

A determination of the water content of the wet films obtained in this experiment showed that in each instance it amounted to approximately 90 per cent of the water present in the emulsion from which it was deposited. Thus the coagulum from the 10 per cent emulsion contained approximately 80 per cent water, which is quite astounding in view of the relative hardness and apparent dryness of the film. Obviously the differing resistances of these

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FIG. 4. FILM RESISTANCE-INTEGRATED CURRENT GRAPH

films must be connected with their differing water contents; it is difficult to see how, if the emulsion droplets were immediately and fully discharged on reaching the anode, such differences could arise.

It is believed that this finding is strong evidence in favour of the ionic mechanism, since coagulation in this way could give a loose chain like coagulum occluding large quantities of water.

# **Geometry of the Electrodes**

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In these experiments only the side of the anode facing the cathode was exposed in order to avoid complications due to the geometry of the system and the varying lengths and therefore resistances of the conducting paths; it is of interest to consider how this does affect the flow of current. Fig. 5 shows three experiments in which the sides of the anode facing and remote from the cathode respectively were exposed. The difference in behaviour is quite apparent and in particular the rates at which the current decreases in the two cases. The vertical lines indicate the dry film weights obtained, the back of the test piece actually receiving ultimately a greater weight of deposit, which is confirmed

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FIG. 5. THE EFFECT OF FACE OF ANODE EXPOSED

by the greater area representing the integrated current. Curve C represents the behaviour when both faces are simultaneously coated and may be compared with curve D, which is the arithmetical sum of A + B. Once again there are interesting differences. The initial current is less than the sum of the individual currents, presumably because the solution cannot carry the combined current, the source of power being ample to supply the current without a drop in voltage. The rate of fall-off in current is slower when the two faces are exposed and the integrated current greater, which agrees with the finding that the weight deposited is also greater. These experiments are cf interest because they demonstrate that the shape, size and other geometrical features of the articles being coated must play a part in the thickness of coating received under any given circumstances.

The explanation of these curves would appear to be as follows. In curve A the voltage gradient across the cell is initially V/I, at which value the deposited film is able to build up an electrical resistance by endosmosis and compaction, so that the deposition rate soon decreases. In case B the conductive path is longer than A and therefore the voltage gradient is less than V/I, and the initial current is therefore less, but at this lower potential gradient the film resistance does not increase so rapidly, the current is better maintained and therefore ultimately a greater deposit is obtained.

In case C a certain amount of the volume of liquid between the electrodes near to the cathode has to carry the current flowing to both faces of the anode;

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this it is unable to do at a rate amounting to the sum of A and B, and hence the initial current is less than the expected total. The result of this is that the voltage gradient between the cathode and each side of the anode is reduced, so that for the reasons given above a greater weight of deposit is ultimately obtained.

#### Effect of Applied Potential

The importance of the voltage gradient across the film has become evident in the foregoing discussion and it is further evident that the extent to which this can increase and the rate at which it will do so must in some way be dependent upon the voltage applied across the electrodes. Since the applied voltage must also control the voltage gradient across the liquid in the cell, it will also influence the extent to which deposition is able to continue after the film resistance has risen to a given value.

Two quite distinct types of behaviour can arise according to whether the deposited film remains electrically conductive or whether it becomes resistant. Fig. 6 illustrates an example where the film retains some conductivity, and



FIG. 6. THE EFFECT OF APPLIED VOLTAGE ON AN ACRYLATE CO-POLYMER EMULSION

here it is seen that at high voltages the current falls off fairly rapidly, but the rate of fall off decreases as the applied voltage is reduced until at low voltage the current remains almost constant. In this instance, which is fairly typical of emulsion systems, there is an optimum voltage as regards the weight of deposit obtained in a given time. Fig. 7 shows the opposite behaviour, where



FIG. 7. EFFECT OF APPLIED VOLTAGE

the current falls off very rapidly, due to the increasing resistance of the film; a similar kind of behaviour occurs at all voltages. There is no optimum value of the voltage at which a maximum yield of deposit is obtained and the greater the potential applied the greater the deposit in a given time. This behaviour is generally characteristic of polymer solutions, but examples of intermediate behaviour exist.

### **Effect of Electrolytes**

The presence of extraneous electrolytes can have a number of different effects upon the deposition of resin, for instance the common ion effect may repress

the ionisation of the salt of a complex ion or the surfactant in an emulsion and so reduce the current carried by the resin to be deposited. Even if the common ion effect is insignificant, much of the current passing may be carried by the electrolyte or surfactant in solution to the detriment of the quantity of resin deposited.

Fig. 8 shows the current-time relationship of an acrylic type emulsion when varying proportions of sodium sulphate are present in the aqueous phase. It will be seen that the current increases as the electrolyte present is increased. The short horizontal lines indicate the current carried by a sodium sulphate solution of the same concentration; the volume occupied by the emulsion droplets would be expected to reduce the conductivity of the electrolyte, and the reduction of the initial current of the emulsion is of the correct order. It is of interest that the current passed by the emulsion containing electrolyte falls off fairly rapidly, whilst this particular emulsion shows no initial decrease of current when no electrolyte is added.



FIG. 8. THE EFFECT OF ADDED ELECTROLYTE (NA2 SO4) ON ACRYLATE CO-POLYMER EMULSION

The actual weight of deposit obtained increases with increasing electrolyte content, but if the areas under the current/time curves are integrated a uniform decrease in the weight of deposit per coulomb is found.

### Effect of pH

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pH may have a profound effect upon both the current passing and the weight of deposit obtained in either solution or emulsion systems. Fig. 9 shows the



FIG. 9. THE EFFECT OF PH ON AN ACRYLIC ACID CO-POLYMER

behaviour of an acrylic acid copolymer which is obtainable as an emulsion at pH 2.5, but which can be solubilised by the addition of ammonia or sodium hydroxide. This graph shows the weight of deposit obtained after four minutes at constant applied voltage as the pH is increased from 2.5 to 12. The points represented by circles were obtained from an experiment in which the resin was solubilised with ammonia and the crosses a corresponding experiment with sodium hydroxide. The very sharp maximum occurs at pH 8, irrespective of the alkali used, although the pH at which the emulsion " clears " is markedly different for the two alkalis. The negligible deposit at high pH values may be due to the re-dissolution of the resin film in the strongly alkaline solution, or because the presence of alkali precipitates ferrous ions formed at the anode as the hydroxide and thereby prevents them from coagulating the polymer.

Many other factors such as the quantity and type of ionic surfactant, the non-ionic surfactant and water soluble non-electrolytes all have an effect upon the quantity and form of the deposit obtained. The effect of pigment and the surfactants with which it is dispersed have not been discussed, but are of primary importance in the functioning of the process. The nature of the metal upon which deposition takes place is another factor which influences the results, and as has been indicated earlier the deposition of the ingredients at the correct relative rates, the build up of by-products formed in the process and replenishment of the bath are all problems which have to be solved.

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Enough has been said, however, to illustrate the extreme complexity of the process, and it must be admitted that although the influence of various factors is gradually being unravelled, there are many steps in the mechanism which are not yet fully understood.

### ACKNOWLEDGEMENTS

The authors thank the Directors of Blundell, Spence & Co. Ltd. for granting permission to publish this paper. Thanks are also due to Mr. J. A. Hasnip and Mr. C. Derrick, who carried out the experimental work involved in the investigation.

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#### REFERENCES

- 1. Crosse & Blackwell Ltd., BP 455,810; 496,945.
- Sumner, C. G., *Trans. Faraday Soc.*, 1940, 35, 272.
  Troelstra, S. A., *Philips Teck. Rev.*, 1951, 12, 293 ; Sylvania Electric Products, BP 899,302.
- 4. Fink, C. G., and Feinleib, M., Trans. Electrochem. Soc., 1948, 94, 309.
- 5. Bockris, J. O'M., "Modern Aspects of Electro-chemistry No. 2," p. 154 (Butterworths Scientific Publication).

- Burden, J. P., and Guy, V. M., Trans. Inst. Metal Finishing, 1963, 40, 93.
  See Shyne, J. J., Org. Fin., 1956, 17, 12.
  Hamaker, H. C., Trans. Faraday Soc., 1940, 35, 279; Gemant, A., Ind. Eng. Chem., 1939, 31, 1233.
- 9. Berry, J. R., Paint Technology, 1963, 27, 13.

#### DISCUSSION

MR. H. M. COOK said he assumed that as the solids in the bath were depleted paint was added to bring the concentration of solids up to strength again, but at the same time there would be a build up of by-products, which meant that ultimately the solution had to be discarded. Was this the case?

MR. MELL in reply, agreed that replacement of the deposited solids which have been removed from the bath was the crux of the process and one had to use various means to make the addition. One way for example, was to surround the cathode with a porous bag to restrict diffusion and so obtained a high concentration of ammonium ions around it and facilitated dissolution of the acid form of the polymer which is fed in at this point.

MR. S. J. REED said Mr. Finn went to some length to point out the film deposited depended upon the attitude of the article. The samples exhibited seemed to be covered with a uniform deposit. How was this obtained?

MR. MELL said the examples were prepared from a type of polymer which rapidly built up a highly resistant film, so that when the coating on the side facing the cathode had built up a resistance, the current flux was diverted to the back, resulting in equal film thickness over all.

MR. F. R. BOYNTON said it was his experience when working with soluble alkyd type polymers, there was a minimum period during which no deposit remained after washing with water. In the first 30-40 seconds up to about 80 or 90 per cent of the total coulombs were passed. A matter of a very small number of coulombs or seconds later, a washable film was obtained. He wondered if the lecturers could explain this. Furthermore, he had also found when a deposit was once formed and then left in contact with the bath, it became resolubilised and could be washed off with water.

MR. FINN in reply said it was this kind of behaviour which led them to put forward the mechanism they had suggested. He agreed with the speaker that a lot of coulombs could be passed without obtaining much washable film. He suggested that an ionic reaction was proceeding and that it gradually converted the initial coagulum to the insoluble form.

MR. MELL said a further point was that one could carry out a deposition and withdraw the panel after about 30 seconds, and find that there was nothing on the panel this did not mean nothing had been deposited. A deposit might have been formed, but which may not have been able to resist the shearing action on removal from the bath. Later on, when electro-endosmosis had compacted the film, it could be withdrawn from the bath. It must not be assumed that because a deposit could not be seen on removal that none had been formed.

MR. FINN asked the questioner for how long his deposition had been carried on.

MR. BOYNTON in reply said if the current was switched off for 2 minutes before withdrawal, he found that when the deposit was washed, the coagulum was washed away. If withdrawal had been immediate this would not have been so.

MR. FINN said they had not observed this but it might be a function of the alkalinity of the solution, which if high would tend to redissolve the deposit.

MR. J. DENNY asked if he correctly understood the lecturers to say there could be no coagulation, if there were no electrolyte present.

