JOURNAL
OF THE
OIL AND COLOUR CHEMISTS' ASSOCIATION

Vol. 47 No. 7 July 1964

TRANSACTIONS AND COMMUNICATIONS

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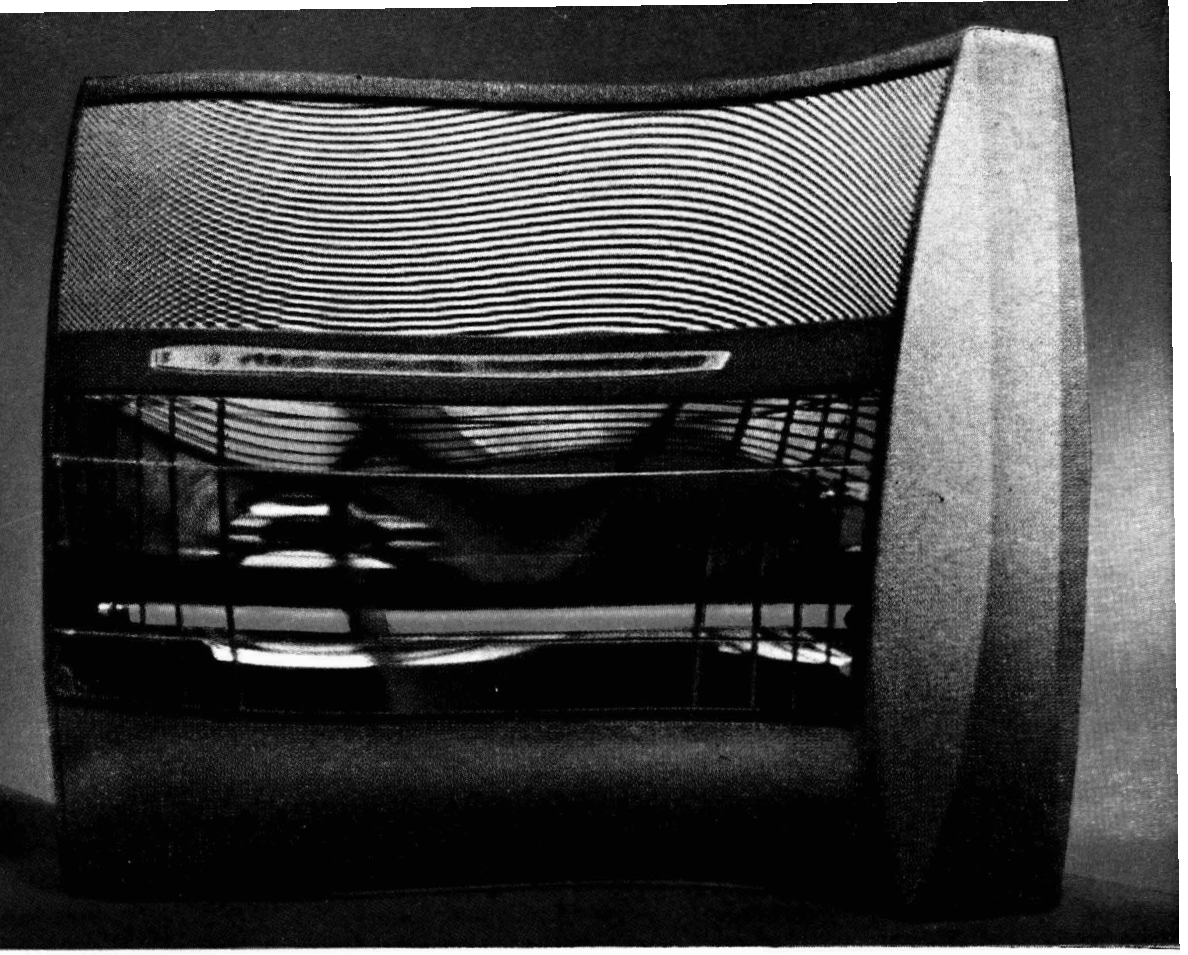

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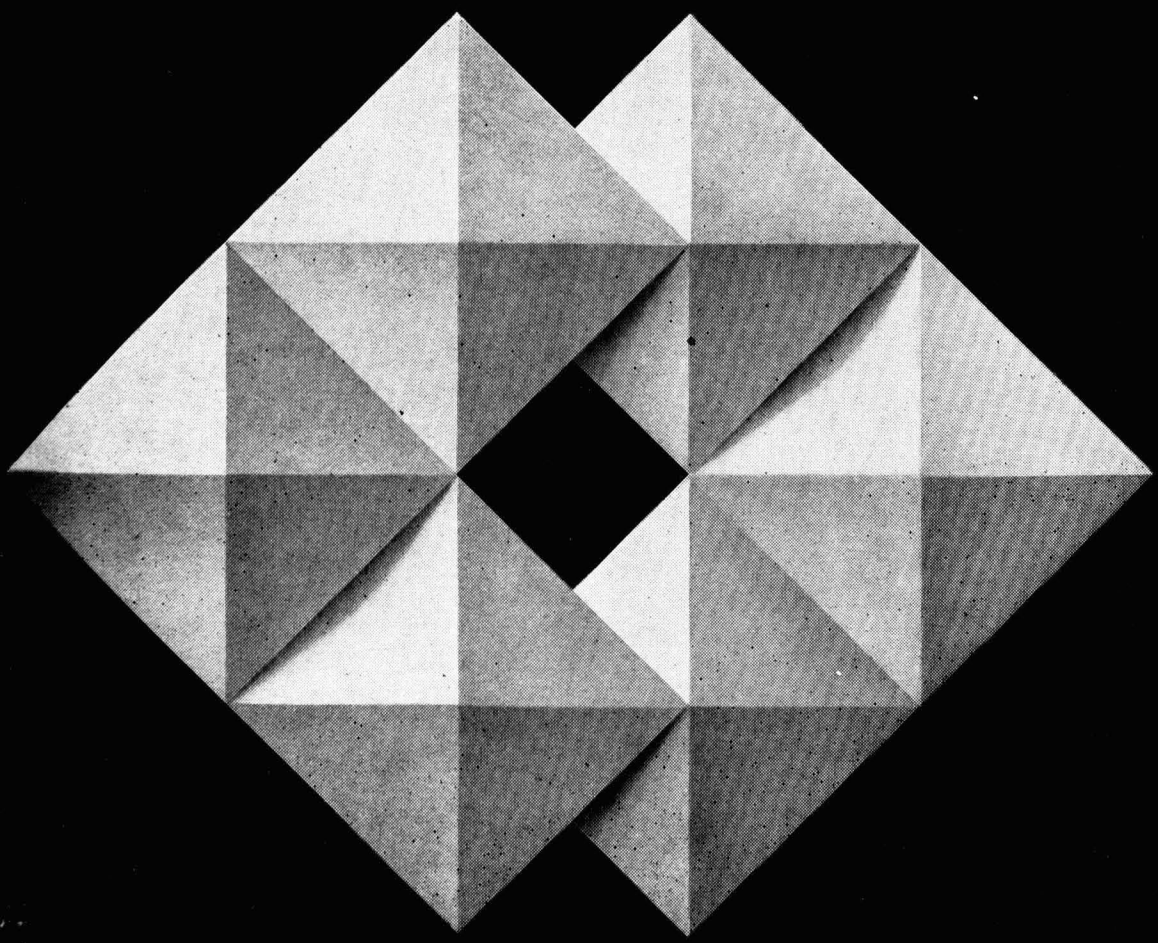

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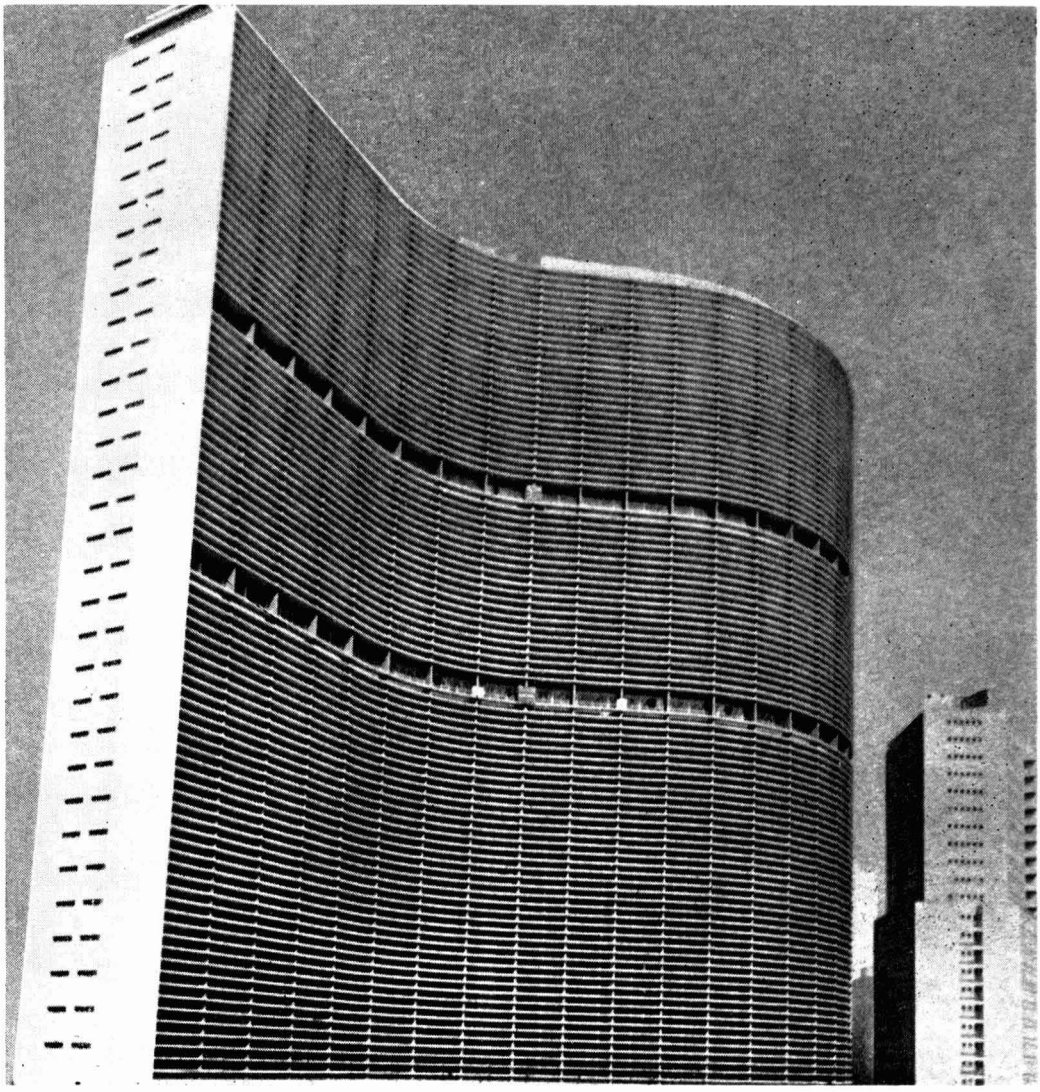

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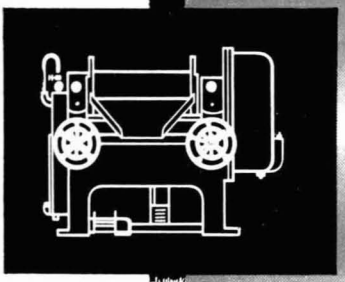

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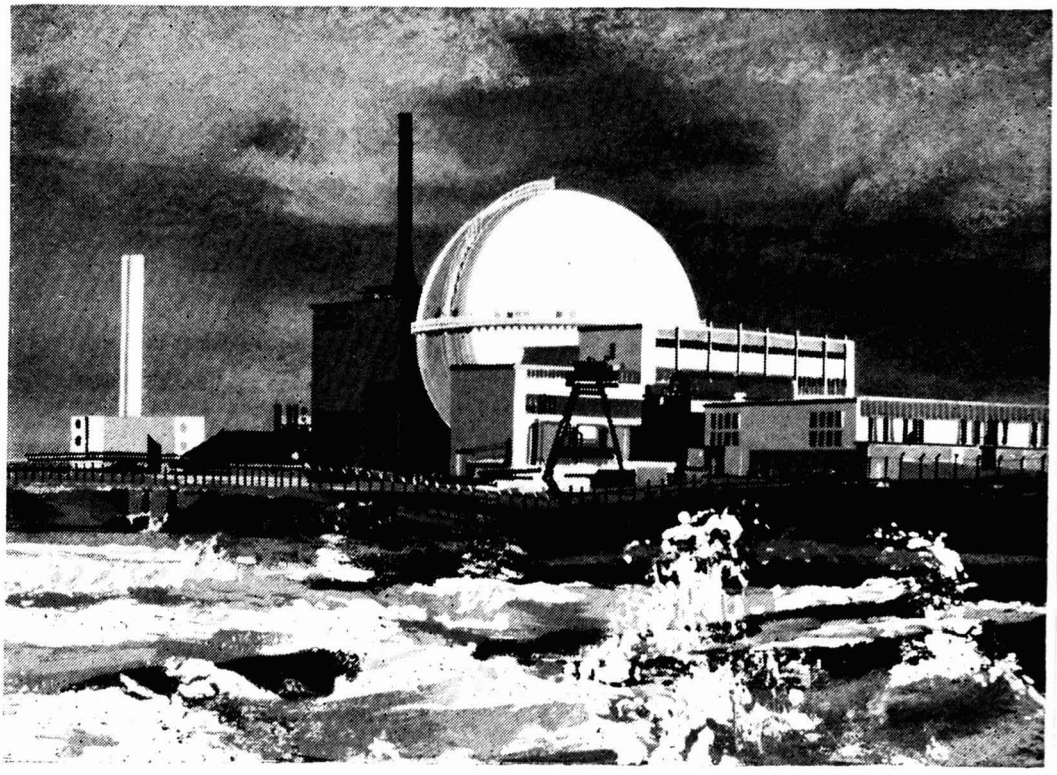

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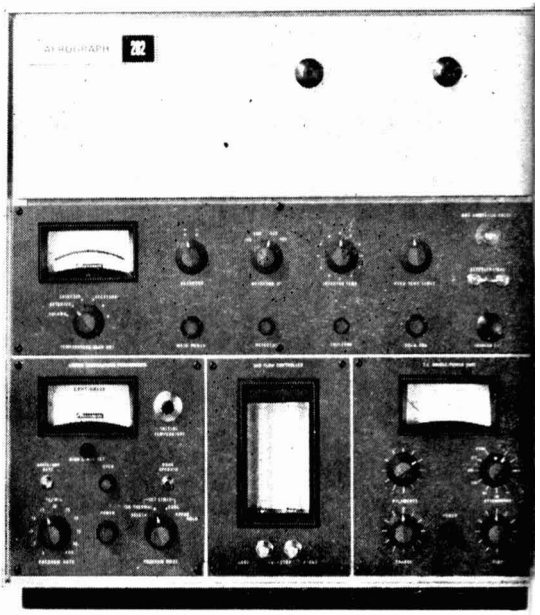

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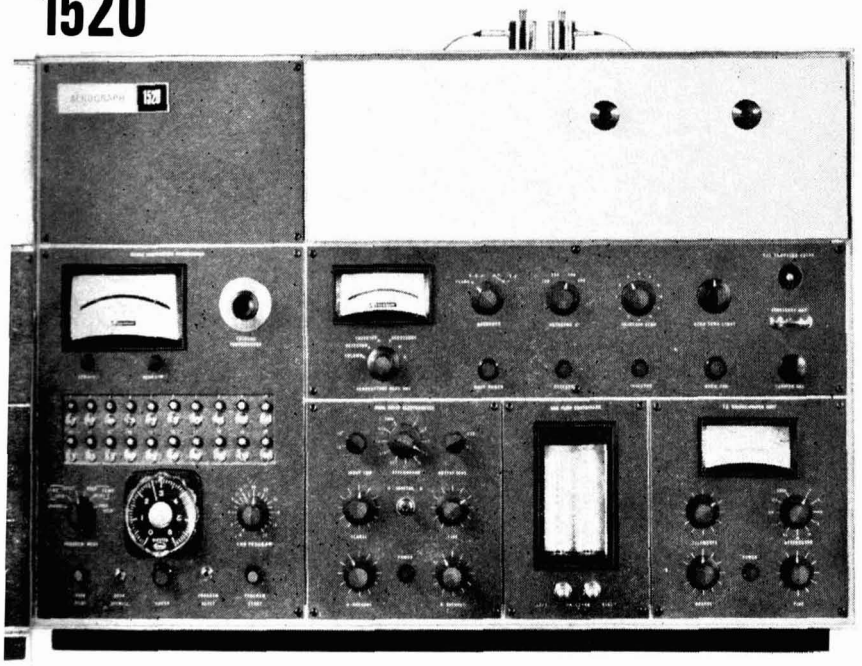

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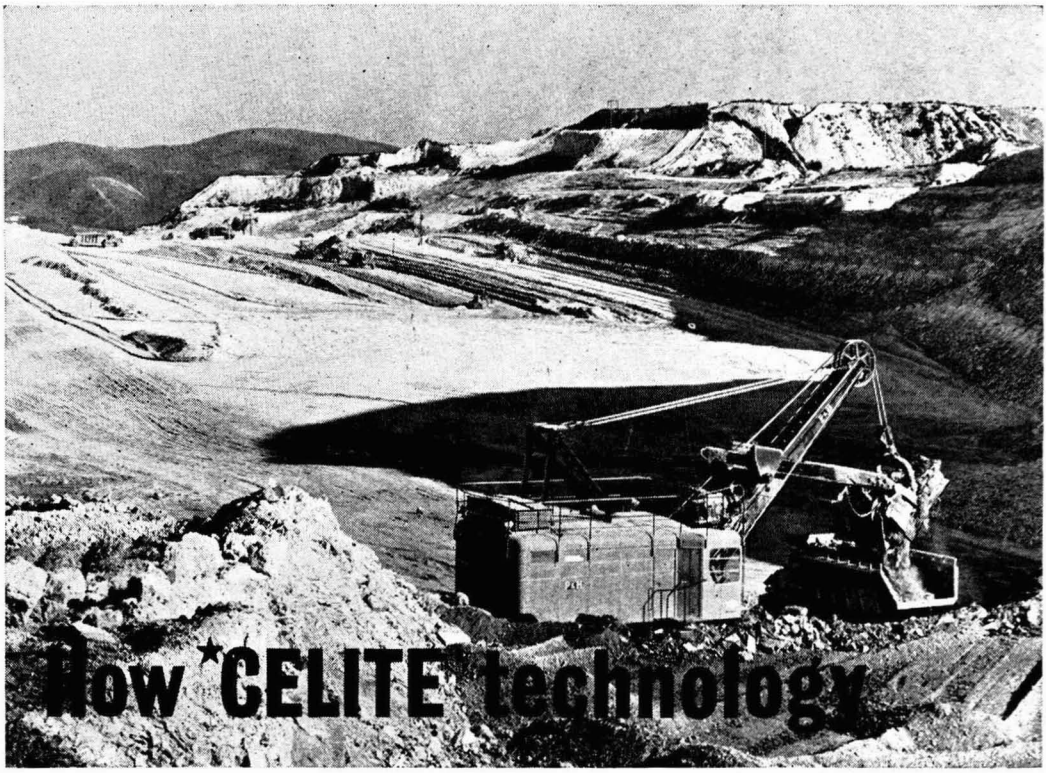

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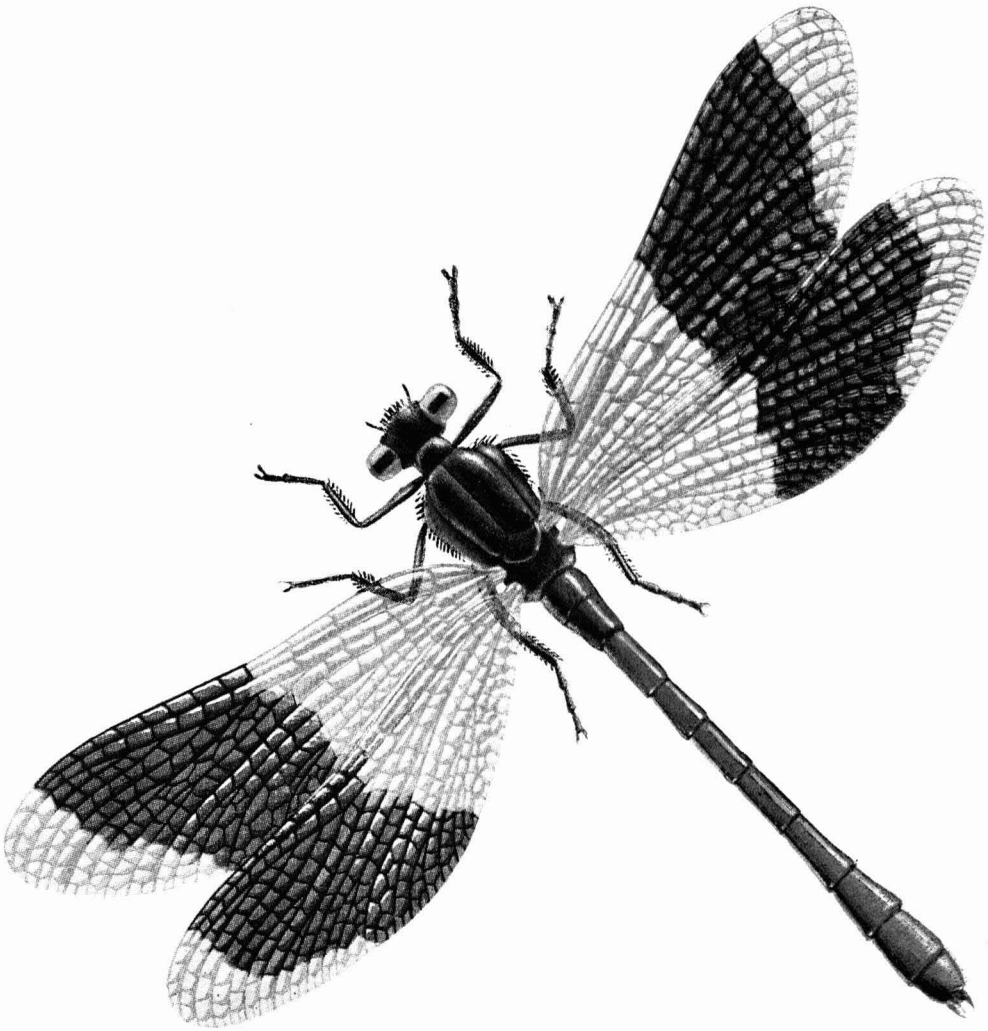

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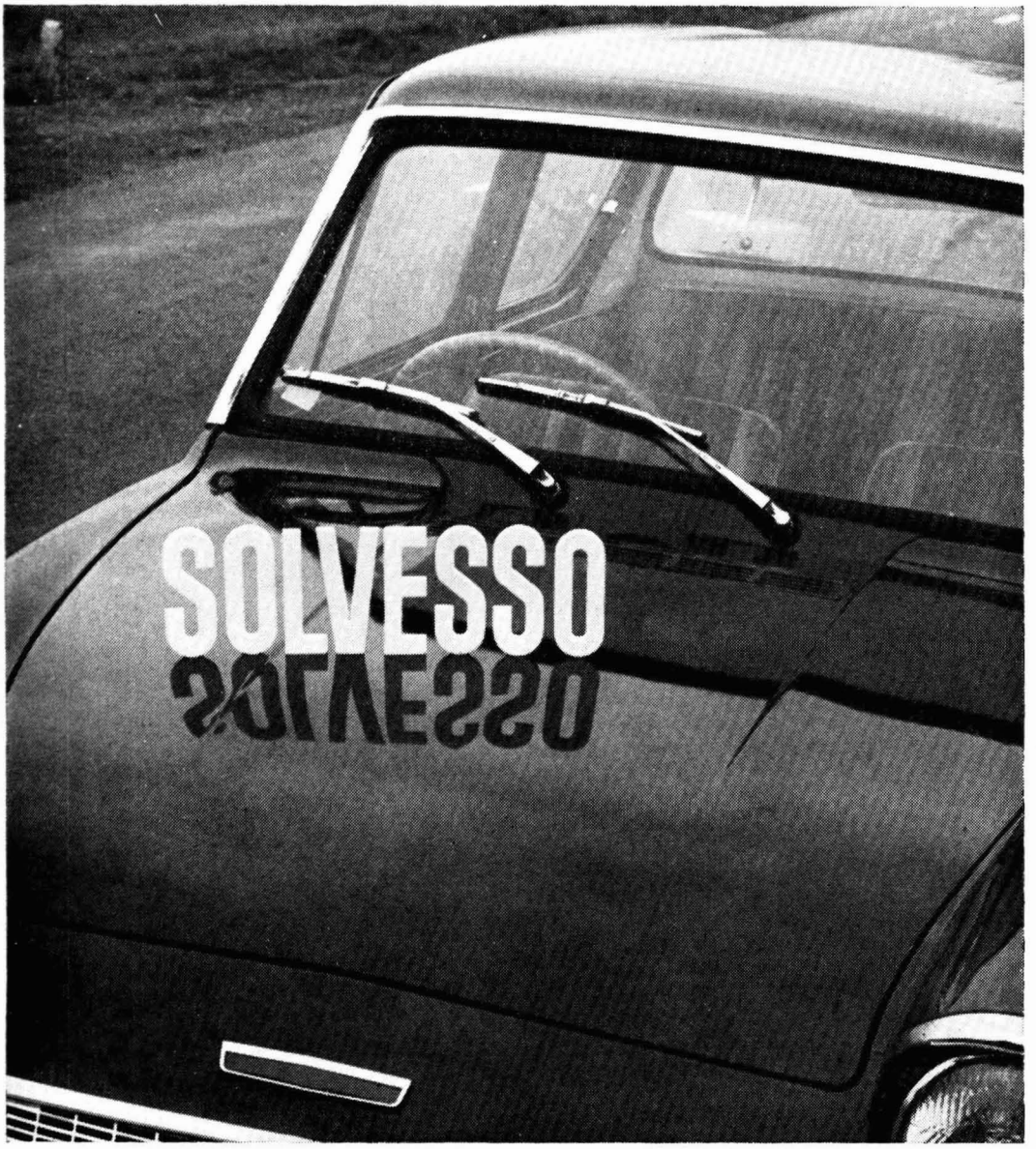

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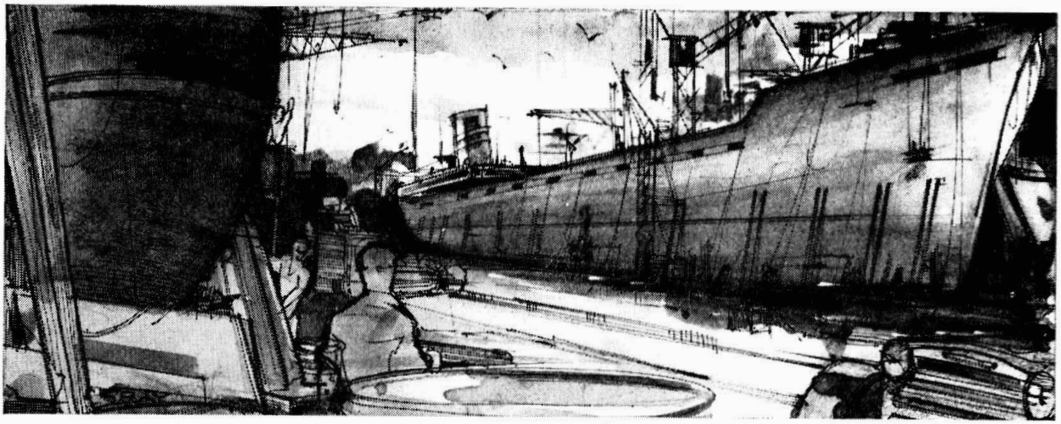

