

JOURNAL OF THE OIL AND COLOUR CHEMISTS' ASSOCIATION



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Colloidal aspects of printing inks

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A chromatographic study of an etching primer

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Cobalt 2-ethylhexanoate systems as accelerators for two pack polyurethanes and their effects on storage stability

R. J. Goodman and J. A. Douek

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--See Editorial

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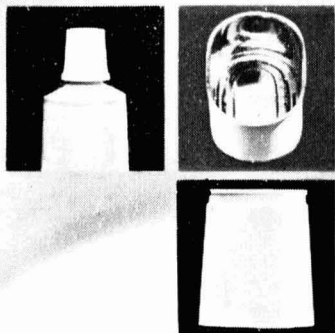
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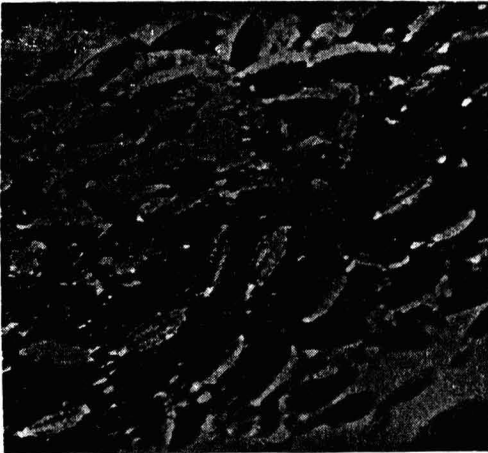
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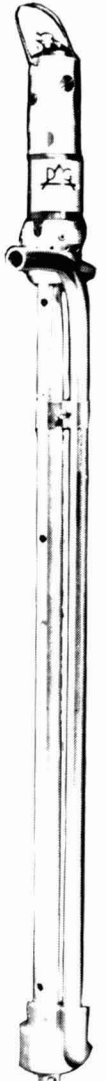
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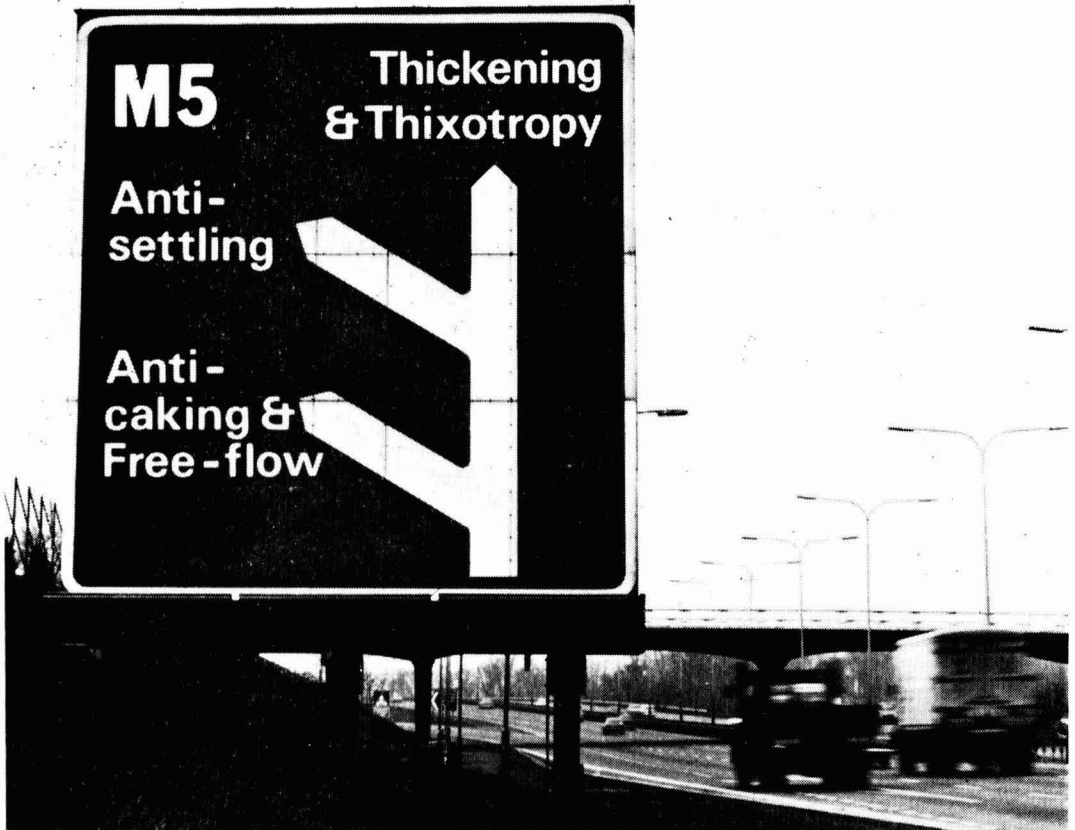
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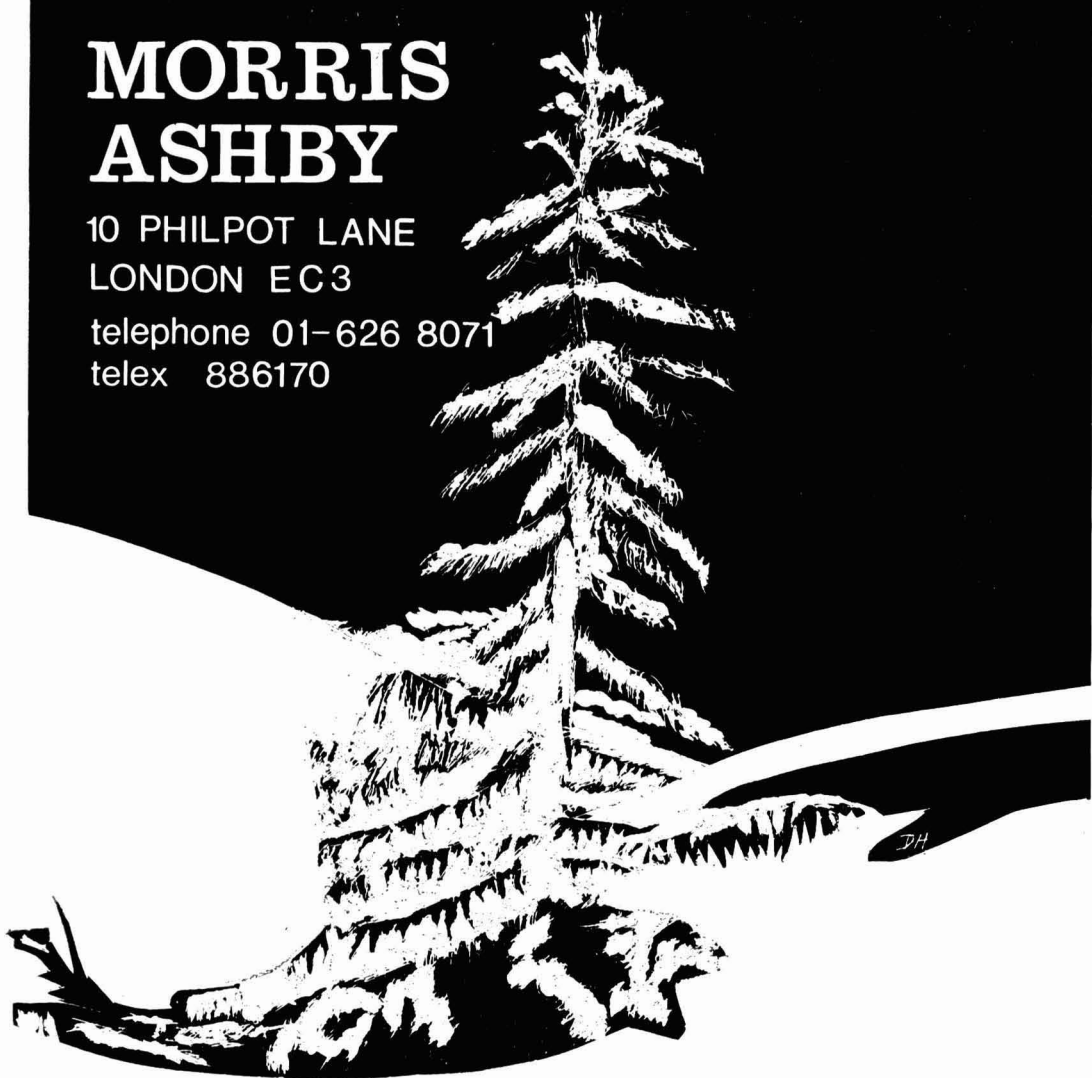
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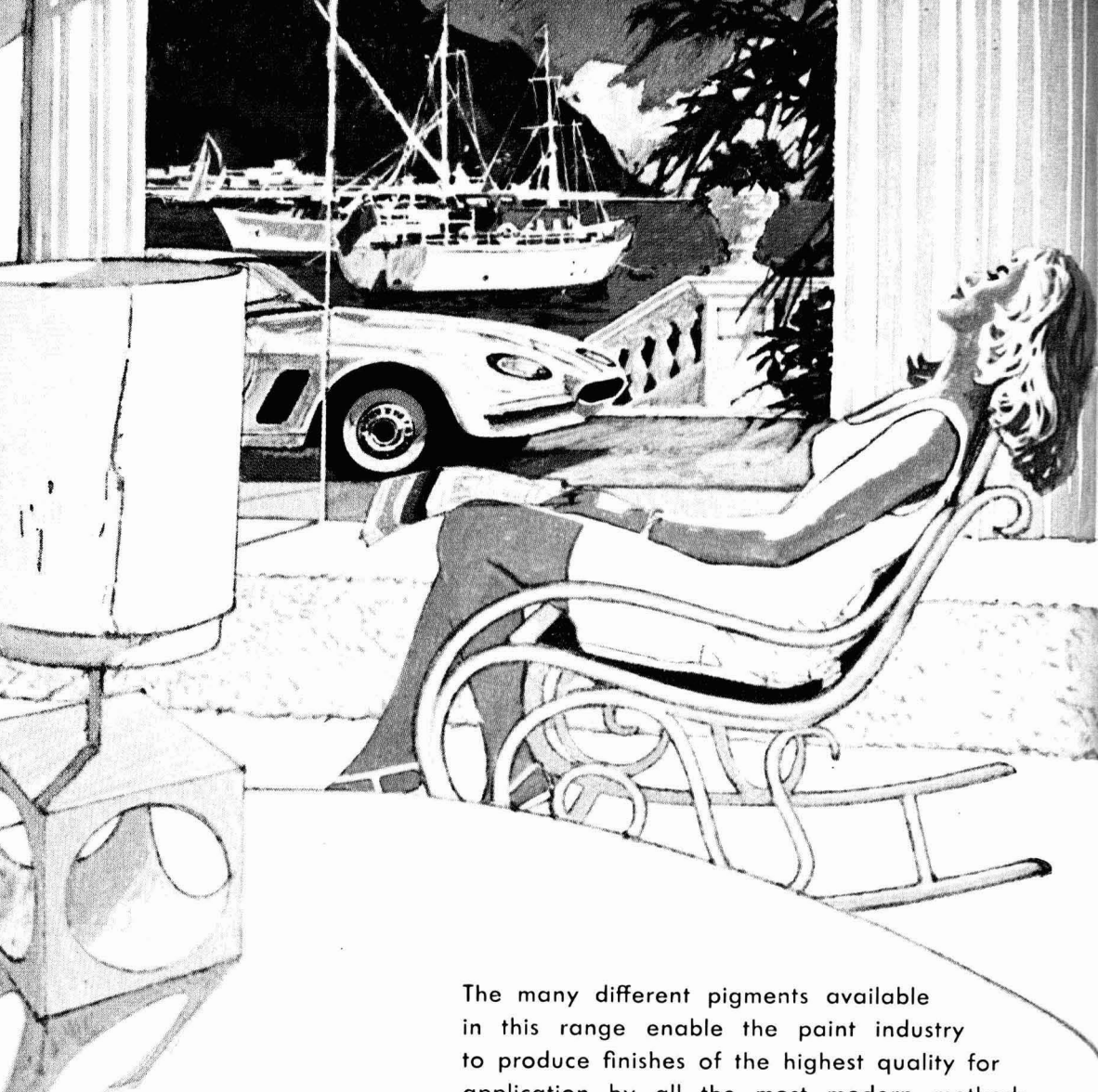
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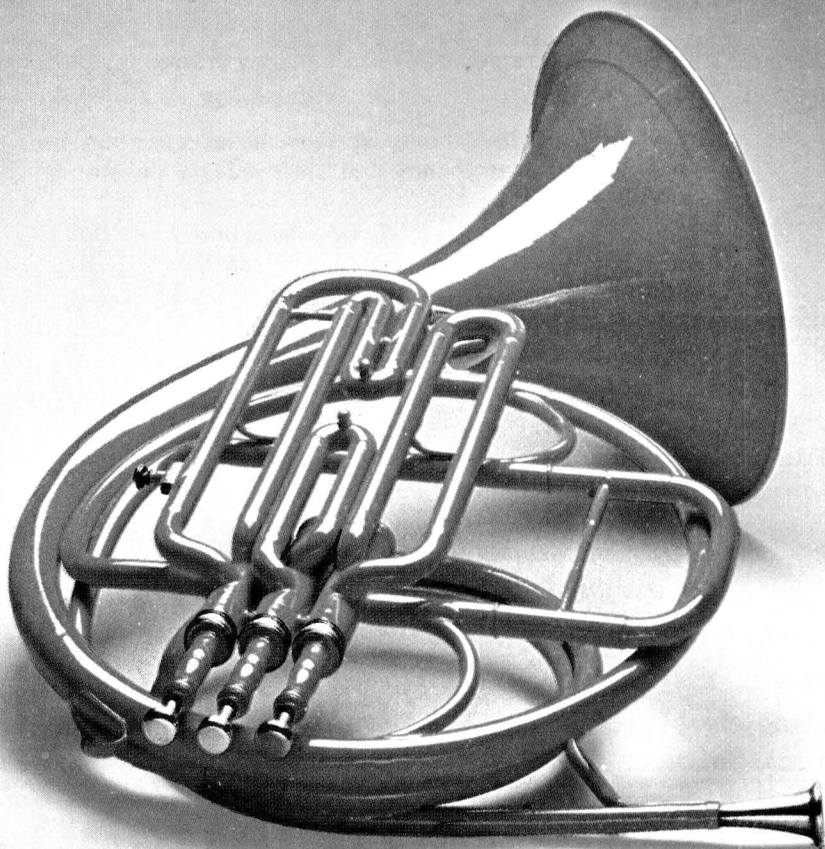
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Transactions and Communications

Composition of water-soluble dehydrated castor oil alkyds

By N. A. Ghanem, M. A. El-Azmirly and Z. H. Abd El-Latif

Laboratory of Polymers and Pigments, National Research Centre, Dokki, Cairo, U.A.R.

Summary

The synthesis of water-soluble DCO/phthalic anhydride alkyds has been attempted by introducing into the alkyd structure a suitable amount of free carboxyl groups. For this purpose maleic acid anhydride (MA), citric acid (CA), and pyromellitic acid dianhydride (PMDA) were employed. PMDA, being a tetrafunctional acid, possesses a high capacity for producing water-soluble resins when used as a partial replacement for phthalic anhydride. Much of the practicability of the alkyds produced and their tendency to gelation depended upon the order of addition of the components and the control of the time and temperature of the various reactions.

Investigation of the resins by a turbidimetric titration technique has shown that the higher the functionality of the modifying acid used, the higher was the polydispersity and the better were the solubility characteristics. It was found that the polydispersity increases with the increase of the quantity of the polyfunctional modifier and with the increase of the oil content.

Water-soluble alkyds modified with PMDA gave films which exhibited promising features, such as favourable hardness and mechanical properties, thermal stability, good resistance to water, acid and alkali (Na_2CO_3 solution), without having any residual tackiness.

Keywords

Binders, resins, etc.

alkyd resin
water soluble resin

*Raw materials used in manufacture
or synthesis of ingredients for coatings*

castor oil
dehydrated castor oil

*Processes and methods primarily associated
with analysis, measurement and testing*

turbidimetric titration

La composition des résines alkydes à l'huile de ricin déshydratée solubles dans l'eau

Résumé

On a tenté d'effectuer la synthèse des résines alkydes à l'huile de ricin déshydratée et à l'anhydride phtalique par l'introduction d'une suffisance de groupements carboxyliques libres dans la structure de la résine alkyde. A ce but on a utilisé l'anhydride maleique (MA), l'acide citrique (CA) et le dianhydride de l'acide pyroméllitique (PMDA). Etant tétra-fonctionnel, celui-ci possède une forte tendance de rendre des résines solubles dans l'eau en remplaçant partiellement l'anhydride phtalique. L'utilité de telles alkydes et également leur tendance de se gélifier dépendent en grande mesure de la séquence dans lequel on introduit les composants et également de l'attention accordée au contrôle de la durée et de la température des diverses réactions.

On a démontré par le dosage des résines au moyens de la titrimétrie turbidimétrique que plus élevée la fonctionnalité de l'acide modificateur employé, plus élevée serait le degré de polydispersion, et également de solubilité. On a trouvé que la polydispersité s'augmente au fur et à mesure de l'augmentation de la teneur en modificateur polyfonctionnel et aussi de la teneur en huile.

Des alkydes modifiées à PMDA rendaient des feuillets mettant en évidence des caractéristiques intéressantes telles que bonne dureté et bonnes propriétés mécaniques, stabilité à la chaleur, bonne résistance à l'eau, à l'acide et à l'alcali (solution de Na_2CO_3) et en même temps aucun "tack" résiduel.

