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Grinding

The behaviour of liquids on rotating rollers

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The analysis of polymeric esters by interesterification and gas liquid chromatography

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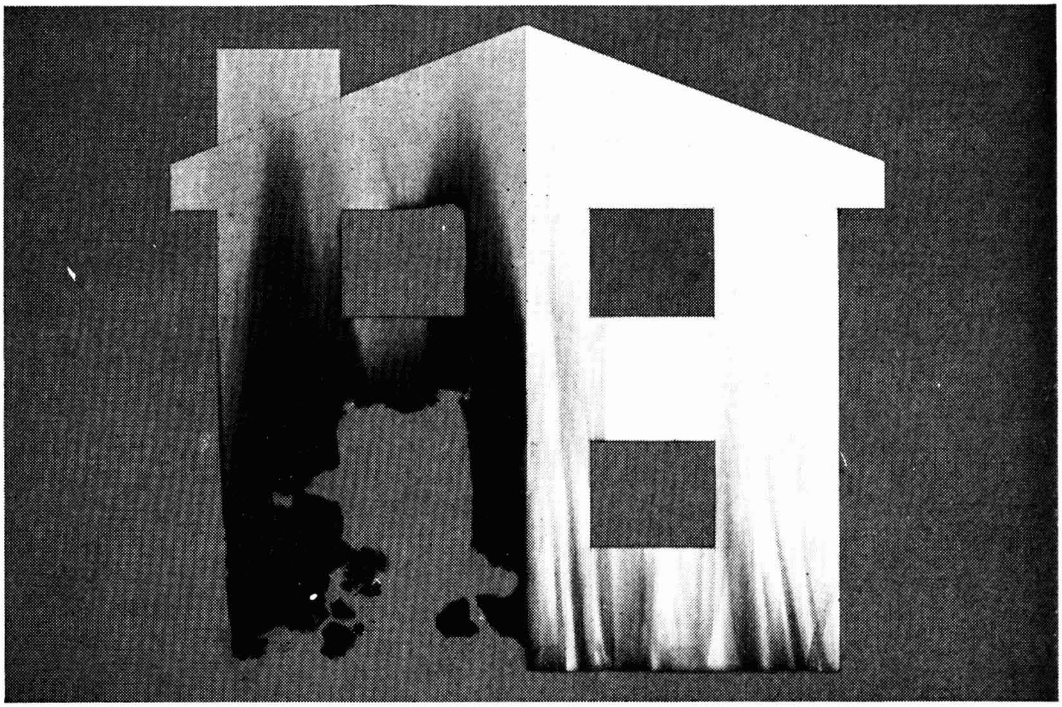


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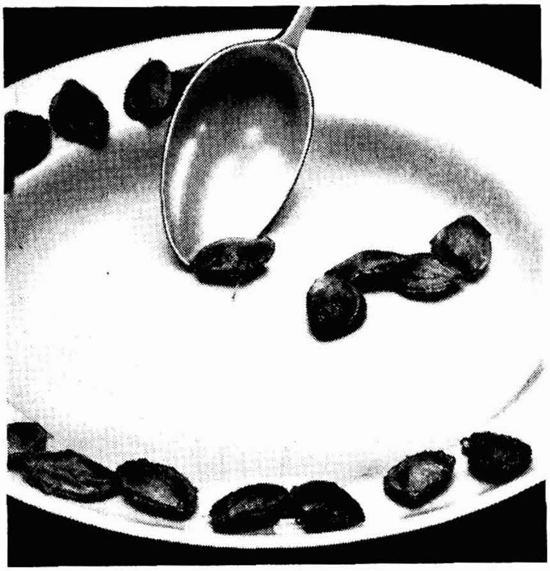

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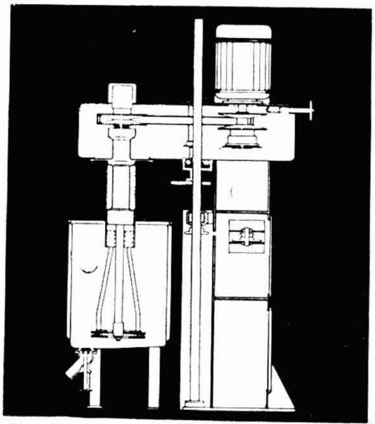

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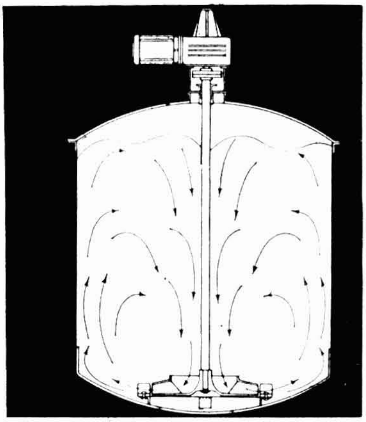

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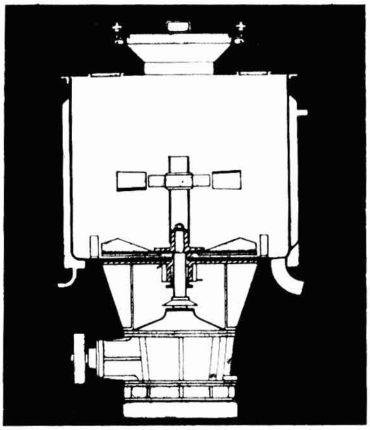

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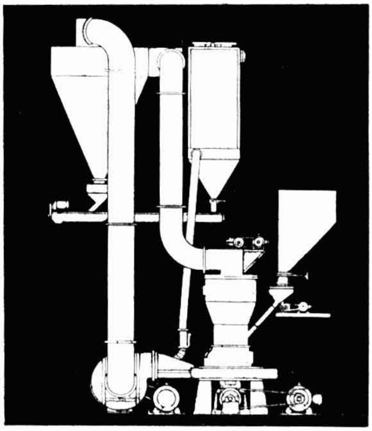

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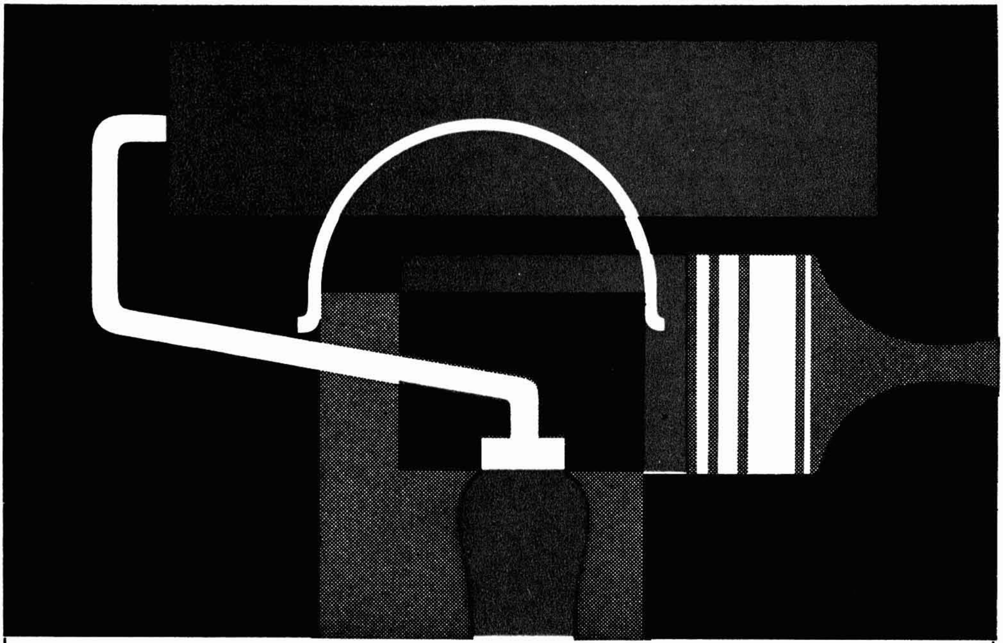

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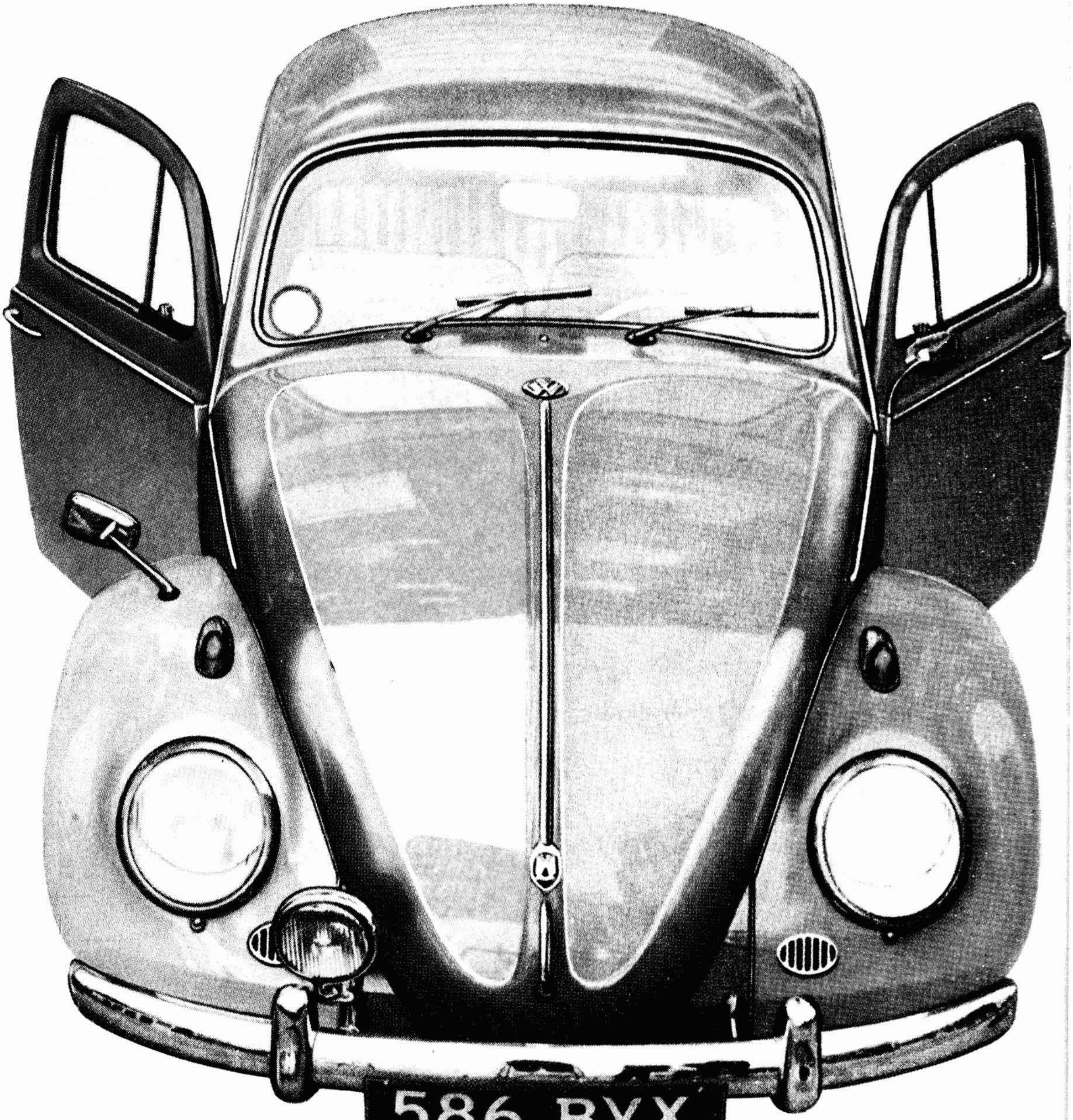

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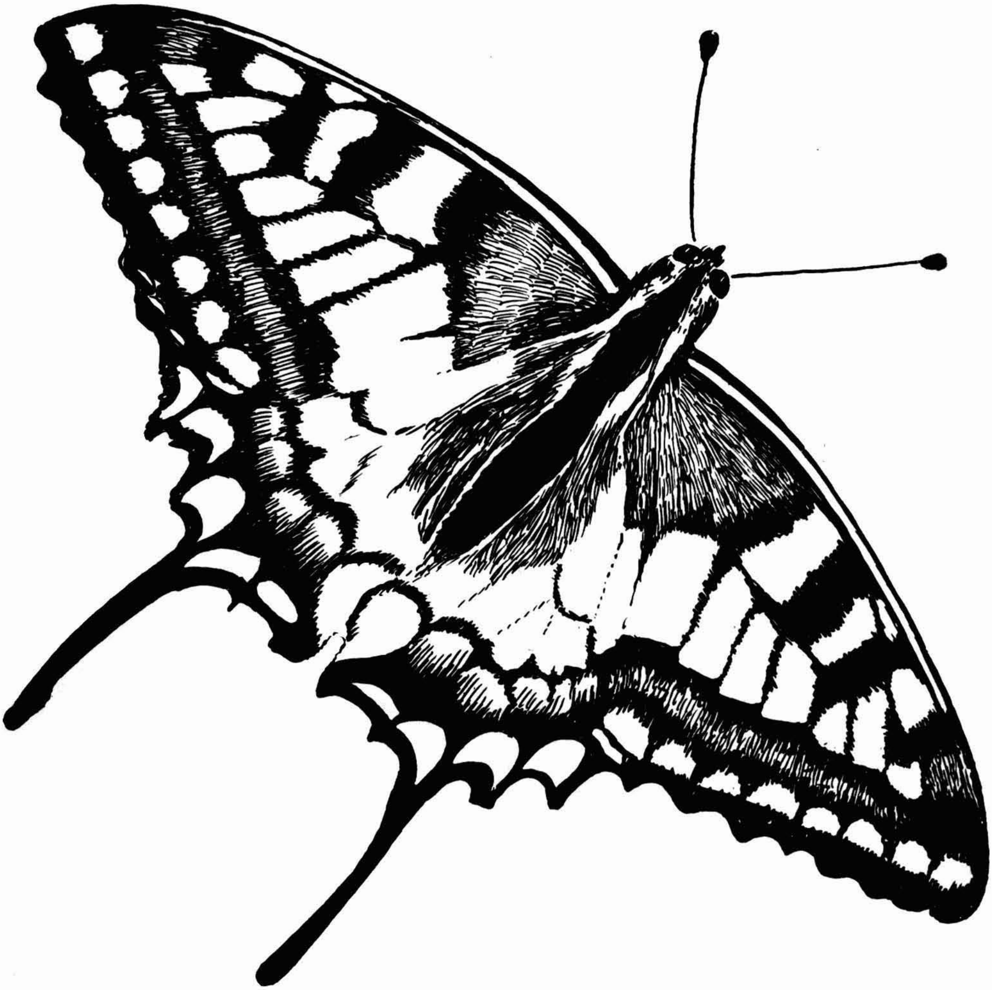

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Transactions and Communications

The analysis of polymeric esters by interesterification and gas liquid chromatography

By J. Rawlinson* and E. L. Deeley

Imperial Chemical Industries Ltd., Paints Division, Wexham Road, Slough, Bucks

Summary

A new method of analysis of polyesters is described, in which the sample is interesterified with an excess of methyl acetate in the presence of a catalyst. The reaction is carried out under pressure at 175°C for one hour. After cooling and removing catalyst residues, the methyl acetate solution of alcohol acetates and acid methyl esters is analysed by programmed temperature gas liquid chromatography on two different columns. Identification of the constituents is made by comparison of their retention times with the retention times of prepared standards, and with the chromatograms of resins of known composition analysed by this technique.

A full qualitative analysis may be made in three hours and the method is much simpler and of greater sensitivity than existing methods. The method may be applied in the presence of other resins of non-ester type.

L'analyse d'esters polymères par chromatographie en phase gazeuse/liquide après leur interesterification

Résumé

On décrit une nouvelle méthode pour l'analyse d'esters polymères qu'il s'agit de l'interesterification d'un échantillon avec un excès d'acétate de méthyle en présence d'un catalyseur. La réaction s'achève sous pression à 175°C dans une heure. Après refroidissement et l'enlévement des restes du catalyseur, on soumet la solution dans d'acétate de méthyle des acétates alcooliques et des esters méthyliques des acides à l'analyse chromatographique en phase gazeuse/liquide, aux températures préordonnées, sur deux colonnes différentes. On fait l'identification des constituants par comparaison de leurs temps de rétention avec ceux des étalons preparés, et également avec les chromatogrammes des résines, dont la composition est bien connue, que l'on a fait analysées par cette technique.

Une analyse qualitative complète peut être effectuée dans trois heures, et la méthode est plus facile et plus sensitive que les méthodes déjà en cours. La méthode peut être utilisée en présence des résines du type " non-ester."

Die Analyse Polymerer Ester mittels Interveresterung und Gas- Flüssigkeitschromatographie

Zusammenfassung

Eine neue Methode zur Analyse von Polyestern wird beschrieben, bei welcher das Prüfmuster mit einem Überschuss an Methylazetat in Gegenwart eines Katalysators interverestert wird. Die Reaktion wird bei 175°C eine Stunde lang unter Druck ausgeführt. Nach Abkühlung und Entfernung von Katalysatorenrückständen wird die Lösung der Alkoholazetate und sauren Methylester im Methylazetat in zwei verschiedenen Kolonnen und bei programmge-

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*Present address : Unilever Research Laboratory, Port Sunlight, Cheshire.

steuerter Temperatur mittels Gas- Flüssigkeitschromatographie analysiert. Identifizierung der Bestandteile erfolgt durch Vergleich ihrer Retentionszeiten mit denen dargestellter Prototypen und mit den chromatographischen Diagrammen von Harzen bekannter Zusammensetzung, die in gleicher Weise analysiert worden waren.

Innerhalb dreier Stunden kann eine vollständige qualitative Analyse ausgeführt werden, und dabei ist die Methode viel einfacher und empfindlicher als die gebräuchlichen. Die Methode ist auch bei Anwesenheit anderer Harze vom Nicht-Estertyp anwendbar.

Анализ полимерных эфиров посредством взаимной этерификации и газовой жидкостной хроматографии

Резюме

Описывается новый метод анализа полиэфиров в котором образец подвергается взаимной этерификации с избытком метилацетата в присутствии катализатора. Реакция производится под давлением при температуре в 175°C в течение одного часа. После охлаждения и удаления каталитических остатков, раствор метилацетата, спиртовых ацетатов и метиловых эфиров анализируется посредством програмной температурной газовой жидкостной хроматографии, на двух разных колоннах. Определение составных элементов производится сравнением их периодов удерживания с периодами удерживания изготовленных норм и с хроматограммами смол известного состава, анализированных этим методом. Полный качественный анализ может быть осуществлен в три часа и метод намного проще и более чувствителен чем существующие методы. Метод может применяться в присутствии других смол не-эфирного типа.

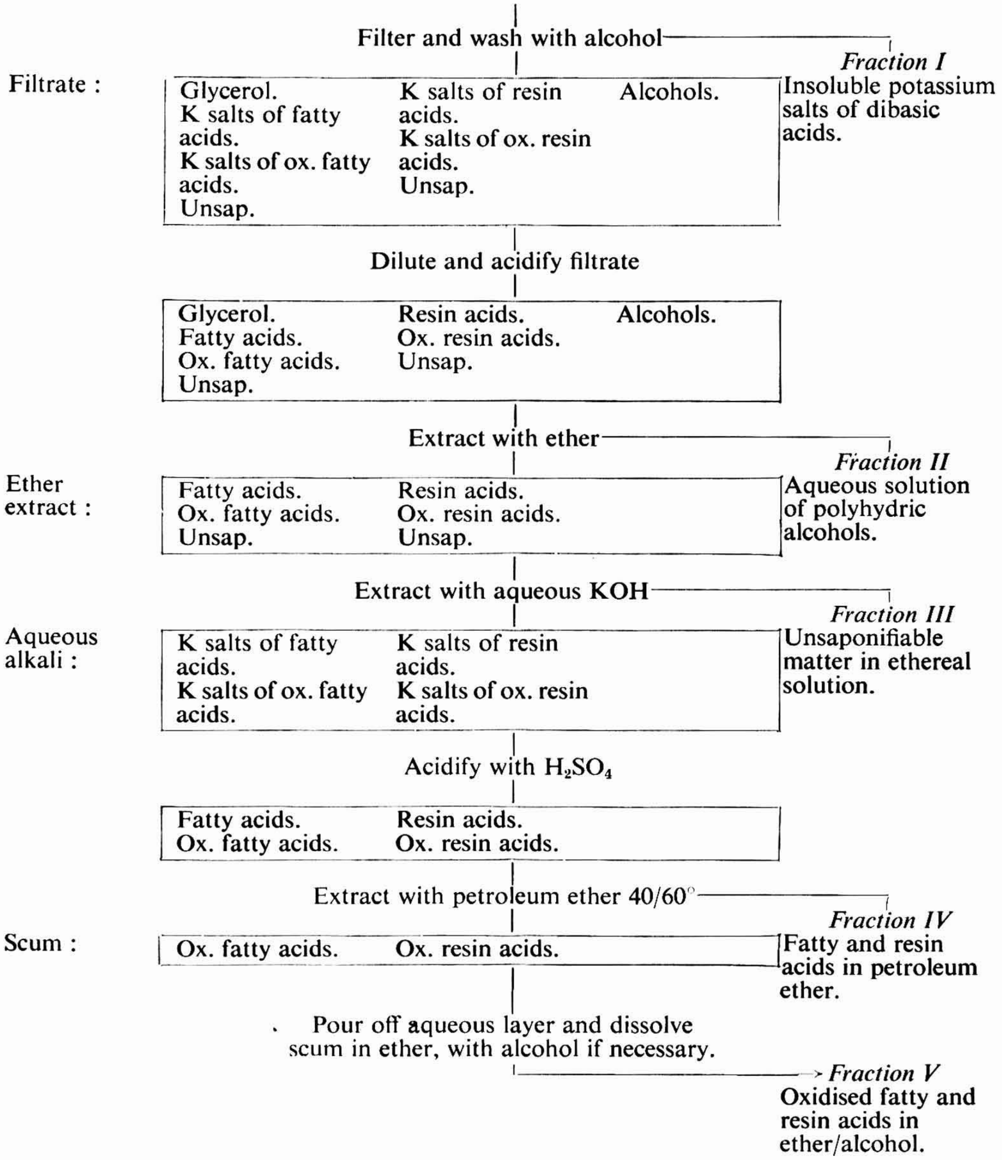
Introduction

Analysis of polymeric ester systems such as oil-modified alkyd resins, linear saturated polyesters, unsaturated polyesters and urethane oils and alkyds is usually carried out by saponification or hydrolysis procedures which attack the ester linkage and allow the alcohols and acids to be recovered for identification and determination. In general the process of saponification followed by separation into alcohol-insoluble potassium salts of dibasic acids, unsaponifiable matter, aqueous solution of polyols, and fatty and resin acids follows the scheme shown in Table 1, in this case a rosin and fatty oil modified alkyd resin.

Table 1

Saponification procedure for analysis of an alkyd resin

Components :	*Fatty oil*	*Modifying resin*	*Alkyd*	*Fractions separated*
Chemical constituents :	Glyceryl esters of fatty acids. Oxidised fatty acids. Unsap.	Resin acids. Oxidised resin acids. Unsap.	Polyhydric alcohols. Dibasic acids.	
		Saponify with dry alcoholic KOH		
	Glycerol. K salts of fatty acids. K salts of ox. fatty acids. Unsap.	K salts of resin acids. K salts of ox. resin acids. Unsap.	Alcohols. K salts of dibasic acids.	



Filter and wash with alcohol

Filtrate: Glycerol. K salts of fatty acids. K salts of ox. fatty acids. Unsap. | K salts of resin acids. K salts of ox. resin acids. Unsap. | Alcohols.

Fraction I Insoluble potassium salts of dibasic acids.

Dilute and acidify filtrate

Glycerol. Fatty acids. Ox. fatty acids. Unsap. | Resin acids. Ox. resin acids. Unsap. | Alcohols.

Extract with ether

Ether extract: Fatty acids. Ox. fatty acids. Unsap. | Resin acids. Ox. resin acids. Unsap.

Fraction II Aqueous solution of polyhydric alcohols.

Extract with aqueous KOH

Aqueous alkali: K salts of fatty acids. K salts of ox. fatty acids. | K salts of resin acids. K salts of ox. resin acids.

Fraction III Unsaponifiable matter in ethereal solution.

Acidify with H_2SO_4

Fatty acids. Ox. fatty acids. | Resin acids. Ox. resin acids.

Extract with petroleum ether 40/60°

Scum: Ox. fatty acids. | Ox. resin acids.

Fraction IV Fatty and resin acids in petroleum ether.

Pour off aqueous layer and dissolve scum in ether, with alcohol if necessary.

Fraction V Oxidised fatty and resin acids in ether/alcohol.

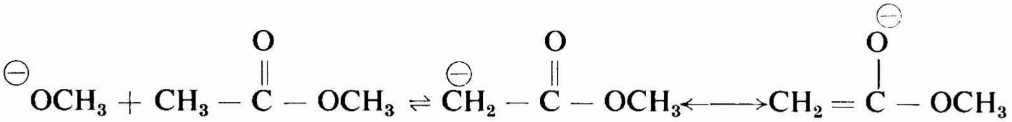
Thereafter, when dealing with an unknown composition, the constituents of the various fractions must be identified. The established procedures involve chemical tests and most of the modern physical techniques of analysis, such as infra-red and ultra-violet spectroscopy, gas liquid chromatography, paper and thin layer chromatography, polarography and nuclear magnetic resonance spectroscopy. Even so, in the complexity of constituents to be expected, identifications are not always unequivocal, particularly in the case of paint vehicles where the polyester may often be mixed with one or more resins of non-ester type. The amount of time spent on such an analysis can fairly obviously be very great.

The acetates of polyols are sufficiently volatile to analyse by gas liquid chromatography, as are the methyl esters of both the dibasic acids and modifying monobasic acids met in polymeric ester systems, and a catalysed interesterification with methyl acetate yields both the polyol acetates and the acid methyl esters. This simple procedure gives virtually a full systematic qualitative analysis on resins which are usually classified in the paint and allied industries as polyesters or modified polyesters, terms which are normally assumed not to include the acrylic and vinyl polymeric esters.

The interesterification reaction and the action of the catalyst

Although references to transesterification techniques in the analysis of either the alcohol or the acid components of esters exist in the literature[1–5], there is no mention of interesterification techniques. Ester-ester reactions are used in the modification of fats[6], but the reactions do not take place as readily as alcoholysis, and a catalyst is needed. Suitable catalysts are essentially the same as those used for alcoholysis i.e. acids, bases, metal salts, etc., and sodium methoxide was found by the authors to be the most reactive and to have least side reactions in polyester systems.

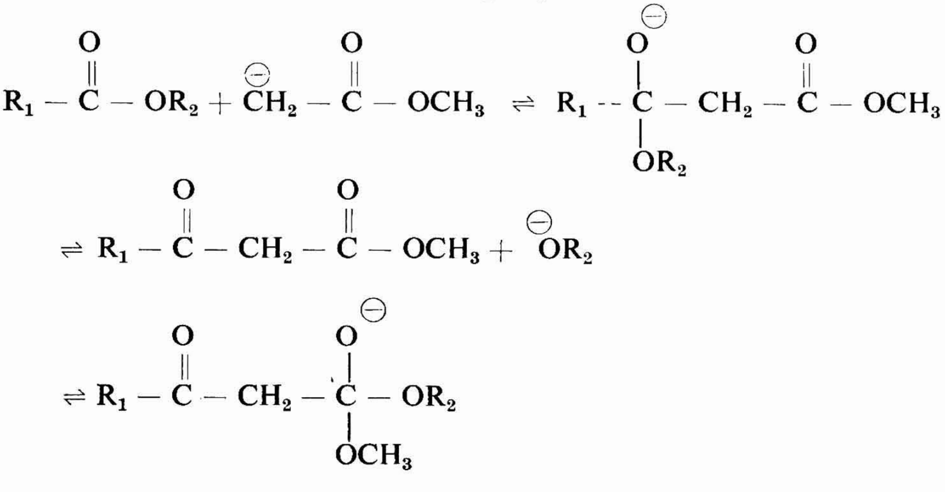
The catalytic effect of sodium methoxide in the reaction is due to the formation of an enolate ion by proton extraction.



$$^{\ominus}OCH_3 + CH_3-\overset{\overset{O}{\|}}{C}-OCH_3 \rightleftharpoons \overset{\ominus}{C}H_2-\overset{\overset{O}{\|}}{C}-OCH_3 \longleftrightarrow CH_2=\overset{\overset{O^{\ominus}}{|}}{C}-OCH_3$$

This enolate ion is then believed to react to form a β-ketoester as shown below[7].

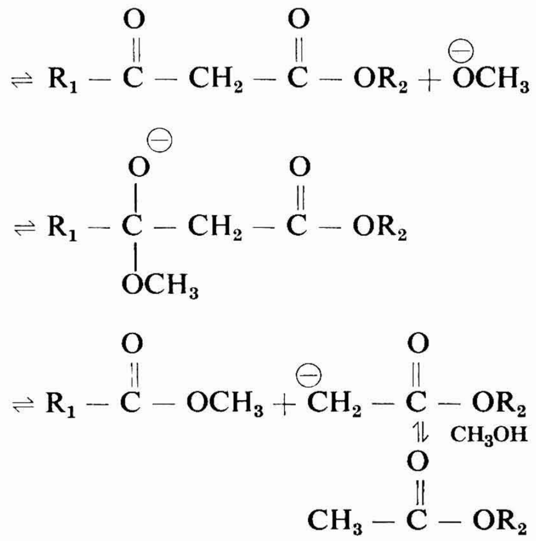
Let the polyester be represented by $R_1-\overset{\overset{O}{\|}}{C}-OR_2$, noting that R_1 and R_2 may contain other reacted functional groups.



$$R_1-\overset{\overset{O}{\|}}{C}-OR_2+\overset{\ominus}{C}H_2-\overset{\overset{O}{\|}}{C}-OCH_3 \rightleftharpoons R_1-\underset{\underset{OR_2}{|}}{\overset{\overset{O^{\ominus}}{|}}{C}}-CH_2-\overset{\overset{O}{\|}}{C}-OCH_3$$

$$\rightleftharpoons R_1-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-OCH_3+{}^{\ominus}OR_2$$

$$\rightleftharpoons R_1-\overset{\overset{O}{\|}}{C}-CH_2-\underset{\underset{OCH_3}{|}}{\overset{\overset{O^{\ominus}}{|}}{C}}-OR_2$$



$$\rightleftharpoons R_1-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-OR_2+\overset{\ominus}{O}CH_3$$

$$\rightleftharpoons R_1-\underset{\underset{OCH_3}{|}}{\overset{\overset{O^{\ominus}}{|}}{C}}-CH_2-\overset{\overset{O}{\|}}{C}-OR_2$$

$$\rightleftharpoons R_1-\overset{\overset{O}{\|}}{C}-OCH_3+\overset{\ominus}{C}H_2-\overset{\overset{O}{\|}}{C}-OR_2 \xrightleftharpoons{CH_3OH} CH_3-\overset{\overset{O}{\|}}{C}-OR_2$$

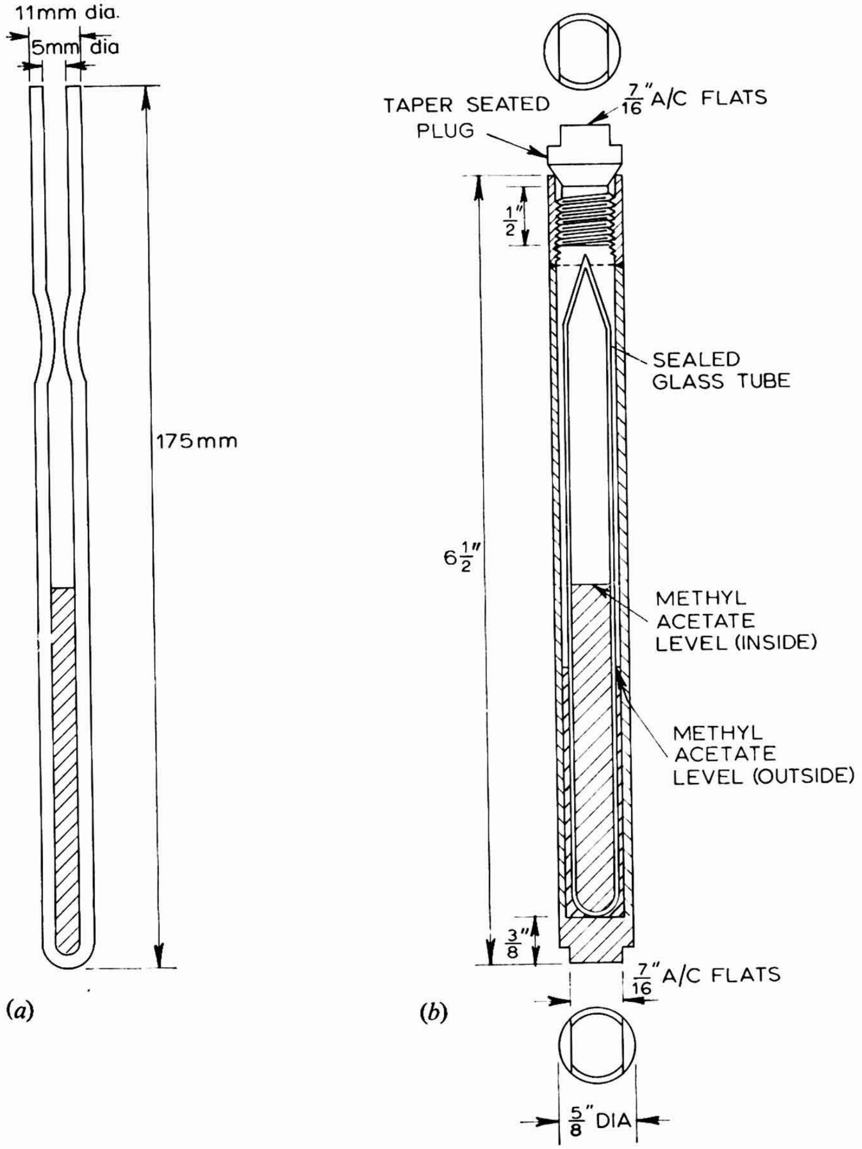
$R_1CO_2CH_3$ is the methyl ester of R_1CO_2H and

$CH_3CO_2R_2$ is the acetate of R_2OH.

The most effective catalyst was found to be a concentrated solution of sodium methoxide in methanol rather than solid sodium methoxide. This is not unreasonable when it is realised that solid sodium methoxide is used to condense methyl acetate to acetoacetic ester[8]. The methanol present makes the latter reaction reversible and degradation of the polyester to simple molecules, rather than condensation of the methyl acetate, takes place. However, some control over the amount of catalyst added must be exercised, since, if too much methanol is present, the polyol acetates tend to hydrolyse to give the free polyol. In addition, if any water is present in the methyl acetate, the polyol acetates are not formed. This is probably because the water destroys the catalyst to give methanol and sodium hydroxide and the latter causes hydrolysis of the acetates formed. In such cases the chromatogram shows only the methyl esters of the acids or those with a reduced quantity of alcohol acetates, the latter being apparently more easily hydrolysed.

Experimental conditions

The interesterification with excess dry methyl acetate catalysed by a methanol solution of sodium methoxide is carried out in a sealed micro-Carius tube by heating under pressure. It has been found convenient to add the catalyst by means of a syringe with a long needle which passes through the constriction in the Carius tube (Fig. 1a) to the resin dissolved in methyl acetate. After sealing, the reaction tube is enclosed in a steel sheath closed by a screwed plug, sealed, if necessary, with Teflon tape (Fig. 1b). Methyl acetate is added to the sheath in order to equilibrate the pressures inside and outside the reaction tube and so prevent breakage. The steel sheath containing the reaction tube fits closely into one of several holes in an electrically heated and thermostatically controlled brass block, where the interesterification reaction is carried out.



(*a*) (*b*)

Fig. 1 (a) Carius tube (b) Carius tube seated for operation under pressure

After cooling, the reaction tube is broken open and the sodium acetate formed is centrifuged off. The methyl acetate solution of alcohol acetates and acid methyl esters is chromatographed on both a polar and a non-polar column and the peaks are identified by comparison with prepared standards and with chromatograms of resins of known composition analysed by this technique.

It is advisable to chromatograph the solution as soon as possible, as changes in the polyol acetate peaks have been observed after standing for one week.

Interesterification conditions

Amount of sample taken	25-40 mg
*Amount of dry methyl acetate	1.5 ml
†Amount of sodium methoxide catalyst solution	30-50 mg
Reaction temperature	175°C
(approximate reaction pressure	25 atmospheres)
Reaction time	1 hour

*Dried to less than 100 ppm water by passing and keeping over $\frac{1}{16}$ in Type 4A Molecular Sieve (British Drug Houses Ltd.).

†Made by dissolving sodium metal in AR methanol to give 25 per cent w/w sodium methoxide.

Gas chromatographic conditions

The conditions below refer to the use of a single column Perkin-Elmer F11 instruments with a flame ionisation detector, but there is no reason why any other suitable instrument could not be used.

Amplifier range	20×10^2
Hydrogen pressure	16 psi
Air pressure	30 psi
Nitrogen pressure	15 psi
Injection block temperature	c. 300°C (Control No. 6)
Sample size	8 μl

(1) *Polyester column*

Length	2 m × $\frac{1}{8}$ in od
Stationary phase	8 per cent w/w 1,4-butanediol succinate on HMDS Chromosorb W, 80-100 mesh (Perkin-Elmer DE 307).

Temperature programme	(a) *for alkyd resins*	(b) *for oil-free polyesters*
Initial temperature	100°C	70°C
Final temperature	200°C	200°C
Programming rate	3 C°/min	4 C°/min

(2) *Apiezon column*

Length	2 m × $\frac{1}{8}$ in od
Stationary phase	25 per cent Apiezon L on 60-80 mesh Celite

Temperature programme	
Initial temperature	100°C
Final temperature	260°C
Programming rate	4 C°/min

These conditions have been optimised so that as complete qualitative data as possible may be obtained on a wide variety of compositions.

Retention times under these conditions of possible constituents of the reaction mixture arising from polyesters normally met in paint analysis are given in Table 2.

Table 2—Retention times of possible constituents

All the retention times are given relative to dimethyl phthalate = 1.00

Column Temperature Programming rate	8% Polyester 70°-200°C 4°/min.	8% Polyester 100°-200°C 3°/min.	25% Apiezon L 100°-260°C 4°/min.
Methyl pelargonate	0.34	0.26	0.64
Propylene glycol diacetate	0.37		0.25
Propylene glycol monoacetate	0.40		0.13
Ethylene glycol diacetate	0.40	0.30	0.22
Dimethyl fumarate	0.41		0.31
Ethylene glycol monoacetate	0.43	0.33	0.11
Dimethyl succinate	0.45		0.28
Methyl benzoate	0.46	0.37	0.52
1,3-Butanediol diacetate	0.49		0.39
Dimethyl maleate	0.52		0.26
1,3-Butanediol monoacetate	0.53		0.25
Methyl laurate	0.62	0.53	1.13
1,4-Butanediol diacetate	0.62		0.54
Dipropylene glycol monoacetate	0.64		0.48
1,4-Butanediol monoacetate	0.65		
Dimethyl adipate	0.66		0.60
Dipropylene glycol diacetate	0.70		0.68
Diethylene glycol monoacetate	0.73		0.41
Methyl *p*-tert-butyl benzoate	0.76		1.09
Diethylene glycol diacetate	0.77		0.63
Glycerol triacetate	0.87	0.82	0.66
Dimethyl azelate	0.89		1.09
Glycerol diacetate	0.96	0.94	0.56
Dimethyl sebacate	0.96		1.23
Trimethylolethane triacetate	0.97		0.91
Dimethyl isophthalate	1.00	1.00	1.15
Dimethyl terephthalate	1.00		1.15
Trimethylolpropane triacetate	1.04		1.04
Trimethylolpropane diacetate	1.16		
Dimethyloltricyclodecane monoacetate	1.62		1.71
Dimethyloltricyclodecane diacetate	1.73		1.75
Trimethylolpropane allyl ether/acetates	0.77 0.91 0.94 1.28		1.05 not found not found not found
Methyl esters of trimellitic acid	very long very long		1.43 1.53
Dimethyl " chlorendate "	very long		1.91
Dimethyl tetrachlorophthalate	very long		2.12
Methyl myristate		0.72	1.40
Methyl palmitate		0.91	1.64
Methyl stearate		1.09	1.99
Methyl oleate		1.13	1.90
Methyl linoleate		1.21	1.90
Methyl linolenate		1.30	1.90
Pentaerythritol tetra-acetate		very long	1.23
Pentaerythritol triacetate		very long	1.21
Methyl ricinoleate (acetate derivative)		very long	2.36
Methyl esters of maleic/fumaric adducts	0.94 0.61 not found		0.80 not found 1.55
Methyl esters of rosin acids	1.5-3.5		2.5-4.0

The method may be applied to the polyester solids but this usually involves an unnecessary step, as the solvents in which most polyesters are carried do not interfere with the analysis. They are normally eluted from the chromatographic column well before any of the reaction products, and the peaks due to them and to the reagent which appear on the chromatograms may be ignored. There is a possibility, however, that high boiling hydrocarbon solvents may hide early reaction product peaks on the Apiezon column.

Polyester systems met with in the paint industry are often used in blends with other resin components of essentially non-ester type. These other resins have been found not to interfere with the reaction but simply to remain dissolved in the methyl acetate reagent, and do not appear on the chromatogram. The effect of nitrocellulose is abnormal in that it inactivates the catalyst, but this may be overcome by increasing the catalyst concentration when it is present.

Results

The chromatograms which are shown are the results of the application of the method to polyesters of known composition or to proprietary materials whose composition was known from prior saponification analysis. The brief comments which are made under the sub-headings (a) to (d) below are not meant to be comprehensive discussions of the results, the details of which may be seen on the chromatograms.

(a) *Alkyd resins*

Chromatograms of the method applied to a wide variety of alkyd resins are shown in Figs. 2-10. It is difficult to detect tung oil in an alkyd resin by this technique because the major constituent, elaeostearic acid, has usually been reacted to form polymeric species whose methyl esters are involatile. It may also be noted that dimethyl terephthalate and dimethyl isophthalate are difficult to distinguish and that the methyl esters of rosin acids are characterised by their very long retention times and somewhat poor resolution.

(b) *Linear saturated polyesters*

Typical chromatograms are shown in Figs. 11-13. Under the conditions given no difficulties were met in the application of the method to linear polymeric esters and to polyurethane pre-polymers.

(c) *Unsaturated polyesters*

Typical chromatograms are shown in Figs. 14-17. Because of reaction of the double bond to give higher molecular weight species, recovery of maleic and fumaric acids is never complete in saponification analysis of this type of resin. On interesterification of polyesters made from either maleic or fumaric acids, which on saponification analysis very often result in the recovery of some of both maleic and fumaric acids, only fumarate is observed. It is assumed that under the conditions of the reaction maleate is completely isomerised to fumarate. In addition, peaks other than dimethyl fumarate are found on the chromatogram in varying amounts. The retention times of those observed are given in Table 2.