MR. MELL said something must be present capable of electrolysis such as surfactant or similar material. It could either be surfactant which was itself producing anions which were continually available, or it could, of course, be solubilised polymer. It could also be extraneous electrolytes.

MR. S. S. DONE asked if they had found in the pigmented paint that these surfactants were equally effective with organic pigments.

MR. MELL in reply said there was no doubt provided one could adsorb the right type of surfactant on the particular pigment concerned electrodeposition would occur. There were certain types of pigment where this was difficult.

MR. S. J. REED said that during the lecture it was said that it was difficult to get the pigment and the resin deposited at the same rate, was it not possible to take the pigment and disperse it in the resin and then emulsify?

MR. MELL said he did not recall saying there was great difficulty. Difficulty could arise if one did not use the correct sufactant. It was possible to incorporate the pigment in the emulsion particle, but he regarded it as practically very difficult to obtain a stable emulsion of a polymer-enclosed pigment particle, which would withstand the ill treatment to which it would be subjected in a deposition bath.

MR. F. ARMITAGE referred to one of the graphs shown by Mr. Finn and said that he would like confirmation that in the case of emulsions the deposit was not related to the number of coulombs of electricity passed through the bath, but in the case of the water soluble polymer the quantity of deposit was directly proportional to the coulombs.

MR. FINN said he did not think so; there was an approximate relationship between the number of coulombs passed and the weight of deposit with both emulsions and soluble polymers.

MR. ARMITAGE then asked what was the main difference in the relationship between the soluble and emulsion polymers.

MR. FINN said that as a rule deposition was very much more profitable electrically with emulsions where there was a high weight/charge ratio, the higher this ratio the greater the amount of deposit for the same current.

MR. ARMITAGE asked if it was not correct to say that the amount deposited was directly proportional to the coulombs.

MR. FINN said approximately, but not exactly.

MR. ARMITAGE said his second question concerned water retention. He understood it to have been stated by the lecturers that the water retention was as high as 70 per cent. How did they deal with dragging and tears when the object was removed from the bath?

MR. MELL said they believed the coagulum was formed by a cross-linking mechanism and that it was firm and rigid, even though it might contain 70 per cent water. The fact that one could wash a deposit containing so much water without dislodging it was one of the factors in favour of ionic coagulation.

MR. ARMITAGE asked if it was necessary to allow more or less flash-off before stoving.

MR. MELL said as the film was so rigid and cross-linked any bubbling or frying resulting from placing the film in the oven immediately occurred to a lesser extent than if the same polymer was applied by dipping. The two examples which had been exhibited were from the same paint. The black specimen in particular showed that the electrodeposited film was not blistered although there had been no flash-off time. The dipped specimen was boiled up in spite of allowing some flash-off time.

MR. ARMITAGE asked if they had any idea of the effect of particle size on electrodeposition.

MR. MELL said that they had not any direct experimental evidence on the effect of particle size. A mixture of solution and emulsion was a possible way of obtaining optimum conditions, although there might be difficulty because the deposition rates might not be equal.

MR. W. J. MCLEAN referred to a previous speaker's remarks about the absence of tears after washing the film. He said he had been having trouble with tears. Immediately after deposition an apparently uniform film was formed, but on washing and allowing to dry for some time tears had developed.

MR. MELL said that they had cases where, after deposition, the film was quite tight and dehydrated, for example the film after removal from the bath might contain only 14 per cent water, but after washing this increased to 70 per cent. Obviously the film had absorbed water during washing. In the case referred to by the speaker it was possible that reabsorption of water had made the film more fluid.

MR. MCLEAN said he had tried without washing and still found he did not obtain a uniform surface.

MR. MELL asked if the current was switched off while the articles were still immersed. If so, water absorption could occur from the paint in the bath.

MR. MCLEAN said that the current had been switched off.

MR. DONE said deposition rates were referred to several times during the lecture and asked whether if this rate were determined for a resin A, and also for another resin B, and both gave the same result, would they still deposit in equal amounts in a mixture?

MR. MELL said they had not enough experimental evidence to give a definite answer to that question, as there was obviously an enormous number of possible combinations. He would have thought that mixing two solutions together, provided each particular resin would deposit at the same rate individually, they would do so when mixed. But with emulsions so many side effects could occur that he would not like to say a mixture would deposit at an equal rate.

DR. L. A. O'NEILL asked if, with alkaline solutions of an alkyd, there was any evidence of the fractionation of the alkyd during its electrodeposition.

MR. MELL said he did not know. To establish that would involve a considerable amount of experimental work. He believed that in a practical system entrainement by

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a large molecule taking small ones with it tended to make the deposition of various size molecules more uniform.

MR. FINN quoted an example of entrainement. They had carried out an experiment with an amino type resin and had obtained no deposition at all, but when it was pigmented with titanium dioxide a deposit was formed. An examination of the film showed the content of amino resin in the deposit was the same as that in the bath, a mixed coagulum being formed.

MR. BOYNTON referred to the theory of ionic coagulation which he understood was due to anodically produced ions acting as a precipitant. If this were so, it would seem to him the crucial experiment was to deposit a film on platinum.

MR. MELL said they had already shown there was considerable evidence for an ionic mechanism and he would describe a further experiment which strongly supported that opinion and which also indicated the effect of the metal upon electro-endosmosis. (This is now included in the text of the paper).

MR. COOK asked if the electro-deposition process was being used to any extent commercially, and if so was the attendance of a paint technologist required to look after the bath.

MR. MELL said he thought it was quite common when operating large paint plants, in the motor industry for example, to have a paint technologist in constant attendance for either dipping or electro-static spraying. In the future, he could see no reason why electrodeposition should not operate as satisfactorily as the ordinary dip bath or electro-static spraying, when once the basic principles had been settled.

MR. DENNY said he was very interested in the question of the porosity of the film. If there was no bubbling when there was no flash-off before stoving, this would indicate the film was very porous. Had any work been done comparing dip applied systems with electrodeposited paint with regard to porosity.

MR. MELL said they had done no permeabilities of the final stoved film, but they did know the corrosion resistance obtained from an electrodeposited paint on a steel panel was at least equal to that of the same paint applied by dipping.

MR. DENNY asked if there was excessive sinkage shown on overcoating.

MR. MELL said they had no real experience and were not able to generalise on this point. They had had some films which were extremely good on overcoating. Porosity could arise in these electrodeposited films due to gas bubbles, gas generated at the cathode can migrate across the bath and become trapped in the film deposited at the anode.

MR. L. J. TASKER said he believed during the early part of the lecture it had been suggested by the lecturers that in order to obtain satisfactorily pigmented systems it was necessary to have the right kind of surfactant adsorbed on the surface of the pigment. Could the speakers give any guidance as to which type of surfactant should be used with specific pigments and extenders.

MR. MELL said he did not think there was any short guide to this problem. The only way one could tackle it was by trial and error.

MR. MCLEAN asked what was the optimum temperature for deposition?

MR. MELL said the effect of temperature on the rate of deposition varied widely with different systems. Some systems were relatively insensitive to temperature, whereas others were remarkably sensitive. A few degrees could sometimes alter the rate of deposition, although in other experiments they had operated up to 80°C, and without any change at all. They found this rather hard to explain. MR. T. BIGGS said Mr. Mell referred to earlier work on the deposition of rubber and he would like to know if their interpretation of the process by ionic coagulation was in agreement with any earlier theories.

MR. MELL said certainly the earlier work on rubber did suggest an ionic coagulation. The literature they had reviewed was rather vague in this respect.

MR. FINN said Fink and Feinleib suggested this mechanism for the deposition of synthetic latices.

MR. BIGGS asked if they believed their experimental work further confirmed this view.

MR. MELL in reply said that this was so, and it was a great pity that the process came to be called electrophoresis since this was misleading, in their opinion electrophoresis was not primarily concerned.

MR. J. S. GEARY referred to the comparison of electrodeposited films and dip applied films, and asked how the lecturers obtained the same film thickness in both cases to enable them to make a comparison.

MR. MELL said they adjusted the solids of the dipped coat until they obtained an equal film thickness.

MR. TASKER asked if they had experience of electrodeposition with metals other than iron, for example aluminium ?

MR. MELL in reply said this was a difficult question because there were so many combinations of metals and resins, and the behaviour of a particular resin may not be the same on different metals. Under the right conditions deposition could be obtained on almost any metallic surface.

MR. TASKER asked if other metals act similarly to iron.

MR. MELL said that in general the answer was yes when there was a metal which could provide suitable ions.

#### CORRESPONDENCE

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#### **IMPORTANT CORRECTION**

Accelerated Weathering of Paint Films

It will be noticed that the grouping of the blocks on pages 92 and 93 of the February *Journal* are incorrect. The following should be the correct groupings :

System B	System C	System D
Fig. 20, Fig. 21	Fig. 22, Fig. 23	Fig. 24, Fig. 25
System E	System F	System G
Fig. 26, Fig. 27	Fig. 28, Fig. 29	Fig. 30, Fig. 31

The inconvenience which this incorrect grouping has caused is very much regretted.

# Correspondence

# TECHNICAL EDUCATION

In recent years the Association has been giving increasing attention to means whereby they can play an active part in the education of chemists entering the paint industry.

The purpose of this letter is to suggest that the Danish system has much merit and that the Association should consider whether it could be adopted for use in this country. The following brief details were given to me in the course of a recent visit to the Paint Research Station, Copenhagen, by the Director, Mr. H. K. Raaschou Nielsen :

During the last year of study for the degree of M.Sc.Chem.Eng. at the Technical University of Denmark, it is normal for the young chemist to spend approximately six months on part-time research, and for those interested in paint, varnish and printing inks, this research is carried out at the Paint Research Station under the control of the Director, who also functions as instructor in paint technology at the Technical University.

At the end of the period a thesis is submitted to a panel of examiners, which in the case of the paint industry includes the Professor of Chemical Industries at the University, a Director of Research from one of the leading Danish companies and Mr. Raaschou Nielsen.

Mr. Raaschou Nielsen showed me a number of theses which had recently been submitted. The standard of work was most impressive.

We know that in England there will be difficulties in adoption because of the differentiation between technological and pure research. Nevertheless the climate of opinion is undergoing change and it may well be possible to find means by which the British paint industry can benefit by a scheme similar to that used in Denmark.

H. A. NEWNHAM.

Spelthorne Metals Ltd., 38 Berkeley Square, London, W.1.

16 January 1964.

# **Bristol Section**

#### **MODERN DISPERSION METHODS**

A very gratifying attendance of 45 members and visitors were present at the first meeting to be held in 1964, on Friday 3 January, to hear a paper by Mr. Wadham on "Modern Dispersion Methods." Mr. Wadham stepped in at the very last moment in place of Mr. R. Ward, who was indisposed.