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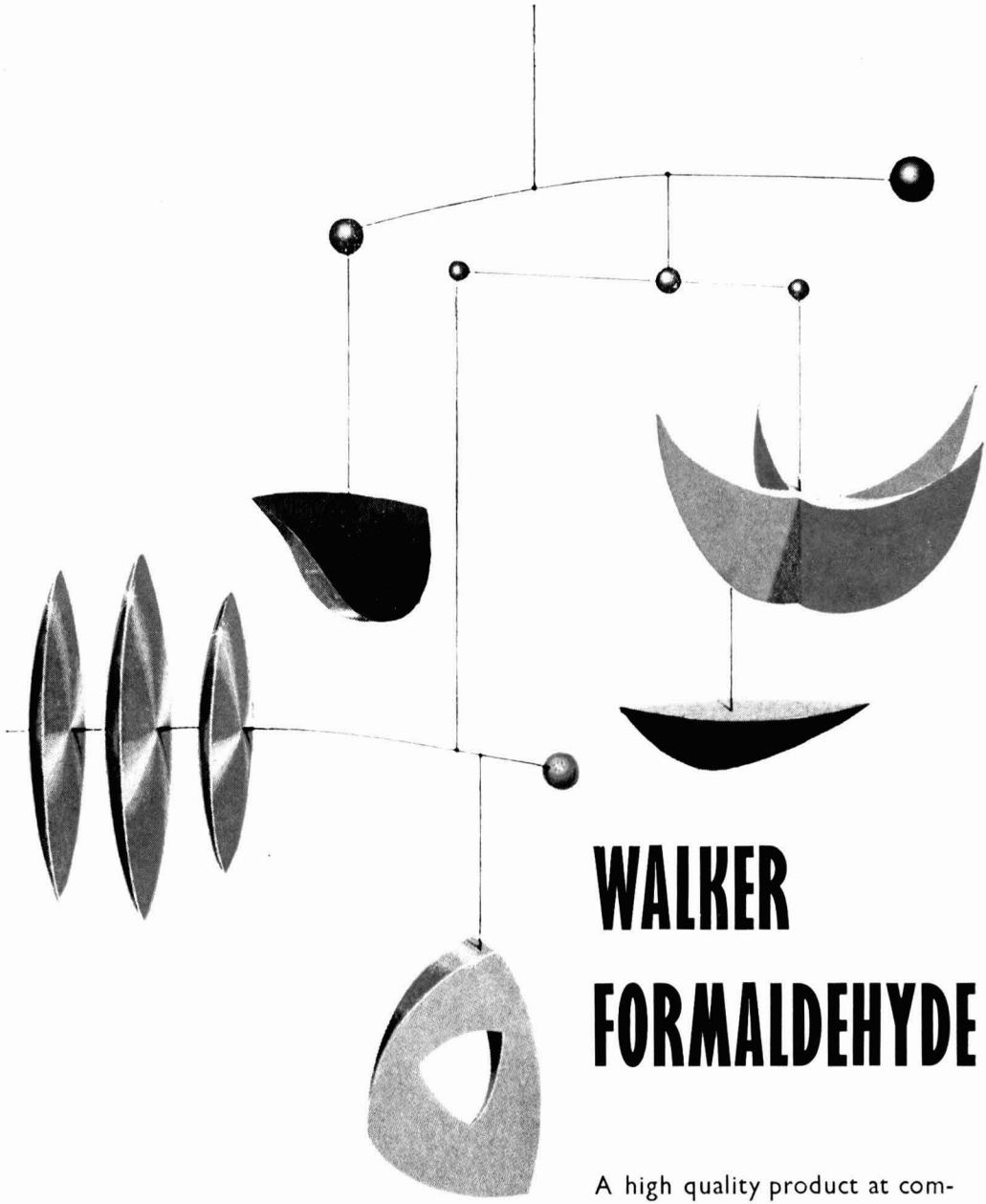

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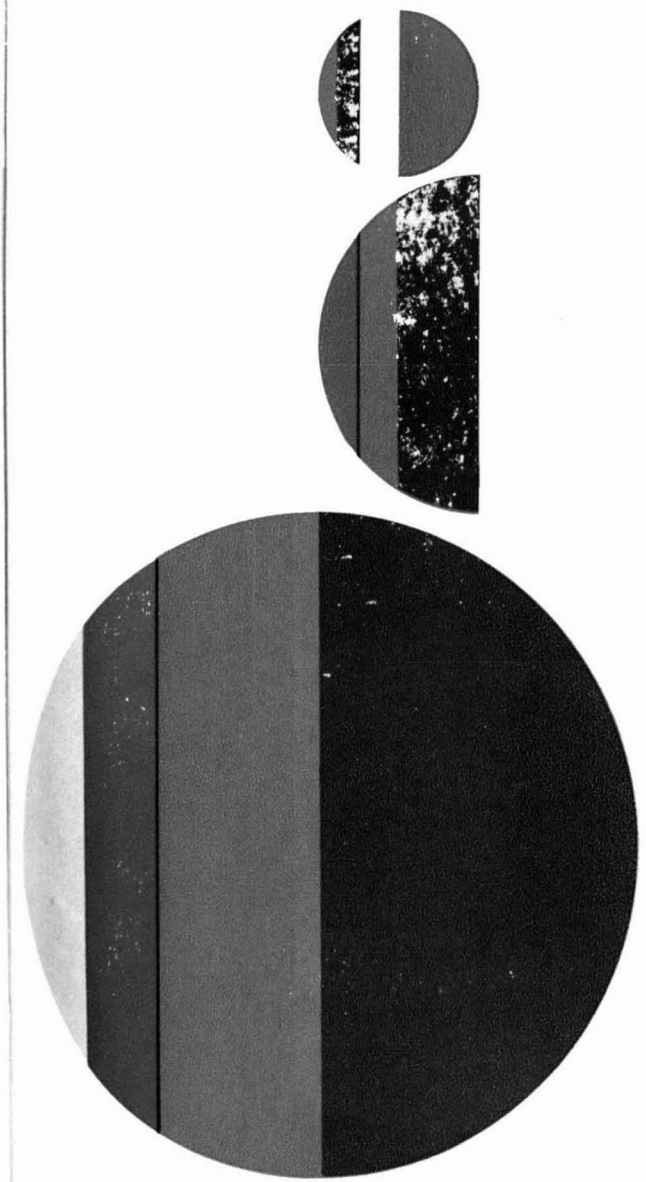

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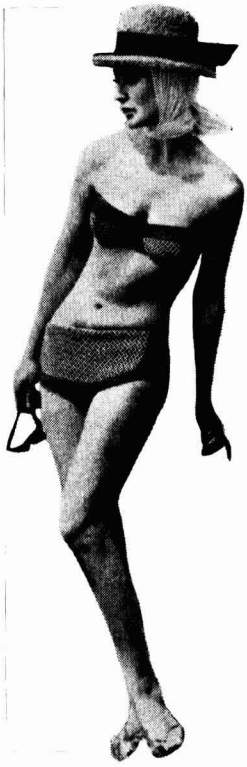

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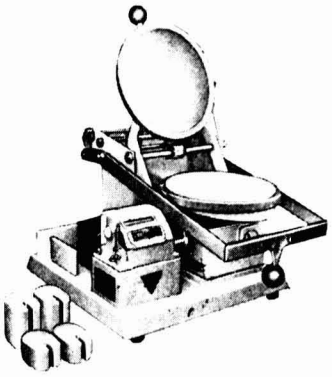

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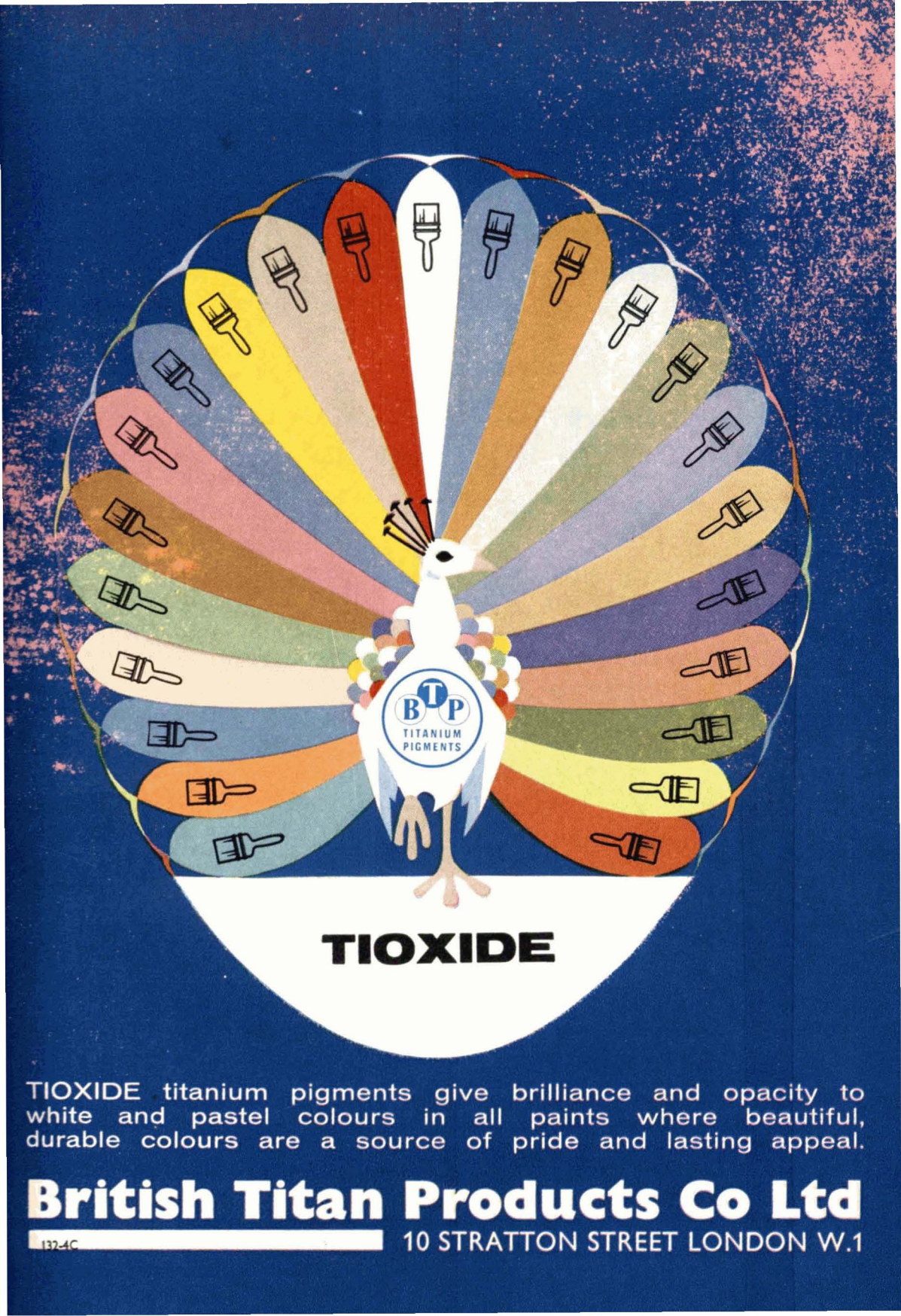

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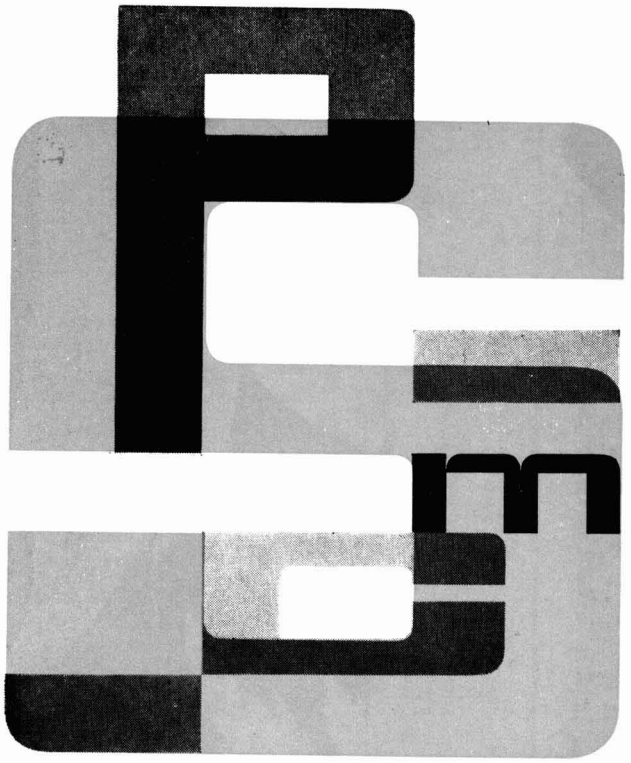

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Vol. 47 No. 7 July 1964

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TRANSACTIONS AND COMMUNICATIONS

Versatility of Chromatographic Techniques in Their Application to Paint Research*

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Summary

This paper summarises and compares chromatographic techniques and describes their applications to problems in paint research. Details are given of the methods used at the Paint Research Station and the results obtained in the analysis of solvent systems in lacquers, the characterisation of commercial turpentines and dipentenes, solvent retention of lacquer films, the fatty acid composition of drying oils, the separation of minor constituents of linseed oil, the analysis of glycerolysis products, the examination of volatiles of natural oils, and the pyrolysis of polymers.

INTRODUCTION

The subject of this paper is the versatility of chromatographic techniques in their application to paint research. It is impossible to do full justice to the techniques which revolutionised the understanding of natural products and played such an important role in biochemical and medical sciences, but their usefulness in paint research is not perhaps so obvious.

The paint research chemist is mostly concerned with improvement of the performance of paint films. This implies correlation of the properties of the paint film with the composition of the original paint. It is a formidable task considering that the paint formulation includes mixtures of various inorganic and organic pigments, polymeric or polymerisable media, plasticisers, catalysts, solvents, etc.—and that the dried, cured or weathered paint films are far removed in their chemical structure from the composition of the original paint ; it is surprising that any correlations can ever be made. In the large array of physical and chemical methods used by the team of workers trying to solve these problems, chromatographic techniques also have something to offer.

*Presented before London Section 20 February 1963 and Manchester Section 8 November 1963.

แผนกห้องสมุด กรมวิทยาศาสตร์

Chromatography is essentially an efficient method of separating mixtures of soluble or volatile compounds, so its uses in a way are restricted. Some examples will be given later, however, of the use of chromatography even in the study of properties and structure of polymeric materials.

But first consider how chromatographic techniques work, what types of chromatographic systems exist and how they compare.

Chromatographic System

Separation in all chromatographic methods is based on unequal distribution of the components of a mixture between two phases. The choice of the two competing phases is of primary importance to the separation. Distribution is influenced by the weak secondary forces acting between the molecules of the solute and the medium. These forces depend on the presence of polar and polarisable groups, shapes and sizes of molecules of both the solute and the medium. In general, therefore, solutes differing in chemical structure distribute themselves unequally between the competing phases which differ in polarity. This effect is usually very small in a static experiment when only one equilibration takes place. It can be magnified, however, by performing a number of successive equilibrations.

In chromatography the continuous repetition of a single equilibration proceeds automatically by letting one of the competing phases move in one direction through the other phase. Imagine a narrow glass tube filled with an adsorbent powder and a solvent percolating continuously through it. This is our chromatographic system. The mixture to be separated is introduced as a small batch at the top of the column without interrupting the flow of the solvent. Various molecules present in the mixture distribute themselves between the stationary and the mobile phase and only those which are in the mobile phase move along the system to the new sites of the stationary phase where new distributions occur. At the same time pure mobile phase reaches the occupied zone of the stationary phase and another distribution takes place. In this way the components of the mixture travel along the system, where the more they are attracted by the stationary phase the longer they are retained. Finally, discrete zones of separated components move along the system and can be detected either on the column, if they are visible or made visible, or after leaving the chromatographic system in different intervals of time. Fig. 1 illustrates the separation of two components of different distribution coefficients.

The principal factor of successful separation is the efficiency of the single equilibration step ; the number of repetitions can only magnify it. The efficiency of the single equilibration depends primarily on the choice of a suitable pair of phases. A rational choice is guided by an understanding of the nature of the interactions between the molecules. Unfortunately only rough correlations between the structure of molecules and the secondary forces of attraction are known and in practice the two-phase systems used are far from perfect. But even if the two-phase system is not the best possible, a successful separation can be achieved by increasing the number of equilibrations. This can be done by increasing the length of the system or by decreasing the fraction of the path needed for a single equilibration (the height equivalent of the theoretical plate).

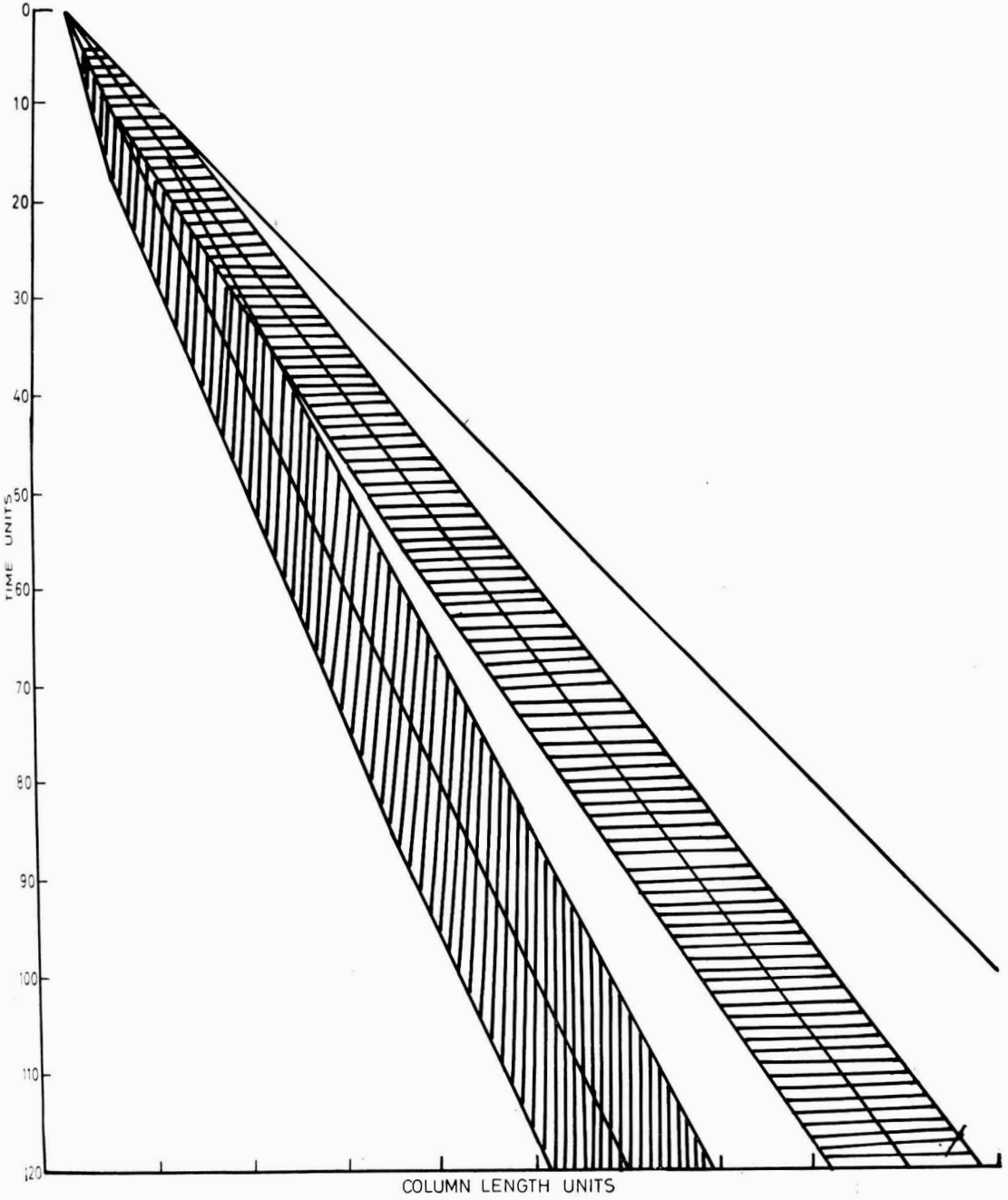

FIG. 1. SEPARATION OF TWO COMPONENTS OF DIFFERENT DISTRIBUTION COEFFICIENTS

Types of Chromatographic Systems

The chromatographic systems met in practice can be roughly divided into : (*i*) packed column chromatography in which the competing phases can be

solid/liquid, liquid/liquid, solid/gas, liquid/gas, (*ii*) capillary column chromatography—liquid/gas ; (*iii*) open column chromatography—paper and thin layer chromatography.

Each of these systems has a number of variables such as the type of both stationary and mobile phase, length of the path, temperature, rate of flow, etc.

Packed Column Chromatography

The oldest chromatographic system is a packed column with a solid/liquid pair of phases. One difficulty encountered in using this system is the poor reproducibility of the results due to the changes in the properties of solid adsorbent powders from batch to batch. Another is that as the solid adsorbent is usually irreversibly changed by the passage of the liquid phase, fresh columns have to be prepared for each experiment.

Packed column chromatography with a liquid/liquid pair of phases is realised by impregnation of the inert powder with the liquid stationary phase. Both phases have to be equilibrated with each other. Changes of temperature during the separation may affect greatly the results.

Both these systems have the advantage that relatively large batches of mixtures can be separated in one experiment. In both systems the composition of the mobile phase can be changed during the experiment to improve the separations. Automatic fraction collectors, by dividing the eluates into small equal volumes, facilitate the detection of the separated zones.

Packed column systems with a liquid/gas pair of competing phases (*gas-liquid chromatography*) have achieved great popularity in recent times. Distribution between the liquid and gaseous phases is determined by the solubility/volatility ratios and only volatile compounds can be separated. The temperature of the system, however, can be maintained at any desired level limited only by the stability of the stationary phases so that the separations of very high boiling compounds can be carried out successfully. This method is capable of great precision and reproducibility when the temperature, pressure and flow of gas are strictly controlled.

Mass transfer between the thin layer of the liquid stationary phase and gas is much quicker than between liquid and liquid so that the system is capable of a large number of equilibrations in a comparatively short time. Columns can be used repeatedly and detection is automatic and very sensitive. Moreover the result of the separation is automatically registered on a chart. The advent of gas chromatography opened new possibilities of quick and reliable analyses of complicated natural mixtures. Separations based on solubility/volatility ratios are much more efficient than those obtained by fractional distillation when only volatility differences are exploited. Quantitative determination of the composition of the mixture can be made using the recorded chromatograms and identification of the components is facilitated by the reproducibility of retention times.

The limitations of the method are that mixtures to be separated have to be volatile at the temperature at which the separation is carried out and although it is possible to work at high temperatures the stability of the stationary phase is the limiting factor. The choice of mobile phases is limited to a few inert gases and this is restricted even more by the type of detectors used. The method

is at its best with very small samples. These limitations, however, apply only to the present stage of the development of this elegant technique. There is perhaps a danger of rash identifications of the separated compounds by their retention times only, especially if only one stationary phase is used for separation.

Capillary Column Chromatography

This forms a branch of gas chromatography. Glass, metal or nylon capillaries are used coated inside with a thin layer of a liquid stationary phase and an inert gas flows through the open space in the middle of the capillary. This system can work only with extremely small samples and requires high sensitivity detectors. Equilibrations proceed very quickly and the length of path can reach hundreds of metres thus providing the opportunity for very subtle separations. On the other hand short lengths of capillary columns can be used to provide separations in a matter of seconds, the chromatogram being displayed on the memory screen of an oscilloscope.

The Open Column Systems

These consist of thin sheets of a stationary phase which is porous enough to allow the liquid mobile phase to move across by capillary action or by gravity, the whole system being enclosed in an air-tight container. This system is represented by two techniques : paper chromatography and thin layer chromatography.

Paper chromatography is a well established technique of great versatility. The stationary phase is usually cellulose with a layer of adsorbed water but in recent years a large number of modified and impregnated papers have come into use, so that the stationary phase can range from a nonpolar hydrocarbon oil to an ion exchanger. An unlimited number of liquid mobile phases can be applied. Several samples can be separated simultaneously on one sheet, thus making it possible to compare the unknown mixture with the mixture of standard compounds, etc. Separation can be carried out with one solvent in one direction and continued at right angles with another solvent. (*Two-dimensional paper chromatography.*) The movement of the mobile phase can be stopped at any time by removing the sheet and evaporating the solvent. Thus the separated zones are immobilised and can be detected by spraying with an appropriate reagent.

The limitations of the method are, the length of the path of the mobile phase is restricted, the movement of the mobile phase is slow, so that one experiment may last up to 24 hours ; the reproducibility of retention factors is not very good due to the difficulties of controlling humidity, temperature, etc. ; only non-volatile compounds can be satisfactorily separated and detected, so that volatile mixtures have to be converted to some non-volatile derivatives ; quantitative estimation is difficult.

In thin layer chromatography (TLC) a layer of adsorbent powder is made to adhere to a glass plate. Adhesion may be increased by addition of a small quantity of Plaster of Paris or starch to the aqueous slurry of the powder before spreading it on the plate. The adsorbent layer may be reactivated by heating to the required temperature in an oven. The same adsorbents as used in the packed columns can be used. A layer of an inert powder can be impregnated with any stationary phase. The advantage of this system over column

chromatography is that separation is more precise and reproducible, takes a short time and is done on a microscale. The separated compounds can be visualised *in situ* by spraying with similar reagents to those used in paper chromatography. TLC can be used to monitor large scale column separations done on the same stationary phase, in order to find the best solvent system and to check the composition of the fractions. TLC separations take less time than on paper (30 minutes instead of several hours). There is less diffusion of zones leading to much sharper separations. When a purely inorganic adsorbent is used, strong reagents (sulphuric acid) can be applied for the general detection of organic compounds. In other aspects the scope and limitations of TLC are similar to paper chromatography. Its particular limitations are the fragility of the thin layer and the tendency of separated zones to air oxidation, due possibly to catalytic effects of the adsorbents.

It is hoped that this short appraisal of chromatographic systems makes it clear that chromatography is an inexhaustible mine of separating techniques. The choice is unlimited, but the best choice is difficult to arrive at. Of course by using other people's choice it can be hoped to get as good separations as they achieved themselves but the challenge is there to find a better, if not perfect, system.

Application of Chromatography to Paint Research

All the above mentioned chromatographic techniques have been used at one time or another at the Paint Research Station. Paper chromatography is used in routine analytical procedures for separations of inorganic ions, dibasic acids, polyalcohols, etc. Column liquid chromatography is used for research into adsorptive properties of pigments but now it is proposed to give some examples of application to paint research problems of gas and thin layer chromatography only.

Two types of gas chromatographic apparatus are used at the Paint Research Station : a double beam thermal conductivity detector apparatus and an argon ionization apparatus. Fig. 2 shows the first, which was built at the PRS

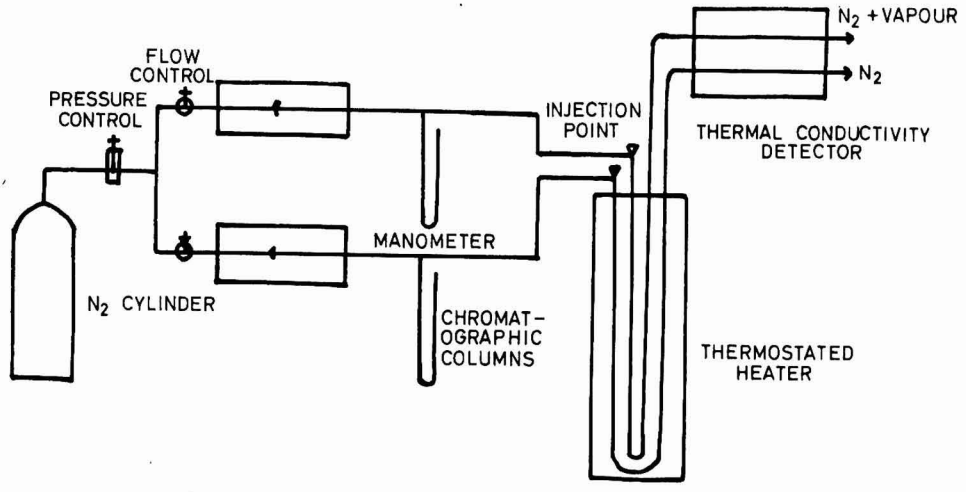

Fig. 2. A Double Beam Thermal Conductivity Detector Apparatus

in 1956. The two cells of this differential detector are connected to the outlets of the identical columns ; in a single experiment one column is used for separation, the other acting as a reference column. At low temperatures, when the stationary phases are stable, each column may contain a different stationary phase, thus giving the means to separate a given sample on two different phases without any change. At high temperatures when there is a possibility of bleeding of the stationary phase into the detector, both columns are filled with the same stationary phases thus giving good stability to the system. The separate heating of the detector and columns is useful when the programmed temperature separation is carried out.