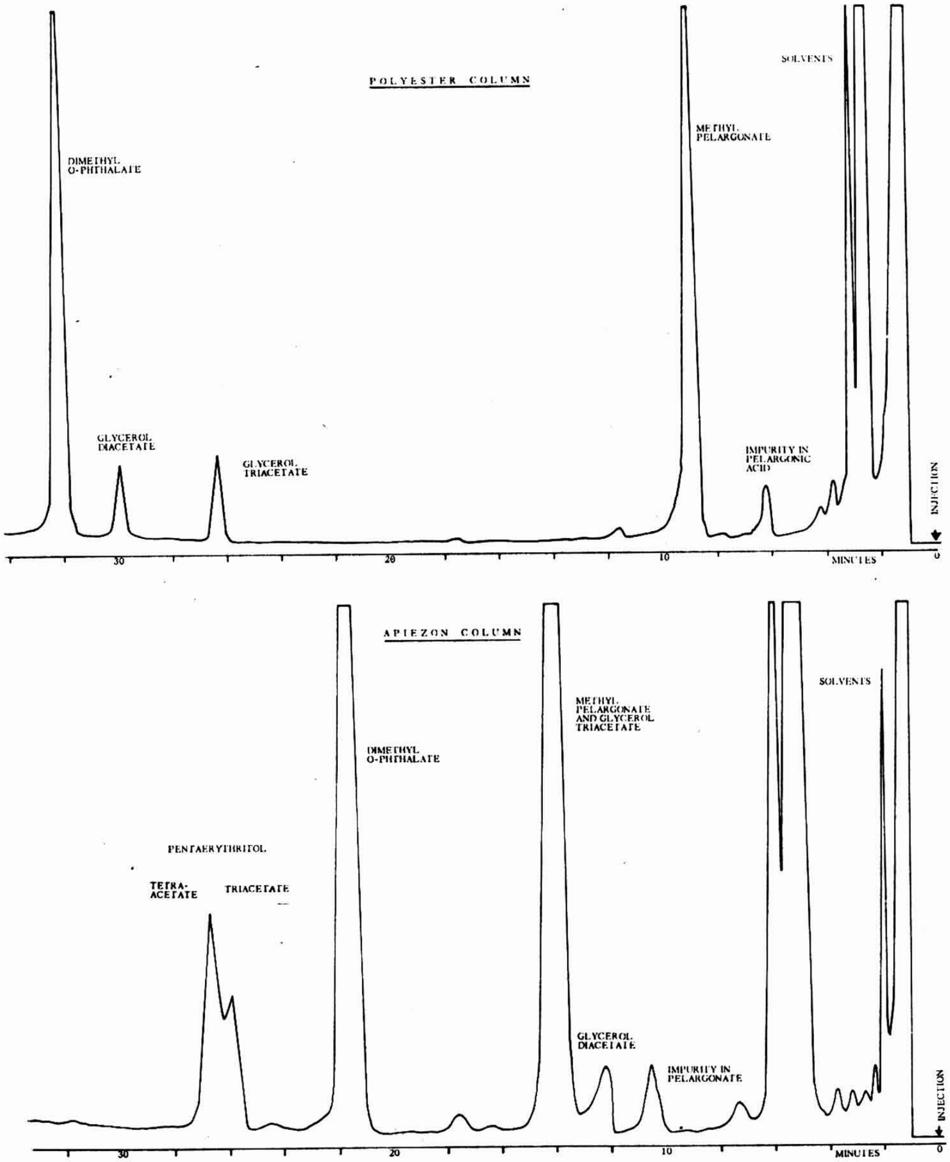


Fig. 2. Pelargonic acid modified glycerol/pentaerythritol o-phthalate alkyd resin

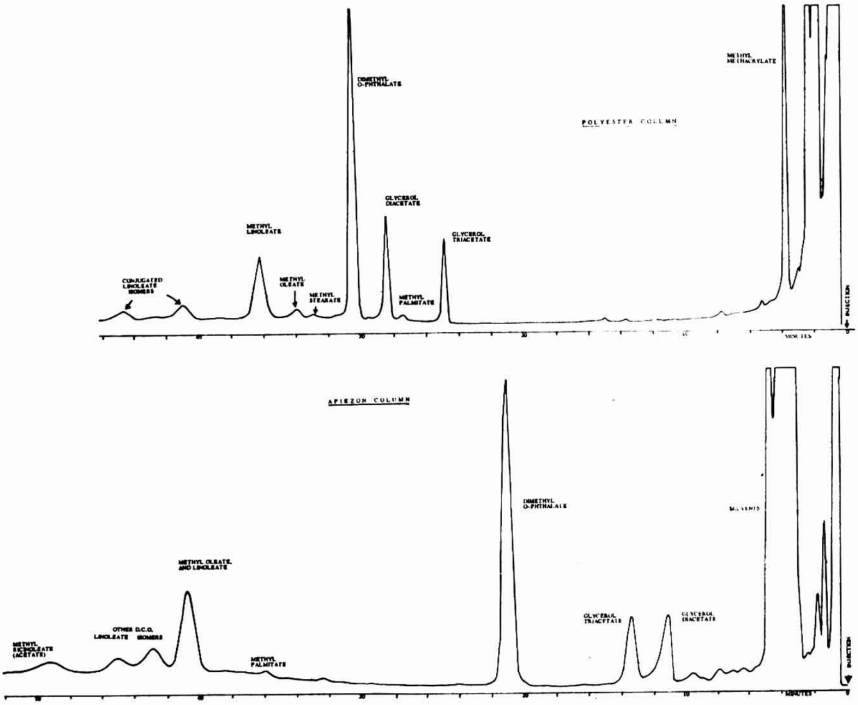


Fig. 3. Dehydrated castor oil modified methacrylated glycerol o-phthalate alkyd resin

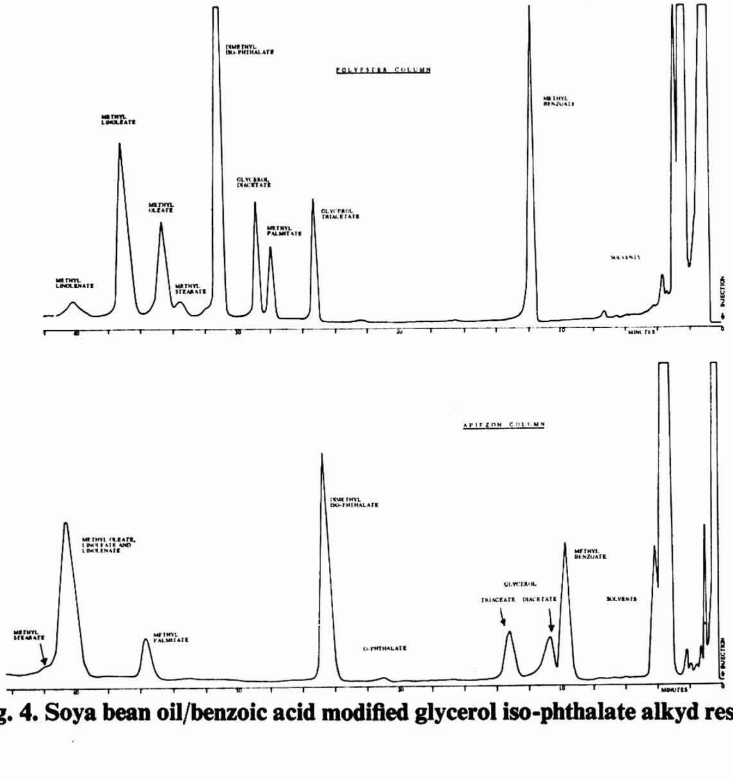


Fig. 4. Soya bean oil/benzoic acid modified glycerol iso-phthalate alkyd resin

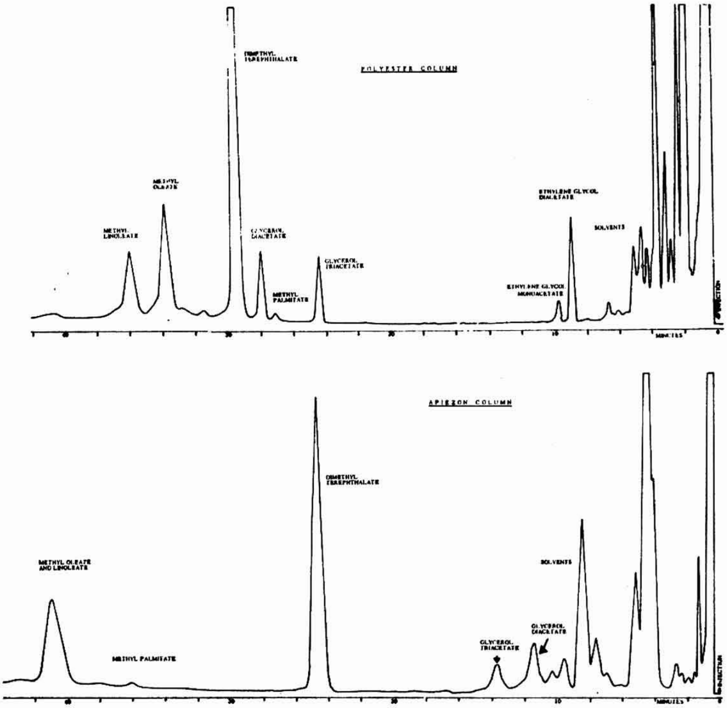


Fig. 5. Tall oil modified glycerol/ethylene glycol terephthalate alkyd resin

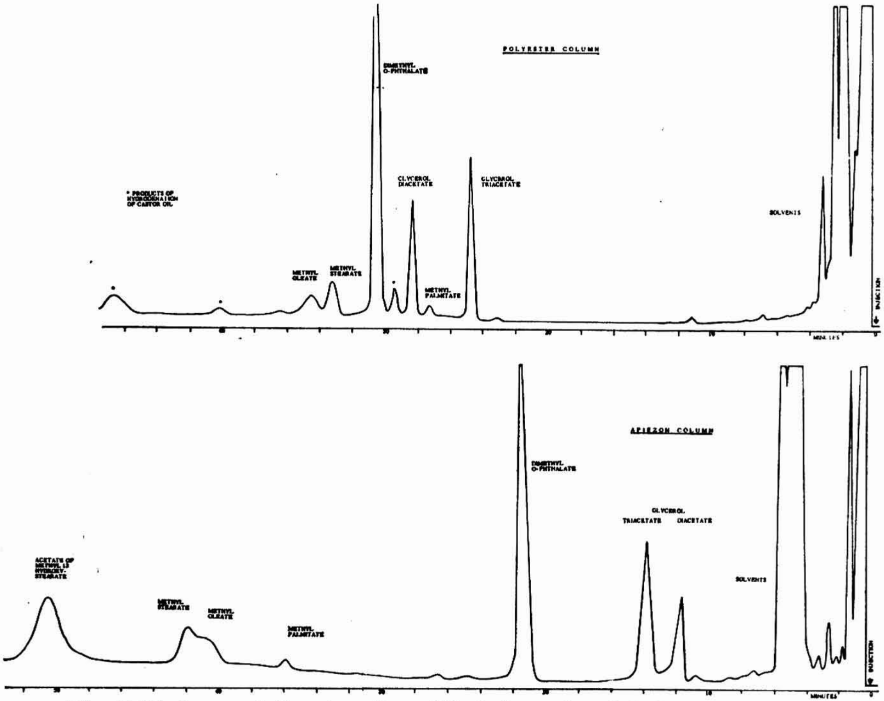


Fig. 6. Hydrogenated castor oil modified glycerol o-phthalate alkyd resin

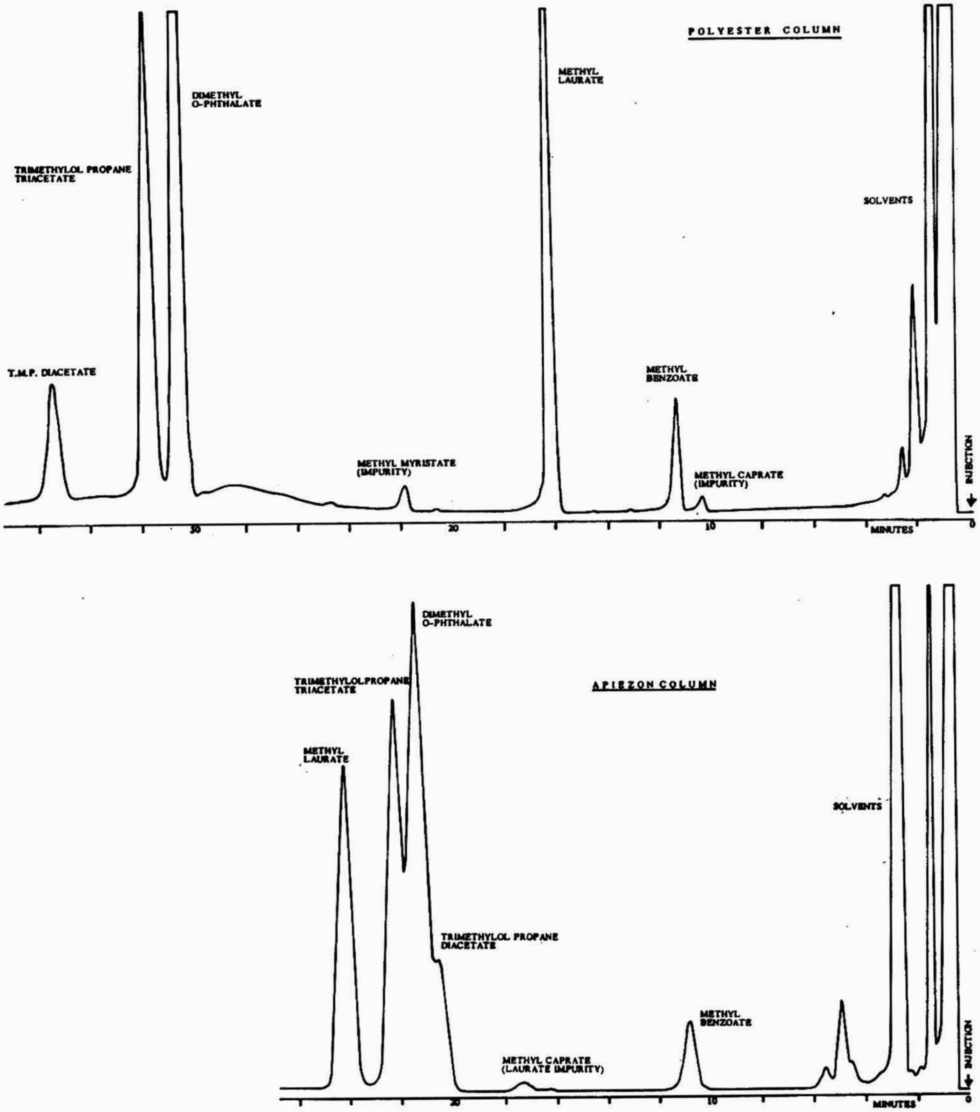


Fig. 7. Lauric acid/benzoic acid modified trimethylolpropane o-phthalate alkyd resin

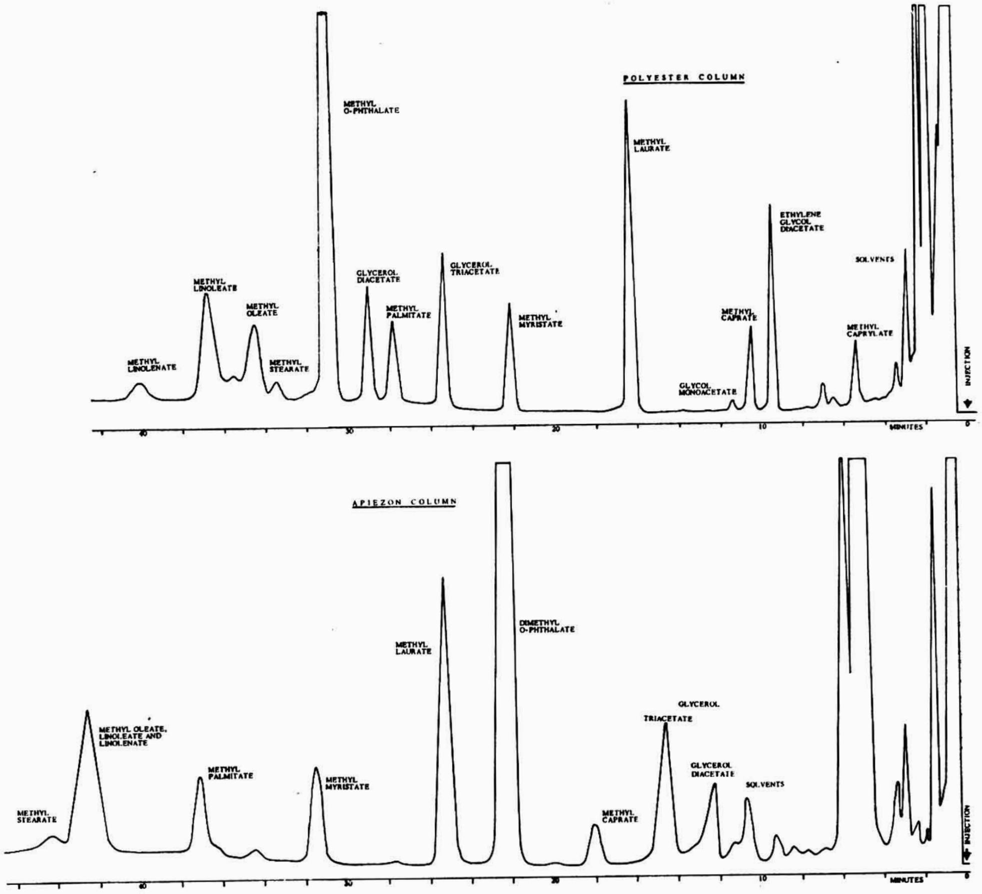


Fig. 8. Coconut oil/soya bean oil modified glycerol/ethylene glycol o-phthalate alkyd resin

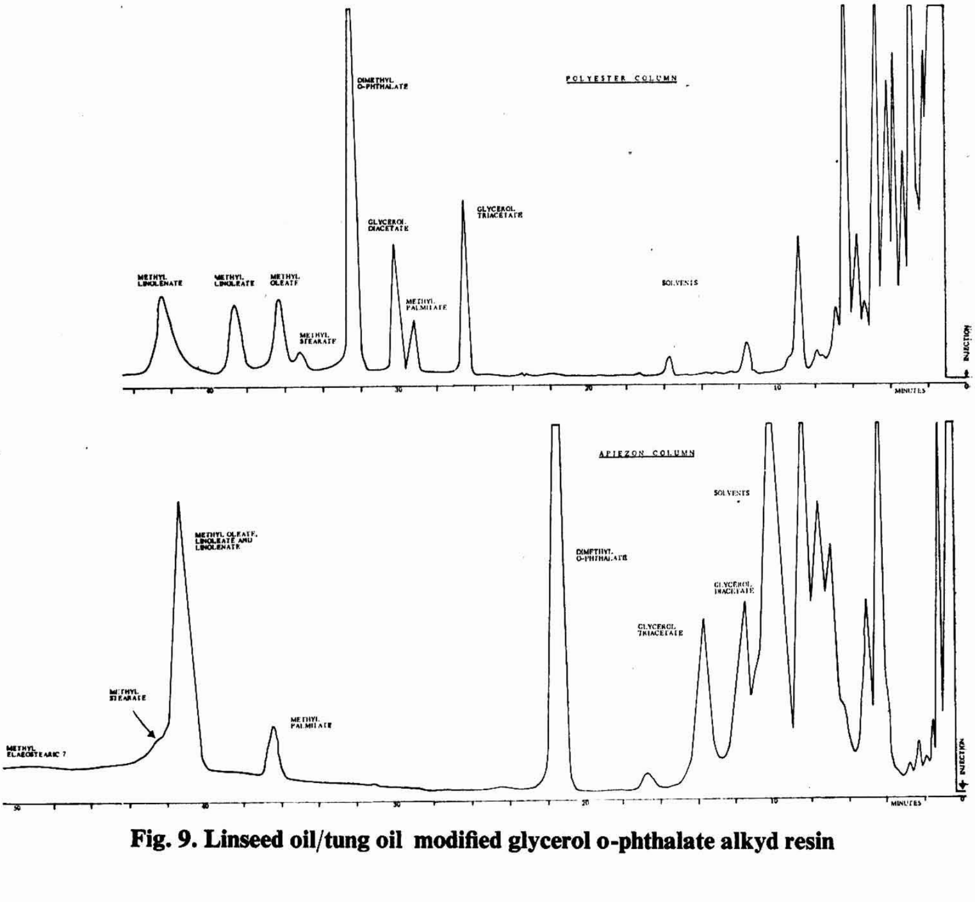


Fig. 9. Linseed oil/tung oil modified glycerol o-phthalate alkyd resin

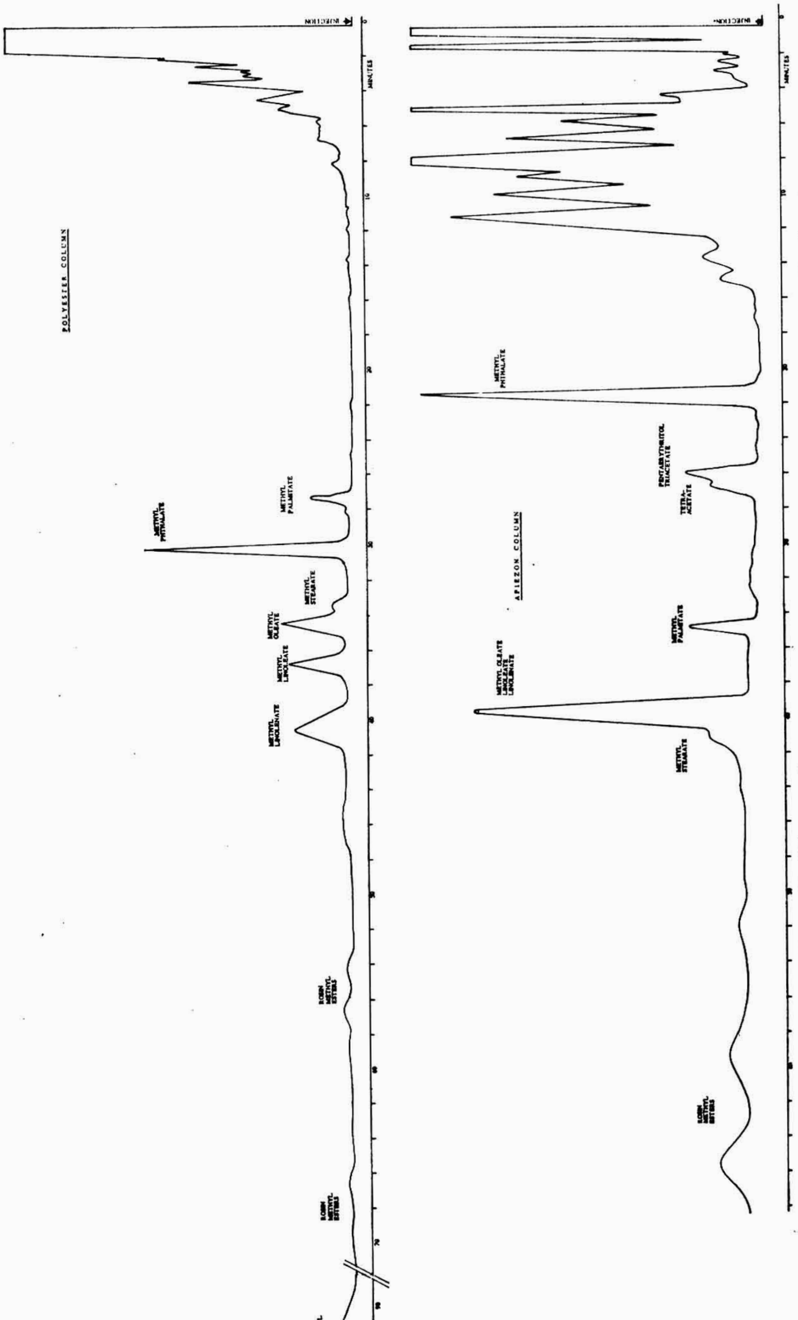


Fig. 10. Rosin modified linseed oil/tung oil modified glycerol/pentaerythritol o-phthalate alkyd resin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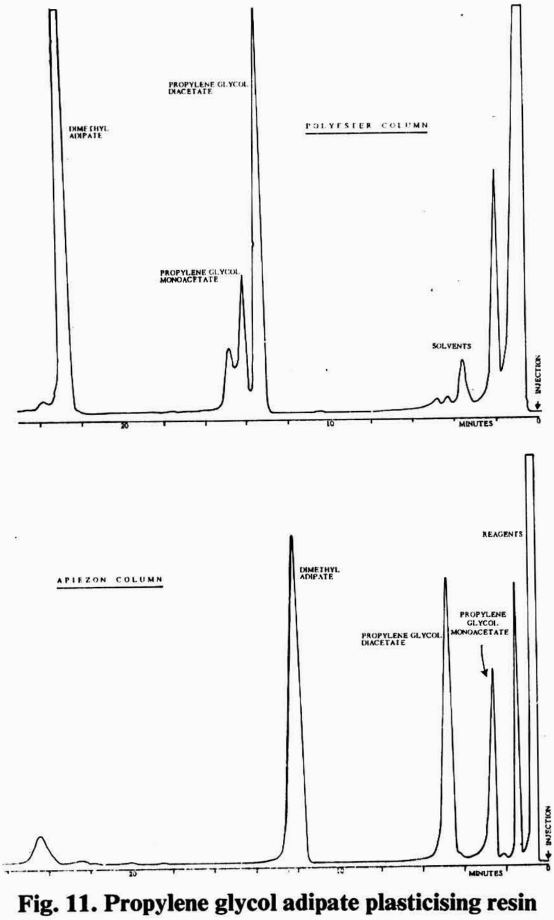


Fig. 11. Propylene glycol adipate plasticising resin

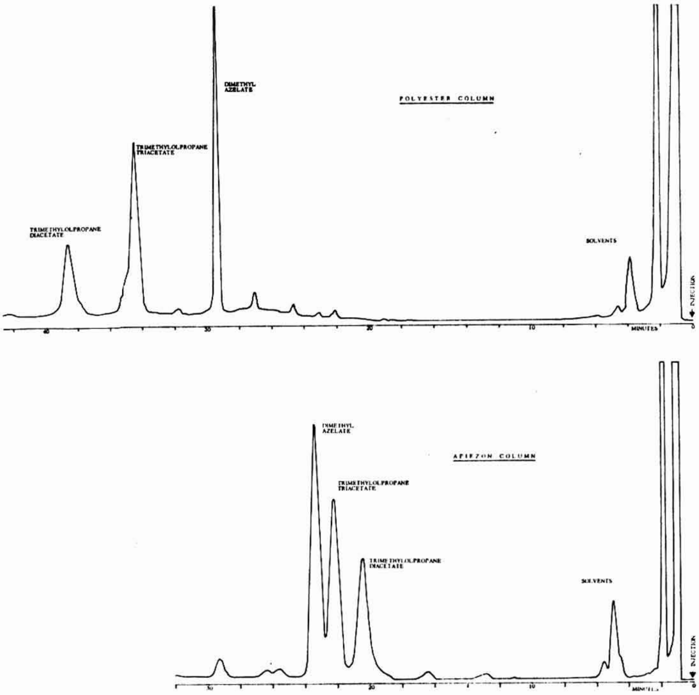


Fig. 12. Trimethylol propane azelate pre-polymer

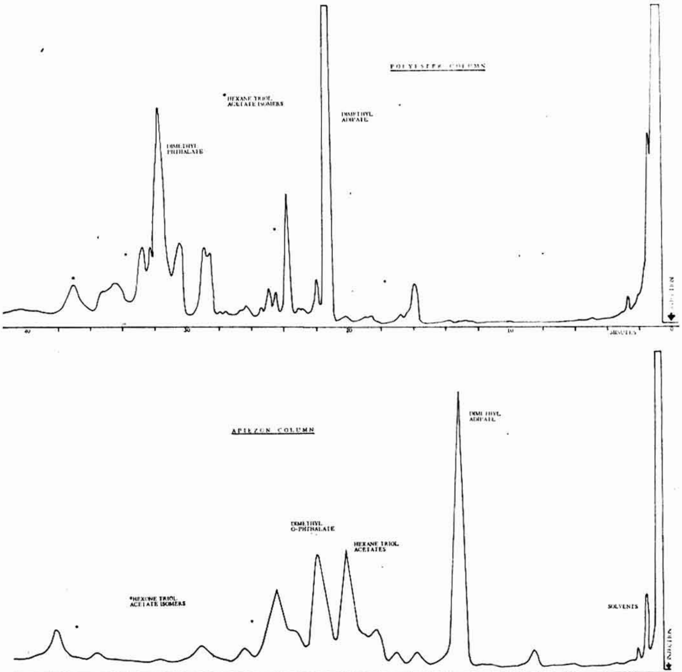
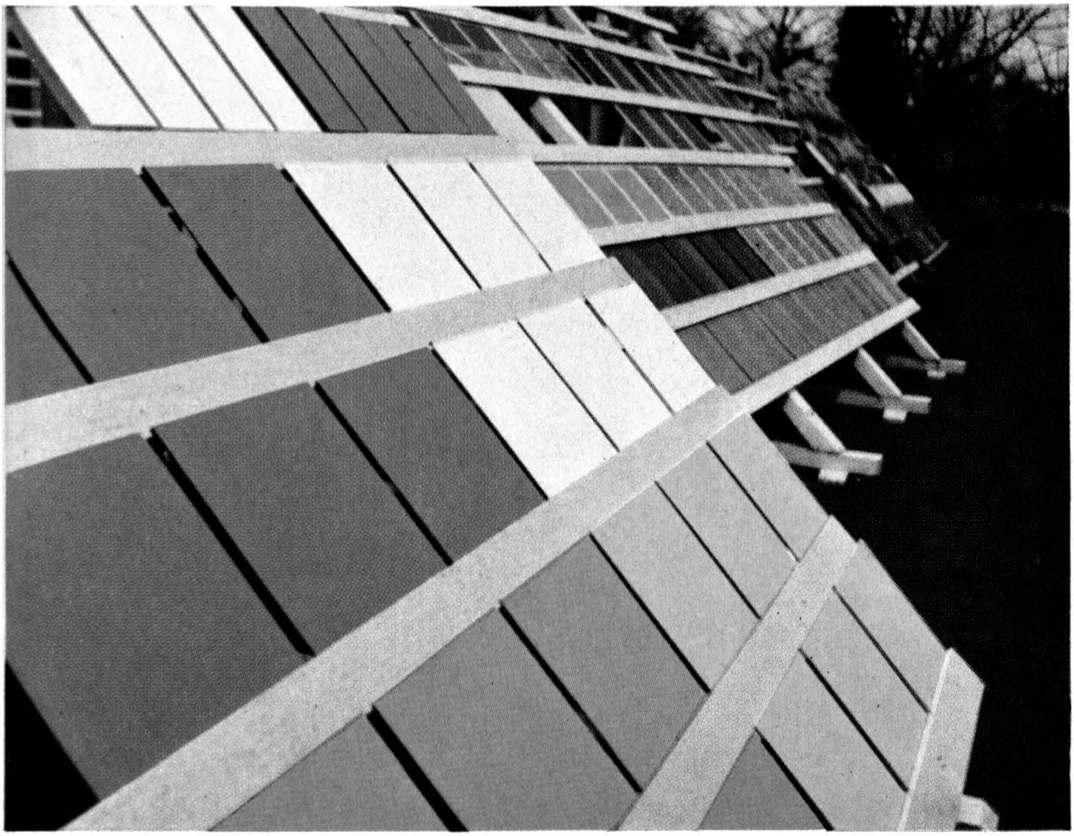


Fig. 13. Hexanetriol phthalate/adipate pre-polymer

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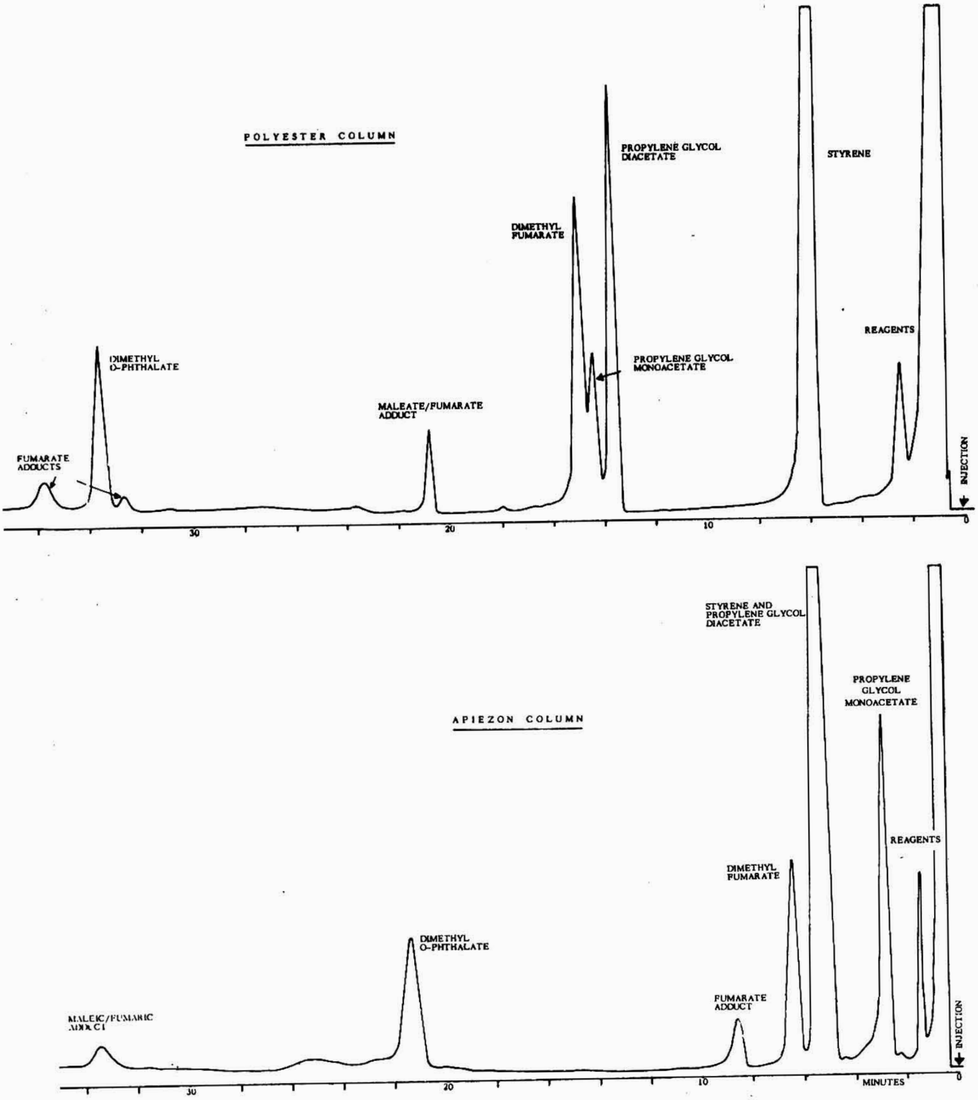

Fig. 14. Styrene thinned 1,2-propylene glycol maleate/o-phthalate unsaturated polyester

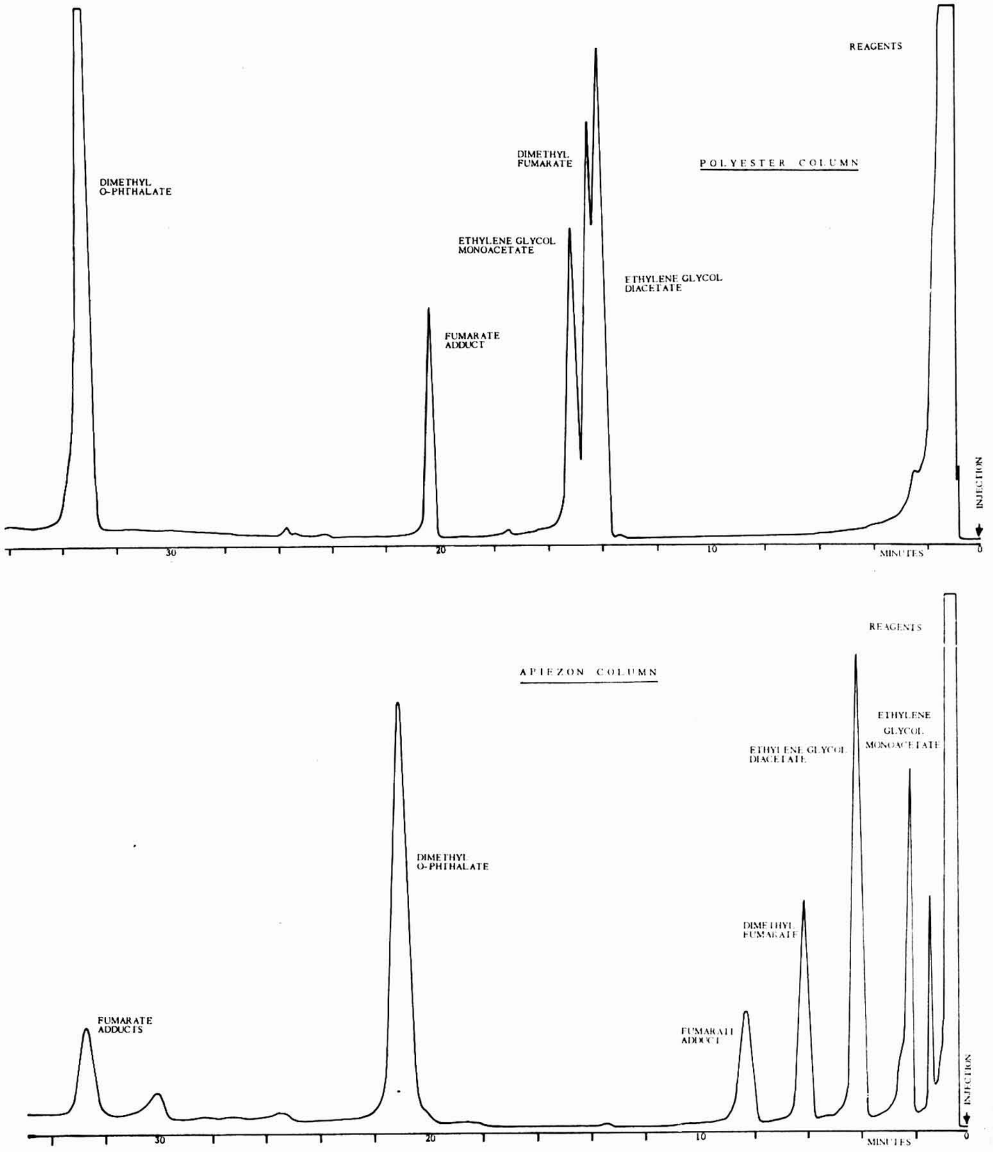

Fig. 15. Unthinned ethylene glycol fumarate/o-phthalate unsaturated polyester

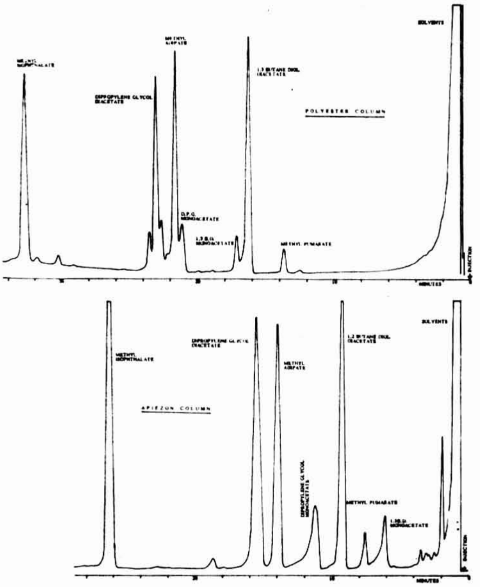

Fig. 16. Unthinned 1,3-butanediol/dipropylene glycol fumarate/isophthalate/adipate unsaturated polyester

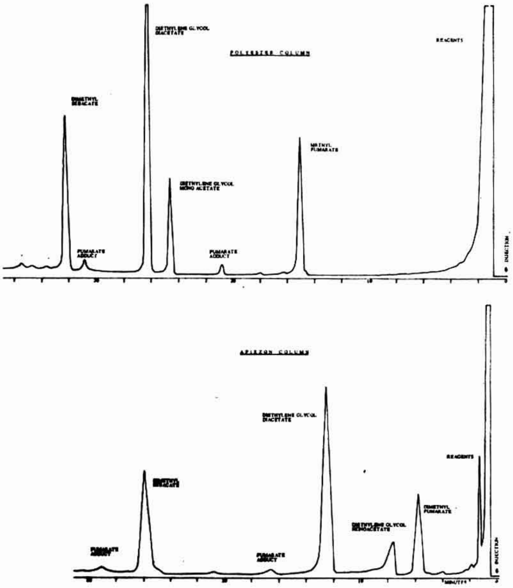

Fig. 17. Unthinned diethylene glycol maleate/sebacate unsaturated polyester

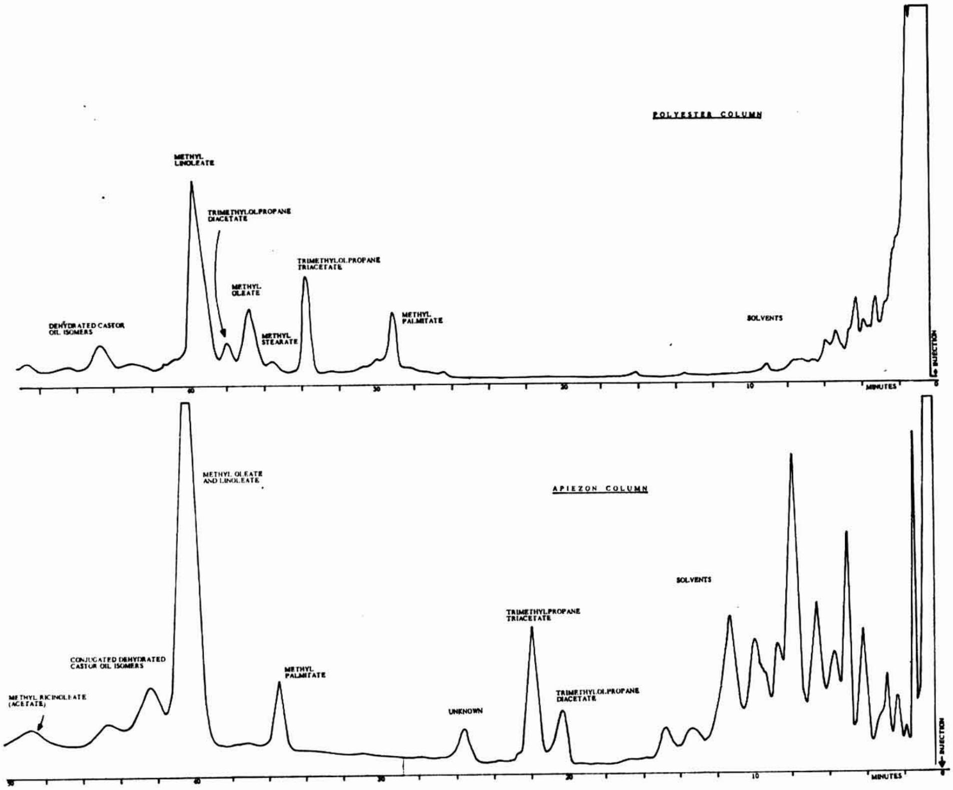

Fig. 18. Trimethylolpropane treated dehydrated castor/soya bean polyurethane oil

(d) *Urethane oils and urethane alkyds*

These may be analysed by this method but no derivatives of the isocyanate are normally seen in the chromatograms, examples of which are shown in Figs. 18-19.

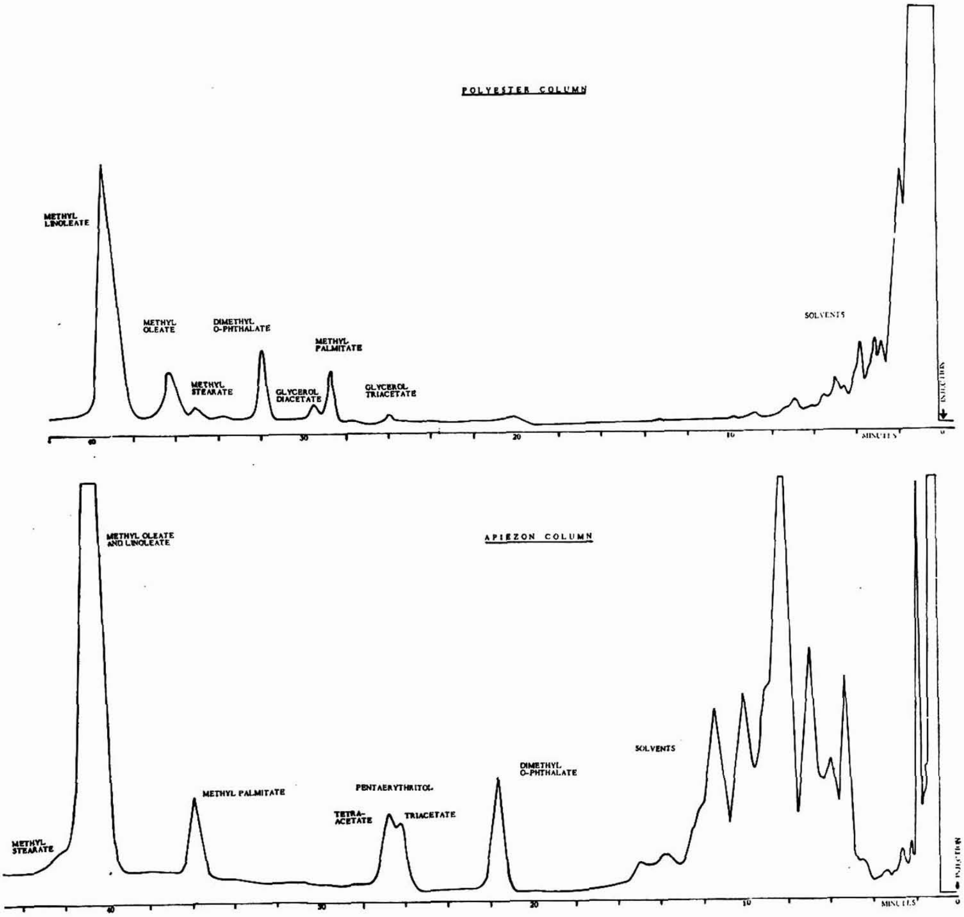

Fig. 19. Pentaerythritol safflower oil o-phthalate polyurethane alkyd resin

(e) *Monomeric ester plasticisers*

These are much simpler systems than any of the foregoing and, even in admixture, it is not anticipated that there would be any difficulty in their analysis by this method.