Defining first his interpretation of the terms mixing, wetting and dispersing, and assuming that grinding was rarely necessary in the production of a paint, Mr. Wadham went on to discuss the factors which must be considered in choosing the right equipment for a particular dispersion problem. Ideally the equipment should be capable of completing the process from start to finish, without having to transfer to other equipment, e.g. stirrers, pugs, ponies, pan mills, high speed mixers, ball mills and attritors. Equipment such as colloid mills, sand mills, roller mills and microflow mills required a premixing operation and often a third "let down" stage. When abrasive conditions were present, precision mills such as roller mills or colloid mills should be avoided.

Horse power requirements of the various machines were discussed. Whilst formulae were available for calculating this, often the basic information was not all available and it became a matter of experience or taking advice from the equipment suppliers. Figures quoted ranged from 50 hp/g of paste for certain twin roll mills to 1 hp/1,000 g for simple mixers.

Other factors which had to be considered in making a choice of new equipment were types of pigment and media, etc., consistency of the product, labour costs, capital expenditure allocated, space available and flexibility to suit varied production. The decision these days had been simplified by improvements in raw materials which made dispersion so much easier.

Mr. Wadham continued by describing typical dispersion problems, indicating the traditional equipment used for such problems compared with present recommendations. The trend was obviously from heavy, slow running, precision machines to light, fast running machines, of which the most interesting were : (*i*) the high speed cavitation mixer with variable hydraulic control of speed, (*ii*) the S type attritor, and (*iii*) the microflow mill.

These were then described in more detail, particular advantages being outlined. The cavitation mixer would cope with a wide range of viscosities and interchangeable containers made the equipment very flexible in use. The attritor was described as a modified ball mill, but with much greater efficiency. The grinding charge was rotated within a stationary vertical cylinder by means of slowly revolving bars. Power consumption was low and particular advantages were that thixotropic materials could be easily discharged while the machine was running, giving 90-95 per cent yields, little or no aeration took place, and special covers allowed operation under vacuum, pressure, or in the presence of inert gases. The microflow mill is the most recent development and its operation was described as being like a multi-roll mill, working inside a cylinder. The cylinder may range from  $3\frac{1}{2}$  in diameter for a laboratory model to 12 in for a 60-gallon machine and might be lined with an aluminium oxide coating for producing whites. Flat blades were driven around the periphery of the stationary cylinder, in addition to grinding rods which were thrown out to the periphery and rotated at approximately half the blade speed. The whole of this inner portion could be taken out for cleaning. Premixed paste was fed through a valve which was set to give the correct dwell time in the machine, dispersion taking place between the rods, blades and inner surface of the cylinder.

The discussion which followed was very capably handled by Mr. Wadham. In answer to Mr. A. B. Lock, he stated that the engineer's view is that dispersion must precede wetting. On dispersion of organic pigments for maximum strength, he considered the best machines were the microflow or S type attritor—care, however, must be taken not to overgrind when strength will be lost. Supersonic methods of dispersion have been investigated, but cost is against this—an experimental set up to disperse 2 ccs of paste required £90 worth of electrical equipment. Following questions on the S type attritor, Mr. Wadham gave more details, such as they are ten to 100 times faster than ball mills, grinding media may be flints or steatite balls from  $\frac{1}{16}$  in diameter, the agitator rotates at 40-80 rpm, a continuous type was being developed but was not yet available, and a typical output of the 100S (50 gallons) model would be 100 gallons of enamel base/hour. Cleaning could be achieved with very low amounts of solvent, and for a complete colour change the ball charge could easily be dropped and replaced.

A vote of thanks, proposed by Mr. D. S. Newton, was well supported by all present.

R. J. W.

# London Section

### WATER-THINNABLE ALKYD MEDIA

The sixth meeting of the session was held at Manson House on 15 January 1964. when, with Mr. M. R. Mills in the chair, Mr. R. A. Brett, of the Paint Research Station, presented a paper entitled "Water-Thinnable Alkyd Media." Several aspects of water soluble alkyd resins for stoving compositions had been studied, including in the definition maleinised oils. With the latter a loss of acidity occurred on reaction with the drying oil, which could lead to reduced solubility in ammonia-possibly due to resistance of the anhydride ring to hydrolysis during the acid value determination and to loss of reactive groups. The use of fumaric acid, particularly with tung oil, enabled full acidity to be retained. In a study of non-oil-modified alkyds the introduction of ether groups improved solubility, but water resistance was likely to be low. The use of alcohols of high functionality gave some improvement, but the best results were given by acids of high functionality, e.g. trimellitic or pyromellitic acid, which enabled good solubility to be obtained, probably due to a more even distribution of carboxyl groups. In film studies, maleinised oils behaved well, but gave poor colour. Non-oil-modified alkyds, which were non-oxidising, gave good colour, particularly when stoved at higher temperatures (180-200°C) to cure by esterification. With a series of alkyd/amino resin condensates based on trimellitic and adipic acid mixtures, it was found that flexibility and water resistance ran in opposite directions; the introduction of capric acid or castor oil produced a similar relation between flexibility and water resistance. An ether modified resin based on 2-methoxy ethanol, however, had improved flexibility and water resistance, and hexamethoxyhexamethylol melamine showed the best results. To study the mechanism of cure of alkyd/amino resins, the rate of loss of base on stoving was studied. There was a rapid initial release, but after one hour there was still a large amount of nitrogen retained in the film. It was found that almost all the amino resin of the melamine type was in the inextractable portion of the film. Problems of use and application had also been studied. With a series of linear polyesters based on phthalic anhydride and a range of glycols solubilised with trimethylamine, the rate of pH change was related to the number of ester groups in the chain. Anomalous viscosity reduction on dilution had also been examined and was thought to be partly due to molecular association involving the hydroxyl terminated molecules. On application, the occurrence of pinholes on stoving had been examined. These pinholes were found to contain a small particle of undissolved resin in the centre, but removal of gel particles from solution before stoving did not entirely eliminate this defect.

In the discussion which followed, Mr. A. R. H. Tawn, Mr. N. R. Fisk, Mr. G. A. Fisher, Mr. M. J. Zissell, Mr. F. Armitage, Mr. A. G. North, Mr. W. O. Nutt, Mr. R. R. Davidson, Dr. P. A. Toseland and Mr. G. N. Stockdale took part. In proposing a vote of thanks to the speaker, Mr. J. R. Berry said that it had been a pleasure to listen to such a well thought out lecture, and congratulated the speaker on his exposition of this complex branch of technology.

V. T. C.

# Manchester Section

# THE LABORATORY EVALUATION OF THE BEHAVIOUR OF COLOURED PIGMENTS ON BALL MILLING

On 13 December 1963, in Manchester, the Section met to hear Mr. H. G. Cook present a lecture on "The Laboratory Evaluation of the Behaviour of Coloured Pigments on Ball Milling."

The lecturer first described a method that had been developed for the determination of the optimum conditions for the dispersion of a pigment by ball milling. It had been found that use of the *Red Devil* paint conditioner for shaking a jar made it possible to disperse, with glass balls, mill bases of a similar viscosity to those used on the large scale. For each pigment examined a range of concentrations had been milled in a 20 per cent solution of a long oil alkyd resin and the rate of elimination of coarse particles determined by taking Hegmann gauge readings at five-minute intervals.

Slides were shown illustrating the effect of varying pigment concentration on speed of dispersion. For most lead chrome pigments, as expected, it had been found that there was an optimum concentration above and below which speed of dispersion was reduced. For the majority of organic pigments this was not so, lower concentrations giving increasingly faster milling until impracticably low concentrations were reached. Under these conditions the preferred concentration became a compromise between speed of dispersion and throughput of the mill. The lecturer suggested that it was likely that these differences in behaviour would run parallel to the differences between pigment groups in the Daniel Flow test.

After dispersion, concentrated resin solution was added to each mill base and any tendency to shock-seeding was then noted. The "let-down" mill bases were tested for flow and it was often found that the pigment concentration chosen for best pigment throughput of the mill had to be lowered in order to avoid shock-seeding or to give reasonable flow from the mill.

Survey of the behaviour of a wide range of pigments had shown, first, that ball mill base formulation was very important for the achievement of rapid dispersion, secondly, that it was virtually impossible to predict the optimum formulation from a knowledge of the product's technological properties. Slides were shown to demonstrate that two phthalocyanine blues, although very different in tinctorial strength, should be ball milled at the same concentration to obtain best results. On the other hand, two phthalocyanine greens, closely similar to each other in general physical properties, gave optimum milling behaviour at different concentrations.

More detailed investigation with a short range of pigments had shown that as the concentration of alkyd resin solution used for ball milling was changed, the further this was above or below 20 per cent, the more critical became the pigment concentration to give satisfactory dispersion.

The basic testing method had also been modified so that rate of development of tinctorial strength could be followed in addition to the rate of elimination of coarse particles. Several pigments developed almost maximum strength as the seed level approached 5 microns, but others continued to develop strength after this. In all cases significant strength increases were obtained as milling continued below 10 microns.

The lecturer concluded by saying that preliminary work on the effect of varying the resin had indicated that changing the solvent had perhaps more effect than changing the resin'.

An active discussion took place during which members of the audience raised questions on flow properties, the effect of solvents, flooding and flotation effects, dilution of stainers, resin viscosity, applicability to sand milling and comparison with flow point methods. Mr. C. Williams, in proposing a vote of thanks to the lecturer, commented that it was a great pleasure to hear such an interesting subject presented by a member of the Section. He congratulated Mr. Cook on the clarity with which the lecture had been presented and on the capable way in which he had dealt with the many questions raised. The audience showed its support by considerable applause.

# PHTHALOCYANINE PIGMENTS : THE RELATIONSHIP BETWEEN PHYSICAL FORM AND PERFORMANCE

On 10 January 1964, the Section met in Manchester to hear Dr. J. D. Easton present a paper, as joint author with Dr. F. M. Smith, entitled "Phthalocyanine Pigments : the Relationship Between Physical Form and Performance."

The lecturer reminded his audience that phthalocyanine colours were among the fastest growing organic pigments; this was caused by their extreme fastness and many uses. Four chemical groups were recognised: copper and metal-free phthalocyanines, halogenated copper phthalocyanine and the heavy metal salts of sulphonated copper phthalocyanine; these showed characteristic spectra in sulphuric acid.

Copper phthalocyanine could be synthesised from phthalic anhydride or phthalonitrile and had then to be converted to a suitable state for pigmentary use. It showed polymorphism and the properties of the *alpha* and *beta* forms were described in detail and the existence of other forms indicated. "Crystallisation" to the *beta* form in use might occur either with or without substantial strength loss, depending on the proportions of *alpha* and *beta* forms in the pigment and on the crystallising agency. This was exemplified in paint and plastics and the mechanism discussed.