The argon ionization detector is much more sensitive than the thermal conductivity one and is used for special problems which will be discussed later.

Analysis of Solvents

The obvious application of gas chromatography is analysis of solvent " mixtures " such as white spirit, petroleum distillates, benzoles, solvent naphthas, etc. The composition of the solvent mixtures can be checked and the presence of some components, which influence their performance in the paint, can be traced. Components of the mixtures can be identified by comparing the retention times of the peaks appearing on the chromatogram with previously accumulated data for the pure compounds on the same stationary phase.

Lacquer solvents analysis is more difficult as these solvents contain a variety of components of widely different nature and volatility. In this case separation on one stationary phase only can be very misleading, as may be illustrated by the following example.

Two samples of solvents for a special lacquer were found to differ in their performance and were believed to contain the same components, a large amount of petroleum ether with small amounts of *iso*-propanol, ethyl acetate and methyl ethyl ketone. Separation performed on a medium polarity dinonyl phthalate stationary phase gave two identical chromatograms for both samples consisting of six major peaks. Petroleum ether separated in the same conditions also gave the same pattern of peaks. Various isomeric hydrocarbons present in the petroleum ether obscured entirely the presence of other components of the mixture. This, however, became obvious only when the mixture was separated on a non-polar *Apiezon* grease stationary phase, on which the hydrocarbon peaks shifted to longer retention times revealing the presence of three other components in one sample and only two in the other.

The component present only in one sample was found to have the same retention time as normal propanol and not *iso*-propanol. The other component had the same retention time as toluene which was not expected to be present. The third could be either ethyl acetate or methyl ethyl ketone as this stationary phase could not separate them. A highly polar polyethylene glycol stationary phase was found to be most useful for this analysis. The aliphatic hydrocarbons were only slightly soluble in this stationary phase and therefore had retention times much shorter than the other components. Ethyl acetate was well separated from methyl ethyl ketone, n-propanol shifted to much longer retention time as was to be expected because of its high solubility in this medium, toluene also gave a well separated peak. Fig. 3 shows the chromatogram obtained. The

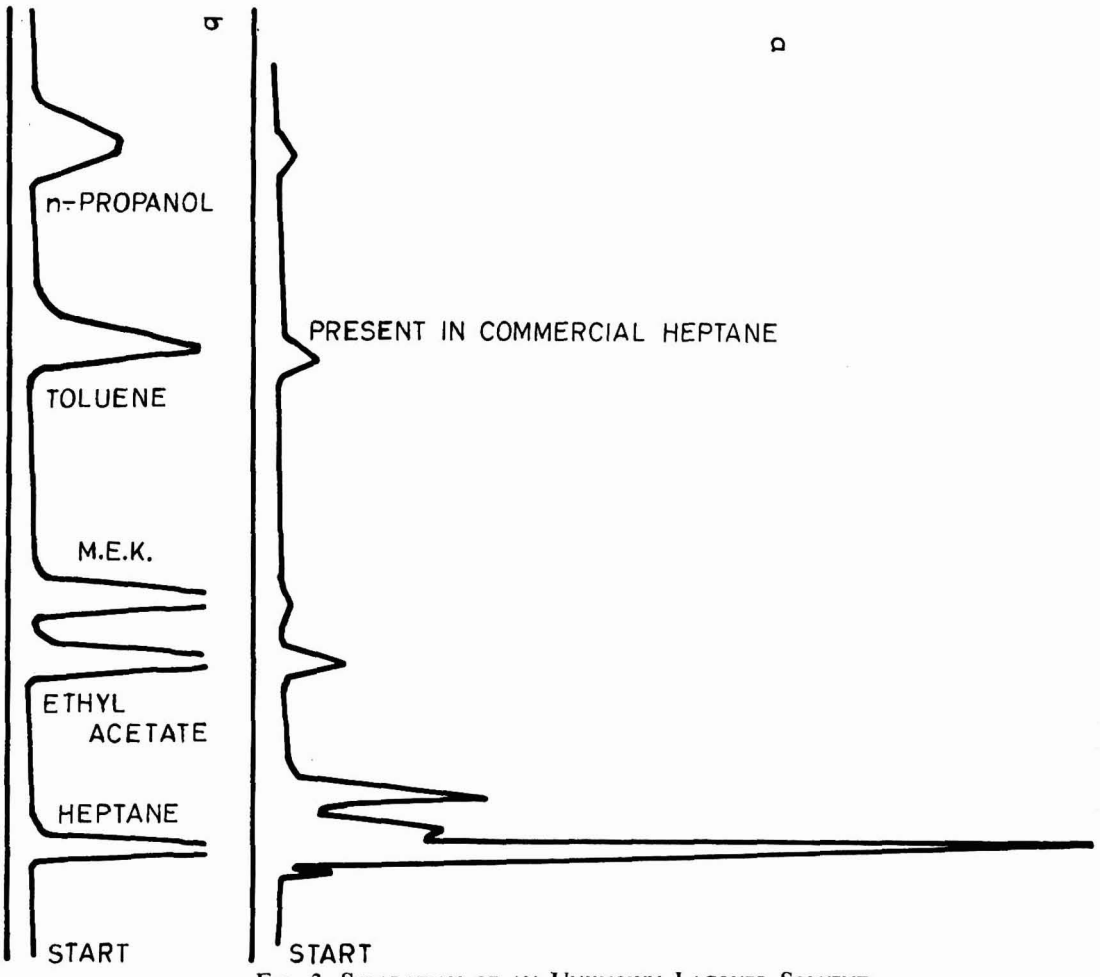

FIG. 3. SEPARATION OF AN UNKNOWN LACQUER SOLVENT

presence of toluene was confirmed by ultra violet analysis. This example illustrates well the importance of the proper choice of the stationary phase as well as the danger of relying on a separation on one stationary phase only.

Characterisation of Commercial Turpentines and Dipentenes

Terpene hydrocarbons are difficult to separate by fractional distillation because their boiling range is narrow (170-186°C) and at these temperatures isomerisation occurs readily. Using gas chromatography with a polar stationary phase in which these hydrocarbons are only slightly soluble, good separations were achieved at temperatures below 100°C thus avoiding any danger of isomerisation. The retention times of eleven pure terpene hydrocarbons were determined on dinonyl phthalate and ethylene glycol stationary phases and these data were used for the analysis of several commercial turpentines.

Fig. 4 shows the chromatograms of three turpentines. The first has Δ3-carene as the major component, the second contains predominantly

α-pinene, the third has three major components γ-terpinene, terpinolene and limonene in nearly equal amounts. Δ3-carene and α-pinene have only one double bond on the ring, terpinene, terpinolene and limonene have two double bonds ; the third turpentine differs considerably therefore from the others. Commercial dipentenes were also separated. Their content of limonene does not exceed 50 per cent, terpinolene and saturated menthane are the other main components.

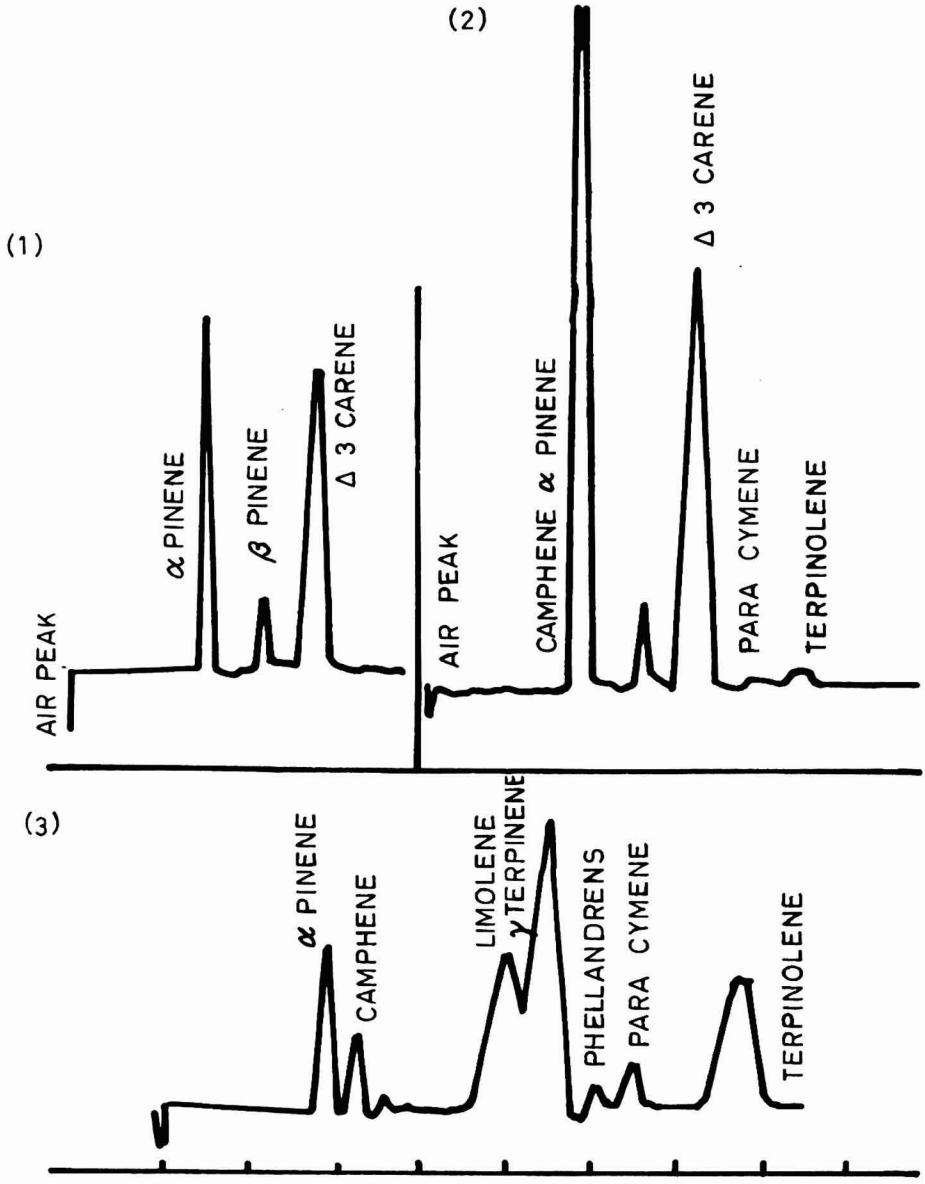

FIG. 4. SEPARATION OF THREE COMMERCIAL TURPENTINES

Fig. 5 shows the chemical structures of some of the components of commercial turpentines.

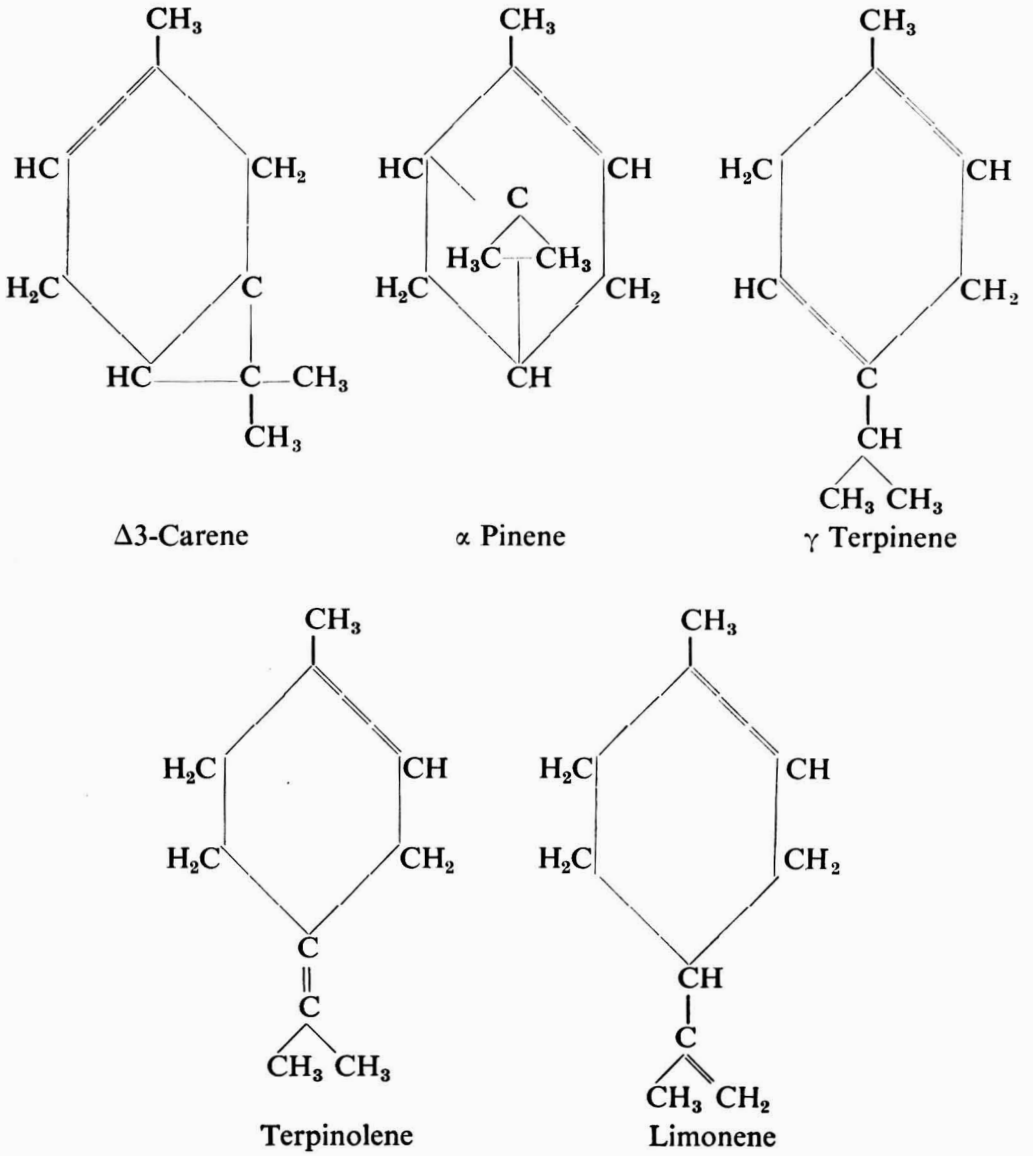

FIG. 5. CHEMICAL STRUCTURES OF SOME COMPONENTS OF COMMERCIAL TURPENTINES

Solvent Retention of Lacquer Films

Usually volatile compounds are the object of analysis by gas chromatography and known stationary phases are used for separation of unknown volatiles. The problem, however, can be reversed and the properties of the unknown compound used as stationary phase can be investigated by passing known

volatiles and observing their retention times, shapes of eluted zones etc. This method was used for the comparison of solvent retention of four lacquer films all containing the same amount of nitrocellulose and tricresyl phosphate and differing only in the type of resin present. Identical columns were prepared containing equal amounts of the investigated lacquers spread as a thin coating on inert solid particles. The behaviour of five solvents was examined on each of these columns. Each solvent was injected alone and the chromatogram gave the retention time and the shape of the peak. Fig. 6 illustrates the result of this comparison. The graphs shown represent superimposed chromatograms of the individual solvents. The longer the retention time the stronger is the solvent retained by the film. The asymmetry and the broadness of the peaks indicate the non-ideal behaviour, i.e., the increased retention time when the solvent concentration decreases.

Lacquer containing a non-drying alkyd exhibits the greatest selectivity of solvent retention and the smallest tendency to retain small concentrations of solvents. Lacquer with maleic resin of high rosin content releases isopropyl acetate, n-butanol and toluene nearly at the same rate and the non-ideal behaviour is very pronounced. Lacquer containing dewaxed Dammar resin shows a marked tendency to retain n-butyl acetate much longer than other components. The graphs illustrate the fact that vapours leaving lacquer films have a mixed composition until the last traces of solvents in both lacquer compositions containing maleic resin. The composition of the vapour phase released from the lacquer with non-drying alkyd changes rapidly at first but the last traces contain n-butyl acetate and butanol.

The Fatty Acid Composition of Drying Oils

Unsaturated glyceride oils are a major raw material of the paint industry and are also of great interest to biochemists and the food industry. Hence a large number of research workers all over the world have applied themselves to finding suitable conditions for the efficient separation of fatty acids by gas chromatography.

As methyl esters are more volatile and less reactive than fatty acids, the separation of the former presents fewer difficulties. The main problem was to find a stationary phase stable enough at the temperatures required for separation and efficient enough to separate the large number of acids of the same carbon chain length but differing in position and number of double bonds. Polyester type stationary phases were found to be more efficient the shorter the carbon chain of the dibasic acid used. The shortest dibasic acid which gave sufficient thermal stability to the polyester was succinic acid, and ethylene glycol succinate polyester is the most efficient stationary phase used up to date. Methyl esters of fatty acids of the same chain length are retained the longer, the more double bonds they possess. On the other hand non-polar *Apiezon* greases retain saturated structures longer than unsaturated, without, however, clear separation of individual unsaturated acids.

The determination of the fatty acid composition of natural oils such as linseed, soya bean, tobacco, etc. has now become a standard procedure.[1] Fig. 7 shows a chromatogram of linseed oil methyl esters. Distinct peaks for linolenate, linoleate, oleate and the saturated acid esters are visible; their

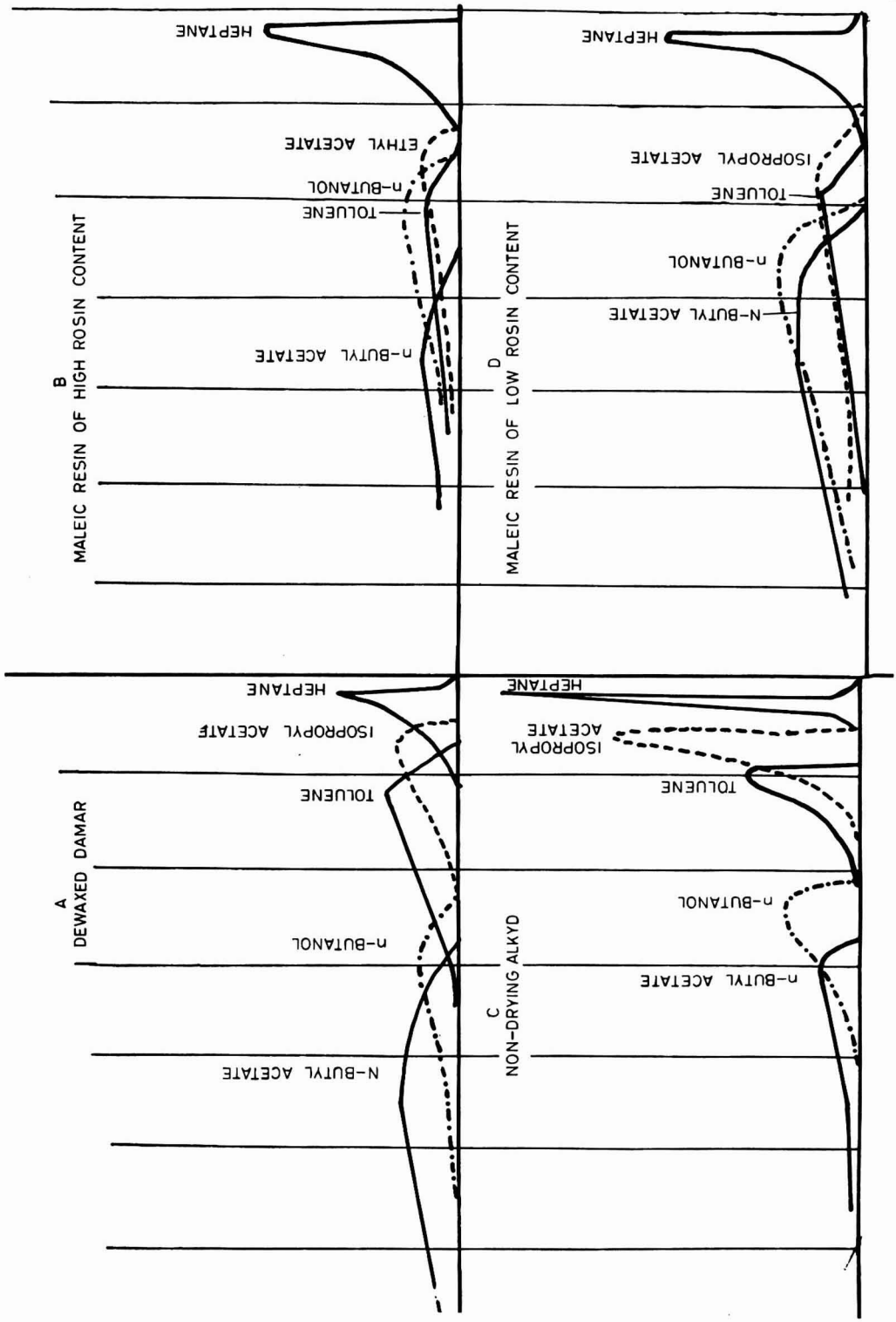

FIG. 6. SOLVENT RETENTION OF LACQUER FILMS

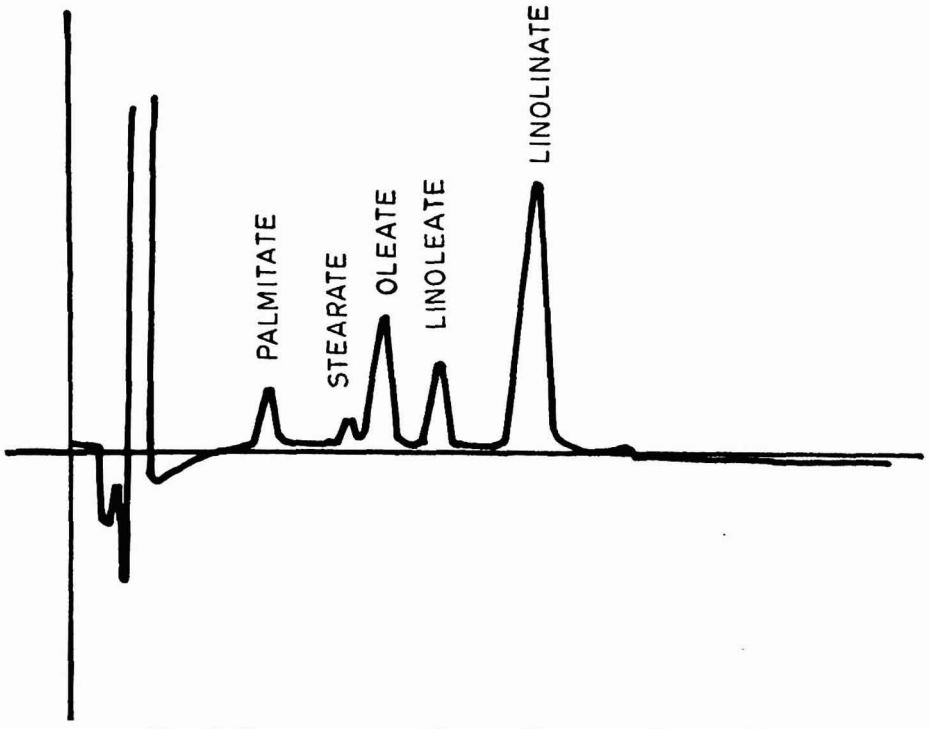

FIG. 7. SEPARATION OF METHYL ESTERS OF LINSEED OIL

proportions may be calculated from the areas under the peaks. Typical fatty acid compositions of some oils are shown in Table I.

TABLE I

METHYL ESTERS OF THE FATTY ACIDS OF DRYING OILS. GAS LIQUID CHROMATOGRAPHY: STATIONARY PHASE: ETHYLENE GLYCOL SUCCINATE POLYESTER. TEMPERATURE 195°C

Methyl esters of acids	Linseed oil	Soya bean oil	Tobacco seed oil	Tall oil (Scandinavian)	Tall oil (American)	Dehydrated castor oil
Palmitic	7	12	5	1	4	1
Palmitoleic ..	—	—	—	1	1	—
Stearic	2	3	1	0.2	1	1
Oleic (+ elaidic) ..	20	28	13	40	41.5	4
Linoleic	14	50	75	35	36.5	23
Unidentified ..	—	—	—	8	3	—
Linolenic	56	7	6	2	3	—
Conjugated linoleic 1 ..	—	—	—	1.5	4	54.5
Conjugated linoleic 2 ..	—	—	—	—	1	
Higher boiling comp.	—	—	1	12.5	6	15.5

The problem of separating and identifying mixtures of acids becomes more complex when heated or modified oils are examined. Dehydrated castor oil is such an example and the chromatogram of the separation of methyl esters of the fatty acids of such oil is given in Fig. 8. Apart from small amounts of palmitate, stearate, and oleate, there is a large peak of non-conjugated linoleate followed by three not very well separated peaks of conjugated linoleates, and lastly a small peak of unchanged ricinoleate.

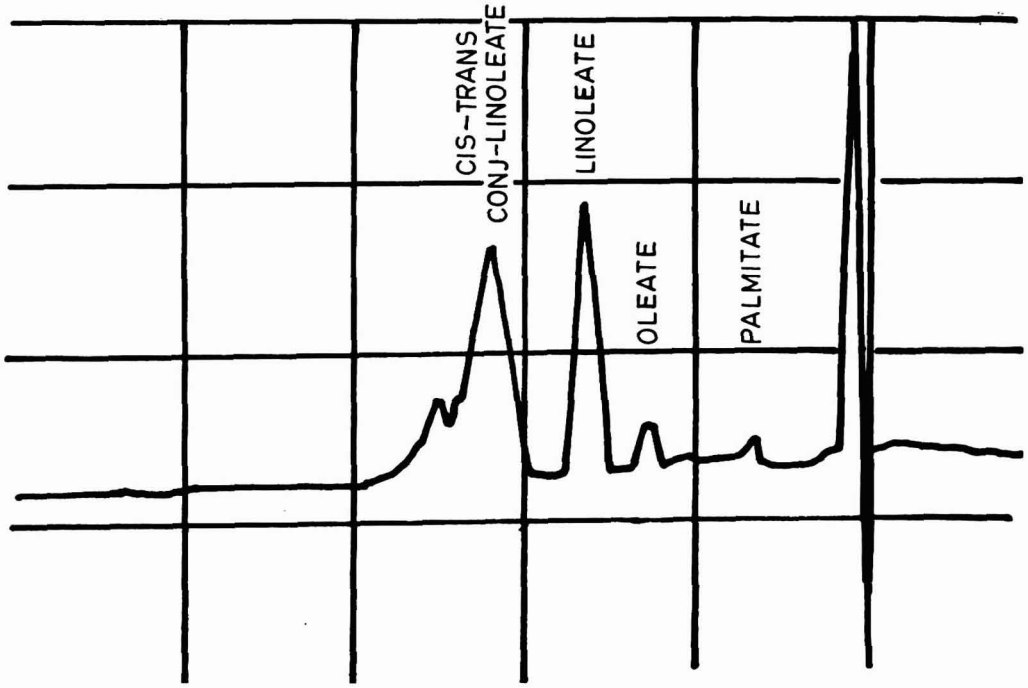

FIG. 8. SEPARATION OF METHYL ESTERS OF DEHYDRATED CASTOR OIL

Another system containing acids of uncertain composition is the monomeric fraction obtained on heat treatment of linseed oil followed by molecular still distillation. The distillate contains not only the original unchanged acids which have not polymerised but also some new acids. Fig. 9 shows the chromatogram of this fraction. Between the linoleic ester peak and the linolenic peak, a peak of an unknown fatty acid ester appears which is possibly the ring compound reported by some authors to be present in this system.[2]

Identification of unknown fatty acids solely from gas chromatographic data is not easy. When the retention times of normal saturated fatty acid methyl esters are plotted on semi-logarithmic paper against the number of carbon atoms in the chain a straight line is obtained. By definition the normal saturated fatty acid esters are represented as integers equal to their carbon chain length. The positions of the unsaturated fatty acid esters fall usually in between, and their positions can be expressed by the carbon number of the corresponding saturated acid ester plus a certain fraction characteristic for one, two, three etc. double

FIG. 9. SEPARATION OF THE DISTILLATE OF MONOMERIC FRACTION OBTAINED ON HEAT TREATMENT OF LINSEED OIL

bonds in the molecule. This equivalent carbon number[3] can be used for identification. Such a plot is shown in Fig. 10. When the equivalent carbon numbers are found for both polar and non polar stationary phases, identification becomes more reliable.