Comparison of interesterification analysis with existing methods

The usual methods of analysis of polyester systems mentioned in the introduction use 1-2 g of solid sample and, if full separation and identification of all likely constituents in an unknown is sought, take a minimum of three days working time and a somewhat longer elapsed time. The interesterification method provides systematic qualitative analysis on 25-40 mg of solids, or proportionately more of a solution, in three hours elapsed time and somewhat shorter working time. In addition the manipulative work is much simpler and the method is of greater sensitivity, as minor ester components may easily be missed in the usual methods unless special efforts are made to detect them, but are unlikely to remain undetected by interesterification. The method, however, is not quantitative in application to the complex systems to be expected in this field of analysis, although in the more simple cases an estimate of the proportions of the constituents may be made from inspection of the chromatograms and by comparing them with standards of similar composition.

Conclusion

The general method which is described, of analysis of polymeric ester systems by interesterification with methyl acetate followed by gas liquid chromatographic analysis of the volatile reaction products, allows of a full qualitative analysis in three hours. The results are systematic in that no constituent is likely to be missed, and they provide a basis on which a quantitative analysis by traditional methods, if so required, may be much more expeditiously and correctly carried out.

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The behaviour of liquids on rotating rollers*

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Summary

Simple lubrication theory is applied to the study of the flow of liquids between rotating rollers, and some of the predictions of the theory are tested experimentally.

The formation of ribs on rotating rollers is one of the phenomena examined and it is found that the critical condition is given by $\frac{\eta U}{\gamma}\left(\frac{r}{h}\right)^{\frac{3}{4}} = \text{const.}$ Beyond the critical condition it is found that the number of ribs per centimetre is determined by independent functions of roller radius, roller separation and the parameter $\left(\frac{\eta U}{\gamma}\right)$.

Reasons are given for assuming that the simple theory may be a good approximation to the conditions existing on a tackmeter and a simple relation is deduced between the tack force, ink viscosity, and speed. Experimental test of the formula shows good agreement between tack force and apparent viscosity if the latter is measured for ink recovered from the tackmeter.

Le comportement de liquides sur rouleaux tournants

Résumé

On se sert de la théorie élémentaire de lubrification pour étudier l'écoulement de liquides entre rouleaux tournants, et l'on essaye expérimentalement certaines prédictions de la théorie.

La formation des nervures sur rouleaux tournants est l'un des phénomènes examinés, et l'on trouve que la condition critique s'exprime par $\frac{\eta U}{\gamma}\left(\frac{r}{h}\right)^{\frac{3}{4}} = \text{constante.}$ Au delà de la condition critique on trouve que le nombre de nervures par centimètre est déterminé par les fonctions indépendantes, du rayon de rouleau, de l'ouverture des rouleaux, et le paramètre $\left(\frac{\eta U}{\gamma}\right)$.

On mentionne les raisons pour supposer que la théorie élémentaire peut offrir une bonne approximation aux conditions qui existent dans un " tackmètre." On déduit un rapport simple entre la force de tack, la viscosité d'encre et la vitesse de rotation. L'épreuve expérimentale de la formule démontre un bon accord entre la force de tack et la viscosité apparente de l'encre receuillie à partir du " tackmètre."

Das Verhalten von Flüssigkeiten auf Rotierenden Walzen

Zusammenfassung

Beim Studium des Durchfliessens von Flüssigkeiten zwischen rotierenden Walzen wird einfach die Theorie des Schmierens angewandt, und einige auf dieser Theorie beruhenden Voraussagen werden experimentell geprüft.

Eines der Phänomene ist die Riffelbildung auf rotierenden Walzen, und es wird festgestellt, dass der kritische Zustand sich aus der Gleichung $\frac{\eta U}{\gamma}\left(\frac{r}{h}\right)^{\frac{3}{4}} = \text{konstant}$ ergibt. Jenseits des

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*Presented to London Section on 20 October 1966.

kritischen Zustandes wird gefunden, dass die Zahl der Riffeln per Zentimeter durch unabhängige Funktionen von Walzenradius, Walzenabstand und den Parameter $\left(\frac{\eta U}{\gamma}\right)$ bestimmt wird.

Für die Annahme, dass sich die einfache Theorie den auf einem Zügigkeitsmesser herrschenden Zuständen gut zu nähern scheint, werden Gründe aufgeführt, und es wird eine einfache Beziehung zwischen Stärke der Zügigkeit, Druckfarbenviskosität und Geschwindigkeit abgeleitet. Experimentelle Prüfung der Formel weist gute Übereinstimmung zwischen Stärke der Zügigkeit und Pseudoviskosität auf, wenn letztere messang mit Druckfarbe, die vom Zügigkeits-messgerät rückgewonnen worden war, vorgenommen wird.

Поведение жидкостей на вращающихся роликах

Резюме

Простая теория смазки применяется в изучении течения жидкостей между вращающимися роликами и некоторые предсказания этой теории испытываются экспериментально. Образование прослоек на вращающихся роликах представляло одно из изучаемых явлений и найдено что критическое условие дается формулой $\frac{\eta U}{\gamma}\left(\frac{r}{h}\right)^{\frac{3}{4}} = \text{const.}$ В закритических условиях найдено что число прослоек на сантиметр определяется независимыми функциями радиуса роликов, зазора роликов и параметра $\left(\frac{\eta U}{\gamma}\right)$.

Даются основания для предложения что эта простая теория может служить хорошим приближением условиям существующим на адгерометре и получено простое соотношение между силой сцепления, вязкостью чернила и скоростью. Экспериментальная проверка этой формулы дает хорошее согласие между клейкостью и видимой вязкостью, если последняя измеряется для чернила извлеченного из адгерометра.

Introduction

The problem of the ink technologist has been, and is, that of relating the behaviour of his products on the machine to physical properties which he can measure and control. In one respect the most convenient property to study is that of viscosity. However, printing inks are non-Newtonian materials and their viscosities, in the sense of Newton, are very dependent on the conditions of test or usage.

The shear rates on an average printing machine vary widely. They are comparatively low in the duct, but on the rollers intermittent shear rates of the order of 10^5 sec^{-1} exist. To study the rheological properties of inks is comparatively easy at low rates of shear and several viscometers are available. At higher rates of shear it is much more difficult for a number of reasons : (*i*) viscosity is usually fairly high so considerable Joule heating occurs, causing significant rise in temperature, (*ii*) in rotational viscometers, at least, the ink sample usually disintegrates at a comparatively low rate of shear which is essentially characteristic of the ink.

In view of these difficulties it is not surprising that very little has been published concerning the correlation of the performance of inks with rheological properties.

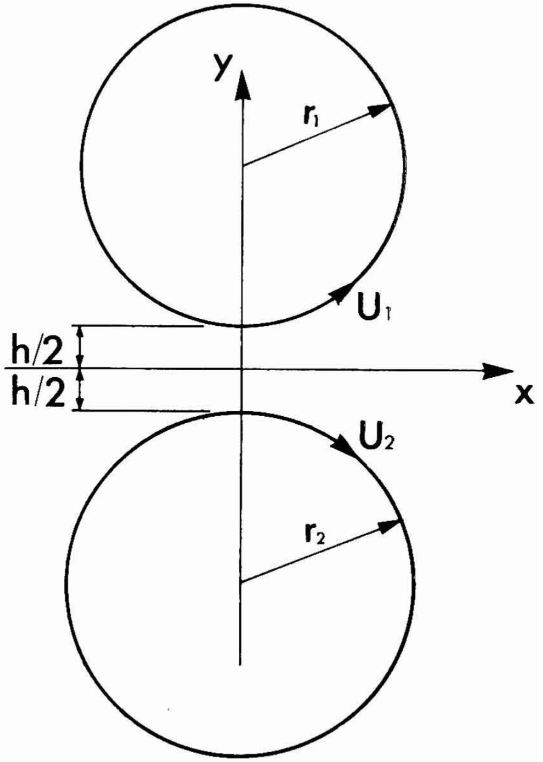

Fig. 1. Co-ordinate axes used in the calculation

Theory of liquid behaviour on rollers

As a first step in an attempt to correlate the behaviour of liquids on rollers with viscous properties it is convenient to have a theoretical relationship to give a guide as to the nature of such a correlation. It was suggested by Sir Geoffrey Taylor that a theoretical study of the system might be possible using lubrication theory. In essence this consists of applying mathematics to study the flow of liquid near the nip between two rollers, where, for practical purposes, it can be assumed that the streamlines are perpendicular to the line joining the centres of the rollers.

If we take axes as indicated in Fig. 1 the differential equation for the motion of the liquid is

$$\eta \frac{d^2u}{dy^2} = \frac{dp}{dx} \qquad (1)$$

Where u is the liquid velocity, η the viscosity of the liquid and p the pressure in the liquid. The roller surface can be represented by $y = h/2 + x^2/2r$ so the boundary conditions are

$$u = U_1 \text{ on } y = h/2 + \frac{x^2}{2r_1}$$

$$u = U_2 \text{ on } y = -\left(h/2 + \frac{x^2}{2r_2}\right)$$

Where U_1, U_2 are the surface speeds of the rollers and h is the separation at the nip.

Integrating equation (1) and using the equation of continuity we obtain for the pressure distribution relative to atmospheric pressure

$$p = -\frac{4\,\eta U}{h^2} \cdot \frac{x}{\left(1 + \frac{x^2}{2rh}\right)^2} \qquad (2)$$

where $U = \frac{1}{2}(U_1 + U_2)$ and $1/r = 1/r_1 + 1/r_2$.

Consideration of this equation shows that if we set $x = n\sqrt{2rh}$ the expression for p becomes

$$p = -\frac{4\,\eta U \sqrt{2rh}}{h^2} \quad \frac{n}{(1 + n^2)^2} \qquad (3)$$

This means that $\sqrt{2rh}$ is a basic length unit for the system and that the pressure distribution curve is always the same on this scale.

The properties of the liquid and the geometry of the system only determine the levels of the maximum and minimum pressures.

The calculation is strictly valid for fully immersed rollers, but, by using suitable values for the radii of the rollers, it is possible to determine the order of magnitude involved and to estimate how close an approximation it may be to the thin film case. For rollers of diameters 3 in with a 10 micron nip the basic unit of length is 0.62 mm. The maximum value of $n/(1+n^2)^2$ occurs when $n={}^1/\sqrt{3}=0.58$. The maximum (minimum) pressure is therefore situated 0.36 mm from the nip. Inserting the values for r, h in equation (3) we obtain

$$p = - 2.469 \times 10^5 \, \eta U n/(1 + n^2)^2$$

and since the maximum value of $n/(1+n^2)^2$ is 0.325 the maximum (minimum) pressure is $8.02 \times 10^4 \, \eta U$ dynes cm^{-2}.

The maximum value of $n/(1+n^2)^2$ is 0.325 and when $n=3$ the value falls to 0.03, so that rather more than 90 per cent of all the pressure change takes place in the range ±3, i.e. ±1.86 mm from the nip. It appears therefore that in the thin film case the menisci in the nip do not have to be too extensive in order to achieve reasonable approximation to the fully immersed case.

Considering the formula for the maximum pressure, we see that for a value of $\eta U=12.5$ the minimum pressure on the outgoing side becomes -10^6 dynes cm^{-2} relative to atmospheric pressure. Under these conditions one must expect cavitation to occur in the liquid[1]. With fully immersed rollers the cavities will be self-healing in the main body of liquid and a line of bubbles will be observed close to the nip.

In the thin film case, self-healing cannot take place and the continuous liquid sheet ends at or before the position of minimum pressure, and webs or filaments form between the two rollers. The nip on the exit side is quite small, not more than 0.36 mm in the case considered here.

It seems likely therefore that the simple theory outlined may be a sufficient approximation to the thin film case for predictions to be made at least of the form which relationships between forces and ink properties should take.

Formation of ribs on rotating rollers

Turning now to phenomena which the theory predicts, it is seen that the pressure in the liquid on the exit side of the nip is below atmospheric. Under extreme conditions this leads to cavitation, but well before this stage in the non-immersed case, it is observed that the liquid surface is not a smooth cylinder but consists of a series of equally spaced thicker rings or ribs.

This rib formation occurs not only with roller application but whenever thin films of fairly viscous liquids are applied by rolling or spreading. Even the familiar brushmarking of paints is thought to be caused by the same mechanism. In the field of printing technology, rib formation is most prevalent with the operations of varnish coating or adhesive application for laminating On the printing machine itself the use of reciprocating rollers randomises the rib pattern and thus minimises its effects.

The foregoing theory has been extended[2, 3] to obtain information about the onset of ribbing and the spacing of the ribs. Qualitatively the mechanism is as follows. When the rollers are at rest, the meniscus has a definite shape depending on the position of the free surface. The pressure drop across the surface on the axis of symmetry will be γ/R where γ=surface tension of the liquid and R is the radius of curvature of the surface. When rotation commences there will be an additional pressure drop due to the motion and the liquid surface will move towards the nip to make R smaller and thus balance the additional pressure. The inward movement of the meniscus will be opposed by the increased volume of liquid coming through the nip and eventually the surface will be distorted. From this approach it was deduced that ribbing should commence when a critical value of the parameter $\eta Ur/\gamma h$ was exceeded.

Experiments have been made to study the onset of ribbing[4]. In these, three pairs of rollers were used so that the effect of roller diameter could be ascertained. The gap between the rollers could be set by means of micrometers. A number of liquids of low viscosity were used, the viscosity being measured by a Ferranti-Shirley viscometer and surface tension by means of the du Nouy torsion balance. The critical velocity at which ribbing commenced was determined by increasing the speed slowly until the ribs appeared. At least three determinations were made and the results averaged.

Data were obtained for three roller pairs, four gap settings and seven liquids. The analysis of the data was made in two stages. First the critical velocity for each roller pair and gap was plotted against γ/η for each liquid. Straight lines were obtained and the slopes calculated. The logarithms of these slopes were then plotted against the logarithms of the ratios gap/roller radius. A straight line of slope $\frac{3}{4}$ resulted, leading to the formula for critical conditions

$$\frac{\eta U}{\gamma}\left(\frac{r}{h}\right)^{\frac{3}{4}} = 10.3$$

From the practical viewpoint, this relationship implies that it is not possible to apply varnish or adhesive films at economic speeds without ribbing and a rib-free film can be obtained only if the ribs can flow out before the film has set.

In the same series of experiments runs were made at higher speeds with more viscous liquids to determine how the spacing of the ribs varied with speed and viscosity. The rib number, i.e. the number of ribs per centimetre, was determined by photographing the rollers and counting the ribs on the negative. Speeds employed were 15, 30, 60 cm/sec.

A preliminary examination of the results showed that above a viscosity level of about 2.4 poise the rib number appeared to be independent of liquid and speed. Statistical analysis confirmed this, so the rib numbers were averaged for each value of the gap and roller pair. The values are shown in Table 1. Each value in the table represents the limiting rib number (N) for each combination of the geometrical variables. Examination of the data in Table 1 showed that the limiting rib number is obtained as a product of two independent functions, one involving the radius only and the other the gap. This is a different situation from the critical condition where the ratio of gap to radius is the relevant parameter. One deduction which can be made from this result is that the rib number is still finite when the gap approaches zero.

Table 1
Experimental values of N summed over viscosity and speed

Gap	Combination A	Combination B	Combination C
1	12.4	11.3	10.4
3	9.1	8.3	7.9
5	6.7	6.5	6.0
7	5.0	4.9	4.7

For the remaining data obtained in these experiments the rib number n was plotted against $\eta U/\gamma$ for each gap-radius combinations. As is to be expected the graphs cut the axis of $\eta U/\gamma$ at a definite value $(\eta U/\gamma)_0$ and it was found that if n/N was plotted against $[\eta U/\gamma-(\eta U/\gamma)_0]$ essentially the same curve was obtained for all values of the gap-radius combination.

Hence it is concluded that the rib number n is determined by three independent functions of the roller radius, the gap and the parameter $\eta U/\gamma$ respectively.

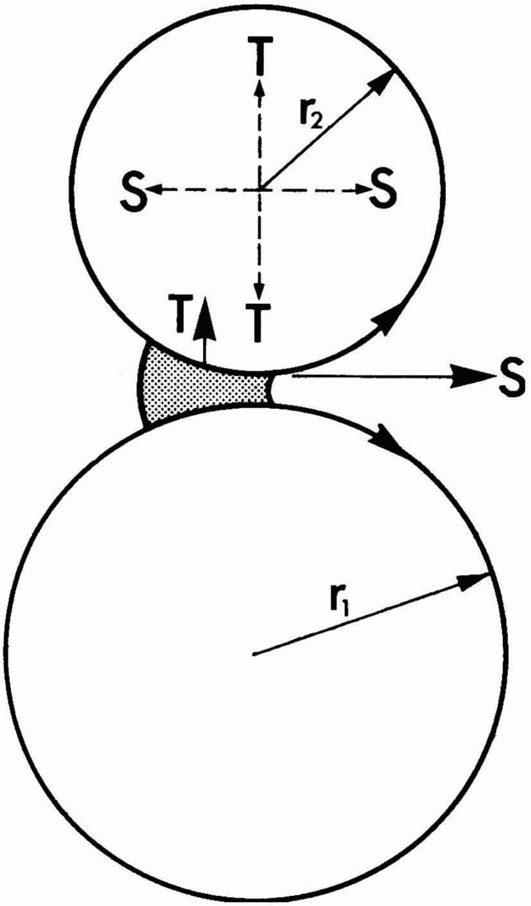

Fig. 2. Force diagram for a tackmeter

Application to the tackmeter

The results of the lubrication theory can be applied to obtain a relationship between viscosity and the force measured on a tackmeter^5. If it is assumed that the theory of the fully immersed case is a sufficiently close approximation to the thin film case the relationship between the tackmeter force and the viscosity of the ink is a simple one.

A tackmeter consists essentially of a rider roller rotating in near contact with a larger drum carrying an ink film (Fig. 2). The rotation of the drum would cause the rider roller to move in precession around the drum if a compensating force were not applied. It is this force which is measured in a tackmeter.

The rider roller is subject to two forces, (1) a force acting to lift it away from the drum due to the pressure developed in the liquid, and (2) a tangential force tending to pull it in the direction of rotation. The normal force is equivalent to a force along the line of centres and a couple, M, in a direction opposing the rotation of the rider roller. The force along the line of centres is balanced by the thrust T between the two rollers. This thrust may be due solely to the mass of the rider roller or may be due to spring loading of the bearings. Likewise, the tangential force is equivalent to a couple tending to rotate the roller in a forward direction, together with a force S acting at the roller spindle.

When the system is in equilibrium and the rider roller rotates at constant speed, the torques acting on it must balance, hence

$$Sr_2 = M + F \tag{4}$$

where F is the frictional torque in the bearings.

It can be shown by integrating the pressure distribution over the inlet side of the nip that

$$M = \frac{2 \pi \eta U r \sqrt{2rh}}{h} \tag{5}$$

and

$$T = \frac{4 \eta U r}{h} \tag{6}$$

Eliminating h between these equations and substituting in (4) we obtain the relation

$$S = \frac{\sqrt{2} \pi r_1}{r_1 + r_2} (\eta UT)^{\frac{1}{2}} + F/r_2 \tag{7}$$

This is a simple equation between force and viscosity which should be amenable to experimental test. In a previous attempt at a correlation between force and viscosity, the value for the latter was taken from the slope of a rheogram. This is equivalent to using the plastic viscosity if the ink is considered as a Bingham body. It was found in this work that, although the equation appeared satisfactory for a single series of inks, different lines were obtained for different series.

However, since the ink is represented by a single parameter it seemed better to use the apparent viscosity instead of plastic viscosity. Ideally one should measure the viscosity at the shear rate occurring on the roller system, but for various reasons, such as temperature rise and instability of the ink in the viscometer, this was not possible. As a compromise, it was decided to measure viscosity at a single rate of shear at a level which it was reasonably certain could be employed for all inks. Fig. 3 (*a*) shows a plot of shear force against square root of viscosity at a single rate of shear. The viscosities in this graph were measured on samples taken from the can of ink and consequently did not allow for breakdown of structure caused by shearing between the rollers. It was known[6] that in some cases at least the structure destroyed by shearing was slow to recover, so a further set of viscosity measurements was made on ink recovered from the rollers of the tackmeter at the end of the experiment. This data is shown in Fig. 3 (*b*). Calculation shows that the correlation coefficient has improved from 0.615 to 0.850 by using the recovered ink.

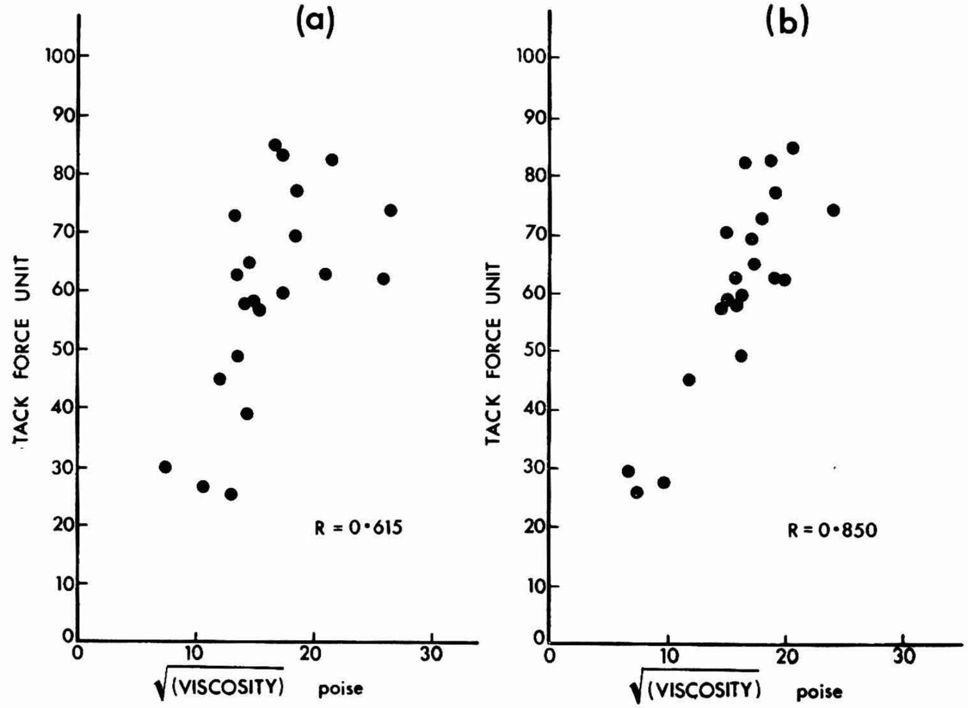

Fig. 3. Tack force versus viscosity at constant speed
(a) Viscosity of samples from can (b) Viscosity of samples from tackmeter

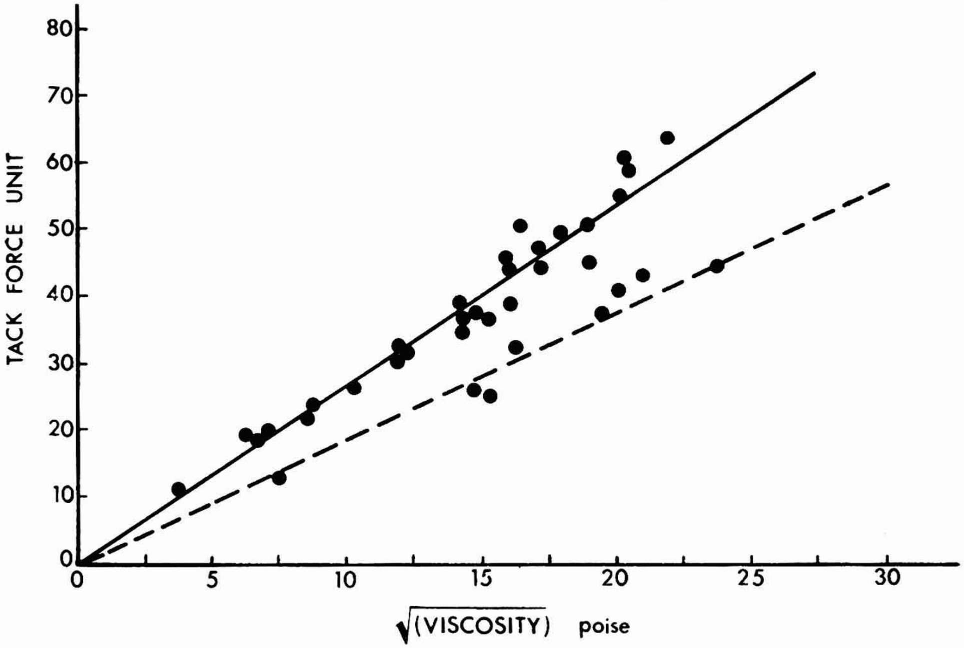

Fig. 4. Tack force versus viscosity for various inks

This result was encouraging, so the measurements were made on a large variety of inks, letterpress or lithographic, from various sources. The results are shown in Fig. 4, in which it is seen that a large majority of the point falls around one line whilst the remainder falls around a second line. Similar lines were obtained for other speeds of rotation. According to equation 7 the slopes of these lines should be proportional to the square root of the speed. A plot of these quantities is shown in Fig. 5, where the linearity is seen to be excellent.

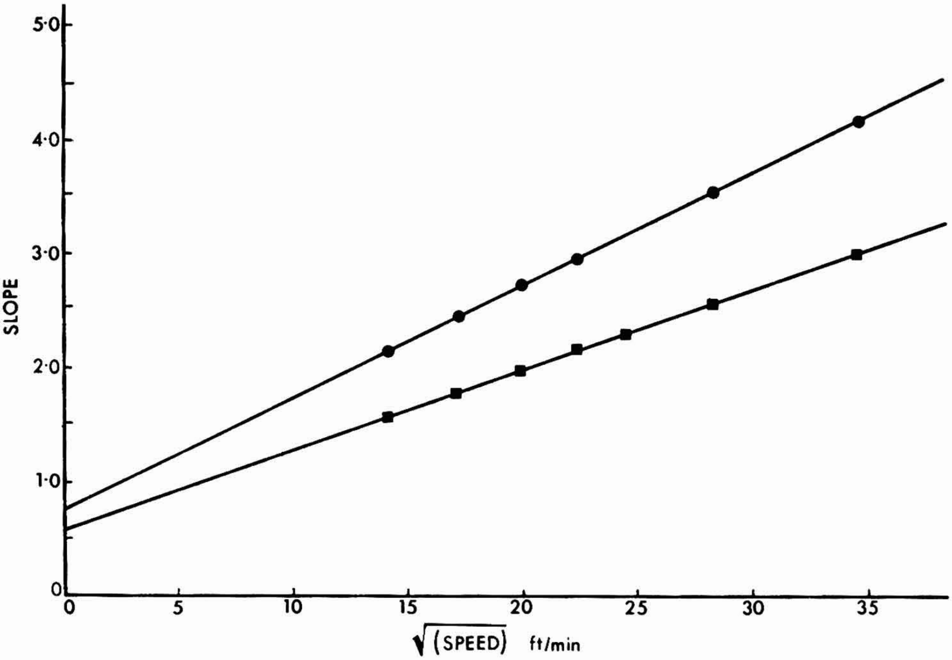

Fig. 5. Slopes of tack force viscosity curves versus speed

Discussion

The overall agreement with the simple theory is promising, but the existence of at least two lines suggests that, although viscosity is the major property involved, a second one is also contributing to the measured force. It is possible that, since most inks are viscoelastic, the other quantity involved will be an elastic modulus. Qualitative support for this hypothesis was obtained by measurements on four suspensions of carbon black in lithographic varnishes which were known to differ in their elastic components. When force was plotted against the square root of the viscosity for these materials the line joining the points cut across the original lines, the most elastic varnish falling near the lower line. If it is assumed that the viscoelastic order of these suspensions is the same as the varnishes, the experiments afford some support for the hypothesis that the tack force is viscoelastic in character.

In this case one must expect the type of force between rolling surfaces to change with speed from being predominantly viscous at low speeds to predominantly elastic at high speeds. The transition would be expected to occur at speeds having some relation to the relaxation time of the ink. The machine time which is relevant to the problem would seem to be the time taken for an ink particle to pass through the nip, i.e. nip width divided by machine speed.

Acknowledgments

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Discussion at London Section

Mr. P. Davies asked what was the usual appearance of the Moiré fringe pattern produced when printing ink ribbed on the rollers?

Mr. C. C. Mill said that with ink ribbing on a roller system the ink film transferred from the forme roller was not of uniform thickness, so that some dots carried more ink than others ; this set up a pattern of its own, related to the rib distribution on the rollers. Reciprocation of the rollers was used to overcome this, but where linear reciprocation was used, interference patterns still occurred occasionally, and it was necessary to use sinusoidal reciprocation to overcome the effect completely.

Mr. A. R. H. Tawn commented that Mr. Mill had said that his experiments with interchangeable rollers of different radii had led to the conclusion that the rib number depended, not on the harmonic mean of the radii (as expected), but on the radius of the interchangeable roller. How did the ink know which was the interchangeable roller?

Mr. Mill said that using one fixed roll prevented complete interchanging the roller system ; this made it impossible to arrive at a final conclusion of the causes of rib growth.

Mr. K. Pond asked whether Mr. Mill attributed the differences in pressure profiles to roller speeds or to roller diameters.

Mr. Mill said that, in the roller coating machine discussed, roll speeds were the same ; distortion occurred in the pressure diagram because of pressure retention at the nip centre axis, possibly due to inertia.

Mr. R. G. Kinsman asked whether any information was available on the magnitude of the ribs as well as their frequency. He observed that some liquids, e.g. polyisobutylene in oil, <30 poise, appeared to produce more peaky ribs than others.

Mr. Mill said that the magnitude and frequency of ribbing was proportional to roller separation. Difficulties occured with narrow gaps, which could mask observations. It was emphasised that viscous effects only, and not viscoelastic effects, were observed.

Mr. J. A. L. Hawkey asked how far the ribbing effect manifested itself at the end of the roller distribution train? What was the position at the final separation on to paper? In smoothing out, Tollenaar and others had suggested that cavitation persisted within the transferred film and the ink film splitting was governed by the position of the voids, which in turn depended on the time of dwell before impression.

MR. MILL considered that the question of films and speeds on a printing machine was rather outside the scope of the paper ; many difficulties were involved in measuring film thickness on roller systems. When the ribbed profile went through a nip it was squashed, but re-formed on emerging from the nip. With low viscosity media, some filtration could also occur ; this factor could lead to preferential vehicle transference.

MR. HADDON asked whether the type of roller used altered the deformation of the liquid.

MR. MILL said that varying the hardness of the rollers did not affect ribbing.

MR. I. DOUGLAS asked how the forces between two rotating rollers were affected if one of the rollers reciprocated axially.

MR. MILL did not consider axial reciprocation to have a significant effect on the force fields occurring in the system.

DR. C. H. WISBEY asked whether the number of ribs tended to diminish with time.

MR. MILL said that their separation on the rollers was maintained, even to the extent of following a displacement of a single rib.

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Grinding*

By A. C. B. Mathews

Coates Brothers & Co. Ltd., Easton Street, London, W.C.1.

Summary

The method of preparation and its influence on the final properties of paint or ink are critically discussed. Practical manufacturing experience provides the data for the conclusions that are reached. The importance and mechanisms of air elimination during the process of milling are examined in some detail.

The flocculated and the agglomerated conditions of dispersions are explained from a simple fundamental point of view, and the adsorbed polymer layer theory elaborated to provide an hypothesis which fits observed performance. Observation indicates that dispersions arenot necessarily flocculated or deflocculated but desirably in a third state for which the author uses the term "micellar." The logical manufacturing recommendations resulting are enumerated. Mills are classified with regard to their performance. A new mill having the advantages of unattended operation on thick consistency material is described.

Broyage

Résumé

On discute critiquement la méthode de préparation et son influence sur les propriétés de la peinture ou de l'encre. Les conclusions sont basées sur les données en provenance des expériences dans la fabrication pratique. On examine en quelque détail l'importance de l'élimination d'air pendant le procédé de broyage, ainsi que les mécanismes d'en achever.

On explique, au point de vue à la fois simple et fondamental, les conditions de floculation et d'agglomération des dispersions, et également on élabore la théorie de la couche de polymère adsorbée afin de fournir une hypothèse en accord avec le comportement observé. Les observations revèlent que les dispersions ne doivent pas être floculées ou défloculées, mais par préférence doivent être dans un troisième état que l'auteur caractérise par le terme micellaire. On énumère les recommandations logiques à propos de fabrication qu'y suivent. Des broyeurs sont classés à l'égard de leur rendement. On décrit un nouveau moulin pour le broyage des pâtes épaisses qui se marche sans l'intervention d'un ouvrier.

Mahlen

Zusammenfassung

Es wird der Fabrikationsprozess und sein Einfluss auf die endgültigen Anstrich- oder Druckfarben kritisch betrachtet. Die gezogenen Schlussfolgerungen basieren auf praktischer Werkserfahrung. Die Wichtigkeit und der Mechanismus der Eliminierung von Luft im Zuge des Mahlprozesses wird ins einzelne gehend untersucht.

Die geflockten und die agglomerierten Zustände von Disperionens werden von einem simplen, fundamentalen Standpunkt aus erklärt, und es wird sehr auf die Theorie von der adsorbierten, polymeren Schicht eingegangen, um eine zum beobachteten Verhalten passende Theorie vorschlagen zu können. Beobachtungen zeigen an, dass Dispersionen nicht notwendigerweise ausgeflockt oder entflockt sind, sondern sich in einem wünschenswerten dritten Zustande befinden, für welchen der Verfasser den Ausdruck " micellar " wählt. Die sich logischer Weise für die Fabrikation ergebenden Ratschläge werden vorgetragen. Mühlen werden hinsichtlich ihrer Leistungen in Gruppen eingeteilt. Eine neuartige Mühle, die vorteilhafter Weise Materialien dicker Konsistenz ohne Aufsicht fertig stellt, wird beschrieben.

Растирание

Резюме

Обсуждаются метод изготовления и его влияние на конечные свойства красок или чернил. Практический производственный опыт является критерием достигнутых

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*Presented to the Thames Valley Branch, London Section 29 September 1966, and to the Southern Branch, London Section, 14 November 1966.

заключений. Подробно рассматривается важность механизма удаления воздуха во время процесса измельчения. Условия флоккуляции и агломерации дисперсий объясняются с фундаментальной точки зрения и развивается теория адсорбированного полимерного слоя для вывода гипотезы соответствующей наблюдаемому действию. Наблюдения показывают что дисперсии не обязательно флоккулируются или дефлоккулируются, но скорее приобретают иное третье состояние, которое автор именует «мицеллярным». Перечисляются полученные логические производственные рекомендации. Мельницы классифицируются по характеристикам их действия. Описывается новый тип мельницы имеющей преимущество работать без надзора с материалом густой плотности.

Introduction

From the users' point of view it is not difficult to distinguish between good and bad paints. The physical conditions in a good paint are very complex and many previous papers on the subject do not attempt to apply theory to practice or to suggest modifications of methods of manufacture likely to lead to improved results.

Consideration of the mechanism of satisfactory and faulty production, and of the final quality, led to the concept of the pigment-vehicle structure of good paint being one in which every primary pigment particle is surrounded by several superimposed adsorbed layers of polymers drawn from the vehicle. The familiar adsorbed mono-layer did not seem sufficient to prevent hard settlement even if the layer consisted of the longest polymer chains in the vehicle standing on end on the surface of the pigment particle.

As the terms aggregate, agglomerate, flocculate, colloid and micelle used freely in this discussion differ in meaning from author to author their definitions for the purposes of this paper are as set out in Fig. 1.

Primary pigment particle (primary for short)	One very small piece of solid (coloured) substance or extender from the powder supplied by the manufacturer.
Aggregates	Clusters of primaries—dry interspersed with air.
Agglomerates	Clumps of primaries, interspersed with some constituent of the vehicle—no air.
Colloids	Graham's original meaning. Amorphous material dispersions. Intermediate between true solutes and suspensions.
Floccules or flocculates	Often reversible structural clumps responsible for false body etc. in a paint.
Micelles	Agglomerates of molecules. They form in concentrated solutions i.e. those thicker than the critical micelle point below which we have molecular dispersions.
Sol	Colloidal solution, i.e. suspension of primaries kept up by Brownian motion.
Gel	Structural colloidal solution. Coagulated sol.

Fig. 1. Definitions of terms

Pre-mixing

The first difficulty met with in manufacture is the elimination of air and its replacement by vehicle. It is not easy to visualise aggregates turning directly into agglomerates ; some action must take place whereby the air occluded in aggregates and adsorbed on the individual particles, is separated and made to escape to the atmosphere.

OCCA Conference

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On adding pigment to some vehicle in a pug, a very few of the separate primaries will go into the liquid, and a large amount of the pigment will remain on top of the vehicle, Fig. 2 (1).

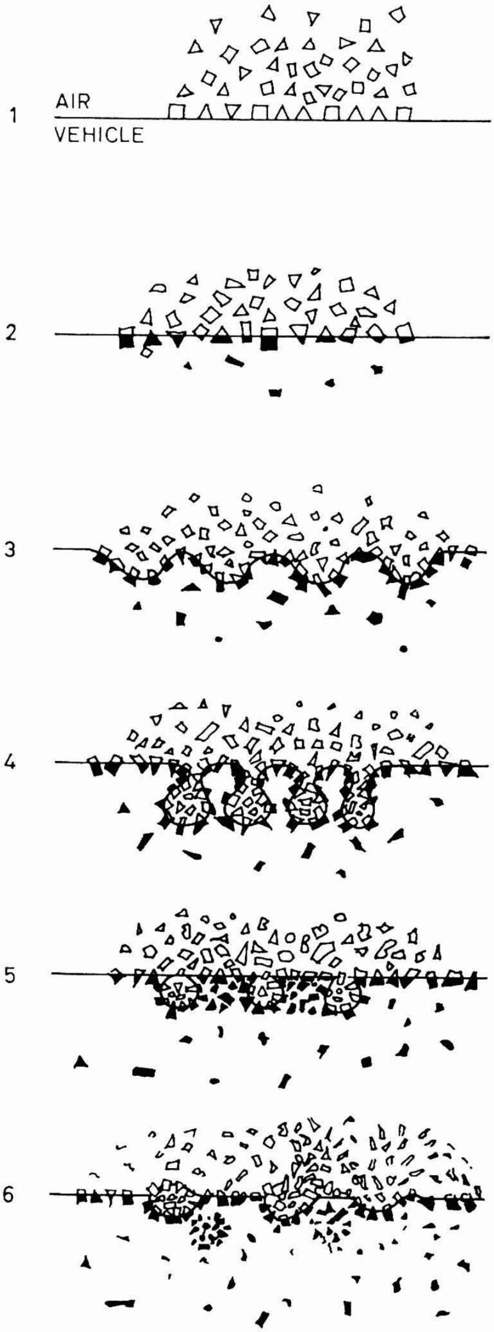


Fig. 2. Air elimination

At the vehicle surface some primaries will be partially submerged Fig. 2 (2). These have a surface expanding effect, Fig. 2 (3) and (4) and, eventually, the surface becomes so convoluted that the folds close up forming bubbles as in Fig. 2 (5). These bubbles, when large, will rise to the surface and between them will be liquid spaces now bounded by partially wetted primaries which become more completely wetted by the pug action bursting the bubbles containing dry pigment. The explosive energy released when a bubble is burst tends to turn the bubble envelope inside out, Fig. 2 (6), forcing partially wetted primaries into the fully wetted state. Kneading of bubbles containing pigment will tend to drive primaries into and through the bubble envelope wall so that a stage is reached when only bubbles free of pigment remain. At the same time the bubbles themselves will be divided and subdivided. This is the general picture of the pugging process which goes on repeating and becoming more intense as the charge thickens up on the addition of more and more pigment.

The smaller the bubbles the greater the internal shearing forces needed to be supplied mechanically by the pug to burst them. Greater force can only be effective in proportion to the increase in consistency of the pug charge, and when the motor is on the point of overload trip, bubbles of irreducible size will remain, however long the pug runs. At this stage some further improvement can often result by " soaking," i.e. allowing the batch to stand, provided the pigment is comparatively easily wetted by the vehicle. In the case of prussian blue, the umbers and certain blacks, which are difficult to wet, the liquid/solid interface is not likely to advance and may actually recede. With these pigments there is, therefore, no virtue in letting the batch stand and soak, and in fact there is considerable danger of spontaneous combustion, aggravated by the bubbles being larger and more plentiful ; thus there will be plenty of air present to support combustion and also less chance of heat dissipation so that oxidation can accelerate to the active combustion stage.

Degrees of wetting

Differences of bad wetting can be shown by taking a palette knife coated with beeswax which, when immersed in water and withdrawn, will be found to be dry. The intriguing question is whether it is wetted when immersed. A second palette knife coated with vegetable black similarly immersed appears silvery due to an intervening layer of air between it and the water causing total internal reflection. It too is dry on withdrawal. Obviously the beeswax, which showed no silvery effect is more wetted than the vegetable black. It is suggested that it is in a " forcibly wetted " state when under water.

Contact angle is the usual measure of wetting, and is well known to be subject to many influences, including time. When wetting is bad, high contact angles are known to decrease, but they will not always do so to the stage where the interface will advance and wetting spread, which is the condition needed for " soaking " in the pug to be beneficial.

Cases are known where, for example, a black and a white pigment, dispersed in sufficient vehicle to give a thick nearly black paste, will, on thinning-out, produce a light grey. One explanation of this unwelcome effect is that the black pigment is " forcibly wetted " by the vehicle in the thick paste condition, but that the mobility conferred by thinning-out results in de-wetting, enabling the dispersed black particles to clump together, thus reducing their pigmenting effect by self-obscuration. This is a very severe case of flocculation.

It is argued from this behaviour that a paint film containing de-wetted primaries will have bad durability. Weak adhesion of vehicle to pigment primaries will result in poor film cohesion. In other words, durability is proportional to goodness of wetting. If wetting is poor the film will fail, first by loss of gloss, then chalking, and finally by wholesale disintegration. If the vehicle is one that shrinks on ageing, the film will craze due to loss of the reinforcing effect that is conferred on it by dispersion of a well wetted pigment —tantamount to good adhesion between vehicle and pigment primaries. In printing inks the defect known as piling could well be due to this cause. The importance of complete air elimination is obvious by this argument.

Stir-in pigments

The American " stir-in " pigments are coated with an easily wetted layer, but for satisfactory use the adhesion of the added vehicle to the coating as well as the coating to the primary must be good, and one must ensure that the pigment coating is not dissolved by the thinner to be used. If the thinner does dissolve the coating, agglomeration is likely and, if serious, a lumpy paint will result. Some reliable mechanism is very necessary to prevent agglomeration, which can be responsible for paints appearing still badly ground after repeated milling.

Roller grinding

The next process to be considered is triple rollering. The action here is the same as in the pug, namely internal shear, but much more intense. This is achieved, without the expenditure of excessive horsepower, by concentration of effort in a very small zone of action, i.e. the nip between the rollers, treating very small portions of the batch in turn. That the shearing action is internal is proved by measurement of the actual separation of rolls showing that this is many times the dimensions of individual primaries. If it were not so the rate of output of such mills would be completely uneconomic.

The action of triple rollering is therefore to reduce further the size of bubbles in the mix that were irreducible in the pug. Aggregates of pigment remaining are broken up, more air is released and the whole batch is unified, resulting in one large agglomerate, ideally now containing no air and ready for thinning out.