Zusammensetzung von Wasserlöslichen Dehydratisierten Rizinusölalkyden

Zusammenfassung

Die Synthese wasserlöslicher dehydratisierter Rizinusöl/Phthalsäureanhydrid Alkydharze wurde durch Einführung einer geeigneten Menge von freien Karboxylgruppen in die Alkydstruktur versucht. Hierfür wurden Maleinsäureanhydrid (MA), Zitronensäure (CA) und Pyromellithsäuredianhydrid (PMDA) benutzt. Da PMDA eine vierfach funktionelle Säure ist, besitzt sie, wenn zum Teil an die Stelle von Phthalsäureanhydrid (PA) tretend, die Fähigkeit wasserlösliche Harze zu erzeugen. Wie weit auf diese Weise erzeugte Alkydharze von praktischem Nutzen sind, sowie ihre Neigung zur Gelierung ist von der Reihenfolge der Zugabe der Komponenten sowie Zeit und Temperatur der verschiedenen Reaktionen abhängig.

Untersuchung des Harzes durch eine turbidimetrische Titrierungstechnik haben gezeigt, dass je funktioneller die benutzte modifizierende Säure, um so höher die Polydispersität und um so besser die Löslichkeitscharakteristika.

Wasserlösliche mit PMDA modifizierte Alkydharze ergaben Filme, die vielversprechende Merkmale besaßen, wie z.B. gute Härte und mechanische Eigenschaften, Wärmebeständigkeit sowie gute Wasser-, Säure- und Alkalien- (Na_2CO_3 Lösung) Festigkeit ohne Anzeichen zurückbleibender Neigung zum Kleben.

Состав водорастворимых дегидратированных алкидов касторового масла

Резюме

Делается попытка синтезировать водорастворимые дегидратированные алкиды фталевого ангидрида путем введения в алкидную структуру подходящего количества свободных карбоксильных групп. Для этой цели применялись ангидрид малеиновой кислоты, лимонная кислота и диангидрид пиромеллитовой кислоты. Так как диангидрид пиромеллитовой кислоты является тетрафункциональной кислотой, он обладает высокой способностью к образованию водорастворимых смол, когда он применяется в качестве частичного заместителя для фталиевого ангидрида. Практичность полученных алкидов и их склонность к желатинизации зависят от порядка добавления компонентов и регулирования времени и температуры различных отдельных реакций.

Анализ смол при помощи техники турбидиметрического титрования показал, что чем выше функциональность применяемой модифицирующей кислоты, тем выше была полидисперсность и тем лучше были характеристики растворимости. Найдено что полидисперсность увеличивается с увеличением количества полифункционального модификатора и с увеличением содержания масла.

Водорастворимые алкиды модифицированные диангидридом пиромеллитовой кислоты, дали пленки которые выявили перспективные характеристики, как например удовлетворительную твердость и механические свойства, термическую устойчивость и удовлетворительное сопротивление против воды, кислот и щелочи (раствора Na_2CO_3), без проявления какой либо остаточной клейкости.

Introduction

The use of water as a solvent for industrial paint systems is one of the major topics currently undergoing intense research and development work in the surface coatings industry.

Water-thinnable paints offer the advantages of ease of application and clean-up. In industrial coatings, they offer the additional benefits of reducing fire and toxic solvent hazards.

Although it is often difficult with molecules of large size to distinguish between emulsions and true solutions, recent polymer chemistry has evolved

hydrophilic polymers which contain polar groups, thus giving water-soluble polymers¹.

Alkyd resins as normally used in the surface coatings industry are oil-modified polyesters, made from oils (or their fatty acids), polyols and dibasic acids. Solvent-thinnable alkyds are normally processed to give a final acid value of 20 or less. If an acid of high basicity is used together with a dihydric alcohol, a resin can be obtained with high acid value (50 or more) which when neutralised with suitable bases become water-soluble¹. Water-soluble oil-modified alkyd resins based on phthalic anhydride are produced by heating to the esterifying temperature the mixed phthalic anhydride, oil and polyol to an acid value of about 30-120, and then neutralising with a suitable base². Brett³ has pointed out that the best results with water-soluble alkyds are likely to be obtained with systems which have been taken to as high a degree of reaction as possible, i.e., those in which the minimum number of carboxyl groups were retained which would ensure solubility in an aqueous base. Therefore, it is important to find the ways in which the degree of the reaction could be increased whilst still maintaining the solubility requirements.

The work described in this paper is concerned with water-soluble alkyds of the stoving type in which solubility is induced by the introduction of the minimum amount of free carboxyl groups in the alkyd resin cooked to the highest possible degree of reaction. In this investigation, two distinct methods have been employed; the first⁴ was to modify the oil (DCO) part of the resin by means of a Diels-Alder reaction using maleic anhydride (MA). The second was to modify the polyester chain by replacing part of the PA with the higher functional CA and PMDA; the use of trimellitic anhydride has been described elsewhere⁵. The preparation of the solvent-thinnable unmodified counterparts of these alkyds at various oil lengths and by different routes has already been investigated, and the relation between the reaction schedules and properties discussed⁶.

Experimental

Materials and methods employed

DCO fatty acids: Samples were kindly supplied by Victor Wolf Limited. A sample of trade name "Dedico" was used in this work.

Dehydrated castor oil: Dehydration was carried out under reduced pressure using Dowex-50 (sulphonated polystyrene/divinyl benzene copolymer) manufactured by Dow Chemical Co. The technique of dehydration has been described previously⁷.

Glycerol: Pure glycerol was obtained from the Kafr El-Zayat factory of the Egyptian Salt and Soda Co.

Diethylene glycol: Pure diethylene glycol of molecular weight 106.04 was obtained from Veb Laborchemie, East Germany.

Triethylene glycol: Analytical grade of molecular weight 150 was obtained from British Drug House Ltd.

Polyethylene glycol: Polyethylene glycol of molecular weight 200 was obtained from Fluka AG., Switzerland.

Phthalic anhydride: Pure scales obtained from Veb Laborchemie, East Germany, MP = 130.8°C.

Maleic anhydride: Analytical grade maleic anhydride of 99 per cent purity, MP = 59-60°C was obtained from Merck AG, West Germany.

Citric acid: Pure crystalline MP = 153°C was obtained from Veb Laborchemie, East Germany.

Pyromellitic acid dianhydride: A sample of 99.5 per cent purity was obtained from Veba-Chemie AG, West Germany.

Alkyd resin preparation: Alkyd resins of different oil lengths were prepared under various conditions. The detailed procedures are given in the experimental section. The reaction was followed by analysis of samples removed after different intervals using a special device⁷.

Analytical techniques

Polydispersity of the alkyd resins: To obtain preliminary information on the molecular weight distribution in the alkyds prepared, turbidity measurements were performed by the method described previously⁶.

Testing the alkyd films: In addition to the acid, iodine, and diene values, viscosity and colour measurements mentioned in a previous publication⁷, the alkyd films were tested for their pendulum hardness, elasticity and water, acid, and alkali (5 per cent Na₂CO₃) resistances using standard techniques^{8, 9, 10}.

Thermogravimetric analysis: A 0.1g section of the dry film was heated in air from room temperature to 600°C at a rate of 5°C/minute. An automatic recording apparatus manufactured by Gebruder Netzsch, West Germany was used.

Alkyd synthesis

Modification of alkyds with maleic anhydride: Two techniques were adopted in the modification of DCO/phthalic alkyds by MA:

The MA was added to the initial polyesterification mixture together with PA after the glycerolysis step was completed, or; the alkyd resin, first cooked in the usual way, was then treated with MA in a second stage of the reaction.

Only short and medium oil length alkyds could be converted to water-soluble resins by either technique. For the preparation of 46 per cent oil length water-soluble alkyds, the suitable proportions of maleic anhydride ranged from 7.5—10 per cent on the weight of the total resin. It was essential to restrict the reaction temperature to 160°C in the first technique, and to avoid gelation in the second stage of the second technique.

For 53 per cent oil length alkyds, higher maleic anhydride proportions were required to attain water solubility but the probability of gelation was increased.

Dehydrated castor oil, or its fatty acids was used when investigating the above techniques.

Modification of alkyds using citric acid: Citric acid was used to modify DCO alkyd resins of oil-lengths 53, 46 and 42 per cent. The glycerolysis step was carried out at 240°C for 1½ hours in the presence of 0.04 per cent LiOH. The glycerolysis product was cooled to 100°C, the PA was added and the mixture heated to 180°C. After 15 minutes at the reaction temperature, citric acid was added and heating was continued for about two hours. Replacement of 15-20 molar per cent PA by citric acid and a reaction temperature not exceeding 180°C were necessary to obtain water-soluble alkyds.

As the oil length is reduced, the organophilicity decreases whilst the hydrophilicity increases. However, premature gelation at low oil lengths becomes more probable. In all the above cases, by introducing polyethylene glycol as a partial substitute for glycerol to the extent of about 15 molar per cent, it was possible to increase the reaction time without the risk of quick gelation. This is important with water-soluble alkyds, where the best results are obtained with systems cooked to a high degree of reaction.

Modification of alkyds with pyromellitic dianhydride (PMDA): The tetrafunctional acid (PMDA) possesses a high capacity for producing water-soluble resins. DCO alkyds of oil-length 62 per cent, 53 per cent and 46 per cent were examined for water solubility by partial replacement of PA with this tetrafunctional acid. Two techniques were used, as shown below.

1. Pyromellitic dianhydride was incorporated at the beginning of the polyesterification reaction, i.e., it was added together with phthalic anhydride after the glycerolysis step has been carried out.
2. Phthalic anhydride, glycerol and DCO, were reacted in the normal order to produce a solvent-thinnable oil-modified alkyd resin, and then finally pyromellitic dianhydride added and the esterification reaction continued to produce a product capable of forming aqueous solutions after neutralisation with ammonia or an organic amine.

The alternative procedure of replacing the drying oil by its fatty acids was employed in some runs.

62 per cent oil length alkyds: As shown in Table 1, modification of the alkyd resin is affected not only by the amount of the polyfunctional acid but also by the mode of its addition. Addition of pyromellitic dianhydride at the beginning of the reaction increased the probability of gelation (technique 1). Treating the already prepared alkyd with the same proportion of PMDA made it possible to obtain water-soluble resins free from the risk of gelation. In view of the high functionality of PMDA, its addition to alkyds of even low acid value (run 4) leads to the formation of water-soluble alkyds. Increasing the percentage of PMDA to 15 molar per cent results in gel formation.

Addition of polyethylene glycol (PEG) in the proportion of 10-30 molar per cent on glycerol decreased the extent of gelation. Other ether glycols—diethylene glycol (DEG) and triethylene glycol (TEG)—gave the same effect as PEG.

53 per cent oil length alkyds: As in the case of DCO alkyds modified with citric acid, decreasing the oil length may lead to easier formation of water-soluble alkyds, but may also make gelation more feasible. The data given in Table 2 show that the addition of 5 molar per cent of pyromellitic dianhydride was sufficient to produce water-soluble resins; increasing the ratio to 10 molar per cent led to the formation of small gel particles in the resin. However, by replacing 20 per cent of the glycerol with polyethylene glycol, gelation was avoided (run 3).

46 per cent oil length alkyds: By further decreasing the oil length, the organophilicity decreased and the hydrophilicity increased making the solubilisation of the resin easier in the polar solvent, water. The results summarised in Table 3 indicate that 3 molar per cent of PMDA (based on PA) were sufficient to

Table 1
Preparation of water-soluble DCO alkyls
62% oil length modified with PMDA and with PMDA/PEG

Run No.	PMDA molar % on PA	PEG molar % on G	Mode of addition	Temperature (°C)	Time (min.)	Acid value (mg. KOH/g.)	Solubility in water	Viscosity (50% SC) GH	Colour GH
1	10	0	One step	180	145	35.87	Small gel particles	Small gel particles	Small gel particles
2	10	0	(1) Resin (2) Resin + PMDA	180 180	60 120	52.58 21.37	Small gel particles	Small gel particles	Small gel particles
3	10	0	(1) Resin (2) Resin + PMDA	180 180	120 30 55	9.64 17.90 13.90	WS Insoluble	D	5
4	10	0	(1) Resin (2) Resin + PMDA	180 180	150 20	8.45 23.14	WS	D	5
5	15	0	(1) Resin (2) Resin + PMDA	180 180	150 20	9.69 Gelled			
6	10	10	(1) MG + PEG + PA (2) Resin + PMDA	180 180	150 45	10.20 25.85	WS	F	5-6
7	15	10	(1) MG + PEG + PA (2) Resin + PMDA	180 180	150 45	17.03 20.45	Partially gelled	Partially gelled	Partially gelled
8	15	20	(1) MG + PEG + PA (2) Resin + PMDA	180 180	150 45	27.47 25.85	WS	E	5-6
9	15	30	(1) MG + PEG + PA (2) Resin + PMDA	180 180	150 45	28.71 31.65	WS	D	5-6

MG = monoglyceride.

GH = Gardner-Holt

Table 2
Preparation of water-soluble DCO alkyds; 53% oil length, modified with PMDA and PMDA/PEG

Run No.	PMDA molar % on PA	PEG molar % on G	Mode of addition	Temperature (°C)	Time (min.)	Acid value (mg. KOH/g.)	Solubility in water	Viscosity (50% SC) GH	Colour GH
1	5	0	(1) MG + PA (2) Resin + PMDA	180	150	64.84	WS WS	C	5-6
					30	38.11			
					60	25.11			
2	10	0	(1) MG + PA (2) Resin + PMDA	180	150	62.71	Small gel particles	Small gel particles	Small gel particles
					30	63.05			
					60	43.27			
3	10	20	(1) MG + PA + PEG (2) Resin + PMDA	180	150	60.43	WS WS	F	5-6
					30	56.59			
					60	40.59			

Table 3
Preparation of water-soluble DCO alkyds, 46% oil length, modified with PMDA and PMDA/PEG

Run No.	PMDA molar % on PA	PEG molar % on G	Mode of addition	Temperature (°C)	Time (min.)	Acid value (mg. KOH/g.)	Solubility in water	Viscosity (50% SC) GH	Colour GH
1	3	0	(1) Resin + PMDA	180	120	45.90	WS	Q	5-6
			(2) Resin + PMDA	180	60	30.90			
2	5	0	(1) Resin + PMDA	180	120	43.60	WS	P	5-6
			(2) Resin + PMDA	180	60	36.22			
3	10	0	(1) Resin + PMDA	180	120	33.10	WS Gelled		
			(2) Resin + PMDA	180	5 15	53.59 —			
4	5	5	(1) MG + PEG + PA	180	120	49.59	WS	K	5-6
			(2) Resin + PMDA	180	60	46.48			
5	5	10	(1) MG + PEG + PA	180	120	46.13	WS	P	5-6
			(2) Resin + PMDA	180	60	45.18			
6	10	10	(1) MG + PEG + PA	180	120	46.13	WS	L	5-6
			(2) Resin + PMDA	180	60	48.70			

obtain water-soluble alkyd resins. Increasing the ratio of PMDA to 10 molar per cent led to quicker and more extensive gelation than in the corresponding case of 53 per cent oil length alkyd.

Gelation could also be avoided by the addition of PEG (runs 4-6).

Water-soluble DCO alkyds prepared by the fatty acid method

For comparison, water-soluble DCO alkyds of oil length 46 per cent were prepared using dehydrated castor oil fatty acids. The three components, fatty acids, glycerol, and phthalic anhydride, were either reacted together and the alkyd produced treated with pyromellitic dianhydride, or the fatty acid and glycerol were first reacted to produce monoglycerides which were then reacted with phthalic anhydride to obtain an alkyd which was allowed to react with PMDA. The results obtained are collected in Table 4, from which it will be seen that, under similar conditions to those applied in DCO alkyds, water-soluble DCO fatty acid alkyds were obtained. However, by using DCO fatty acids, it was possible to increase the amount of PMDA without causing gelation (run 3). It seems that in the fatty acid method, the concentration of the reactive α -hydroxyl groups of the glycerol becomes insufficient to cause gelation with pyromellitic dianhydride, which is the case with DCO alkyds. It is also possible that by using fatty acids instead of the oil, more uniform alkyd structure would be produced, which in turn facilitates dissolution. Turbidimetric titration studies throw light on this question.

Discussion

Molecular weight distribution by turbidimetric titration

Molecular weight distributions of water-soluble alkyds were determined using the technique previously used for solvent thinnable alkyds.⁶

The turbidimetric titration curves obtained generally indicate that water-soluble alkyds have a narrower molecular weight distribution than ordinary alkyds reacted at higher temperatures. Naturally the use of high temperatures in alkyd preparation provides the conditions for all types of side reactions, such as oil polymerisation and branching of the chain molecules of the glyceryl phthalate alkyds, and this will result into a product of high polydispersity. On the other hand, it was found that the molecular weight distributions of the water-soluble alkyd resins were broader than conventional alkyds reacted at the same or slightly higher temperatures. It is well known that, in preparing water-soluble alkyds, the polyesterification reaction is often stopped at a high acid value, i.e., the chain length of these resins will be relatively short. This is shown from the precipitation threshold values (γ_s) for the water-soluble alkyds, which are almost always greater than those for conventional alkyds (precipitation threshold, γ_s , being the fraction of the non-solvent present at the onset of turbidity). It is usual to associate the volume fraction of non-solvent at some significant precipitation point with the average molecular weight of the sample¹¹. The incorporation of polyfunctional acid branching units in the formulation of water-soluble resins will increase the number of branches per chain. This, together with relatively short chain length will naturally lead to a considerable increase in the polydispersity.

A comparison of the turbidimetric titration curves of the water-soluble resins of different types reflects the effect of the amount and type of the modifying

Table 4
Preparation of water-soluble DCO fatty acid alkyds, 46 per cent oil length, modified with two different proportions of PMDA

Run No.	PMDA molar % on PA	Mode of addition	Temperature (°C)	Time (min.)	Acid value (mg. KOH/g.)	Solubility in water	Viscosity (50% SC) GH	Colour GH
1	5	(1) FA + G + PA (2) Resin + PMDA	180 180	150 60	40.44 40.64	WS	M	6
2	5	(1) Fatty MG + PA (2) Resin + PMDA	180 180	150 30	37.00 43.88	WS	O	6
3	10	(1) FA + G + PA (2) Resin + PMDA	180 180	150 60	28.55 48.32	WS	R	5-6

acid and of the other variables on the polydispersity of the final product.