Although the identification of the fatty acids in the triglycerides of a drying oil is of the greatest importance for the characterisation of its performance in the paint film, the presence of some other components may also have an influence. For instance oxidation is affected by the presence of natural antioxidants, the amount of " foots " may be related to the phospholipid content, waxes present in the oil may affect the gloss of dried films and the colour of films may be influenced by natural colouring matters.

For the best method of studying these components, thin layer chromatography is used. In contrast to gas chromatography, thin layer chromatography can be carried out without any special apparatus. Devices for preparing the plates and

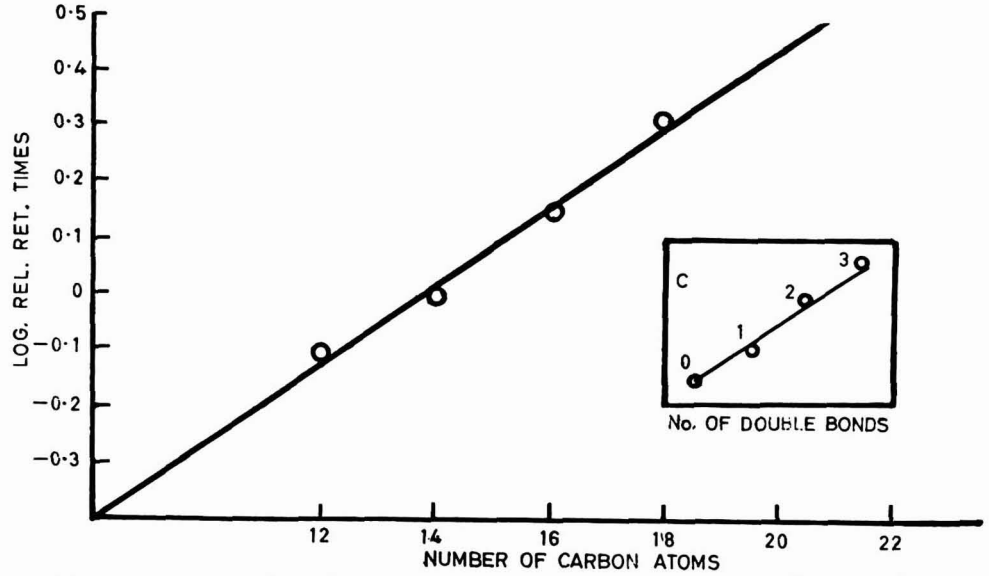

FIG. 10. THE PLOT OF LOG RETENTION TIMES AGAINST NUMBER OF CARBON ATOMS OF METHYL ESTERS OF FATTY ACIDS

carrying out the various operations can be purchased but at the Paint Research Station these have not been found necessary.

Separation of Minor Components of Linseed Oil

Separation by thin layer chromatography using silicic acid as adsorbent depends mainly on the type and number of oxygen-containing polar groups present in the molecule. The main components of oils, triglycerides, occupy a narrow zone on the plate although they vary in unsaturation. Components varying in hydroxyl or carboxyl content separate clearly.

Raw linseed oil was separated by TLC on silicic acid plates using continuously changing concentration of diethyl ether in petroleum ether (20-60 per cent) during the experiment, a method developed at the Paint Research Station.[4] In this system hydrocarbons travel to the solvent front and very polar compounds remain on the base line. The separated components were visualised by spraying the plate with 50 per cent sulphuric acid, followed by heating at 120°C. Apart from the major triglyceride spot, eleven smaller spots were detected. Identification was made by comparing the retention factors with standard compounds run on the same plate, specific reagents, and by infrared analysis of the material extracted from the separated zones. A semiquantitative estimation of the proportions of minor components was done by taking a photograph of the plate and measuring the optical density of the spots along the path of the separation.

The following minor components were identified : long chain alcohol and sterol esters, tocopherol esters, free tocopherols, fatty acids, triglycerides with polar groups on the fatty chains (epoxy and hydroxyl), diglycerides, sterols, a yellow compound with keto groups and finally phospholipids. Fig. 11 gives some of the structures of the compounds present as minor components in linseed oil.

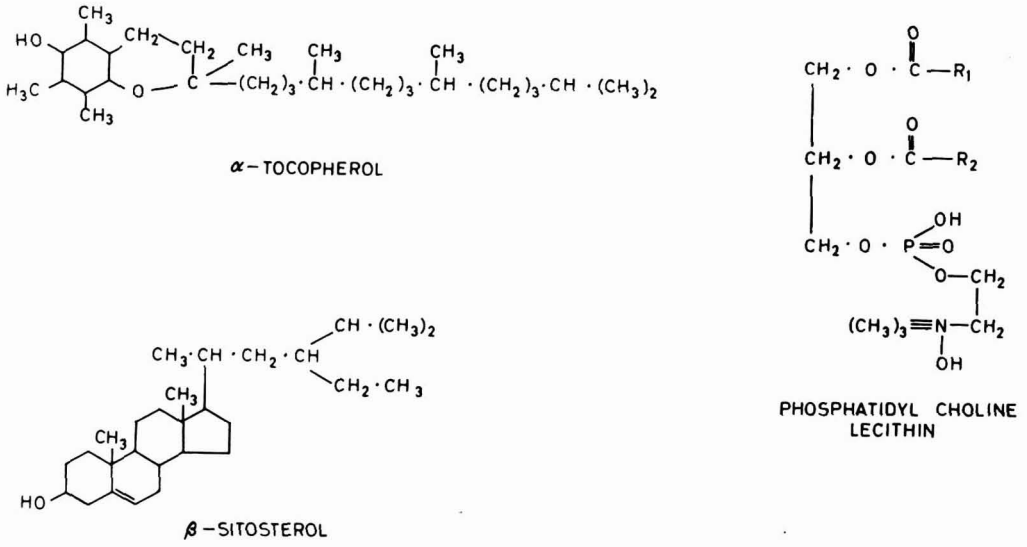

FIG. 11. STRUCTURES OF SOME COMPOUNDS PRESENT IN THE MINOR COMPONENTS OF LINSEED OIL

As the phospholipids stayed on the base line during the main separation and could not be identified properly, another solvent system was used for their separation. First, the phospholipids were separated from the other components on a thin layer plate by using acetone as the mobile phase. The phospholipids remained on the base line and all the other components travelled to the solvent front. (Advantage was taken of specific insolubility of phospholipids in this very polar solvent.) Acetone was evaporated from the plate and the plate was developed a second time using a solvent system in which the main phospholipid types are known to separate.[5]

The linseed oil phospholipids were compared with soya bean phospholipids run on the same plate. The linseed oil phospholipids were found to consist mostly of one type—phosphotidylcholine, whereas the soya bean phospholipids are composed of almost equal amounts of several types.

Column chromatography using silicic acid as adsorbent is much less efficient for separation of the minor components of linseed oil than TLC. When raw linseed oil was separated on a silicic acid column, the non-polar esters and triglycerides were eluted with petroleum ether leaving other minor components on the silicic acid. The elution was monitored by testing the composition of eluates on a TLC plate. The triglycerides eluted were still yellow due to the presence of tocopherols and their esters. A completely colourless linseed oil was obtained by passing it through a double layer column containing a silicic acid layer and below it a charcoal layer. The charcoal layer removed the non polar yellow components. A film made of this completely colourless linseed oil did yellow on ageing and exposure to ammonia as much as untreated linseed oil, showing that the yellowing of linseed oil films is not connected with the presence of natural colouring matters in the original oil. Moreover the oil was unstable and gelled easily due to the absence of antioxidants.

Analysis of the Products of Glycerolysis

Another example of application of thin layer chromatography in paint research is the use of this technique for the analysis of the products of the glycerolysis reaction, known in the industry under the name of monoglycerides. From the reaction mixture of linseed oil and glycerol a mixture of glycerol, 1- and 2-mono, 1:2- and 1:3-diglycerides and triglycerides is obtained. The separation of mono-, di- and triglycerides of linseed oil has been carried out on silicic acid coated plates using continuously changing concentration of diethyl ether in petroleum ether (composition changing from 10 per cent ether to 60 per cent during the experiment). All the components separated clearly and their proportion could be estimated. The same technique was applied for the separation of the mixture of pentaerythritol esters of linseed oil fatty acids and of a mixture obtained from the reaction of pentaerythritol and linseed oil. The last mixture contained both glycerides and pentaerythritol esters. Table II illustrates these separations.

TABLE II

RF VALUES OF GLYCERIDES AND PENTAERYTHRITOL ESTERS OF LINSEED OIL OBTAINED WITH CONCENTRATION GRADIENT DEVELOPMENT

Compound	Mixture 1	Mixture 2	Mixture 3
Glycerol, penta	0	0	0
2-Monoglycerides	0	—	0
Mono-penta esters	—	0.09	0.09
1, -Monoglycerides	0.19	—	0.18
Di-penta esters	—	0.30	0.28
1, 2-Diglycerides	0.38	—	0.37
Tri-penta esters	—	0.46	0.46
1, 3-Diglycerides	0.47	—	0.47
Tetra-penta esters	—	0.79	0.79
Triglycerides	0.82	—	0.81

Thin layer chromatography was also used to follow the course of glycerolysis reaction.[6] Linseed oil and glycerol were reacted in the presence of sodium hydroxide catalyst at 235°C for two hours with continuous stirring. Samples of the reaction mixture removed every ten minutes were delivered to weighed containers, cooled, weighed and diluted with acetone to give 5 per cent solution of each sample. A large silicic acid coated plate was spotted with ten solutions of these samples. Care was taken to deliver exactly the same amount of solution on each spot. The plate was developed by a mobile phase of composition changing from pure petroleum ether to 50 per cent solution of diethyl ether. The dried plate was sprayed with concentrated sulphuric acid and heated until dark spots developed.

Fig. 12 shows the photograph of a TLC plate. The trains of spots for each time of reaction showed clearly the gradual decrease of triglycerides as well as the increase of mono- and diglycerides up to 30 minutes of reaction, but later the changes became small. A photograph of the plate was taken and the negative was scanned on an optical densitometer, so that a plot of optical

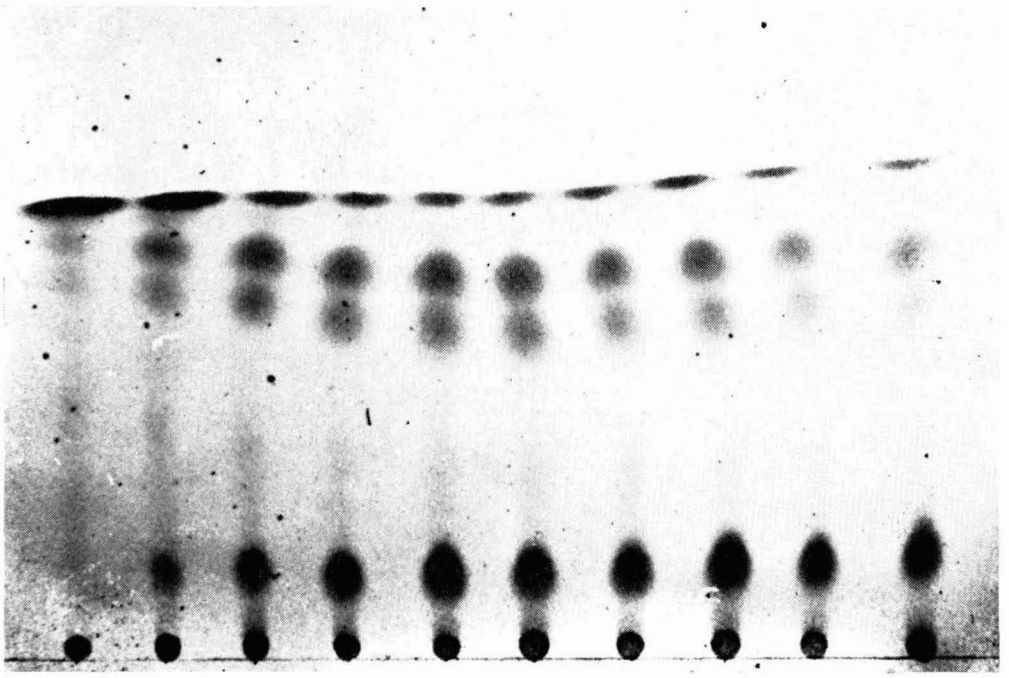

FIG. 12. A PHOTOGRAPH OF A TLC PLATE OF THE SAMPLES OF GLYCEROLYSIS REACTION MIXTURE

density against distance could be obtained. When the negative was scanned in the direction parallel to the base of the plate, along the spots of one type of component, the changes of concentration of a given species during the reaction could be estimated more accurately. Fig. 13 shows the graph obtained for monoglycerides.

Thin layer chromatography was also used to get a glimpse of the distribution of triglycerides of various drying oils. The triglycerides could be separated into groups of different total unsaturation. This was done on plates coated with inert powder impregnated with a non polar stationary phase such as squalane or undecane. The mobile phase was of high polarity (acetic acid). The separated triglycerides were exposed to iodine vapour thus giving brown spots on the plate ; the retention factors increased with the degree of unsaturation of the triglycerides. Various oils could be differentiated clearly by the number and the positions of the triglyceride types.

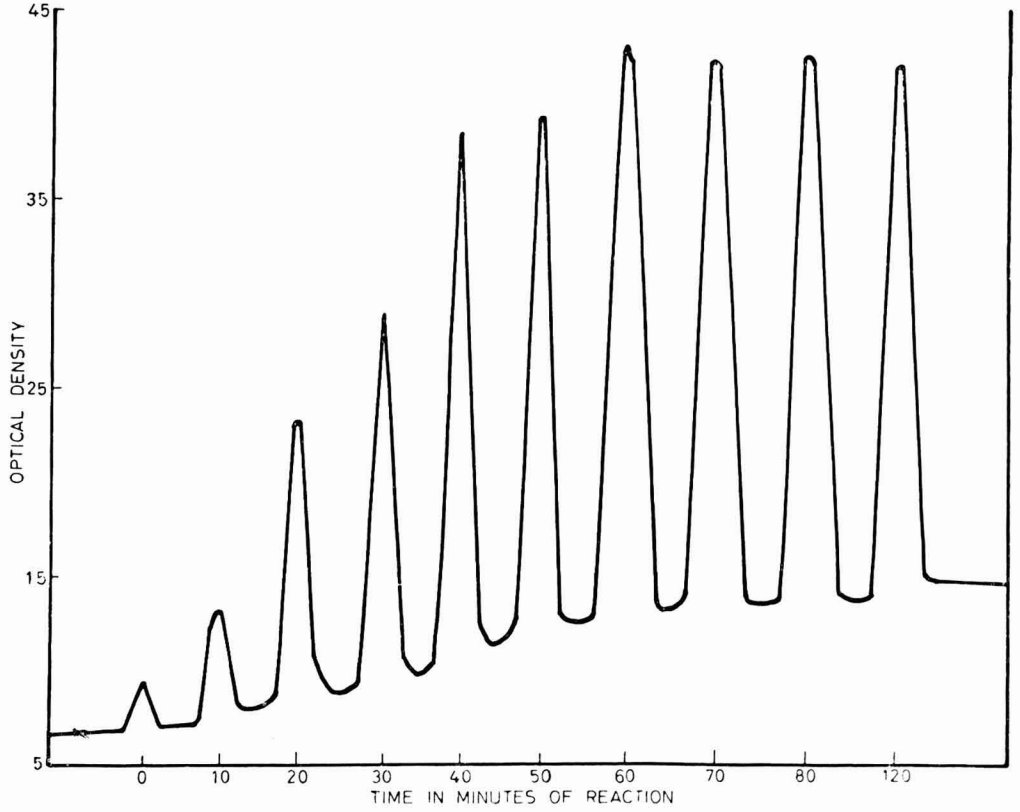

FIG. 13. GLYCEROLYSIS OF LINSEED OIL. CONCENTRATION OF MONOGLYCERIDES AT VARIOUS TIMES

Examination of Volatiles of Natural Oils

In the examination of oils, both gas chromatography and thin layer chromatography have their uses and they are in a sense complementary. The presence of volatiles in the natural oil or evolution of volatiles during the autoxidation process can be detected and to some degree identified by gas chromatography, using the highly sensitive argon detector. For this purpose the apparatus is provided with a bypass, which can be heated to any suitable temperature. The oil to be examined is kept in the bypass for a time required to accumulate sufficient amount of volatiles in the gaseous phase and then the contents are swept into the column by argon flow. The volatiles separate in the column in the usual way and appear as a series of peaks on the chromatogram.

When the autoxidation products are investigated, air is admitted to the by-pass and a catalyst is added to the oil to promote autoxidation. In this way it is a simple matter to detect the presence of volatiles, but identification proves to be difficult. The autoxidation products of linseed oil consist predominantly of propionaldehyde and formic acid but a large number of minor components are also detected. These consist of higher saturated and unsaturated aldehydes but some other compounds are also present which have not yet been identified.

The by-pass on the argon detector apparatus can be used for the detection of trace components not only in paint films but also in printed papers, lacquer films, the residual monomers in synthetic polymers, etc. The volatiles evolved during the curing of paint films can also be examined in this system.

The sensitivity of the argon detector is such that a sample of the gaseous phase from above the solution (of a lacquer) can be taken by a gas syringe and injected into the column, thus giving the composition of the vapour phase above a solution, a paint in a container, or even a paint film.

Pyrolysis of Polymers

Thermal degradation of polymers depends primarily on the molecular structure of the polymers. Separation and identification of volatile products of pyrolysis can therefore throw some light on the structure of a polymer. If a polymer could be identified solely by its volatile pyrolysis products gas chromatography could be used for its analysis. In many cases this was found to be true.

These experiments were realised in practice in the following way. The usual packed column was provided with a pyrolysis unit[7] consisting of a platinum coil sealed inside a short glass tubing. This unit is placed on the top of the column. Fig. 14 gives a diagram of such a unit. Nitrogen is made to flow through the coil straight into the column, the coil being heated to any required temperature by an electric current. The polymer is deposited on the coil by dipping it in a solution of the polymer in a volatile solvent, the solvent evaporated and the loaded pyrolysis unit connected to the column. Usually one has to wait and see if any volatiles are released from the polymer without heating the coil—these may be due to the presence of residual solvent or monomer entrapped in the polymer. A current sufficient to obtain the given temperature of pyrolysis

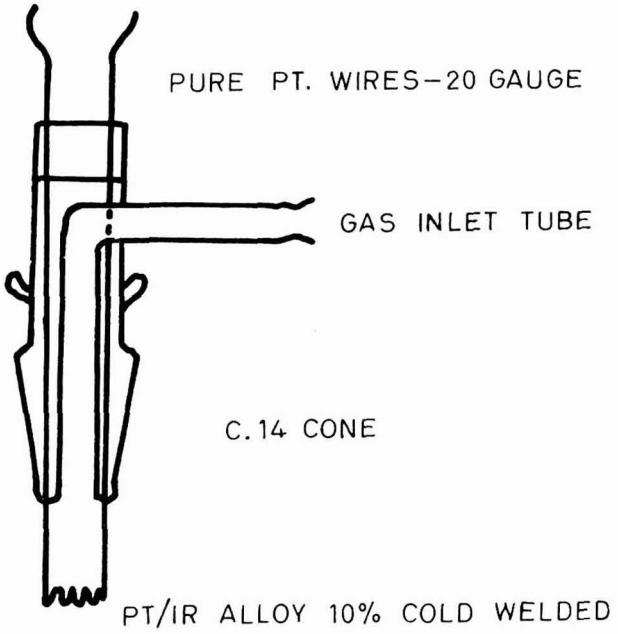

FIG. 14. DIAGRAM OF PYROLYSIS UNIT

is switched on for 10 or 20 seconds. The volatiles are swept into the column as soon as they are formed thus minimising any secondary reactions between the highly reactive products.

Volatiles are separated in the usual way by their passage through an appropriate column and a pattern of peaks appears in due time on the recorder chart. The pyrolysis products may consist of gases and compounds of varying volatility. One set of conditions may not be adequate to cope with separation. Usually, however, the conditions suitable for separation of medium range volatility compounds are employed as most monomers and other characteristic degradation products can be separated in these conditions.

A series of homopolymers of methacrylate, acrylate and styrene type gave a high proportion of monomers in the pyrolysis volatiles and could be easily identified. Copolymers gave different patterns of peaks than the mixtures of corresponding homopolymers—so that copolymers could be differentiated from the mixtures of homopolymers. Some copolymers, however, could not be differentiated from each other, i.e., acrylic acid/butyl methacrylate from the copolymer containing maleic or methacrylic acid instead of acrylic. On the other hand in some cases even the proportion of the monomeric constituents of a copolymer could be evaluated. Fig. 15 shows some of the results of pyrolysis of copolymers.

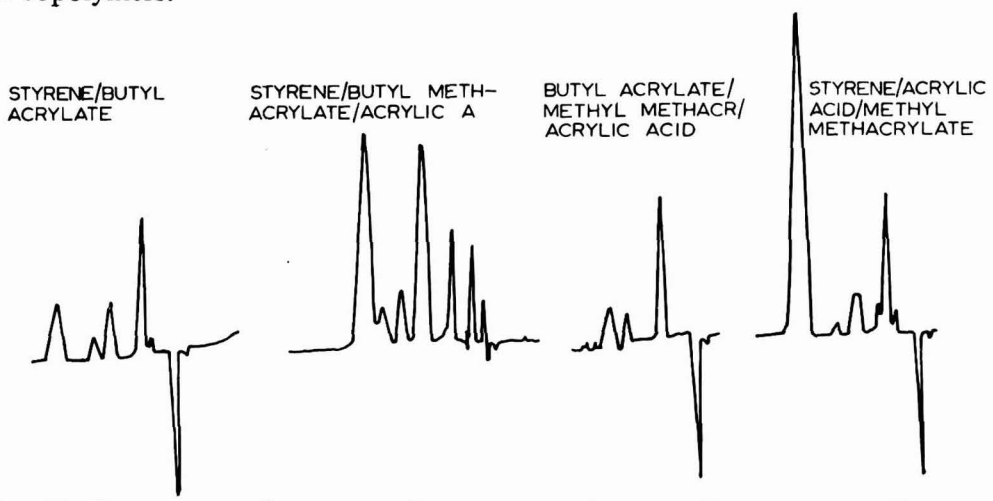

FIG. 15. PYROLYSIS OF COPOLYMERS. SEPARATION OF VOLATILE COMPONENTS OF PYROLYSIS

The detection of the volatile products of pyrolysis can be used not only for identification of polymers but also for the study of their thermal stability. The temperature of the coil could gradually be increased, thus giving information about the behaviour of the polymer at various temperatures. In some cases the pyrolysis coil may be placed in the bypass instead of at the top of the column, thus avoiding contamination of the column with high boiling pyrolysis products.

CONCLUSIONS

The number of applications of chromatographic techniques to paint research seems to be infinite although only a few have been mentioned. Chromatographic separation methods do not have a sound theoretical basis yet and a rational

choice of the competing phases is still difficult. There is, however, a growing tendency to rationalise the chromatographic systems—and the near future may bring spectacular improvements in these methods. It must not be forgotten that the research worker is not alone and that teams of other research workers, who, perhaps, are never met but whose work can be read and appreciated in so many scientific journals, do most of the basic research.

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DISCUSSION

MR. A. R. H. TAWN said that one of the problems in using GLC as a means of quantitative analysis was the measurement of the peak areas on the recorder chart. Of the more obvious methods, a recent publication on this subject had given triangulation, cutting-out and weighing, and measurement by Planimeter as the order of preference. He asked the lecturer which of these methods she considered to be the most satisfactory and, as several integrating recorders were now available, whether any of these instruments gave satisfactory results.

MRS. S. M. RYBICKA said that in any quantitative approach the first consideration was the equal response of the detector to all the components of the separated mixture. In this respect she preferred the thermal conductivity detector to the Argon detector, because she felt that the former was more likely to give reproducible equal response. The measurement of peak areas always involved errors, but she thought that the errors of triangulation and cutting-out were of the same order. Triangulation was easier and more suitable for narrow symmetrical peaks. The Planimeter gave large errors especially for small peaks, and was, therefore, unsatisfactory. So far as automatic integrators were concerned she had no experience of their use, but she felt that although some of the errors experienced by the manual methods might be excluded, there would still be difficulties, e.g. with the base line drift, not well resolved peaks, etc.

DR. H. WARSON asked what the procedure was when a solvent mixture contained water and whether it was possible to have a preliminary short ancillary column with glycerol or polyglycol to retain the water. He also asked whether the gas density bridge was the only detector which gave the area under the peak as a strictly molar quantity. He also queried the quantitative interpretation of pyrolysis chromatograms.

MRS. RYBICKA said that to determine water it was necessary to use a very polar stationary phase, e.g. polyethyleneglycol. Using nitrogen as the mobile phase a negative peak was obtained with water. Small amounts of water, 0.1 per cent or less, could be estimated correctly with previous calibration as the response of the thermal conductivity detector was very high for water vapour. The Argon detector was not suitable for the determination of water and its sensitivity to other components dropped when water entered the detector. If it was desired to remove a large quantity of water a short column of diglycerol on top of the main column would retard the water sufficiently to enable the estimation of the other solvent peaks. Alternatively the direction of the carrier gas could be reversed when the water vapour started to leave the diglycerol column, thus removing it from the system.

She thought that the gas density balance detector was most reliable and was the best detector for quantitative analysis. So far it had not been used very much due to difficulties in construction, but there were now several commercial instruments of this type available. It certainly gave a response on the basis of molecular weight.

She said that she had no faith in quantitative results in pyrolysis experiments. Such results as had been quoted in the lecture had been based on the knowledge of the amount of monomer used to prepare the polymer.

MR. TAWN commented that the lecturer had suggested that TLC could be used to monitor large-scale column chromatography. He thought that this implied that the two techniques did the same thing and gave the same results. Mrs. Rybicka, however, had achieved by TLC the exceedingly difficult separation of 1.2- and 1.3-diglycerides in a linseed oil glycerolysis product, which he and his colleagues had failed to achieve some years ago, using the same adsorbent and solvent system, in a column. The lecturer had also reported TLC as being superior to column chromatography in the separation of phospholipids. He asked Mrs. Rybicka to comment on this apparent anomaly.

MRS. RYBICKA replied that when she suggested that TLC could be used to monitor large-scale column chromatography she meant that the solvent system could be tried out first on TLC using the same adsorbent as on the column. The column might be imperfect due to the unevenness of the powder packing or channelling and this could be checked by examining the composition of the eluates by TLC. The comparison of the separation achieved on both systems might be used to improve the column performance.

MR. D. GRIME asked whether the lecturer had found any difficulty in the pyrolysis technique from the retention of solvent by the polymer film as such solvent would be expected to appear in the pyrogram. He suggested that pyrolysis of block and random co-polymers would be expected to give different pyrograms by giving different products in, e.g., the "unzipping" process, and asked Mrs. Rybicka whether she had any experience of the pyrolysis of this type of polymer.

MRS. RYBICKA replied that one of the diagrams demonstrated clearly the possible misleading effect of residual solvent in the polymer film. Two peaks were found with methyl methacrylate, one of which was found, on using a much lower temperature, to be due to residual solvent. It was necessary to be very careful to remove all residual solvent by heating at a much lower temperature for a sufficient time before carrying out the pyrolysis experiment. No work had been carried out as yet on polymers of the type quoted in the second question.

DR. WARSON, in proposing a vote of thanks, gave an example of the way in which the use of GLC had assisted in the manufacture of higher purity vinyl esters by the unexpected detection of ethylene glycol diacetate in the reaction products. Suitable modifications to the reaction conditions had resulted in the elimination of this undesirable by-product, which could not have been found by any other method.