Ultimate elimination of air

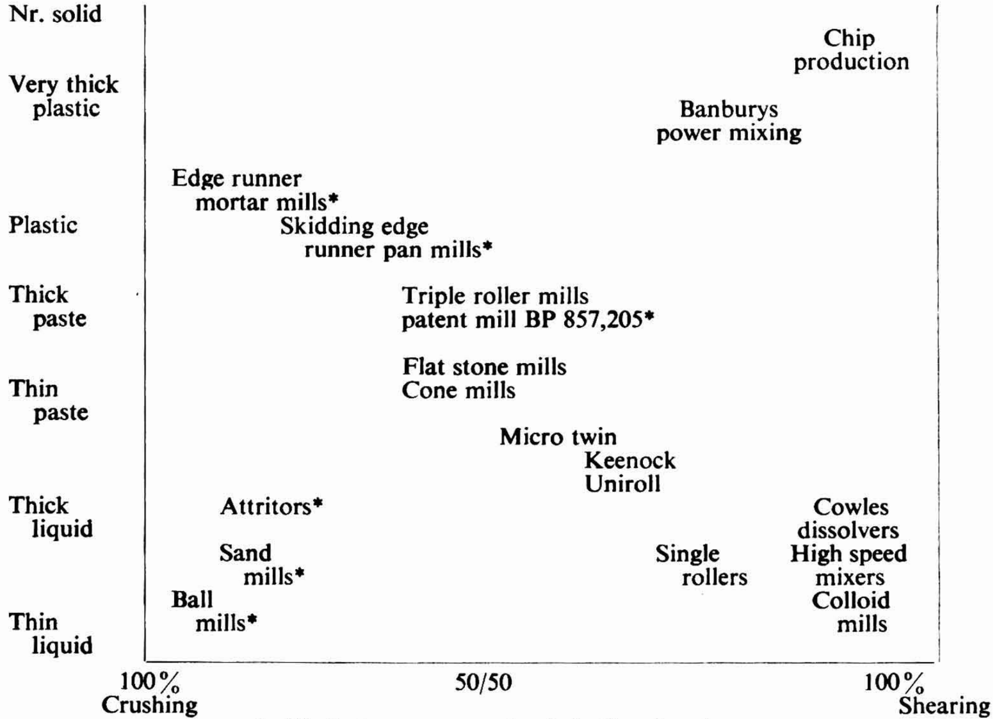
The ultimate disappearance of the very small bubbles is an interesting speculation. It is known that for very finely divided pigments the surface area increases very considerably as particle size gets really fine. Assuming that effective internal shear normally divides one very small bubble into two, each of approximately half the original volume, but totalling more than the original area, we shall get a rapid increase in total surface area as the process proceeds. On surface tension theory the total free energy is in consequence considerably increased at an accelerating rate as bubble size is reduced. This demands an appreciable amount of work, which to be effective demands a high viscosity of the mix, if it is achieved at slow speed. These two factors explain the very high power needed if the process is to be carried out expeditiously.

However many times the bubbles are divided, smaller and smaller ones still remain, and the ultimate disappearance is not explained. Again on surface tension theory the excess pressure inside a submerged bubble is directly proportional to the surface tension, and inversely proportional to the radius of the bubble. If this holds true for very small bubbles the pressure could become very large indeed for microscopic bubbles. It is suggested that ultimate complete air elimination could be due to pressure solution of the remaining air into the vehicle, from which it diffuses out when near a free surface, this condition being well provided on a triple roller mill for example.

Alternatively, milling conditions may favour coalescence of small bubbles once they are freed of dry pigment by kneading action. This mechanism appears to operate in the new paste mill described later.

Classification of mills

Fig. 3 shows mills arranged according to their capabilities. Mills can either crush or rub, or combine these two actions. On the left of the chart would be placed mills performing by 100 per cent crushing ; hammer mills used for the preparation of metallic pigments would be an example. On the right would be placed a mill that operates by 100 per cent shear ; the single roller bar mills provide the nearest approach to this condition.



*mills that can run unattended after charging

Fig. 3. Classification of mills

Vertically the mills are positioned according to their most efficient working consistency, thus highest up on the chart are high powered pugs and chip production mills, both well over to the right of the diagram.

It is maintained without much fear of disagreement that the need for a crushing action with modern pigments is very much less now that pigment manufacturers supply materials whose largest particles are much smaller than those that would be acceptable in a good quality enamel and even in printing inks. Crushing is effective mostly for particle size reduction and shearing mostly for wetting. Shearing is therefore the action primarily required in modern paint or ink manufacture. Internal shear must be relied on for the sake of output rate and the thicker the mix the more effective will this action be.

Of course, if a fine pigment is aggregated, due to inadequate washing for example, some crushing action is an advantage. At the extreme stiffness used in Banbury power mixing and, in the ultimate, in chip production, the intense internal shear is quite sufficient to break up normal aggregates and even to reduce the particle size of soft materials.

It will be seen that triple roller mills occupy a central position on the chart, Fig. 3, and they are indeed the most versatile mills; they provide good crushing when necessary and then finish their job with first-rate shearing action. Also, as every ink maker knows, they are de-aerators *par excellence*. To get rid of minute air bubbles from a paste, the only practical machine to use is the roller mill, and a possible explanation of the mechanism has been put forward above.

Compared with ball mills the triple roll mill has the disadvantage that a premix in a pug is needed, and also constant attendance by a mill man. To get over both such disadvantages the mill shown in Fig. 4 was devised by the author to provide exactly equivalent performance to that of a triple roller mill, even to the extent of getting rid of air.

In the several laboratory sized mills made, air is eliminated during the early stages in the form of large discrete bubbles. The action of the mill is such that the paste is forced by means of an extruder type screw pump through a multiple ball-bearing thrust race where the balls are very much more enveloped by their tracks than in a normal mechanical bearing. It is this feature that provides the necessary shearing action because true rolling can only take place at one point and over the rest of the line contact the ball makes with the track shearing takes place. This mill performs well on ink and paint, but awaits scale-up. A special feature is the detached stirrer, which is effective in preventing channelling of the batch.

Thinning out

After milling, the next operation in paint or liquid ink making is thinning out. It is known that this must be done slowly, and with the thickest addition first. Not only is this mechanically expedient, but, as will appear later, there are also imperative theoretical reasons for so doing. If thinning is carried out in the wrong order and/or too fast, the so-called colloidal shock may lead to an unstable product. The paint will suffer from clumped agglomerates or strong floccules and exhibit bad flow, bad gloss, apparent bad milling and

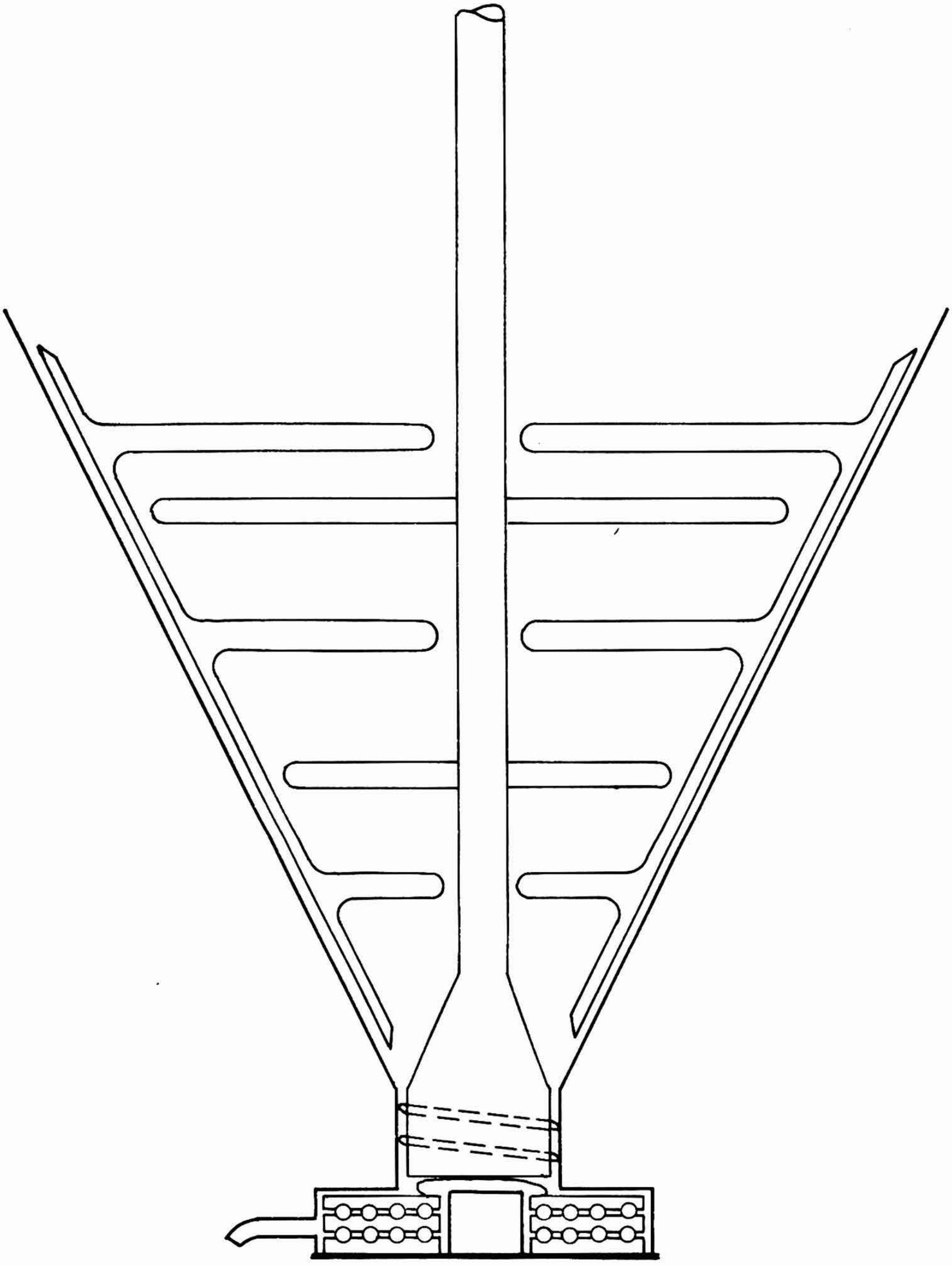


Fig. 4. Line contact paste ball mill. (B.P. 857, 205)

poor opacity or colour value. That such defects were avoided by the old craftsman methods of manufacture can be proved by examination of old samples of gloss paint or enamels made 40 years or so ago. Some of them will be found to be in excellent condition, needing very little stirring to redisperse a definite but not hard settlement, and yielding films showing very good flow and gloss. It is to account for such properties, and correlate many facts of manufacturing experience, that the idea of the multiple adsorbed layer on each primary is put forward.

Storage properties

In considering the differences in response to stirring between one kind of settlement and another, the first obvious conclusion was that hard rock-like settlements were densely packed primaries practically free of vehicle, whereas those that redispersed easily were not so tightly packed, being interspersed with some constituent of the vehicle. The question of the part played by *adsorbed layers on primaries* then arises : the adsorbed layer of vehicle-solid on each primary has been well established by experimental determination using, for example, solutions of purified materials such as stearic acid in benzene. Monolayer adsorption in such experiments is general, but a monolayer of even a very long chain polymer scarcely seemed adequate to account for long-term easy stirring of settlement in paints. Vehicles in common use always contain a spectrum of polymers and it seemed reasonable that a primary could adsorb a first layer of most preferred polymer, which itself could then adsorb a layer of another solid constituent from the vehicle, and so on, depending on the number of vehicle constituents capable of being adsorbed on each other. In this way, each primary would become encased with a thick adsorbed total layer and could behave as an entity. Such entities would have an average density very much less than the density of the primary, and, in spite of Stoke's law, it would on balance settle less, and less tightly. Such multi-layers would have to be thick and robust to resist squeezing out and deformation due to gravity forces, and keep the primaries sufficiently separated to reduce attractive forces between them, so preventing agglomeration.

Multi-pigment enamels presented a difficulty because it did not follow that different pigment primaries would all prefer the same first adsorbate. However, this should not matter provided the outer layers were more or less the same. For this to happen, the conception of multi-layers is vital ; the more the better.

To prevent both bad settlement and agglomeration, these entities need to be as similar as possible, at least as far as their outer surfaces are concerned.

Interim conclusions

So far, therefore, it would seem that to make good paint one should comply as much as possible with the following conditions :

(1) Choose pigments all preferring to adsorb the same polymer for the first layer.

If this is impossible :

(2) Provide a wide range of molecular sizes of polymers in the vehicle so that each primary can select its own first choice, the second layer will then be nearer the average and so on until the outer layers are all the same. It follows that greater amounts of the outer polymers are needed in the vehicle.

(3) Adopt the mill-base or concentrate method of manufacture, the outer layers all coming from the added vehicle, thus having a better chance of all being the same.

The order of adsorbed layers—Traube's rule

A lead as to the natural and stable order of the adsorbed layers is necessary at this stage and it is suggested that Traube's rule provides this. Traube's rule is variously stated, one version says that : " In aqueous solution surface tension decreases as an homologous series is ascended".[1] It is argued that surface tension is directly related to contact angle, contact angle is inversely related to wetting, and wetting is directly related to adsorption : therefore, adsorption at a surface will increase as one ascends an homologous series.

If this is true for substances in aqueous solution there is no apparent reason why it should not be so for non-aqueous solutions, and surely polymers of increasing molecular weight correspond very well to ascending an homologous series[12]. It can be expected therefore that, other things such as polarity being equal, the longest chain polymers will be more readily adsorbed to form the inner adsorption shell on a primary, and the shortest ones will form the outer layers.

Varnishes

A consideration of varnishes, i.e. pigment-free vehicles, in respect of their physical composition, is relevant to the discussion. It used to be considered essential for high quality varnishes to be matured and there is no doubt that gloss, flow and brushability were improved by this treatment, poetically described 40 years ago as " letting the fire die out." What is really happening is that the mobility conferred by thinning after final cooking to body, and keeping the tanked varnish warm for six or 12 months, allows polymer orientation, forming stable micelles clustering round real or imaginary nuclei. By the same arguments as put forward above for paints, the highest molecular weight polymers will be in the centre, and subsequent layers will each be of shorter chains with the lowest molecular weight polymers clustering in the outermost ill-defined layer.

Micelles in varnish

Fig. 5 is reproduced from the first of three papers given in 1933 by W. E. Wornum[2] and classifies Varnish Micelle behaviour, the papers explaining much of the performance of varnishes, based on the micelle conception.

Fig. 6 gives a two dimensional idea of a micelle formed from polar molecules (a), and non-polar (b). Polar molecules will cluster radially, and non-polar ones more in a laminar formation. There is, of course, the possibility of mixed types ; much of A. E. Alexander's[3] work on biophysical chemistry is illuminating on micelle formation and behaviour.

The varnish micelles must be understood not to have hard boundaries, just a gentle grading, a vignette effect. Now consider what happens during their formation : the biggest, relatively immobile, long-chain molecules cluster

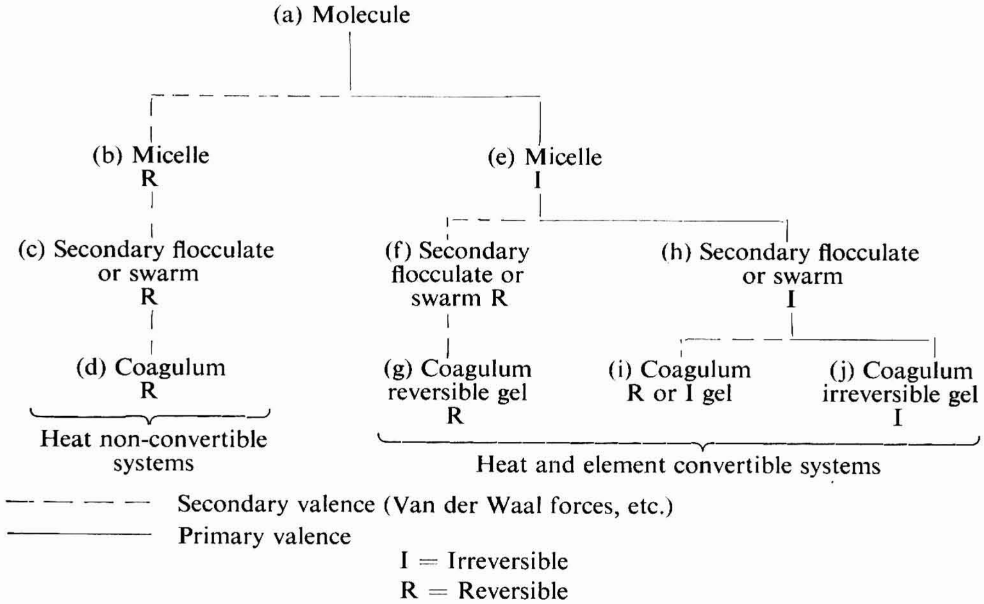


Fig. 5. Structural diagram of disperse phase

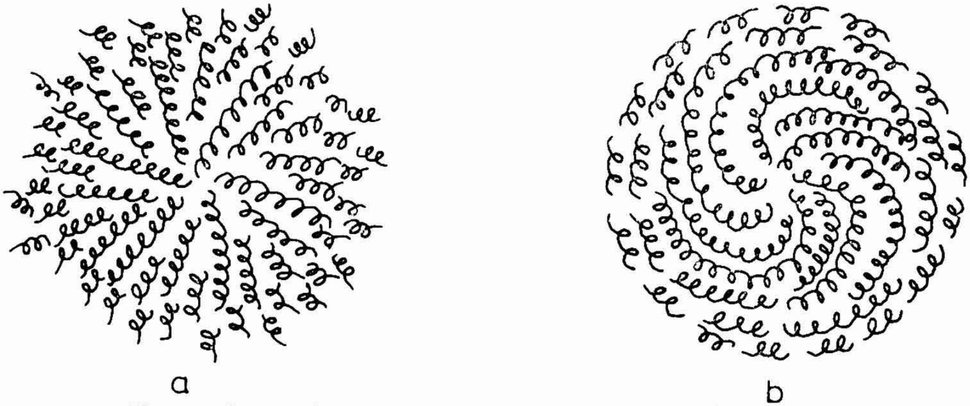


Fig. 6. Mixed chain length polymer micelles, (a) polar, (b) non-polar

together first, collecting lighter and lighter molecules outwards, the solvent retreating farthest. This could well be the mechanism of syneresis. The excluded solvent augments the liquid phase which is itself freed of the heavy, high viscosity molecules, now immobilised in the fully formed micelles' entities.

In consequence one observes increased mobility of these higher concentration resin agglomerates dispersed in a lower viscosity liquid phase, now much more Newtonian than it was, and all this at the same concentration of solids as in the original unmatured varnish. This state of affairs will obviously result in better flow and brushability. For good gloss, good flow is essential, but also necessary, is a good, clear homogeneous surface resulting from the uniformity of composition of the outer layers of the micelles.

Micelles in paint

The picture is very similar for good paint, except that a pigment primary is the nucleus for each micelle.

In a paper by Dintenfass[4] it is pointed out that primaries, particularly crystalites, are heterogeneous as far as adsorption is concerned. There are also inactive areas in this respect. Such being the case, the single pigment enamel picture first considered is probably hypothetical although it served a useful purpose, as a stepping stone to the mixed pigment example, which now becomes the general case for both single and mixed pigment enamels. Fig. 7 is a representation of a primary with attraction for two polar-type polymers on different areas of its surface, and yet it has a uniform outer layer of short-chain polymer molecules.

The diagrams show :

(1) Lower concentration of solvent in the micelle.
(2) Absence of long chains in the liquid phase.
(3) Different high molecular weight polymers in the first layer.
(4) Uniform low molecular weight polymers in the outer layer.
(5) Long-chain polymers concentrating on points (this appears necessary from geometrical considerations and could result from electrical causes).
(6) Reasonably uniform total layer thickness tending roughly to a spherical shape.

Flocculation and agglomeration

The literature is very confusing concerning flocculation. By the definitions adopted for this paper, agglomeration occurs when two or more primary centred micelles come together and stick.

The literature indicates that deflocculation, or full dispersion, is desirable, recognisable by hard dense settlement ; surely most undesirable ! And yet, we have the contradiction demonstrated by very old paint samples in good condition where the settlement is not hard, and it is manifestly fully dispersed to give such good flow and gloss, and no trace of colour unevenness. There must be a third state, represented by such paints for which the term " Micellar " is suggested, because they consist of dispersions of pigment-nucleated micelles, each as illustrated on Fig. 7.

Micellar paint

If a paint is not micellar, shown by its having false body, voluminous settlement and poor flow, or by severe hard settlement, it will be so because of defects in the multi-layers adsorbed on the primaries. If fast thinning, for example, partially dissolves away thin parts of the envelopes so that areas of primaries are insufficiently protected, two or more such entities can come together and stick. This is agglomeration which can in practice be so severe as to be irreversible. If areas of multi-layer adsorbed envelopes are absent completely from primaries, again two or more can come very close together, and this is flocculation. In general, flocculation is much more reversible than agglomeration, but the film from flocculated paint will have poor durability. With both

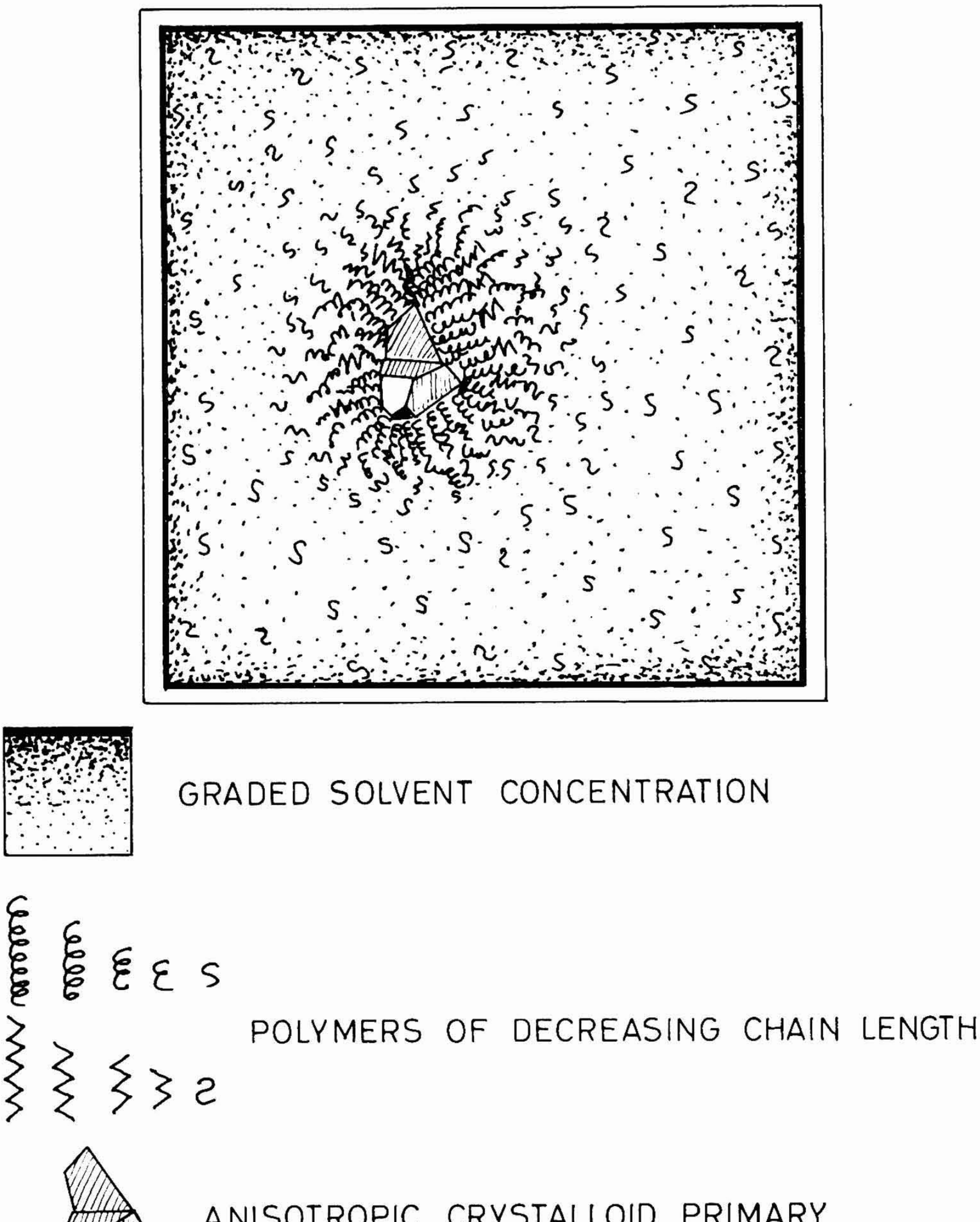


Fig. 7. Pigment primary and its environment as in a micellar paint

flocculated and agglomerated paints, flow and gloss will be poorer than for the same paint in a truly micellar state (as defined above).

Obviously the character of the pigment will have a very great bearing on flocculation and such false-body promoting primaries as china clay, talc etc. must be so by virtue of the fact that they possess very few active adsorption sites. One can also appreciate that their performance as thixotropy promoters is somewhat variable.

It is possible that some light is thrown by these considerations on the leafing of metallic pigments, supplied in the form of thin plates coated with stearic acid. Referring to Fig. 7 and the concentrated adsorption shown there on a point of the primary, it is suggested that this takes place all round the sharp edge of each plate, and that there is little or no adsorption anywhere else. Agglomeration thus takes place edgewise and the paint leafs.

General support for the above interpretation is given by a statement by A de Waele[5] who states, " given a sufficiently thick and undeformable adsorbed layer, coalescence of primary particles will be inhibited."

Thixotropic vehicles

Standardised thixotropic vehicles are now available and they relieve the paintmaker of reliance on the uncertain performance of china clay, bentonite and the like. Applying similar logic it could be that their behaviour is due to the presence of slightly *agglomerated* micelles. It would be preferable to say structurally reversible *flocculated* micelles, if flocculated in this connection was not a contradiction of the definitions adopted. One can imagine that possibly molecular shape is responsible and that the set-up state consists of a weak jigsaw of reversible cross linkages. Whatever their *modus operandi*, their use in a true micellar paint would inhibit any settlement indefinitely while preserving all the other desirable properties of such paint.

The role of the thinners

The role of the thinner must now be considered. If agglomeration is due to adsorbed multi-layers of uneven thickness on primaries, shock thinning will dissolve away most or all of the layer in the thin places and the paint will be susceptible to colloidal shock. If the thinner is preferentially adsorbed on the primary, the adhesion of the envelope will disappear, and the cohesion of the applied paint film will be weakened, moreover mass coalescence of naked primaries will occur. In this way the paint loses all its useful properties besides showing a rock-like settlement.

Paint bought from the shop and its performance

Fig. 8 is a schematic representation of a micellar paint made from normal (not thixotropic) vehicle, after indefinite standing. The top layer is clear liquid phase, free of the highest viscosity molecules and ideally nearly Newtonian. In this connection Dintenfass[5] says " flow is only possible if free liquid is present." The middle layer consists of loosely spaced micelles, each with a pigment primary as a nucleus and pervaded by the liquid phase. They are

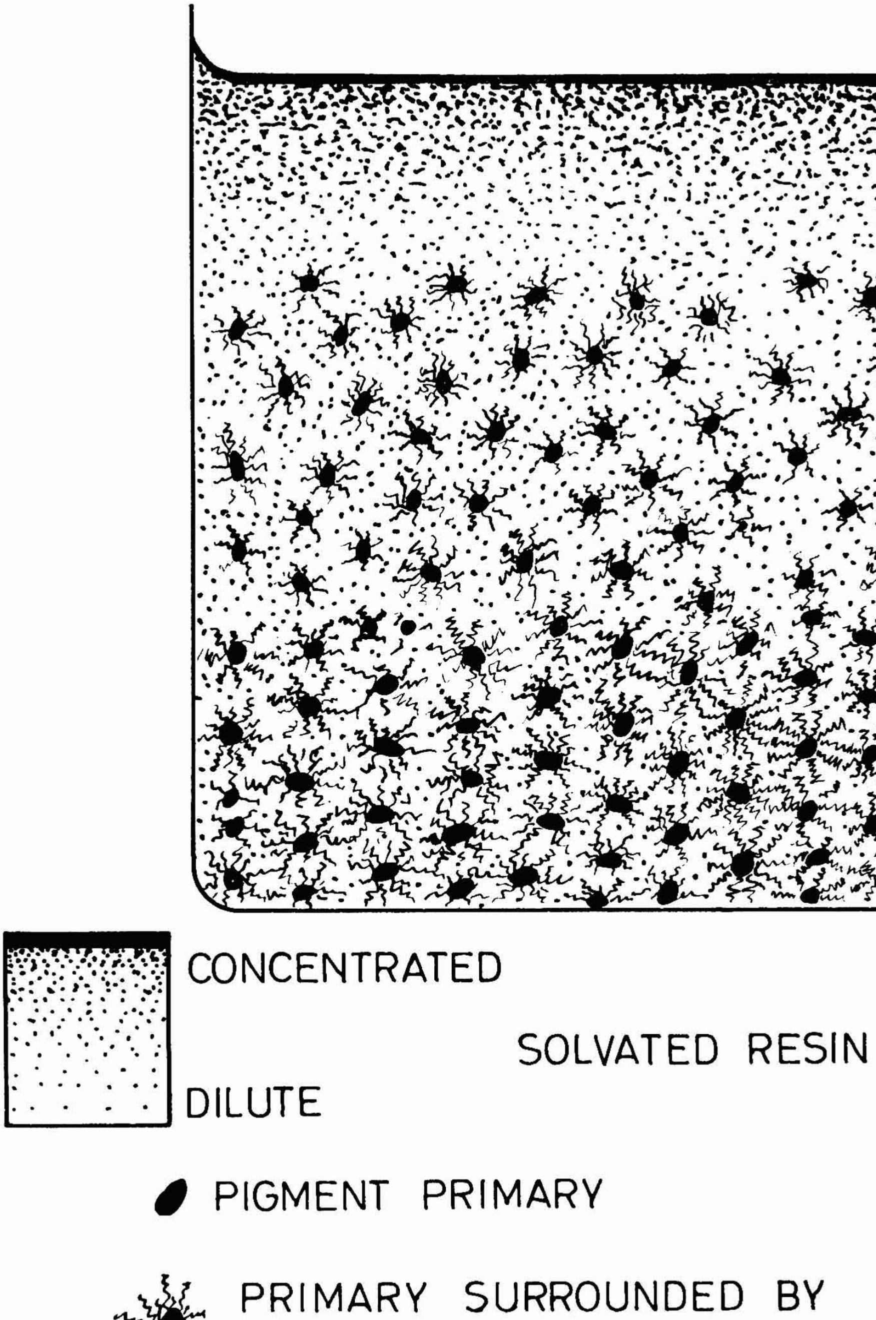


Fig. 8. Settlement of paint in the micellar condition

presumably smaller than those in the diffusely defined bottom settlement layer where there is no or very little liquid phase. Coalescence is prevented by the adsorbed multilayers of polymers, a condition that makes re-dispersal easy as the settlement has a plastic or even jelly character. In this connection it is significant to note that there will be small chance of first-adsorbed-layer adhesion to the primary changing on drying of a micellar paint film because there is no solvent here to evaporate. Dintenfass[7] warns against bad durability due to two possibilities of loss of adhesion in this region. The first is chemical interaction between the adsorbed layer and the primary, and the second is such reaction photo-chemically promoted.

Previous evidence of multi-adsorbed layers

It is obvious that nearly the whole of the foregoing argument depends for its validity on the existence of multi-adsorption layers, and it must be confessed that relevant literature references are few and far between. The first found by the author is in 1949 when Alexander and McMullen[8] make a tentative suggestion that the existence of multi-layers would explain what was otherwise an anomaly.

The second is in a book by K. W. Allen[9], who is rather more positive about their existence. The third is a recent paper by Sherwood and Rybicka[10] who have proved, by differential solution, the existence of two adsorbed layers. The present author is convinced, however, that the multi-layer theory must ultimately be verified by future experimenters in this field as it so adequately and unfailingly explains all the phenomena which he has met with in practice.

Recommendations

On the basis of the arguments presented in this paper the author recommends the following milling procedures, which must give in his opinion optimum manufacturing conditions :

(1) Give the pigment its first contact with the highest molecular weight constituent of the vehicle, or at least with its most preferred adsorbate from the complete vehicle.

(2) Exclude solvent at this stage if at all possible, but eschew at all costs any solvent which would be adsorbed in preference to solid constituents of the vehicle.

(3) Eliminate all air at as early a stage in the milling as possible.

(4) Make additions in descending order of molecular weight.

(5) Add thinners and drier last.

(6) Give the best opportunity possible for re-orientation to a stable adsorbed layer order to take place and compensate for any incorrect order of additions made during manufacture.

Condition (1) carries the pre-requisite that milling needs to be at a thick consistency because the highest molecular weight fraction of the vehicle will not constitute a large proportion of the total and will be of very high viscosity.

Clearly the production process best complying with the indicated requirements is the chips method, the unassailed excellence of the product being manifest by the maximum gloss, flow, colour value and transparency achieved, closely followed by power mixing, by Banbury for instance. The latter process can suffer from pocketing, necessitating a final refining process. Adequate conditions, however, can be, and are, achieved by pug and roller mill methods, or by using the patent mill shown in Fig. 4.

Milling by ball mill, attritor, sand mill or high speed mixer starts with the disadvantage that only comparatively thin consistencies can be dealt with, and so solvent generally has to be present during the milling, which for the reasons already given can be dangerous.

It is worth noting in passing that ball mills really are very deficient in shearing action. Only over a very restricted range of mill-base consistency will the balls in the cascade layer provide on impact effective shearing action, as in thin media the action of the ball is a bounce and not a shear. It is for this reason that ball mill grinding times are usually protracted and that sand mills and attritors mill faster since these provide more shear, but still, be it noted, only at point contacts.

Mechanism of good paint manufacture by less preferred methods

It is necessary to explain how good paints are made by these processes. First, as previously explained, the mill-base or concentrate method of production is helpful, but the main reason must be re-orientation, if adsorption layers are initially put down in unstable order. Desorption can readily take place and is the first step towards the assumption of correct layer order for the micellar condition. The great hazard is the risk of agglomeration during the re-orientation process ; this is very real and explains those instances where repeated single roller refining fails to produce a satisfactory result, and the batch has to be saved by rejecting refractory agglomerates by centrifuging.

The worst process of all for producing a high quality glossy enamel is fairly obviously the so-called sludge grind. It gives the maximum chance of the first adsorbed layer being solvent. Any subsequent polymer layer adsorbed will have transient foundations which evaporate when an applied film is dried.

With high speed mixer production the only chance of success is for the pigment to be very fine and free of strong aggregates. At the same time it must have a strong affinity for a solid constituent of the vehicle, to the exclusion of the thinner. It is established that high speed mixing carried on too long leads to agglomeration. Cowles Dissolvers and similar machines are useful for their original purpose of dissolving chips, and although the foundation adsorbed layer by this method is extremely well anchored, it is advisable not to prolong treatment any longer than is necessary for fear of agglomeration.

In connection with *ab initio* paint production by high speed mixer, an interesting view is put forward by H. E. Weisburg[11]. He says that the " success attainable is directly proportional to the dilatancy of the vehicle." One would have thought that any contribution to dilatancy made by the pigment would also be useful, but in general the theory seems acceptable. Dilatancy plus high speed is equivalent to a thick consistency, but the same risk of agglomeration re-appears as the mixer slows down, and the spurious high viscosity disappears.

Numerous papers on subjects of fundamental interest to milling have been concerned with the theory of adsorption and coalescence. This paper has related basic considerations to practical uses, and it has shown that adhesion is of primary importance. A very interesting and well constructed paper by W. A. Zisman[12] entitled "The Influence of Constitution on Adhesion" is strongly recommended as supporting reading.

Finally it is submitted that the most promising line of development towards better and more profitable milling should be directed to improving the chip and power mixing methods now available.

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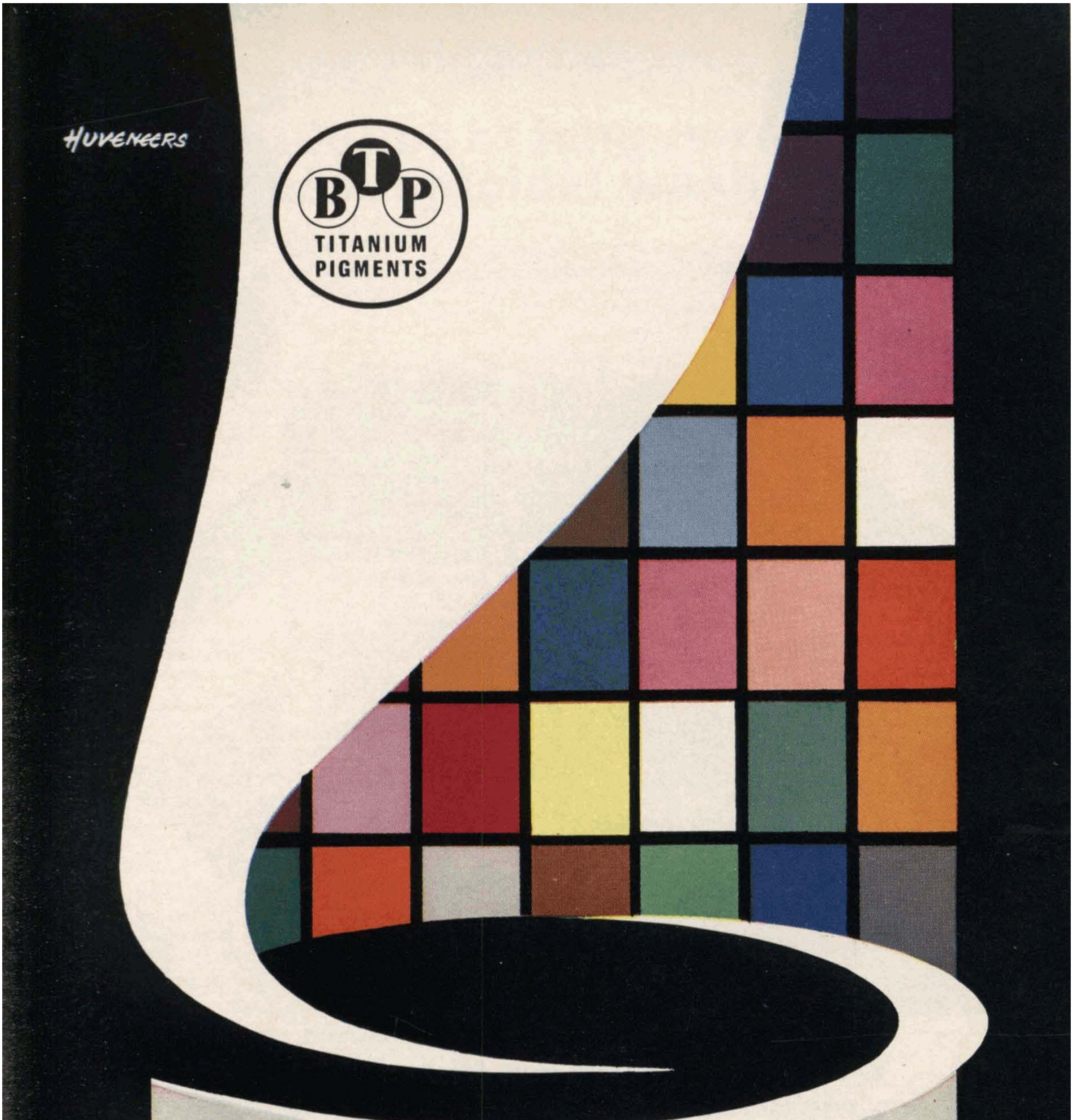
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PURE BRISTLES

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The formulation of fungus-resistant paints and fungicidal washes*

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Summary

The effectiveness as mould inhibitors of di-(phenylmercury) dodecenyl succinate, pentachlorophenol, N-trichloromethylthio-phthalimide, para-toluene sulphonamide, and zinc oxide in an alkyd enamel paint is investigated for indoor use in Melbourne and also in a humid tropical environment in Lae, New Guinea. The paint films are analysed for residual fungicide after various conditions of exposure.

The fungicides and zinc oxide are found of use for indoor application only at comparatively high concentrations. In Lae the effect of nearly all the fungicides is very short-lived, owing to the instability of the compounds under the prevailing climatic conditions. Indoors in Melbourne the loss of fungicides from the paint is slower and hence they have a longer effective life.

Fungicidal washes have been found useful for suppressing the growth of mould in two industrial establishments.

La mise au point des formules de peinture résistante à végétation mycelienne

Résumé

On a examiné, dans une peinture à l'alkyde, l'éfficacité en tant qu'inhibiteurs de moisissure pour l'usage à l'intérieur des composés suivants, di-(phényl-mercure) dodecenyle succinate, pentachlorphénol, N-(trichlormethylthio)-phtalimide, para toluène sulfamide et l'oxyde de zinc. D'ailleurs le rendement des fongicides a été vérifié à l'environnement humide des tropiques à Lae, Nouvelle Guinée. Afin de mieux comprendre les observations, on a déterminé la perte de fongicide en provenance des feuils de peinture sous des conditions divers d'exposition.

On a trouvé que les fongicides et l'oxyde de zinc sont éfficace pour l'usage à l'intérieur seulement aux concentrations assez élevées. A Lae l'effet de toutes les fongicides était de très courte durée à cause de l'instabilité des composés précites sous le régime climactérique. A l'intèrieur la perte de fongicide est plus légère et ainsi les peintures y restent éfficaces plus longtemps.

Die Formulierung pilzbeständiger Anstrichfarben

Zusammenfassung

Es wurde in einer alkydharzebundenen Anstrichfarbe für Innen die Wirkung folgender Pilzverhütungsmittel geprüft ; Das Di(phenyl)-quecksilbersalz der Bernsteinsäure, Pentachlorphenol, N-(Trichlor-methylthio)-Phthalimid, Paratoluolsulphonamid und Zinkoxid. Auch im tropischfeuchten Klima von Lae in Neuguinea wurde die Wirksamkeit der Fungizide geprüft. Die Anstrichfilme wurden auf unter verschiedenen Exponierungsbedingungen erlittene Verluste an Fungiziden hin analysiert, um die gemachten Beobachtungen besser verstehen zu können.

Man fand, dass die Pilzverhütungsmittel sowie Zinkoxid für Innenanstriche nur bei verhältnismässig hoher Konzentration von Nutzen waren. In Lae war die Wirksamkeit aller Fungizide von sehr kurzer Dauer. Der Grund dafür ist die Unbeständigkeit der untersuchten Verbindungen unter den in Lae herrschenden Verhältnissen. Der Verlust an Fungiziden aus den Anstrichfilmen geht innen langsamer vor sich, und dehar bleiben dieselben wirksam.

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*Adapted from a talk given by E. Hoffmann at the eighth OCCA Convention, Victor Harbour, South Australia, July, 1966.

Формуляция красок дающих защиту против плесени

Резюме

Исследовалась эффективность, в качестве подавителей плесени, ди-(фенил ртути) додецилен сукцината, пентахлорофенола, Н-(трихлорометилтио) – фталимида, паратолуол сульфамина и окиси цинка в алкидовой краске для применения внутри помещений. Ценность этих фунгисидов также проверялась во влажной тропической среде в Лаэ, в Новой Гинее. Выполнены анализы потерь фунгисидов в красочных пленках при различных условиях выветривания, с целью установления лучшего понимания этих наблюдений. Найдено что фунгисиды и окись цинка эффективны внутри помещений только при сравнительно высоких концентрациях. В Лаэ эффект всех фунгисидов продолжался очень короткое время. Причиной этого была неустойчивость исследованных составов в климатических условиях преобладающих в Лаэ. В помещениях иотеря фунгисидов из краски происходит медленее и потому они остаются эффекптвными.

Introduction

In 1961 the Housing Commission of Victoria invited the Division of Building Research to try to develop a more mould-resistant paint than those that were commercially available.

The incidence of mould growth in the Commission houses tended to be much higher than in other dwellings, and this caused a considerable expense for repainting.

There are basically two reasons for this high susceptibility to mould. (1) The construction of the commission houses, which have prefabricated single concrete walls 3.5 in thick. The heat loss through such a wall is somewhat larger than in the normal brick veneer or weatherboard dwelling. Consequently, the temperature on the inside of an exterior wall tends to be lower than that of a wall in the usual cavity construction. This can lead to condensation of water vapour on the wall and to saturation of the paint film with water, a condition which is favourable to the growth of mould. (2) The Commission houses usually have more persons per unit of floor area than other houses, and often are very poorly heated in winter time, or are heated by kerosene appliances which generate a great amount of steam. This raises the relative humidity of the air in the dwelling and leads eventually to a large condensation of water on the cold walls.

Numerous compounds have been proposed as additives to make a paint film more resistant to the growth of fungus. The usefulness of these substances is tested by exposing panels coated with paints of the appropriate formulation outdoors in regions where mould growth occurs, and the appearance of these panels gives an indication of the suitability of the formulation. This at least gives some indication of the mould resistance of the product, but such a procedure is quite useless for indoor assessment. Painted panels attached to walls on which mould growth is known to occur will usually not show any mould, although the painted wall surrounding it may have plenty. The reason for this is that the panel is better heat-insulated than the wall ; less condensation will occur, the paint film will be drier, and consequently there will be less opportunity for fungus to grow. Assessment of mould resistance in an indoor environment is therefore usually based mainly on the Vicklund and Manowitz test[1] or on some modification of it. After many years of comparing the assessments of these laboratory tests with the actual performance in the field most workers are probably convinced that no correlation exists. For instance, Reyne[2] has the following to say about the method. " There is no correlation between results of these tests and the mildew resistance of these paints under conditions of use. We have records of paints containing 1½ oz of mildewcide which have failed the test but did very well on a two-year exposure programme. Conversely, paints that passed the test and contained only ¼ oz of mildewcide per gallon of paint failed on exposure."

It is not enough simply to note whether or not any growth occurs, and for a better understanding of the action of a fungicide it is desirable to determine how stable it is under the conditions of exposure. Stability of a compound is clearly a necessary but not a sufficient condition for its efficiency. Paint films were therefore exposed on suitable substrates in various environments, and the coatings were analysed at appropriate intervals to determine how much of the added fungicide remained.