Pigments resistant to crystallisation, Dr. Easton explained, could be either already in the *beta* form or stabilised in the *alpha* form by, for example, introduction of chlorine. The pigmentary *beta* form showed cleaner shades and better flow in threeand four-colour printing inks. Crude copper phthalocyanine in the *beta* form could be converted to *alpha* form pigment by acid solution or swelling and the properties of the product depended greatly on the conditions used. The benefits of suitable after-treatment were shown in the colouring of rubber.

Grinding crude copper phthalocyanine in the *beta* form with an inorganic salt gave increased colour strength and increased content of *alpha* form. If this process was combined with a solvent treatment a *beta* form pigment was obtained. The mechanism of these changes was discussed.

Flooding, flotation and flocculation in paints containing blue and white pigments were illustrated and possible mechanisms outlined. Phthalocyanine pigments resistant to these defects could be prepared by incorporation of a polar-substituted phthalocyanine; this could operate by either reducing flocculation of blue or by increasing association with white.

Normal phthalocyanine green was prepared by chlorination of copper phthalocyanine, but the yellower greens were either metal-free polychloro-phthalocyanine or copper polychlorobromo-phthalocyanines. Although polymorphism was not known for phthalocyanine green, acid pasting and salt grinding could be used as finishing techniques. In addition solvent treatment increased crystallinity and improved strength, cleanliness and dispersibility of the pigment.

The lecturer felt that the future of phthalocyanine pigments was likely to lie in moderate extensions of the shade range, combined with the production of tailor-made physical forms for specific applications.

During the discussion which followed several speakers raised questions concerning newer physical forms, the use of X-ray crystallography, flotation and flocculation, the value of *alpha/beta* mixtures and the effect of aqueous chlorine on phthalocyanine blues. Mr. W. F. McDonnell, in proposing a vote of thanks, made the point that satisfactory performance of new pigments in the pigment maker's laboratory did not necessarily mean that the same results would be obtained in different media and under different conditions of dispersion. He felt that the lecture had provided an excellent review of the topic and congratulated Dr. Easton and Dr. Smith on their capable presentation and handling of the discussion. The audience showed their strong support for these views by considerable applause.

I. S. M.

# **Midlands Section**

#### SURFACE COATINGS SYMPOSIUM

A meeting of the Section, held at Birmingham Chamber of Commerce on 17 January 1964, took the form of a symposium. Mr. A. R. G. Warne was the Chairman and three papers were presented, entitled "Plastic Coatings," by Mr. J. Land, "Hypalon Coatings," by Mr. C. A. Sharp, and "Rubber-like Polymers," by Dr. A. Lowe.

#### **Plastic Coatings**

Mr. J. Land said that early developments of plastic coatings were restricted to the bonding of calendered pvc on to steel and the application of plastisols to formers by hot dipping. With the development of self-adhesive organosols and plastisols it became possible to use paint-industry techniques with raw materials from the plastic industry.

His company, having particular interest in chemical resistance, had developed a self-adhesive "rigisol" based on a pvc homopolymer. Test films had withstood 30,000 hours of accelerated weathering and adhesion was still good. On one building site alone, 500,000 ft<sup>2</sup> of this coating had been used.

In reply to questions, Mr. Land said that application was by roller coating and that curtain coating was also successful. When the substrate was hot-rolled steel it was shot-blasted, but was not galvanised or primed; aluminium required etching with caustic soda. On deep drawing, the coating followed completely down to the breaking point of the metal. At drill-holes there was sometimes corrosion, but the corrosion creep was very limited. Recoating was possible and epoxy-resins were favoured for this.

#### Hypalon Coatings

Mr. C. A. Sharp explained that although rubber-based paints had been used for a number of years, there was difficulty in obtaining coloured paints due to oxidative breakdown. In 1952 *Hypalon* was introduced by treating polyethylene with gaseous chlorine and sulphur dioxide. A typical *Hypalon* had one chloro group for every seven carbon atoms and one sulphonyl chloride group for every 90 carbon atoms. The chlorine provided internal plasticisation and the sulphonyl chloride groups gave centres for vulcanisation.

Having no unsaturation and no chromophoric groups, *Hypalon* was unattacked by ozone, was resistant to oxidation and gave water-white solutions in aromatic hydrocarbons and chlorinated solvents. A range of types was available, the less soluble types being used in the rubber industry and the more soluble types being suitable for surface coatings.

Metal oxides were used as curing agents in conjunction with rubber accelerators like MBTS. Tribasic lead maleate was the preferred curing agent and it also functioned as a colour stabiliser. Cure was slow at room temperature and could be accelerated by heating. Faster cure might be obtained by using two-pot systems incorporating 2-mercapto-imidazoline and di-*ortho*tolyl guanidine. Epoxy resins and polymides also serve as curing agents.

Mr. Sharp then dealt with pigmentation and solvents for making paints for brushing, spraying, hot spraying, dipping and roller coating. The pigment might be incorporated using rubber mills to form chips or by ball mill using 10 per cent of the *Hypalon* initially and incorporating the rest later.

In answer to a query, he said that compatibility with other resins was usually adequate to permit the incorporation of 5-10 per cent *Hypalon* in normal paints to improve hardness and surface tack.

#### **Rubber-like Polymers**

Dr. Lowe said that most synthetic rubbers are obtained by polymerisation of unsaturated compounds like butadiene. The introduction of polyurethanes represented a most significant development. Polyurethanes were formed by the reaction between di-isocyanates and dihydroxyl compounds and properties could be modified by choice of diol. Crystallinity, which gives high tensile strength, could be built in by using blocks of polyesters like polyethylene adipate.

By using a deficiency of diol, polymers with isocyanate end-groups are obtained and these might be cured by reaction with water or with diamines. Rate of cure might be improved by heating and by incorporating a small amount of branching in the polyester.

If a deficiency of isocyanate was introduced, the polymer may be compounded with further isocyanate during rubber making. For this application there were advantages in using polyester-amides from materials like ethanolamine.

The principle of building blocks into polymers to give an infinite variety of endproducts was one which could be applied to surface coatings. The isocyanate-ended polymer, reacting with atmospheric moisture, required more branching and this tended to reduce the rubber-like characteristics, but the products were still essentially rubbers.

Replying to questions, Dr. Lowe said that isocyanates with low molecular weights were most suitable for coating metals. They have good adhesion and excellent resistance. To reduce hazards from toxicity, adducts of isocyanates with polyols are used.

A vote of thanks to the three lecturers was proposed by Mr. L. R. Seaborne.

L. R. S.

#### TRENT VALLEY BRANCH

The first technical meeting of this Branch was a visit to the Research Department of the Engineering Division of British Railways at Derby on 13 January.

Members and visitors were given a brief introductory description of the various sections of the Research Department by Mr. S. Wise and then conducted in small groups through the laboratories. Research was carried out in all facets of railway engineering, from improvements in permanent way laying and fixing to vehicle design

and wagon control. The service sections were fully equipped, much use being made of a recently installed digital computer.

The visit concluded with a brief business meeting, Mr. Law proposing a vote of thanks to the staff of British Railways who had sacrificed their evening and given the Trent Valley Branch such an interesting visit.

J. L. P.

# **Newcastle Section**

### WATER-THINNABLE ALKYD MEDIA

A lecture on "Water-Thinnable Alkyd Media" was given by Mr. R. A. Brett (Paint Research Station) to the fourth meeting of the Section on 2 January 1964. The Vice-Chairman of the Section, Mr. E. L. Farrow, was in the chair.

The lecture covered work done during the past few years at the PRS. By defining alkyds generally, Mr. Brett was able to include maleinised oils, where the main work had been on the reactions between oils and maleic anhydride. It was found that the acidity of these products was below that calculated from the starting materials, and this was undesirable because the minimum maleic anhydride should be used to attain solubility in dilute alkali in order to leave as much of the oil unsaturation as possible available for film formation. The loss of available acidity was attributed partly to difficulty of hydrolysis of the anhydride groups in the adduct and partly to some reaction which caused their total loss. Use of fumaric acid avoided this with conjugated oils, but not with unconjugated ones.

Alkyds, without oil modification, had been prepared according to three approaches in order to attain water solubility with the highest possible degree of reaction : (*i*) introduction of ether groups *via* polyglycols, (*ii*) use of high-functionality polyols, (*iii*) use of high-functionality acids, e.g. trimellitic anhydride (TMA) and pyromellitic acid. The solubilising effects in the second and third groups were attributed to wide molecular weight distributions, and in the case of the third group also to the fact that free carboxyl groups were found in the high molecular weight fractions to a much greater extent than when a difunctional acid was used.

Film studies showed the maleinised oils to yellow badly, probably owing to the action of nitrogenous base (used for solubilising) on the drying oil fatty acids. The non-oil-modified alkyds required high stoving temperatures to remove the base and attain cure by esterification in the film.

In order to progress beyond this point, attention was turned to combinations of water-soluble alkyds and phenolic- or amino-resins. Three types of alkyd were investigated : TMA/adipic acid/diol; TMA/capric acid/diol; TMA/castor oil/diol, and a partially methylated trimethylol MF resin. In none of the systems could a satisfactory combination of flexibility and water resistance be obtained, and substrate wetting was also a problem. It had been concluded that the MF resin was not a satisfactory cross-linking agent, and that either one etherified with 2-methoxyethanol, or hexamethoxymethylmelamine, would offer better possibilities.

Studies on the mechanism of the curing of water-soluble alkyd/MF systems were concentrated on the rate of loss of base from the alkyds alone, since this must precede the curing reaction (alkyd carboxyl groups with MF resins). In general the rate of release declined with increase in molecular weight of the base, and it was thought that as much as 50 per cent of the amount initially present could be retained in a normal stoving schedule. A radiochemical method of determining the retained base was being explored. Work had also been done on the distribution of amino-resin between the MEK-soluble and MEK-insoluble portions of the cured films. The greater proportion (80-97 per cent) was in the insoluble fraction.

Problems with the alkyd/MF systems included storage stability, anomalous viscosity reduction behaviour and film defects on application. On storage, a fall of pH, clouding and even separation into layers could occur; a reduction in the number of ester groups per unit weight of resin reduced pH changes, which presumably were due to hydrolysis of the alkyds; secondary hydroxyl groups appeared to be associated with clouding more than did primary groups. Anomalous viscosity reduction appeared to be due to the presence of chains terminated by hydroxyl groups at both ends; termination by carboxyl groups and branching of chains reduced the anomalies. Application defects could occur immediately on application or at various stages of stoving. "Cratering" occurred at the very beginning of stoving and it had been found that each crater had a solid particle at its centre and a thin film of resin over the "crater" surface. Improvements were made by eliminating dust, adding solvents or a non-ionic surfactant, or by filtering off gelled particles, but none cured it completely. The cause of the phenomenon was obscure and might be due to stresses within the film due to earlier curing of its upper layers.