Use of Gas-Liquid Chromatography in the Field of Drying Oils and Oleoresinous Media*

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Summary

The limitations of using GLC for qualitative work is noted and the methods for overcoming some of these limitations discussed. The experimental procedure for obtaining chromatograms of methyl esters from processed oils and alkyds is then described and the results discussed.

INTRODUCTION

Gas-Liquid Chromatography (GLC), or Vapour Phase Chromatography as it is sometimes called, is a comparatively new tool for the chemist, for it was in 1942 that Martin and Synge[1] first indicated the basis of the method, and not until 1952 did James and Martin[2] show the far-reaching possibilities for analysis of volatile substances. During the last decade there has been an increasing volume of literature concerning use of GLC in many branches of science and industry, including analysis of vegetable drying oils and solvents,[3] but not including much else of direct bearing to the paint industry. The present paper is an attempt to describe some preliminary work and future possibilities concerning analysis by GLC of processed drying oils, oleoresinous media and resins used in surface coatings.

EXPERIMENTAL

A *Pye Argon Chromatograph* has been used in the conventional manner for the experimental work described. It was found convenient for expelling the sample from the micro-pipette, and for washing it, to have a rubber teat instead of small bore rubber tubing. A typical simple chromatogram is given in Fig. 1 for the methyl esters of linseed oil fatty acids, showing peaks due to methyl palmitate, stearate, oleate, linoleate and linolenate. Once the position of the peak arising from a pure substance is known then, in general, when it appears from a mixture it can be provisionally identified and later confirmed by using a column of different polarity as described by Haslam[3] for solvents.

Limitations of qualitative analysis include the following :

(*i*) Constituents with the greatest volatility may not be noticed, as they may occur as one peak, perhaps with the peak due to a solvent deliberately added.

(*ii*) Constituents of low volatility may not give peaks that can be distinguished.

(*iii*) Non-volatile constituents are not recorded.

*Given before the Midlands Section on 18 January 1963.

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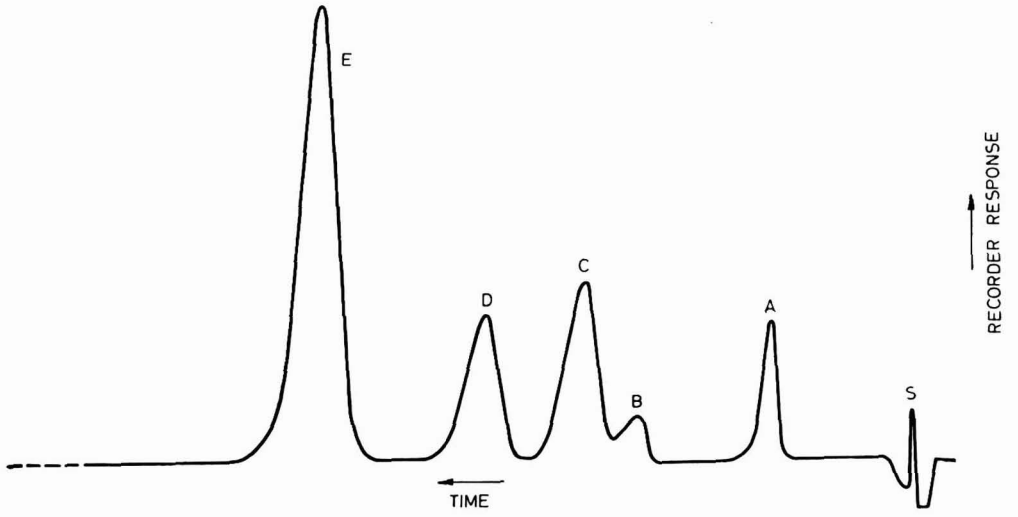

FIG. 1. METHYL ESTERS OF LINSEED OIL FATTY ACIDS
The peaks are lettered as follows : S, solvent ; A, palmitic ; B. stearic ; C, oleic ; D, linoleic ; E, linolenic. Polyethylene glycol succinate column, 160°C

(*iv*) Some substances may change (decompose, isomerise, etc.) during passage through the column, especially when a pre-heater is used.

(*v*) Two or more substances may have the same retention time.

(*vi*) Even when retention times are different, a substance may not appear as a separate peak or even as a " shoulder " because of swamping.

(*vii*) Some constituents may be altered or lost during preparation of the sample.

Certain of the above limitations may be overcome, partially at least, for example : (*i*) by obtaining a separate chromatogram at a low temperature, or by temperature programming ; (*v*) and (*vi*) by using a column with a different polarity, or by using a longer column. With a capillary column separation of *cis* and *trans* isomers[4] of fatty acids is possible.

On the preparative scale, GLC is used for obtaining fractions after they pass through the detector, usually having a very high degree of purity. Examination of the constitution of an unknown can then proceed by other techniques, such as infrared spectroscopy or nuclear magnetic resonance.

Quantitative Aspects

The area under a peak, usually calculated from the dimensions of the triangle comprising the sides of the peak and the base line, is a measure of the quantity of substance that has passed through the detector. For some detectors, for example the katharometer, it is standard procedure for a factor to be determined for converting area to weight. The argon detector is one for which the claim is made that area is directly proportional to weight, and though this has been found to be so in some cases,[5] there is by no means complete agreement that this proportionality is always true.

For quantitative work special attention must be made to water[6] ; since it often passes through polar columns much more slowly than might be anticipated, reduces sensitivity and greatly interferes with quantitative work. A flame ionisation detector, unaffected by water, is convenient for aqueous samples. Using an argon detector for quantitative work that is required to be as accurate as possible, all samples should be free from water and the argon dried, for which a molecular sieve is recommended. In this paper most of the work described is technological and of a semi-quantitative nature carried out at temperatures above 150°C, so that these special precautions were not taken.

Removal of water is, however, necessary when using an internal standard, a procedure that involves adding to the sample a known proportion of a pure substance, such as methyl myristate, preceded and followed by quantitative analysis. The change in composition as calculated from the peaks compared with the theoretical change shows if all the constituents of the original sample appear on the resulting chromatogram. This calculation is particularly valuable when examining samples which contain a proportion of non-volatile polymers, such as methyl esters derived from heat-treated products.

In the chromatogram of methyl esters of fatty acids, the peak due to stearic acid may be insufficiently separate from the oleic peak for the triangle to be accurately drawn. In such cases it may be useful to use the relationship that the width of the peak at the base is proportional to the distance from the air peak. Knowing the position of one end of the base, the position of the other end can be marked, and after drawing the first side, the other can then be drawn in with fair accuracy.

Crude and Refined Oils and Acid Oils

When Hilditch first wrote " The Constitution of Natural Fats," the determination of fatty acid composition was extremely tedious. Nowadays results that are believed to be much more accurate are obtained very quickly, and have been widely published. The common fatty acids may be readily identified, but " unusual " acids can be troublesome ; there is still some doubt concerning two of the major peaks, close to that of ordinary linoleic acid, given by tall oil fatty acids. From some oils the number of peaks on the chromatogram obtained by GLC is very large, especially marine oils, for example, 50 peaks have been obtained from cod liver oil,[7] many of which may be hitherto unknown, or at least unsuspected acids.

The straight line obtained by plotting log retention time against number of carbon atoms for the homologous series consisting of the methyl esters of straight chain saturated fatty acids can be usefully extended to unsaturated chains. The point corresponding to the logarithm of the retention time for any other acid (the methyl ester is understood) can be put on the straight line, and the corresponding chain length can then be read off. For example, for a polyethylene glycol succinate or adipate polyester column, oleic acid gives a reading of approximately 18.3. This is called the Equivalent Chain Length (ECL), a concept introduced by Miwa and co-workers.[8] The idea is most useful, simplifies thinking considerably, and could obviously be extended to other compounds. In the polyester columns just mentioned the ECL of oleic acid is 0.3 higher than the corresponding saturated acid (stearic acid is 18.0

by definition), and in fact the introduction of one double bond into a saturated straight chain fatty acid always appears to raise the ECL by about 0.3. The two isolated double bonds of linoleic acid raise the ECL to about 18.8, while conjugation of double bonds raises the value considerably more.

On the technical side, fatty acid composition is of particular importance for non-yellowing oils, notably soya bean oil, since this oil contains several per cent of linolenic acid, the constituent believed to give rise to the yellowing of linseed oil. An average analysis of soya bean oil is 9 per cent linolenic, 50 per cent or slightly more of linoleic, together with oleic, stearic and palmitic acids, sometimes with traces of lauric and myristic acids. From the fatty acid composition the iodine value of an oil can be calculated. For non-conjugated crude oils the result is found to be within two or three units of the Wijs iodine value, while for refined oils the agreement is better.

Where free fatty acids are put through a column the peaks obtained are very poor, flat and skew, apparently caused by association. Good peaks can be obtained by taking certain measures, for example, by washing the support with very dilute hydrochloric acid before coating with the liquid phase, and by incorporating stearic acid[2] or phosphoric acid.[9] In all the original work described in this paper, the methyl esters are used.

Preparation of Methyl Esters

Methyl esters of fatty acids may be readily prepared by direct esterification or by ester interchange. Methanolysis of triglycerides is often preferred owing to the greater convenience and speed ; although the yield may not be so high, it is sufficient for quantitative work for technological purposes.

Methanolysis was used for routine analysis of paint oils as long ago as 1954,[10] and may be brought about by a variety of catalysts. A suitable and convenient reagent, in which sodium methoxide is the catalyst, is prepared by allowing 1 per cent by weight of sodium metal to dissolve in AR methanol. When an alkali refined oil is shaken with 100 per cent excess of this solution for five minutes, and the mixture allowed to stand, free glycerol settles quickly. The upper layer, essentially methyl esters in methanol solution, is preferably washed with salt solution and then dried (filtering is sometimes sufficient) before analysing by GLC.

With viscous oils especially it is more convenient first, to make a solution in an inert solvent, for example, in one-half volume of toluene. The methanolysis procedure just described then works well for vegetable oils, processed oils and products containing these oils up to acid values of about eight. After addition of the methanolysis reagent the liquid may be warmed with subsequent mixing by careful agitation, or in difficult cases the mixture may be heated under reflux. After standing, a sample of the upper layer can be used without further treatment for the chromatograph, but it is always better to wash the sample first in order to avoid contamination of the column with traces of soap, etc. For oils or media of high acid value preliminary esterification or removal of the free fatty acids is necessary for methanolysis to proceed.

Removal of the free acids by extraction with methanol is too tedious to be practical. There are several methods for converting to the corresponding methyl esters : (*a*) With dimethoxy propane,[11] (*b*) The standard method of

refluxing in methanol solution with sulphuric acid as catalyst, (*c*) Similarly, using boron trifluoride as catalyst, (*d*) With diazomethane.[12]

Methods (*c*) and (*d*) are quick and the most convenient. Diazomethane has the advantage of esterifying rosin acids, but requires good fume extraction. By using boron trifluoride (which also requires care) dissolved in methanol, only two minutes' refluxing is required for complete esterification (Metcalfe and Schmitz[13]). If this reagent is not easily obtained, boron trifluoride/ether complex may be used. For an acid oil containing about one-half free fatty acids, a suitable procedure is as follows :

> To 1 ml acid oil add 12 ml of a reagent made by slowly adding one volume boron trifluoride/ether complex to three volumes methanol and reflux for 15 minutes. Allow to cool, add 10 ml toluene and wash with 30 ml salt solution. Dry the upper layer by filtering through paper wetted with toluene.

The solution obtained contains the methyl esters of the free acids in the sample of acid oil together with the triglycerides and other constituents originally present. This solution may be examined by GLC to obtain the composition of the methyl esters. It may also be heated with the methanolysis reagent (sodium methoxide in methanol) when the triglycerides are methanolysed to give the methyl esters of all the acids of the acid oil. If the solution is opalescent after washing and filtering, it may be clarified with a little ether. The constitution of both the free and combined acids of a highly acidic oil may thus be determined. For linseed acid oil the proportion of linolenic acid is found to be well below that in linseed oil.

The composition of the free fatty acids of raw linseed oil has been investigated by esterification with diazomethane followed by chromatographing the methyl esters in the presence of triglycerides. Results are given in Table I.

TABLE I

PERCENTAGE COMPOSITION OF THE FREE FATTY ACIDS OF THREE SAMPLES OF RAW LINSEED OIL

	Palmitic	Stearic	Oleic	Linoleic	Linolenic
Sample 1	10.4	3.0	27.5	22.3	26.8
Sample 2	11.4	3.3	24.9	20.2	40.0
Sample 3	8.9	5.3	26.2	21.8	37.7

Diethylene glycol succinate liquid phase ; 160°C, 1,500 volts, 50 ml/sec.

For comparison, the average composition of the three raw linseed oils is 6 per cent palmitic, 4 per cent stearic, 20 per cent oleic, 15 per cent linoleic and 55 per cent linolenic acids. Since more than one-half the linseed acid oil consists of the free acids present in the raw oil it is evident that the linolenic acid content and similarly the iodine value are both much lower than for the original oil.

For the kind of work just described with linseed oil or linseed acid oil no special precautions are usually necessary. With oils such as tung or oiticica,

however, it is advisable to use an inert atmosphere when preparing or working with the methyl esters.

The effect on fatty acid composition has been found for the procedure used for determination of the percentage unsaponifiable matter in linseed oil, namely, heating under reflux for one hour with N/2 ethanolic potassium hydroxide. After liberation with mineral acids the fatty acids were esterified with methanol using boron trifluoride as catalyst. On the chromatogram a new peak appeared, about 3 per cent of the total area. Under the conditions described for saponification, it appears that at least 3 per cent of the acids are isomerised (probably conjugated).

Processed Oils

When drying oils are processed commercially by polymerisation or oxidation, the main changes that take place arise in the fatty acid chains—isomerisation, polymerisation, oxidation, scission. These changes can obviously be investigated by GLC after conversion to the corresponding methyl esters. A simple case is that of the heat bodying of refined linseed oil, where it has been shown[14] for a cook at constant temperature that the reciprocal of the percentage of linoleic and linolenic acids gives a straight line when plotted against cooking time. The oleic acid content in the experiments described tends to fall, but since the variation is near the outside limit of experimental error, this point merits further investigation. A typical chromatogram of a polymerised linseed

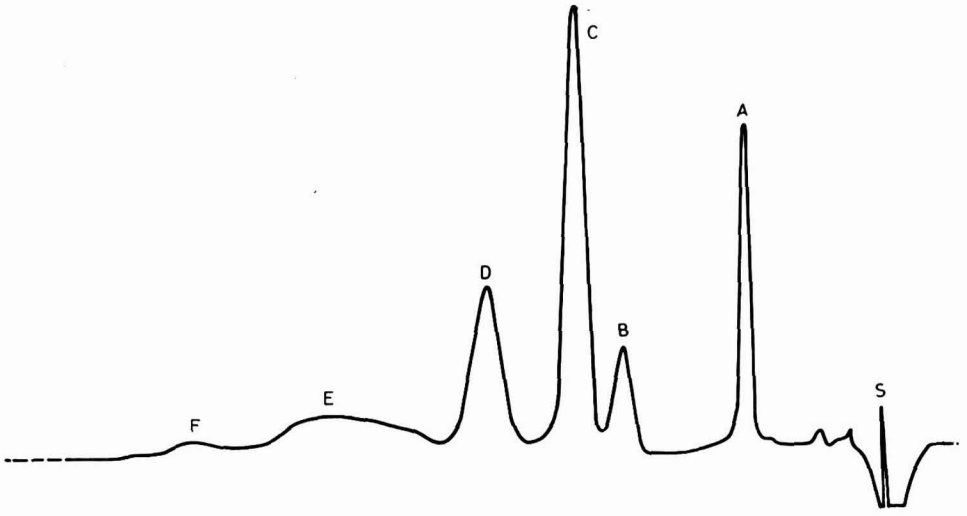

FIG. 2. METHYL ESTERS FROM A 60 POISE LINSEED STAND OIL

S, solvent peak ; A, palmitic ; B, stearic ; C, oleic ; D, linoleic ; E and F, linolenic and new peaks. Polyethylene glycol succinate column, 160°C

oil is given in Fig. 2. The limitations of a quantitative examination of a chromatogram such as this include the following :

(*i*) Any of the five peaks due to palmitic, stearic, oleic, linoleic and linolenic methyl esters may hide peaks due to methyl esters of closely allied isomers or other acids or indeed peaks due to other types of chemical compound.

(*ii*) Substances with a much shorter retention time than methyl palmitate, if present, are not separated from the solvent peak.

(*iii*) Methyl esters of high molecular weight acids such as dimers are not shown. (Work at high temperatures has been described whereby methyl esters of dimer acids and even triglycerides such as tripalmitin[15] have been recorded.)

(*iv*) The " linolenic acid peak " is undoubtedly a complex one which would be separated into different constituents by a longer column, especially by a capillary column.

Similarly, mixed stand oils may be examined by GLC. When a mixture of linseed oil and tung oil in the proportion of 3 to 1 is heated on the manufacturing scale, the proportion of eleostearic acid (originally about 20 per cent) falls almost to zero at the time that the property of webbing in a foul atmosphere (burnt coal-gas) is lost. On the other hand, when tung oil is heated alone the property of webbing is retained, and the proportion of eleostearic acid falls only slowly, being still as high as 60 per cent in a 15 poise oil.

For commercially produced oxidised oils the changes in fatty acid composition are less than those that occur in polymerised oils. Evidently the increased viscosities are obtained by reaction of a smaller proportion of unsaturated fatty acid chains than is required in the virtual absence of oxygen.

When drying oils or mixtures of oils are processed, the following generalisation may be made. Except for conjugated acids present in small amounts (less than one-third) in the original oil, then in the final product sufficient of all the monomeric acids remain unpolymerised to indicate the pattern of fatty acid distribution in the starting mixture, i.e. by using GLC to examine an " unknown," the class of triglyceride oil is usually quickly established, and from economic and other considerations the identity of the oil or oils may be deduced.

At the present time there are seven main classes of drying oils used commercially, all with their own characteristic chromatograms. These are :

(*a*) Linolenic rich, namely linseed oil containing about 60 per cent linolenic and 15 per cent linoleic acid.

(*b*) Linoleic rich with some linolenic, namely soya bean oil containing about 60 per cent linoleic and 10 per cent linolenic acid.

(*c*) Linoleic rich with very little or no linolenic acid, namely the seed oils of tobacco, sunflower and safflower.

(*d*) Dehydrated castor oil. There is a characteristic group of three peaks due to isomeric linoleic acids (one is conjugated) with sometimes a trace of ricinoleic acid.

(*e*) The triply-conjugated oils, tung and oiticica. On both polar and non-polar liquid phases eleostearic and licanic acids occur in characteristic positions after the other C_{18} acids (as is shown by their ECLs).

(*f*) Tall oil fatty acids, variable in composition, but characterised by consisting mainly of oleic acid and 9 : 12 linoleic acid together with peaks apparently due to linoleic isomers. There are traces only of palmitic, palmitoleic, stearic and linolenic acids.

(*g*) High iodine value fish oils. The large number of the fatty acids and the high content of palmitoleic acid characterise these oils. Later peaks than that due to linolenic acid are present because of acids having more than three double bonds and 18 carbon atoms.

Even after processing these seven classes of oil usually retain sufficient of their characteristics of composition for a processed oil to be identified by GLC.

An oil that has been dried in air may be considered as a type of processed oil. The fatty acid composition during the earlier stages of drying may be followed by GLC.

Alkali refined linseed oil was flowed out on to glass microscope slides and the films were allowed to dry vertically in air without driers. After two days the films were sticky and after three days were as tack-free and as hard as this oil can become in a few days. After varying times a slide was stripped of its film by the vapour from boiling toluene (cyclohexanone was added for the dry film) and the resultant solution was subjected to methanolysis. Fatty acid compositions were found as in Table II. The linolenic peak had a shoulder which is included in the percentage of linolenic. A small peak of ECL 15.1 was also formed. A clearer picture of the changes is obtained if the figures in Table II are converted to a constant figure for the saturated acids as in Table III.

TABLE II

PERCENTAGE COMPOSITION OF THE MONOMERIC FATTY ACIDS IN LINSEED OIL DURING DRYING

	Palmitic	Stearic	Oleic	Linoleic	Linolenic
Original oil	5.0	3.8	18.0	14.6	58.6
After one day	6.6	4.3	21.0	14.5	53.6
After two days	7.1	4.9	27.5	15.2	45.3
After three days	9.4	5.0	26.9	14.4	44.3

Diethylene glycol adipate liquid phase : 175°C, 1,250 volts, 50 ml/sec.

TABLE III

PERCENTAGE COMPOSITION FROM TABLE II CONVERTED TO CONSTANT SATURATED ACIDS

	Saturated	Oleic	Linoleic	Linolenic
Original oil	8.8	18.0	14.6	58.6
After one day	8.8	19.3	13.3	49.2
After two days	8.8	22.7	12.7	37.7
After three days	8.8	18.7	10.0	30.7

It is interesting and perhaps surprising that even when the oil had reached the " dry " stage, the unpolymerised linolenic content was still one-half that of the original oil.

Alkyds and Oleoresinous Varnishes

When vegetable oils are heated in the presence of resins and other substances which do not react with the fatty acid chains, it might be expected from the results already given for mixtures of vegetable oils that in the final product unaltered saturated and monounsaturated acids are present together with most of the original reactive acids, except conjugated acid when present in minor amounts ; this is borne out by experiment.

Methyl esters of the constituent acids may usually be prepared from alkyds and oleoresinous media by the simple direct methanolysis procedure already described. Preliminary thinning (e.g. with ½ to 1 volume toluene) and warming with the methanolysis reagent is often advisable. If methanolysis is stopped by high acidity then preliminary esterification with methanol using boron trifluoride as catalyst, or with diazomethane if the acidity is due to rosin acids, is necessary. If any glycerol layer separates, it should be removed before washing (which is advised in order to prolong column life) and drying by filtering. The product contains most of the solvents in the original sample.

Pentaerythritol alkyds are methanolised as quickly as glycerol alkyds. The pentaerythritol solidifies after separating, so that the methanolysis procedure is a quick qualitative test for this polyhydric alcohol.

GLC analysis of alkyds has led to the conclusion that during alkyd manufacture less of the reactive monomeric unsaturated fatty acids are lost by polymerisation than during stand oil manufacture (as might be anticipated from the lower temperatures used). In addition, the acids used in the alkyd cook also form methyl esters which can be identified on the resulting chromatogram.

Table IV shows the fatty acid compositions of three laboratory-made glycerol alkyds, one from linseed oil, one from soya bean oil and the other from linseed/soya in the ratio 3/1. The quantitative results, although with a

TABLE IV

PERCENTAGE COMPOSITION OF THE MONOMERIC FATTY ACIDS FROM THREE ALKYDS

	Saturated	Oleic	Linoleic	Linolenic	Others
Linseed alkyd	14	19	13	49	5
Soya alkyd	15	30	40	7	8
Linseed/soya alkyd	11	21	25	38	5
Linseed oil, average	10	20	15	55	—
Soya bean oil, average.. ..	13	23	54	10	—

lower accuracy than usual are sufficient to demonstrate that the proportion of monomeric linolenic acid lost by polymerisation in the linseed oil cook is small, probably less than one-tenth.

Fig. 3 shows the peaks due to methyl esters from a commercial tung oil alkyd. Here the peaks caused by the two isomeric eleostearic acid peaks occupy an area in relation to the total area due to all the fatty acids not much different from the proportion in tung oil itself.

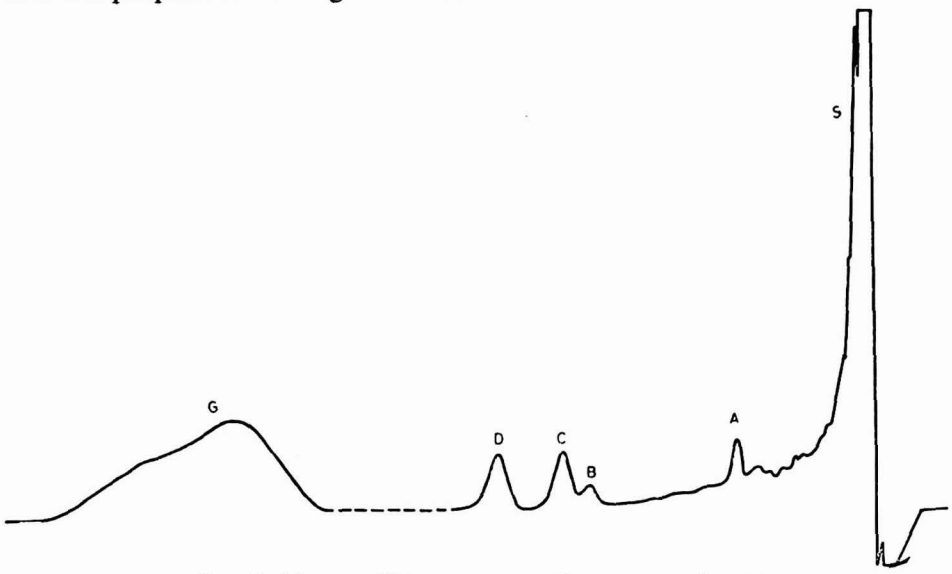

FIG. 3. METHYL ESTERS FROM A COMMERCIAL ALKYD

S, complex solvent peak ; A, palmitic ; B, stearic ; C, oleic ; D, linoleic ; G, α- and β-eleostearic peaks. There is no peak due to dimethyl phthalate. Polyethylene glycol adipate column, 175 °C

Particular note should be made of the peak due to dimethyl phthalate, which for the glycol adipate column used has an ECL of 17.3. Since the area of this peak relative to the total area of the various peaks depends on (*i*) the proportion of phthalic in the alkyd and (*ii*) the proportion of fatty acids not lost by polymerisation (which is related to the extent of the cook), some quite useful information can be deduced from it.

The dimethyl esters of isophthalic and terephthalic acids have different ECL's from that of dimethyl phthalate, so that the particular phthalic acid or other acids used in an alkyd can be readily identified. Methyl benzoate if present appears before the palmitate so that a low temperature chromatogram is required for identification.

The main differences between the two common polyester phases for GLC of unsaturated acids are (*a*) the adipate columns are rather more stable to higher temperatures ; (*b*) the succinate columns have a slightly better resolving power for oleic and stearic peaks. The ECL's of methyl esters for the two liquids are very similar, but for dimethyl phthalate they are quite different. The ECL is about 17.3 on a polyadipate column and 18.7 on a polysuccinate column. Thus in one case the peak due to dimethyl phthalate appears before stearic acid, and in the other, after oleic acid.

Pyrolysis

Several papers have been published on the examination by GLC of the products of pyrolysis of polymers such as polystyrene and polymethacrylate resins, but

very little if any on the applications of pyrolysis to the polymers and other complex products used in the surface coatings industry.

In the experiments to be described a pyrolysis unit available commercially based on that described by Parriss and Holland[16, 17] has been used. Fig. 4 shows the result of a pyrolysis of a medium viscosity linseed stand oil at 600°C for ten seconds followed by passage through a polyester column. The pattern of peaks obtained include a striking set of three close to one another which are also obtained from heat treated tung oil, so that polymerised eleostearate chains are not thereby distinguished from a polymerised non-conjugated system. Nevertheless, it would seem likely that there must be some differences between the pyrolysis products of conjugated and isolated double bond systems which could be recorded and which would be of great use for the analysis of products containing oils.