The range of experiments was widened by testing the mould resistance of various paint formulations exposed in tropical humid conditions at Lae, New Guinea.

Experimental

Evaluation indoors

Evaluation of paint indoors was carried out in dwellings in which a comparatively high degree of disfiguration had necessitated redecoration. All the rooms in which mould growth occurred were redecorated after washing the walls with methylated spirits. All the houses were painted within a few months of each other. The dwellings were inspected after each winter season, when mould is most prolific, and any mould growth was washed off with a hypochlorite solution. All paints tested were of the same composition except for the fungicide. The zinc oxide paints had the same pigment volume concentration as the original paint, part of the extender being replaced by zinc oxide.

It was not always possible to inspect all the houses after a winter season because some were closed ; this accounts for the variation in number of houses inspected per season as given in Table 1.

Analytical work

The paints containing the fungicides and the corresponding blanks were brushed out on sheets (12 in × 6 in) of plastic film attached to hardboard panels and exposed to the desired conditions. An appropriate amount of the paint film was scraped off after exposure and analysed for residual fungicide. Exposures were carried out :

(1) outdoors at Highett, Victoria.
(2) in a fog room at 20°C.
(3) in a constant temperature room at 20°C and 65 per cent RH.
(4) in a hot room at 38°C and 25 per cent RH.
(5) outdoors at Lae, New Guinea.

Table 1

Incidence of mould growth on a flat alkyd enamel paint containing fungicides or zinc oxide

Fungicide	Season 1		Season 2		Season 3		Average (%)
	Houses	Per cent affected	Houses	Per cent affected	Houses	Per cent affected	
Control	11	55	15	47	13	77	59
Mercury as di-(phenylmercury) 0.05%	10	20	11	82	19	37	45
0.1%	13	23	7	29	17	47	35
dodecenyl succinate 0.2%	8	0	9	22	11	27	18
Pentachlorophenol 1%	14	57	16	32	16	50	46
2%	22	5	24	13	20	25	14
N-trichloromethylthio-phthalimide 1%	21	10	23	17	24	33	20
Para toluene sulphonamide 4%	11	0	19	16	19	32	19
Zinc oxide 1.5 lb	18	22	20	5	17	18	15
(per gallon) 3.0 lb	15	13	16	6	14	14	11

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

Exposure at Lae, New Guinea

Separate sets of hardboard panels were exposed at Lae, New Guinea. In each case, one set was coated with a paint containing the fungicide and another set without fungicide.

The intensity and extent of mould growth was assessed at intervals of about three months.

Fungicidal washes

To be effective a fungicide must be on the surface, and the fungicidal property of the paint film is related to the concentration of the fungicide. To add large amounts of fungicides to a paint is uneconomical and may change the properties of the coating in an undesirable way.

In a thin surface layer, a high concentration of the fungicide could be made fairly cheaply, even if a comparatively expensive material were used, and such a wash could be repeated if necessary without great expense.

Washes of this kind could be formulated in many ways, e.g. by making a solution or even an emulsion of the fungicide or fungicide mixture for direct application to the surface, or by suspending or dissolving the fungicides in a film-forming material. In this way a better bond of the mildew-inhibiting material to the surface could be expected.

The present experiments were carried out with fungicide dissolved in a 5 per cent solution of a suitable silicone. The latter was chosen because such a formulation makes the surface water-repellent. This in itself is likely to inhibit mould growth, and seems to be effective in places where the conditions for mould growth are not favourable. However, the addition of a fungicide is necessary when the environment is highly favourable to the growth of fungus. Experiments were carried out in a dye works and a malt house, where such conditions exist.

Results of the survey on the incidence of mould growth indoors on a flat alkyd enamel paint containing various fungicides and zinc oxide are given in Table 1, and characteristic figures of the loss of fungicides from paints exposed to various conditions are given in Table 2.

Detailed studies of rates of loss have been published for some fungicides[3–9]. Table 3 gives the area covered by mould and its intensity rating per affected house (average over the second and third seasons).

Fig. 1 shows the mould growth on two gloss enamel paint films exposed at Lae, New Guinea, one of which contained 0.3 per cent mercury as di-(phenylmercury) dodecenyl succinate. The effect of fungicidal washes on the growth of mould in a dye works is shown in Fig. 2, and Fig. 3 shows the effect in a malt house.

Table 2

Some characteristic loss figures of fungicides at various locations

Fungicide	Outdoors at Highett	Fog room at 20°C	Constant temp. room at 20°C and 65% RH	Hot room at 38°C and 25% RH	Outdoors at Lae, New Guinea
di-(phenylmercury) dodecenyl succinate (3, 4, 5, 6, 7)*	74% after 14 months	49% after 8 months	49% after 6 months	—	80% after 6 months
Pentachlorophenol (8)*	55% after 24 months	100% after 4 months	65% after 24 months	100% after 4 months	80% after 14 months
N-trichloromethylthio-phthalimide†	40% after 24 months	30% after 24 months	10% after 24 months	38% after 24 months	No results yet
Para toluene sulphonamide (9)*	100% after 16 months	100% after 6 months	10% after 24 months	62% after 22 months	96% after 4 months

*The figures refer to publications in which a detailed study on the persistence of the fungicide in paint films is reported.

†Unpublished results.

Table 3

Average area covered by mould and its intensity rating per affected house (average over seasons 2 and 3)

Fungicide	Average area covered by mould (sq ft)	Intensity rating
No fungicide (control)	40	trace to strong
Di-(phenylmercury) dodecenyl succinate		
0.05 % Hg on total weight of paint	78	strong to very strong
0.1 % Hg ,, ,, ,, ,, ,,	36	trace to strong
0.2 % Hg ,, ,, ,, ,, ,,	94	very strong
Pentachlorophenol		
1 % on total weight of paint	52	trace to strong
2 % ,, ,, ,, ,, ,,	23	trace to weak
N-trichloromethylthio-phthalimide		
1 % on total weight of paint	17	trace to weak
Para toluene sulphonamide		
4 % on total weight of paint	18	trace to weak
Zinc oxide		
1.5 lb per gallon	9	trace to weak
3.0 lb per gallon	19	trace

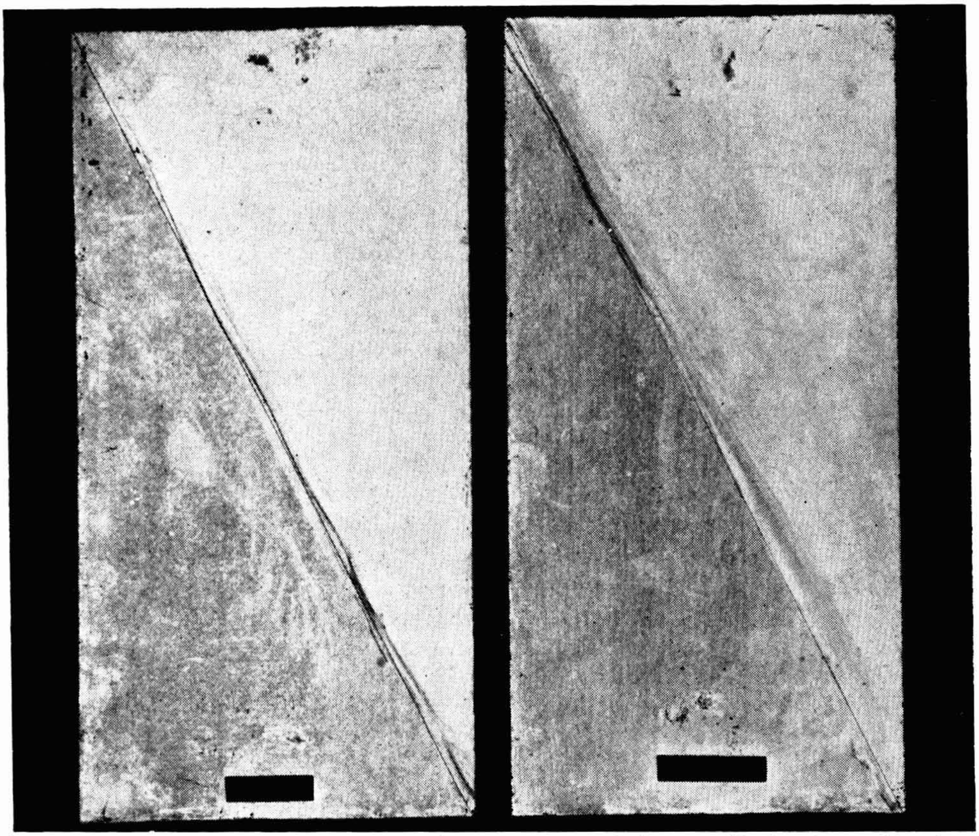

Fig. 1. Mould growth on a gloss enamel paint at Lae, New Guinea. Half of each panel has been cleaned with a hypochlorite solution. The paint on the left hand panel contained 0.3 per cent di-(phenylmercury) dodecenyl succinate

Fig. 2. Effect of fungicidal washes on mould growth in a dye works. The squares (3 ft × 3 ft) were washed free of mould and the lower half was treated with a 5 per cent silicone solution containing fungicides—(1) Blank ; silicone solution only. (2) D-(phenylmercury) dodecenyl succinate. (3) Para toluene sulphonamide. (4) Pentachlorophenol. (5) Salicylanilide. (6) N-trichloromethylthio-phthalimide. (7) Mixture of 1, 4 and 6

Discussion

The results in Table 1 have been statistically analysed and only those cases which show an effect significant at the 5 per cent level or better are dealt with here. No other effects could be shown to be significant with the present set of data.

Di-(phenylmercury) dodecenyl succinate as fungicide

When the investigation started, the Housing Commission of Victoria was using a flat enamel paint containing 0.014 per cent mercury as di-(phenylmercury)-dodecenyl succinate as a fungicide. As far as mould growth was concerned, the results were not satisfactory, and some improvement was sought by increasing the concentration of the fungicide in the paint. The compound was applied at levels of 0.05, 0.1, and 0.2 per cent mercury on the weight of the paint.

With 0.05 per cent mercury the incidence of the attack of mould decreased to 48 per cent of that of the blank (level of significance 2 per cent) only in the

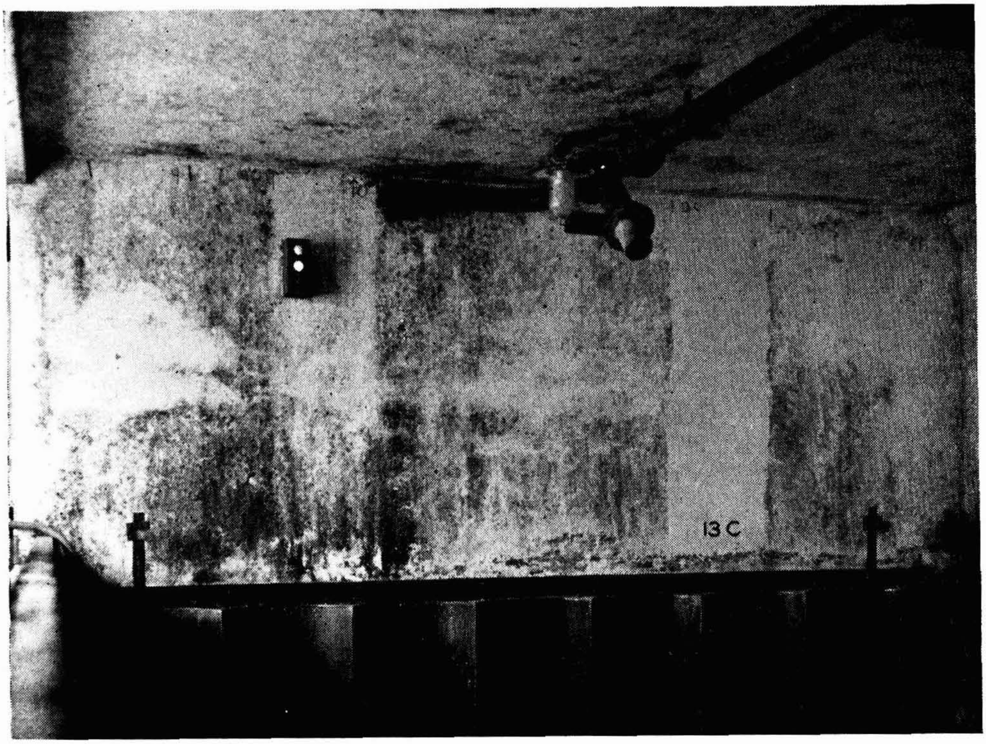

Fig. 3. Effect of fungicidal washes on mould growth in a malt house. Strip 13C has been treated with a silicone solution containing Pentachlorophenol, Salicylanilide, and N-trichloromethylthio-phthalimide. Adjacent strips of the same width were left untreated

third year. With 0.2 per cent mercury the incidence of the attack of mould in the first season was reduced to zero and in the second season to 35 per cent, compared with the blank. The significance level in each case is <1 per cent. Phenylmercury compounds in this concentration range show a very high activity in the Vicklund and Manowitz test. The reasons for the indifferent success in the field are firstly the rapid loss of the compound from the paint film[3–7], and secondly the formation of mercury sulphide (non-fungicidal) by reaction with traces of hydrogen sulphide, which are present in the atmosphere of every dwelling[10–12]. A range of other phenylmercury compounds have been investigated[6, 8] and all are quickly lost from the paint film.

Exposure at Lae

Eleven different paint formulations[5] were exposed at Lae, New Guinea, each containing about 0.28 per cent mercury on the dry paint film, and a comparison was made with the same paints without fungicide. At the same time the paint film was analysed for residual mercury. There was little difference in the strength of the fungus growth on the various panels with the exception of a paint containing 3 lb zinc oxide per gallon, which showed better results than the control for about 13 months.

The analysis showed that between 70 and 80 per cent of the mercury on the upper side was lost after six months, and somewhat less on the under side. The minor effect of the fungicide is therefore not surprising.

The somewhat higher mould resistance of the paint containing zinc oxide and the phenylmercury compound is not due to a smaller loss of fungicide, and the reason for the better service is not apparent.

Figure 1 shows the appearance of an alkyd gloss enamel after exposure for 13 months. One of the panels is the blank, the other contained 0.26 per cent mercury on the film as di-(phenylmercury) dodecenyl succinate. Half of each panel has been washed with hypochlorite solution to restore the original colour.

Pentachlorophenol as fungicide

Pentachlorophenol has been repeatedly proposed as a fungicide in paint[8], and addition of 1 or 2 per cent was investigated. Two per cent reduced the incidence of mould growth to 9 per cent in the first season (level of significance <1 per cent), to 28 per cent in the second (level of significance <5 per cent), and to 32 per cent in the third season (level of significance <5 per cent) compared with the control.

Gloss and flat enamel paints were also exposed at Lae and the observations can be summarised as follows : On the upper side of the panels, coatings containing pentachlorophenol had a slightly better appearance up to ten months, but there was no difference thereafter. On the under side the gloss paint films were slightly better up to seven months, whereas the flat coatings containing pentachlorophenol showed a slight difference in appearance throughout the whole time.

From Table 2 it can be seen that the loss in the tropics is very fast, and the loss in the constant temperature room is much slower. This explains the observed behaviour as to the growth of mould. It is estimated[8] that to keep a better appearance even for 14 months the paint film would have to contain about 6 per cent pentachlorophenol. The figures in Table 1 seem to indicate that the paint film exposed indoors becomes less resistant as it ages, but this cannot be proved on a statistically significant level. Nevertheless, the analytical results support this view. An addition of from 4 to 5 per cent would appear to be necessary to obtain a coating which would remain active indoors for from five to six years.

N-trichloromethylthio-phthalimide as fungicide

Another fungicide which has been proposed is N-trichloromethylthio-phthalimide, and this has been tried on a 1 per cent level. The incidence of mould growth was lowered in the first season to 18 per cent (level of significance <1 per cent), in the second to 36 per cent (level of significance 5 per cent), and in the third season to 43 per cent (level of significance <1 per cent) compared with the control. It would seem that the effect wears off as the paint ages, although it is not statistically significant and the reason for this could be different from the case of pentachlorophenol. From Table 2 it can be seen that the rate of loss from the paint film is much lower than in the previous case and it may be that the cause of apparent deterioration is due to a too slow diffusion of the fungicide to the surface. It seems very likely that the addition of 2 to 3 per cent N-trichloromethylthio-phthalimide to paint would increase the fungus resistance above the improvement obtained with a 1 per cent addition.

Para toluene sulphonamide as fungicide

Para toluene sulphonamide has been proposed as a fungicide and is of interest because of its comparatively low toxicity. In the first season the incidence of mould growth was reduced to zero (level of significance <1 per cent), in the second to 34 per cent (level of significance 4 per cent), and in the third to 42 per cent (level of significance 1 per cent) compared with the control. The effectiveness again appears to decrease with the age of the film.

Panels coated with gloss and flat enamel paints containing para toluene sulphonamide were also exposed at Lae, but no improvement was evident in the performance of the films containing the fungicide.

The observations can be readily understood from the analytical results, which show that the fungicide was nearly all lost from the paint film in only four months (Table 2). In the constant temperature room the loss was only 10 per cent after 24 months.

Zinc oxide as a fungistatic pigment

Zinc oxide has been fairly successful as a fungistatic pigment in paints for use outdoors, although there are exceptions. It was therefore of interest to see what degree of mould control could be achieved with this type of coating used indoors.

Zinc oxide was added at levels of 1.5 lb and 3 lb per gallon. With the lower level the incidence of mould growth fell in the second season to 11 per cent (level of significance <1 per cent) and in the third season to 23 per cent (level of significance <1 per cent). With 3 lb zinc oxide per gallon the incidence of mould growth fell in the first season to 24 per cent (level of significance <2 per cent), in the second to 13 per cent (level of significance <1 per cent) and in the third season to 18 per cent (level of significance <1 per cent).

Considering only those formulations which showed an improvement in all three seasons, i.e. 2 per cent pentachlorophenol, N-trichloromethylthio-phthalimide, para toluene sulphonamide, and 3 lb zinc oxide per gallon, it appears that zinc oxide is the best because it is non-poisonous and very stable.

Concurrently with the formulation of zinc oxide alkyd paints, two of the suppliers to the Housing Commission of Victoria also tried to formulate latex paints containing zinc oxide. Of the latices available in Australia, a few were found to be compatible with this pigment and eventually it was found possible to incorporate as much as 4 lb zinc oxide per gallon. These paints also had a superior covering power to the alkyd paints containing zinc oxide and were therefore used for redecoration. It does not necessarily follow that zinc oxide will have the same beneficial effect in a latex as in an alkyd medium, but so far the results are very encouraging. In 25 houses being kept under close observation, only one showed mould growth after about 18 months, which in most cases included two winter seasons.

The average area in sq ft and intensity of mould in an affected house is shown in Table 3. The data are not extensive enough for them to be amenable to statistical analysis, but they give an indication of the extent to which mould growth occurs in the dwellings under observation. It is pertinent to make a few comments in order to remove any misunderstandings. The paints containing 0.05 per cent and 0.2 per cent of mercury, but not that containing 0.1 per cent, show a considerably higher coverage of mould than the control. This is because two of the affected houses showed an above-average growth, for which there is no evident reason. It is worthwhile to bear in mind that small amounts of toxicants can sometimes stimulate mould growth[14]. The quantities of phenylmercury compounds used are very much smaller than those of the other toxicants (maximum 0.2 per cent mercury as compared with a minimum of 1 per cent of other toxicants). Further, the phenylmercury compounds can react with traces of hydrogen sulphide contained in the atmosphere of a dwelling, and this introduces a further complication.

Apart from this exception there is a rough correlation between the effectiveness of a fungicide measured by the number of houses affected by mould and the area covered by it and its intensity.

Figure 2 shows the effect of the fungicidal washes in a dye house, and was taken one year after the washes were applied over a pva paint. Squares 3 ft × 3 ft were cleaned by washing with hypochlorite solution, and the lower half only of each square was treated with the fungicidal preparation. Mould started to appear after three months.

The composition of the fungicidal washes is given in Table 4. It is impossible to know in advance what concentration of fungicide would be effective and the quantities used were therefore arbitrary. However, some guidance as to the concentration needed was derived from the activity of the fungicides in the usual bio-assay test, e.g. phenylmercury compounds are very active so a comparatively low concentration was used, whereas pentachlorophenol seems to be much less active and consequently a much higher concentration was used.

Square 1 shows that a silicone solution, which makes the paint film water-repellent, has no mould inhibiting properties under the very favourable conditions for growth existing in the dye house. A silicone solution containing di-(phenylmercury) dodecenyl succinate was used on square 2, and, although the concentration of mercury was very much higher than would be used in a paint, the treatment was not effective. This is probably due to the rapid disappearance of the fungicide from the film[3, 4, 5].

Square 3 demonstrates the effect of an addition of para toluene sulphonamide to the silicone solution. This compound has recently been recommended as a fungicide for use in paint, but it is not only ineffective in a silicone solution but seems to encourage mould growth. That the addition of fungicides to a coating sometimes increases mould growth has already been mentioned, and has also been observed for para toluene sulphonamide[14]. The present authors have shown[9] that para toluene sulphonamide decomposes in the paint film and it may well be that the decomposition products can be used as food by the fungi.

Squares 4, 5 and 6 demonstrate the efficacy of pentachlorophenol, salicylanilide, and N-trichloromethylthio-phthalimide respectively. An improvement was achieved in each case, the pentachlorophenol being inferior to the other two.

Square 7 shows the result of an addition of a mixture of fungicides to the silicone solution. This is the most effective treatment and is probably due to a synergestic action of the fungicides used.

To prove whether a fungicidal wash was effective in a malt house, a different procedure from the previous one was adopted. The wall shown in Fig. 3 was divided into strips 1 ft wide and existing mould was cleaned off with a hypochlorite solution. The wash to be tested was applied to one strip and the adjoining strips were left untreated.

The first wash tried was No. 7 (Table 4), but this proved to be ineffective in this environment. It is of interest to note that it has been shown[15] that *Pullularia pullulans* from different sources does not exhibit the same growth behaviour on the same paint film, and this probably applies to other kinds of fungi growing on organic coatings. This, together with the more plentiful food available in a malt house, is very likely the reason that a formulation which performed well in the dye house was not successful in the malt house. Formulation 13C, which had a total fungicide concentration of 48 per cent on the silicone resin, proved to be very effective indeed, as shown in Fig. 3. Because of a misunderstanding, the wall was washed with hypochlorite solution after the photograph was taken at eight months, including the strip 13C which was then mould-free. Mould again began to grow everywhere except on 13C, and 27 months later mould was just beginning to appear on the treated strip. From this behaviour it is concluded that the fungicides are so strongly bonded to the surface that washing does not remove them.

Probably many fungicides and binders other than silicone could be used, and may show advantages over the formulation used at present. The practicability of controlling mould growth with fungicidal washes has been established.

The solutions are best applied with a cotton rag as application by brush sometimes leads to streakiness, especially on glossy surfaces, and they should not be worked too strongly into the paint film, which could be damaged by the solvent. The solutions spread easily on flat or semi-gloss surfaces, but difficulties may be encountered in applying them on gloss surfaces.

Conclusions

1. It is possible to increase the mould resistance of paint for indoor use by adding fungicides, but to achieve a significant effect the concentration must be higher than most manufacturers realise, and none of the fungicides in the concentration range used make the paint film absolutely resistant. The greatest reduction of mould growth was obtained with the addition of 2 per cent pentachlorophenol. This compound decreased the occurrence of mould growth to 24 per cent of that of the control.

2. The most widely used fungicide, di-(phenylmercury) dodecenyl succinate, does not give much improvement in the concentration range (<0.2 per cent)

Table 4

Concentration of fungicides (on the silicone content of the wash) and solvents used

		Mercury as di-(phenylmercury) dodecenyl succinate (%)	Para toluene sulphonamide (%)	Pentachloro-phenol (%)	Salicylanilide	N-trichloro-methylthio-phthalimide (%)	Solvent mixture (vol. parts)	
							Shell solvent X55	Methylethyl acetone
Dye Works	1	—	—	—	—	—	1	0
	2	1	—	—	—	—	1	0
	3	—	14	—	—	—	2	1
	4	—	—	11	—	—	—	—
	5	—	—	—	14	—	2	1
	6	—	—	—	—	3	1	0
	7	1	—	6	—	1.6	2	1
Malt House	Strip 13C	—	—	20	16	12	3	1

in which it is usually added, and it can give rise to sulphide staining. Although only di-(phenylmercury) dodecenyl succinate has been tried for painting the houses of the Housing Commission of Victoria, the analytical behaviour of other phenylmercury compounds makes it likely that what has been said about di-(phenylmercury) dodecenyl succinate applies to other organic mercury compounds.

3. Fungicidal paints used indoors were also tested outdoors at Lae, New Guinea, and proved of little value. This is due to their high rate of loss from the paint film under tropical humid conditions.

4. Coatings formulated with zinc oxide were also tried indoors and proved successful. A formulation containing 3 lb zinc oxide per gallon reduced the incidence of mould growth to 19 per cent of the control. At the present time the Housing Commission uses a latex paint containing 4 lb zinc oxide per gallon.

5. Many paint firms add some fungicide to latex and alkyd paints to make the film fungus-resistant, but the amounts used are usually too small to be effective. From the number of complaints received at the Division of Building Research concerning paint failures due to mould, the opinion was formed that there is no need for the addition of fungicides unless the coatings are used in humid tropical regions or in some special cases where a large condensation of water occurs on the walls for long periods of time. Mould does occur in houses on occasions, but this can easily be controlled by such simple methods as washing it off with bleach solution or improving the ventilation.

6. If a special fungus-resistant paint is needed for indoor use, a formulation containing zinc oxide is the most appropriate one at the present stage of knowledge.

7. For industrial establishments fungicidal washes appear to be useful. They can be applied at more frequent intervals than paint and it is comparatively easy to find out what fungicides and what concentration should be used.

8. If a fungicide is offered by a supplier for addition to coatings the paint manufacturer should insist on being provided with data to show how stable it is in the paint film under conditions of exposure conducive to the growth of mould.

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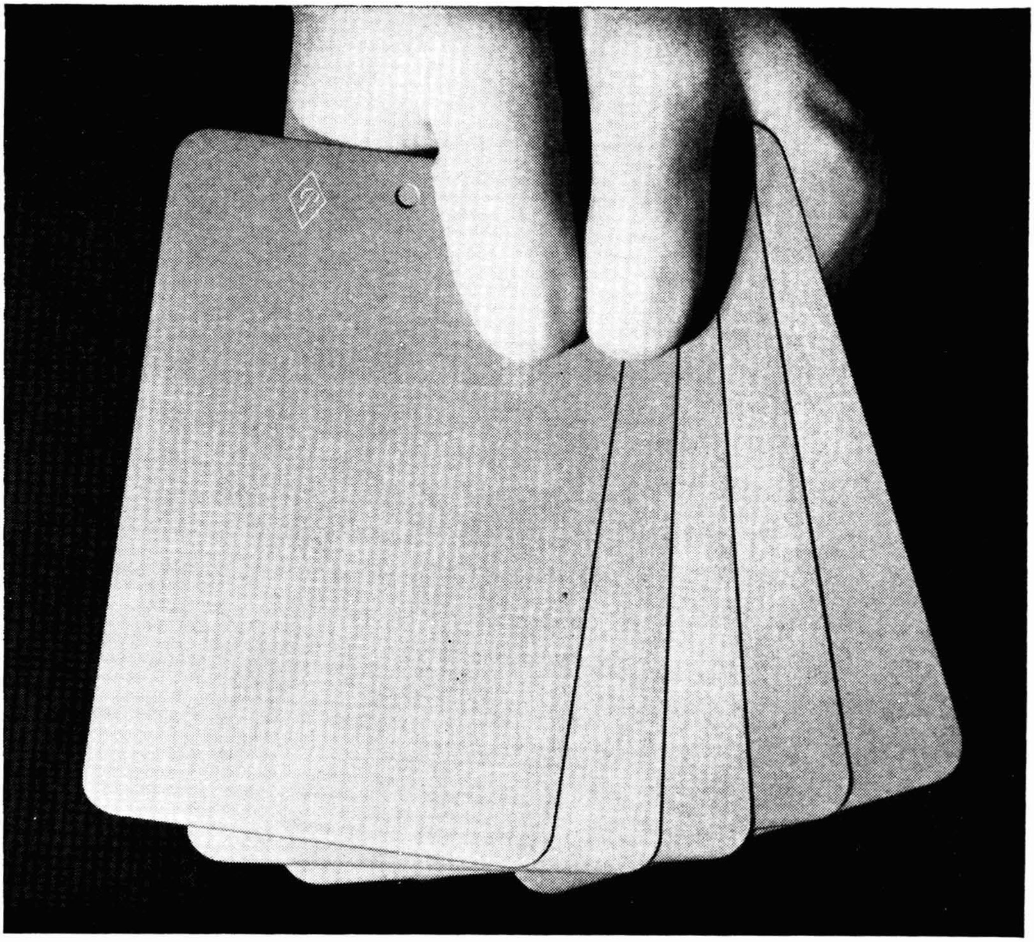

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The glycerolysis step in the production of oil modified alkyd resins: Part IV

Some new aspects

By N. A. Ghanem and F. F. Abd El-Mohsen

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Summary

Some new aspects of the glycerolysis of the linseed and cottonseed mixed triglycerides are presented. The reaction rate does not increase to any appreciable extent with the increase of the molar concentration of glycerine even under very efficient stirring. Oxygen seems to retard the glycerolysis reaction, as it is found that the reaction time is almost doubled when the glycerolysis is carried out in absence of a blanket of inert gas. Standard curves are devised, from which the percentage of monoglyceride formed at any stage can be determined from the turbidity temperature of the mixture in ethyl alcohol. A method is proposed whereby, from experimental knowledge of the amounts of glycerol and monoglycerides, the remaining amounts of diglycerides and triglycerides can be calculated. The reaction mixture components are thereby fully assessed.

L'étape glycérolytique dans la fabrication des résines alkydes modifiées à l'huile. IVème Partie: Certains aspects nouveaux

Résumé

On présente certains aspects nouveaux sur la glycérolyse des triglycérides mixtes d'huiles de lin et de coton. La vitesse de réaction n'accroît pas d'un degré important selon l'augmentation de la concentration molécullaire de glycérine, même sous des conditions d'agitation très effectives. Il paraît que l'oxygène fait retarder la réaction de glycérolyse, puisqu'on a trouvé que la durée de réaction est presque doublée dans le cas que l'on effectue la glycérolyse en l'absence d'une atmosphère de gaz inerte. On trace des courbes étalonnées afin de déterminer le pourcentage de monoglycéride, formé à chaque étape, par la température de turbidité du mélange avec de l'alcool d'éthyle. On propose une méthode où, grâce au dosage de glycérine et de monoglycéride, on peut calculer les restes de di et triglycérides. Ainsi les constituants d'un mélange de réaction sont complètement déterminés.

Die Glycerolysen-Stufe in der Fabrikation Ölmodifizierter Alkydharze: Teil IV Einige Neue Gesichtspunkte

Zusammenfassung

Es werden einige neue Gesichtspunkte bezüglich der Glycerolyse gemischter Leinöl- und Baumwollsamenöl- Triglyceride vorgetragen. Selbst bei sehr intensivem Rühren erhöht sich die Reaktionsgeschwindigkeit nicht wesentlich mit dem Ansteigen der molaren Glyzerinkonzentration. Scheinbar verzögert Sauerstoff die Glycerolysenreaktion, da man findet, dass sich die Reaktionsgeschwindigkeit beinahe verdoppelt, wenn die Glycerolyse beim Fehlen einer inerten Gasschicht durchgeführt wird. Es wurden Normkurven entwickelt, mit Hilfe deren der Prozentgehalt an gebildetem Monoglycerid in jedwedem Stadium aus der Trübungstemperatur der Mischung in Äthylalkohol bestimmt werden kann. Auf Grund experimenteller Kenntnis des Gehaltes an Glyzerin und Monoglycerid wird ein Weg vorgeschlagen, mit Hilfe dessen die restlichen Mengen von Di- und Triglyceriden berechnet werden können. Die einzelnen Bestandteile der Reaktionsmischung werden auf diese Weise lückenlos mengenmässig nachgewiesen.

Глицеролизная стадия в производстве масло-измененных алкидных смол

Резюме

Описываются некоторые новые характеристические черты глицеролиза смешанных льняных и хлопковых триглицеридов. Скорость реакции не увеличивается в заметной степени с повышением молярной концентрации глицерина, даже при весьма тщательном перемешивании. Кислород повидимому тормозит глицеролизную реакцию, так-как найдено что время реакции почти удваивается если глицеролиз протекает в отсутствии поверхностного слоя инертного газа. Получены нормальные кривые из которых можно определить процент моноглицерида образовавшегося на любой стадии, из температуры помутнения смеси в этиловом спирте. Предлагается метод при помощи которого, из экспериментальных данных о количестве глицерина и моноглицеридов, могут быть вычеслены остаточные количества диглицеридов и триглицеридов. Составные элементы смеси реакции таким образом полностью оцениваются.

Introduction

In a series of recent publications [1-3], the process of conversion of triglycerides to monoglycerides by glycerol was thoroughly investigated. The reaction was found to be strongly catalysed by minute amounts of basic catalysts. The relative efficiencies of the insoluble catalysts applied in equal weights were found to be in direct correlation with their basicity[2], and a mechanism was put forward[3] showing that glycerolysis takes place through the attack of hydroxyl ion on the carbonyl group of the glyceryl ester linkages. Nevertheless, it was proved that the reaction was subject to heterogeneous catalysis[1] and followed the pattern of a zero order reaction similar to the case of the decomposition of hydrogen peroxide with a gold surface as catalyst [4,5]. To prove whether the reaction is essentially heterogeneous or that the basicity of the catalyst is the decisive factor, NaOH, a powerful glycerolysis catalyst soluble in the reaction medium, was used in comparable concentration. No marked increase in the rate over that in a parallel run with the less basic catalyst LiOH was observed. This substantiates the argument that the reaction is activated at the surface of a solid catalyst, the basicity of which plays a secondary role. This example of a heterogeneously catalysed liquid/solid reaction is rare compared with the numerous industrially important gas/solid catalytic reactions. As such, the glycerolysis reaction is of zero order, and its rate should be independent of the reactants concentration. It will be shown in a following section that this is actually the case.

Some other aspects of interest will also be discussed. The periodic acid method of quantitative determination of the amount of monoglycerides in a glycerolyzed mixture is time consuming. By setting up a standard curve relating the percentage of monoglyceride to the temperature at which turbidity starts to appear at various stages of glycerolysis upon addition of a known volume of ethyl alcohol and cooling, the glycerolysis can be followed without having to carry out the laborious chemical analysis. The curves for two mixed triglycerides are demonstrated. A similar method employing methyl alcohol was proposed by Runk[6].

The glycerolysis of oils is usually carried out under a blanket of inert gas for the preservation of colour. It will be shown that the presence of oxygen has the additional disadvantage of retarding the glycerolysis reaction.

The glycerolysis reaction proceeds from triglycerides, diglycerides through to monoglycerides. It is never complete ; the product, assuming no side reactions, always consists of an equilibrium mixture of the above components plus glycerol in variable amounts, depending on the stage of conversion. Glycerol and monoglycerides can be determined experimentally[7]. A method of calculating the other two components, viz., diglycerides and unreacted triglycerides is presented.

Materials and methods

Materials :

Refined mixed triglycerides of cottonseed and linseed were used. The glycerol was above 99 per cent purity, the rest being water. The physical and chemical constants and sources of these materials, as well as a description of the glycerolysis setup, are given in detail in a previous publication[1].

Methods :

Turbidity method : To 5 ml of 95 per cent ethyl alcohol placed in the usual test tube, 2 ml of the hot glycerolysis mixture were added. A thermometer (100°C scale) was immediately immersed and the mixture, while allowed to cool, was thoroughly homogenised with the thermometer. The temperature at which turbidity started to appear was recorded and called henceforth the turbidity temperature.

Quantitative periodic acid method : The method[7] based upon the oxidation of two adjacent hydroxyl groups by means of periodic acid was used and has been described in a previous publication[1].

Determination of glycerol : The mixture solution in chloroform was shaken with a known volume of distilled water to extract the glycerol. An aliquot of the aqueous extract was analysed by the periodic acid method.

Results and discussion

1. *The effect of excess glycerol on monoglyceride formation :*

To examine the effect of excess glycerol on the rate of monoglyceride formation, several runs were performed at a fixed temperature and catalyst concentration using different molar amounts of glycerol. In run 1 the molar ratio of 1 glycerol to 1 oil is insufficient to establish theoretically complete conversion to monoglyceride. In runs 2 and 3 this ratio was 2 : 1 which is exactly stoichiometric with respect to formation of monoglycerides.

In runs 4 to 9 various excesses of glycerol were used. The results are summarised in Table 1 from which the absence of any decrease of the reaction time (increase of the reaction rate) upon increase of the glycerol concentration can be observed.

Fig. 1. shows the change of the turbidity temperature with reaction time in the glycerolysis of cottonseed oil as an example. It indicates the value of using a slight excess of glycerol. At 2 : 1 glycerol : oil ratio the reaction proceeds quite normally except near the equilibrium point where, due to the lack of enough

Table 1

Effect of glycerol content on the glycerolysis of cottonseed and linseed oils
Reaction temperature=240°C. Catalyst : PbO (0.02 per cent on weight of oil)

Run No.	Glycerol/oil				Time to reach max. MG content		Colour (Gardner)	
	Molar ratio		% glycerol					
	Cotton-seed oil	Linseed oil	Cotton-seed oil	Linseed oil	Linseed oil	Cotton-seed oil	Linseed	Cotton-seed
1	1 : 1	—	9.38	—	—	48	—	6-7
2-3	2 : 1	2 : 1	17.16	17.31	43.5	44	7-8	6-7
4-5	2.5 : 1	2.5 : 1	20.57	20.74	35	45	7-8	6-7
6-7	3.28 : 1	3.3 : 1	25.3	25.67	39	45	7-8	6-7
8-9	4 : 1	4 : 1	29.29	29.51	40	46.5	7-8	6-7

glycerol and the contribution of the reverse reaction, the reaction becomes slow. This sluggishness is absent when the molar ratio is increased to 2.5 : 1 and higher. The curve representing the 4 : 1 ratio is intentionally shifted 10 minutes to the right for the sake of clarity. This increase in the glycerol concentration was found to have practically no effect on the extent of glycerolysis.[3,8]

2. *Retardation of the glycerolysis reaction by atmospheric oxygen :*

Runs performed in the absence of an inert gas blanket were found to proceed at a lower rate and to give a product of inferior colour.

Typical examples are summarized in Table 2.

Table 2

Reaction in presence and absence of a blanket of inert gas (CO_2)

Reaction temp. °C	Catalyst	Oil	Time taken to reach maximum MG content (minutes)			
			in presence of CO_2		in absence of CO_2	
				Colour		*Colour*
220	0.02 % PbO	Linseed	78.5	6-7	147	9-10
230	0.02 % LiOH	Linseed	65	7	110	9-10
230	0.02 % NaOH	Cotton-seed	130	4-5	270	12-13

The reaction time was roughly doubled, which should aid side reactions, and the product's colour was darker. It is concluded that atmospheric oxygen acts as a retarder of the glycerolysis reaction.

3. *Correlation between the turbidity temperature and the percentage of monoglyceride formed :*

Examples of using the periodic acid method of following the reaction course are given in Fig. 2, and examples of using the turbidity temperature method are given in Fig. 3, for several reaction temperatures.