Effect of the type of modifying acid: It is quite expected that the introduction of polyfunctional modifying acids in the formulation will increase the probability of branching, i.e., the greater the functionality of the modifier the more probable will be the branch formation.

The turbidigrams given in Fig. 1 indicate that DCO alkyd resins modified with only 10 molar per cent of the tetrafunctional modified pyromellitic dianhydride have a wider distribution of molecular sizes than the corresponding DCO alkyd of the same oil length modified with even higher proportions of the trifunctional citric acid. This broadening of the range of molecular sizes increases the solubility of pyromellitic dianhydride-modified DCO alkyds in water. In addition, with this high functionality acid, the distribution of residual carboxyl groups amongst the various molecular species in the alkyd would be different from that obtained from citric acid. Naturally, pyromellitic dian-

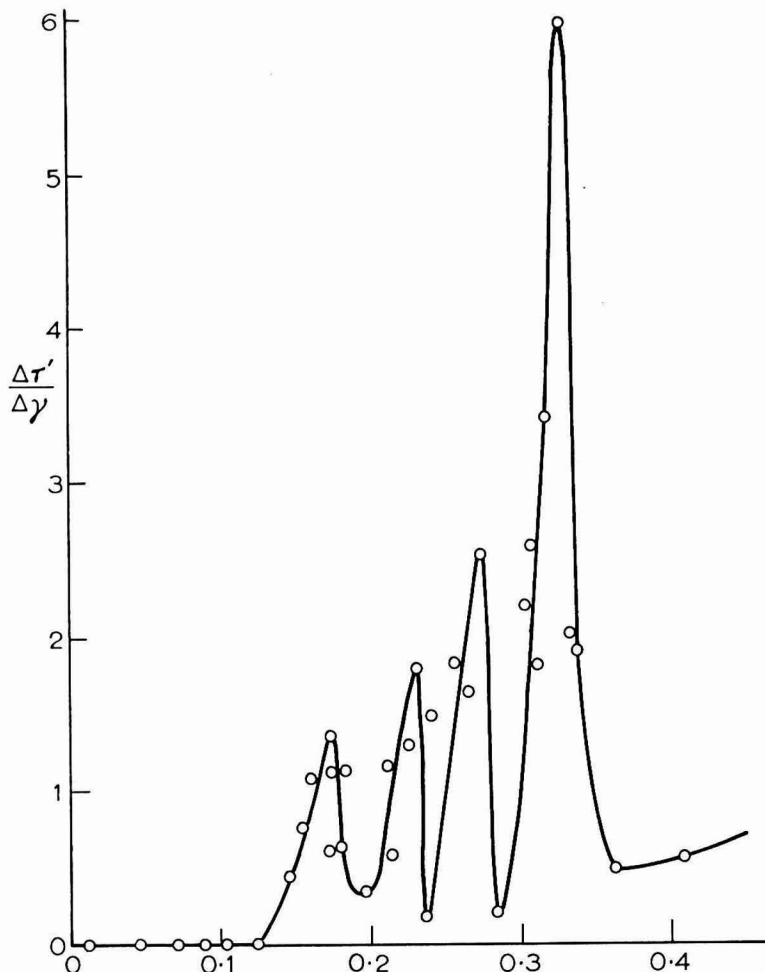
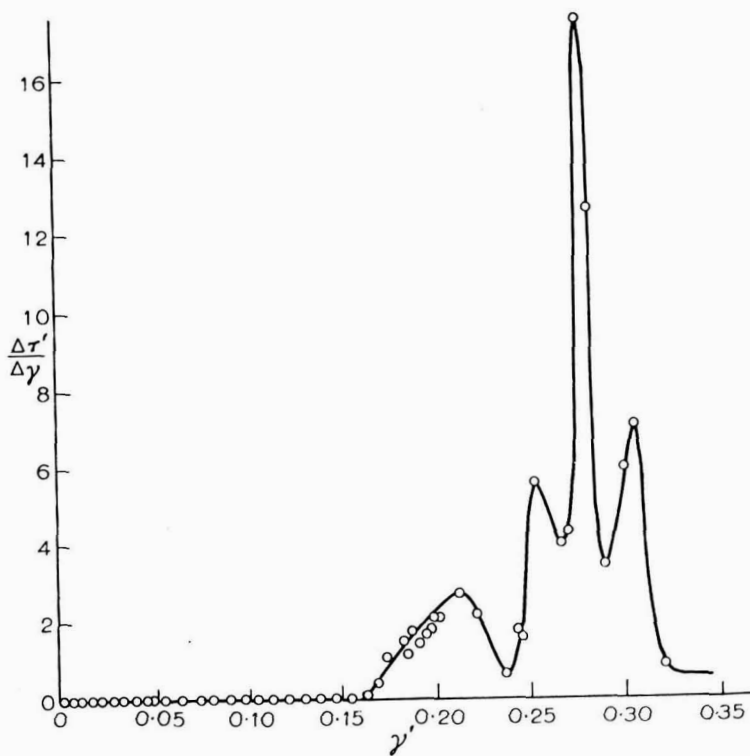


Fig. 1. Turbidimetric titration curves of water-soluble DCO alkyd of 46 per cent oil length:
(a) Resin from MG + PEG + PA treated with PMDA; 10 mole per cent.



(b) Resin from MG + PEG + PA + CA; 15 mole per cent directly

hydride will give a more efficient distribution of carboxyl groups throughout the alkyd molecules than does citric acid in terms of solubilising potential. Thus, by using pyromellitic dianhydride, the most difficult component of the alkyds to solubilise, namely the high oil content alkyd, is provided with a relatively high proportion of carboxyl groups to give a water-soluble resin.

Effect of the concentration of the modifier introduced: The concentration of the modifier (MA, CA or PMDA) was found to have a considerable effect on the molecular weight distribution. Fig. 2 illustrates the turbidimetric titration curves of DCO fatty acid alkyds modified with pyromellitic dianhydride. The high concentration of the polyfunctional modifier tends to increase the number of branch forming units, and consequently increases the heterogeneity. On

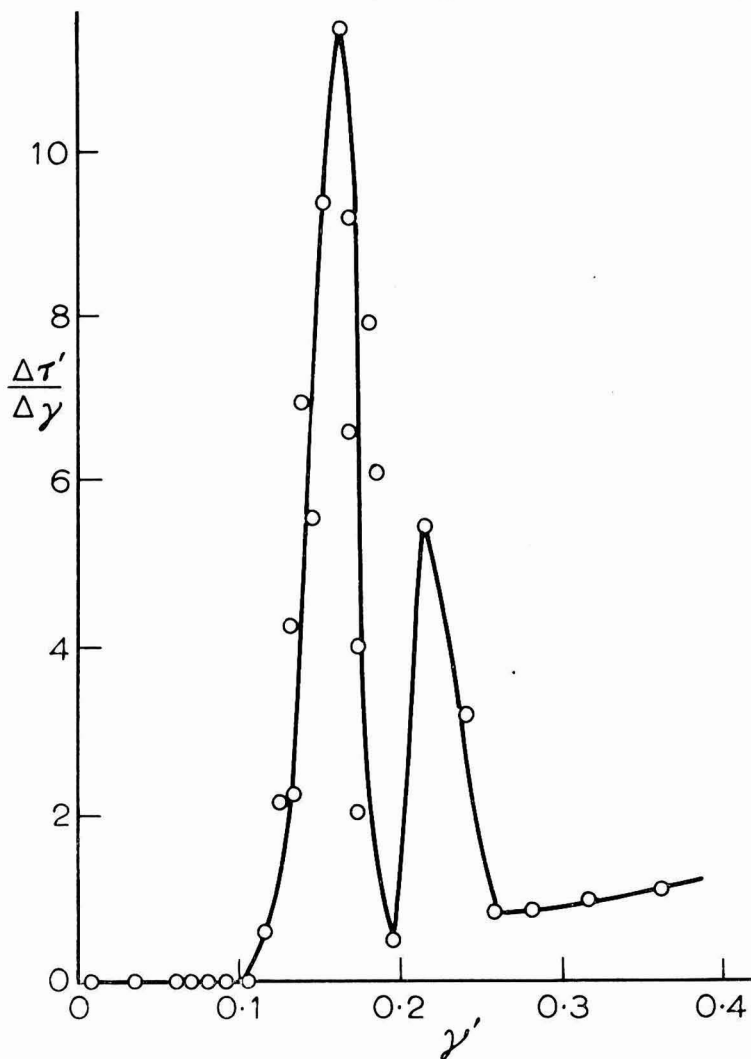
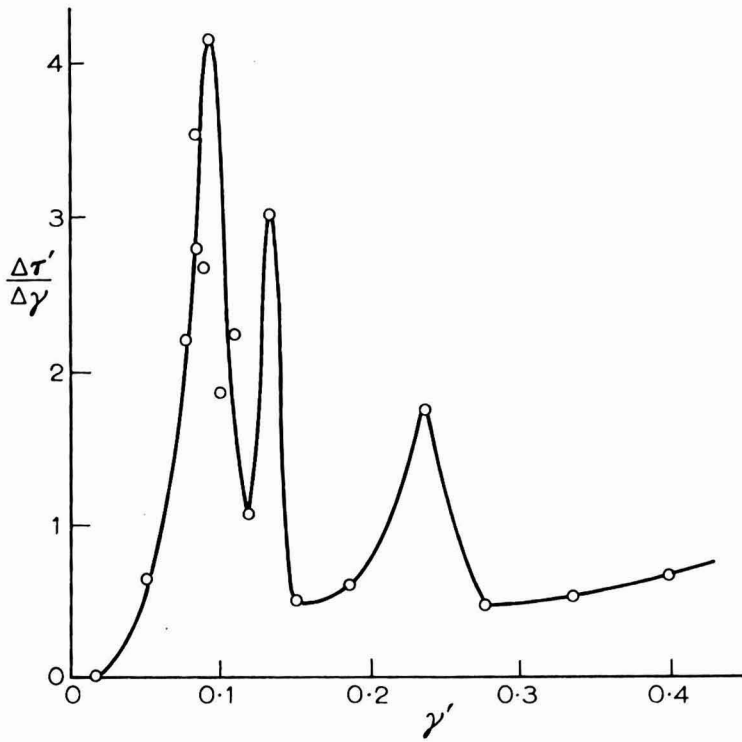


Fig. 2. Turbidimetric titration curves of water-soluble DCO alkyd of 46 per cent oil length:
(a) Resin from DCO FA + G + PA treated with PMDA; 5 mole per cent;



(b) Resin from DCO FA + G + PA treated with PMDA; 10 mole per cent

the other hand, the decrease in the number of branch-forming units will eventually lead to the decrease in the heterogeneity of the resin formed. Fig. 3 illustrates this effect; the partial replacement of the trifunctional component—

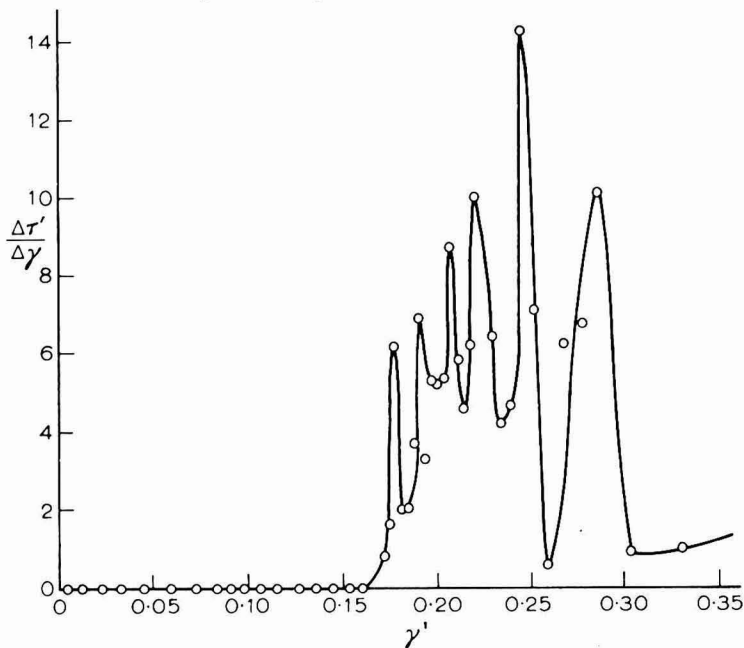
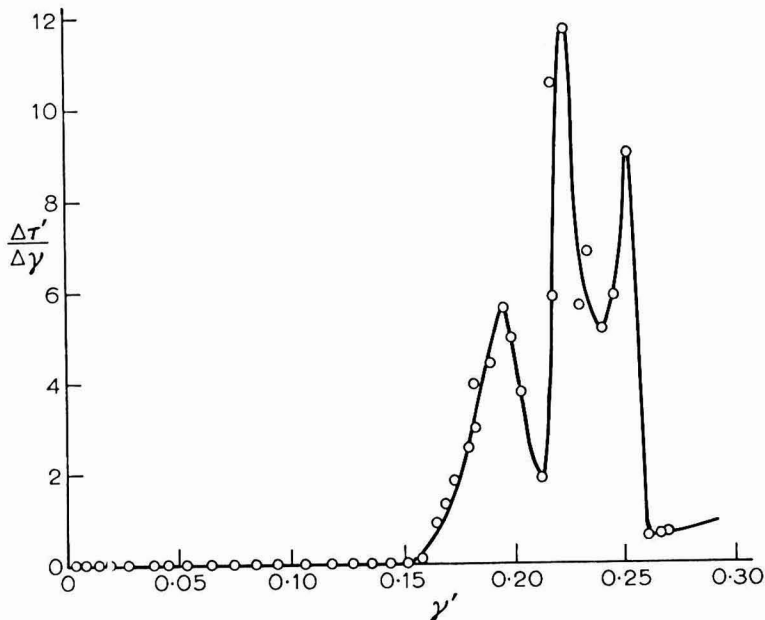


Fig. 3. Turbidimetric titration curves of water-soluble DCO alkyd of OL = 46 per cent:
(a) Resin from MG + PA + CA; 18 mole per cent directly;



(b) Resin from MG + PEG + PA + CA; 18 mole per cent directly

glycerol—by the bifunctional PEG in citric acid modified DCO alkyds decreased the heterogeneity.

Effect of the oil length: It was found that, with the usual solvent-thinnable alkyd resins, the heterogeneity of the resins increased as the oil-content of the alkyd resin increased⁶. It is interesting to find that this relation exists also for DCO water-soluble alkyds.

Results of the turbidimetric analyses of pyromellitic dianhydride modified DCO alkyds of oil lengths 53 per cent and 62 per cent are shown graphically in Fig. 4.

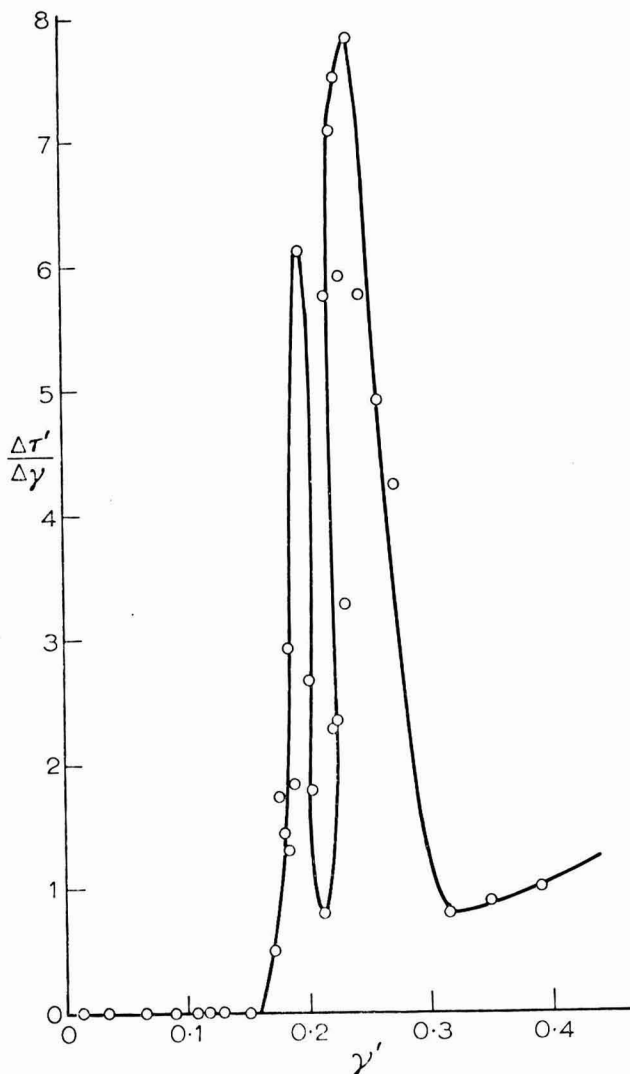
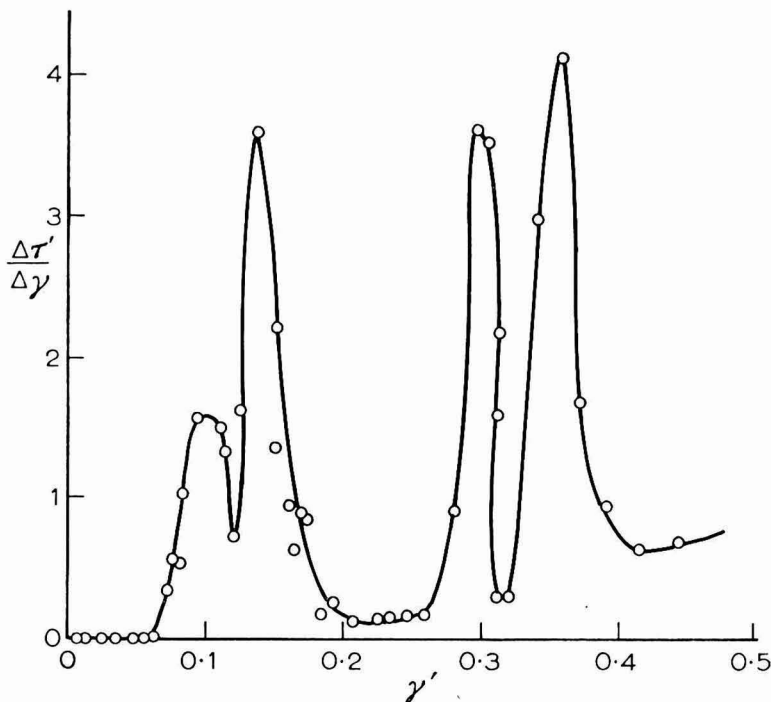


Fig. 4. Turbidimetric titration curves of water-soluble DCO alkyd.
(a) Resin from MG + PA treated with PMDA; 10 mole per cent; OL = 53 per cent



(b) Resin from MG + PA treated with PMDA; 10 mole per cent; OL=62 per cent

It is clearly shown that an increase in the oil length leads to a wider molecular weight distribution; the heterogeneity of the glycerolysis mixture is increased and this is reflected by the heterogeneity of the final resin prepared.