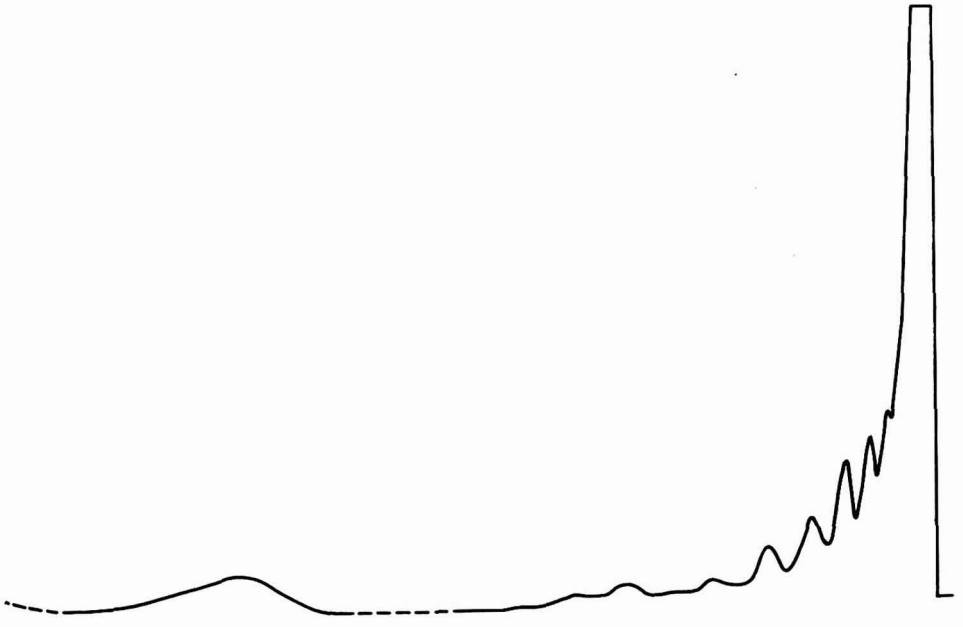

FIG. 4. PYROLYSIS OF A 30 POISE LINSEED STAND OIL

600°C, 10 seconds. Polyethylene glycol adipate column, 175°C

Oil-soluble resins and doubtless most resinous materials give a typical pyrogram after pyrolysis under suitable conditions. Fig. 5 shows the pattern from a coumarone resin. Several peaks are given by phenolic resins, which probably include those of the phenols used in manufacture. Although it is certain that it would be a considerable task to investigate the patterns of peaks given by pyrolysis of the varnish resins, the likely reward would be a quick and certain method of identifying the resin constituents of varnishes. It would seem that the same method would also be useful for the examination of paints and dried films.

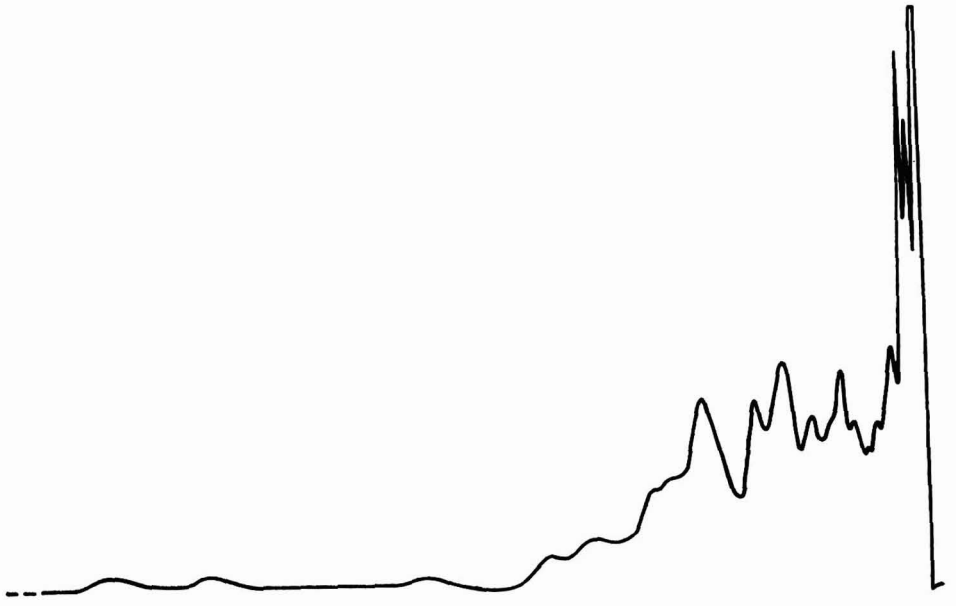

FIG. 5. PYROLYSIS OF A COUMARONE RESIN
600°C, 10 seconds. Polyethylene glycol adipate column, 175°C

CONCLUSION

In conclusion, it can be stated with certainty that, in this paper, only a few of the possible applications of GLC to the field of drying oils, resins and paint media have been described or indicated. There is no doubt that investigations by GLC of free acids, methyl esters and of other compounds from processed media containing oils or resins, and of surface coating materials in general, including partly or wholly dried films, will provide many valuable quick qualitative and semi-quantitative analytical methods useful for technology and for many research problems.

ACKNOWLEDGEMENT

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The Gas Chromatographic Analysis of Residual Oil on Electrolytic Tinplate

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Summary

A method is described for the determination of oil films on electrolytic tinplate. Using gas chromatography microgram quantities of dioctyl sebacate may be quantitatively estimated while the presence of other materials may be established simultaneously.

INTRODUCTION

Electrolytic tinplate, when manufactured, is coated with a minute film of dioctyl sebacate to inhibit rusting and oxidation during storage and to act as a lubricant during subsequent mechanical forming operations. Surface coatings are normally applied to the tinplate without any prior surface preparation.

The concentration of dioctyl sebacate on the tinplate is somewhat variable, 0.1-0.3 g per base box appearing to cover most cases. (A base box is that quantity of tinplate which covers an area of 31,360 sq in. The total surface area therefore being 62,720 sq in.)

Three methods[1] have been used to determine oil film weight. The oldest procedure involving the removal of oil from about 500 in^2 of plate with a suitable solvent in a Soxhlet extractor, evaporation of the solvent and weighing of the residual oil. While the oil recovered in this way is normally 3 to 4 mg, losses and the difficulty in establishing constant weight detract from the value of the method which requires approximately four hours.

To allow a measure of production control a more rapid procedure depending on the spreading of extracted oil on a clean water surface using the Hydrophil Balance[2] has been developed. This uses a small sample of plate and requires less than one hour.

A combination of these two methods has been developed by the *Metal Box Company.*[1] A large sample of tinplate is refluxed with benzene in an extractor ; the extract being concentrated to 5 ml. The extract is directed on to a clean water surface using a microlitre syringe. The quantity of solution which can be applied to the surface before a permanent lens of oil appears forms a measure of the concentration of the extract.

While these subjective procedures are suitable for production control, caution in the interpretation of the oil film values obtained must be made. The ability of the oil to form a film may vary with age and conditions encountered during transportation and storage. As the oil film values are calibrated in terms of the expected oil, contamination on the sheet or material extracted from the apparatus may possibly influence the results.

Where finishing failures have occurred it is desirable to obtain more information than is possible from the above procedures. Using gas chromatography, a procedure is reported where the extracted oil after concentration is estimated quantitatively for dioctyl sebacate while the presence of other materials is indicated simultaneously. Other materials if present may be estimated quantitatively after their identity has been established by using retention data or unambiguously after infrared spectroscopic examination of a sample collected by preparative gas chromatography.

With a gas chromatograph employing an ionisation detector the limits of detection are about 1 ppm while with the newer detectors the sensitivity is even greater.

EXPERIMENTAL

A section of tinplate (50 in^2) was guillotined into 1 in. strips and the oil film extracted with chloroform for two hours in a Soxhlet apparatus. The chloroform extract consisting of about twice the free volume of the extractor was transferred to an evaporation vessel for concentration.

The evaporator described by Riddle[3] and shown in Fig. 1 has been used successfully. With the flask in position one, evaporation on a steam bath was

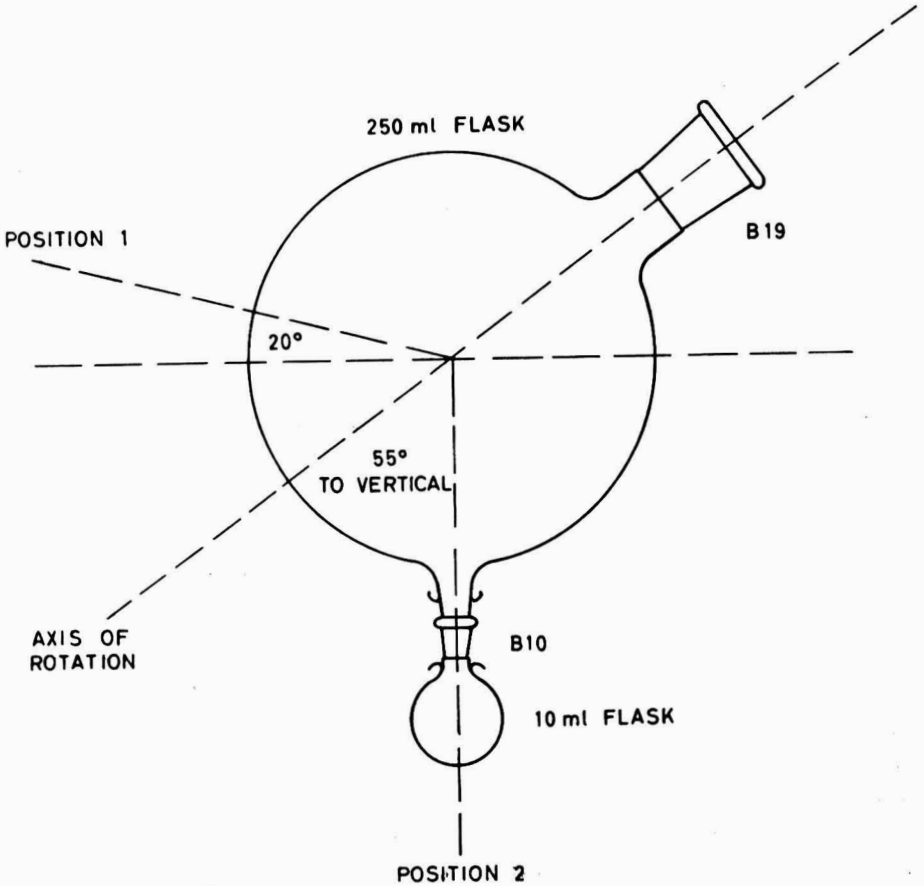

FIG. 1. EVAPORATION VESSEL

continued until a few mls of residue remained, when the flask was rotated to position two and the evaporation continued to about 1 ml. The 5 ml flask was then removed from the larger flask and evaporated to dryness using a jet of air and without heat. A solution for analysis was prepared by the addition of 20 μ l of chloroform from a microlitre syringe. 1 μ l samples of this solution were injected into the gas chromatograph with a 10 μ l Hamilton syringe.

Gas chromatography was carried out using an instrument marketed by *CSR Chemicals Pty. Ltd.* The instrument is fitted with a flame ionisation detector, and a simple, one valve, impedance converter type amplifier feeding a 5 mv, *Leeds and Northrup Model H Recorder*. This instrument has now been replaced by a *Perkin-Elmer Model 800*, which gives considerably improved sensitivity. The column consisted of a 4 ft $\times$ 4.5 mm inside diameter straight glass tube, and was packed with 1½ per cent $\frac{W}{W}$ LAC-IR-196 (diethylene glycol adipate polyester, obtained from *Cambridge Industries Co. Inc.*, 101 Potter Street, Cambridge, Mass.) on 100-120 mesh *Dry-Sil* treated celite 545. Column temperature was 220°C and the injection operated at 300°C. Nitrogen was used as carrier gas at an inlet pressure of 12 lb/in^2 and flow rate of 60 ml/min as measured by the use of a soap bubble flow meter (uncorrected).

Discussion

Calibration is carried out by injecting 1 μ l samples of chloroform solutions of pure dioctyl sebacate. Peak areas are measured with a planimeter and a simple three of four point calibration line drawn. For those cases where the highest accuracy is not desired, a solution of dioctyl sebacate is taken, close in concentration to that of the sample for analysis, and the ratio of the peak areas is used to calculate the dioctyl sebacate concentration in the analysis sample.

Solutions for calibration should be injected on the same day as the analysis is carried out since the polyester stationary phase ages with use and this will effect the quantitative accuracy of the results. The column has a " life " of approximately 100 hours at 220°C before its performance deteriorates noticeably.

Two typical chromatograms are given in Figs. 2a and 2b. Fig. 2a shows a chloroform solution of dioctyl sebacate, while Fig. 2b shows a typical trace resulting from chromatography of a tinplate extract. Note particularly the succession of small peaks following the off-scale solvent peak. This clearly shows the presence of a small amount of mineral oil on the sheet and indicates a major advantage of the gas chromatographic method, that of immediately showing the presence of other contaminants on the surface of the sheet, providing that they are sufficiently volatile. With suitable modifications to the gas chromatographic conditions the method could certainly be extended to hydrocarbon oils and other contaminants on metal sheeting.

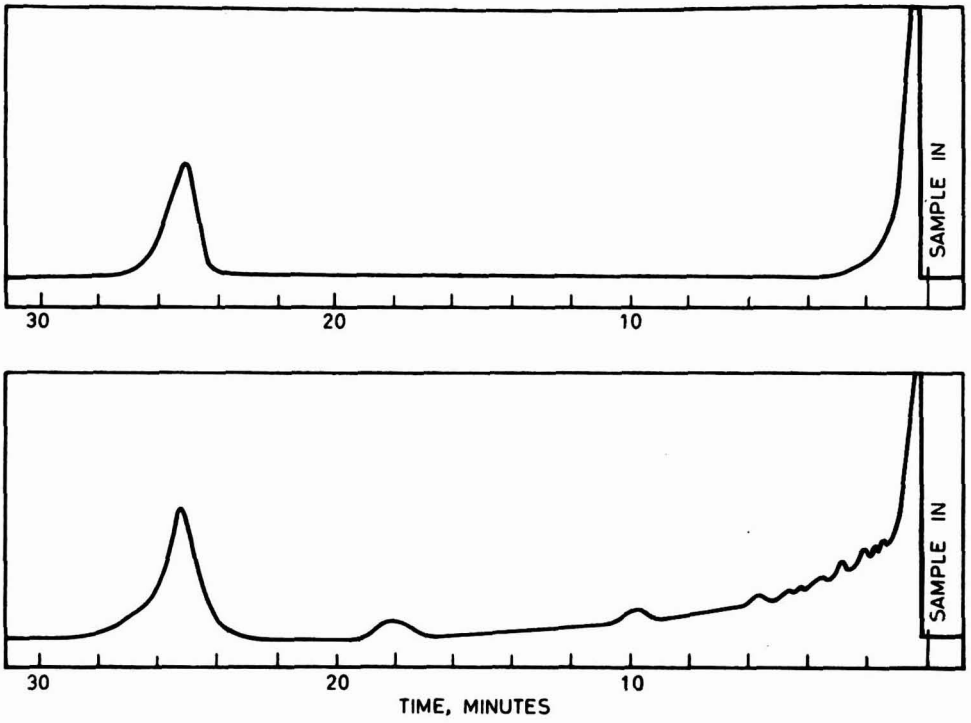

FIG. 2 (*a*). TOP : CHROMATOGRAM OF EXTRACT CONTAINING DIOCTYL SEBACATE ONLY
FIG. 2 (*b*). BOTTOM : CHROMATOGRAM OF EXTRACT CONTAINING MINERAL OIL

The loss of sebacate during the evaporation step is negligible ; a theoretical estimate of this loss using the Rayleigh Equation is shown in the appendix.

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APPENDIX

ESTIMATION OF LOSS OF DIOCTYL SEBACATE DURING EVAPORATION FROM CHLOROFORM

The loss of dioctyl sebacate during evaporation of a chloroform solution at constant temperature may be estimated using an integrated form of Rayleigh's Equation.

$$\log \frac{y_1}{x_2} = \alpha \log \frac{y_1}{y_2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 1$$

x_1, x_2 = Concentration (moles, weight or volume) of solvent at start and completion of evaporation.

y_1, y_2 = Concentration (moles, weight or volume) of dioctyl sebacate at start and completion of evaporation.

$$\alpha = \frac{\text{Vapour pressure of solvent}}{\text{Vapour pressure of solute}}$$

Let the per cent solute lost during a given isothermal evaporation be

$$c = \left(\frac{y_1 - y_2}{y_1}\right) 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

The elimination of y_1/y_2 by combining equations 1 and 2 produces a general equation in terms of per cent solute lost during any given isothermal vaporisation.

$$\log (100 - c) = 2 - \frac{1}{\alpha} \log \frac{x_1}{x_2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

The vapour pressure of dioctyl phthalate at 61°C has been determined by a logarithmic plot of pressure against the reciprocal of the absolute temperature as approximately 0.003 mm and the value of α has been calculated to be approximately 250,000. By evaluation of equation 3 considering a volume decrease of 100 to 1 ml $\left(\frac{x_1}{x_2} = 100\right)$ it is apparent that the value of c is negligible.

Gas Chromatographic Analysis of Solvent Mixtures Using Sequential Application of Solubility and Functional Group Tests

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Summary

The separation of compounds in a solvent mixture cannot be accomplished with certainty by a single gas chromatographic analysis nor can an identification of the peaks obtained be achieved by relying on retention data alone.

A method employing solubility tests and functional group identification is described which, when used in conjunction with retention volume data, allows positive identification.

An index of retention volume data of relevant compounds more extensive than previously reported and determined on columns of different polar properties (dinonyl phthalate and silicone oil) is included.

INTRODUCTION

While a number of workers have described the application of gas chromatography to the identification of solvent mixtures used by the surface coatings industry, it is well known that a positive analysis cannot be obtained by a single gas chromatographic examination.

Whitham[1] supplemented the usual chemical and physical tests by gas chromatography by first examining the sample mixture then fractions obtained by use of the fluorescent indicator absorption technique developed by Ellis and Le Tourneau.[2] Haslam *et al*[3] have used gas chromatography on columns of different polarity and infrared spectroscopy to resolve complex solvent mixtures. Infrared techniques are not successfully applied to multi-component mixtures, but a peak consisting of a single or two superimposed components when trapped out can readily be identified. While the advantages of this procedure conducted on a micro-scale are recorded it has been found that larger samples are usually available. Also infrared spectrophotometry, if available, will not always allow a quantitative determination.

The application of colour reactions to gas chromatographic effluents has been reviewed by Walsh and Merritt.[4] Dubois and Monkman[5] have investigated several colour reactions for the qualitative determination of functional groups and determined the limits of detection of these reactions.

One further scheme[6] involved directing effluent gas on to a strip of a colour reagent mixed with an inert paste which was moved past the outlet tube at the same speed as the recorder chart. In this way, direct visual correlation was made of the location of a particular class of compound in the chromatogram.

In the authors' experience, the preliminary solubility classification not only reduced the need for such extensive examination by colour reagents but also indicated the presence of the very commonly used glycol ethers. These compounds are very difficult to detect by colour tests.

In practice, factors complicating gas chromatographic analysis of solvent mixtures are the wide range of boiling points of the common organic solvents likely to be used and also the widespread use of mixed aliphatic and aromatic petroleum fractions as diluents.

Thus, a typical chromatogram of a solvent mixture containing such a diluent could show at least a dozen peaks, half of them belonging to the complex mixture of paraffins, isoparaffins and aromatics in the diluent.

Programmed temperature gas chromatography was examined by Esposito and Swann[7] for rapid determination of mixtures of simple solvents possessing a wide boiling range, but the presence of commercial hydrocarbon fractions interferes with the unambiguous identification of the component peaks.

Characterisation of thinner mixtures may be greatly simplified by application of a series of solubility tests to the mixture, examining residues in sequence by gas chromatography and observing the effect of the removal of particular classes of compounds from the mixtures. These data then permit accurate interpretation of the identity of the peaks involved by relative retention volume data. The procedure adopted is outlined in Table I and is based on a macro separation scheme developed by Hall[8] where the insoluble fractions were further examined by physical and chemical means.

Hydrocarbon mixtures may be separated from polar solvents, and to some extent the aromatic component of these hydrocarbon mixtures may also be removed. Such mixtures may then be identified as a whole by their characteristic " fingerprint " chromatogram. Detailed study of such material commonly used in Australia has been conducted.[9]

Gas chromatographic analysis was carried out at 130°C using two different stationary phases, dinonyl phthalate and silicone SE30. This temperature provided the most suitable balance between separation of lower boiling components and spreading of peaks of the high boilers. Retention data on the two columns provide a further means of confirming the identification of peaks,[3, 4, 10] but in most cases the dinonyl phthalate column only need be employed.

Use of a thermal conductivity detector enabled simple colour tests to be applied to the effluent gas to differentiate between acetone and ethyl alcohol in the first stages of the chromatogram, as well as to characterise other peaks when necessary.

TABLE I

SOLUBILITY CLASSIFICATION SCHEME

SOLVENT MIXTURE				
				GC Sample
	Extract with 10% brine	Insoluble	All except MeOH, EtOH	GC Sample
	Extract with H_2O	Insoluble	Esters, many alcohols and acetone, hydrocarbons, etc.	GC Sample
		Removed	Water-soluble alcohols and ketones, glycol ethers	
	Extract with 85% H_2SO_4	Insoluble	Hydrocarbon diluents and chlorinated solvents	GC Sample
		Removed	Esters, other alcohols, ketones and "polar" solvents	
	Extract with conc. H_2SO_4	Insoluble	Aliphatic, hydrocarbons and chlorinated solvents	GC Sample
		Removed	Aromatic hydrocarbons and unsaturates	

METHOD

The solubility tests have been conducted on a very small scale and although 10 ml of solvent is normally required for examination this has not seriously affected the applicability of the method.

Three solvent samples of 2.5 ml were each mixed and vigorously shaken with a similar quantity of water, 85 per cent sulphuric acid and concentrated sulphuric acid respectively in 5 ml stoppered graduated cylinders. Smaller vessels may be equally satisfactory but were not available. The samples, after shaking, were allowed to stand and on separation the residue examined. The treatment with 85 per cent sulphuric acid was conducted by a gradual addition of acid and continual cooling under running water. Under these conditions aromatic and unsaturated hydrocarbons are essentially unaffected and trials on larger samples have shown that reproducibility of about 1 per cent is normally encountered. The effect of these solubility tests on the compounds for which retention data are available is shown in Table II. Solvents of low water solubility are shown in the table as insoluble while partially soluble materials are shown as per cent soluble at 20°C. By variation of acid strength removal of olefins

can be achieved within reasonable limits, as described by Ashton,[11] but the separations are incomplete and the test is not specific. Trials with mixed hydrocarbons have shown that errors of 5-10 per cent are experienced.

A simple gas chromatograph (*Shimadzu GC-2B*) using a hot wire detector was used in conjunction with a *Leeds & Northrup Speedomax G Recorder*. A modified injection system employing a rubber septum was necessary as the bulk sampling device was unsatisfactory. The operating conditions used are shown below.

Bridge current	200 mA.
Oven temperature	130°C.
Injection block temperature	150°C.
Gas flow	40-50 ml/min. helium.
Inlet pressure	10 lb/sq in.
Columns	6 ft $\frac{1}{8}$ in ID copper.
Column packings	25 per cent dinonyl phthalate and 25 per cent silicone SE30 respectively on 40-50 mesh acid washed *Celite*.
Chart speed	40 in/hour.

The comparative properties of the columns used are as follows :

	DNP	*SE30*	*Ref.*
Theoretical Plates $N = 2\pi\left(\frac{h\,x}{area}\right)^2$ (Benzene)	860	510	12
$N = 16\left(\frac{x}{w}\right)^2$	560	350	13
Effective Peak Number EPN $= \frac{2_{\Delta}x - (w_a + w_b)}{(w_a + w_b)}$ Benzene/toluene	3.5	4	14

The notation used is shown in Fig. 1.

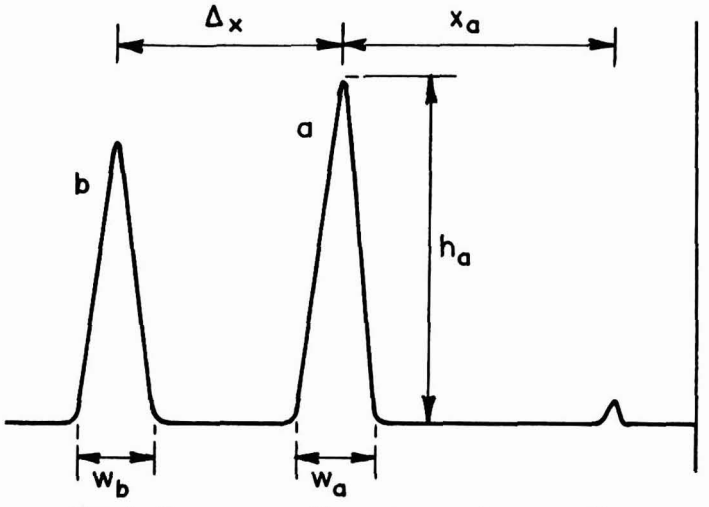

FIG. 1. COMPARATIVE PROPERTIES OF COLUMNS USED

The oven temperature of 130°C has given good results over the wide-boiling range of solvents likely to be encountered. While this is higher than temperatures more commonly used, the response of the thermal conductivity detector was improved for compounds with high boiling points and the conditions were also selected so that the spread of these peaks was kept to a minimum while the peaks of low boilers were not eluted so rapidly that excessive superimposition occurred.

The identification can be made by determination of relative retention volumes or for routine work it is preferable to adjust the gas flow slightly such that the elution time of benzene always occurs at the same time. In this way a direct visual comparison with previous examinations can be made which is invaluable in the identification of " fingerprint " chromatograms of various hydrocarbon fractions.

The sample size normally used is 0.2-5.0 μl, quantitative determinations are made by comparison of peak areas. The sample size for each injection may be varied according to the proportion of insoluble residues recovered from each solubility characterisation or else a constant volume may be used. The principal value of the former is that a rapid visual appreciation of the effect of each operation on individual components is achieved.

The accuracy of the method has been found to be 1-2 per cent, which is quite satisfactory for the majority of purposes. By comparison with a mixture or mixtures prepared on the basis of the analysis the accuracy can be vastly improved.

A recent index of chromatographic data prepared by McWilliam[15, 16] indicates that comprehensive lists of retention data for many common solvents are not readily available and so retention volumes determined on the two columns are shown in Table II.

Confirmatory colour reactions were applied to the effluent gas mixture by passing it through a stream splitter of negligible volume to avoid intermixing of components and into micro-tubes containing test solutions. Whenever a positive result was obtained, the set of reagents was immediately replaced by a fresh set so that the presence of similar compounds with greater retention times would not be masked.

Compounds giving significant response to the tests adapted from Dubois and Monkman are classified in Table II as follows :

A. Alcohols

Reagent : 10 per cent solution of ceric ammonium sulphate in water.

K. Ketones

Reagent :	2 : 4-dinitrophenylhydrazine	2 g.
	Conc. sulphuric acid	4 ml.
	Methyl alcohol	30 ml added carefully.
	Water	10 ml.

C. Chlorinated Hydrocarbons

Beilstein test (green coloration imparted to a flame). This test is applied to a small sample of the solvent residue which was insoluble in conc. sulphuric acid.