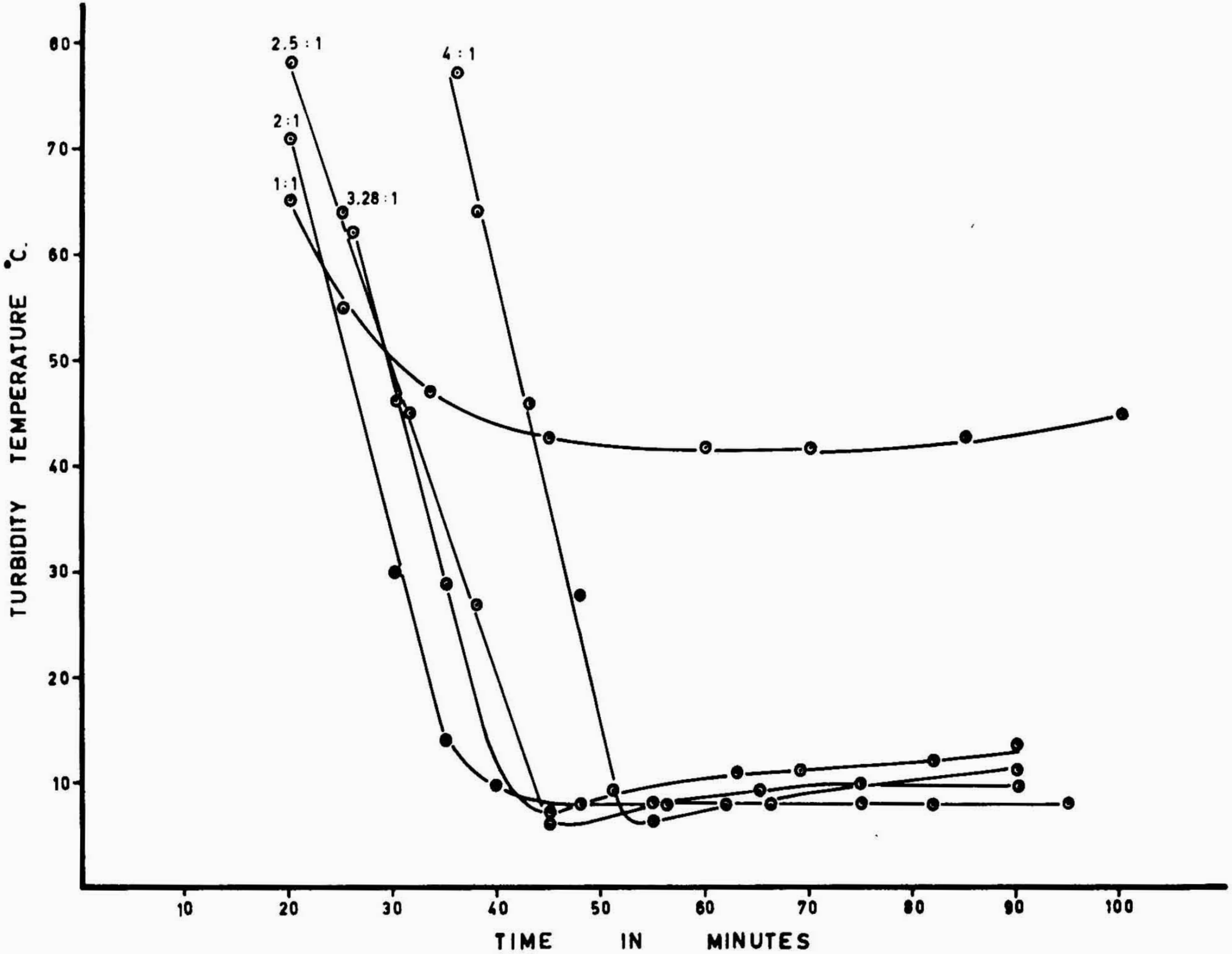

Fig. 1. The glycerolysis of cottonseed oil followed by the turbidity temperature method

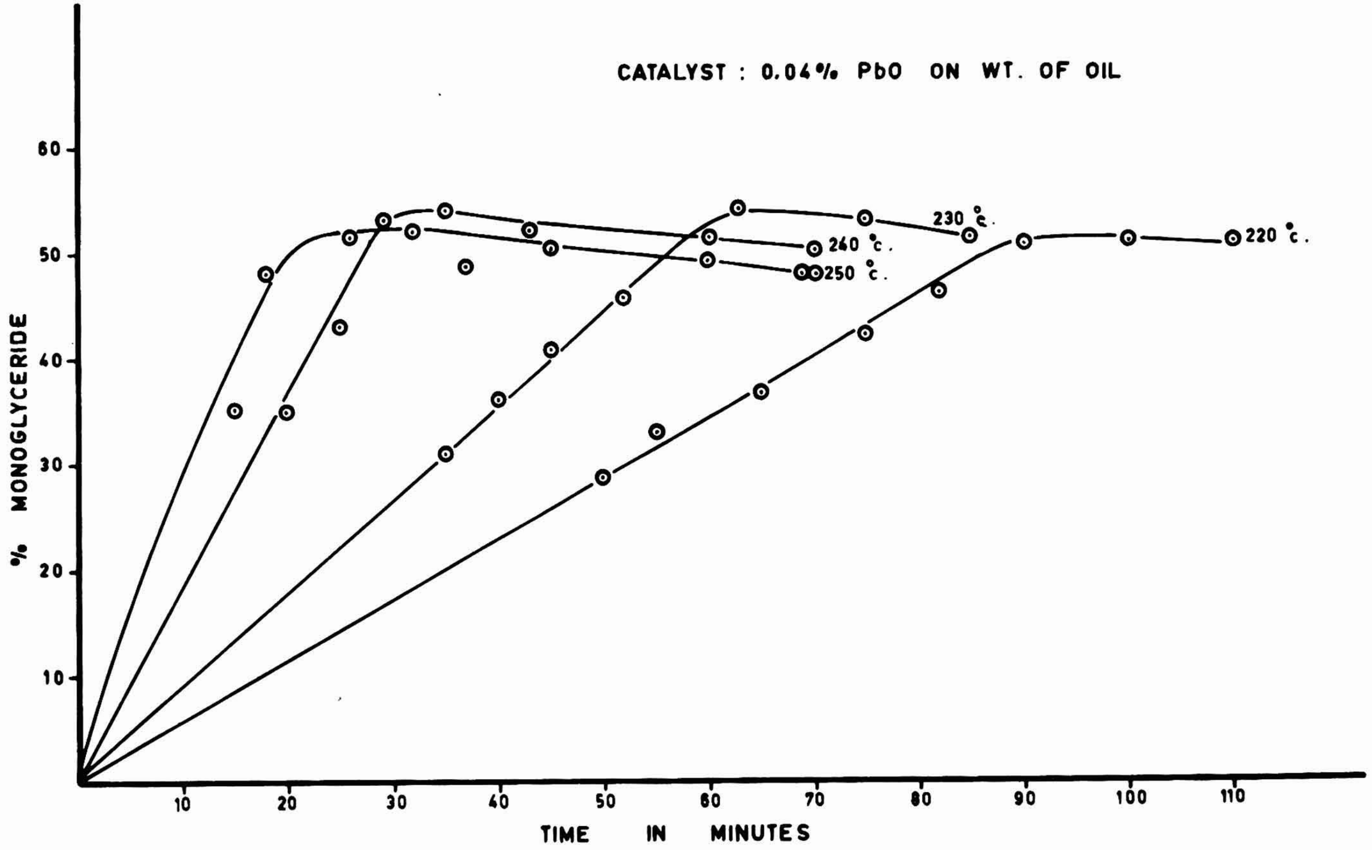

Fig. 2. The conversion of triglycerides to monoglycerides followed by the periodic acid method

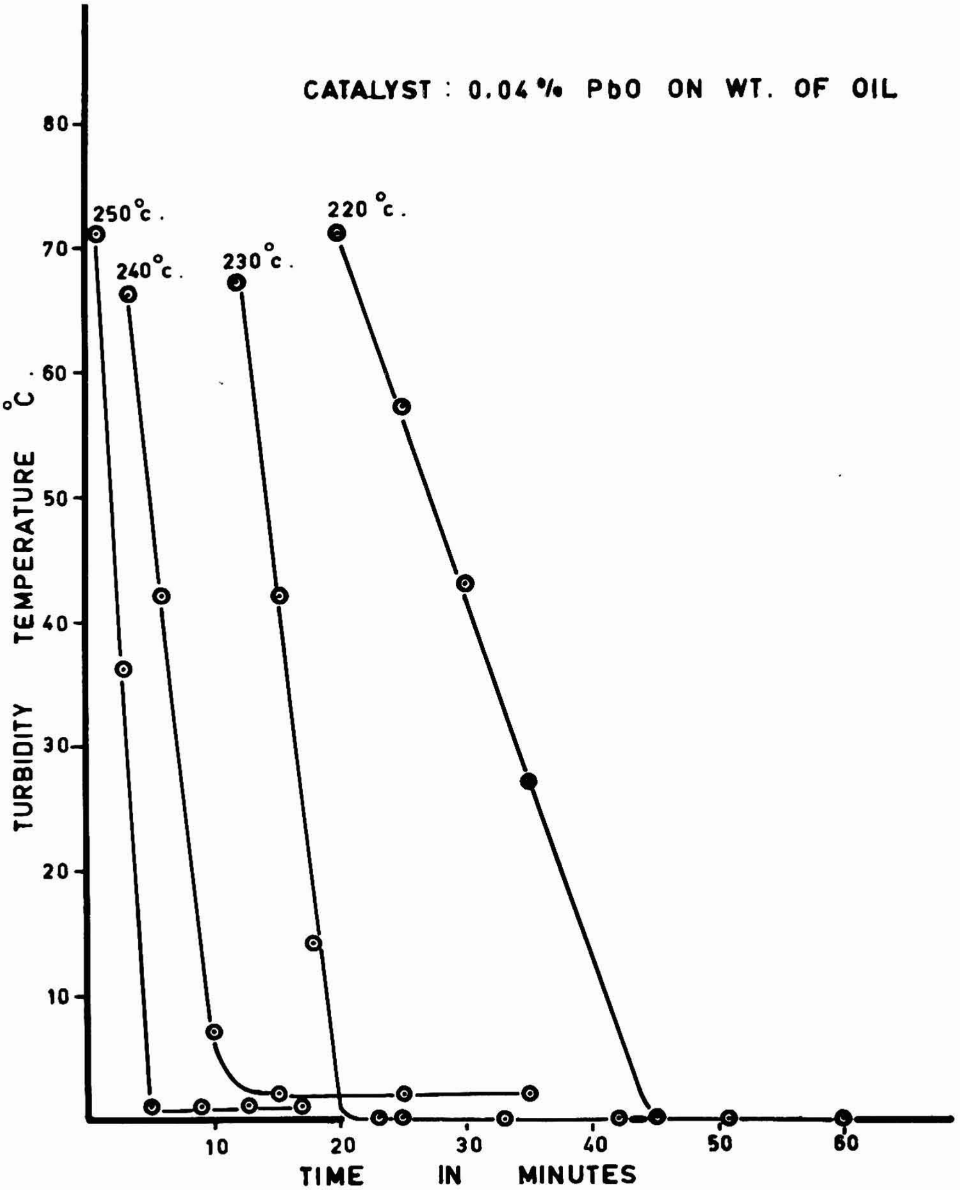

Fig. 3. The conversion of triglycerides to monoglycerides followed by the turbidity temperature method

In production, it is not practicable to use the periodic acid quantitative method to determine the percentage of monoglyceride because it is time consuming. A correlation between this and the turbidity temperature method is given in Fig. 4 for the two different mixed triglycerides of linseed and cottonseed oils from the data accumulated in previous work.[1,2] It can be observed that the turbidity temperature at any degree of conversion is always lower for the more

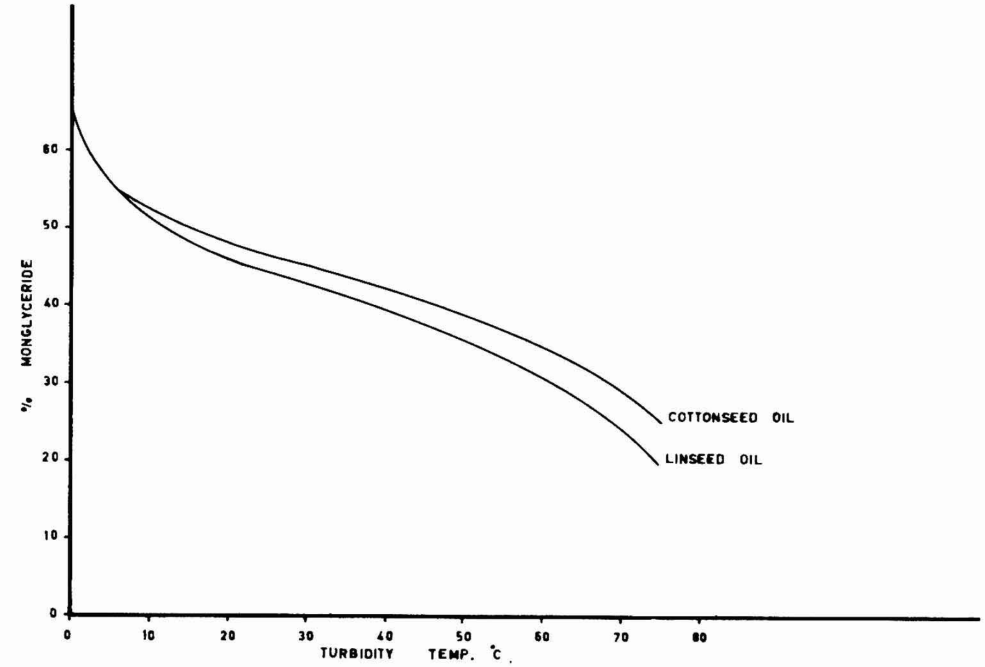

Fig. 4. The determination of the percentage monoglycerides from the turbidity temperature in ethyl alcohol

unsaturated linseed mixed triglycerides. A standard curve can be plotted for any mixture of triglycerides.

4. *Calculation of di- and triglyceride contents from the amounts of glycerol and monoglyceride found by analysis:*

According to the following procedure, the di- and triglyceride contents can be calculated from a knowledge of the amounts of glycerol and monoglycerides obtained by analysis. The detailed calculation with respect to one run is given below followed by Table 3 in which the results of applying the same procedure to several other runs are collected.

Run 2 :

The molar ratio of glycerol to cottonseed oil was .. .. .. = 2 : 1
2 mol glycerol 92 × 2 .. .. = 184 g
1 mol cottonseed oil .. .. = 888 g
Weight of mixture .. .. = 1072 g
Per cent of monoglyceride (by analysis) .. .. = 40.5%

$$\therefore \text{No. of mols of monoglyceride } \frac{1072 \times 40.5}{100 \times 356} = 1.21$$

where 356 is the mol weight of MG
Per cent of glycerol (by analysis) .. .. = 9%

$\therefore$ No. of mols of glycerol $\dfrac{1072 \times 9}{100 \times 92}$ = 1.04

Total no. of mols of fatty acids in the mixture 3×1 .. .. = 3

Total no. of mols of glycerol $2 + 1$ .. .. = 3

No. of mols of fatty acid present in di- and triglyceride $3 - 1.21$ = 1.79

No. of mols of glycerol present in di- and triglyceride $3 - (1.21 + 1.04)$ .. .. = 0.75

Suppose x represents the no. of mols of diglyceride and y represents the no of mols of triglyceride.

$$\therefore x + y = 0.75 \qquad (1)$$

$$\text{and } 2x + 3y = 1.79 \qquad (2)$$

$$\text{Hence, } y = 0.29$$

$$x = 0.46$$

Per cent of diglyceride .. .. $= \dfrac{0.46 \times 662 \times 100}{1072} = 26.7\%$

Per cent of triglyceride .. .. .. $= \dfrac{0.29 \times 888 \times 100}{1072} = 23.8\%$

The mixture therefore consists of :

40.5% monoglyceride + 9% glycerol + 26.7% diglyceride + 23.8% triglyceride .. .. = 100 %

These calculations are based, of course, on the assumption that no glycerol is lost by evaporation or in side reactions and that the oil is subject only to glycerolysis during the reaction time.

Table 3

The calculation of di- and triglycerides from a knowledge of the monoglycerides and glycerol contents in glycerolyzed mixture

Run no.	Mono-glyceride %	Glycerol %	Diglyceride %	Triglyceride %	Total %
	By analysis		By calculation		
3	51.05	7.77	21.44	19.84	100.1
4	53.8	9.8	30.6	5.5	99.7
6	55	15	17.77	11.86	99.63
7	56.75	14.78	20.83	7.39	99.75
9	56	18.9	17.78	7.04	99.72
41 ref. (2)	60	9.5	16.66	13.47	99.63

[*Received 23 November 1966*

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Next month's issue

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

"The influence of additives and calcination on the pigment properties of TiO_2. Parts III & IV," *by V. Blechta, Lavička and Z. Blechta.*

"Metallo-organic primer Coatings," *by Faulkner.*

"A micro-electrophoresis apparatus for the investigation of pigment suspensions," *by Wiseman,*

"Formulation of fungus resistant paints. Addition of para toluene sulphonamide," *by Hoffman, Saracz and Barned.*

Editorial

Suite . . . et fin?

Continuing our brief history of the English chair we enter the 18th century, the " golden age of English furniture." Craftsmanship reached its greatest heights, though technical innovations were few, and the designer was the dominant figure.

The Dutch influence, marked under William and Mary, declined in Queen Anne's reign and what may be called a truly English style emerged. " Easie " chairs had already made their appearance and there were even winged " sleeping chayres " with backs that could be let down on iron ratchets. Veneer and marquetry remained, but the wilder forms of decoration lost favour for a time. The first quarter of the century is distinguished for its graceful, rhythmic style and for the introduction of the cabriole leg and the chair back curved to fit the shape of the relaxed spine. Strength was often sacrificed for delicacy and dowels tended to be used instead of the mortice and tenon joint.

The early Georgian period saw the redevelopment of robust styles, and the taste of the wealthy for ornate splendour heralded the baroque which, in the opinion of many authorities, came as close to vulgarity as some of the creations of a century later. A major factor in this development was the disastrous winter of 1709 when most of the walnut trees in Europe were killed by frost. Ten years later the French tried, too late, to conserve their dwindling stocks and placed an embargo on the export of the timber. Mahogany was introduced from the West Indies, and its strength and texture permitted the designer to incorporate expanses of deeply and crisply carved ornament not practicable with walnut. Further specialised types of chairs were introduced, largely through the influence of architects, like William Kent, who started to design furniture to harmonise with their building styles and to accord with the functions of different rooms. In the withdrawing room, for example, would be found upholstered chairs with low backs and wide seats, reminiscent of the farthingale chairs of a century earlier, clearly designed to accommodate the dress of the period. The extreme of specialisation is to be seen in chairs for reading and writing, which were straddled by the occupant who rested his elbows on padded supports and leaned into a " back " carrying a small desk or shelf at chest height.

The exploitation of mahogany continued in the mid-Georgian period when the fantastically carved, asymmetrical rococo style emerged from the baroque, but by no means all the furniture of this period was heavily decorated. Chairs have always tended to reflect changes of taste more sharply than other pieces, but interest in what are now famous and valuable antiques, originating in the rich houses of the past, should not be allowed to obscure the more moderately fluctuating simpler styles of the country. There, stools and settles were more common than chairs until the middle of the century and one of the most permanent of all chair styles, the Windsor, was born of the country craftsmen. Even in the great houses, the stool remained, usually as part of a suite comprising a dozen or more pieces.

Thomas Chippendale was born in Yorkshire in 1718, the son of an Otley joiner. As a young man he set up business in London where he achieved a considerable but not exceptional status. Recent research has shown that his abilities were not as great as those of his major competitors, like William Vile who, with his partner John Cobb, produced some of the greatest pieces of all time under Royal patronage. There is no evidence that Chippendale himself ever worked for Royalty, though he did do some fine work for the nobility, for example at Harewood and Badminton. His posthumous reputation rests largely on a pattern book, *The Gentleman and*

Cabinet Maker's Director, which he originally published in 1754 and which ran to three editions. Therein are to be found designs in the style and precise proportions commonly associated with his name. It is now believed that these were the work of two of his employees, Lock and Copland. Many prominent craftsmen subscribed to *The Director* and adapted or simplified its designs, but not a single piece described in it can be unequivocally attributed to Chippendale's own hand. Chippendale's greatest work was done in his later years, around 1770-80, when he made some beautiful furniture under the direction of Robert Adam.

The Director was typical of the pattern books which appeared during the 18th century and continued into the next. They were really catalogues, and Chippendale's was not the only reputation dependent on such publications. George Hepplewhite, a craftsman of undoubted ability, is commonly, but erroneously, credited with the invention of the shield-back chair. In fact " Hepplewhite " is not an original style at all ; most of the designs appearing in his *Cabinet Maker's and Upholsterer's Guide*, published in 1788, after his death, closely followed Robert Adam. Two quaint designs appearing in *The Guide* were for the *confidante* and the *duchesse*. The former consisted of a settee to the ends of which were attached small chairs, set at an angle. The *duchesse* was also of composite construction, comprising two facing chairs separated by a stool. Hepplewhite's firm was small and its output must have been insignificant compared with that of many contemporary workshops. Most of the extant " Hepplewhite " chairs date from the last decade of the century and were made by other craftsmen to designs which were simplified versions of those published in *The Guide*.

If Chippendale and Hepplewhite are remembered because of their publications, they were at least accomplished craftsmen, which is more than can be said of Thomas Sheraton, who set up in London as a drawing master about 1790. He had served for some years as a journeyman cabinet-maker, but he lived " by his exertions as an author " and there is no evidence that he made a single piece of any consequence. His influence, which was great, stemmed from his four-part *Drawing Book* (1791-94) and the less important *Cabinet Dictionary* and *Encyclopaedia* which followed it. He was a fluent inventor and, although favouring a squarish style with vertical emphasis, he made use of the vase and lyre motifs in filling his chair backs. He was a great exponent of the virtues of mahogany and advocated a light form of construction in which superfluous timber was pared away down to the last ounce.

Late Georgian was, of course, followed by Regency, but the latter term is an exceedingly vague one when applied to furniture. Whilst every age has produced its good, bad and indifferent, none has produced such variety of style and craftsmanship as the Regency period ; but, having said that, we hasten to point out that, the more recent the period, the greater the variety of its surviving products.

The Industrial Revolution was slow to affect the woodworkers, and particularly the chair makers, who had always tended to hold themselves aloof from the general craft of cabinet making. During the years 1779-93, Bentham had invented most of the " modern " woodworking machines, but they made little difference to production until " Regency " was well advanced. The resultant decline in craftsmanship hardly affected chair making until some 20 years after cheap cabinet work had made its appearance. Then the depreciation in the value of money as a result of the French war led to a displacement of expensively wrought curved surfaces by plainer forms. Metal, particularly brass, enrichment did become popular, however. To our readers, perhaps the most interesting feature of the period was the introduction of French polishing in England around 1815, and throughout the 19th century many of the older pieces were stripped and refinished in this medium.

Few can be unaware of what has happened to style and craftsmanship since Regency merged with Victoriana, and the Great Exhibition announced yet another reversion in taste. It has been fashionable until very recently to deride the products of the late 19th and early 20th century, but these hardly belong to history and have yet to be seen in full perspective. The machine now appears to have been tamed and a new elegance is emerging. Just what this owes to our grandparents will not, perhaps, be appreciated for another hundred years.

Reviews

PHOTOCHEMISTRY

By J. G. CALVERT and J. N. PITTS, JR. New York: John Wiley & Sons Inc., 1966. Pp. xvii + 899. Price 150s.

Professors Calvert and Pitts are both prolific workers in the photochemical field and they admit in their preface that they are not alone: " In recent years the growth of photochemistry has been stimulated anew by the keen interests of not only the physical chemists but also the physical-organic, organic, and inorganic chemists, molecular spectroscopists, kineticists, and photobiologists." Workers concerned with polymers and coatings can consider themselves as coming under one or more of these classifications, and it cannot be denied that never in the history of our industries has interest in photochemistry been so intense, ranging as it does from lightfastness, yellowing and photochemical degradation on the one hand to radiation curing of films on the other.

The book is aimed at those of advanced undergraduate level and beyond—quite a long way beyond, in the reviewer's opinion, and unless the authors' universities are offering first degrees in photochemistry, there will be few undergraduates who can spare the time to concentrate on the subject to the extent of mastering more than a fraction of this book's contents.

The approach is essentially academic with few concessions to applied interests. The development of the subject is logical and thorough, starting with the pure physics of light, the interaction of light with atoms, and the photochemistry of simple molecules like oxygen and the hydrogen halides. Primary photophysical processes of polyatomic molecules are next considered and lead into a more descriptive discussion of the photochemistry of the various classes of organic compounds. This section concludes with a brief comparison of the effects of non-ionising ultraviolet radiation, gamma rays and electron impact which, though brief, does at least help us to put our thinking about such topics as electron beam curing of coatings into proper perspective. The remaining third of the book is concerned with the more practical aspects of photochemistry: a chapter on the determination of the mechanism of photochemical reactions (concerned essentially with principles) is followed by an excellent account of experimental methods which gives useful guidance to would-be photochemists about the selection of primary radiation sources, the choice of optics and reaction cells, the measurement of light intensities and the determination of quantum yields. An appendix of eight tables of photochemical data, and the comprehensive author and subject indexes, complete a thoroughly fundamental and workmanlike volume. Numerous references to the original literature are given and a healthy proportion of these are to very recent work. A feature of the book is the provision, at the end of each chapter, of a number of really searching problems for solution by the reader. He who succeeds in working through them can rest content that his grasp of the subject has reached the research level.

The book is exceedingly well produced and its price, though high by students' standards, is not out of line with present-day trends. Those who seek a really firm basis for their work on photochemical topics will be well served; the book is not for dabblers in the subject.

A. R. H. TAWN.

THE CHEMICAL FORMULARY, VOL. XIII

Editor in Chief, H. BENNETT. New York: Chemical Publishing Company Inc., 1967. Pp. 447. Price $8.00.

Volume XIII differs little in form and content from its predecessors. Presumably the recipes it contains are new to the series, but they are presented with the usual gaily abandoned inconsistency, under the usual topical headings comprising, among others, inks, paints and lacquers, soaps and cleaners, cosmetics and drugs, foods and beverages, polish, paper, and . . . pyrotechnics. The preface warns against expecting too much of a starting-point formulation (many are obviously culled from the literature of raw material suppliers), and advises consultation with professional chemists regarding commercial production. Fair enough, but it is difficult to imagine any serious manufacturer using such a compilation for his inspiration let alone his instruction. A responsible publisher has, however, seen fit to produce 13 such volumes, so presumably someone must read them.

> *Enthusiastic, hardworking technologist with own bath-tub, seeks contact with gentleman willing to take financial interest in the manufacture of a glue for preserving rock samples, a cod-liver oil ointment (without cod-liver oil), powdered Worcestershire sauce, health food all purpose pork sausages, a paper coating for metals, or military incendiaries. Or would consider acting as consultant to manufacturer having formula but no instructions for production of aerosol laundry starch (nitrous oxide propellant), coconut and soya hand soap, gravy for turkey pot pie, neoprene garden hose or lithographic ink. Write Box ....*

A. R. H. TAWN.

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.)*

An increase of capacity of 25 per cent is claimed by **British Celanese** for the Celacol methyl cellulose plant of their Spondon works. Further expansion is in hand and should be on stream at the end of the year.

Elvacite 6026 acrylic resin, a new solution grade polymer, is announced by **Du Pont.** The resin, a low molecular weight copolymer of methyl methacrylate and n-butyl methacrylate, is supplied as a 50 per cent solution in toluene, and is commercially available from Du Pont de Nemours International SA. The polymer, it is claimed, has excellent solubility in ethylene glycol, monoethyl and diethyl ethers, and most esters, ketones and chlorohydrocarbons, and is compatible with such resins as cellulose acetate, butyrate, nitrocellulose, chlorinated rubber, and some vinyls, epoxies and silicones.

Perkin-Elmer Limited announce a new extended range infra-red spectrophotometer, the Model 457, scanning from 4,000 to 250 cm^{-1}. The Model 457 is claimed to be the first instrument of its type to scan this range and to offer such a consistently high level of performance. The instrument operates on the double-beam, optical null principle, using two diffraction gratings, and recording on a continuous " flow chart," with no gap for grating change-over.

ICI Ltd. have developed a new safety colour for fire engines. The colour, a " psychologically unpleasant " yellow, in the green part of the spectrum, is claimed to be more eye catching than the traditional red, and was developed for the Coventry Fire Brigade. The paint is designated Dulux Coventry Fire Brigade Yellow P339-7419.

A new type of test meter has been developed by **Henry W. Peabody (Industrial) Limited** for the dual purpose of testing the electrical resistance of paint and the voltage output of the Ransburg range of electrostatic hand guns.

The new meter, the S.595, incorporates a switch enabling coating material resistance or gun current to be read from the same dial. A simple socket plug allows the interchange of both output tester and paint probe.

Bodying agent CVP, a new paint additive, has recently been introduced by **Cray Valley Products Limited.** The additive is claimed to improve sag resistance, brushability and pigment suspension of a variety of air drying paints and, at the levels recommended for use, to have no significant effect on the gloss of the paint or on stability.

Polyvinyl Chemie Holland NV have recently introduced a new solvent soluble acrylic copolymer, NeoCryl B-723, which, it is claimed, contributes many important performance advantages not previously available to formulators of coatings. These include : improved adhesion to bare steel and polished aluminium, upgraded colour and durability properties without detracting from adhesion with solution vinyls, and outstanding water and moisture resistance.

Also by Polyvinyl Chemie is a new booklet on suggested floor polish formulations with AC-polyethylene waxes.

A new zinc silicate primer, " Zinsil," is announced by **Detel Paints Ltd.,** a member of the Albright & Wilson Group. The primer is claimed to represent a significant breakthrough in bringing to the market a zinc silicate at a much lower cost than has previously been possible without in any way reducing the technical qualities of this type of primer.

Barter Trading Corporation Limited (a Tennants Consolidated Limited subsidiary) have recently been appointed UK agents for **Norsk Spraengstofindustri A/S,** the Norwegian synthetic resin manufacturer.

Barter will now offer the entire range of Norsk's surface coating resins, including the well-known Dynomin and melamine resins.

A new 100 ft splitting column for the hydrolysis of oils and fats is now on stream at the Bromborough Pool, Cheshire, works of **Price's (Bromborough) Limited.** A large increase in the output of oleochemical derivatives is expected.

Cyanamid of Great Britain Limited and **Texaco UK Limited** have recently announced the formation of a joint venture in the United Kingdom, to be known as Jefferson Chemicals UK. The company will manufacture and market petrochemicals at a site of 150 acres in Llanelly in South Wales. Initial production will include morpholine, piperazine and specialty amine chemicals.

Management offices are being established in London; at present sales offices will continue at Cyanamid's offices in London.

Victor Wolf Limited have recently published a new specification chart of their main fatty acids, showing not only the usual chemical and technical data but also details of constituent acids and other important information.

Using a new technique of colour selection, paint manufacturers **Blundell-Permoglaze Limited** have reduced by more than two-thirds the number of undercoat colours needed for use with their complete range of Permoglaze, Pammel and British Standard 2660 range of gloss finishes.

Previously the 144 gloss finish colours in the company's ranges required 76 undercoat colours. Now, for the same glosscoat colours, only 24 undercoat colours, including white, are needed.

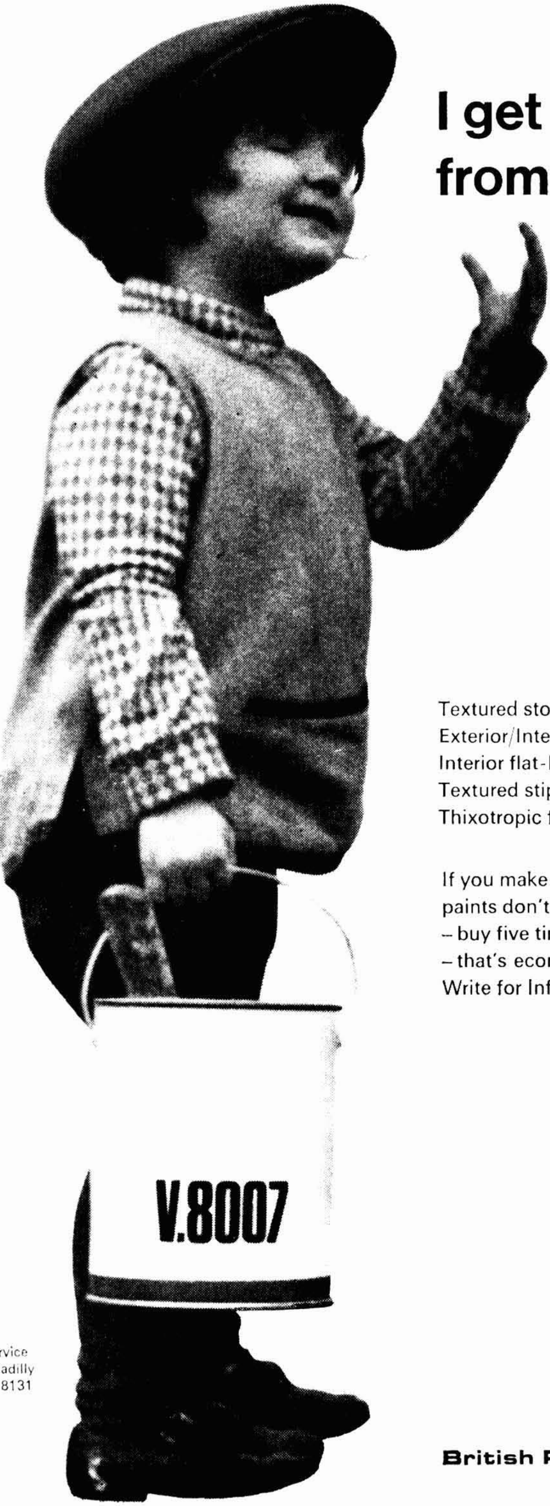
Jenson & Nicholson claim that their rate of filling small cans has virtually doubled due to the use of filling machines designed by **Neumo Ltd.** Double and probably treble the rate of filling 5- to 45-gallon containers using the latest Neumo designed variable height machine is predicted by the company.

ICI Ltd. has recently added Monolite Fast Yellow GXS to its range of organic pigments. The new pigment is a red-shade yellow of, it is claimed, high strength and excellent all-round fastness, making it of particular value in the pigmentation of high-quality stoving finishes, as well as finishes for commercial vehicles, etc. and high-quality packaging inks.

British Resin Products Limited announce the addition of Epok D.2103 to their range of thermosetting acrylic resins. The resin is xylol/petrol resistant, and has been developed to meet the very demanding specifications set by leading motor car manufacturers. It conforms in all other respects to the high performance standards applicable to motor car stoving enamels, and is particularly recommended for outstanding application properties in metallic finishes.

Also new by BRP is a " cold press " polyester resin, Cellobond A262/287. This resin is claimed to be a new approach to cold press moulding ; systems based on Cellobond A262/287 and Cellobond promoter X777/11 can be used with both MEKP and BP catalysts.

" Cool-set Inks," an entirely new range of screen process inks for high speed printing of paper and board, have recently been introduced by **Sericol Group Limited** in conjunction with their subsidiary companies, Screen Process Supplies Limited and Industrial Colours Limited. The new inks are claimed to have the properties of ability to be dried under cool-jet air or natural air, exceptional screen stability and self-solvency, an attractive scuff-proof and semi-gloss finish, easy printing and sharp definition, economy in use due to outstanding coverage and saving in production costs, and complete resistance to creasing and cutting on paper and board.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Bristol

The use of computers to control batch reactions

The 153rd meeting of the Bristol Section was held at the Royal Hotel, Bristol, on Friday 27 January 1967, with the Chairman, Mr. R. J. Woodbridge, presiding.

After the usual preliminaries, Mr. Woodbridge introduced Mr. J. M. F. Drake and Mr. I. G. Kennard, of IBM (United Kingdom) Ltd., who presented a programme entitled " The use of computers to control batch reactions."

The subject was covered in three parts ; firstly, a paper by Mr. Drake, which gave a general introduction to electronic computers and the way they may be used to solve a wide range of problems. This was followed by a film, " Process Control," after which Mr. Kennard gave a talk on " Computers in process control."

Mr. Drake described how the electronic computer was now used for a very wide range of applications, from simple repetitive scientific calculations to complex management control of industrial businesses. In such operations the computer could be programmed to perform tedious work cheaply, with speed and accuracy, whilst at the other end of the scale processing problems too large to be practicable by manual operation could be undertaken.

The technological advance in electronic computers had been rapid and modern systems could perform upwards of 120,000 additions per second in their central processing units. These units incorporated magnetic backing storage systems which allowed vast numbers of characters to be stored in a readily accessible form on magnetic tapes, discs and drums.

Mr. Kennard referred to the use of a computer to replace the " three-term " analogue controller. It was practicable to collect analogue signals directly from processing plants, which were then digitised in an analogue digital converter, for transmission directly into the computer. A computer thus suitably programmed could simulate the action of the " three-term " controller (as currently used for quality control), the output to the control process valves, etc., being available from the computer in digital or analogue form as required. This method of control was known as direct digital control (DDC) and by this technique the process control computer could replace up to several hundred analogue loops.

The computer approach could be considered to be cheaper and was also able to provide more responsive and stable control. Furthermore, the computer could be programmed to exercise supervisory control by integrating and optimising the control over many loops in a manner which was not practicable with conventional analogue controllers. Thus by programming and determining the end point of batch reactions, the computer did in fact carry out two jobs simultaneously. Such techniques were referred to as " multi programming."

Mr. D. S. Newton opened a most lively discussion on the various aspects and possibilities of process control, during which Mr. Drake and Mr. Kennard elaborated on the many points raised.

In proposing a vote of thanks, Mr. D. N. Fidler referred to the ability of the speakers in bringing to more simple terms such a complex subject ; the vote of thanks was warmly supported.

F. E. R.

Hull

Powder coatings

The eighth technical meeting of the session was held at the Royal Station Hotel, Hull, on 6 March, with the Section Chairman, Mr. L. W. Wynn, in the chair. A lecture on " Powder coatings " was given by Messrs. F. E. Bassford and B. Y. Downing, of BIP Ltd.

Mr. Bassford explained that electrostatic spray methods had first been applied to thermoplastic materials such as nylon, pvc and teflon, and had been extended to thermosetting resins about five years ago, using epoxies. About three years ago BIP had started the development of a self-curing, thermosetting system based upon an alkyd resin.

The requirements of the alkyd were that it should be pale, its melting point should be such that the powder did not cake on storage, and that whilst it should fuse and cure at an elevated temperature after application, it must be capable of being fused and compounded with pigments, etc., without premature gelation.

The stages in the preparation of the powder for application were :

(1) The resin, disintegrated to pass a 60 mesh sieve, was dry blended with the pigments, for which purpose a dry ball mill or a special cone blender was used.

(2) The blend must be fusion compounded, a process in which heat and high shear were essential. Screw extruders had been found very satisfactory, the machine in use being capable of operation over a range of speeds and, by change of the stators, at a range of shear rates.

The temperature was maintained at 85-90°C, and the speed of the screw varied from 100 to 1,000 rpm. A die head was used to give a ribbon suitable for subsequent granulation. This also had an effect on the shear, as it caused a back pressure. The feed hopper was water cooled and fitted with a vibratory mechanism to give a consistent feed of powder.

(3) The paste from the extruder was collected on trays and, when cool, was reduced by a rotating knife and then disintegrated in a pin hammer mill.

The formulation contained pigments, extenders and colouring matter ; a tensioning additive, such as polyvinyl butyral (3-5 per cent) to prevent cissing when the powder is applied and fused ; a thixotropic agent, usually 0.5 per cent Aerosil, to reduce sagging in thick films ; and a lubricant to minimise caking, for example, 0.5 per cent zinc stearate, although too much stearate caused blooming and loss of gloss.

The pigments used must be heat stable. TiO_2 with an extender was generally used, and where tinting materials were used they were added in the fusion compounding stage, since the use of mixed powders in the gun led to speckled finishes.

Mr. Bassford finally compared the properties of alkyd and epoxy systems when applied by this technique, and stated that there still remained a lot of development work to be done to finalise the product.

Messrs. Wynn, Gilroy, Gamon and Adamson took part in the lengthy discussion which followed. A vote of thanks was proposed by Mr. Geary, and was passed in the usual manner.

Seventeen members and five visitors were present.

S. R. F.

London

Classification of industrial paint systems

A meeting of London Section was held at Imperial College, London, S.W.7, on 22 March, to hear Dr. J. A. W. van Laar, of Philips, Eindhoven, give the European Liaison Lecture entitled " Classification of industrial paint systems." The President, Dr. S. H. Bell, was in the chair.

Dr. van Laar began by describing the need for a system of classification of industrial paints which were applied in a controlled manner to a range of types of substrate involved in the manufacturing operations of a large company. These finishing operations covered a wide range of products, and were also carried out in many countries by labour with varying degrees of skill, so that operations which could be performed satisfactorily in an advanced industrialised country might not be possible elsewhere. The aim was always to produce finished products of uniformly good quality by whatever means were available. There were certain difficulties in the establishment of such a classification system, including a need for satisfactory standard tests, and frequently a lack of knowledge of the basic phenomena involved in deterioration on exposure to various kinds of conditions.

The basic principles which had been used in classification were based on qualities of performance rather than on composition ; due regard was paid to composition where necessary. Secondly, the paint film was considered always in relation to the substrate. Finally, tests must be realistic, even at the expense of speed of testing. The classification system was based on four co-ordinates : (1) resistance to climatic conditions. Here four categories were specified, two for indoor exposure and two for outdoor, in a series of increasing severity ; (2) mechanical qualities, which consisted of two categories, extremely good and normal ; (3) a quality which had been loosely described as smoothness, meaning texture, freedom from blemishes, etc., and which was the basis of visual appearance ; and (4) gloss, which was specified instrumentally.

There was an inter-relationship between these factors ; for example, improving the resistance to climatic conditions might also change the mechanical properties ; the type of machining operations performed before application of the surface coating would affect a number of properties. The classification system enabled the designer to specify the requirements needed in the mass production of products to be used in a range of climates, with regard to the facilities available for application in each case. Such specifications greatly simplified costing procedures. As the designer specified in terms of properties, the manufacturing and finishing departments concerned were then free to translate these in terms of mechanical finishing procedures and paint systems which would meet the requirements.

For the classification of climatic conditions, three basic factors were involved, light, humidity and corrosive conditions. The resistance to various climatic conditions was expressed in terms of the number of days required to produce a specific effect, and simple logarithmic relations were found for the various individual categories of performance. Dr. van Laar described some interesting work on the incidence of filiform corrosion. He then showed examples of the detailed classifications used, which would specify the mechanical working and finishing operations required to produce products of the required properties.

Dr. L. Valentine, Mr. P. Davies, Mr. T. R. Bullett and Mr. T. E. Adams contributed to the discussion. Mr. R. N. Wheeler, Chairman of London Section, proposed a vote of thanks to Dr. van Laar for an outstanding lecture, in which a great deal of thought had been given to the philosophy behind paint performance and paint testing.

V. T. C.

Manchester

The conservation of paintings and the detection of forgeries

At a meeting of the Manchester Section on 10 February, held in the Manchester Literary and Philosophical Society building, Mr. A. R. Ashton, consultant restorer of the North-Western Museum and Art Gallery Service, gave a lecture entitled " The conservation of paintings and the detection of forgeries." The meeting was attended by Mr. W. McDonnell, in the chair, and 66 members and visitors.

Mr. Ashton first described in detail the complex structure of classical paintings from the substrate, which could be canvas or wood, proceeding through the various ground coats and background colour coats to the composition and characteristics of the top paint coats, comprising the main subject matter and decorative layers of the painting.

Mr. Ashton then gave an account of modern methods of conservation. Chemicals and polymers could be of some assistance in supporting and consolidating weak substrates, etc., but there was still no substitute for painstaking, highly skilled manual work in the cleaning and repairing of damaged areas of a painting.

The disastrous floods in Florence in 1966 provided a topical basis for the lecture, and Mr. Ashton gave a vivid account of the scale of problem facing restorers now working in Italy and how it was being tackled.

Mr. Ashton then dealt with forgery in paintings and showed how this could be detected both from a layer-by-layer examination of the painting and by modern instrumental methods. Instances of now very valuable old paintings being discovered below later often mediocre work were not unusual and provided a rewarding area of work for restorers. Similarly, an exceedingly valuable Rembrandt had been discovered below a modern painting in a recent case of art smuggling.

The lecture was illustrated with many excellent slides, and in addition Mr. Ashton recounted some humorous experiences from his work at home and abroad.

A lively and quite lengthy discussion followed in which many of those present took part, confirming the wide interest in this fascinating subject. Mr. C. Williams proposed the vote of thanks to round off a most interesting and entertaining meeting.

D. A. P.

The development of alkyd based powder coatings

The Manchester Section met on 16 March 1967 at the Strand Hotel, Brunswick Street, Liverpool, to hear a paper entitled " The development of alkyd based powder coatings," by Messrs. Bassford and Downing, of BIP Chemicals. The Vice-Chairman, Mr. W. F. McDonell, and 65 members and guests were present.

The speaker traced the development of powder coatings from their introduction about 20 years ago, and pointed out that the method was an adaptation from the technique used for solvent finishes. Intrinsically high build coatings were obtained, with a limit on thickness caused by the development of a residual field. The thickness limit could be raised by introducing antistatics, or by heating the objects. Early thermoplastic polymers did not give good adhesion, breaks leading to peeling. Efforts were then made to develop thermosetting systems, for example epoxides which were hard and chemically resistant.

The lecturer's own work had been in the field of modified alkyd resins. For the preparation of satisfactory powders, the curing temperature had to be higher than the melting point in order that compounding could proceed. After cure a hard resin was required to give a good powder.

The development of the process to the present stage, which was suitable for continuous operation, was described. The constituents were pre-ground to pass 60 mesh and cone blended. Compounding, involving the application of heat and shear, was in a Vickers screw extruder. Disintegration was achieved in a pin/disc mill, and finally powder classification was done in a Cascade sieve to give a 120-200 mesh product.

The basic formulation of the powders was described. They were mainly white (TiO_2), but phthalocyanine blues and greens, cadmium reds and yellows and carbon black were suitable for coloration. Colour must be introduced at the compounding stage as mixing coloured powder finishes gave mottled results. Extenders (talc and calcium/magnesium carbonates) and zinc stearate to prevent powder caking were other components.

Powder particle size had little effect on application properties, but when coarser than 100 mesh, a mottled surface resulted, when finer than 200 mesh, a dusty powder was produced.

Finally, a comparison of alkyd powder coatings was made with epoxy powders and two solvent based finishes, acrylic/melamine and alkyd/melamine, in terms of physical properties and chemical resistance. It was stated that at present the quality of the finished produced is not equal to that from solvent based enamels, but that provided some deficiencies were overcome, the products would occupy their own niche in the coatings field.

There followed a detailed and informative discussion, at the close of which the vote of thanks was proposed by Mr. J. F. J. Rule.

D. A. P.

Midlands

The Newton Friend Lecture

Materials and skills of the jeweller

The annual Newton Friend Lecture of the Midlands Section was held at Birmingham Chamber of Commerce on Friday 10 March and, as is customary, members' ladies were invited. The subject, " Materials and skills of the jeweller," proved very popular and there was a good attendance of members, ladies and visitors. Three lecturers each gave a short paper.

Mr. R. W. Dew began his paper on " Precious metals " by explaining that the term " precious metals " referred to nobility : that is stability to oxidation and resistance to acids. The precious metals comprised gold, silver and six metals of the platinum group. Some of them were so familiar in the context of jewellery and adornment that the extent to which precious metals contributed to everyday life tended to be overlooked. The speaker then outlined the history, rate of production, properties and major uses of each metal.

Mr. N. Harper spoke on " The background of gem diamonds." Diamonds were first found in India, then in Brazil, in South Africa a hundred years ago and more recently in Russia. After describing the nature of the mineral and its geographical occurrence, Mr. Harper outlined the complex methods used to win diamonds from the earth and the reasons for their high cost. Only a fifth of the diamonds found were suitable for gems, and the rest were used in industry for grinding. Diamond was the hardest substance known and could only be cut by diamond itself. The cutting and polishing of gems, using diamond dust on phosphor bronze wheels, was a very skilled and slow process.

The third paper, entitled " Joys of creating," was given by Mr. J. Rossiter. He said that the general term " the jewellery trade " comprised a number of separate and distinctive trades like designers, enamellers, goldsmiths, silversmiths, chasers, mounters and setters. Methods of producing hand-made jewellery had changed very little over the last 200 years and technology had had little impact. There had been changes in fashion, and the introduction of purchase tax after the war had influenced design. Centrifugal casting, which had been introduced since the war, was a development of the lost-wax method, but used centrifugal force to force the metal into a plaster mould. Newer finishing techniques included trichlorethylene-degreasing and ultrasonic cleaning.

After a discussion period, which included contributions from some of the ladies, Mr. D. J. Silsby proposed a vote of thanks to the speakers.

L. R. S.

Newcastle

A scientist turns to crime

The fifth ordinary meeting of the Section, on 2 February, consisted of a lecture by Mr. K. J. Kimber, of the Northern Forensic Science Laboratory, Gosforth, Newcastle upon Tyne. Mr. Kimber reviewed the history of forensic science in this country, starting with the establishment of laboratories at Hendon and elsewhere in the 1930s. He then gave a talk on case histories, illustrated by many slides of excellent quality. On 7 February a party from the Section paid an evening visit to the laboratory, during which the staff spent much time and energy explaining their work.

D. M. J.

Tall oil

The sixth ordinary meeting of the Section, on 2 March, took the form of a works visit to British Oxygen Chemicals Ltd., Birtley, Co. Durham, followed by lectures.

The afternoon visit was made by 42 members, and after an introduction by Mr. J. Oxley the party was divided into three sections, each of which was taken for a tour of the tall oil distillation plant and the analytical and technical service laboratories. Tea was then provided, and with about 30 more members present the evening meeting began.