The discussion was contributed to by Mr. Bravey, Mr. Deeks, Mr. Laws, Mr. Farrow, Mr. Maugham, Mr. Wall and Mr. Baxter. Though the work reported had been done on clear films, pigmented films had been tested and showed similar patterns of behaviour. Maleic acid was no better than the anhydride in reaction with oils, since it formed the anhydride. Wetting of substrates was better if long-chain fatty acids were included in the alkyds. The use of higher stoving temperatures than 120°C had not been investigated, either in order to drive off the solubilising bases or to cure the hexamethoxymethylmelamine. Mr. Wall had noticed a tendency for viscosities to drop on storage ; Mr. Brett said that hydrolysis of ester groups would cause this, but a commoner observation in his experience was separation into layers, the lower thick and the upper thin. The reaction causing loss of maleic acidity was tentatively ascribed to formation of keto-acids.

The vote of thanks was proposed by Mr. A. Laws.

D. M. J.

# Scottish Section

#### FORENSIC MEDICINE

In More's Hotel, Glasgow, on Thursday 9 January 1964, the Section held their fourth meeting of the session under the chairmanship of Dr. D. Atherton. On this occasion the lecturer was Dr. E. Rentoul, of the Department of Forensic Medicine, Glasgow University.

Dr. Rentoul explained that his lecture would be concerned with the medical-legal aspects of criminal investigation and the problems which were involved.

He began by outlining the various steps taken when a sudden unexplained death occurred. In the first place the police were called in along with—in Scotland—two doctors. In addition, in some circumstances, the procurator fiscal was also present. Only after the police had completed their initial investigation and given their assent could the doctors proceed with their examination.

It had to be decided whether or not a crime had been committed and while making their decision the doctors were required to keep a very open mind. If this were not done a wrong conclusion could be arrived at and, as a result, a murder could possibly be mistaken for accidental death. Forensic medical experts were then faced with three problems : (a) the identification of the deceased, (b) the time of death, and (c) the cause of death whether it be natural, accidental or homicidal.

Identification could sometimes be relatively easy when the relatives of the deceased could be found. But even in these same circumstances the problem could turn out to be far from straightforward as murderers often tried to render their victims unrecognisable. However, in this connection dentists could be helpful as they kept very detailed records.

As to the time of death this was not easy to establish and at best could be given to within two hours. But in those cases where long periods of time had elapsed before the corpse was found it was quite impossible to state the time of death unless firm evidence from another source was available. Dr. Rentoul said that the most accurate method of determining the time of death was based on the rate of cooling of the body, but this had limited application and there was really no method available which could exactly pinpoint the time of death.

The third problem—what was the cause of death ?—could sometimes be easily solved. It was here that doctors had to form an unbiased opinion as to the cause of death. This was of major importance and on it depended whether further police action would be taken. Also, in coming to their decision they had to find information which might be required by a jury.

In the second part of his lecture, Dr. Rentoul showed a large range of slides illustrating various types of wounds inflicted by murderers, injuries received in road accidents and the effect on the body of a variety of abnormal conditions. These all proved of very considerable interest.

To conclude, Mr. W. Horsburgh thanked Dr. Rentoul for an extremely interesting and educational lecture. Mr. Horsburgh was obviously fully aware of the impact it had on the Scottish Section members attending as his vote of thanks was given —as he said—on behalf of the Oil & Colourless Chemists.

T. B. H.

#### EASTERN BRANCH

#### INAUGURAL LECTURE

The first meeting of this newly formed Branch of the Scottish Section was devoted to a lecture by Mr. H. G. Cook on "The Systematic Technical Evaluation of Coloured Pigments."

In providing technical data for coloured pigments (for use in paints), three principles should be followed. First, all testing should be strictly comparative. Secondly, tests should be on a realistic basis in actual paint vehicles, so that it is a system rather than an individual pigment substance that is examined. Finally, results should, wherever possible, be expressed in objective, numerical terms. The paint formulator must decide from these comparative, objective results which pigments suit his purpose.

The work carried out to compile data on four different properties, dispersibility, opacity, heat fastness and weather fastness, for a large range of pigments, was described.

For dispersibility optimum mill-base formulations were determined by measuring speed of dispersion on a *Red Devil* paint conditioner under conditions where one minute's dispersion was roughly equal to one hour's ball milling. Conditions taken into consideration for optimum pigment/resin solution ratios included discharge consistency and absence of shock as well as speed of dispersion.

March

Two film thicknesses at three pigment volume concentrations were used to determine the contrast ratios for each pigment. The ratio was obtained from reflectance measurements. Graphs of contrast ratio against PVC were shown for several pigments to illustrate the assessment of opacity.

Heat fastness was determined at different depths of shade and under different stoving conditions. The former were the International Standard Textile Shade depths of 1/3, 1/25 and 1/200, and the importance of equal visual depths was emphasised. In assessing the change of shade the ISO Grey Scale was used for comparing contrast ratios and expressing them numerically on a 1-5 scale. Fastness to stoving after overspray with white was also estimated by a Grey Scale for staining.

Testing of weathering fastness had many variable factors to contend with and could not properly be accelerated. Various locations were used and exposures carried out at equal visual depths and at the same time. A range of shade depths was used and also different media, since both factors influenced durability. The Grey Scale was again used to describe changes after three, six, 12 and 24 months' exposure and patterns were also assessed for gloss.

Other pigment properties of value to the paint manufacturer were listed.

In the discussion, Mr. Bennett queried dispersibility differences between phthalocyanine blues with and without surface coating. Mr. Cook explained that a small proportion of xylene in the grinding medium could reduce the difference.

Mr. Humphrey and Mr. Cook discussed the Daniel method of dispersibility testing compared with the method described.

Mr. Sim raised practical questions on flotation, flooding and flocculation problems in the paint factory. The last phenomenon was considered the most serious to deal with.

Mr. Bullions queried equating the *Red Devil* dispersion tests with large-scale ball mill practice, and was assured by Mr. Cook that under correct conditions of capacity and ball charge the recommended optimum ratios gave good results and comparisons between pigments.

Mr. McVey raised the point of mixtures of pigments. For processing properties generally these could be predicted, but for performance and weathering, mixtures of pigments could behave anomalously.

Mr. Phillips was interested in the difference between various weathering sites, and Mr. Cameron asked if any of the tests were used as manufacturing controls. Mr. Cook concluded by mentioning certain special tests which might be used for manufacturing control.

At the end of the meeting, Mr. Sim accorded a vote of thanks to Mr. Cook, to the members of the newly formed Branch for their support, and to Mr. Bullions for his pioneering work which had resulted in the formation of an Eastern Branch of the Scottish Section.

# FATTY ACIDS, THEIR NATURE AND USES IN INDUSTRY

This Branch held its second meeting on 13 November 1963, when Mr. J. J. B. Jesse gave a lecture on "Fatty Acids, Their Nature and Uses in Industry."

After a preliminary survey outlining the historical development of the fatty acid industry and the sources and manufacture of the individual fatty acids, Mr. Jesse gave details of specific applications, depending on, firstly, the physical properties of the acids.

The hardening of paraffin wax with stearine for candles, the uses of stearine in cosmetic creams and the formulation of buffing compounds using stearine and other fats as the matrix for holding the abrasive were examples given.

The reason for the efficacy of small additions of oleines and other fatty acids in special lubricants for metal rolling, pressing, cutting and drawing operations was explained by the strong polar attraction of the carboxyl group of the amphipathic fatty acid molecule to metal surfaces. This left a hydrocarbon chain projecting outwards from the surface.

Oleines and other fatty acids and their derivatives were present in processing yarn lubricants for natural and synthetic fibres.

In the moulding of many products, small additions (about 1 per cent) of fatty acids such as stearine are frequently used to give easy release from the mould. Varied examples were given, such as both thermoplastic and thermosetting resin powders, metallic powders for sintering, and pharmaceutical tablets, etc. Stearic acid performs as a mould release in rubber compounding in addition to being an activator for the vulcanisation accelerator.

Coatings of the compounds on to certain pigments rendered these more easily dispersible in organic media, and stearic acid could give flow properties to certain minerals. Ore flotation methods using fatty acids such as oleic were described.

The second part of the lecture related to those uses linked to chemical reactivities of the fatty acids, beginning with all varieties of soaps and their uses in toiletries and industrial emulsions, including the emulsion polymerisation of S-B rubbers. Solvent soaps in hand cleaners, firelighters and disinfectants were mentioned. In foam rubber production and as latex additives fatty acid uses were described.

Insoluble metallic soaps, from either fusion or double decomposition processes, were used in wire drawing, in plastics as stabilisers and in lubricating greases. Fatty acid in waterproofing limestone dust (as used in coal mines for the suppression of dust explosion) and also cement for wet storage were described in some detail.

The uses of fatty monohydric alcohol esters as plasticisers, lubricants, oiliness additives, film strength improvers and in various pharmaceutical roles were described.

Polyhydric alcohol esters were widely investigated as emulsifiers. Also in this classification were the plasticising alkyds and the air-drying alkyds. Vinyl esters, their preparation and use co-polymerised with vinyl acetate, were outlined.

The methods used to obtain nitrogen derivatives, fatty amides, alkanolamides and nitriles were given and typical uses were quoted ; amides as slip agents, mould release, rubber and waterproofing compounds ; alkanolamides as foam boosters in detergents and shampoos, and nitriles, after reduction to the fatty amine, as cationic additives for bitumens.

Reduction to fatty alcohol by hydrogenation or by sodium reduction gave alcohols for use in alkyl sulphate detergents.

March

Fatty ketones had newer applications such as slip agents, and mention was also made of fatty anhydrides, ketenes and mercaptans with specific uses.

Hydrogenation of mixed fatty acids can be selective for the polyunsaturated compounds so that these might be separated from the monounsaturated acids.

12-hydroxystearic acid was used in lithium grease and was derived from ricinoleic acid by hydrogenation. Other products such as epoxidised, sulphated and sulphurised unsaturated acids were described.

The oxidative cleavage of oleic acid by ozone to form pelargonic and azelaic acids was given as an example of a modern commercial development, and to close Mr. Jesse gave some details on sulphated and dehydrogenated hydroxyacids.

Questions on some of the above topics were raised by Mr. Hutchinson, Dr. Atherton, Mr. Pringle and Mr. Gower, who also accorded Mr. Jesse a vote of thanks from all those at the meeting.

P. A. G.

#### STUDENT GROUP

#### SOME ASPECTS OF PAINT MARKETING

Under the chairmanship of Mr. D. M. Stewart, the Section's Student Group held their fifth meeting of the session in More's Hotel, Glasgow, on Saturday 11 January 1964. The lecturer on this occasion was Mr. G. McVey, who spoke on "Some Aspects of Paint Marketing."