TABLE II

	BP (°C)	Solubility* Classification	Confirmatory colour reaction	Relative retention volume Benzene = 1.0	
				DNP	SE30
Alcohols					
Methanol	64.5	1a	A	0.190	0.150
Ethanol	78.3	1a	A	0.294	0.234
Isopropanol	82.3	1	A	0.354	0.308
tert-Butanol	82.5	1	A	0.430	0.380
Allyl alcohol	97	1	A	0.616	0.045
n-Propanol	97.2	1	A	0.562	0.440
sec-Butanol	99.5	1 (18%)	A	0.735	0.650
Isobutanol	107.2	1 (9%)	A	0.730	0.590
n-Butanol	117.7	1 (8%)	A	1.180	0.805
2-Methyl butanol	129.8	2	A	1.920	1.31
n-Pentanol	138	2	A	2.280	1.54
4-Methyl-2-pentanol	139	2	A	2.95	2.10
2-Ethyl butanol	147	2	A	3.66	2.33
2-Methyl-1-pentanol	148	2	A	3.30	2.20
n-Hexanol	157	2	A	4.23	2.79
Cyclohexanol	161	2	A	5.18	3.29
Pentoxol	165	1	A	6.40	4.13
n-Heptanol	172	2	A	7.9	4.7
Di-iso-butyl carbinol	178	2	A	9.45	5.58
2-Ethyl hexanol	184	2	A	11.0	6.80
Ketones					
Acetone	56.1	1	K	0.364	0.327
Methyl ethyl ketone	79.6	1 (27%)	K	0.690	0.585
Di ethyl ketone	102.7	2	K	1.27	1.10
Methyl n-propyl ketone	102.3	2	K	1.21	1.04
Methyl iso-butyl ketone	116.2	2	K	1.67	1.37
Methyl n-butyl ketone	127.2	2	K	2.03	1.75
Mesityl oxide	128.3	2	K	2.69	1.84
Methyl iso amyl ketone	144.7	2	K	3.56	2.65
Ethyl butyl ketone	147.6	2	K	2.40	1.84
Methyl n-amyl ketone	151.4	2	K	3.45	3.00
Cyclohexanone	156.7	2	K	5.51	3.47
Pentoxone	160	1 (28%)	K	5.32	3.59
Ethyl n-amyl ketone	168	2	K	4.30	3.15
Di-iso-butyl ketone	169.4	2	K	6.30	4.86
Di acetone alcohol	169.2	1	A, K	5.00	2.42
Isophorone	215.2	2	K	25.4	11.4
Esters					
Methyl formate	31.5	1 (30%)	—	0.191	0.232
Ethyl formate	54.3	1 (8%)	—	0.368	0.346
Propyl formate	81.3	2	—	0.707	0.666
Butyl formate	106.8	2	—	1.39	1.23
Methyl acetate	57.1	1 (32%)	—	0.390	0.334
Ethyl acetate	77.2	1 (9%)	—	0.629	0.594
Isopropyl acetate	89	2	—	0.760	0.810
n-Propyl acetate	101.6	2	—	1.130	1.07
sec-Butyl acetate	112	2	—	1.42	1.46
tert-Butyl acetate	98	2	—	0.975	0.940
Isobutyl acetate	116.5	2	—	1.44	1.40
n-Butyl acetate	126.5	2	—	2.14	1.92

TABLE II—*Continued*

	BP (°C)	Solubility* Classification	Confirmatory colour reaction	Relative retention volume Benzene=1.0	
				DNP	SE30
n-Amyl acetate	148	2	—	3.90	3.30
Methyl propionate ..	79.9	1 (7%)	—	0.716	0.680
Ethyl propionate ..	99.1	2	—	1.07	1.04
Isopropyl propionate ..	111.3	2	—	1.28	1.30
n-Propyl propionate ..	123.4	2	—	1.94	1.82
Methyl *Cellosolve* acetate	144.5	1	—	3.10	2.35
Cellosolve acetate ..	156.4	1 (23%)	—	3.82	3.06
Butyl *Cellosolve* acetate ..	192.2	2	—	9.20	7.50
Allyl acetate	103	2	—	1.10	1.00
Ether compounds					
Ether	34.6	2	—	0.256	.320
n-Propyl ether	91	2	—	0.800	0.980
n-Butyl ether	142.2	2	—	2.55	3.12
Propylene oxide	35	1 (60%)	—	0.281	0.274
1, 4-Dioxane	101.5	1	—	1.41	1.13
Methyl *Cellosolve* ..	124.6	1	A	1.11	0.695
Cellosolve	135.6	1	A	1.69	1.16
Isopropyl *Cellosolve* ..	142	1	A	2.30	1.61
Butyl *Cellosolve*	171.1	1	A	5.37	3.63
Methyl *Carbitol*	194	1	—	4.60	3.25
Carbitol	201	1	—	6.35	5.44
Butyl *Carbitol*	230	1	—	10.5	12.45
Hydrocarbons					
Aromatic					
Benzene	80.1	3	—	1.00	1.00
Toluene	110.6	3	—	1.94	1.86
Ethyl benzene	136.2	3	—	3.38	2.93
o-Xylene	144.4	3	—	4.42	3.54
m-Xylene	139.1	3	—	3.64	3.08
p-Xylene	138.4	3	—	3.70	3.12
Aliphatic					
n-Pentane	36.1	4	—	0.228	0.354
n-Hexane	68.7	4	—	0.414	0.650
n-Heptane	98.4	4	—	0.820	1.22
n-Octane	125.7	4	—	1.55	2.19
n-Nonane	150.7	4	—	2.87	3.60
n-Decane	174.0	4	—	5.23	6.40
n-Undecane	195.8	4	—	9.30	10.5
Isohexane	58.0	4	—	0.361	0.61
Isooctane	99.0	4	—	0.805	1.18
Cyclohexane	80.7	4	—	0.775	1.07
Trans-decalin	185	4	—	9.18	9.10
Cis-decalin	195	4	—	11.86	11.3
Chlorinated hydrocarbons					
Methylene chloride ..	39.8	4	B	0.487	0.33
Chloroform	61.7	4	B	0.873	0.65
Carbon tetrachloride ..	76.5	4	B	1.230	0.98

*Solubility classification : 1. Soluble in water. 1a. Soluble in brine. 2. Soluble in 85 per cent sulphuric acid. 3. Soluble in concentrated sulphuric acid. 4. Insoluble in concentrated sulphuric acid.

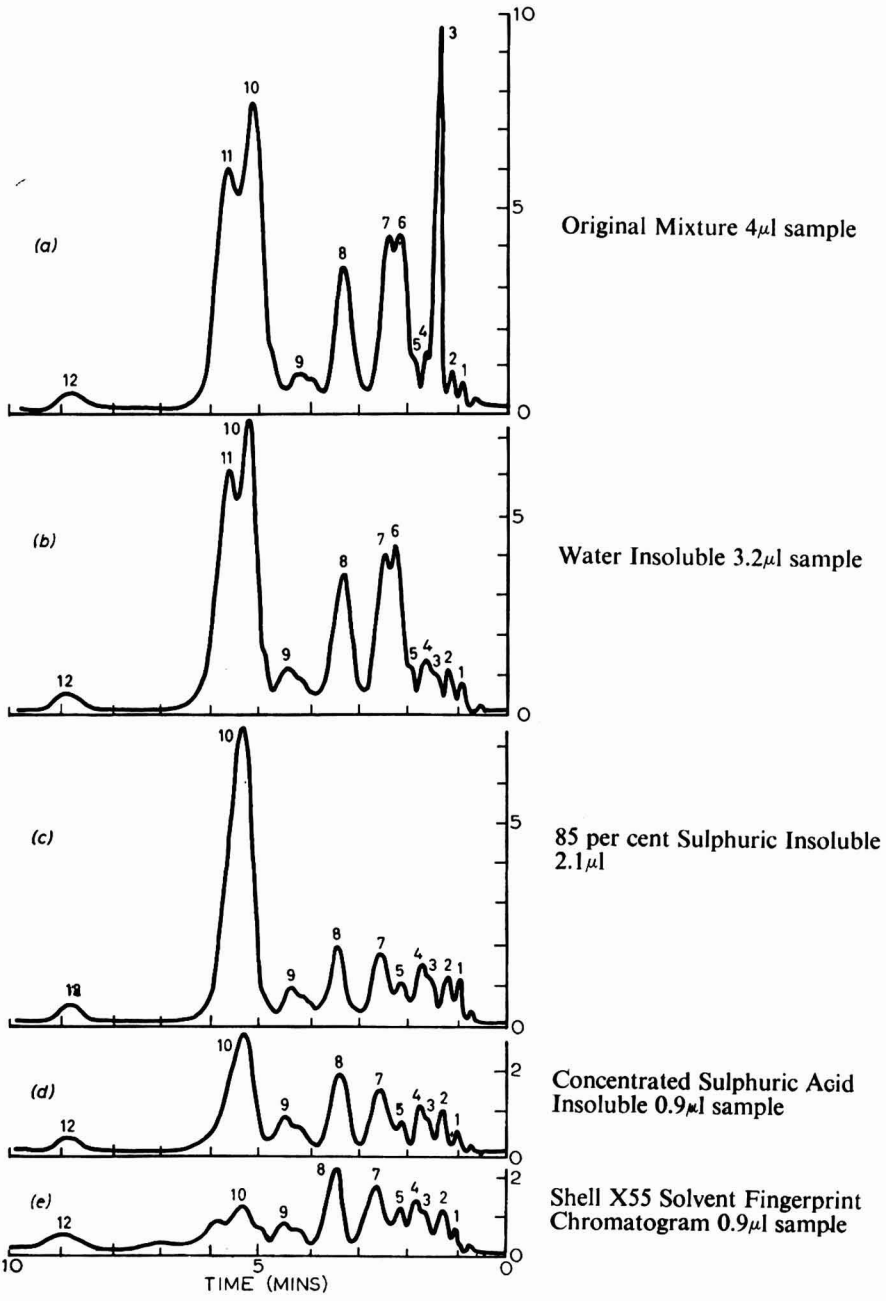

FIG. 2. GAS CHROMATOGRAMS OF SOLVENT MIXTURES SHOWING EFFECTS OF SEQUENTIAL SOLUBILITY EXAMINATION

EXAMPLE

The solvent mixture used by Hall[8] was analysed according to the sequential solubility method with the following results :

Solvent	Percentage soluble	Percentage residue	Sample for GC (Original mix=4μl)
H_2O	13	77	3.2
85 per cent H_2SO_4	48	52	2.1
Conc. H_2SO_4	70	30	0.9

The chromatograms obtained are shown in Fig. 2, the curves being :

(*a*) Original solvent mixture.

(*b*) Elimination of water solubles with removal of peak 3 and a change in peak 7.

(*c*) Elimination of 85 per cent H_2SO_4 solubles with removal of several more substances at peaks 6, 7, 8 and 11.

(*d*) Extraction with conc. H_2SO_4 resulted in a large decrease in peak 10 and a slight effect on peak 12.

Interpretation of these results from the tables of relative retention volumes enabled the peaks to be identified as 3, ethyl alcohol ; 6, ethyl acetate ; 7, methyl ethyl ketone ; 8, n-butyl alcohol ; 10, toluene ; 11, butyl acetate ; and 12, a trace of the isomeric xylenes.

The remaining peaks were the components of a hydrocarbon mixture.

(*e*) By examination of a reference collection of typical fingerprint chromatograms of more commonly used commercial petroleum fractions, Shell X55 was selected as the most likely solvent and a check run of comparative sample size confirmed this. (An apparent discrepancy in (*d*) in the proportion of toluene remaining is explained by the incomplete extraction of this compound by conc. H_2SO_4.[11])

Each component was then estimated quantitatively by comparison of peak areas with reference chromatograms.

TABLE III

DETERMINATION OF SOLVENT COMPOSITION

Composition		Hall's Method	Solubility Classification and GC
Ethanol	10.0	10.0	10.2
n-Butanol	7.0	8.8*	7.1
Ethyl acetate	6.0	5.4	6.2
n-Butyl acetate	20.0	20.6	20.3
Methyl ethyl ketone	5.0	5.0	5.1
Shell X55	27.0	26.7	25.0
Toluene	25.0	23.5	26.0
		100.0	99.9

*Determined by difference.

ACKNOWLEDGEMENTS

The authors wish to thank *Union Carbide Aust. Ltd.*, *Shell Chemical (Aust.) Pty. Ltd.* and *CSR Chemicals Pty. Ltd.* for supplying samples of their principals' products.

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Review

ANALYSIS AND CHARACTERIZATION OF OILS, FATS AND FAT PRODUCTS. VOL. I

By H. A. BOEKENOOGEN (Editor). Interscience Publishers, 1964. Pp. xii+421.

Introducing this book, the editor expresses the intention of publishing from time to time a number of chapters on certain topics of an analytical nature for the benefit of those engaged in the investigation of fats in the widest possible sense. Of the nine contributions by different authors presented here, only four deal with analytical techniques as such and the remainder with their application to specific problems. Although the publication of miscellaneous collections is not uncommon nowadays, the policy has certain disadvantages when the various subjects discussed have an important theme in common. Here we have a rather curious position in which the second chapter—on the assay of essential fatty acids—pays scant attention to the thiocyanogen method so strongly recommended in the first, and completely ignores the possibility of separating cis and trans isomers by means of their urea inclusion compounds described in the third. Indeed, it is difficult to understand why this contribution was included in the first volume at all, in spite of its general excellence. It would have been expected that such important topics as absorption spectroscopy and the various chromatographical techniques would have been dealt with first in separate chapters, rather than merely as a means of determining the essential fatty acids. Another chapter which appears to be out of place describes attempts to estimate foots in linseed and other oils. After pointing out the inadequacy of the methods included in various official specifications and leaving the reader in some doubt as to what it is that has to be measured, a number of abortive attempts to solve the problem are described. It would have been better to have waited until a generally acceptable method had been found.

The type of treatment accorded by the various authors to their subjects is by no means uniform. The more useful chapters are extremely well written and, after giving a general introductory survey, describe methods of analysis in terms giving the impression that they have been selected as the result of long practical experience. Judged from this point of view, those dealing with the assay of essential fatty acids, the application of urea inclusion compounds, dilatometry of fats and the analysis of monoglyceride and related emulsifiers can be warmly recommended. A short chapter on nuclear magnetic resonance spectra fails because it gives no descriptions of the apparatus and techniques employed in producing the spectra.

A chapter on the use of ion-exchangers for the analysis of detergents would have been recommended had it been written in a clearer style. The author is not completely at home with the English language and to follow his argument sometimes requires more than the usual amount of concentration. Considering that only two of the contributions are written by English-speaking authors it is pleasing to note that this defect is noticeable only in two others. A certain quaintness of style is not altogether unacceptable, but when it leads to obscurity

or confusion it must surely detract from the value of the work. In the chapter on the classical chemical methods in fat analysis it has led to palm oil being confused with palm kernel oil on more than one occasion, and to the extraordinary statement that the calculation of the acid value is based on the molecular weight of a given fatty acid or fatty acid mixture. This contribution can also be criticised on the grounds that too strong a bias has been shown towards the work of one particular school of fat chemistry, with which the author was once associated. Readers who may be deterred by a formidable list of references, more than two-thirds of which are to journals in languages they cannot understand, may find it profitable to consult the first volume of any of the editions of Lewkowitsch published at the turn of the century and still to be found on the shelves of many libraries. The language difficulty does not seriously affect the clarity of a chapter on the analysis of butter and cheese, but the authors use too much space with subjects like the estimation of moisture, fat, solids-not-fat, etc., which are important in dairy chemistry but have little general interest, and too little on the determination of composition and detection of adulteration which are problems common to other industries. Their suggestion that the fatty acid composition of butter fat, and even the glyceride mixture occurring in it, might be simulated by the admixture of materials derived from other sources is an intriguing one which ought to have been developed further.

A publication which sets out to present information to assist both industrial analysts and research workers to keep abreast with progress made by their opposite numbers should itself be up-to-date. A study of the references contained in this volume suggests that most of the chapters were completed in 1960 at the latest. Although an opportunity was doubtless given for last-minute adjustments, these can never really compensate for any serious loss of time. On the whole, the book is well produced and contains much valuable information of an assorted character. It is to be hoped that at least some of the weaknesses noted will not be repeated in subsequent volumes.

M. R. MILLS

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.)*

GLOVERS CHEMICALS LTD. have sent us a booklet describing their range of anionic surface active agents.

The Secretary of State for Scotland, The Rt. Hon. Michael Noble, M.P., opened the new factory of BJN PAINTS (SCOTLAND) LTD. on 11 May. The factory situated at East Kilbride, Lanarkshire, replaces the old factory in Forbes Street which has been zoned as a new housing area.

BASF AG have introduced a 25 per cent plastic emulsion called *Latekoll D* that can be converted into a clear highly viscous liquid solution by the addition of ammonia. The Company reports that its main features are the yielding of emulsion paints with high resistance to water and that it prevents or reduces the formation of serum.

From ANDERMAN & CO. LTD. we have received the catalogue of gas chromatographic chemicals produced by E. MERCK.

EDITORIAL COMMENT

Powder Coatings

The current " State of the Art " of any newly developed product is often difficult to determine. Shell Chemicals have, by their recent demonstration at their Technical Service Laboratories at Egham, done their best to remedy this in the case of Powder Coatings, their application and performance.

Laboratory tests designed to show the outstanding chemical resistance of this type of product were exhibited by Shell themselves, and they enlisted the aid of the manufacturers of equipment who demonstrated the current and development plant used for electrostatic spraying and fluidised bed application.

Examples of electrical equipment, expanded metal grilles and pipes coated by this technique were available for examination, the powder coatings used being supplied by various paint companies and applied by trade enamellers.

All in all a well-balanced picture of a product which will undoubtedly gain an important place among the heavy duty surface coatings in the next few years.

New South Wales Section

What Can the Paint Industry Provide? Architects and Engineers State Their Requirements

The April meeting of the New South Wales Section was held in conjunction with the Royal Australian Institute of Architects and the Australian Institute of Engineers.

The three speakers, Mr. W. Lucas (Architects), Mr. C. Putt (Engineers) and Mr. A. E. Cameron (OCCA), each spoke on the above topic from the viewpoint of his profession. Afterwards Mr. D. M. Martin (OCCA) joined them to form a discussion panel to answer questions from the audience.

Mr. Lucas criticised what he considered the paint industry's preoccupation with purely decorative coatings for visual effect, sales advertising and frequent changes in colour trends causing unnecessary repainting, to the exclusion of developing other properties, e.g. sound absorption, flame retardance, solar absorbence, etc. Modern architects are showing a tendency to use material not requiring painting (timber, copper, aluminium, brick, stone, etc.) because paint performance is not good enough.

Mr. Putt, speaking on maintenance problems with ferrous metals, considered that a more sophisticated and more highly capitalised approach to industrial painting is needed in Australia. More emphasis must be placed by paint manufacturers on advising clients of the correct procedure of surface preparation, the proper paint for the job, and the correct system at the right film thickness. Insufficient rigid recommendations are given. The industrial customer wants protection from corrosion, and in most cases all he is getting is paint. Mr. Putt considers that it would be appropriate for the paint industry to take the leading part in ensuring correct industrial application of their products.

Mr. Cameron spoke on the efforts of the paint industry to educate builders and architects on what paints are available and how to use them, of the lack of training of engineers and architects on protective coatings and of the inadequacy of painting specifications on even the largest building projects. Mr. Cameron suggested that poor initial design in buildings and plant often caused maintenance problems.

An interesting discussion followed, in which some of the questions posed were : (*a*) " What is the paint industry doing to provide a satisfactory clear finish for exposed timber ? " (*b*) " Why do paint manufacturers change a product which a customer may have been using satisfactorily for some time ? Why not print an accurate analysis on the label ? " (*c*) " Do engineers use the right materials, as probably the inclusion of as little as 0.4 per cent Ni to mild steel could vastly improve corrosion problems ? "

L. J.

Victorian Section

Static Hazards in the Paint Industry

The April technical meeting of the Victorian Section was held in the Union Hall, University of Melbourne, when Mr. John Cordner spoke to 79 members on " Static Hazards in the Paint Industry."

The oil and petrochemical industries have given the lead to other manufacturers in studying this problem, prompted by such major accidents as the explosion and fire at a petrol tanker in Dusseldorf just prior to the last war, when 34 people were killed. This was directly attributed to a flash from static electricity discharge.

Static electricity belied its name because by nature it was a dynamic force. An electrical double-layer formed at the junction of any two dissimilar materials and when these were separated a static charge built up. The hazard only occurred when

this voltage became very big and a discharge took place. It should be remembered that materials normally thought of as insulators could store up large amounts of static electricity ; for example, plastic materials.

Three conditions must be satisfied for a hazard to exist : (1) An explosive atmosphere must exist. (2) An accumulation of charge must take place. (3) A sufficient potential gradient must build up to ionise the gas in the vicinity of the charge, to allow discharge to take place.

The obvious counters to these conditions were : (*i*) Careful factory practice—adequate ventilation, use of inert gas blankets. (*ii*) It was impossible to avoid generating a charge, but static earthing and certain other measures could prevent the charge accumulating. (Fine solid particles are a particular hazard because of their high specific area.) (*iii*) A radio-active source could be used to ionise the adjacent air to a point where a continuous, safe discharge takes place.

In handling solids, large static charges accumulated during mixing, grinding or pouring. An instance was cited of a point discharge occurring at an imperfection in a sheet of plastics film over which powder was moving.

Liquids built up charges during operations such as pumping, filtration and agitation. Sampling of tanks of inflammable liquids should be delayed for a time after any of these operations in order to avoid static flash to the sampler. The settling of solids in liquids had been known to build up high static voltages. The mixing of dissimilar liquids could also be a static source and the agitation of emulsions was a particularly serious hazard.

The most effective remedy to combat static electricity was to use efficient earthing. Conductors should be massive to provide a path of low resistance and to minimise loss of efficiency by corrosion. Moving parts must be earthed by means of a separate brush and collector ring, as grounding through bearings is inefficient. Portable earth leads should clamp tightly to equipment ; screw clips were not desirable. Danger points to watch for which could defeat static earthing were localising of earthing by paint, plastic gaskets and rust.

The lecture was comprehensively illustrated by a colour film showing the build-up of static charges in liquids, solids and gases, the effect of subsequent discharges and the means of avoiding them.

At question time, Mr. Cordner made the following comments :

It was possible that some paints could be made conductive by incorporating polyethylene glycol in them, but the speaker had no personal experience of this. One of the simplest and most effective ways of detecting static electricity build-up was the gold-leaf electroscope of school physics days. This will readily detect a potential of 500 volts, which was not a dangerous pressure. No minimum voltage could be specified as the danger threshold to cause ignition of hydrocarbon vapour, as this would also be influenced by factors such as the physical shape of the object collecting the charge ; but partial ionisation of air takes place at 5,000-20,000 volts and hence a flash became possible in this region. Below 5,000 volts an induced corona discharge could leak the charge safely away. As early as 1898 it was realised that magnesium oleate could be added to an inflammable liquid in order to prevent static build-up, but the dosage required was massive. It was unlikely that organo-metallic driers in a paint system would be present in sufficient quantity to perform a similar function. Current anti-static liquids were usually chromium organic acid complexes such as chromium dialkyl salicylate. The case quoted by a questioner, the pumping at high speed of de-ionised water through polyethylene piping, was considered by Mr. Cordner to be a textbook example of a set-up to generate large quantities of static electricity, both materials being insulators and difficult to earth.

The trouble would, of course, occur at the discharge point. The lecturer agreed that the liberal use of water in a paint company had probably contributed to the rarity of static fires in the industry, but cautioned his audience not to become complacent because of their good record to date in Australia, as the danger still existed and was very real.

In thanking the lecturer for his talk, Mr. C. Bray quoted the familiar example of static electrical build-up on the driver of a car in very dry weather. However, he felt reluctant to avoid the unpleasant shock from static discharge he experienced when he subsequently touched a metal component of the car, by dragging an anti-static belt behind his vehicle and driving with anti-static boots on.

The long question period and the presence of many visitors at the meeting attested to its importance and excellent presentation.

D. W. B.

SEVENTEENTH TECHNICAL EXHIBITION 1965

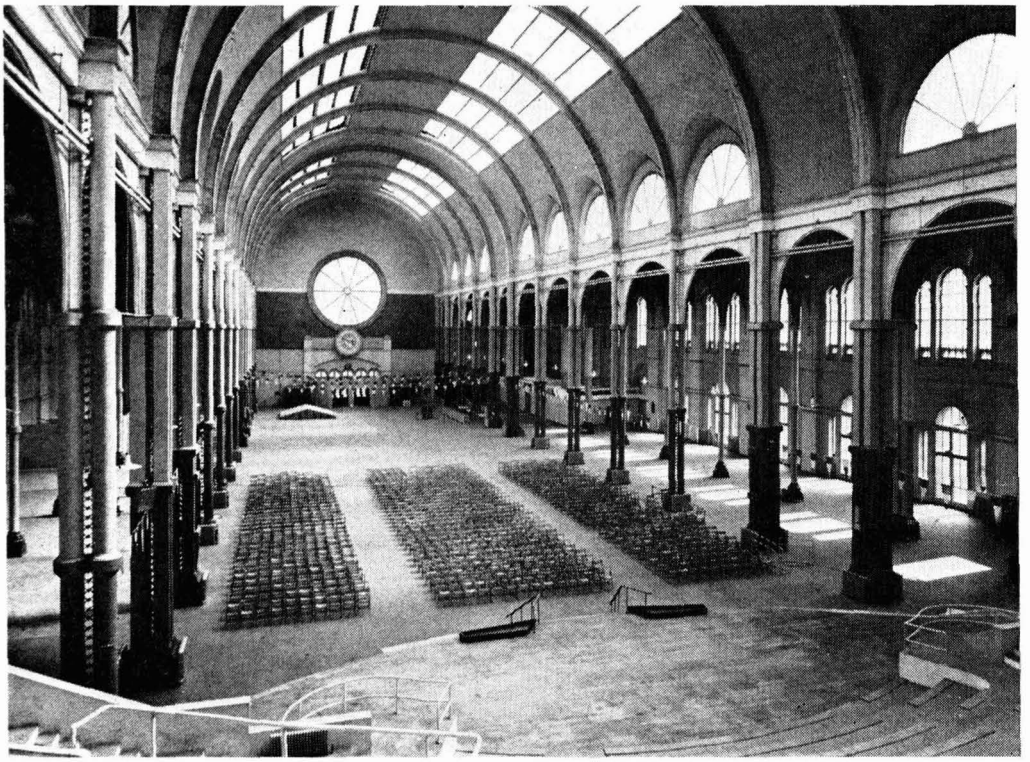

Photo by *Leslie Bryce, A.I.B.P., A.R.P.S.*

THE GREAT HALL OF ALEXANDRA PALACE

NEW VENUE AND LONGER EXHIBITION PERIOD FOR 1965

The growth in popularity of the Exhibition, which is one of the most important annual events for the surface coating industries amongst both exhibitors and visitors, has been so marked in recent years that it has been necessary to curtail the size of stands in order to accommodate all the companies whose applications were received by the closing date (in the preceding September), and many visitors have expressed the wish that the Exhibition should be open for a further day.

The Exhibition Committee has also taken into consideration the difficulties which arose in the preparation of the 1964 Exhibition because of the unofficial ban on overtime operated by carpenters, painters and labourers, which naturally meant that the weekend build-up period was lost; the Committee feels that exhibitors would therefore welcome a longer build-up period before the weekend.

Accordingly, the Committee has made arrangements for the 1965 Seventeenth Technical Exhibition to take place at Alexandra Palace, London, on the following dates and times :

Monday 22 March ..	3.00 p.m.-6.30 p.m.
Tuesday 23 March ..	10.00 a.m.-6.00 p.m.
Wednesday 24 March	10.00 a.m.-6.00 p.m.
Thursday 25 March	10.00 a.m.-6.00 p.m.
Friday 26 March ..	10.00 a.m.-4.00 p.m.

Photo by *Leslie Bryce A.I.B.P., A.R.P.S.*

A CORNER OF ONE OF THE TWO RESTAURANTS AT ALEXANDRA PALACE

The Committee is pleased that it has been able to arrange continuity of tenure at Alexandra Palace so that the Exhibition will take place in March each year.

It is felt that by extending the Exhibition for an additional day, this will not only allow overseas visitors greater time to visit the stands, but will also allow more companies in the United Kingdom an opportunity to arrange for their technical personnel to visit the Exhibition in rotation.

From the exhibitors' point of view, two of the advantages of the new arrangements will be that all contractors for interior fitments will be able to enter the Hall on the Thursday preceding the Exhibition and also that all the stands will be accommodated in the Great Hall.

There are ample free car parking facilities available at Alexandra Palace and the journey by road from Central London is relatively easy. Alexandra Palace occupies a commanding position high on the North London hills and is less than two miles from the North Circular Road and only four miles from Euston. A free bus shuttle service will be operated from Wood Green Station on the Piccadilly Underground Line to and from Alexandra Palace ; the journey from Central London to Wood Green takes approximately 18 minutes. Visitors arriving at the West London Air Terminal can board the Piccadilly Line trains at Gloucester Road Station. Those arriving at main line stations will also find it is not a difficult journey and a map will be included in the *Official Guide* showing main line, Underground and bus services, together with suggested routes for those travelling by car.

There are adequate catering facilities at Alexandra Palace and there are two

restaurants with full dining facilities, together with two buffets and several bars.

The Exhibition Committee wishes to make known as widely as possible the rules governing participation in the Exhibition, which exhibitors agree to accept when sending in their application forms. The rules state that companies exhibiting shall present technical advances in the paint, printing ink and allied industries relating to :

(*i*) New products ;

(*ii*) New knowledge relating to existing products and their use ; or

(*iii*) In suitable cases, existing knowledge which is not generally available in the consuming industries.