Dr. K. Ennor gave an outline of the history and uses of tall oil, culminating in the erection of this, the first tall oil fractionation plant in Britain, in 1966. The raw material used was Scandinavian tall oil ; this had more dienoic fatty acids than did the American, and when made into paint media dried better, and also showed less yellowing.

Mr. S. Redfern dealt with the analysis of tall oil products. One of the most important problems had been the determination of rosin acids in tall oil fatty acids, and Mr. Redfern reviewed the available methods of selective esterification and titration. The other main method of analysis was gas-liquid chromatography, and methods of preparing and chromatographing the methyl esters were described. The linoleic acid peak had a shoulder which was attributed by American workers to a conjugated form, but Mr. Redfern accepted the identification by Finnish workers of this constituent with cis-5, 9, 12-octadecatrienoic acid. This acid, although a triene, resembled linoleic acid in its drying and yellowing properties, since the double bond at position 5 was so remote from the others.

Analysis of " distilled tall oil " (which is defined as having a rosin content of over 10 per cent) showed that the rosin was significantly different from " tall oil rosin," the product of distillation, since it contained less abietic and more pimaric types of acid. Also the fatty acids averaged nearer 19 than 18 C-atoms, a fact which had caused discrepancies when attempting to calculate compositions from acid values.

Questions included some on the technical properties of the distilled tall oil rosin fraction, whether it would react with maleic anhydride, and how it would behave in an alkyd ; the authors expected that significant differences would be found, though they were not sure. Other questions related to the differences in fatty acid compositions of tall oils from warmer and cooler growing areas, the latter in general giving more diene.

The Chairman, Mr. E. L. Farrow, thanked BOC for their hospitality, the lecturers for their presentations, and Mr. Edbrooke for organising the function. The party then repaired to the Lambton Worm for beer and snacks, again provided by the hosts.

D. M. J.

Scottish

Aerosol paints

The second meeting of 1967 was held in the Lorne Hotel, Glasgow, on Thursday 9 February, at 6 p.m., when Mr. A. Rattan presented a paper on " Aerosol paints."

The first aerosol, said Mr. Rattan, appeared as an insecticidal spray during World War II. This early " bug bomb," as it was called, was both cumbersome and expensive, and the modern aerosol pack bore little resemblance to its early predecessor. The modern aerosol consisted of a can, valve, product and propellant. On depressing the actuator, a gasket was deformed, thus exposing an orifice in the stem and allowing the contents of the can to be discharged.

As propellants, fluorinated hydrocarbons were probably the most effective, used either singly or in mixtures one with another, although butane was normally used for water-based products. Careful choice of container was essential if corrosion was to be avoided.

The discharge rate for a pack should be of the order of one gramme per second, this requirement being met by valve design, propellant loading and adjustment of the viscosity of the product, the latter being some 20 seconds Ford Cup No. 4 for a paint. The broad principles of formulation for various finishes were discussed including nitrocellulose lacquers, synthetic enamels, acrylics and polyurethanes. In the main, production of a satisfactory product system depended on the choice of the correct solvent mixture along with a proper balance of resin and propellant. Although fluorocarbons constituted the preferred propellants in this country, hydrocarbons were used in the USA and one American company had developed a paint pack using propane alone as propellant. Using only 15 per cent of this propellant on the total formulation, it was claimed that the spray consisted of 100 per cent paint, due to the high volatility of the propane.

Pressure filling was the most normal method of filling aerosol packs. In this process, the can was filled with a predetermined quantity of the product, the headspace purged with the heavier propellant vapour, the valve swaged on, and propellant finally introduced, under pressure, through the valve assembly. Alternatively, cold propellant could be added to chilled product at about −40°C in the container and the valve swaged on. This method was not, however, recommended for paint aerosols, since precipitation of the resin used could occur. The Omni-Pak method was demonstrated, in which any shade of paint was filled, under pressure, by means of fairly simple equipment into a package which already contained propellant and the necessary solvent blend. Installation of this machine could cost a retailer some £100 and the filling operation could be carried out in a few minutes.

The testing of aerosol paints was described, and various characteristic paint defects, such as bubbling, cratering, orange peel, sagging, blushing, loss of gloss and colour change, were dealt with, along with such application difficulties as jetting and valve blockage.

Correct spraying technique was described and demonstrated. It was necessary, for example, to ensure that the aerosol container was not too cold, otherwise a poor spray or jet would be obtained. Best results were obtained with two to three passes at a distance of about 12 in from the surface.

A. MCL.

The use of microscopy in the investigation of paint defects

At a meeting of the Scottish Section, held in the Lorne Hotel, Glasgow, on Thursday 9 March, Mr. H. Wells delivered a lecture on "The use of microscopy in the investigation of paint defects." At the outset, Mr. Wells stated that, at the Chemical Inspectorate, Woolwich, his department was concerned specifically with the laboratory investigation of paints—decorative, industrial, and specialised finishes for aircraft, etc. Thereupon he set out to illustrate the types of problems encountered with a range of coloured slides of unusually high quality. These covered the following subjects :

(*a*) Photomicrographs of paint sections, flakes of faulty paint film, metallic powders, etc.

(*b*) Methods of handling (by means of vacuum probes) microscopic particles and of mounting sections for examination in molten wax, cold-curing polyester resin and cold-curing epoxide resin. This last method has been found to be the most successful and has been adopted for general work in this field.

(*c*) Methods of viewing prepared specimens, types of microscopes used and methods of illumination. Mr. Wells said that a stereoscopic microscope was sometimes employed ; but, usually, an ordinary instrument was found more suitable. As for illumination, a "dark ground" vertical illuminator was found to give the clearest image. High magnification was not essential and ×60 to ×100 was adequate for this type of work. Slides showing a variety of subjects—paint films on metal, wood, etc. —were shown to illustrate these points.

(*d*) Micrometer eyepieces used for determining the dimensions of specimens and the use of coloured filters at the light source.

(*e*) Reagents used for the identification of components in the paint layers in the specimens. Materials such as calcium plumbate could be easily identified and tests had even been devised for such an inert pigment as titanium dioxide.

(*f*) The use of UV illumination, which is often advantageous where normal illumination fails, although by far the majority of microscopic investigations of paint sections were done in the latter. Very occasionally, infra-red illumination was used.

Mr. Wells gave very detailed explanations of the operation of both standard and stereoscopic microscopes and of the auxiliary apparatus necessary for manipulating and illuminating paint section specimens. Details of the chemical reagents used in micro-analysis were given and, in conclusion, he showed a range of slides illustrating some of the sophisticated techniques in micro-analysis.

Following the lecture, Mr. Wells very kindly answered a large number of questions which ranged from the choice of photographic equipment required to methods of polishing specimens. This lecture indeed proved extremely impressive and, as Mr. Pisacane said in his vote of thanks, was enjoyed by everyone.

T. B. H.

Notes and News

OCCA 19

The Association's Information Centre, showing the displays featuring the Paint Technology Manuals, the Introduction to Paint Technology and the Scarborough Conference

The Nineteenth Technical Exhibition was held on 13-17 March 1967 at Alexandra Palace, London. The attendance over the five days the Exhibition was open was estiestimated at 11,500. The international nature of the Exhibition was shown by the attendance of representatives from the following 30 overseas countries : Argentina, Australia, Austria, Belgium, Canada, Ceylon, Czechoslovakia, Denmark, Finland, France, Eastern Germany, Western Germany, Holland, Iceland, India, Ireland, Israel, Italy, Lebanon, Morocco, Norway, Poland, Portugal, Singapore, South Africa, Spain, Sweden, Switzerland, USA and USSR.

Twelve firms were exhibiting for the first time. The increased overseas interest was also shown by the fact that 29 of the stands were of exhibitors from eleven foreign countries, including the USA as well as Europe. The greatest number were of Dutch and German firms. In addition, the products of many other overseas manufacturers were shown by agents in this country.

Exhibition Luncheon

The Exhibition Luncheon was held on Monday 13 March at the Savoy Hotel, London, W.C.2., and was attended by over 250 members, exhibitors and guests. The Rt. Hon. George Darling, P.C., M.P., Minister of State at the Board of Trade, was the principal guest and responded to the Address of Welcome by the President of the Association, Dr. S. H. Bell.

Dr. Bell, in welcoming the guests, exhibitors and press, referred to the older " image " of paint in the eyes of the general public. This was in contrast to the modern technological developments which had taken place in the surface coating industries. OCCA provided the means by which the scientific background and technological progress of these developments could be presented and discussed, with its annual programme of over 100 lectures to Sections and Branches, and with the Journal of world-wide repute. Attention was also paid to educational efforts for younger people, with organised visits to the Exhibition of students from the upper forms at schools, and the Association's books for students. The " Introduction to Paint Technology " had now reached 13,000 copies distributed, while the Technical Training Manuals had already reached 4,000 copies for each of the six volumes.

Mr. G. Darling officially opened the Exhibition by cutting the traditional tape, watched by (left to right) Dr. S. H. Bell (President), Mr. A. S. Fraser (Chairman, Exhibition Committee) and Mr. R. H. Hamblin (General Secretary)

Dr. Bell welcomed the Guest of Honour, the Rt. Hon. George Darling, and referred to the fact that the finished products of our industries were used in the form of very thin layers of surface coatings. Yet despite this, the annual turnover of the paint industry was about £150 millions (1965 figures), with export sales of about £11 million, with also nearly £2¾ million for printing ink exports. There was in addition a very considerable " hidden " export—a word which seemed rather inappropriate for surface coatings on finished goods—which was quite substantial in amount and which was of great importance in giving protection and sales appeal. He then extended a welcome to the official guests :

Cyril Sweet, *Master*, and Barrett G. Wilson, *Clerk*, *of the Worshipful Company of Painter-Stainers*, N. A. Iliff, Esq., *President of the British Plastics Federation*, Dr. T. J. Drakeley, *President of the Institution of the Rubber Industry*, L. Morton Wood, Esq., *President of the Society of Dyers and Colourists*, J. Smethurst, Esq., *Chairman of the British Colour Makers' Association*, and A. Tremain, Esq., *Chairman of the Surface Coating Synthetic Resin Manufacturers Association*, R. T. Bowes, Esq., *President of the Society of British Printing Ink Manufacturers*, P. A. J. Sturge, Esq., *President*, and K. S. Flory, Esq., *Director*, *of the Paintmakers Association*, Dr. G. L. Riddell, *Director of the Printing Packaging and Allied Trades Research Association*, L. W. Robson, Esq., *President*, and Dr. L. Valentine, *Director*, *of the Research Association of British Paint Colour and Varnish Manufacturers*, and R. N. Wheeler, Esq., *Chairman of London Section.*

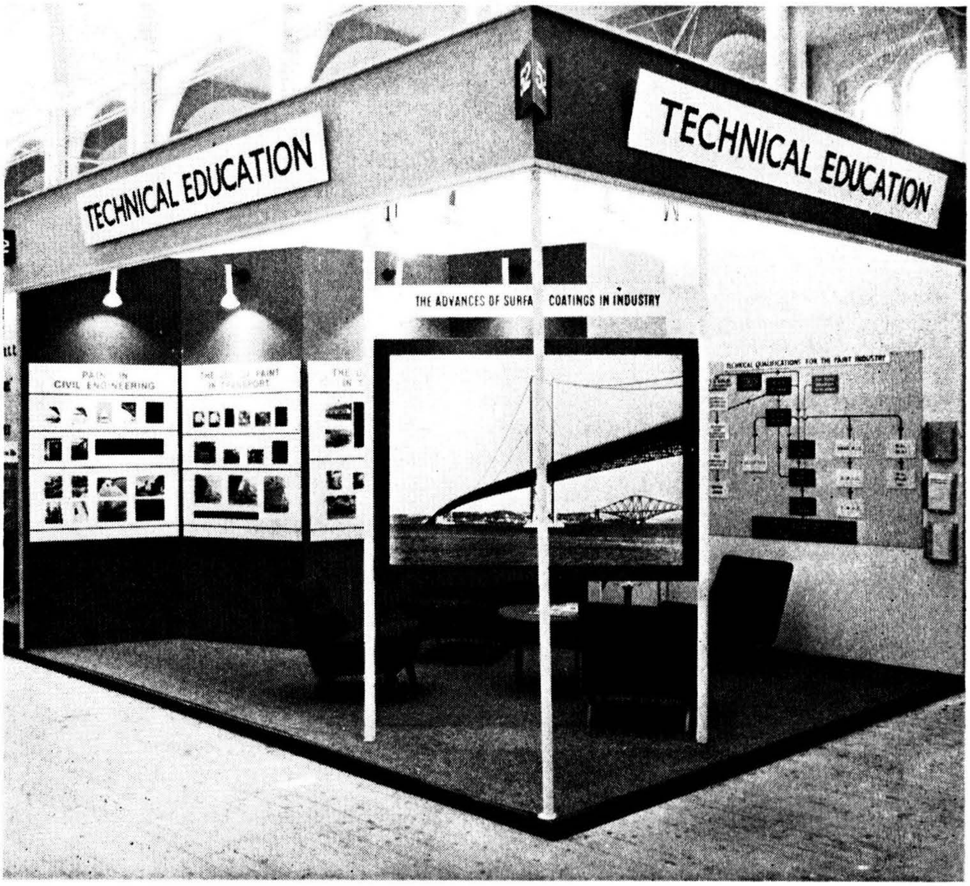
The Rt. Hon. George Darling, P.C., M.P., thanked Dr. Bell for the interesting and informative Address of Welcome. He referred to the fact that this was a Technical Exhibition, which provided an opportunity for direct contact on a technical level between suppliers and consumers, which resulted in a beneficial two-way flow of information and ideas. He referred to the great advance in the last 20 years in the use of colour, in almost every aspect of our national life, and in particular in the decoration of our homes, offices, factories and schools, where brighter more attractive colours now predominated. He thanked the Association for its hospitality, and wished the Exhibition every success.

The official opening ceremony was performed at 3 p.m. at Alexandra Palace by Mr. George Darling, who then made a tour of the stands accompanied by the President, Dr. Bell, the Chairman of the Exhibition Committee, Mr. A. S. Fraser, and the General Secretary, Mr. R. H. Hamblin.

Technical Report

Technical Education

The main value of the Technical Education stand lies in the expert advice obtainable from the staff, and this was of the customary high standard. An attractive display covered the uses of paint in civil engineering, illustrated by photographs of the recently constructed Forth and Severn Bridges, and the use of paints in the field of transport by land, sea and air. A further exhibit dealt with printing inks, and included an item of considerable historic interest lent by Dane & Co. Ltd., the first example of the trichromatic process demonstrated at the Exhibition of 1878, and astonishing in the way which the colours had been preserved. Modern examples of trichromatic printing were also shown.

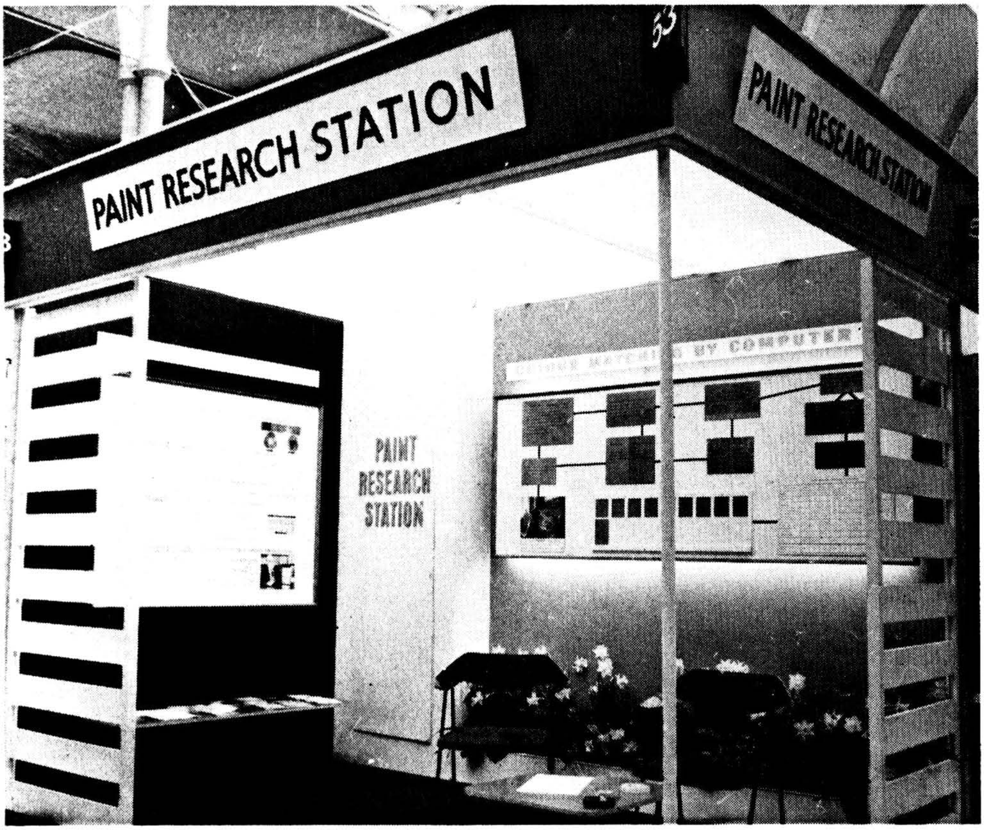


The theme of the Technical Education stand was " The advances of surface coatings in industry," featuring the new Forth and Severn Bridges

Again, parties of sixth form science students were invited to visit the Exhibition. 204 students from ten schools attended over three days, during which short introductory talks were given, prior to the students seeing the Exhibition, by Mr. P. Birrell, Mr. J. Bravey and Mr. G. H. Hutchinson. The talks stressed the variety of scientific interests involved in the industry, and the opportunities for an interesting career for young people.

Research Association

The Paint Research Station stand was devoted to colour and colour matching, stressing work on the prediction of the colour of pigment mixtures. An historical chart showed the progress in this field from the days of Newton to the recent work of Dr. Duncan at the PRS. By a simplification of the theory, analogue methods may be used, such as the Davidson and Hemmendinger Colorant Mixture Computer. With full calculations with a digital computer, where both absorption and scattering coefficients were used, colour matching could be extended to deep and saturated colours. One particular advantage of the digital computer technique was that as well as a formulation, so-called tinting factors were produced, by means of which the corrections necessary to the first match could be made in a single stage. The use of the digital computer technique was illustrated by a series of nine matches of a standard made from a variety of sets of four pigments selected from a basic range of eight coloured paints and white, including information on the costs of each formulation.



The Paint Research stand had a theme of "Colour and colour matching"

Technical Press

The Paint Manufacture stand showed the range of technical publications produced, together with a display featuring the journal.

The Paint Oil and Colour Journal display included the new edition of the Year Book, technical publications concerned with surface coatings technology, and a range of technical books.

Paint Technology showed " Anti-Corrosion Methods and Materials," which has recently been taken over by Sawell Publications Ltd., and the 1967 Paint Trade Manual of Raw Materials and Plant.

Translation and Technical Information Services showed their range of technical publications concerned with the surface coatings industries, including the new series of abstracts of papers appearing in the Russian Paint Journal, Lakrokrasochnye Materialy i ikh Primenenie. In addition, surveys of the patent literature were shown, including one on titanium dioxide pigment manufacture and one on electrophoretic deposition of paint.

Pigments

ALLIED CHEMICAL CORPORATION showed the range of Harmon light fast organic pigments, with particular emphasis on their use in automobile finishes. The use of highly transparent hydrated ferric oxide dispersions as " gold paste " for the production of a range of colours for coating metals and foils was shown. A new flocculation resistant carbon black for use with thermosetting acrylics was featured. ANCHOR CHEMICALS showed the well known *Dixie* and *United* carbon blacks. VICTOR BLAGDEN exhibited pigments from SPCM, including a range of predispersed pigments for use in rotogravure inks, and new yellow pigmentary dyestuffs giving improved colour, lightfastness and flow in offset printing inks.

BRITISH TITAN PRODUCTS featured three new grades of titanium dioxide, *Tioxide R.HD2*, a multipurpose grade giving ease of dispersion in aqueous and non-aqueous systems, and suitable for all types of mills, *Tioxide R.CR6*, a new high opacity rutile pigment, free from organic treatment, designed for air drying and stoving media, but which could also be used in gloss latex paints. *Tioxide R.XL* was a new rutile pigment, of lower titanium dioxide content, for use in latex paints producing increased opacity. Another exhibit was concerned with the choice of pigments and other factors for accurate matching of touch-up low bake acrylic enamels for autobody repairs.

FARBENFABRIKEN BAYER displayed two new grades of rutile titanium dioxide pigments, *Bayertitan R.KB2* and *R.FD1*, with improved colour, brightness and opacity, and also gloss retention in air drying and stoving finishes. A new micronised yellow iron oxide pigment, *Yellow 3910*, had improved ease of dispersion. Three new high temperature resisting inorganic pigments, *Light Yellow 8 G*, *Light Yellow 3 R* and *Light Blue 2 R*, had high lightfastness and weathering resistance. The *Helio Fast P* range of easily dispersed pigments were of particular value in flamboyant lacquers and flexographic and gravure inks. Two new cadium pigments, *Cadmopur Orange 3 RS* and *Yellow 15 GN*, were also shown.

BASF UNITED KINGDOM showed new phthalocyanine blue and green pigments with improved colour strength. Also on display were red and magenta shades of copper ferrocyanide complex pigments, particularly for newspaper printing, and a new red polycylic pigment with good fastness and heat stability. BUSH BEACH AND SEGNER BAYLEY showed two new Degussa carbon blacks, *FW 200* especially developed for thermosetting acrylics, and *300* for rotogravure inks. CORNELIUS CHEMICAL COMPANY exhibited the speciality pigments of the Mearl Corporation.

CIBA CLAYTON displayed *Cromophtal Red A3B*, which is now available, used in mixtures with light fast molybdate orange, and used with carbon black to produce maroon shades for car finishes. The *Microlith A* series of pigments, based on ethyl cellulose as the carrier resin, are designed for flexographic and alcohol based gravure inks, being especially suited to systems containing nitrocellulose. These pigments have good lightfastness and resistance to most materials encountered in packaging. The use of *Orasol* soluble dyestuffs on a thermosetting acrylic medium was displayed, showing good bleed resistance on overspraying and stoving. CROXTON AND GARRY showed the *Midas Gold* dispersions from RBH Interchemical Corporation for use in metallic car finishes based on acrylic, alkyd and nitrocellulose media. *Phloxine Red Toner 21.2310*, available as dry pigment or dispersed in letterpress, offset or gravure media, offered improvements over lithol pigments.

DURHAM RAW MATERIALS in an interesting technical display showed the possibilities of electrodeposition of top coats over conventionally deposited zinc flake primers, and also the electrodeposition of zinc flake primers, followed by electrodeposition of a top coat. Panels illustrated the good corrosion and weathering resistance. Other technical displays illustrated the use of *Zinc Flake 1100* and *Ultrafine Zinc Dust* in heat resistant paints, and in various media including inorganic silicates. Primers based on zinc dust which were suitable for spot welding were also shown.

11,500 people are estimated to have attended the Exhibition, and good use was made of the seating area in front of the Information Centre

Geigy (UK) showed extensions to their range of predispersed and easily dispersible pigments. *Irgalite Red PDS.3* is a toluidene red available in granule form and suitable for high speed dispersion equipment. Two new members of the recently introduced *Irgazin* range were *Red GLT*, an azo pigment, and *Violet 6 RLT*, a dioxazine pigment. Ferrocyanide cationic dye complexes shown were *Irgalite Brilliant Pink FB*, *Deep Green FB*, and *Yellow Green FG*. New ink pigments on show were *Rubine L4BC*, a calcium

4B toner, *Yellow L10G*, a 10G arylamide pigment, *Yellow LBAW*, a *m*-xylidide *bis*-arylamide yellow, and *Blue LGB*, a phthalocyanine. *Yellow PR2*, a green shade *bis*-arylamide yellow, and *Rubine PR4* were introduced for high speed dispersion in publication gravure inks.

FARBWERKE HOECHST displayed panels after two years exposure showing the good colour retention of the quinacridone pigments *Permanent Red E3B* and *Permanent Pink E*. The improved gloss and tinting strength of *Hansa 10 GX* and *Hansa 5 GX* were illustrated. A new surface treated azo *Yellow DHG.24* showed improved colour and strength in printing inks. A new flushed pigment (in linseed oil) *Reflex Blue AG conc. 30* was now available. *Permanent Brown HFR* was a new pigment of the mono-azo naphthol A.S. series.

IMPERIAL CHEMICAL INDUSTRIES featured two new ranges of easily dispersible pigments, the *ED.P* series for paints, and *ED.I* series for viscous printing inks. The paint pigments which will be available are *ED.P Monolite Fast Scarlet RN* (toluidine red), *Fast Yellow GH* (arylamide yellow G), and *Fast Yellow 10 GH* (arylamide yellow 10G), and the printing ink pigments will be *ED.I Monastral Fast Blue BX* (*alpha* form phthalocyanine blue), *ED.I Rubine Toners 4 BT, 4 B*, and *2 B*, and *ED.I Monolite Yellow GL* (light-fast benzidine yellow) and *10 GH*. Other new pigments include *PX Monolite Yellow GT*, a benzidine yellow with easy dispersion in ink media such as gravure inks. Improved flow properties and gloss are also obtained. *Monolite Fast Red 2 YS* is a further development of a dibromoanthranone vat pigment, with improved strength and fastness even in very pale tints. *Monolite Fast Yellow GXS* is a monoazo pigment dyestuff with good fastness to overspray. *Supra Fast Primrose Chrome 10 GS* is a chrome pigment with improved light-fastness.

IMPERIAL SMELTING CORPORATION showed a display of panels illustrating the use of zinc orthophosphate as an anti-corrosive pigment. Zinc phosphate primers showed corrosion protection equivalent to red lead, but in contrast to the latter, can be used in sprayed coatings. Furthermore, zinc phosphate primers can be formulated for rapid drying and confer good intercoat adhesion. INDUSTRIAL COLOURS showed the improved range of *Flare* fluorescent pigments, including the *610* range for stir-in paints, screen inks, and paper coatings.

The display of KEMISK VAERK KOEGE featured a new *epsilon* form of copper phthalocyanine, *Isol Phthalo Blue E 7543*. This is redder in hue than the *alpha* form pigments, and is at present available in an unstabilised form, but will shortly become available as a crystallisation resistant grade. A new grade of the *beta* form pigment, *Isol Phthalo Blue BC.2.7546* is specially suitable for the new European Standards for a trichromatic blue. Two new low-haze toluidine reds were shown, *Isol Toluidine Red LHG 8501* and *LHB 8502*. Several new types of BON pigments were shown, *Isol Bona Red N4R 7523*, a manganese salt, with good flow properties and light fastness in inks ; *Rubine BKB 7529*, a 4B rubine pigment, and *Red N7R.7524*, a calcium salt with better light fastness and rheological properties. Three new easily dispersible benzidine yellow pigments were shown, *Isol Benzidine Yellow GA.PR.9500, GB.PR.9501*, and *GRA.PR.9505*, and a dispersible phthalocyanine, *Isol Phthalo Blue BGA.PR.9520*. These pigments may be dispersed in low polarity solvent based media by high speed mixing. Pigment dispersions in vinyl resins VYHH, VMCH, VAGH, in nitrocellulose RS and SS, and in polyamide resin were available, as well as aqueous dispersions.

KRONOS TITANIUM PIGMENTS exhibited a new pigment, *Kronos RN.CX*, the equivalent of the American produced *Titanox RA.NC.1*, a general purpose pigment of high durability. Of particular interest was the display of the use of the Zeiss Interference Microscope in the study of surface haze associated with poor pigment dispersion and with the loss of gloss in weathering. The advantages of using new grades of pigments with improved dispersion characteristics were demonstrated. Also in display were the

The President, Dr. S. H. Bell (third from left), and the Director of the Paint Research Station, Dr. L. Valentine (second from left), with an informal group of Directors of foreign Research Organisations who visited the Exhibition. (Left to right) Mr. A. Caillez (Laboratoire de at Profession IVP, Belgium), Dr. R. Bult (Verfinstituut TNO, Netherlands), Mr. P. Rabanl (Laboratoire peintures et vernis), Mr. H. K. Raaschou Nielsen (Central Laboratory of the Danish Paint and Varnish Industries) and Mr. B. Hemberg (Svenska Färgindustriens Forskningslaboratorium, Sweden)

results of natural weathering tests in which panels had been exposed on a world-wide basis, at sites ranging from Florida to Britain, Scandinavia and South-East Asia.

LAPORTE INDUSTRIES displayed a new grade of rutile titanium dioxide, *Runa RH42*, of general applicability. The exhibit featured the results of measurements of hiding power over a range of pvc's in long oil alkyd, melamine-alkyd, and copolymer emulsion media. Dispersibility of the pigment by Cowles dissolver and sand milling was illustrated. MCKECHNIE CHEMICALS illustrated the use of lithopone in water soluble resin systems, including the results of salt spray tests on paint systems pigmented with lithopone and anti-corrosive pigments. Electrolytic copper pigment for anti-fouling compositions was shown as an 80 per cent paste in white spirit or xylene, with stabilising additives to prevent surface oxidation.

PFIZER showed their established range of iron oxide pigments, and *Stay Steel* stainless steel flake pigment. A new strong brown *BN 65* giving a clean lilac tint when reduced with titanium dioxide was introduced. The high purity range (97-98 per cent Fe_2O_3) of *Kroma Reds* with low water soluble content were particularly suited for paints for electrodeposition. Two new high temperature resistant pigments, *Kromatherm Yellow Y 2030* and *Y 2835* were shown. These are zinc titanium ferrites, and are stable up to 425°C. REX CAMPBELL & COMPANY showed cadmium pigments and cuprous oxide for anti-fouling paints of improved dispersibility suitable for use with high speed dispersion equipment.

SPELTHORNE METALS showed a technical display of the use of metallic lead pigments in various types of media. Results were shown of variations in pigmentation level in a range of media, including oil based, alkyd, vinyl-toluene alkyd, and chlorinated rubber paints ; the effect of the percentage metallic lead content and pvc, for natural coastal and industrial exposure. The use of metallic lead in water soluble primers was displayed, as was the use of a metallic lead primer for zinc coated steel. In all cases a study of the optimum pigmentation conditions had been made.

SWADA (LONDON) displayed their recent developments in the *CQ* range of fluorescent pigments specially formulated for plastics, with increased temperature stability up to 250°C, which allows considerably more freedom in blending and fabrication techniques. N.V. TITAANDIOXYDEFABRIEK TIOFINE showed various improvements made in their *Tiofine* range of pigments, including the *R60* and *R70* grades with improved ease of dispersion. Four grades of anatase and five of rutile are now available. VUORIKEMIA OY also showed new grades of titanium dioxide, *Finntitan RR2* and *RD2*, with improved dispersibility.

Extenders

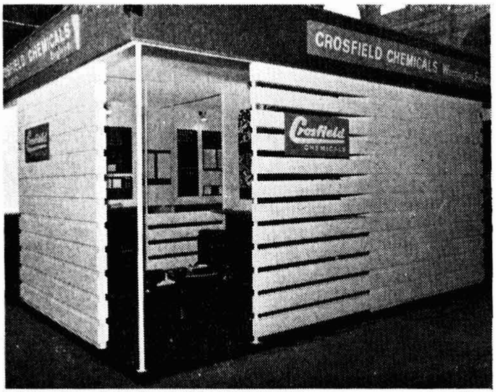
BERK showed *Dicalite* extenders and various grades of calcined and surface coated clays from the Georgia Kaolin Company, USA. BUSH BEACH & SEGNER BAYLEY showed the use of *Aerosil* as a thickener, and flow control agent. JOSEPH CROSFIELD & SONS showed the use of *Microcal ET* calcium silicate, *Alusil ET* aluminium silicate, and *Neosyl ET* fine silica in latex paints, as partial replacement for titanium dioxide in formulations. The good colour of these extenders showed to advantage in high pvc formulations. The *Gasil* range of micronised silica gels were exhibited for use as wetting agents, anti-blocking aids, and in paper coatings.

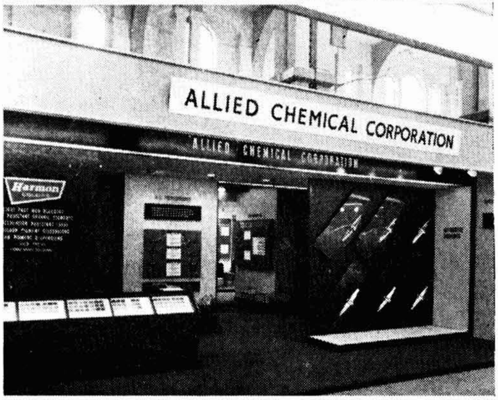
CROXTON & GARRY displayed a fine grade of precipitated calcium carbonate, *Hakuenka OT*, with a high degree of transparency for use in inks. *Millicarb*, used in iron oxide primers and road marking paints was also on show. ENGLISH CHINA CLAYS showed the use of the clays *Speswhite*, *Grade A*, and *GSH(S)* in decorative alkyd and polyvinyl acetate copolymer emulsion paints. China clays *GSH(S)* and *BMM* were used in a series of iron oxide/zinc tetroxychromate primers in comparison with other extenders and unextended primers. *BMM* grade gave good results in terms of the absence of blistering and corrosion. The use of a coarse extender, *Lee Moor S 2 G* in the formulation of emulsion type textured wall paints was displayed.

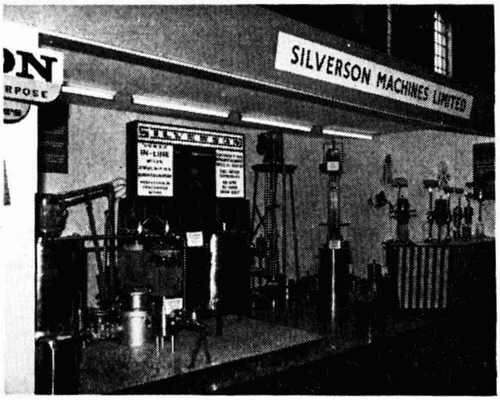
LAPORTE INDUSTRIES illustrated the properties of *Laponite*, a synthetic sodium magnesium lithium fluoro silicate clay, as a gelling agent in emulsion paints. NORWEGIAN TALC (UK) showed the results of an extensive series of comparisons of a wide range of extenders in air drying and stoving systems, and the effects of the type and amount of dispersing agent used with extenders in emulsion paints. A new finer grade of *Microdol 275* was on show. PECHINEY-SAINT-GOBAIN showed *Peintal*, a new white alumina extender for interior and exterior emulsion paints. PLUESS-STAUFFER showed *Omya BLP* 3, a crystalline calcium carbonate with a hydrophobic coating for use in solventless polyurethanes, *Omya BSH* as an extender for zinc rich primers, and *Syloid ZH.1* a molecular sieve material.

Oils and fatty acids

BRITISH OXYGEN CHEMICALS featured a range of Vantal products from their fractionation plant. Attention was drawn to the much reduced yellowing tendencies of white







alkyd paints based on *Vantal A1* and *A4* fatty acids. Improvements in the purity and colour of C_8 and C_9 acids, particularly 2-ethyl hexoic, 3.5.5.-trimethyl hexoic and iso-octoic acids, were demonstrated by NOVADEL. A wide range of dehydrated castor oil fatty acids of varying conjugation were shown by VICTOR WOLF, a new development product being *Iso-Dedico*, having 34 per cent trans-trans conjugated diene. Booklets and leaflets were available on new uses for these materials, including, for example, the manufacture of urethane oils. YOUNGHUSBAND STEPHENS exhibited their range of drying oils, clarity and paleness being emphasised. A very pale safflower oil was now available in reasonable quantities.

Resins—emulsion polymers

BASF United Kingdom introduced a new fine particle size emulsion polymer, *Acronal 290 D*, suitable for use in matt and gloss paints for interior or exterior purposes.

British Oxygen Chemicals drew attention to the advantages of high-solids emulsions in terms of storage costs and general versatility. Such emulsions were exemplified by *Vandike 8085*, a vinyl acetate/butyl acrylate copolymer of 61 per cent solids content, and *Vandike 550*, a polyacrylate type of 55 per cent solids. Examples of the applications of these emulsions in wood primers and undercoats for conventional alkyd systems, fire-retardant paints and textured finishes were shown.

Dunlop Chemical Products Division demonstrated recent developments in their *Polimul* range of emulsions, including a new vinyl acetate/VeoVa 911 copolymer suitable for use in primers and finishes for structural steel. Further details in the formulation of water thinned gloss paints based on a mixture of *Polimul DS.4611*, a small particle size emulsion, and *Polimul 1160*, an alkali soluble acrylic polymer, were available. A special feature represented graphically the relation of raw materials cost per gallon of paint to various contrast ratios.

Harlow Chemical Company were exhibiting for the first time, and showed a wide range of vinyl acetate and acrylic homopolymers and copolymers. In particular, a vinyl acetate/ethylene copolymer *DM 10* and vinyl acetate/versatate copolymers *DM 20* and *DM 21* were featured with panels illustrating the exterior durability of the products. The performance of an intumescent fire-retardant emulsion paint was also shown.

Lennig Chemicals featured several of their 100 per cent acrylic emulsions in the *Primal* range, the water vapour resistance of *Primal AC 34* when used in wood primers being demonstrated. A priming and undercoating system based on *Primal AC 22* was also shown.

Vinyl Products gave prominence to their vinyl acetate-ethylene copolymer emulsions. A new polymer type had been developed in which the ethylene was introduced as grafted side chains, the resulting improvement in scrub resistance being illustrated. Other exhibits included a display of panels showing the use of *Vinamul 6865*, a vinyl acetate-acrylic emulsion, in primers and undercoats in which good flow properties were emphasised. Results from exposure trials demonstrated the freedom from chalking, cracking and excessive dirt pick-up of the wood primer.

A newcomer to the exhibition, Polyvinyl Chemie Holland, showed their *Neocryl* range of polymer emulsions designed primarily for use in floor polishes, including metal bound types, which resist alkaline detergents but are readily removed by ammonia. Kingsley & Keith had further information on the vinyl acetate/styrene copolymer emulsion *CIS 0246* from Staperm Ltd. introduced last year, together with a wide range of vinyl acetate, styrene and acrylate polymers and copolymers introduced during the past year from Pontyclun Chemical Co. A range of vinyl acetate/ethylene copolymer dispersions developed for adhesives and paper coatings were displayed by Bush Beach & Segner Bayley.

Resins—water thinnable

CIBA (ARL) introduced *X83/343*, a liquid hardener, specially designed for use with *Araldite* liquid epoxy resins in the formulation of water-dispersible coating systems. Cray Valley Products announced a new low cost resin, *Resydrol P420*, for use in water thinned stoving primers or coloured finishes. A complete water thinnable system for industrial stoving finishes, with filler and primer based on alkyd types and a water soluble acrylic top-coat, was shown by Farbenfabriken Bayer. Also exhibited was an interesting newcomer, *Ercusol I 60*, described as an acrylic based self-cross-linking dispersion copolymer, which could be used for air drying or stoving coatings, and gave particularly good adhesion to galvanised steel.

Nederlandse Castor Oliefabriek demonstrated the use of *Newcowel TNAC*, an air drying polyester-acrylic copolymer, in high gloss water dilutable paints of good colour retention. Scado-Archer-Daniels introduced *Scadosol A46*, a new development product in their water soluble range, giving improved air drying properties and flow characteristics in gloss paints.

Electrodeposition

BASF United Kingdom introduced a new water thinnable thermosetting acrylic resin, *Luhydran*, particularly for the electrodeposition of one-coat systems in pale and white shades. Cray Valley Products emphasised their continued progress in the development of water soluble resins for application by electrodeposition with examples of anti-corrosive primers based on *Resydrol E451*, pastel shade finishes based on *Resydrol E474*, flamboyant finishes based on *Resydrol E475* and white finishes based on *Synocryl 841S*.

Nederlandse Castor Oliefabriek showed a modified grade of *Necowel L 2075* for use in primers applied by electrodeposition, improvements in corrosion resistance being demonstrated with test panels. A recently developed water dispersible synthetic fatty acid ester adduct, *Necowel HO*, was particularly suitable for high voltage electrodeposition, and extremely good throwing power was claimed. Information on another resin designed for high voltage application was available in the Scado-Archer-Daniels stand. This resin, *Arolon EP 7992-15-104*, could be used for clear coatings, primers or one-coat self priming enamels, satisfactory film thickness being achieved at 200-400 volts in 1-2 minutes.

Pluess-Staufer introduced *Plusaqua 178*, a new resin for electrodeposition, being particularly designed for use in white and pastel finishes. Shell Chemicals UK featured their water soluble ester resins, *Epikote DX-15* and *DX-16*, specially developed for electrodeposition. Of particular interest was a continuous strip bath exhaustion test in operation to demonstrate the stability of a primer based on *DX-16*. Durham Raw Materials displayed panels showing electrodeposited coatings on a zinc rich primer. They also demonstrated that zinc rich primers (containing *Zinc Flake 1100*) could themselves be electrodeposited, followed by a top coating applied by electrodeposition.

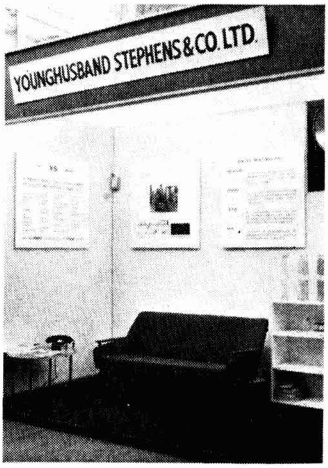
Resins—polyurethane

Victor Blagden showed a range of *Cargill* polyurethane resins that are now being manufactured in the United Kingdom. These included new moisture curing types that could be used in seamless flooring. Imperial Chemical Industries featured new developments in moisture curing prepolymers, including *Suprasec 1285*, a prepolymer of a polyisocyanate with coal tar, which is film forming itself. It can also be further reacted with *Daltolac 2200*, a polyether, or with castor oil to give high build finishes of excellent resistance. Also exhibited were *Daltosec 2140* and *Daltosec 1140*, two new prepolymers, for use in flooring compositions.

Lancashire Tar Distillers drew attention to a range of special pitches for use in one-pack moisture curing and two-pack polyurethane/pitch compositions for application to structural steel work. J. H. Little announced the production of *Sovermol*, a new hydroxyl containing component for polyurethane lacquers. With this unsaponifiable polyol, coatings of good flow and excellent chemical resistance can be obtained. Plastanol showed *Hythane 1*, the first of a series of urethane modified alkyd resins now being developed. Panels demonstrating the hardness and abrasion resistance of films compared with conventional alkyds were displayed.

Societe des Usines Chimiques Rhone-Poulenc had further information available on their range of *Scurane* polyurethane resins, including *Scurane VIP 60 AB*, a blocked


PECHINEY-SAINT GOBAIN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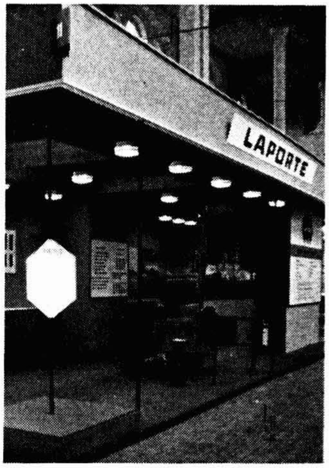
LAPORTE


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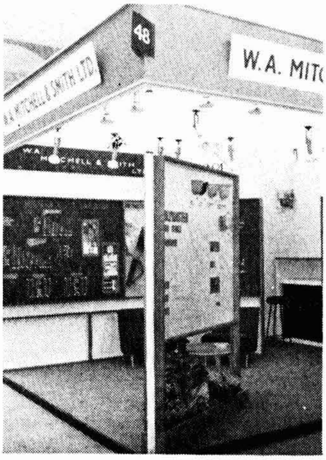
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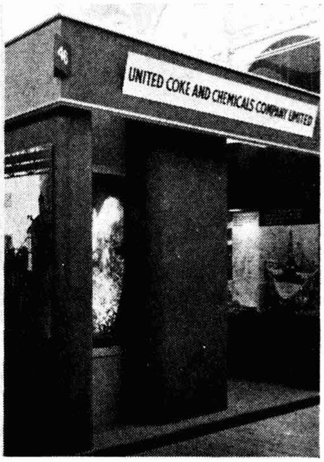
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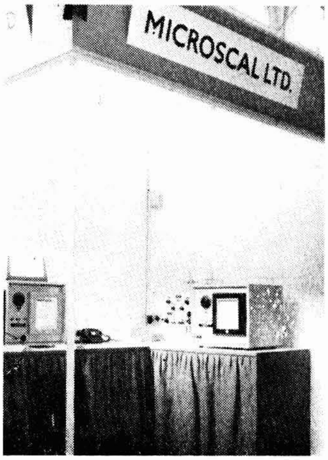
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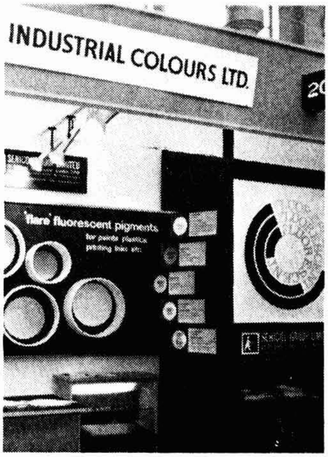

INDUSTRIAL COLOURS LTD.
'flare' fluorescent pigments
for paints plastics printing inks etc.