Comparison of film properties of water-soluble alkyd resins

Solubility characteristics: In preparing solutions of the alkyds in water, it was found that the resin solutions have high viscosity, even at low solids content. This was overcome by using ethyl alcohol as coupling solvent. The most suitable solvent mixture was water : alcohol in the ratio 80:20 by weight. The use of ammonia as solubilising agent gave rise to solutions with poor storage stability. The instability was probably due to the volatility of ammonia and consequent regeneration of the carboxyl groups in the alkyd, rendering the resin insoluble in the aqueous system¹². It was noted, however, that aqueous solutions of non-volatile organic bases, such as triethylamine, gave a greater solubilising effect than ammonia for the same stoichiometric quantities, thus enabling higher degree of reaction to be achieved whilst still retaining the water-soluble properties and much improved storage stability (several months). Triethylamine was used in most of the experiments as the solubilising base.

The most stable solutions were those of PMDA-modified resins. Moreover, when different ether glycols—diethylene glycol (DEG), triethylene glycol (TEG) and (PEG)—at 20 molar per cent on glycerol, were incorporated in 10 molar per cent pyromellitic-modified DCO alkyds, it was observed that

glycols with higher ether oxygen content (TEG and PEG) gave alkyd resins of better solubility in aqueous solvents.

Film properties: Aqueous solutions of the alkyd resins were prepared according to the following composition by weight: 50 solid resin: 40 water: 10 ethyl alcohol. After preparation of the films, they were dried either at room temperature or stoved at 130°C after being allowed to stand in the air for one hour in the presence or absence of water-soluble drier (0.05 per cent Co or Mn in the form of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ or $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$.)

It was observed that use of water-soluble driers shortened the drying time. Stoving the films enhanced drying, but it introduced rapid yellowing, especially with maleic and citric acid modified DCO alkyds. In addition to yellowing on stoving, the films in the case of maleic and citric acid modified alkyds suffered from residual tackiness.

An interesting observation was the remarkable shortening of the drying time upon incorporation of a small amount of hydrogen peroxide with the resin solution in the presence of the water-soluble drier. A similar effect has been observed with organic solvent soluble alkyds and alkyd/melamine combinations, where the addition of certain organic peroxides, in presence of small amounts of metallic driers, improved the film hardness and reduced the stoving time and temperature.¹³

Alkyds modified with PMDA exhibited more promising features than those modified with MA or CA; no residual tackiness was observed and the hardness, mechanical properties and water, acid, and alkali resistances were favourable.

The great solubilising capacity of the tetrafunctional PMDA makes it more suitable for the production of water-soluble phthalic alkyds of long oil lengths.

It is most likely that these properties can be further improved by incorporating other water-soluble amino resins.

Thermogravimetric analysis: Thermogravimetric analysis was demonstrated as a useful tool in the investigation of copolymer composition and in the determination of thermal stability of polymers. Its usefulness in the coatings and polymer fields has been demonstrated in a recently published review¹⁴ and in recent investigations in this laboratory¹⁵ on special polyesters. It was also useful in demonstrating the loss of fugitive plasticiser from a polyvinyl acetate latex film on ageing.¹⁴

The thermograms of 62 per cent oil length alkyd made from previously dehydrated castor oil are shown in Fig. 5.

- (a) A 62 per cent oil length alkyd which was made water-soluble by incorporating 10 molar per cent of pyromellitic dianhydride and 10 molar per cent diethylene glycol.
- (b) A 62 per cent oil length alkyd which was made water-soluble by incorporating 10 molar per cent of pyromellitic dianhydride and 10 molar per cent triethylene glycol.
- (c) Solvent-thinnable DCO alkyd resin of 62 per cent oil length.

From this figure it may be seen that films obtained from the water-soluble resins modified with PMDA and various ether glycols have a somewhat higher

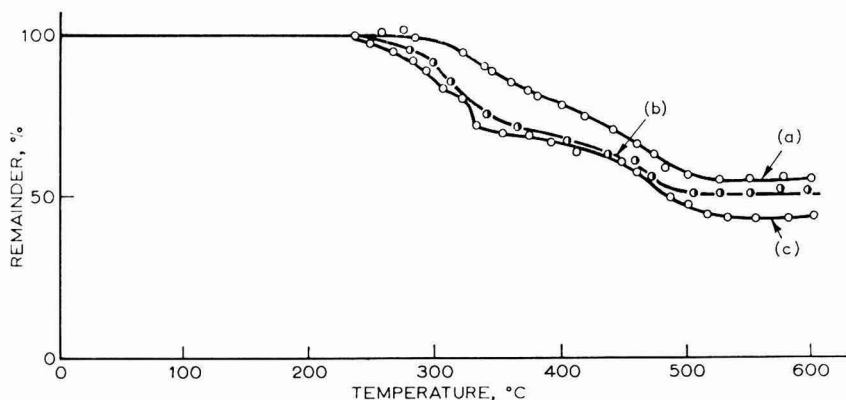


Fig. 5. Thermograms of:

- (a) DCO alkyd of OL = 62 per cent (resin treated with PMDA; 10 mole per cent; 10 mole per cent DEG);
 (b) DCO alkyd of OL = 62 per cent (resin treated with PMDA; 10 mole per cent; 10 mole per cent TEG);
 (c) Solvent-thinnable DCO alkyd resin of OL = 62 per cent

thermal stability than the corresponding solvent-thinnable alkyd; the temperature of extensive decomposition for the former two resins ranges from 250-275°C, whilst that of the last was about 225°C; moreover, at 600°C, (a) and (b) lost about 45 to 50 per cent of their weight whilst the loss in weight of (c) was greater than 55 per cent.

The above results show that partial substitution of PA by PMDA during the alkyd reaction has led to a more complex composition than that characteristic of unmodified DCO alkyds.

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Colloidal aspects of printing inks*

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Summary

The technique of using the Joyce-Loebl disc centrifuge has been extended to determine the particle size of pigments in printing inks. It is shown that the particle size is not homogeneous, but a high proportion of the particles are within the limits of size generally ascribed to colloids. The upper limit of the colloidal size range is estimated to be in the region of 0.2μ to 0.3μ .

It is found that the tendency of pigments in printing inks to settle during storage is related to the extent to which the pigment particles are greater than the upper limit of the colloidal range. It is shown that in some cases the degree of dispersion of the pigment in an ink is improved when the ink is diluted.

An explanation of this effect and some of the flow properties of inks is possible on the basis of colloidal theory.

Keywords

Equipment primarily associated with analysis measurement and testing
disc centrifuge

Types and classes of coating
printing ink

Properties, characteristics and conditions primarily associated with bulk coatings
particle size distribution

Miscellaneous terms
colloid chemistry

Aspects de la nature colloïdale des encres d'imprimerie

Résumé

On a développé la technique opératoire du centrifugeur à disque de Joyce-Loebel afin de permettre la détermination de la grandeur particulaire des constituants pigmentaires d'encres d'imprimerie. On démontre que la grandeur particulaire n'est pas uniforme, mais qu'une proportion élevée se trouve dedans les limites accordées en général à l'état colloïdal. On considère que la limite supérieure des grandeurs colloïdales se situe entre 0.2μ et 0.3μ .

On trouve dans le cas des encres d'imprimerie que la tendance des pigments de se déposer lors du stockage des encres est liée à la mesure où les particules pigmentaires dépassent la limite supérieure de grandeur particulaire. On démontre à l'égard de certaines encres que le degré de dispersion du pigment s'améliore lors que l'on dilue l'encre.

Il est possible, sur la base de la théorie des colloïdes, de donner une explication de cet effet ainsi que de certaines caractéristiques de l'écoulement d'encres d'imprimerie.

Druckfarben Kolloidal Gesehen

Zusammenfassung

Die Joyce-Loebl Scheibenzentrifugentechnik wurde nunmehr auch auf die Bestimmung der Teilchengröße von Pigmenten in Druckfarben ausgedehnt. Es wird aufgezeigt, dass die Teilchengröße nicht homogen ist, sondern, dass die Größe eines hohen Prozentsatzes der Teilchen innerhalb der im allgemeinen den Kolloiden zugerechneten Grenzen liegt. Die obere Grenze des Gebietes kolloidaler Größe wird als in der Gegenf von 0.2μ bis 0.3μ geschätzt.

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Es wurde festgestellt, dass die Tendenz von Pigmenten in Druckfarben sich beim Lagern abzusetzen, in Beziehungen zu dem Ausmass steht, in welchem die Grösse der Pigmentteilchen die obere Grenze des kolloidalen Gebietes übersteigt. Es wird gezeigt, dass der Dispersionsgrad des Pigmentes in der Druckfarbe in manchen Fällen durch Verdünnung letzterer verbessert wird.

Auf der Basis der Kolloidtheorie ist es möglich, diese Auswirkung sowie einige der Verlaufseigenschaften von Druckfarben zu erklären.

Коллоидные аспекты печатных красок

Резюме

Технология применения дисковой центрифуги Джойс-Лосбля пспользована для определения величины пигментных частиц в печатных красках. Показано что величина частиц не однородна, но что большая пропорция частиц лежит в пределах размера обычно приписываемого коллоидам. Верхний предел коллоидного размера оценивается в области от 0·2 до 0·3 мк.

Найдено что склонность пигментов в печатных красках отстаиваться во время хранения, связана с степенью на которую пигментные частицы превышают верхний предел коллоидного диапазона. Показано что в некоторых случаях степень дисперсии пигмента в печатной краске улучшается когда краска разбавлена.

Возможна интерпретация этого эффекта и некоторых свойств потока печатных красок на базисе коллоидной теории.

Introduction

It is stated in Kingzett's Chemical Encyclopaedia (p. 243) that the term colloid state "is now applied to a state of matter characterised primarily by the degree of sub-division; all materials can be obtained either spontaneously or by artificial methods, as colloidal dispersions. The characteristic range of size of colloidal particles is from 1 millimicron to 200 millimicrons in diameter (1 millimicron = 10^{-7} cm); particles smaller than this are of molecular size and form normal solutions, whereas larger particles begin to show the properties of an ordinary suspension in that they become visible in a microscope and tend to settle out under gravity. Subject to this definition of size, the disperse phase may be gaseous, liquid or solid, and so may the dispersion medium."

E. K. Fischer, in his book "Colloidal dispersions," p. 2 states that "The limits of colloidal particles have been variously stated, but sizes between 1 micron and 1 millimicron encompass the usual extremes."

The colloid state is therefore seen to be a dispersion of one phase in another, with the particles of the dispersed phase falling within a certain size range. It can also be seen from these two quotations that there is considerable uncertainty about the value of the upper size limit.

With regard to printing inks, the author knows of no official definition, and would himself define them as solutions or dispersions of colouring matter in suitable liquid vehicles which, when applied in a thin layer to substrates, especially paper, dry quickly and leave a distinctively coloured film.

Where dyestuffs are used as the colouring agents, they will be in solution in the vehicles and the inks will therefore not be colloidal dispersions. Where insoluble dyestuffs or pigments are used, they will be dispersed in the vehicles, and part or all of the pigment may be in the colloidal state.

With these definitions of colloidal dispersions and inks in mind, the title can be interpreted as implying or assuming that printing inks based on pigments are colloidal dispersions, and therefore many of the phenomena and properties associated with the colloidal state should apply to printing inks. In turn some of these phenomena and properties may provide clues to the explanation and perhaps solution of some of the problems encountered with inks.

Particle size of pigments in inks

The first question to be asked is whether the particle sizes of pigments in inks do lie in the accepted colloid range, whether this extends to 0.2μ or to 1μ . Before considering this question, it must again be emphasised—quoting E. K. Fischer—that “The powdered solids of commerce consist of aggregations of smaller particles. To convert them into dispersions in liquids, mechanical work must be performed, and the forces and stresses imposed on the aggregates through the liquid cause them to break up into smaller units.”

Consequently particle sizes calculated from nitrogen surface area measurements on the powders are not related to the particle sizes of the pigments in printing inks.

Particle sizes calculated from nitrogen surface areas, do however, give the basic particle size of the pigment and indicate whether the ink would be in the colloidal state if the pigment were completely dispersed.

Using the simple formula:

$$d_3 = \frac{6}{\text{density} \times \text{surface area}} \text{ microns}$$

It is found that, for a carbon black of specific surface area $100\text{m}^2 \text{g}^{-1}$ and density 1.8, the d_3 basic particle size is 0.033 microns or 33 millimicrons.

For a phthalocyanine blue, of surface area $60\text{m}^2 \text{g}^{-1}$ and density 1.5, the basic particle size is 0.066 microns, and for a titanium dioxide of surface area $10\text{m}^2 \text{g}^{-1}$ and a density of 3.9, the basic particle size is 0.151 microns.

The basic sizes of these three well known and widely different pigments are all well inside the colloid range. Consequently, if, in printing inks based on them, the pigments were completely dispersed to their basic particles, the inks, by definition, would be colloidal dispersions.

There is no evidence, however, to prove that this is the case. What little experimental evidence is available demonstrates that, in paints and inks, the level of dispersion achieved either in the laboratory or in practice is seldom 100 per cent and the pigments are still in a somewhat aggregated form.

It is believed that, in most paints and inks, the mean pigment particle size lies somewhere between 0.1 and 1 micron. Paints are mentioned because there are more data relating to them and they are often made using the same pigments and the same dispersing techniques that are used for printing inks. If this is a true picture of the situation, then it can be deduced that, in most printing inks, the bulk of the pigment is less than 1 micron and is therefore in the colloid range. The word bulk is used because an ink can have the majority of the pigment particles under 1 micron and therefore in a colloidal state, and a minority of

the particles appreciably greater than 1 micron and therefore outside the colloid range. Such an ink would be partly an ordinary dispersion.

The experimental data for the particle size of pigments in printing inks are so scanty as to be almost non-existent. This is largely due to the experimental difficulties encountered in size measurement. These difficulties are primarily due to the small sizes and low densities of pigments.

Fischer's book describes at least ten ways of measuring particle sizes in the colloid range, namely:

- nitrogen adsorption
- optical microscope
- electron microscope
- adsorption from solution
- sedimentation
- elutriation
- permeability
- diffusion
- X-ray examination
- turbidimetry

and to these can be added another more recent technique:

- ionic (Coulter Counter).

Three of these techniques, nitrogen adsorption, permeability and X-ray examination are applicable to powders only and not dispersions. The optical microscope, elutriation and the Coulter Counter methods are not sufficiently sensitive for pigments. Adsorption from solution is now known to be dependent on the particle size of the solid particles, and diffusion can only apply to aqueous systems. Electron microscopy can only be used with films and not with wet inks. The theory of turbidity relationships with particle size is not yet fully developed. This leaves only sedimentation as a possible technique for application to printing inks and this is effective only when gravity has been replaced by centrifugal force. The Joyce-Loebl disc centrifuge is a commercial instrument which has been used for particle size measurement in printing inks; it works well with aqueous flexographic inks and gives reproducible results, some of which are illustrated below.

Aqueous flexographic inks

Fig. 1 gives the particle size distribution of a commercial aqueous ink of this type. The pigment here is a basic dye complex, Pigment Blue 1. The size distribution is very fine indeed, 80 per cent of the pigment being under 0.1 micron in size. This ink is by definition, therefore, a true colloidal dispersion. Unfortunately, this size measurement was made some years ago and no storage trials were carried out. Despite the fine dispersion, the pigment is not completely dispersed.

Fig. 2 gives the size distribution curve of a commercial red, aqueous, flexographic, ink, containing 20 per cent by weight of a Barium Lithol pigment, Pigment Red 49.

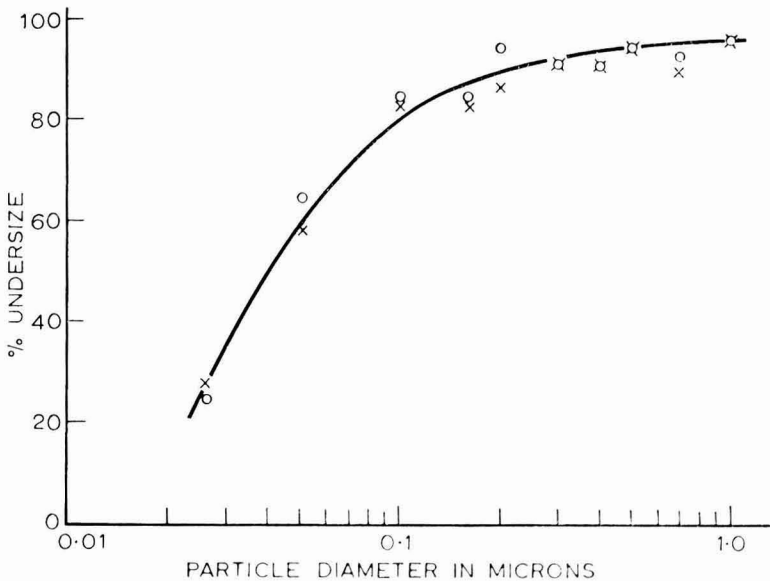


Fig. 1. Particle size distribution of CI Pigment Blue 1 in a commercial aqueous flexographic ink

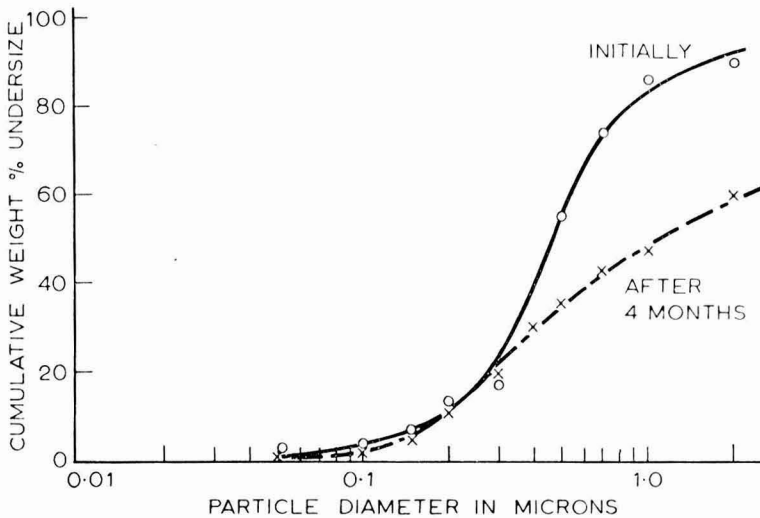


Fig. 2. Barium lithol red aqueous flexographic ink. Pigment content 20 per cent

The size distribution of the red pigment is much coarser. The 50 per cent diameter is 0.475μ , but 15 per cent by weight is above 1 micron and 8 per cent above 2 microns in size.