The Committee stipulates that exhibitors should present a technical theme, that is, to display in a technical manner the technical developments in raw materials, plant or apparatus illustrated by experimental evidence. Furthermore, it is a feature of the Exhibition that technically or scientifically trained people should be available on the stands throughout the official hours of opening.

Copies of the *Invitation to Exhibit* and application forms have already been dispatched to companies both in the United Kingdom and on the continent of Europe ; applications for stand space must be returned to the General Secretary by **Wednesday 9 September 1964.**

There will be no charge for admission and copies of the *Official Guide* will be available without charge both prior to the Exhibition and at Alexandra Palace. All members of the Association, wherever resident, will be sent a copy of the *Official Guide* as soon as these are available early in 1965. It is felt that members appreciate receiving copies of the *Official Guide* well in advance of the Exhibition dates in order that they can plan their itineraries. Copies of the *Official Guide* will also be sent to paint and printing ink companies in the United Kingdom and individually to scientists and technologists on the continent of Europe. Any non-member, company, or organisation wishing to receive a copy of the *Official Guide* before the Exhibition should notify the General Secretary before the end of the year.

It was particularly gratifying to the Committee to learn that the visitors to the Sixteenth Technical Exhibition included representatives from at least 30 countries. The countries recorded in the overseas visitors' books on the OCCA information stands were Argentina, Australia, Belgium, Canada, Denmark, Egypt, Eire, Finland, France, Germany, Holland, Hong Kong, Hungary, India, Italy, Japan, Jordan, Jugoslavia, New Zealand, Nigeria, Norway, Pakistan, Poland, Portugal, South Africa, Spain, Sweden, Switzerland the USSR and the United States.

A feature of the Exhibitions, which will be repeated at the Seventeenth Technical Exhibition, has been the stand devoted to Technical Education, on which information on technical courses and careers will be available. The Committee has decided once again to invite parties of sixth form science students to visit the Exhibition, when they will be given short introductory lectures by members of the Association.

An Exhibition Luncheon will be held at the Savoy Hotel, London, W.C.2, on Monday 22 March, prior to the Opening Ceremony. So popular has this function become in recent years that it has not been possible to accommodate all the requests for tickets. A form of application for Luncheon Tickets will be enclosed with each copy of the *Official Guide*.

Companies who have not previously exhibited and would like to have their names submitted to the Committee for consideration should write to the General Secretary, R. H. Hamblin, M.A., F.C.I.S., F.C.C.S., Oil and Colour Chemists' Association, Wax Chandlers' Hall, Gresham Street, London, E.C.2.

Bristol Section

Annual General Meeting

The 20th Annual General Meeting of the Bristol Section was held at the Royal Hotel, College Green, Bristol, 1, on Friday 24 April. A rather disappointing figure of only 18 members was present.

Minutes of the previous AGM were read and approved. Arising from these, it was stated that the Committee had decided not to arrange any further works visits unless there was a specific demand for them—this decision being forced by the generally poor attendance on previous visits.

Next followed the Committee report and reports from the Treasurer and Publications Secretary. The Chairman, Mr. L. Brooke, thanked the retiring Committee members for their valuable support. The Committee for 1964-65 was then elected with the following results :

Chairman : Mr. L. J. Brooke.

Chairman-Elect : Mr. R. J. Woodbridge.

Hon. Secretary : Mr. D. N. Fidler.

Hon. Treasurer : Mr. W. J. McWaters.

Hon. Publications Secretary and Hon. Research and Liaison Officer : Mr. L. Tasker.

Representative on Council : Mr. R. J. Woodbridge.

Hon. Auditor : Mr. C. C. Pearce.

Committee : Mr. R. Dennis, Mr. P. L. Gollop, Mr. I. S. Cox, Mr. C. G. Phillimore and Mr. J. R. Taylor.

Finally, the Chairman asked the views of members present to the Section tackling a research project during the coming year —to mark the Section's " coming of age." Views on this were rather mixed, and it was agreed, since the number present was rather small, to circulate all members and leave to the Committee to act on the response.

The meeting was then closed, but was followed by a film show, capably projected by the Chairman.

R. J. W.

Manchester Section

Presentation to Past Chairman

After the Summer Committee Meeting, held on 8 May, an informal dinner party was held, which was attended by Committee and Sub-committee members. After the meal, the Chairman (Mr. H. F. Clay) paid tribute to the tireless way the past Chairman (Mr. J. Smethurst) had carried out his duties. He commented on the efficient way Mr. Smethurst had conducted the business of the Section during the past two years, and the innovations he had introduced. He then presented to Mr. Smethurst on behalf of the Committee a silver sauce boat which he hoped would serve to remind him of his successful term of office and the best wishes and thanks of the members.

In reply, Mr. Smethurst thanked Mr. Clay and the committee for the kind remarks, good wishes and very acceptable gift which he was sure would delight and remind both him and his wife of his enjoyable term of office. He thought that if he had been successful in the position, it was because of the loyal and full support of the whole committee. Mr. Smethurst concluded by saying that he hoped Mr. Clay would find his two years of office just as enjoyable and he would, as a loyal committee member, help him in any way possible.

W. F. McD.

Newcastle Section

Photograph by *Dr. T. Banfield*

DINNER DANCE, 3 APRIL 1964, HEXHAM

The photograph shows (*left to right*) Mrs. Arnold, Mr. J. G. N. Smith (*Chairman*), Mrs. Smith, Dr. J. E. Arnold (*President*), Mrs. Hamblin and Mr. R. H. Hamblin (*General Secretary*)

LADIES' NIGHT

Ladies' Night, now an annual event in the calendar of the Newcastle Section, was held on Friday 3 April at the Royal Hotel, Hexham. Nearly 100 members and guests were present this year and the Section was honoured by the presence of the President and Mrs. Arnold. The General Secretary and Mrs. Hamblin also made the long journey North to Hadrian's Wall, and Dr. Arnold made reference to his exploration of this ancient Iron Curtain in a short speech which followed the dinner. A new innovation was to have the local branch president of the Federation of Master Painters and Decorators, Mr. W. Connor, as a principal guest.

Dancing continued until 1 a.m. and welcome cups of hot soup provided on leaving helped to keep out the cold during the long journeys home to Newcastle, Billingham and Carlisle.

J. A. W.

MR. M. J. HEAVERS

Mr. M. J. Heavers, an Ordinary Member attached to the Manchester Section for many years has joined *Kronos Titanium Pigments Limited*, the United Kingdom subsidiary of National Lead Company.

Mr. Heavers who has had many years' experience in the surface coatings industry has been the Honorary Social Secretary of the Manchester Section for four years and is also the representative of the Section on Council.

ASSOCIATION NOTICES

Applications for Membership

It is felt that members would like to be reminded of the standard of competence for the election of candidates to Ordinary Membership of the Association, as laid down by the Council, when they are sponsoring candidates for election. The qualifications for the granting of Ordinary Membership at the present time are :

1. A degree in a scientific subject or any generally accepted equivalent qualification ; or any technological qualification in a subject covered by the Association.

2. Or where there is adequate evidence of the technical competence of the candidate other than the obtaining of the qualifications mentioned above, the qualifying period of practice in the industries covered by the Association shall be normally not less than seven years.

Associate Membership is open to those employed in the industries who do not qualify for Ordinary Membership.

The Council has further resolved that Junior Membership should be open without restriction to the age of 21 years and may be extended to 25 years of age, where candidates are following courses of technical study to the satisfaction of their employers or technical college lecturers.

Retired Members

Council also wishes it to be widely known that in 1962 it introduced a reduced membership subscription rate for members who have retired from business. This applies to a member who has completed 20 years as an Ordinary or Associate Member and has retired from business, and normally has reached the age of 60 ; he may apply for his name to be retained on the Register of Members at an annual subscription rate of £1 1s. and he will retain the same rights of membership as the class of membership to which he was attached upon retirement.

Members wishing to avail themselves of this concession should write, in confidence, to the General Secretary at the address shown on the front cover of this *Journal*, giving the relevant information under the four headings : (*a*) name, address and Section, (*b*) date of election, (*c*) date of retirement, (*d*) age.

Change of Address

Members changing their address are urged to inform the General Secretary's office immediately so as to avoid any misdirection of mail. This is particularly important as far as the *Journal* is concerned.

Will members please note that since membership of the Association is entirely on an individual basis, if notification of the change of an address for a company is sent to the Association's office this will not necessarily guarantee the change of address in the Association's records of the member concerned unless the name of the member is stated on the communication.

Binding of the "Journal"

Members will be pleased to know that W. Heffer & Sons Ltd., Hills Road, Cambridge, will undertake the binding of back volumes of the Association's *Journal* sent in by individual members, at a cost of 21s. per volume.

Members wishing to avail themselves of this facility should send the parts direct to W. Heffer & Sons Ltd., enclosing a remittance of 21s. and ensuring that notes bearing their names and addresses are enclosed with the parcels.

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

ASTFALCK, ANTHONY NOEL, Carst & Walker Pty. Ltd., PO Box 5500, Johannesburg, South Africa. (*South African*)

BENSON, PETER HEYS, Drynamels Ltd., Hall Green, Birmingham, 28. (*Midlands*)

BETTISON, ROBERT AMES, PO Box 14-130, Auckland, New Zealand. (*New Zealand*)

BRAMHILL, COLIN, B.SC., 16 Adelphi Drive, Scartho, Grimsby, Lincs. (*Hull*)

CHITTENDEN, RICHARD, B.SC., Mander-Kidd Ltd., Old Heath Town Road, Wolverhampton. (*Midlands*)

EDWARDS, ERNEST HAROLD, 4 Selwyn Street, Blackburn, Victoria, Australia. (*Victorian*)

EVANS, ROBERT GIBSON, A.R.I.C., 1 Lilac Avenue, Humberstone, Leicester. (*Midlands*)

GREEFF, MATTHEUS PHILIP, B.SC., 30 Piet Joubert Street, Krugersdorp, Transvaal, South Africa. (*South African*)

JELLIS, RICHARD LESLIE, B.SC., 9 Forest Edge, Buckhurst Hill, Essex. (*London*)

JOHN, ELWYN CLIVE, 14 Brettonwoods Avenue, Harrietwood, Durban, Natal, South Africa. (*South African*)

KERCHISS, ROMAN ROBERT, RK Chemical Company, The Laboratory, Great Chishill, Royston, Herts. (*London*)

LYONS, BARRY JOHN, 57 Marchant Avenue, Reservoir, Victoria, Australia. (*Victorian*)

O'REGAN, BARRY PHILLIP, B.SC., Ciba Co. Pty. Ltd., Orion Road, Lane Cove, New South Wales, Australia. (*New South Wales*)

ROBINSON, ALAN ELLWOOD, B.A., 38 Inglis Road, Ealing Common, London, W.5. (*London*)

ROBINSON, FRANCIS DERRIK, B.SC., " Frays," Stallingborough Road, Healing, Grimsby, Lincs. (*Hull*)

RUSSELL, REX HAMILTON, M.SC., Presso Iannini Via Carissimi 5, Milan, Italy. (*Overseas*)

SAWYER, ROBERT SARGENT, B.SC., B.CH.ENG., PO Box 3714, Johannesburg, South Africa. (*South African*)

WILSON, GAVIN DOUGLAS, B.SC., " Barfields," 43 Oaken Grove, Maidenhead, Berks. (*London*)

Associate Members

BASTEIN, T. EBERHARD H., 368 Pine Avenue, Ferndale, Randburg, Transvaal, South Africa. (*South African*)

HUTCHINGS, GRAHAM JOHN, PH.C., c/o Esso Standard NZ Ltd., Box 3001, Auckland, New Zealand. (*New Zealand*)

LAPHAM, JOHN HENRY WATSON, B.A., PO Box 3429, Durban, Natal, South Africa. (*South African*)

PAGETT, JOHN ARTHUR, 8 Hood Street, Old Toongabbie, New South Wales, Australia. (*New South Wales*)

PRIDE, DOUGLAS MAXWELL, c/o Swift & Co. (Trading) Pty. Ltd., 149 Milton Street, Ashfield, New South Wales, Australia. (*New South Wales*)

STEPHANI, WOLFGANG V., PO Box 1521, Durban, Natal, South Africa. (*South African*)

VICKERS, RAYMOND HAROLD, A. C. Hatrick Ltd., Patiki Road, Avondale, Auckland, New Zealand. (*New Zealand*)

WILLIAMS, JOHN, 11 Abbotsbury Road, Hayes, Kent. (*London*)

WILMSHURST, ALFRED GEORGE, 12 Sylvia Street, Lower Templestowe, Victoria, Australia. (*Victorian*)

Junior Members

BRAITHWAITE, TREVOR JAMES, 16 Scott Street, Germiston, South Africa. (*South African*)

MORPETH, LIONEL, 18 Holly Avenue, Dunston, Gateshead, 11, Co. Durham. (*Newcastle*)

SKIPSEY, DAVID, 43 Wellington Court, Felling, Gateshead, 10, Co. Durham. (*Newcastle*)

WILLIAMS, WINSTON ROGER ASHLEE, 90 Upton Road, Slough, Bucks. (*London*)

Forthcoming Events

(Note: Details are given of meetings arranged 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.)

Wednesday 1 July

OCCA Council Meeting.

London Section. Visit to Shell Centre at 6 p.m.

Thursday 16 July—Sunday 19 July

Sixth Australian Convention, Meyer Chalet, Warburton, Victoria.

Tuesday 18 August

West Australian Section. A discussion between members and Mr. Wichett (Timber Research Laboratories), regarding the Painting of Karri.

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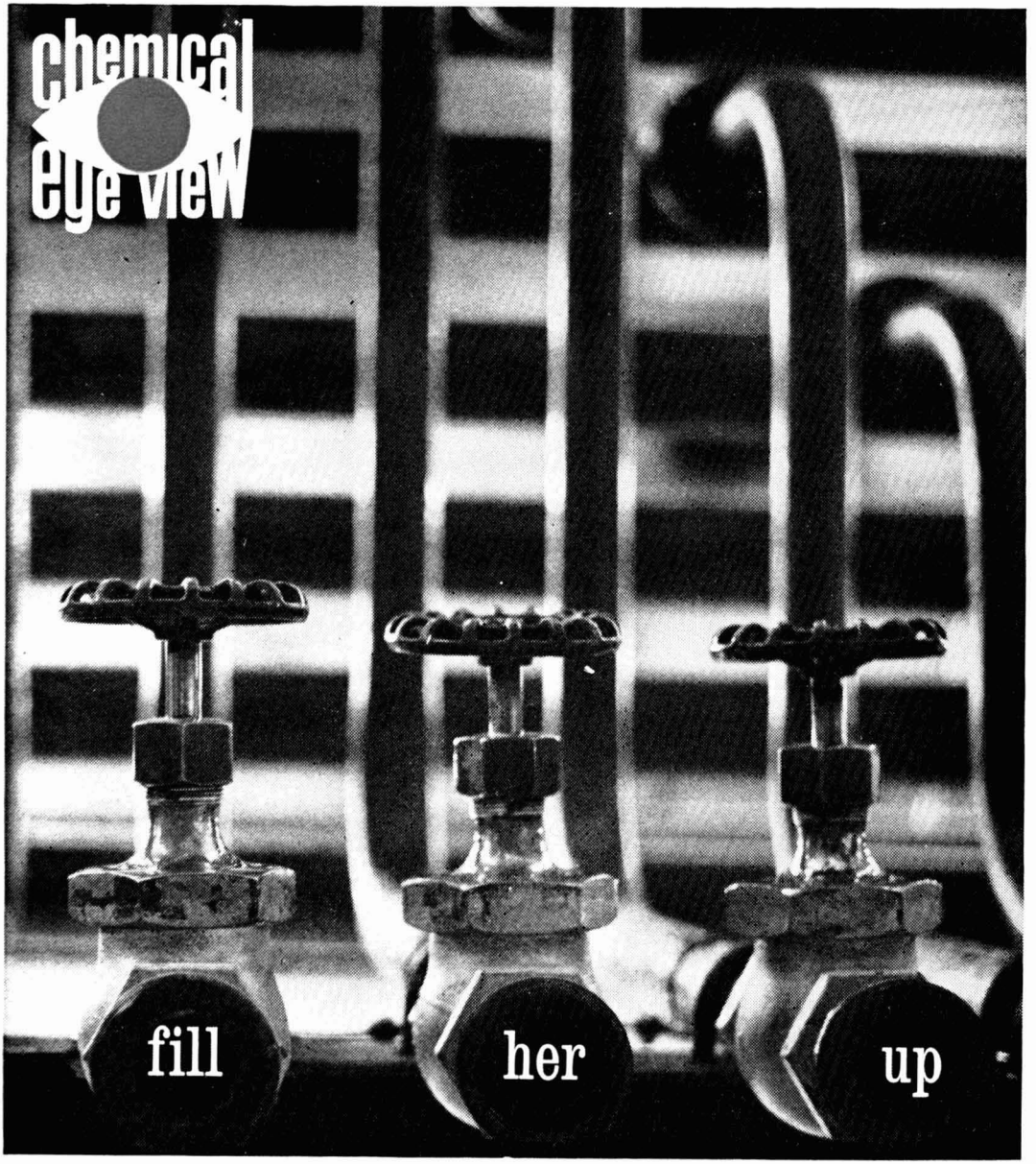

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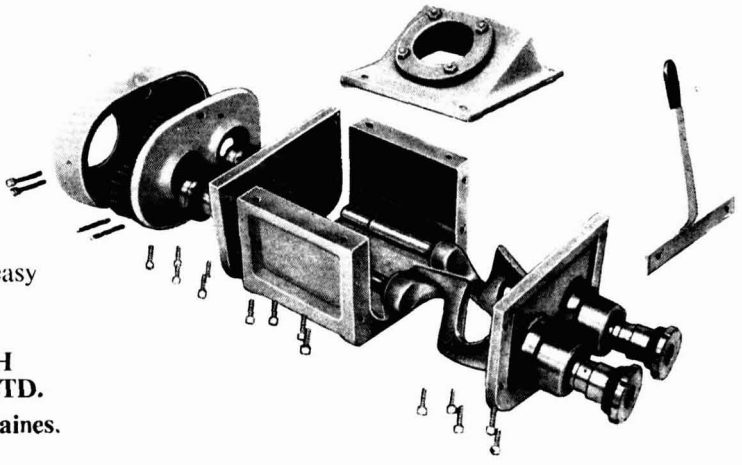

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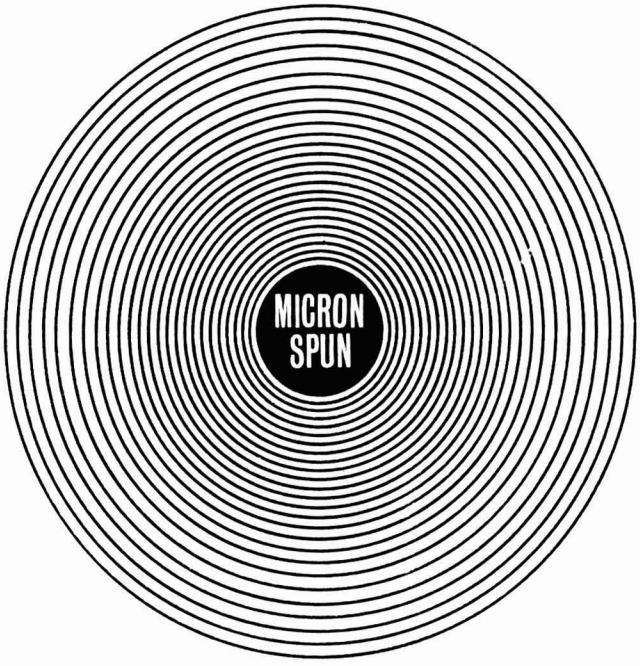

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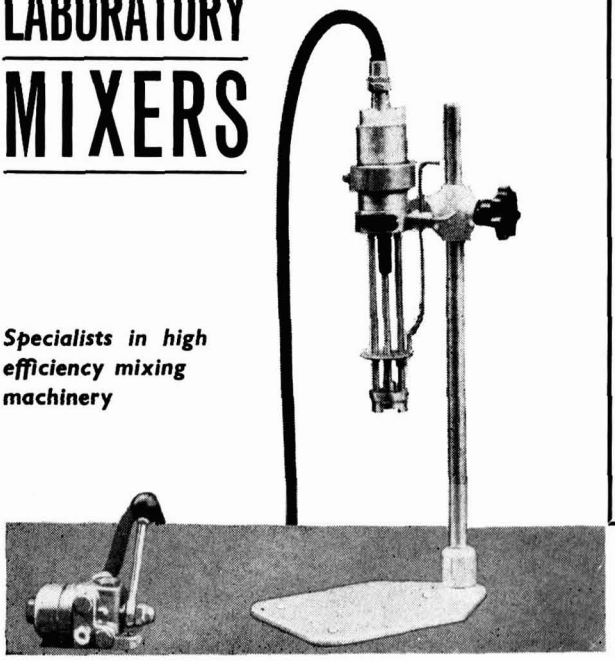

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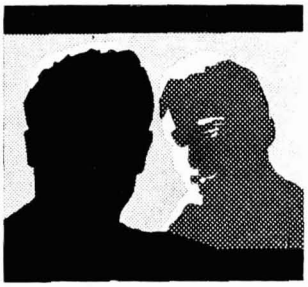

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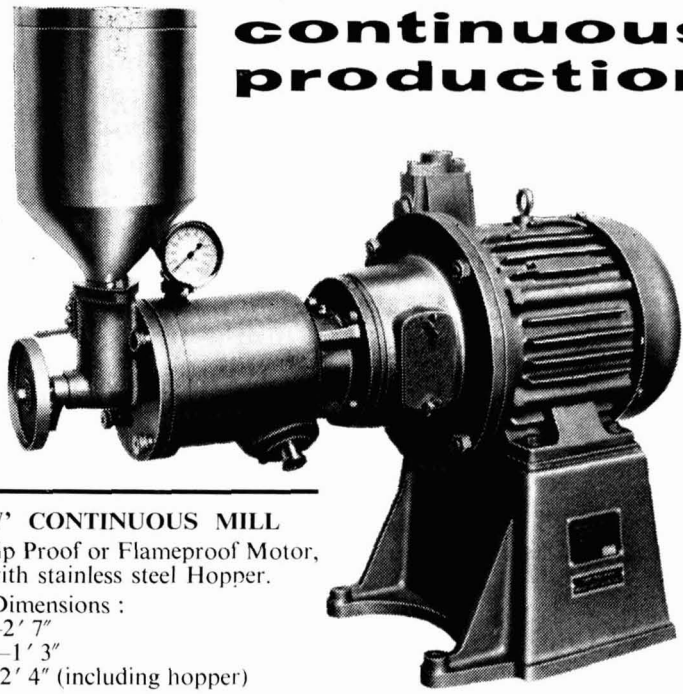

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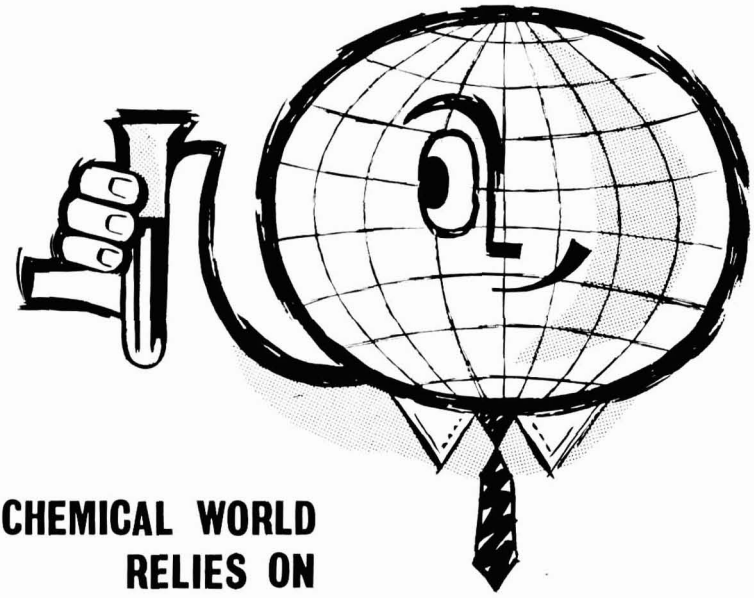

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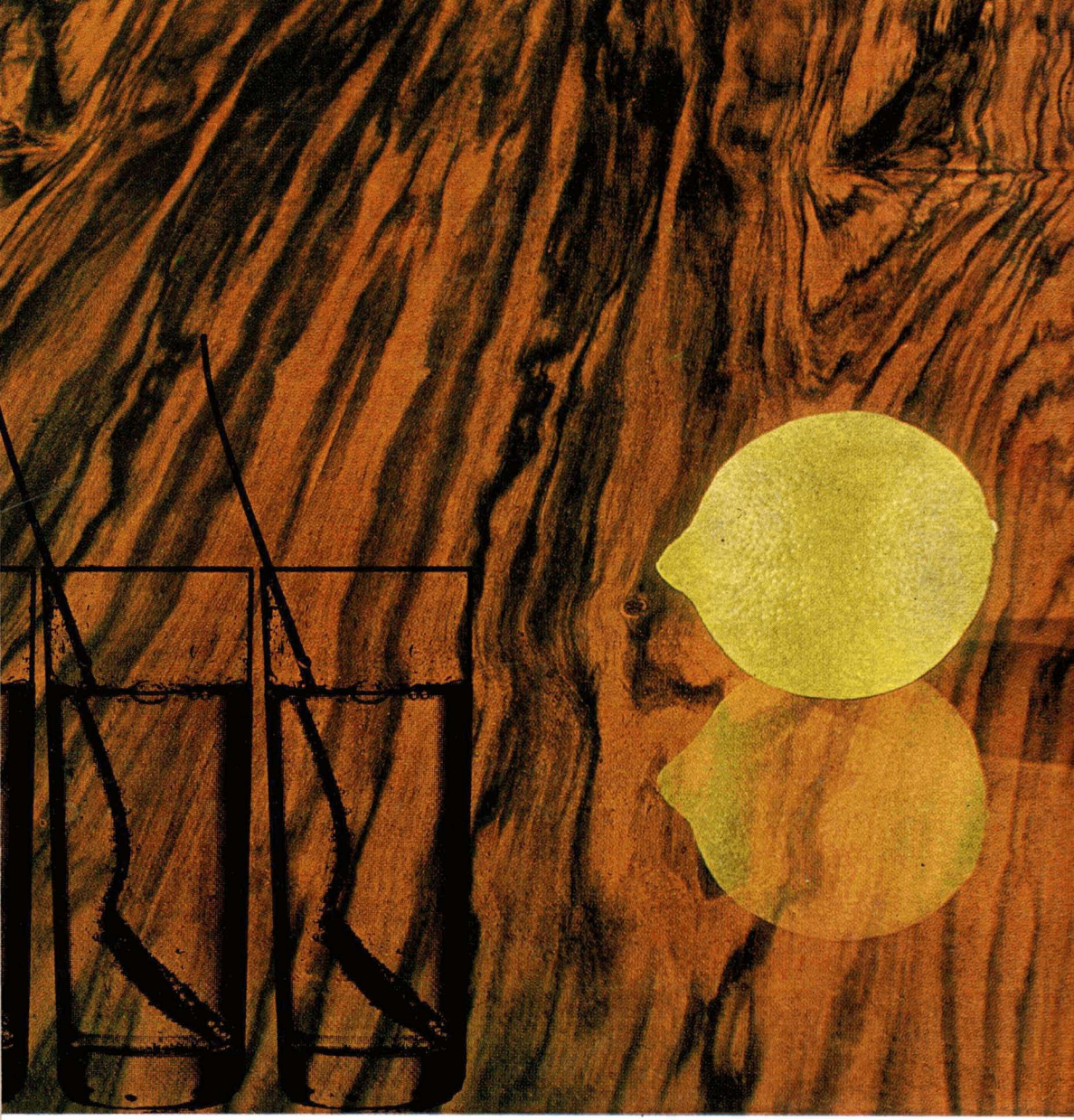

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