NORWEGIAN TALC (U.K.) LIMITED

polyisocyanate. SVENSKA OLJESLAGERI AKTIEBOLAGET introduced a new air drying urethane oil, *Soretan 364L*, based on safflower oil, having better colour retention than a linseed based product. It was recommended for boat and floor varnishes to give high abrasion and water resistance.

Resins—epoxy

CIBA (ARL) introduced *Araldite X83/341*, a new liquid hardener for solvent-free coatings and flooring compounds based on epoxy resins. It was particularly suitable for pale finishes and was effective at temperatures as low as 5°C, and 95 per cent relative humidity. This company also had information available on a new dry pigmentation technique for the manufacture of epoxy powder coatings. Colour matching was greatly simplified and well formulated dry pigmented powders showed excellent stability.

Special pitches suitable for epoxy/pitch compositions were displayed by LANCASHIRE TAR DISTILLERS and UNITED COKE & CHEMICALS.

New low temperature curing agents for epoxy finishes were introduced by the ANCHOR CHEMICAL CO. and SHELL CHEMICALS UK. Further information was available from CORNELIUS CHEMICAL CO. on the use of reactive polyamides, *Genamids 971* and *972*, and polyamide/epoxy adducts, *Versamids X-230* and *X-280*, in epoxy compositions.

Resins—thermosetting acrylic

FREDK. BOEHM introduced two new thermosetting acrylic resins of low odour, viz. *Albacrol VP 65/001*, suitable as sole medium for appliance enamels, and *Albacrol VP 65/002*, for use in combination with melamine resins in automotive finishes. PLASTANOL had information on a recently developed hydroxyl containing acrylic resin, *Acrysol 100*, designed for automotive finishes and curing at 120°C, but which could also be used for coating domestic appliances, chemical resistance being increased by stoving at 150°C. FARBENFABRIKEN BAYER had on display a range of coloured finishes based on *Baycryl L530*, a thermosetting acrylic which cures at relatively low temperatures.

Resins—alkyd (drying oil modified)

CRAY VALLEY PRODUCTS introduced a new thixotropic alkyd into their range, *Gelkyd 357W*, for producing fully gelled decorative gloss finishes. An interesting newcomer was a short oil linseed alkyd, *Synolac 49C*, supplied in trichlorethylene and designed for use in trichlorethylene thinned paints of air drying and stoving types. FARBENFABRIKEN BAYER introduced the newly developed *Alkydal S51* and *S64*, soya oil type alkyds for semi-gloss finishes having particularly good mar resistance.

J. H. LITTLE featured a new use for *Lioptal 541*, a phenolic modified short oil alkyd, in air drying primers. Particularly good adhesion and resistance to solvents were noted.

NEDERLANDSE CASTOR OLIEFABRIEK showed speciality alkyd resins, *Necoftal 4060X*, an air drying short oil alkyd, designed for fast air drying industrial finishes or for airless spray fillers, and *Necoftal LO 2655*, a medium oil alkyd, for automotive repair finishes. NORSK SPRAENGSTOFINDUSTRI introduced a new DCO alkyd, *Dynotal C-41X*, for use with amine resin in low temperature stoving enamels and *Dynotal T-73*, a tall oil alkyd designed for inexpensive decorative finishes. PLASTANOL had several new resins on show, including *Hytex 1* a long oil isophthalic alkyd developed specially for printing inks and having exceptional wetting properties, and a new range of acrylated alkyds, *Acrysol 1X* for fast drying low bake enamels, *Acrysol 2 AH* for roller coatings and *Acrysol 3X* for very fast drying finishes with good solvent release. A new urethane modified alkyd, *Hythane 1*, was also described (see also under Resins—polyurethane).

SCADO-ARCHER-DANIELS introduced *Scadonal 47-ML-70* a new medium oil soya alkyd with good resistance to yellowing at 80-100°C and suitable for white radiator paints. SURFACE COATING SYNTHETICS featured *Surkyd 131*, a long oil terephthalic alkyd specially developed for the printing ink industry. Also shown were a series of charts indicating viscosity/concentration relationships of various alkyds blended with *Surcovar 3884*. SVENSKA OLJESLAGERI AKTIEBOLAGET introduced a new safflower oil modified alkyd, *Soalkyd 3033*, having good colour retention and high build. FREDK. BOEHM exhibited a recently developed air drying alkyd of low linolenic acid content, *Pioneer AF 529*, particularly suitable for white and light tint radiator finishes.

Resins—alkyd (oil free)

KUNSTHARSFABRIEK SYNTHESE introduced a new series of oil free plasticising alkyds, details of *Setal 170 BX-67* and *Setal 171 BX-67* being available. These resins have been specially developed for coil coating applications in conjunction with hexamethoxy methyl melamine as cross-linking agent. Florida exposure trials showed that the exterior durability of these systems was superior to conventional alkyd/melamine compositions. NEDERLANDSE CASTOR OLIEFABRIEK also showed an oil free alkyd suitable for coil coating, *Necoftal OF 3570*. This was an isophthalic type and could be cured in one minute at 260°C to give very hard coatings of high impact resistance.

Resins—amino

BIP CHEMICALS featured their range of *Beetle* amino resins, emphasising the excellent compatibility of the liquid hexamethoxy methyl melamine *BE 670* with other media. FREDK. BOEHM showed their new highly reactive melamine resins, including *Pioneer RF3* and *Pioneer VP40/601*, the latter having extremely low odour. NORSK SPRAENGSTOFINDUSTRI introduced two new types of urea resins, *Dynomin UB-30* and *Dynomin UI-38*, specially developed for electrostatic spray application. Both resins may be used in either acid catalysed or stoving compositions. SVENSKA OLJESLAGERI AKTIEBOLAGET showed a new very fast curing isobutanol modified melamine resin, *Soamin M30*.

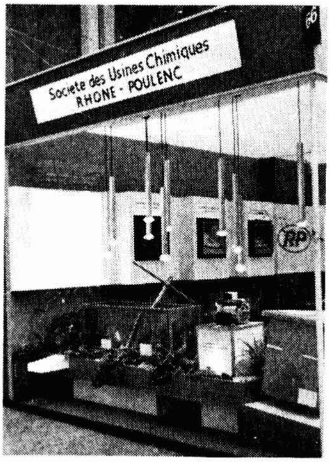
Resins—polyamide

ALLIED CHEMICAL CORPORATION showed their range of *Mykon* non-reactive polyamide resin for use in flexographic inks with information on alcohol solubility and moisture sensitivity. AMOCO featured a new single polymer system, *Amoco AI Polymer*, which could be cured to a poly (amide-imide), particularly suitable for wire coatings. BRITISH CELANESE had information on soluble polyamides for use in adhesives and surface coatings, and CORNELIUS CHEMICAL COMPANY exhibited their wide range of polyamides, featuring *Versamid 712A*, a new alcohol soluble type for printing inks. W. A. MITCHELL & SMITH introduced *Mitchanol 16*, a modified polyamide resin developed for printing on difficult surfaces. The newly developed *Polyamides No. 10* and *No. 11* were exhibited by VICTOR WOLF. These materials are readily soluble in ethyl and propyl alcohols and are designed for flexographic inks.

Resins—unsaturated polyester

BASF UNITED KINGDOM introduced *Ludopal LR 8214*, a new highly reactive polyester with a very short curing time suitable for production-line coatings on furniture. New polyester resins were also shown by W. A. MITCHELL & SMITH. These included *Polymaster resins 1537* and *1592*, both amine modified polyesters combining good can stability with fast cure, and *Polymaster resins 9000*, *9100* and *9200*, combinations of which could be used to produce taint-free coatings in contact with, for example, wines or dairy produce.


FREDK. BOEHM LTD
FREDK. BOEHM LIMITED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CADOSET
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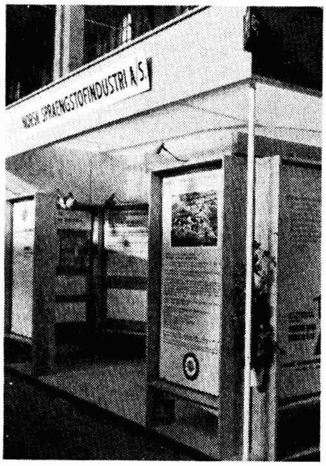
ACRYLIC RESIN FOR
INDUSTRIAL ENAMELS
SCADO-ARCHER-DANIELS N.V.
RESINS FOR ROLLERCOATING
PIGMENT WETTING PROPERTIES


NORSK SPRAENGSTOFINDUSTRI A/S.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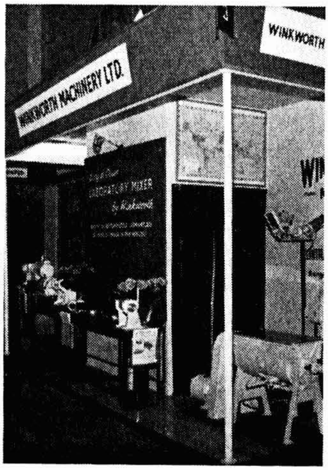
WINKWORTH
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LABORATORY MIXER
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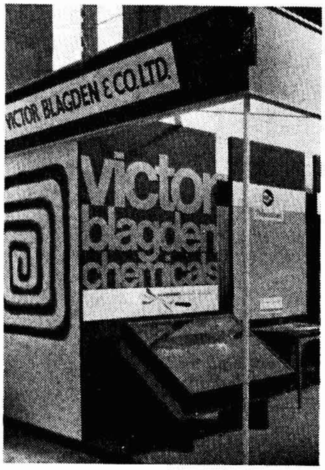

VICTOR BLAGDEN & CO. LTD.
victor
blagden
chemicals

Resins—miscellaneous

ALLIED CHEMICAL CORPORATION had information on a range of low molecular weight polyethylenes and polyethylene copolymers, and illustrated the improvement in mar resistance of paints that could be obtained with small additions of these materials. BRITISH CELANESE showed their petroleum resin *PR 107/35* in solid, solution and three emulsion forms. Information on the use of this resin in emulsion form as an extender for synthetic polymer latices was available. A new grade of polyvinyl butyral resin, *BWT 1884*, having extra polar groups to improve adhesion to metal, was shown by BUSH BEACH & SEGNER BAYLEY. Two styrene-maleic anhydride copolymers were exhibited by CORNELIUS CHEMICAL COMPANY, *SMA 3000 AS*, useful as a stabiliser for acid stable emulsions and *SMA 1440 H*, a surfactant for pigment dispersion.

FARBWERKE HOECHST gave prominence to *Hostaflex PP66*, a chlorinated polypropylene resin, and demonstrated its use in underwater paints and for road marking compositions. A range of coloured panels also illustrated the use of a carbamate resin, *Uresin B*. HERCULES POWDER COMPANY introduced a new range of modified terpene resins, *Terpalyns*, with information on their uses in adhesives and surface coatings. IMPERIAL CHEMICAL INDUSTRIES illustrated the development of high build coatings with *Alloprene* chlorinated rubber. POLYVINYL CHEMIE HOLLAND showed applications of their *Neocryl* range of acrylic bead polymers. *Neocryl B731*, for example, could be blended with alkyd type media for decorative and industrial paints to improve air drying properties and recoatability time. SCADO-ARCHER-DANIELS featured a new two component curing system, *Aroflint 1010*. This consisted of an alkyd resin with reactive carboxyl groups and a fatty acid ester with free epoxy groups. Air drying and stoving compositions based on this mixture had particularly high build and excellent adhesion to a wide variety of substrates (e.g. reinforced polyester resins). SOCIETE DES USINES CHIMIQUES RHONE-POULENC illustrated the use of their vinyl resins on a model ship, showing a full system consisting of a wash primer based on *Rhovinal B*, a polyvinyl butyral resin, followed by a second coat based on *Rhodopas AXRH*, a pvc/pva copolymer and an anti-fouling paint based on *Rhodopas AX 85/15*. Also featured was *Rhovinal F*, a polyvinyl formal resin, suitable for use in wire enamels.

Chemicals

AMOCO CHEMICALS has further information available on the uses of isophthalic acid, noting particularly *IPA 95* (95/5 isophthalic/terephthalic acids) and *IPA 75* (70/30 isophthalic/terephthalic acids) in formulations for polyesters and alkyds, including the oil free type. Dimethyl terephthalate (*DMT*), purified terephthalic acid (*TA-33*) and a technical grade of terephthalic acid (*TA-12*) were also featured. IMPERIAL CHEMICAL INDUSTRIES indicated that a new fine powder grade of pentaerythritol was now available, suitable for incorporation by stirring into intumescent paints to provide a source of heat released carbon dioxide. A new low cost polyol derivative, *CML 3* liquor was also available as a raw material for alkyds, waxes and polyesters. LAPORTE INDUSTRIES had data sheets available on a wide range of glycidyl ethers, including brominated types for the preparation of flame-retardant resins. A chart indicated the use of *Howflex CP*, dicyclohexyl phthalate, in thermoplastic acrylic finishes to increase solids content and improve gloss. REX CAMPBELL & COMPANY displayed their range of plasticisers and solvents and information was available on latest developments.

Solvents

CARLESS CAPEL & LEONARD showed their established range of solvents, with the addition of *Aliphatic Solvent 15/40*, and *Naptha 14/80*, both intended primarily for the fabric proofing industry. IMPERIAL CHEMICAL INDUSTRIES featured the use of isobutanol in a display of technical information concerned with flash points of solvent mixtures, together with general technical data on the use of isobutanol in surface coatings. The use of trichlorethylene was again featured, with particular reference to rapid flash-off.

LANCASHIRE TAR DISTILLERS featured their well known *Puresol* range of light hydrocarbon solvents. Solvent recovery facilities are available. SHELL CHEMICALS UK showed the use of organic solvent additions in electrodeposition, to improve stability, flow, and ease of make up. Also on show were their well known range of *Shellsol* and *Oxitol* solvents. UNITED COKE & CHEMICALS showed their range of high purity aromatic solvents.

Additives, driers, fungicides, surfactants etc.

BERK showed their *Bentone*, *Strodex* organic phosphate wetting agents, and *Phelam* fungicides. BRITISH CELANESE showed the results of work on the water retention of *Celacol* and *Courlose* cellulose ether. An interesting suggestion was the use of acrylic fibres for texturing and reinforcing surface coatings and plasters, where their good physical and chemical resistance would be advantageous. BUSH BEACH & SEGNER BAYLEY exhibited the new *AM Wax* from BASF, and *A Wax*, for anti-rub and scuff properties in inks, and for use in matting acid catalysed lacquers.

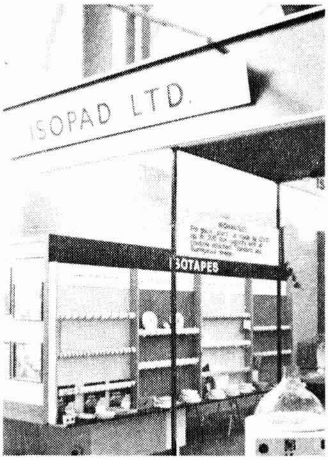
BYK GULDEN LOMBERG showed a number of new products. *Bykanol* is an anti-gelling agent for paints. *Bubble Breaker* is a silicone-free anti-foaming agent for latex paints. *Disperbyk* is an anionic surface agent for use in emulsion paint as a wetting and dispersing agent for inorganic and organic pigments. It may also be used in solvent based paints. *Lactimon*, an anti-floating agent, is an acid salt of a high molecular unsaturated organic acid with a fatty amine, combined with a compatible silicone, and is effective in preventing Bénard cell formation in many systems, and as a wetting and dispersing agent. In addition, technical information about the well-known *Anti-Terra U*, *Byk P104* and *P104S*, and *Byketol* agents was displayed.

CROXTON & GARRY showed a range of wetting and dispersing agents from Lucas Meyer, *Colorol F* for alkyd systems, *Colorol 20* for nitrocellulose, *Colorol E* for water based paints and *Colorol 30* for polyester resin systems. Also displayed was *Syloid ZH1*, a molecular sieve material recommended for addition to zinc rich primers to adsorb water and prevent gas build up.

DANIEL PRODUCTS COMPANY, a newcomer to the Exhibition, showed a number of new products designed for specific purposes. A series of opacity boosters consist of combinations of light fast pigments designed to increase the effective hiding power and mask the yellowing of white enamels. *Tint-Ayd UL.20.14* is for use with non-yellowing whites, and panels illustrated a considerable improvement compared with lampblack. It is compatible with almost all solvent and water-based paints. *Tint-Ayd 233*, a combination of mineral violet and ultramarine, and *Tint-Ayds 233A, B, and C*, combinations of quinacridone magenta and indanthrone blue, were suitable for decorative and stoving finishes. *Visc-Ayd 812* is a two-pack bodying agent which can be incorporated into the millbase or added to the finished paint, and is claimed to maintain the viscosity increase on storage. *Disperse-Ayd 7*, a deflocculant, is particularly recommened for fine particle carbon blacks in vinyl toluene and acrylic systems. *Slip-Ayd SL50* and *SL78* consist of low molecular polyethylene dispersions for improving the surface properties of coatings.

DURHAM RAW MATERIALS featured *Nuosperse 657*, a film forming dispersing agent for non-aqueous media, suitable for use in dispersing titanium dioxide and other pigments in a range of media, including plasticisers. The *Nuosyn* range of driers based on synthetic acids were displayed, with technical information on their stability in mixtures at high dilution. GRACE GMBH showed *Daxad 30*, a low foaming dispersing agent for water based systems, giving improved flow, levelling and holdout in high pvc emulsion paints. The *Syloid* range of fine particle porous silicas were used as flatting and anti-blocking agents ; some grades were surface treated for special applications. HERCULES POWDER COMPANY presented a technical display of work on the use


MOLTENI-MILAN
AGENTS G.J. SKLICH LTD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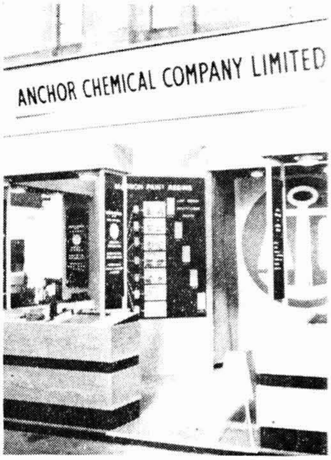
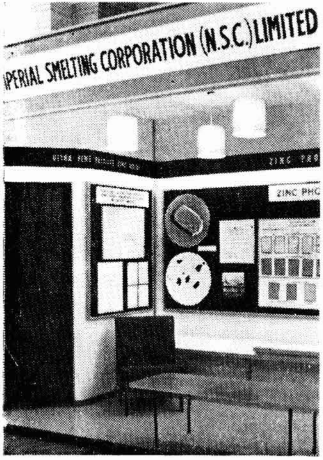
ISOTAPES


ANCHOR CHEMICAL COMPANY LIMITED


AKTIEBOLAGET SWEDEN
SOAB


FARBENFABRIKEN BAYER
BAYER


DURHAM RAW MATERIALS LIMITED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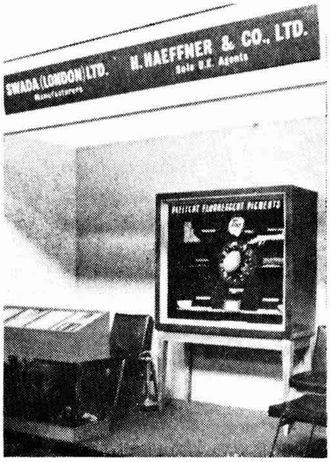
ZINC PHO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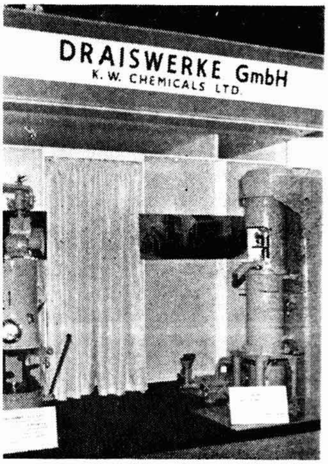
Manufacturers
H. HAEFFNER & CO., LTD.
Sole U.K. Agents


DRAISWERKE GmbH
K. W. CHEMICALS LTD.

of *Natrosol* hydroxyethyl cellulose in PVA emulsion systems, in which the effects of surfactant and protective colloid were studied. KINGSLEY & KEITH showed the Olin Chemicals *Omadine* anti-bacterial and anti-fungal agents.

J. H. LITTLE showed the Henkel International range of additives. *Product 963*, consisting of a neutral salt of a polycarboxylic acid with amine derivatives, has a wide range of activity against flooding, floating and settlement, and is claimed to be an effective anti-settling agent for metallic pigments. *Dehydrophen CF*, an alkyl aryl polyglycol ether, may be used as a non-foaming wetting agent for emulsion paints. Technical information was available about a number of other well-known products including the range of *Airdrin* driers. NOVADEL displayed the range of *Siccatol* dryers, based on synthetic acids, including *Barium Siccatol*, *Noury Drier 10*, and *Noury Drier 775*, based on zirconium siccatol.

REX CAMPBELL displayed *Copper Butyl Phthalate* and *Copper Octoate*, used as pigment dispersion aids especially suitable for use with difficult pigments such as carbon black and prussian blues in high shear conditions, e.g. in the production of colour chips in nitrocellulose. Thixotropic additives from Baker Castor Oil Co. include *Thixin R* and *Thixatrol ST* for controlling sagging and improving flow. The latter is especially suitable for use in zinc rich primers. *MPA*, another thixotropic additive, gives only a small viscosity increase. *POST 4* is a new liquid stir-in post additive for sag correction of finished paints. TITANIUM INTERMEDIATES exhibited information on the use of triethanolamine titanate in the formulation of thixotropic dispersion paints, and the use of organic titanates as catalysts in a variety of reactions. VICTOR WOLF showed a range of slip and anti-blocking agents, and *Vinco* stabilisers for PVC plastisols and organosols.

Laboratory apparatus and instruments

APPLIED RESEARCH LABORATORIES, a new exhibitor, demonstrated the most recent Bausch and Lomb spectrophotometers, including the new *Precision Spectrophotometer*. Also on show was the *Spectronic 600E*, a less expensive recording spectrophotometer with special reflection spheres capable of measurement of glossy or matt surfaces. WILLIAM BOULTON exhibited a new air driven laboratory high speed dissolver, with many obvious applications in paint laboratories. COULTER ELECTRONICS exhibited the *Coulter Counter Model B* with the *Volume Converter Model M*, which gives directly cumulative or differential volume or weight distributions. Also available was information about the *Numinco Orr* surface area/pore volume analyser, the mercury penetration porosimeter, and an air displacement porosimeter.

ELCOMETER INSTRUMENTS displayed a comprehensive range of paint and surface coating testing instruments, including the well-known *Erichsen* equipment. Of interest was a working model of the cup deep drawing testing machine, capable of extending to 8 mm at an operating pressure of 6 tons. A new thickness testing instrument was the *Inspector* thickness gauge, a single legged instrument for use with coatings on ferrous substrates. FERRANTI showed the well-known *Ferranti-Shirley* cone and plate viscometer, with emphasis on the additional equipment which is available. The automatic flow curve recorder enables a rapid standardised test procedure to be used with non-Newtonian materials, and the automatic cone and plate setting unit was shown. Also displayed was the *Ferranti Portable Viscometer*.

GUNTER STIERAND KG, a newcomer to the Exhibition, showed a very full range of testing equipment for surface coatings, including two new items; the *Stierand Paint Inspection Gauge*, to determine the thickness and number of coats of paint films and plastic coatings ; with its full range of cutting tips the instrument is capable of readings down to two microns. The *Stierand Flexibility Tester* is a new instrument for testing the elasticity of wood finishes, and is a type of reverse indentation tester, the elasticity of the film being measured by the number of concentric rings shown by the lacquer film after indentation. ISOPAD showed a laboratory scale combined mantle heater and control unit. LIVINGSTON ELECTRONICS showed the recent developments in the *Color-Eye*, including the use of a large integrating sphere, designed primarily for textile measurement. Analogue computers for the conversion of colorimeter difference readings into NBS units of colour difference were again featured. RUDOLPH MEYER'S INCORPORATED showed again the *Tack-O-Scope* tack measuring instrument and the *IGT Printability Tester* in their latest forms.

MICROSCAL, a new exhibitor, had in operation two models of the *Microscal Flow Microcalorimeter*. This instrument is capable of detecting physical and chemical interactions at the solid/liquid interface, the sensitivity being of the order of a few microcalories ; the more sensitive instrument fitted with a DC amplifier has a sensitivity of 2 microcalories. Using this technique, the interactions of solutions of paint media and other materials with pigments were demonstrated, illustrating displacement and replacement effects. THE PYRENE COMPANY showed the range of standardised test panels available, in steel, zinc and aluminium ; panels with phosphate and chromate pretreatment are available, and also buffed steel panels. RESEARCH EQUIPMENT (LONDON) exhibited their comprehensive range of test equipment. The production model of the *ICI Cone and Plate Viscometer* was on show. This stabilises the sample at 25°C in 15 seconds, so that extremely rapid operation is possible on a routine basis. The *ICI Pneumatic Micro Indentation* apparatus was again on show ; this operates over a range of between −20°C and 90°C, and its sensitivity is such that an indentation of 6 microns gives a 5 in deflection on the recorder chart.

SANGAMO CONTROLS showed an improved version of the *Weissenberg Rheogoniometer*, which is capable of studying a variety of rheological properties of a wide range of materials. SHEEN INSTRUMENTS (SALES) showed a wide range of paint testing equipment. The *ICI Rotothinner* is now available for measuring viscosities up to 340 poise, and a new version was produced for testing gel strength of non-drip emulsion paints. The portable *PJA Glossbox* can be used on site at any angle. An automatic recorder was now available for the Rocker Hardness and Pendulum Hardness instruments. A 20° ASTM glossmeter has been developed. The *ICI Automatic Film Applicator* was also on show. TORRANCE & SONS exhibited the new 3½ in laboratory *Microflow Mill Mark III* especially suitable for the production of gravure and flexographic inks. WINKWORTH MACHINERY showed the latest version of the laboratory size *Z-blade mixer Model 22*, with interchangeable Z blades and ribbon blender. This has been redesigned for ease of dismantling and cleaning.

Manufacturing equipment

AMF INTERNATIONAL, exhibiting for the first time, showed a range of *Micro-Klean* filter cartridges. Two types were suitable for the paint industry, one being a wound element not susceptible to solvent attack, and the second a heavy duty resin bonded filter element with greater efficiency over long periods of use. WILLIAM BOULTON showed for the first time the *Podmore Boulton Vibro Energy Continuous Automatic Grinder*, in which vibro energy is applied to an attritor type mill. Also on show was the range of vibro energy mills and paint and ink strainers, and high speed dissolvers. BERK showed the *Afco Snap-Ring* calibrated filter bags.

DH INDUSTRIES showed a range of manufacturing equipment. The *Pamasol Micromat* automatic rotary aerosol pack filler from Willi Mader, Switzerland, was on show. Mixers from Peter Küpper AMK, West Germany, and a sealed pressurised sand mill from Ateliers Sussmeyer, Belgium, were exhibited. DRAISWERKE had on show the *Perl Mill*, with recent modifications made since it was shown at last year's Exhibition. The mill may now be used with high viscosity, high solids millbases, and cooling devices can be fitted to the upper portion as well as to the body of the mill. Models for vacuum operation are available. The *Drais Torrmat* disperser was on show. EUTOPLAST COAT-

INGS, a new exhibitor, offered versatile equipment for flame application of plastics and other coating materials.

HIBBERD, ROCKALL & CRAIG, at the Exhibition for the first time, showed a wide range of spray application equipment, including equipment for airless spray, and other application equipment, from the Iwata Air Compressor Mfg. Co., Japan. Their associate, RUDOLF NEULINGER, showed an extensive range of dispersion equipment, including the *Sferomat* bead mill, with discs placed eccentrically on the shaft, and a contraflow cooling system. A standard high speed dissolver, with a variable speed range from 400-2,200 rpm was on show. ISOPAD placed emphasis on equipment for use in areas defined by the 1966 Code of Practice for flameproof equipment. *Isotapes Type ITB2F* and *ITW2F*, surface heating equipment, and controls for use in these areas were shown, together with their wide range of heating tapes and panels.

MARCHANT BROTHERS exhibited a new inclined 2-speed 6 in × 16 in triple roll mill, with low level loading and built in safety features to eliminate damager due to overloading. A large *Model 913 NVH* triple roll mill from VEB Maschinenfabrik Heidenau, fitted with a pan lift, was on show. Other mills were on show, with some minor modifications. MASTERMIX ENGINEERING COMPANY showed the *V.E.H. Disperser*, a variable speed range high speed disperser with a self-contained hydraulic system. The *Mastermix P.M.D.* was claimed to require considerably less power than other machines of similar throughput, with no increase in dispersion times. A range of portable mixers was on show.

DR. MEAZZI, a new exhibitor, showed a new *Vibrofiltro*, a vibrating filter for paints, varnishes and lacquers. Easily replaceable sieves of bronze, stainless steel, silk or nylon are available. Also on show was a self-priming diaphragm pump. MILLROOM ACCESSORIES & CHEMICALS showed the *Rotamix*, a turbo mixer available in a wide range of sizes, the twin headed *Biotomix*, and various other mixing equipment. A new item is an adjustable hydraulic support stand. MOLTENI OFF. MECC. exhibited a range of up to date dispersing equipment, including the *Montani* heavy duty planetary mixers, for use under vacuum where dehydration and deaeration were required, also a mixer for extremely viscous materials operating at up to 2,400 rpm. The range of *Microsfera* continuous grinders was shown, together with other mixing equipment. pumps and vibratory sieves.

NOVADEL had on display a variable rate powder feeder, the *Vari-feeder*. PREMIER COLLOID MILLS showed a range of mixing equipment covering the complete range of viscosities. SILVERSON MACHINES showed their complete range of mixers, mills and emulsifiers, including a complete set-up of three units in line to convert raw materials into finished products on a one-run basis. The *Abramix*, for highly abrasive materials, was also shown. STEELE & COWLISHAW showed a scale model of the *Pinto Agitomic Emulsifier*, and the range of newly designed universal horizontal twin-blade mixers, together with other items from their extensive range of mixing and dispersion equipment

TORRANCE & SONS exhibited the new *Microflow* mills, which are especially suited to the production of gravure and flexographic inks. Throughputs of the 15 in model ranged from 140 lb/hr for benzidine yellow and fanal blue to 650 lb/hr for white pigments. A final effective maximum particle size in the range of 2-3 microns is claimed. The *Mark V Cavitation Disperser* was on show, having variable speeds up to 2,600 rpm at constant torque. Other equipment on show included triple roll mills and the *Attritor* disperser. WINKWORTH MACHINERY showed their ribbon blade *Contra Flow Mixers*, available in a range of sizes, together with Z-blade and other mixing equipment.

Acknowledgements

The Honorary Editor is indebted to the following members of the Association who gave so much of their time to assist in the reporting of the Exhibition : N. Ashworth, M. J. Atkins, R. McD. Barrett, J. C. Bearman, L. J. Brookes, J. K. E. Burke, T. R.

Bullett, W. Clark, J. S. Cox, P. C. Daley, S. Duckworth, H. Foster, K. B. Gilkes, J. R. Green, H. R. Hamburg, R. F. Hill, S. Hodgson, G. L. Holbrow, A. G. Holt and colleagues, V. F. Jenkins, J. R. Kitchen, C. H. Morris, W. F. McDonnell, D. S. Newton, L. A. O'Neill, J. Pooley, T. I. Price, E. F. Redknap, F. E. Ruddick, J. F. J. Rule, P. Sharp, D. G. Soar, L. Tasker, W. G. Topham, J. R. Taylor, R. N. Wheeler and L. W. Wynn.

The Honorary Editor particularly wishes to thank Mr. R. A. Brett and Dr. V. T. Crowl (Honorary Publications Officer of London Section), who have organised the reporting, collated the reports and comments received, and written the final report.

OCCA Conference, Scarborough

20-24 June, 1967

Interfacial Behaviour

Although the date for registration for the biennial technical Conference was given as 1 April, this was at the request of the hotel managements, who naturally wished to allocate rooms for this period in June as early as possible. However, arrangements have been made for accommodation for late applicants, as it is appreciated that in present circumstances many members and visitors may not have been able to plan a visit nearly three months in advance. Anyone wishing to attend this important technical Conference should, therefore, send in an application form as soon as possible to the General Secretary at the address shown on the Conference brochure. If further copies of the brochure are required, these can be obtained from the address on the front cover of the *Journal*.

There will be four main technical sessions at which 11 papers will be presented. Reprints of the summaries published in the November 1966 issue of this *Journal* are available on application ; biographies of the lecturers appeared in the October issue. In addition to the technical sessions there will be three workshop sessions, but all the available places at these sessions have now been filled.

The Conference registration fees are £8 for members, £12 for non-members, £5 for wives and £4 for junior members.

Social events will include a civic reception and the Association's dinner-dance, as well as coach tours, theatre party and a sea trip.

Bristol Section

Taken at the Bristol Section Dinner-Dance, the photograph shows (left to right) Mr. N. Cochrane (Chairman, West Riding), Mrs. Cochrane, Mr. R. J. Woodbridge (Chairman, Bristol), Mrs. Woodbridge, Dr. S. H. Bell (President), Mrs. J. H. A. Quick, Mr. J. H. A. Quick (Chairman, Irish), Mrs. C. H. Morris, Mr. C. H. Morris (Chairman, Midlands)

Annual Dinner-Dance

The Annual Dinner-Dance of the Bristol Section was held on Friday 20 January 1967 in the Mayfair Suite of the new Entertainments Centre, Bristol, when the Chairman, Mr. R. J. Woodbridge, and Mrs. Woodbridge welcomed some 150 guests and members, in particular the guest of honour, Dr. S. H. Bell, President of the Association.

Other guests present were the Chairman of the West Riding Section, Mr. N. Cochrane, and Mrs. Cochrane; the Chairman of the Midlands Section, Mr. C. H. Morris, and Mrs. Morris; the Chairman of the Newcastle Section, Mr. E. L. Farrow, and Mrs. Farrow, and the Chairman of the Irish Section, Mr. G. H. A. Quick, and Mrs. Quick.

The delightful and pleasing decor of the new venue in no small way contributed to the warm and friendly atmosphere which was again most evident and characteristic of the Section's functions.

After dinner, Mr. Woodbridge introduced Dr. Bell, who, in his usual warm and friendly manner, expressed his pleasure at being present. Mr. Quick wittily and briefly responded on behalf of the guests.

The evening continued with dancing until 1 a.m., when the South Wales contingent reluctantly left to motor their way home over the new Severn Bridge in traditional Welsh weather conditions.

Irish Section

Social evening

On Saturday 25 February 1967 the Irish Section became known to the television viewing public in the Republic of Ireland when 19 members visited the studios of Radio Telefis Eireann at Montrose.

Our worthy Honorary Treasurer, John Kershaw, became a TV personality when he was called from the audience to take part in the quiz show " Quicksilver." He was well on the way to leaving the studio with a handsome cheque in his pocket when unfortunately the " Sound of Music " beat him.

Following the show the party was shown round the studios by Chris Darby, a director on the news section and presentation officer. Our thanks are also due to him for obtaining the tickets for us.

To conclude what was a most enjoyable evening we retired to the Montrose Hotel, where our friend John had to put up with a certain amount of good natured ribbing.

Thames Valley Section

Meeting of Council

At the meeting of Council held on 6 April a petition was received from the Thames Valley Branch of the London Section requesting that Section status should be accorded to the Branch, which was founded in 1963 and which had successfully organised three sessions of technical meetings.

The petition had been duly endorsed by London Section Committee and Council was pleased to accede to the request so that with effect from the Annual General Meeting of the Thames Valley Branch on 12 April the Branch achieved the status of a Section of the Association.

The Chairman of the Branch, Mr. A. G. Holt, will, therefore, become a member of Council and the Section will, in due course, appoint a further representative on Council, in the usual way.

Members attached to the Thames Valley Branch will, in the summer months, be sent a notice asking if they wish to transfer from the London Section to the Thames Valley Section, and rules for the new Section will be adopted at a General Meeting of the Section early in the next session.

The formation of the Thames Valley Section means that there are now ten full Sections in the UK and Ireland, with three Branches of Sections. The congratulations of Council are extended to the new Section with best wishes for its future success.

New Zealand Section

Annual Convention

The fifth Annual Convention of the New Zealand Sections is to be held at Wairakei from 11-13 August 1967. Anyone interested should contact the Honorary Secretary, Mr. G. D. Leathley, 27 Konini Road, Titirangi, Auckland, New Zealand.

The London College of Printing is to hold a course in Statistical Quality Control from 5-9 June 1967. The course offers to those involved in quality control or production management in the printing and allied industries an opportunity to study the principles and applications of statistical quality control.

The Borough Polytechnic is to hold a two-day course on the Fundamentals of Surface Coating Technology on 28-29 June 1967. This is intended to provide a general background knowledge for technical and sales representatives, and will also be suitable for scientifically qualified entrants to the industry.

Economic and commercial factors will be considered as well as the principles of paint formulation, raw materials, film formation, application, and consumer problems.

The American Association of Cereal Chemists and the American Oil Chemists' Society have announced that a Joint Annual Meeting will be held in Washington D.C. from 31 March-4 April 1968, with headquarters in the Washington-Hilton Hotel.

An estimated 2,000 registrants from industries operating in the cereal, oilseed, pulse, fat, oil, lipid and emulsifier fields will hear about 250 technical papers and view more than 125 exhibits, and a technical and industrial exposition.

The Plastics and Polymer Group of the Society of Chemical Industry are planning a technical visit to the research establishment in Israel in the early spring of 1968, provisionally 21 April to 5 or 6 May. The visit is intended to take in the Weizmann Research Institute, the University of Jerusalem, the Haifa Technion and some other items of more general interest. An alternative programme will be available for ladies.

Anyone interested should contact: H. Warson, B.SC., PH.D., F.R.I.C., 284 Warwick Road, Solihull, Warwickshire.

A series of one-day seminars entitled The Physical Chemistry of Surface Coatings is to be held by the Borough Polytechnic. The first, Macromolecules in Solution, was on 27 April, and others are to follow in the near future.

Hilditch Memorial Lecture

Professor T. P. Hilditch, C.B.E., F.R.S., the first holder of the Campbell Brown Chair of Industrial Chemistry in the University of Liverpool, and an Honorary Member of the Association, died on 9 August 1965 after an eminent career in the field of oils and fats.

In September 1966 an appeal was launched to establish a memorial lecture as a tribute, to which the Association contributed. The first Hilditch Memorial Lecture has now been arranged for 18 July, having the title " Oils and Fats in the 70's." The lecture will be delivered by Dr. J. G. Collingwood, Director of Unilever Limited.

News of Members

Mr. C. Williams, an Ordinary Member attached to the Manchester Section, has been appointed Commercial Manager of Styrene Co-Polymers Ltd.

Mr. Williams was previously responsible for the Northern Sales of Cray Valley Products Ltd., and is an active Committee member of the Manchester Section, holding the office of Programmes Officer.

Mr. J. H. Grimshaw, an Associate Member attached to the London Section, and Managing Director of Horace Cory & Co. Ltd., has been appointed Chairman of the Company. Mr. Grimshaw was a founder member of the Manchester Section, and is a past member of Council.

Mr. M. R. Wilson, an Ordinary Member attached to the London Section, and formerly production manager at Pfizer's Bromley fine-chemicals plant, has been appointed works manager of the Pfizer Chemical Division at Stalybridge, near Manchester.

Mr. W. D. Aspinwall, an Ordinary Member of the Irish Section, has taken up the post of General Manager in the overseas organisation of the Coates Group of Companies, relinquishing his position as General Manager of the Glenside Printing Ink Co.

Mr. A. Nutton, an Ordinary Member attached to the London Section, retires as Managing Director of Novadel Limited as from 31 March 1967.

Mr. Nutton has served with Novadel for 30 years, first joining as Technical Sales Manager. He will remain a Director of the Company after retirement.

Mr. P. J. Gay, an Ordinary Member attached to the Hull Section, and Past President of the Association, has been appointed Technical Sales Executive of the Storry Smithson Group.

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

AIREY, DAVID LAWRENCE, J. Bibby & Sons Ltd., King Edward Street, Liverpool 3. (*Manchester*)

ALSTON, ERIC, B.SC., 2 Annie Street, Ramsbottom, Via Bury, Lancs. (*Manchester*)

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Forthcoming Events

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

Thursday 18 May

New South Wales Section. " A Review of Polymer Latex Dispersions for Paint," by Mr. P. T. Willmott, Polymer Corp. Pty. Ltd.

Thursday 15 June

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

Tuesday 20 to Saturday 24 June

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

Oil and Colour Chemists' Association

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

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

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

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

PUBLICATIONS

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

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

Paint Technology Manuals

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

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

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

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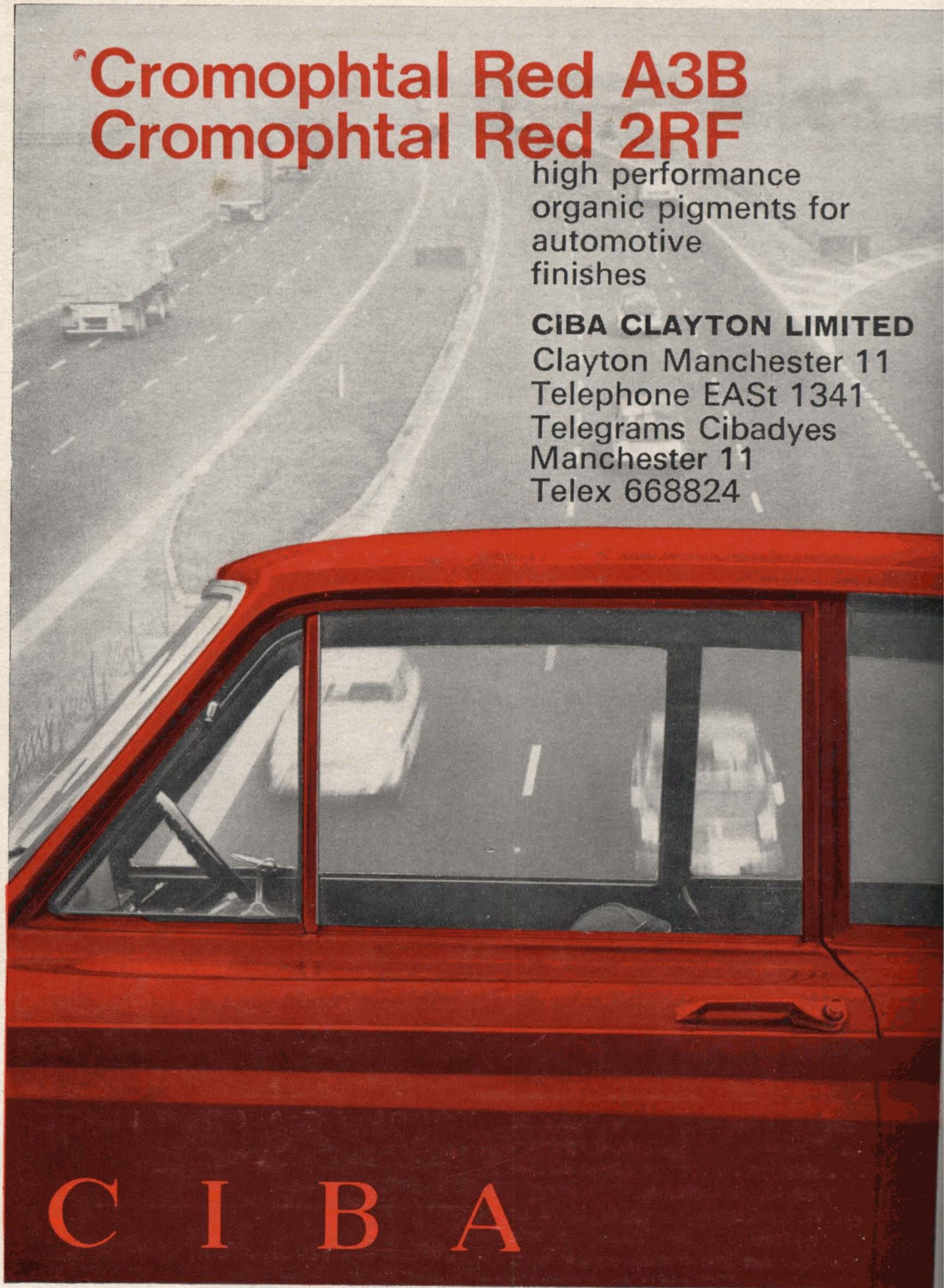

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