Mr. McVey introduced his subject by pointing out the connection between advertising and selling as parts of a marketing plan. He dealt with selling to (a) consumers and (b) to retailers at some length, emphasising that the sale always took place "in the mind of the customer," and that, in selling, attention had therefore to be paid to this factor.

Going on to advertising, Mr. McVey stated that this required to create a public attitude to a product and should meet merchandising at the "scene of sale" in order to be fully effective. He showed, however, how "brand loyalty" could affect this process.

To produce good advertisement, agents required to know a great deal about the product to be sold. They had to acquire information on its uses, properties, selling features, advantages over competitive products and possible future developments. In addition they had to be given details of such things as the selling seasons for the product, the value of the total market and the structure of the sales force which would handle it.

Mr. McVey, to conclude his lecture, discussed the relative advantages of press, cinema and television advertising. He showed how—contrary to expectation—the last mentioned could prove a really cheap form of communication as in one instance, which he cited, the advertising cost worked out at 6d. per 1,000 viewers, a figure which could not have been equalled by using an alternative advertising method.

Mr. D. M. Stewart, after a lengthy question period, thanked Mr. McVey for a really interesting and informative lecture.

T. B. H.

#### SECTION PROCEEDINGS

# Victorian Section

#### PHOSPHATED STEEL

On Monday 11 November, Mr. J. H. Geyer, of the United States, addressed a technical session of this Section.

Mr. Geyer explained how zinc phosphate coatings were deposited on steel surfaces when the chemical balance of the treating solution was upset at the metal liquid interface. The deposit of zinc phosphate adhered strongly to the steel surface because its crystal structure could align itself exactly with the crystal structure of the steel; this gave rise to an interchange of an electromagnetic force between the crystals and the surface and caused a pseudo-metallurgical bond. The zinc phosphate crystals might be pure rhomboids or in some circumstances they might be body centred or face centred crystals. Coatings in which the zinc phosphate crystals were pure rhomboids have a lower density than the others and the crystals showed a significant tendency to fracture under mechanical stress when hard paint films were applied over them. Introduction of iron or calcium into the coating gave body or face centred crystals; this increased the density of the crystals and increased the strength considerably. Iron for this type of modification came from the dissolved metal; calcium was introduced through the phosphating chemical.

All zinc phosphate coatings contained combined water and adsorbed free water. If the phosphate coating had not been applied under the correct conditions, it was possible to find a layer of acicular crystals on top of the rhombic crystals deposited originally. These acicular crystals lost their water of crystallisation readily; if such a coating was painted and then baked, the water of crystallisation was lost as steam which caused blow holes in the paint. These acicular crystals also caused poor adhesion as they were not bound strongly to the primary crystal deposit.

A properly deposited zinc phosphate coating consisted of an adherent layer of rhombic crystals, each abutting but never quite touching its neighbour. Paints laid down on such a coating penetrated the capillaries between crystals, giving rise to a mechanical bond of considerable strength. The coating would not corrode or decompose in corrosive atmospheres so that the possibility of under-film corrosion was greatly reduced.

Manganese phosphate was used for coating wearing surfaces such as piston rings. The manganese phosphate crystals sheared parallel to the metal surface and consequently it provided a smooth barrier between the wearing surfaces, so preventing galling and welding.

Iron phosphate was a common prepaint treatment and these coatings were noncrystalline. The coatings comprise mixtures of iron oxide and iron phosphate.

After question time, Mr. J. Young thanked the speaker on behalf of the meeting.

D. W. B.

# 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.)

PEROX CHEMICALS CO. LTD. announce that they are now manufacturing pigmented dispersions. This is a result of taking over the manufacture of *Estarex* range of pigmented dispersions from TRIANGLE DISPERSIONS (COLOURS) LTD. The production of *Estarex* will be carried out at Perox's Sheerness works.

As from 1 April 1964, P.R. CHEMICALS LTD. will terminate their agreement with VICTOR BLAGDEN & CO. LTD., who are acting as their sales agents. This move is caused by reorganisation within P.R. Chemicals.

POWELL & Co. announce the introduction of a drum rotator for mixing, blending, tumbling and cleaning. It is reported to revolve 40/50-gallon drums containing liquid materials up to 900 lb and dry materials up to 750 lb gross weight.

The South African subsidiaries of FEDERATED PAINTS LIMITED and of BLUNDELL-PERMOGLAZE are to merge in order to allow a wider coverage of the South African market.

BURTS & HARVEY LTD. have announced the closure of their works at Spring Hill, Southampton, Hants., and the transfer of the manufacturing activities previously carried out there to their main works at Belvedere, Kent.

O.C.C.A. DINNER DANCE-FRIDAY 10 APRIL Savoy Hotel, London, W.C.2

(See page 266)
### SIXTEENTH TECHNICAL EXHIBITION, 1964

The Exhibition will provide both a focus Wednesday 18 March : 10 a.m. to 6.30 p.m. for the technical display of advances in Thursday 19 March : materials, equipment and technology by the suppliers to the industries covered by the Oil and Colour Chemists' Association *i.e.* the paint, printing ink and allied industries, and a forum for direct discussion between the technical men of suppliers and consumers. It will take place at the Royal Horticultural Society's Old and New Halls Vincent Square. (entrance : London. S.W.1), and the hours of opening will be:

Monday 16 March : 3 p.m. to 6.30 p.m. Tuesday 17 March : 10 a.m. to 6.30 p.m. Exhibition.

10 a.m. to 6 p.m.

So heavy was the demand for space by the closing date for applications that the Exhibition Committee was forced reduce the allocation of space to some companies and to draw up a waiting list of late applicants. Plans of the layout of the stands in the two halls are given overleaf, together with a numerical list of exhibitors, six of which have not shown at previous OCCA Exhibitions, and a further 17 were not showing at last year's

AME PARK NEW HALL THE OLD HALL NCENT BUS ROUTES TORIA STN 

How to reach the Old and New Halls

The Exhibition Luncheon will be held at 12.45 p.m. on Monday 16 March at the Savoy Hotel London, W.C.2. The Guest of Honour, The Rt. Hon. Lord Drumalbyn, Minister of State, Board of Trade, will respond to the Address of Welcome delivered by the President, Dr. J. E. Arnold.

The opening ceremony will take place at the entrance to the Old Hall (Vincent Square) at 3 p.m., immediately prior to the admission of visitors.

Underground stations near to the halls are Victoria. St. James's Park and Westminster ; there are also frequent bus services to Victoria Street and Vauxhall Bridge Road, which are within easy walking distance of the Exhibition Halls. A sketch map is





LAYOUT OF OLD HALL

It is suggested that visitors to the Exhibition start at the Vincent Square entrance to the Old Hall, where stands 1-41 are situated, and then proceed *via* the side exit of the Old Hall across Elverton Street to the New Hall, where stands 42-95 are located.



LAYOUT OF NEW HALL

### March

### NUMERICAL LIST OF EXHIBITORS

#### Stand

264

- 1. Blagden, Victor, & Co. Ltd.
- 2. McKechnie Brothers Ltd.
- 3. Chemische Werke Hüls A.G.
- 4. Kingsley & Keith (Chemicals) Ltd.
- Winkworth Machinery Ltd. 5.
- 6. Carless, Capel & Leonard Ltd.
- 7. Bakelite Ltd.
- 8. Premier Colloid Mills Ltd.
- 9. Scott Bader & Co. Ltd.
- 10. Boehm, Fredk., Ltd.
- 11. Oil & Colour Chemists' Association 55. Resinous Chemicals Ltd. Information Bureau
- 12. Technical Education
- 13. Croxton & Garry Ltd.
- 14. Frenkel, Leon, Ltd.
- 15. Bush, Beach & Segner Bayley Ltd.
- 16. Ferranti Ltd.
- 17. Hardman & Holden Ltd.
- 18. Spelthorne Metals Ltd.
- 19. Evans Electroselenium Ltd.
- 20. Boake, A., Roberts & Co. Ltd.
- 21. Vicker-Armstrongs (Engineers) Ltd.
- 22. Paint Research Station
- Svenska Oljeslageri Aktiebolaget
- 24. Amoco Chemicals Corporation
- 25. BIP Chemicals Ltd.
- 26. Johns-Manville Co. Ltd.
- 27. Cray Valley Products Ltd.
- 28. Tar Residuals Ltd.
- 28. Dougherty, M. E., Ltd.
- 29. British Resin Products Ltd.
- 29A.Bibby, J., & Sons Ltd.
- 30. Universal Oil Co. Ltd.
- 30. Seaton, John L., & Co. Ltd.
- 30. Premier Oil & Cake Mills Ltd.
- 31. Plastanol Ltd.
- 32. Dunlop Chemical Products Division
- 33. Lennig Chemicals Ltd.
- 34. British Celanese Ltd.
- 35. Novadel Ltd.
- 36. Lancashire Tar Distillers Ltd.
- 37. Kronos Titanium Pigments Ltd.
- Mo och Domsjö Aktiebolag
- 39. Beck, Koller & Co. (England) Ltd.
- 40. Research Equipment (London) Ltd.
- 41. (British Red Cross Society)
- Scado-Archer-Daniels NV
- 43. Campbell, Rex, & Co., Ltd.
- 43. Chemical Supply Co. Ltd., The
- Oliefabriek 44. Nederlandse Castor " Necof " NV
- 45. Elliott, H. J., Ltd.

### Stand

- 46. Tin Research Institute
- 47. Torsion Balance Co. (Great Britain) Ltd., The
- 48. Neville Cindu Chemie NV
- 49. Boulton, William, Ltd.
- 50. Paint, Oil & Colour Journal
- 51. D. H. Industries Ltd.
- 52, 53. Mitchell, L. A., Group of Companies, The
- 54. Surface Coating Synthetics Ltd.
- 56. Union Carbide Ltd.
- 57. Allied Colloids Ltd.
- 58. Pascall Engineering Co. Ltd.
- 59. Styrene Co-Polymers Ltd.
- 60. Vinyl Products Ltd.
- 61. Geigy Co. Ltd., The
- 62. Distillers Co. Ltd., The
- 63. Burts & Harvey Ltd.
- 63A. Titanium Intermediates Ltd.
- 64. Dow Chemical Co. (UK) Ltd.
- 65. Torrance & Sons Ltd.
- 65. Holmes Bros. Paint Machinery Ltd.
- 66. Berk, F. W., & Co. Ltd.
- 67. Kunstharsfabriek Synthese NV
- 68. Sheen Instruments (Sales) Ltd.
- 69. British Oxygen Chemicals Ltd.
- 70. Wolf, Victor, Ltd.
- 71. Farbenfabriken Baver AG
- 72. SCC Colours Ltd.
- 72. Smith, J. W. & T. A., Ltd.
- 72. Cornbrook Chemical Co. Ltd.
- 72. Cromford Colour Company Ltd.
- 73. British Titan Products Co. Ltd.
- 74. Imperial Chemical Industries Ltd.
- 75. Steele & Cowlishaw Ltd.
- 76. British Oil & Cake Mills Ltd., The
- 77. Shell Chemical Co. Ltd.
- 78. Amalgamated Oxides (1939) Ltd.
- 79. Ciba Clayton Ltd.
- 80. Ciba (ARL) Ltd.