Much of the pigment is in a colloidal state, but much of it is outside the colloid range. This ink is stable on dilution 1 : 3 with water, but its behaviour on storage for three months is very interesting. On redetermining the pigment particle size distribution, and comparing it with the original curve, it was

found that the percentage of finer particles—below about 0.3 microns—had not altered, but particles greater than 0.3 microns had coarsened markedly. There was some sedimentation in the ink sample. This could have been predicted from colloid theory. The particles in the true colloidal state were stable on storage, those outside it were not. The colloidal limit of size in this case appears to be 0.3μ .

Similar results were obtained with a commercial blue aqueous flexographic ink based on a copper phthalocyanine blue, Pigment Blue 15, at 17 per cent concentration by weight. Fig. 3 shows the size distribution curve obtained

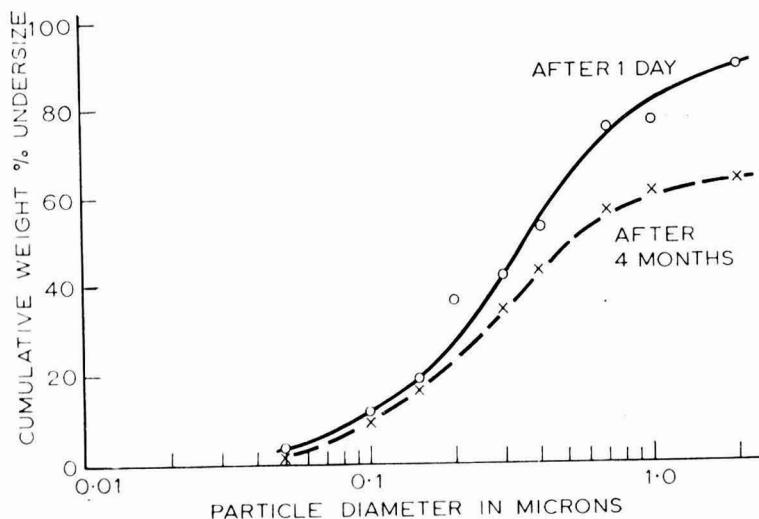


Fig. 3. Phthalocyanine blue aqueous flexographic ink. Pigment content 17 per cent

for this ink on the disc centrifuge. The 50 per cent diameter is 0.360μ , but 20 per cent of the pigment by weight is over 1 micron and 10 per cent over 2 microns. Again part of the pigment is in a true colloidal state and part is definitely outside this range. Consequently, on storage one would expect the fine particles to be unaffected and the coarser ones to settle out. This is confirmed by comparing the original size distribution with that taken after standing for four months. The percentage of particles under 0.2μ has not altered on standing. Here the upper colloidal size limit appears to be 0.2μ .

Similar results were also obtained for a commercial red aqueous flexographic ink based on chlorinated para red, Pigment Red 4. The size distribution curves are shown in Fig. 4. Again, the fine particles are largely unaffected on seven weeks' storage. The upper colloidal size limit here appears to be 0.2μ .

A practical result of this work should be to encourage ink makers to ensure that the bulk of the pigment particles in their inks is below about 0.3μ . This would ensure that the pigment particles will be in the true colloidal state and that the ink will therefore have a long storage life. Otherwise, the particle size distribution will coarsen on standing. This coarsening of part of the organic pigment will result in a marked weakening of strength in the ink, accompanied by other disadvantages such as loss of brightness and gloss. This is because

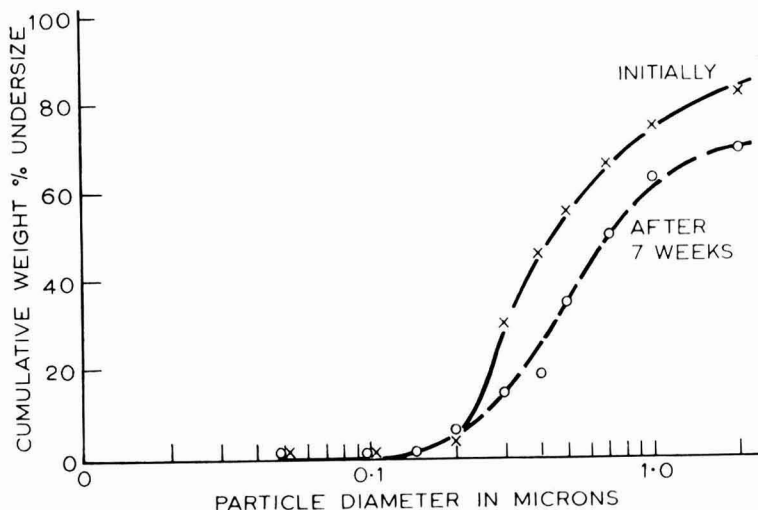


Fig. 4. Para red aqueous flexographic ink. Pigment content 25 per cent

these properties of pigmented systems have been shown to be very dependent on the particle size of the pigment.¹

It is of interest to note from these results that 0.3μ appears to be the upper size limit of the true colloid range, at least for this type of system.

It is possible that similar phenomena and arguments would apply to gravure inks, both aqueous and solvent based, but there are no published particle size data for such inks. The author has not yet been able to use the disc centrifuge for solvent-based gravure inks, because the perspex disc is attacked by the solvents. Would such an upper limit of particle size of a true colloidal dispersion be anticipated from colloid theory for any particular pigment independent of the vehicle present?

Oil-based inks

Similar arguments should also apply to oil-based inks, such as letterpress and lithographic inks, but again there is a lack of particle size data. There is no obvious reason why the same Joyce-Loebl technique could not be used for determining the pigment particle size distribution in such inks. However, even if the technique proves to be suitable, it is very slow and, whilst not neglecting it, the author has used an indirect technique for determining the 50 per cent weight diameter.

This technique depends on having a master curve for any given pigment. The colour strength/particle size curves for a number of important printing ink pigments have been determined, including phthalocyanine blue and green, anilide, *m*-xylylide and *o*-anisidide yellows, calcium 4B toners, manganese 2B toners and dinitraniline red. The conditions under which these curves were determined have been described in a previous paper.² Fig. 5 shows a typical curve obtained for phthalocyanine blue.

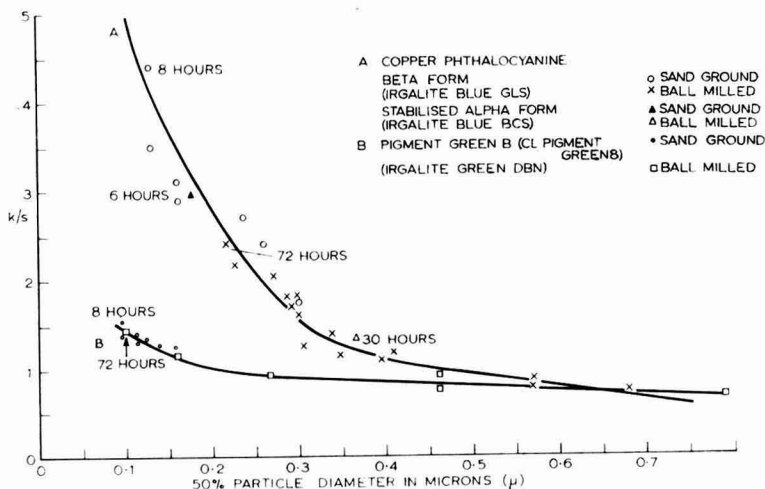


Fig. 5. Particle size of paint stainers/colour strength of titanium dioxide reductions (1 : 12.5)

A sample of the ink to be examined was stirred into the same standard white paint based on Beckosol P470, to a known ratio of pigment to titanium oxide. From the coloured paint so obtained, a film was prepared and after drying, its K/S value was determined. The corresponding 50 per cent diameter was read from the master curve and this is the 50 per cent diameter of the pigment in the ink.

In this technique the ink is being used as a paint stainer. Most oil ink vehicles are perfectly compatible with Beckosol P470, so that there should be little, if any, disturbance to the pigment dispersion during the mixing. This indirect technique is much quicker, but it gives only a mean diameter and not a complete size distribution.

The results obtained from three commercial litho printing inks are as follows:

Ink pigment	50% Diameter (μ)
Calcium 4B, 39%	0.26
<i>m</i> -xylylide yellow, 20%	0.52
anilide yellow, 20%	0.43

With 50 per cent diameters of these orders, much if not all of the pigments in the inks must be in the colloidal range. Similar values have been found for many other letterpress and litho inks. It can therefore be argued that, in letterpress and litho inks, the greater proportion of the pigment is in the colloid state and, therefore, such inks are essentially colloidal systems.

With all types of pigment inks, therefore, it is probable that most of the pigment is in the colloidal range. However, it may well be that it is the pigment particles outside the colloid range that really control some very important properties of inks, particularly the storage properties.

Application of colloid theory to inks

If inks are true colloidal systems, it would seem that knowledge of their properties might be gained from the huge literature on classical aqueous colloids. However, apart from the above prediction of stability depending on particle size, not much springs to mind.

This is not really surprising. The colloid systems so intensively studied in the past have usually been aqueous and dilute. Inks are mainly non-aqueous (but not always) and their pigment content is usually high. In litho inks it can reach 40 per cent and even in flexographic and gravure it can be about 10 per cent. It is doubtful whether the theories developed for dilute aqueous colloids will apply in such circumstances. The pigment concentrations in inks are so high that the difficulties in the mathematics involved in applying classical theories appear to be insuperable.

This is unfortunate as stability is an important property of inks. It is an important property in itself in so far as it affects storage properties, and it also appears to be closely related to the flow properties of the inks and to the dispersibility of the pigments in the inks.

The two mechanisms put forward to explain the stability of pigment dispersions, i.e. why the pigment particles do not aggregate, are based on electrostatic repulsion and steric hindrance.

The former postulates an electric double layer around each pigment particle, the presence of these layers giving rise to an energy barrier which will prevent flocculation of the pigment. According to this theory, known as the DLVO theory, this energy barrier can be formed in both aqueous and non-aqueous systems, even where the systems can be regarded as largely non-ionising. It is not, therefore, restricted to aqueous dispersions.

The steric hindrance theory assumes that molecules of surfactants, resins or polymers can be adsorbed from solution on to pigment surfaces. These molecules usually have a long chain length and have a limited freedom of movement. The presence of these adsorbed chains on the surfaces of pigment particles prevents them from approaching each other close enough to allow van der Waals forces of attraction to come into play and cause flocculation. Absorption of this type has been confirmed in both aqueous and non-aqueous systems, so that this stabilising mechanism is not restricted to any one system.

It is probable that the DLVO mechanism is applicable in aqueous pigmented flexographic inks, and the steric hindrance mechanism in other inks, but this has never been proved.

Although mathematical difficulties have prevented the detailed application of either theory to inks because of their high pigment content, both theories imply that, as the pigment content of a dispersion is increased, so the stabilising forces preventing aggregation will be decreased. This may well be the explanation of the experimental finding that, when inks are diluted, there is a slight decrease in particle size of the pigment i.e. a slight increase in dispersion.

A study of Figs. 2 and 3 illustrates this point.

In Fig. 2, the size distribution curve of a commercial red aqueous flexographic ink containing 20 per cent by weight of a barium lithol red pigment is given.

From the curve, the 50 per cent mean diameter can be read off and is found to be 0.475μ . Fig. 6 gives the size distribution curve of a 1 : 3 dilution of this ink with water and from it the 50 per cent mean diameter is now seen to be 0.420μ .

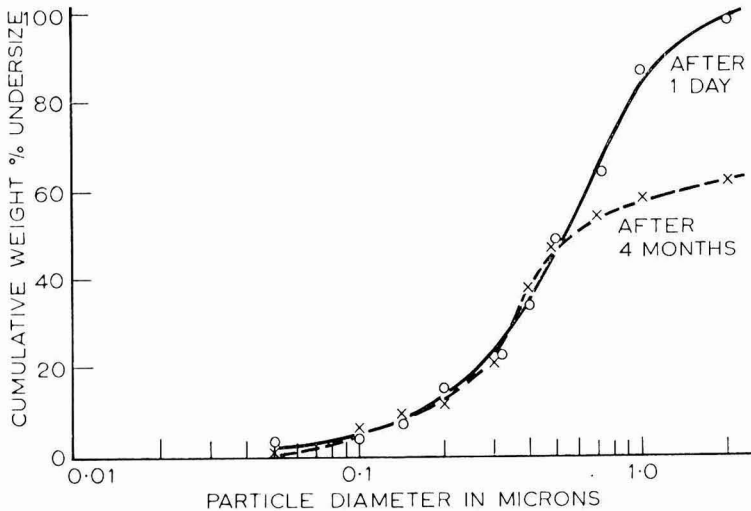


Fig. 6. Barium lithol red aqueous flexographic ink. Pigment content 20 per cent. Ink diluted 1 : 3 with water and allowed to stand

In Fig. 3, the size distribution curve for a commercial phthalocyanine blue aqueous flexographic ink containing 17 per cent pigment is shown. The 50 per cent diameter is 0.360μ . Fig. 7 shows the size distribution curve for a 1 : 3 reduction of this ink with water. The 50 per cent diameter is now 0.295μ .

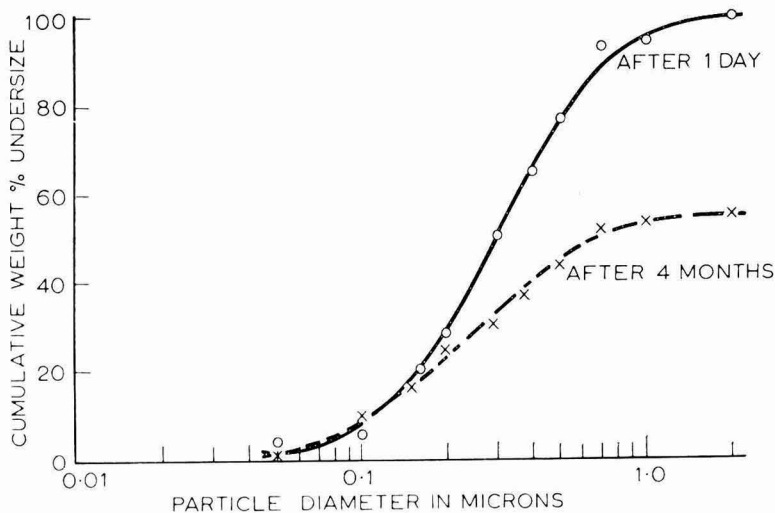


Fig. 7. Phthalocyanine blue aqueous flexographic ink. Pigment content 17 per cent. Ink diluted 1 : 3 with water and allowed to stand

The improvement in dispersion on diluting these two inks is small but definitely outside the limits of experimental error. The dilution in each case was accomplished with gentle stirring by hand, so that there is no question of the improvement being brought about by mechanical forces.

It is also interesting to note that these two inks were made by the same manufacturer. The aqueous flexographic ink based on chlorinated para red was made by a different company, and coarsened quite markedly on diluting 1 : 3 with water, the 50 per cent diameters being 0.450μ and 0.820μ .

It is believed that the improvement in dispersion in the first two inks on dilution is real, and it is of interest to consider whether this can be explained in terms of colloid chemistry.

The same phenomenon occurred with some commercial lithographic inks which were examined. The purpose of the examination was to see if they were stable on dilution despite their initial high pigment content. In earlier attempts to measure the particle size distribution of pigments in such inks³, inconsistent and coarse results were obtained. These had been attributed to dilution shock occurring when the inks had been diluted to the pigment content of 0.5 per cent by weight that is necessary for centrifugal sedimentation. Later work had established that dilution shock was indeed the cause of the erratic results, but it also established that this shock did not occur when the ink was diluted with a varnish, but when the diluted ink was injected into a solvent in the spinning disc for centrifugal sedimentation.

This could be explained by the action of the solvent stripping the absorbed polymer or resin molecules from the pigment. Whether this was true or not, it was found that, by introducing some resin into the solvent, or spin fluid, in the disc, the particle size results obtained were much finer and more consistent.

At the same time, a photosedimentometer attachment was fitted to one of the disc centrifuges to speed up the measurement of particle size distribution. This followed the changes in pigment concentration at a fixed depth in the cell during the centrifugal sedimentation by recording variations in the intensity of a beam of light after passing through the suspension. These variations were printed on a recorder which gave a graph of turbidity against time. From the speed of rotation and instrument constants, the time axis was altered to a size axis and from the recorder curve an uncorrected cumulative weight percentage undersize curve was obtained. This recorder tracing was obtained in an hour, so that the particle size distribution measurement was appreciably speeded up.

Three commercial lithographic inks were examined in this way to see how they behaved on dilution. The first difficulty was to dilute them with a varnish without causing any extra shear. This difficulty was due to their high viscosities and hence could be overcome by heating the inks before dilution. This enabled them to be diluted with mid litho varnish merely by hand stirring.

The original inks and the diluted inks were examined on the disc centrifuge using the photosedimentometer attachment, their size distribution curves were obtained and their 50 per cent diameters read from them. The results obtained are listed below.

Red litho ink based on a calcium 4B toner, CI pigment Red 57, containing 39 per cent pigment:

<i>% Pigmentation after dilution</i>	<i>50% Diameter (μ)</i>
39.0	0.275
10.19	0.210
7.00	0.180
3.69	0.220
2.12	0.220
1.09	0.250
0.73	0.230

The particle size distributions given by this method, whilst not absolute, owing to an unknown calibration factor, should be comparable. The results show clearly that there is a small but definite reduction in particle size, i.e. a small but definite increase in dispersion, as the ink is diluted. Further dilution brings a slight coarsening, but even the most dilute ink is no coarser than the original.

Yellow litho ink based on a *m*-xylylide yellow pigment CI Pigment Yellow 13 at a concentration of 20 per cent:

<i>% Pigmentation after dilution</i>	<i>50% Diameter (μ)</i>
20	—
10	0.58
5	0.525
2	0.520
1	0.530

The dilutions were made by warming and stirring in the mid litho varnish. The master dispersions for measurement on the disc centrifuge were made by diluting the various inks with white spirit containing 5 per cent of a resin (Beckosol P470). Master dispersions could not be obtained from the original full strength ink without applying shear and therefore running the risk of altering the dispersion.

Again there is a small but definite increase in dispersion on initial dilution, but this increase is not progressive with further dilution.

Yellow litho ink based on an anilide yellow, CI Pigment Yellow 12, at a concentration of 20 per cent:

<i>% Pigmentation after dilution</i>	<i>50% Diameter (μ)</i>
20	—
5	0.450
2	0.335
1	0.305
0.5	0.315

Again the full strength ink was too viscous for measurement and again there appears to be an improvement in the dispersion level on dilution with varnish. In this case the improvement is quite marked.

This improvement in dispersion on dilution is also considered to be real and it would be interesting to have the views of colloid chemists on a possible explanation. The author believes that any level of dispersion represents an equilibrium between a stabilising mechanism and the forces of attraction and that at high levels of particle concentration the equilibrium is displaced and can only be maintained at a coarser level of particle size.

The results for these three commercial litho inks also show that pigments behave very differently. Using standard vehicles and standard milling techniques, they differ in the level of dispersion achieved and in the flow properties of the resultant inks. It is believed that this is probably due to differences in their adsorption capacities for the resins in the ink vehicle and this belief implies faith in the steric hindrance mechanism of stability rather than in the DLVO theory.

Some indirect evidence can be obtained from flow measurements on various inks made in the author's laboratories. In these experiments, a β phthalocyanine blue was dispersed into a standard mid litho varnish at different pigmentation levels, namely 10 per cent, 15 per cent, 20 per cent, 25 per cent and 30 per cent.

At each pigmentation level, the degree of dispersion was altered by varying the amount of shear applied. As the grinding was performed with an Engelsmann automatic muller this was achieved by varying the number of revolutions of the grinding plates and the load on the plates.

The viscosity was measured at a shear stress of 7,000 dynes cm^{-1} using a relaxation technique on a Shirley-Ferranti viscometer. In this way it was possible to determine the effect of pigment dispersion and concentration on the flow of the inks.

The actual dispersion level achieved was determined by the indirect method already described. The inks were assessed for colour strength by treating them as paint stainers and making standard reductions of them with a white paint. The colour strengths of dry films of the reductions were measured on a spectrophotometer and the corresponding 50 per cent diameters were read from a master curve for this particular pigment.

The effect of particle size and pigment concentration on the flow properties of the ink at a low rate of shear are shown graphically in Fig. 8. From this graph, it can be seen that, at low concentrations, the viscosity is independent of the particle size. As the pigment concentration rises, the viscosity is independent of particle size until a certain size is reached and further reduction in size markedly increases the viscosity. At high levels of pigmentation, the viscosity is very dependent on size throughout the whole size range.

From these results, it might be inferred that the viscosity is controlled by the number of particles present in the ink, as the number is obviously dependent on the pigment concentration and the particle size. If this was the only controlling factor, then identical sets of curves should be obtained for different pigments provided their densities are similar.

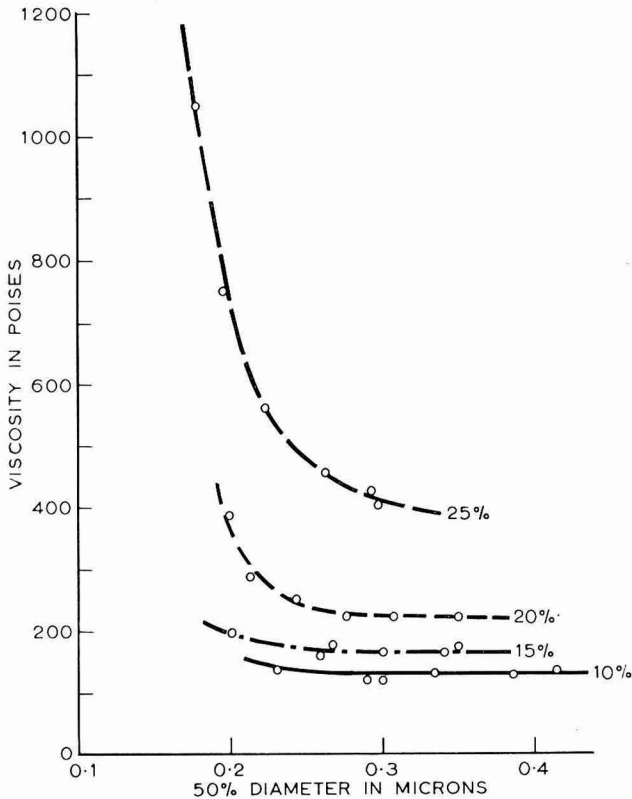


Fig. 8. Blue GLSM lithographic inks. Viscosity/50 per cent diameter at different pigment levels

Fig. 9 shows a corresponding set of curves for another pigment in the same medium. The pigment here is a calcium 4B toner, Rubine 4BP, CI Pigment Red 57, which has a density of 1.60 compared with that of 1.59 for the blue. Although the curves for the red are similar to those obtained from the blue in general characteristics, they are by no means identical (see Fig. 10). For any given combination of particle size and pigmentation level, the viscosity of the red ink is appreciably higher than that of the blue ink.

It can be seen from results of this nature that, although concentration and level of dispersion are two important parameters affecting the flow properties of inks, they are not the only criteria. There must be at least one other parameter and this may well be the thickness of the adsorbed layer of resin on the pigment. Assuming that the pigments do adsorb the resin, and that they vary in their adsorption capacity, then it is easy to conceive, first, that such adsorbed layers would affect the viscosity, and secondly, that a densely packed multilayer would have a markedly different effect from a loosely packed monolayer.

Thus, the third parameter can be understood qualitatively in terms of pigment adsorption, that is in terms of a steric hindrance mechanism of stability. On

the other hand, it is hard to visualise how an electric double layer mechanism, such as is postulated by the DLVO theory, could appreciably affect the viscosity.

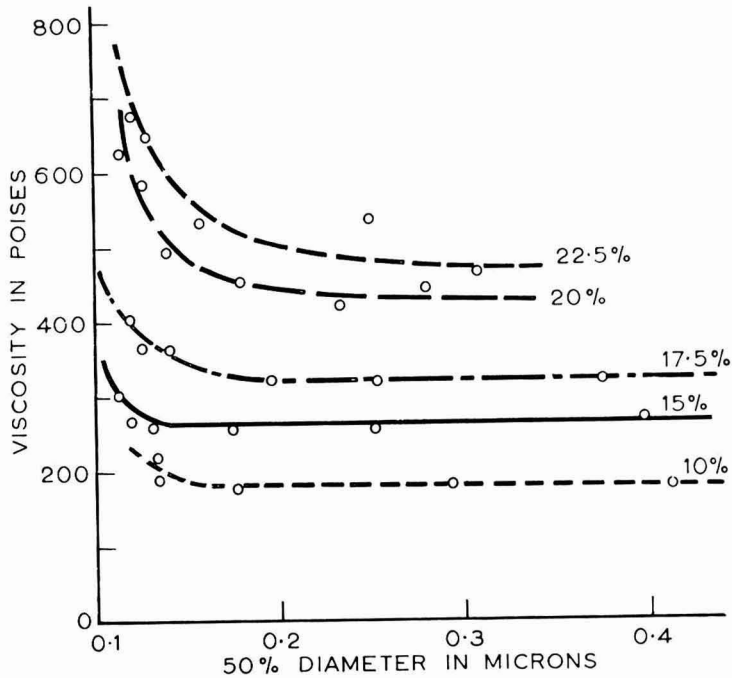


Fig. 9. Rubine 4BP lithographic inks. Viscosity/50 per cent diameter at different pigment levels. Test conditions: 25°C, 7,000 dyne cm⁻²

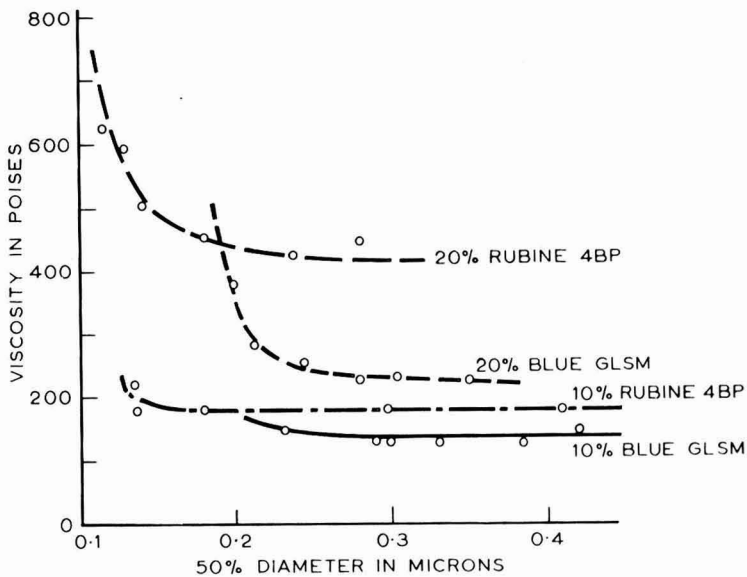


Fig. 10. Rubine 4BP and Blue GLSM lithographic inks. Comparison of flow properties. Viscosity/particle size at pigment levels of 10 per cent and 20 per cent

Conclusions

The work described leads to a number of conclusions, as shown below.

The pigment particles in commercial printing inks are not homogeneous in size, but the evidence is that a high proportion of them are well inside the colloidal range.

The upper limits of the colloidal range are stated in the literature to be from 0.2μ to 1μ . These experiments would indicate that the upper limit is in the 0.2μ to 0.3μ region.

The storage properties of one class of inks, aqueous pigmented flexographic, can be related to the extent to which their particle size distributions lie in the true colloidal range.

It has been shown that inks can improve in dispersion on dilution. This can be explained qualitatively in terms of colloidal theory.

The flow properties of inks appear to be explicable partly in terms of colloidal theory.

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2. *idem* 1972, **55**, 663.
3. Lombard, G. A., and Carr, W., *Printing Technology*, 1969, **13**, 148.

Discussion at the London Section

PROFESSOR G. D. PARFITT said that the DLVO theory predicted that, for colloidal dispersions in non-aqueous media, the stability to flocculation increased with particle size. Furthermore, a preliminary application of this theory by Albers and Overbeck to concentrated systems showed that the stability decreased as the particle concentration increased. This appeared to be in accord with the data presented.

DR W. CARR expressed agreement.

PROFESSOR PARFITT queried the statement that adsorption from solution depended upon particle size.

DR CARR said that, with an aggregated or agglomerated pigment, fresh surface was exposed as the large particles were broken down during milling. He considered that all measurements of adsorption from solution should be accompanied by a particle size distribution measurement.

MR P. G. RICHARDSON asked whether pigment particle shape should be considered amongst the factors determining printing ink flow. Were pigments essentially spherical or amorphous when in their ultimate particle size?

DR CARR replied that he had not discussed particle shape as he did not consider it to have any significant effect. It was not known how the shapes of aggregates related to the shapes of the primary particles.

MR N. CASSON commented that he assumed that Dr Carr meant that the range of particle shapes in commercial pigments was limited, so that it was not an important factor in controlling viscosity.

A SPEAKER said that Dr Groszcek of BP Chemicals had made various shapes of graphite particles, and could probably make these materials available.

DR CARR pointed out that electron microscopy had shown that carbon blacks were spherical in shape.

DR J. H. CHAPMAN asked whether Dr Carr was implying that the particles in practical printing inks were sufficiently aggregated to be, in effect, spherical.

DR CARR replied that he had not assumed this; however, the shear in making inks would tend to round off the particles.

MR CASSON remarked that Dr Carr had referred to viscosity measurements made at a constant shear stress on suspensions at different concentrations and degrees of dispersion. The variation of viscosity with shear stress might give additional information on the state of the pigment. Had such measurements been made?

DR CARR said that he had been limited in his experimental work by the number of variables it was practicable to deal with, and so he had not been able to include this factor.

PROFESSOR K. S. W. SING asked whether there was evidence to show that the BET nitrogen adsorption method provided a measurement of the total surface area within the aggregates, i.e. of all of the particles within the aggregates.

Further was it possible to arrive at a straightforward analysis of the adsorption from solution data? Did this method ever provide a measure of the total area, e.g. by the use of small polar solute molecules?

DR CARR said that his hypothesis was that the nitrogen molecules were small enough to penetrate all the available surface. By contrast, in a liquid ink medium the polymer molecules were so large that they could not enter all the aggregates. He had studied the effect of time of milling on adsorption of resins from solution, and had found very marked time-dependency effects.

A SPEAKER enquired if the polymer was anchored to the pigment by chemisorption, or whether physical adsorption forces were acting. If the latter were the case, the polymer could be removed under shear.

DR CARR replied that it was not possible to determine which type of adsorption occurred.

MR D. F. A. JONES asked whether dilutions of the inks produced any noticeable increase in colour strength.

DR CARR replied that it was difficult to measure the strength of a thin transparent ink film.

MR S. EL SAYYAD (in a written contribution) asked whether Dr Carr had carried out any work on the electrical properties of printing inks. What was the origin of the charges on organic pigment particles? How would polymer adsorption influence the magnitude of the zeta potential at the interface?

DR CARR said that he had not measured electrokinetic potentials of pigment particles in inks. The inks or paints would have to be diluted to such an extent that the final dispersion would bear no resemblance to a practical pigment dispersion. Neither had he measured dielectric constants of inks.

Concerning the origin of the electrical charges on organic pigments, there were various possibilities, e.g. adsorption of surface-active agents, proton exchange with the solvent, the effects of traces of water and ionisation of groups in the pigment molecules. In non-aqueous media, a large surface potential could be produced from a small number of surface charges.

Dealing with the third point, zeta potentials in general changed on addition of polymers to charged dispersions, either because of the extension of the Stern plane into the solution (then the thickness of the adsorbed layer) or by the adsorption of polymer on sites previously occupied by charged species. Both of these effects would lower the zeta potential as measured by electrophoresis. A mechanism which would increase the zeta potential was that of ions being forced out of the Stern layer into the diffuse double layer. He had usually found that, if the particle was charged, its electrophoretic mobility decreased on adsorption of polymer.

A chromatographic study of an etching primer

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Summary

A number of papers has been published on the mode of action of two-pack etching primers and suggestions made as to the chemical reactions occurring between the various ingredients. This paper reports an attempt to study the reactions which occur on mixing the acid and base components of the etching primer, separating the products of reaction by thin layer and dry column chromatographic techniques. The results appear to confirm the commonly held view that a chromium (III) phosphate/resin complex is formed but indicate that some change in the original butyral resin occurs, possibly prior to complex formation.

Keywords

Types and classes of coating
Etching primer

Une étude d'un "wash primer" au moyens de la chromatographie

Résumé

Plusieurs articles ont été publiés au sujet de la mode d'action des "wash primers" à deux emballages et où l'on suggère les réactions chimiques qui puissent se produire entre les divers composants. Cet exposé rend compte d'une tentative à étudier les réactions qui se produisent lors du mélange des composants acide et alcalin du "wash primer" au moyens des techniques de chromatographie en couche mince ou sur colonne sèche pour effectuer la séparation des produits de réaction. Les résultats semblent à confirmer l'avis largement cru, à savoir, qu'il s'agit de la formation d'un complexe entre le phosphate de chromium (III) et la résine, mais en même temps ils indiquent qu'un changement dans la résine butyral se produit avant, peut-être, la formation du complexe.

Eine Chromatographische Untersuchung von einem Washprimer

Zusammenfassung

Einige Abhandlungen über das Verhalten von Zweikomponenten-Washprimern wurden veröffentlicht, und Vorschläge hinsichtlich der zwischen den verschiedenen Bestandteilen stattfindenden Reaktionen gemacht. In diesem Artikel wird versucht, die Reaktionen zu studieren, welche beim Mischen von sauren und basischen Komponenten stattfinden, indem die Reaktionsprodukte durch Dünnschicht- und Trockenkolonnen-Chromatografiertechniken getrennt werden. Die Ergebnisse scheinen die allgemein vertretene Ansicht zu bestätigen, dass ein Chrom (III) Phosphat Harzkomplex gebildet wird, deuten jedoch darauf hin, dass sich möglicherweise vor der Komplexbildung in dem ursprünglichen Butyralharz etwas geändert hat.