87. Paint Manufacture

- 81. Crosfield, Joseph, & Sons Ltd.
- 82. Price's (Bromborough) Ltd.
- 83. National Adhesives Ltd.
- 84. Marchant Brothers Ltd.
- 85. Silverson Machines Ltd.
- 86. Durham Raw Materials Ltd.

### Stand

- 88. Armour Hess Chemicals Ltd.
- 89. Esso Petroleum Co. Ltd.
- 90. Hercules Powder Co. Ltd.
- 91. Sturge, John & E., Ltd.
- 92. Barter Trading Corporation Ltd.

#### Continued from page 261]

will be available throughout the period of be present to talk to the school parties; the Exhibition and a full restaurant introductory lectures will be given in a service will be available from 12.30-2.30 p.m. on the second, third and fourth the Technical Education stand will be days.

The Association's Information Bureaux will be situated on Stand 11 in the Old Hall (Tel. VICtoria 5040) and on Stand 93 in valuable contribution to the advancement the New Hall (Tel. TATe Gallery 0320). These telephone numbers are available on the days of the Exhibition only, as are all the numbers included in the Exhibition Official Guide. Copies of the Official Guide have been circulated to all members of the Association, as well as being sent to There will also be representatives from chemists and technologists individually on the British Red Cross Society at Stand 41. the Continent of Europe and paint and printing ink manufacturing firms in the the Society of Dyers and Colourists the United Kingdom. obtain copies of the Official Guide without stand in the New Hall (stand 93) a display charge from the Association's offices, and organised by the Society. they will also be freely available at the Exhibition.

schools to send parties of senior students will be appearing in the May issue of the taking "A"-Level science to visit the Journal. Any inquiries concerning the Exhibition, and 31 schools in the Greater Exhibition should be addressed to the London area have arranged parties for General Secretary, R. H. Hamblin at the the mornings of the Exhibition. A special Association's offices, Wax Chandlers' Hall, stand has again been devoted to Technical Gresham Street, London, E.C.2.

### LATEST INFORMATION FROM EXHIBITORS

went to press.

### Stand 1-Victor Blagden & Co. Ltd.

in the Official Guide, this Company will qualities of Resin 2400 based enamels are be exhibiting Resin 2400 manufactured said to be similar to those based on by CARGILL INC. of the United States. conventional alkyds.

Stand

- 93. Oil & Colour Chemists' Association Information Bureau
- 94. Laporte Titanium Ltd.
- 95. Paint Technology & Associated Publications

Education, on which representatives from reproduced on page 261 showing the technical colleges in London, together with position of the halls. Buffet facilities representatives from industrial firms, will separate lecture hall. The theme of Analysis in the Paint and Printing Ink Industries."

> The annual Exhibitions have made a of scientific knowledge in the surface coating industries. Last year the Exhibition attracted well over 10,000 visitors, including a large number from 30 overseas countries. For the assistance of exhibitors and visitors, interpreters will be in attendance. To commemorate the 80th anniversary of Non-members may Association is pleased to incorporate in its

A full report on the Exhibition, together with extracts from the luncheon speeches Invitations have again been extended to and a review of the outstanding exhibits,

The following information was received It is claimed that this resin is suitable for from exhibitors after the Official Guide the production of interior gloss and semigloss enamels. It is a water soluble resin

and enamels based upon this are reported to dry in 6-8 hours and to approach their In addition to the products mentioned ultimate hardness in 48 hours. The work [Continued on page 266

### Ltd.

The Company will be showing a new product of the Trojan Powder Company, is also to be shown. It is claimed that this This product Di-Methylol Propionic Acid product combines the high activity of the is a tri-functional compound containing two primary hydroxyl groups. It is reported active dimethyl dithiocarbamate group. to offer a simple means of producing It is reported to be compatible with both water solubility in alkyds, polyesters, and oils suitable for use in both air drying and stoving finishes.

#### Stand 31—Plastanol Ltd.

Two new water-thinnable resins, one for use in primers that are to be applied by conventional dipping methods and one designed for primers that will be applied by electro-deposition will be shown.

Two new vinvl modified alkyd resins will also be shown. Details are as follows : *Plastvrol S-77X* is a styrene modified alkvd which is claimed to give very fast drying. spray applied coatings of good colour and mechanical properties, Plastyrol S-99X is also a styrene modified alkyd and is designed to meet the demand for quick drving spray finishes of high gloss where gloss is the governing factor.

### Stand 57-Allied Colloids Ltd.

A new magnetic pigment, Magnetic Pigment 345 BASF, for use in magnetic printing inks, carbon paper, etc., will be shown for the first time.

### Stand 66-F. W. Berk & Co. Ltd.

the following extra items. Afco Calibrated either water or a variety of low-cost Strainer Bags manufactured in the United organic solvents and solvent blends; and States by the AMERICAN FELT CO. They EHEC 75, likewise water-soluble and are designed to remove oversize particles soluble in organic solvents particularly from paint and other liquids. They are chlorinated hydrocarbons. EHEC 75 is made to exact specifications giving particle thus of particular interest for use in washsize cut-off at intervals between 5 and 100 off paint removers. Latest Natrosol applicamicrons. It is claimed that they are tions will also be featured.

### **ASSOCIATION DINNER-DANCE**

Members may like to be reminded that at the beginning of January, and return the Association Dinner-Dance will take them as soon as possible. The price of the place at the Savoy Hotel, London, W.C.2, ticket is 3 gns. each, and non-members on Friday, 10 April. Requests for tickets wishing to obtain forms should write so far received have been heavy, and immediately to the General Secretary of the members wishing to reserve places should Association at the address shown on the complete the forms which were circulated front cover.

Stand 4-Kingsley and Keith (Chemicals) almost free from clogging thus making long continuous runs possible.

> The new Berk fungicidal additive Phelam Phenyl Mercury group with the fungicidally water- and oil-based systems.

> Products of the DEXTER CHEMICAL CORPORATION marketed under the name of Strodex will also be shown. Strodex PK-90 when used in latex paint formulations is reported to take the place of a combination of several dispersing wetting and emulsifying agents. It is claimed to have exceptional wetting and dispersing properties together with improved washability, wet adhesion and storage stability.

### Stand 70-Victor Wolf Ltd.

A late development of this Company is a lubricant suitable for pvc and polythene sheets. Samples of sheets containing this lubricant will be shown on the stand and compared with sheets that do not contain this lubricant.

### Stand 90-Hercules Powder Company Ltd.

Owing to a printer's error a line was missed from this Company's Official Guide Editorial. The relevant paragraph should read :

Cellulose derivatives. Attention will be called to the notable solubility characteristics of two new products, Klucel, a F. W. BERK & Co. LTD. will be exhibiting non-ionic ether outstandingly soluble in

1964



THE PALACE HOTEL, TORQUAY, CENTRE FOR THE ASSOCIATION'S CONFERENCE, 1965

It is felt that members would like to have afternoon. These sessions, at which numinformation on the dates and venue of bers will be limited and admission will the next Association Conference. It will be by ticket only, will not neccessarily be take place at Torquay from 25 to 29 May related to the main theme of the 1965 : the delegates will be accommodated Conference. in various hotels in the town, with the Conference headquarters again at the Palace Hotel

informal discussion sessions on the Friday on the cover before 31 December 1964.

## Full details will be sent to members

early in 1965, but non-members wishing to receive registration forms should write to In addition to the normal Conference the General Secretary of the Association, programme, it is proposed to hold Mr. R. H. Hamblin, at the address shown

### Scottish Section

### ANNUAL DINNER-DANCE

The Annual Dinner-Dance of the Scottish Section was held in the Kintyre Suite, Central Hotel, Glasgow, on Friday 17 January 1964.

On arrival the guests were received by the Chairman, Mr. A. Fraser, Mrs. Fraser, the President of the Association, Dr. J. E. welcomed the top table guests and in

Arnold, and Mrs. Arnold. At the top table during the dinner, in addition to those above, were Mr. J. Smethurst (Chairman of Manchester Section), Mrs. Smethurst, Mr. J. G. N. Smith (Chairman of Newcastle Section) and Mrs. Smith.

Following the meal, Mr. Fraser officially



The Top Table at the Section's Dinner Dance showing from left to right, Mrs. Smith, Mr. J. Smethurst (Chairman, Manchester Section), Mrs. Arnold, Mr. A. S. Fraser (Chairman, Scottish Section), Mrs. Fraser, Dr. J. E. Arnold (President), Mrs. Smethurst, Mr. J. G. N. Smith (Chairman, Newcastle Section)

his remarks included Dr. H. A. Hampton, he said, were trying to emulate, and to the Immediate Past President, and his wife. recent formation of the Eastern Branch. He referred specifically to the fact that this was Dr. Arnold's first time in Scotland on a purely social occasion and expressed the hope that it would indeed prove an enjoyable visit. At this point Mr. Fraser then presented each to Dr. Arnold. Mr. Smethurst and Mr. Smith a souvenir of their visit to Scotland-a haggis (complete with Dr. Arnold faced up to his unflinchingly; Mr. Smethurst watched his suspiciously; Mr. Smith, it appeared, gave his a friendly nod.

In his speech, Dr. Arnold expressed pleasure at his being able to attend this Scottish function ; it was, he agreed, his first purely social visit to Scotland although he had come up to the north many times on business. In a few well chosen phrases work being done by the Scottish Section, success, its Student Group, which other Sections,

Mr. Fraser thanked Dr. Arnold for his kind remarks. He then went on to present officially to Mr. A. McGuire the Whittaker Golf Trophy. (To everyone's amusement Mr. McGuire not only agreed to speak but burst into a veritable flood of poetry.)

On behalf of the guests, Mr. Smethurst, "export documents"). in a short speech, congratulated Mr. Fraser and the Scottish Section Committee for their efforts in organising the function. He thanked him for his kind hospitality which, he said, was so much appreciated and enjoyed. To this Mr. Fraser replied, concluding his remarks by thanking his Social Sub-Committee, especially Mr. J. S. Hutcheson, for all their efforts in ensuring the success of the evening.