Хроматографическое исследование грунтовых реактивных красок

Резюме

Был опубликован ряд статей о характеристике действия двухкомпонентных грунтовых реактивных красок и были выдвинуты предположения о химических реакциях происходящих между различными отдельными компонентами. Настоящая статья описывает

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попытку изучить реакции вызываемые перемешиванием кислотных и основных компонент грунтовой реактивной краски, разъединяя продукты реакции при помощи хроматографической техники тонкого слоя и сухой колонки. Результаты повидимому подтверждают широко распространенное мнение что образуется комплекс хромовой (III) фосфатной смолы, но указывают что происходит некоторое изменение в исходной масляной смоле, возможно до образования комплекса.

Introduction

The term etching primer is used to describe a material applied to metal surfaces prior to the application of conventional paints in order to improve the adhesion of the latter and to afford some degree of protection against corrosion. The two-pack etching primer studied comprises a base component, consisting of a dispersion of zinc tetroxochromate in an alcoholic solution of polyvinyl butyral resin to which is added an alcoholic solution of phosphoric acid (the acid component) shortly before application.

The reactions which occur when a film of etching primer is applied to a metal surface may conveniently be considered under two headings: interactions between chemical components in the primer film and reactions between certain components of film and metal. Many suggestions have been made¹⁻⁵ as to the reactions involved, but the view most commonly held is that a complex co-ordination compound is formed between chromium (III) phosphate and hydroxyl groups present in the resin. The oxidation of the primary alcohols present in the mixture by chromium (VI) results in the formation of chromium (III); chromium (III) has, of course, marked co-ordinating properties, forming compounds in which it commonly exercises a co-ordination number of six.

In the present work the products of the reactions which occur on mixing the acid and base components of the etching primer have been investigated using thin layer and dry column chromatography, and the separated components analysed qualitatively by atomic emission spectroscopy.

Experimental procedure

The compositions of the acid and base components of the etching primer used are shown in Table 1.

Table 1
Composition of the etching primer

<i>Base component</i>								<i>Parts by weight</i>
Polyvinyl butyral (resin)	13.1
Zinc tetroxochromate (pigment)	12.1
Methyl ethyl ketone	36.1
<i>iso</i> -Propyl alcohol	33.5
Water	3.1
								97.9
<i>Acid component</i>								<i>Percentage by weight</i>
ortho-Phosphoric acid	14.1
<i>n</i> -Butanol	69.8
<i>iso</i> -Propyl alcohol	14.7
Water	1.4
								100.0

The etching primer was mixed to give a normal brushing consistency in the proportion base:acid 2:1. The samples used for thin layer and dry column chromatography were taken 24 hours after mixing, thus allowing time for appreciable amounts of complex to be formed; the reactions would not, however, have gone to completion at this stage.

Thin layer chromatograms were run using glass plates (5 × 20cm) coated with a layer of Kieselgel HF_{254 + 366} 0.3mm thickness (a silica gel absorbent containing two inorganic phosphors which fluoresce when irradiated with light of wavelength 254nm and 366nm respectively). The chromatographic behaviour of the separate components, polyvinyl butyral, zinc tetroxochromate and phosphoric acid was studied using 1 per cent solutions in the appropriate solvents. The developing solvents investigated were tetrahydrofuran (THF), *n*-butanol/*iso*-propyl alcohol (IPA)/water (70:15:15), methyl ethyl ketone (MEK)/*iso*-propyl alcohol (1:1), methyl ethyl ketone/*iso*-propyl alcohol (90:10), and ammonium chloride/ammonia/water (6g: 100ml: 100ml) (Table 2).

The resin and phosphoric acid spots were detected by irradiating the plates with ultraviolet light (254nm), when the spots quenched the fluorescence of the absorbent. The plate with the resin chromatogram was subsequently sprayed with concentrated sulphuric acid and heated in an oven at 105° for 30 minutes; the charred area confirmed the identity of the spot assigned to the resin. Phosphoric acid was identified by the pink colour it gave on spraying the chromatogram with a weakly buffered solution (pH = 7.8) of methyl red/bromocresol green. The yellow pigment was easily detected without any chromogenic procedure.

For thin layer chromatography of the etching primer a small sample, which had been mixed 24 hours previously, was thinned slightly with MEK to enable it to be applied to the plate. The solution (5μl) was spotted on to the plate and the chromatogram was developed using the solvent MEK/IPA (90:10), the solvent front being allowed to move about 10-15cm. The plate was removed, dried in a warm oven to remove solvent, developed again using the NH₄Cl/NH₃ solvent which was allowed to run about 5-8cm. The plate was removed, dried and examined under ultraviolet light. Two identical but separate chromatograms (I and II) were developed on another plate using the procedure just described. Chromatogram I was covered while II was sprayed with the indicator reagent (methyl red/bromocresol green) to detect the presence of free phosphoric acid. Chromatogram I was then sprayed with sulphuric acid and the plate heated to detect the presence of organic material.

The separation of reaction products using a larger sample of the mixed etching primer was achieved using dry column chromatography.⁶ A nylon tube (24in × 1in) sealed at one end was filled with alumina (activity II) to within 2in of the top; the activity of the alumina was shown to be similar to that of the Kieselgel used for thin layer chromatography, so that it did not require pre-treatment.⁶ A small hole was made in the bottom of the tube to allow the solvent to flow through the column.

A sample (*ca.* 5g) of reacted primer was diluted to 25ml with MEK and this solution (3ml) was pipetted on to the column. Elution was commenced with the solvent MEK/IPA (90:10) and was allowed to proceed until the solvent

front had almost reached the bottom of the column. The eluting solvent was changed to the $\text{NH}_4\text{Cl}/\text{NH}_3$ mixture and elution was continued until there was a clear separation between the green and yellow bands. The displaced solvent was collected and the bottom inch of the alumina column was cut off and added to this solution. The portions of the column containing the green and yellow fractions were extracted with concentrated nitric acid and with the $\text{NH}_4\text{Cl}/\text{NH}_3$ solvent respectively.

Each of the three extracts was carefully evaporated just to dryness and ammonium chloride was removed from the yellow component by heating the residue in a crucible.

A qualitative analysis of the residues was made using a Hilger medium quartz spectrograph. Comparison was made with standard samples containing zinc, chromium and phosphate.

The samples were incorporated in potassium bromide discs and their infra-red spectra determined with a Unicam SP.200 infra-red spectrophotometer.

Results and discussion

The results of the preliminary investigation of the individual components of the etching primer by thin layer chromatography are given in Table 2.

Table 2
R_f values of components in various solvents

Component	Developing solvent				
	THF	n-butanol/ IPA/water (70 : 15 : 15)	MEK/IPA (1 : 1)	MEK/IPA (90 : 10)	$\text{NH}_4\text{Cl}/\text{NH}_3/\text{H}_2\text{O}$ (6 : 100 : 100)
Resin	0.91	0-0.89	0.94	0.96	—
Phosphoric acid	0-0.9	0-0.69	0-0.72	0	—
Pigment ..	—	—	—	—	0.93

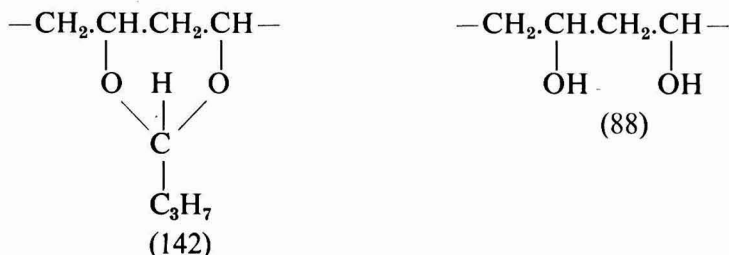
Where R_f values are given as from zero to a particular value, the component appeared on the plate as a long streak usually with distinct spots at the origin and at the head of the streak. This indicated that the component was only partially soluble in the developing solvent and no clear separation could be obtained. The results show that the best separation of resin and phosphoric acid is achieved with the solvent MEK/IPA (90:10). The zinc tetroxychromate pigment was almost insoluble in the organic developing solvents but dissolved in the $\text{NH}_4\text{Cl}/\text{NH}_3$ solution and gave a high R_f value.

Examination under ultraviolet light of the thin layer chromatogram plate obtained with the mixed etching primer showed three spots, one at the origin (A), one near to the first (organic) solvent front (B), and one near to the second ($\text{NH}_4\text{Cl}/\text{NH}_3$) solvent front, (C).

Spot B was colourless and visible only under ultraviolet light but spots A and C were green and yellow respectively. The R_f values for B and C were 0.93 and 0.89, respectively, in close agreement with the values previously found for the resin and pigment in these solvents. The spraying of the plate with concentrated sulphuric acid caused charring of both spots A and B, but C was not affected. The green fraction A thus appears to have resulted from the reaction of the acid and base components of the etching primer and the action of concentrated sulphuric acid indicates that it contains organic material. No pink colour was obtained when the plate was sprayed with methyl red/bromocresol green indicator, indicating the absence of free phosphoric acid in each of the separated fractions.

The first solvent fraction obtained by dry column chromatography yielded a slightly discoloured white solid on evaporation. Examination of this solid by atomic emission spectroscopy showed the absence of zinc, chromium and phosphorus, and it might, therefore, have been regarded as unchanged resin; however, comparison of its infrared spectrum with that of the pure resin showed that the two spectra differ, while comparison with the spectrum of polyvinyl alcohol revealed marked similarities. Thus the alcohol and the colourless residue exhibit a strong broad band centred at 3,300 and 3,200 cm^{-1} , respectively, while the pure resin exhibits a much weaker band at 3,500 cm^{-1} . The mass of the colourless residue which was recovered corresponded to *ca.* 52 per cent of the calculated amount of resin present in the etching primer solution added to the column.

Comparison of the molecular weight of the butyral fraction of the resin chain with that of the alcohol fraction resulting from hydrolysis indicates, however, a change from 142 to 88



so that the weight of the recovered fraction (not involved in the formation of the resin complex) would necessarily be appreciably less than that of resin applied to the column.

Examination of the green and yellow residues by atomic emission spectroscopy showed the presence of zinc, chromium and phosphorus in both these fractions. These results, together with those from thin layer chromatography, suggest that the green fraction represents primarily a phosphatochromium (III)-resin complex formed by reaction of the acid and base components of the etching primer.

Conclusions

The separation of the products of reaction of a two-pack etching primer by thin layer and dry column chromatography has resulted in the isolation of

the following three fractions:

- (i) a colourless fraction which appears to be the unreacted portion of the polyvinyl butyral resin, though chemically modified possibly as a result of hydrolysis of the acetal groups in the original resin.
- (ii) a green fraction which contains a phosphatochromium (III)-resin complex. The nature of the resin in this complex is uncertain, but it seems likely that some hydrolysis of the resin occurs followed by formation of the green complex.
- (iii) a yellow fraction, which shows that the chromate (VI) is not completely consumed by the reduction to chromium (III) even 24 hours after mixing the acid and base components of the primer. The yellow fraction, however, also contains phosphate and cannot be regarded as simply unreacted pigment.

Acknowledgments

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Cobalt 2-ethylhexanoate systems as accelerators for two-pack polyurethanes and their effects on storage stability

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Summary

Previous work has shown that the behaviour of cobalt 2-ethylhexanoate systems in unsaturated polyesters changes with time¹. Initially, a complex of cobalt 2-ethylhexanoate functions as a monomer, but after three weeks there is a considerable loss in activity accompanied by dimer formation. With a two-pack polyurethane the cobalt systems behaved in a similar way. A mechanism is postulated to explain the modes of action of the different cobalt systems used as accelerators.

Keywords

Binders, resins, etc.

urethane two-pack polyol resin

Driers

cobalt 2-ethylhexanoate

Properties, characteristics and conditions primarily associated with bulk coatings and allied products

storage stability

Les systèmes à base de 2-éthylhexanoate de cobalt entant qu'accélérateurs des polyuréthanes a deux emballages et leur influence sur la stabilité au stockage

Résumé

Les études préalables ont démontré que le comportement des systèmes à base de 2-éthylhexanoate de cobalt dans des résines polyesters non-saturées se dépend de l'âge du système. Au début un complexe de 2-éthylhexanoate de cobalt se comporte comme un monomère, mais après trois semaines il y aura une diminution importante de l'activité accompagnée par la formation du dimère. Dans le cas d'une polyuréthane à deux emballages le comportement de ces systèmes à base de cobalt était semblable. On propose un mécanisme pour expliquer les modes d'action des différents systèmes à base de cobalt employés en tant qu'accélérateurs.

KOBALT 2-ÄTHYLHEXANOAT SYSTEME

als Beschleuniger für Zweikomponenten Polyurethane und ihr Effekt auf Lagerungsstabilität

Zusammenfassung

In vorangegangenen Arbeiten wurde gezeigt, dass sich das Verhalten von Kobalt 2-Äthylhexanoat Systemen in ungesättigten Polyestern mit der Zeit ändert. Zunächst verhält sich ein Kobalt 2-Äthylhexanoatkomplex wie ein Monomer, nach drei Wochen hat sich die Aktivität jedoch erheblich verringert. Gleichzeitig findet Dimerbildung statt. Das Verhalten von Kobaltsystemen in Zweikomponenten Polyurethan ist ähnlich. Ein Mechanismus wird vorgeschlagen, um das Verhalten der verschiedenen als Beschleuniger benutzten Kobaltsysteme zu erklären.

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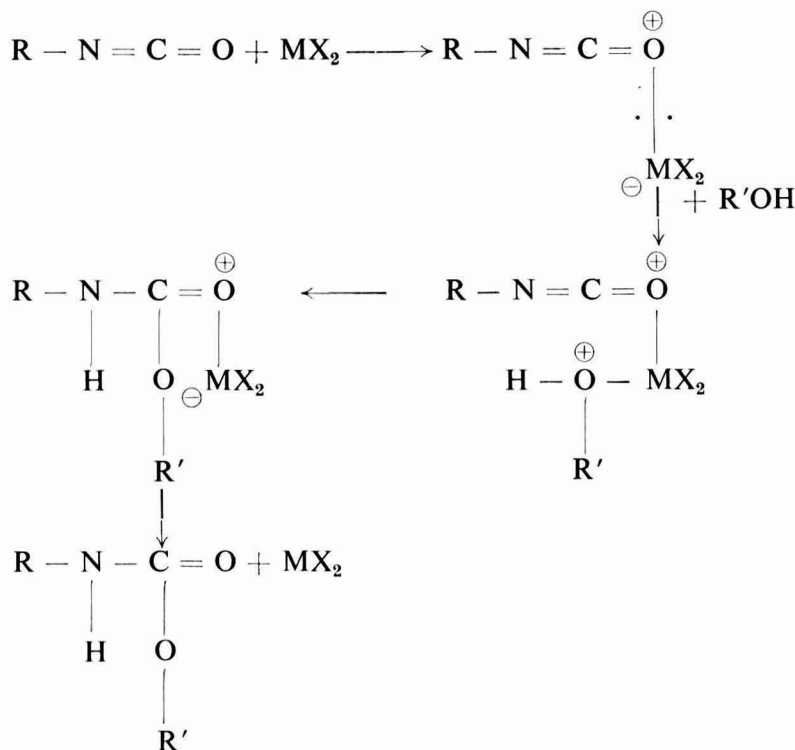
Кобальт 2-этилгексаноатные системы в качестве ускорителей для двух-компонентных полиуретанов и их влияние на стабильность в хранении

Резюме

Более ранние статьи показали что поведение кобальт 2-этилгексаноатных систем в ненасыщенных полиэфирах изменяется со временем. Вначале комплекс кобальт 2-этилгексаноата действует как мономер, но после трех недель обнаруживается значительная потеря в активности, сопровождаемая образованием димера. С двух-компонентным полиуретаном поведение кобальтовой системы было таким же. Постулируется механизм объясняющий характеристики действия различных кобальтовых систем применяемых в качестве ускорителей.

Introduction

The two most likely mechanisms that have been proposed to explain the action of organo-metallic compounds as accelerators in the urethane reaction are due to two groups of workers. Britain and Gemeinhardt² suggested that one metal atom co-ordinates both the isocyanate and hydroxyl groups of the reactants to itself:



(MX₂ is an organometallic compound or Lewis Acid, e.g. AlCl₃, BF₃).

Smith³, however, considered this mechanism to be improbable because it required the attack of one electron deficient centre on another. On the basis of a report by Frisch, Reagan and Thir⁴, who worked with organotin compounds in conjunction with 1-methoxy-2-propanol and phenyl isocyanate,

Smith considered that the urethane reaction occurred via the formation of intermediates of structures A and B (see Fig. 1).

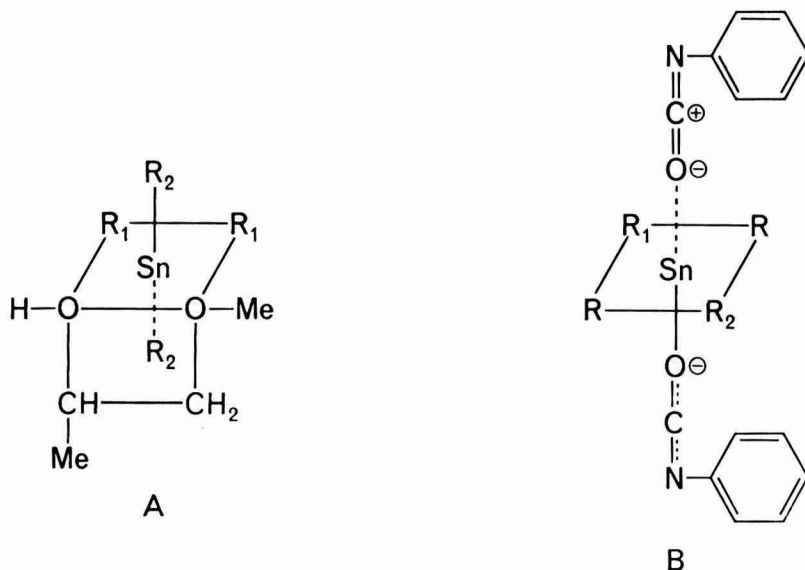


Fig. 1. Intermediate structures proposed by Smith³

Recently Pronina⁵ has shown that when cobalt octoate is used as an accelerator for the reaction between phenyl isocyanate and butanol it forms complexes with butanol and phenyl isocyanate which decompose to give the urethane, PhNH.COObu. It was found that cobalt octoate—(BuOH)_x complexes were less catalytically active than those of Co octoate—(PhNCO)_x.