Dancing continued until 1 a.m. in a he thanked Mr. Fraser for the gift presented very gay atmosphere, which seemed to and also for the invitation, which he had indicate that the Scottish Section Dinnerbeen pleased to accept. He referred to the Dance was once more an outstanding

NEWS OF MEMBERS



Mr. R. Gill receiving a gift from Mr. C. R. Petrie (Chairman of International Paints Ltd.), to mark his retirement from the company. On Mr. Gill's right is Mr. C. R. Preston, Managing Director of the company

Mr. R. Gill, an Ordinary Member attached Gill held the position of Works Manager. to the Newcastle Section and a Past Chairman of that Section, has retired from International Paints Ltd. after 36 years' Member attached to the Newcastle Section, service. At the time of his retirement Mr. has been appointed Mr. Gill's successor.

Mr. F. N. Foster, an Associate Member Honours List for his work in connection attached to the London Section, has been with the RAFVR. We congratulate the appointed London Sales Manager of the Wing Commander on this honour, which L. A. Mitchell Group of Companies.

Wing Commander R. W. F. Samson, an Ordinary Member attached to the Scottish Mr. M. Hess, an Ordinary Member

Mr. H. Nicholson, also an Ordinary

is in addition to the DFC and Bar he obtained during the Second World War.

Section, and Managing Director of Ault attached to the London Section, has and Wiborg (Scotland) Ltd., has been retired from Mander Bros. Ltd. after awarded the O.B.E. in the New Year's nearly 25 years' service in managerial Mr. R. Kitchen, an Ordinary Member attached to the West Riding Section, won first prize worth £50 in a recent competition organised by Paint Technology with an essay entitled "A Method of Solution for some Problems Encountered in the Formulation of Emulsion or Latex-based Surface Coatings for Application by a Curtain Coating Machine."

We congratulate Mr. Kitchen on this achievement.

### EXECUTIVE SECRETARY OF THE AMERICAN FEDERATION DIES

Members will be distressed to learn of the death, on 31 January, of Mr. C. Homer Flynn, Executive Secretary of the Federation of Societies for Paint Technology and one of the most respected and wellknown men in the paint industry. Mr. Flynn, who died in the Jefferson Hospital, Philadelphia, was 64 years of age and leaves a widow.

Members who had the opportunity of meeting Mr. Flynn will appreciate the loss which the Federation, and indeed the paint industry as a whole in the USA, has suffered by his passing. This Association was always encouraged by Mr. Flynn's willingness to co-operate in matters of common interest and benefit to our two organisations.

### VII FATIPEC CONGRESS

The FATIPEC Congress will be held on be an evaluation of the methods in use for 25-29 May 1964, at Vichy. The theme of the determination of the size of particles the Congress will be "Various interactions too small to be measured by sieve.

(Vice-President) is presenting a lecture at one of the Plenary Sessions.

Members requiring further information should contact the organisers at the following address : l'Association Francaise des Techniciens des Peintures et Vernis, Post Box No. 5, Puteaux (Seine), France.

### PROGRESS IN THE CHEMISTRY AND TECHNOLOGY OF PIGMENTS

The Department of Colour Chemistry and Dyeing of the University of Leeds is to hold a three-day residential course on " Progress in the Chemistry and Technology of Pigments." It is intended as a postgraduate course for those interested in pigments both as consumers and producers, the theoretical aspects of pigments and the practical application of these principles will be covered.

Further information and prospectus can be obtained on application to Dr. D. Patterson, Department of Colour Chemistry and Dyeing, University of Leeds. Leeds 2.

### GRANT TO BRADFORD INSTITUTE OF TECHNOLOGY

grants Among totalling over £8,000 received by the Bradford Institute of Technology, from the Department of Scientific and Industrial Research was one for £3,600 for investigation into particle size analysis. One aspect of the work will

### **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**

ACTON, FRANCIS JOHN, 119 Heol Lewis, Rhiwbina. Cardiff. (Bristol) BUTLER, PETER, B.SC., 47 Bannard Road, Maidenhead, Berks. (London) COUGHLAN, THOMAS NOEL, 24 Iona Green, Mayfield, Cork, Ireland. (Bristol) LEMMON, PETER JAMES, Bayer Dyestuffs Limited, 46 High Street, Burnham, Bucks.

(London)

### 1964

LONG, FRANCIS JOHN, M.A., D.PHIL., B.SC. (OXON), M.S. (ENG.), ICI (Paints) Ltd., Wexham (London) Road, Slough, Bucks. MITCHELL, SEWARD JOHN, Blundell Spence & Co. Ltd., Argyll Avenue, Trading Estate, (London) Slough, Bucks. RANE, SHRIDHAR K., Hardcastle & Waud Mnfg. Co., Netavali Baug, Kalyan, Bombay, (Overseas) India. RECKLESS, FRANK NORMAN, A.R.I.C., M.C.I.C., 36 Church Street, Apt. 507, Weston, (Overseas) Ontario, Canada. RUBENS, BERNARD LOUIS, 6 Rowlands, 2 Powell Road, Rose Bay, New South Wales. (New South Wales) Australia. SHARP, PETER FRANK, B.SC., 33 South Road, Sully, Penarth, Glam. (Bristol) SOUSTER, PHILIP ANTHONY LESLIE, B.A., 12 Lime Close, Carshalton, Surrey. (London) WELLS, RONALD SIDNEY, Church Cottage, Cog Road, Scully, Penarth, Glam. (Bristol) WOOD, DONALD MILNES, B.SC., 13 Villa Road, Bingley, Yorks. (West Riding)

### Associate Members

JORDAN, PETER VINCENT, Bayer Dyestuffs Ltd., 46 High Street, Burnham, Bucks. (London)

SILSBY, LEONARD FRANCIS, 27 Covert Road, Northchurch, Berkhamsted, Herts.

(London)

### **Forthcoming Events**

(Note: Details are given of meetings in the United Kingdom up to the 15th of the month following publication, and in South Africa and the Commonwealth up to the 15th of the second month after publication.)

### Monday 2 March

Hull Section. "Recent Advances in Polyurethanes," by R. Kershaw, at Royal Station Hotel, at 7.15 p.m.

#### **Thursday 5 March**

Newcastle Section. " The Photochemistry of Paint Film Degradation," by Dr. Tuesday 10 March G. H. J. Neville, at Royal Turks Head Hotel, Grey Street, Newcastle upon Tyne, at 6.30 p.m.

### Friday 6 March

Newcastle Section-Junior Group. Thursday 12 March "Printing Inks," by F. J. Morpeth, at Rutherford College of Technology, Northumberland Road, Newcastle upon Tyne, at 3 p.m.

Society of Dyers and Colourists. "Defective Colour Vision-Its Nature and Diagnosis," by K. McLaren, at Royal Society, Burlington House. London, W.1, at 6.15 p.m. (Members of the Association have been invited to attend this lecture.)

#### Monday 9 March

Bristol Section. Annual Dance at Ashton Court Country Club.

London Section—Southern Branch. "Variations on Urethane Oils," by A. C. Jolly, at Polygon Hotel, Southampton, at 7.30 p.m.

West Riding Section. "Water Thinnable Alkyd Media," by R. A. Brett (Paint Research Station), at Great Northern Hotel, Wellington Street, Leeds, at 7.30 p.m.

Scottish Section. " Recent Developments in Paint and Printing Ink Media," by G. H. Hutchinson, at More's Hotel, Glasgow, at 7.30 p.m.

### Friday 13 March

Manchester Section. Discussion Evening on new apparatus and experimental techniques presented by Association Members at the Strand Hotel, Liverpool, at 6.30 p.m.

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#### SECTION PROCEEDINGS

### Saturday 14 March

Scottish Section-Student Group. Annual General Meeting at 10 a.m. Followed by Tutorial at 10.30 a.m. "Alkyd Resins," by M. Young (Junior).

"Paint Analysis," by J. Bowden (Intermediate).

"Recent Trends in Paint Technology," by A. T. S. Rudram (Senior).

### Monday 16 March

Sixteenth Technical Exhibition at the Royal Horticultural Halls, S.W.1, at 3 p.m., preceded by the Exhibition Luncheon at the Savoy Hotel, W.C.2, at 12.15 p.m. for 12.45 p.m.

### Tuesday 17 March to Thursday 19 March

Sixteenth Technical Exhibition at the Royal Horticultural Halls, London, S.W.1. 10 a.m. to 6.30 p.m. (Thursday 10 a.m. to 6 p.m.).

#### Friday 20 March

Bristol Section. "Solventless Coatings," by A. McIntosh, at Royal Hotel, College Green, Bristol, at 7.15 p.m.

Bristol Section-Irish Branch. Annual General Meeting at 7.30 p.m. followed by a lecture, "Material Management," by C. Hancock.

Midlands Section. Joint Meeting with the Thursday 9 April Plastics Institute at The James Watt Institute, Gt. Charles Street, Birmingham, 3, at 7 p.m.

### **Tuesday 24 March**

London Section. "Cross Links Between Plastics, Paint and Textile Polymers," by Dr. L. Valentine (Paint Research Station). Joint Meeting with Plastics and Polymer Group, SCI, at 14 Belgrave Square, London, S.W.1, at 6.30 p.m.

### Wednesday 25 March

Scottish Section-Eastern Branch, Annual General Meeting at North British Hotel, Princes Street, Edinburgh, followed by a lecture, "Pigment Dispersion," by Dr. S. H. Bell (Paint Research Station), at 7 p.m.

### Friday 3 April

Newcastle Section. Ladies Night at the Royal Hotel, Hexham.

Newcastle Section—Junior Group. "Durability Testing," at Rutherford College of Technology, Northumberland Road, Newcastle upon Tyne, at 3 p.m. Scottish Section. Annual General Meeting at 6 p.m. at St. Enochs Hotel, Glasgow. Smoking Concert at 7.30 p.m. at Eglinton Arms, Eaglesham.

### Monday 6 April

Midlands Section—Trent Valley Branch. Annual General Meeting, venue to be announced.

### **Tuesday 7 April**

London Section—Thames Valley Branch. Annual General Meeting to be held at the White Hart Hotel, Beaconsfield, Bucks, at 7 p.m. followed by films at 7.45 p.m.

### Wednesday 8 April

Scottish Section—Eastern Branch. **Pigments**—Relation " Phthalocyanine Between Physical Form and Performance," by Dr. F. M. Smith and Dr. J. D. Easton, at North British Hotel, Princes Street, Edinburgh, at 7.30 p.m.

Newcastle Section. Annual General Meeting, venue to be announced.

### Friday 10 April

OCCA Dinner Dance at the Savoy Hotel, London, W.C.2.

#### Monday 13 April

London Section—Southern Branch. 4th Annual General Meeting at Queens Hotel, Portsmouth.

#### **Tuesday 14 April**

West Riding Section. Annual General Meeting, venue to be announced.

#### Wednesday 15 April

West Riding Section. Visit to the Metal Box Co. Works.

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### **OIL AND COLOUR CHEMISTS' ASSOCIATION**







### SIXTEENTH TECHNICAL EXHIBITION



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