It would appear that the work of Pronina lends support to the Britain and Gemeinhardt approach.

Object of the work

The behaviour of cobalt 2-ethylhexanoate systems in a two-pack polyurethane was investigated with special reference to storage stability, and this behaviour compared with that of the same systems in unsaturated polyesters.

Experimental

Reaction system

A 10g portion of a "polycaprolactone triol (PCPO300)" (Union Carbide) was reacted with 7.35g of isophorone diisocyanate (IPDI) (Veba Chemie) to give an isocyanate:hydroxyl ratio of 1.20:1.00. The excess of isocyanate was added to compensate for loss of some isocyanate groups owing to reaction with atmospheric moisture.

Accelerators

Cobalt 2-ethylhexanoate: This was prepared by the method of Richardson⁶. Basically, an aqueous solution of cobaltous acetate tetrahydrate (Co(OOCCH₃)₂ · 4H₂O) was added to an aqueous solution of sodium 2-ethyl-

hexanoate ($\text{Na OOCCH. (C}_2\text{H}_5)_3 \text{ (CH}_2)_3 \text{ . CH}_3$). The product was extracted with mixed hexanes and evaporation of solvent yielded a sticky violet tar. Analysis gave a cobalt content of 17.4 per cent which approximated to the theoretical value of 17.1 per cent. The tar was redissolved in toluene to give a 10 per cent solution.

2,2'-Bipyridyl: Analar 2,2'-bipyridyl was recrystallised from ethanol. The solid (MP 70°) was dissolved in toluene to give a 10 per cent solution.

Complex A (2 : 1 cobalt 2-ethylhexanoate : 2,2'-bipyridyl) and complex B (2 : 2 cobalt 2-ethylhexanoate : 2,2'-bipyridyl): The two complexes A and B were prepared by mixing toluene solutions of the cobalt 2-ethylhexanoate and 2,2'-bipyridyl in the correct molar ratios and then diluting to give a 1 per cent w/v cobalt concentration.

Methods of assessment of properties

Gelation times: The two-pack polyurethane system was assumed to have gelled when material adhering to a glass rod dipped in the reaction mixture no longer flowed from it.

Drying times: Touch and hard drying times were estimated by use of a Beck Koller drying recorder.

The establishment of accelerator level required in two-pack polyurethanes to give the best compromise between pot life and drying

Cobalt 2-ethylhexanoate: Portions of the 10 per cent cobalt 2-ethylhexanoate solution were diluted with toluene to give the metal concentrations as the percentage of the solids in the reaction mixture listed below. Gelation and drying times are summarised in Table 1.

Table 1
Variation of gelation and drying times with cobalt content

% Cobalt	Gel time	Touch dry	Hard dry
0.05	> 60 h	> 80 h	—
0.10	60 h	> 80 h	—
0.20	50 h	60 h	70 h
0.35	7 h	50 h	—
0.50	33 min	40 h	60 h
1.00	20 min	—	—

2,2'-Bipyridyl: The 10 per cent toluene solution of 2,2'-bipyridyl was added to the reaction mixture to give 1, 2 and 5 per cent of 2,2'-bipyridyl on the total solid content of the system. In all three cases gelation and drying times were greater than 100 hours.

Complexes A and B: The solutions of complexes A and B containing 1 per cent w/v cobalt were added to the reaction mixture so as to give 0.25, 0.35 and 0.45 per cent of cobalt metal on total reaction solids. The drying and gelation times are recorded in Table 2.

Table 2
The variation of gelation and drying times at different percentages of cobalt for complexes A and B

% Cobalt	Complex A			Complex B		
	Gel time (min)	Touch dry (min)	Hard dry (h)	Gel time (min)	Touch dry (min)	Hard dry (min)
0.25	300	840	> 36	25	70	230
0.35	205	460	> 24	10	40	130
0.45	100	350	22	5	—	—

Comparison of efficiency of cobalt 2-ethylhexanoate and complexes A and B in systems containing 0.35 per cent cobalt metal

By following hardness build-up: This was measured by comparison of the depth of indentation of a loaded stylus using a Monk microindentation apparatus. A known volume of the polyol:isocyanate:accelerator mixture was placed in the centre of an aluminium panel, which was spun for a fixed length of time on an ICI film spreading apparatus to give a dry film approximately 0.002 in thick. The panels were then dried at room temperature and humidity for one day, five days and 14 days. After these times a small disc was punched out and the hardnesses compared.

By determination of the loss of unreacted isocyanate: Films of the reactants mixed with the different accelerators were cast on a sheet of high density polythene at a thickness of 0.004in and allowed to cure at room temperature and humidity for 1, 5 and 14 days. After these time intervals the films were peeled from the polythene and their infra-red absorption at $2,270\text{ cm}^{-1}$ compared. The results for this experiment are summarised in Table 3.

Table 3
Variation of hardness and unreacted isocyanate with accelerator type

Compound	Microindentation results			% Absorption at $2,270\text{ cm}^{-1}$		
	1 day	5 days	14 days	1 day	5 days	14 days
Cobalt 2-ethylhexanoate	μ Not dry	μ 5.0	μ 3.5	Not dry	80	70
Complex A	3.55	2.0	0.8	50	30	10
Complex B	0.60	0.4	0.2	24	0	0

Determination of concentration of metal using complex B in reaction mixture to give optimum gelation and drying times

A range of concentrations of cobalt metal between 0.025-0.30 per cent w/v

in the reaction mixture was studied with respect to gelation and drying characteristics. In addition, the intensity of absorption of the isocyanate peak at $2,270\text{ cm}^{-1}$ was recorded after 24 hours' curing and the film hardness after 72 hours' curing. The results are summarised in Table 4.

Table 4
Variation of gelling, drying, hardness build-up and amount of unreacted isocyanate in systems containing varying quantities of complex B

% Cobalt	Gelation and drying			% Absorption at $2,270\text{ cm}^{-1}$ (24-hour cure)	Film hardness indentation after 72 hours' curing (μ)
	Gel time	Touch dry (h)	Hard dry (h)		
0.025	6 h	>24	>24	63	2.42
0.05	5 h	5	18	49	1.35
0.10	19 min	4	16	9.5	1.00
0.15	16 min	$3\frac{1}{4}$	$10\frac{1}{2}$	1.0	0.80
0.30	12 min	$1\frac{1}{4}$	$3\frac{1}{2}$	0.0	0.5

The best compromise between gelation and drying times was obtained at a level of 0.05 per cent cobalt metal.

Determination of the influence of atmospheric moisture on the curing of two-pack polyurethanes

Films were cured under dry nitrogen* in a glove-box to determine whether atmospheric moisture affected curing time.

The drying time of films containing 0.05 and 0.30 per cent of cobalt metal as complex B were recorded under dry nitrogen and compared with the result obtained for curing in the normal atmosphere as it is improbable that oxygen plays any part in the reaction. Additionally, the amount of isocyanate left

Table 5
Influence of atmospheric moisture on the curing of two-pack polyurethanes

% Cobalt	Nitrogen		Air		% Absorption at $2,270\text{ cm}^{-1}$ (two weeks' cure)
	Touch dry (h)	Hard dry (h)	Touch dry (h)	Hard dry (h)	
0.05	48	—	5	18	60
0.30	6	50	$1\frac{1}{4}$	$3\frac{1}{2}$	25

*"White spot" nitrogen was dried by passing through molecular sieves, concentrated sulphuric acid and phosphorus pentoxide.

in the film after two weeks' cure was indicated by measuring the intensity of absorption of the isocyanate band at $2,270\text{ cm}^{-1}$. The results obtained are summarised in Table 5

The storage stability of two-pack polyurethanes containing cobalt accelerators

In this experiment, the storage stabilities of systems containing 0.05 per cent cobalt metal were followed. The relative inactivity of cobalt 2-ethylhexanoate and 2,2'-bipyridyl taken alone may have offered definite storage advantages. Distribution of complexes or components between the two reacting portions were investigated. The distributions studied were:

1. complex in the isocyanate portion
2. complex in the polyol portion
3. cobalt 2-ethylhexanoate in isocyanate; 2,2'-bipyridyl in polyol
4. 2,2'-bipyridyl in isocyanate; cobalt 2-ethylhexanoate in polyol.

The reactants were mixed every month for six months and the gelation and drying times together with the indentation hardness after 24 hours cure were measured.

The results are summarised in Tables 6-9.

Table 6
Storage stability of systems containing complex B
(2 : 2 cobalt 2-ethylhexanoate : 2,2'-bipyridyl)

Distribution	Time	Gel time (h)	Touch dry (h)	Hard dry (h)
1	Initially 1 month	5 1	5 3	18 12
2	Initially 1 month	5 >144	5 Not dry in 180	18 —
3	Initially 1 month	5 $1\frac{1}{2}$	5 4	18 13
4	Initially 1 month	5 >144	5 Not dry in 180	18 —

For distributions 2 and 4 measurements were carried out every month for six months but as the results after one month were essentially constant they are not recorded in Table 6.

For distributions 1 and 3 measurements were not carried out after one month, because of isocyanurate formation⁸.

Table 7
Storage stability of systems containing complex A

Distribution	Time	Gel time (h)	Touch dry (h)	Hard dry (h)
1	Initially 1 month	15 2	40 3½	~100 20
2	Initially 1 month 2 months 3 " 4 " 5 " 6 "	15 16 16 17 19 19 19	40 42 41 45 49 48 47	~100 100 ~105 ~105 ~110 ~105 ~110
3	Initially 1 month	15 2½	40 5	~100 30
4	Initially 1 month 2 months 3 " 4 " 5 " 6 "	15 16 17 17 19 19 20	40 42 45 46 49 49 51	~100 ~100 ~105 ~105 ~110 ~110 ~120

For distributions 1 and 3 readings were not taken after one month, as isocyanurate⁸ formation had probably occurred.

Table 8
Storage stability of systems containing cobalt 2-ethylhexanoate

Distribution	Time	Gel time (h)	Touch dry (h)	Hard dry (h)
1	Initially 1 month	80 2	~100 4	180 18
2	Initially 1 month 2 months 3 " 4 " 5 " 6 "	80 85 78 82 88 89 93	~100 ~100 ~100 ~105 ~115 ~110 ~120	180 185 180 185 190 195 200

No readings were taken after one month for distribution 1, as isocyanurate⁸ formation had probably occurred.

Table 9
 Indentation hardness values after 24 hours' cure

Indentation in μ ($\frac{1}{16}$ in radius needle; 4g weight)							
	Initially	1 month	2 months	3 months	4 months	5 months	6 months
Co 2EH in NCO	Not dry	3.2	—	—	—	—	—
Co 2EH in OH	Not dry	Not dry	Not dry	Not dry	Not dry	Not dry	Not dry
Complex A in NCO	Too soft for reading	4.1	—	—	—	—	—
Complex A in OH	Too soft for reading	Too soft	Too soft	Too soft	Too soft	Too soft	Too soft
Co in NCO/Bipy in OH	Too soft for reading	5.6	—	—	—	—	—
Bipy in NCO/Co in OH	Too soft for reading	Too soft	Too soft	Too soft	Too soft	Too soft	Too soft
Complex B in NCO	4.9	2.8	—	—	—	—	—
Complex B in OH	4.9	Not dry	Not dry	Not dry	Not dry	Not dry	Not dry
Co in NCO/Bipy in OH	4.9	2.6	—	—	—	—	—
Bipy in NCO/Co in OH	4.9	Not dry	Not dry	Not dry	Not dry	Not dry	Not dry

Co 2EH = Cobalt 2-ethylhexanoate.

Bipy = 2,2'-dipyridyl.

Discussion

The use of cobalt 2-ethylhexanoate, 2,2'-bipyridyl and complexes A and B as accelerators in a two-pack polyurethane system showed that, whereas cobalt 2-ethylhexanoate was a good accelerator for the reaction between polyol and isocyanate, (short gelation times) it was a poor accelerator for the reaction between isocyanate and atmospheric moisture (long drying times). Complex formation between cobalt 2-ethylhexanoate and 2,2'-bipyridyl, which alone does not accelerate isocyanate reactions, improved accelerator activity with respect to reaction both of isocyanate with polyol and of isocyanate with atmospheric moisture. Complex B (2:2 cobalt 2-ethylhexanoate: 2,2'-bipyridyl) was approximately twenty times more active than complex A at the same metal concentration.

Comparison of hardness build-up in three active systems at the best overall concentration of cobalt metal (0.35 per cent) showed (Table 3) that complex B was the most efficient accelerator followed by complex A, which was in turn followed by cobalt 2-ethylhexanoate. A further indication of the efficiency of complex B was the complete loss of isocyanate after only five days' cure, as shown by disappearance of infra-red absorption at $2,270\text{ cm}^{-1}$.

Complex B was investigated further to determine the concentration of accelerator in the reacting system necessary to give the most useful gelation and drying times. This was found to be 0.05 per cent as cobalt metal. For a range of cobalt metal concentrations between 0.025 and 0.30 per cent it was found that the intensity of the isocyanate absorption (Table 4) was inversely proportional to cobalt concentration. Decrease in intensity of isocyanate absorption was accompanied by the production of a harder film. This means that, as concentration of cobalt increases, so isocyanate reacts more quickly

with polyol and atmospheric moisture generating urethane and urea linkages, which in turn react with isocyanate generating allophanate and biuret linkages. The net result is a hardening of the film. The cross-linking reactions occurring in a two-pack polyurethane are:

1. $R.OH + R'NCO \longrightarrow R'-NH.CO.R$ urethane
2. $H_2O + R'NCO \longrightarrow R'NH.CO.OH \xrightarrow{-CO_2/R'NCO} R'NH.CO.NHR'$ urea
3. $R'NH.CO.R + R'NCO \longrightarrow R'NH.CO.N.R'.CO.R'$ allophanate
4. $R'NH.CO.NH.R' + R'NCO \longrightarrow R'NH.CO.NR'.CONHR'$ biuret.

In order that reactions two and four occur, it is necessary to have atmospheric moisture. To determine the contribution atmospheric moisture makes towards the curing of the film, polyurethane films containing 0.05 per cent and 0.30 per cent cobalt metal as complex B were cured under dry nitrogen for two weeks. In addition, the drying times of these films were measured and found to be significantly different from the drying of similar films in the atmosphere. (Table 5). After two weeks the percentage of isocyanate in the films, as indicated by intensity of absorption at $2,270\text{cm}^{-1}$, was found to be significant. This indicated that reaction of hydroxyl groups with isocyanate was slower than reaction of the latter with water in the presence of complex B. The implication is that complex B is a very good moisture curing catalyst.

In order that cobalt 2-ethylhexanoate systems may be suitable for use as accelerators for two-pack polyurethanes, they must not cause storage instability. In the investigation concerning storage stability it was found that storage of metal species in the isocyanate pack was inadvisable owing to possible isocyanurate formation,⁸ as indicated by the drastic change in drying and gelling after only one month's storage (Tables 6, 7, 8). Cobalt 2-ethylhexanoate and complex A in polyol was stable after storage for six months, whilst complex B in polyol showed very poor stability. The level of cobalt in cobalt 2-ethylhexanoate and complex A was too low to be of any commercial use. Significant increase of the metal levels in these cases would result in premature gelation coupled with poor drying. The conclusions of this investigation are:

storage of either cobalt 2-ethylhexanoate or complex A in the polyol portion of the polyurethane gives constant gelling and drying characteristics even after six months;

storage of complex B in polyol results in drastic loss of activity after one month. After this period the accelerator is less active than cobalt 2-ethylhexanoate.

Nature of accelerator

It appeared that the nature of the cobalt species did not change with time with either uncomplexed cobalt 2-ethylhexanoate or complex A. However, in the case of complex B a drastic change in nature occurred. Moreover, it appeared, on the basis of storage results, that complex B changes to a species similar in nature to cobalt 2-ethylhexanoate.

It has been shown that cobalt 2-ethylhexanoate, in dilute solution in aromatic solvents, probably has a dimeric structure^{1,6}, as shown in Fig. 2.

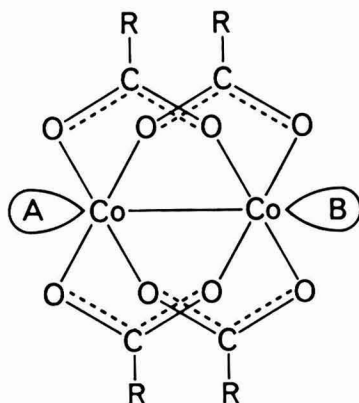


Fig. 2. Dimeric structure of cobalt 2-ethylhexanoate in dilute solutions in aromatic solvents (I)

A, B represent empty d_{z^2} orbitals into which electrons can be donated

If one mole of 2,2'-bipyridyl is added to the dimer above, the ligand field due to bipyridyl is not strong enough to break up the dimer. The complex obtained will consist of one bonded nitrogen atom and a free nitrogen atom, see Fig. 3.

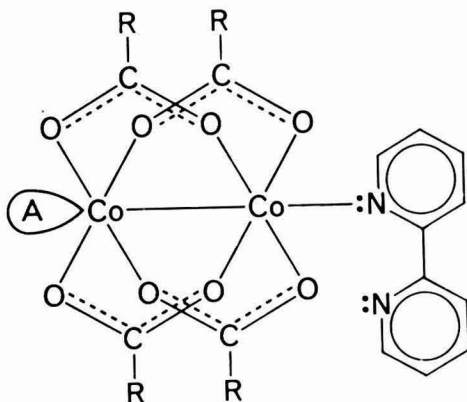


Fig. 3. Complex (II) formed by addition of one mole of 2,2'bipyridyl to (I)

A represents empty d_{z^2} orbital available on only one cobalt atom

If two moles of 2,2'-bipyridyl are added to (I) the ligand field is probably strong enough to break up the dimer. In this case, the complex obtained will be monomeric with respect to cobalt and the latter will be chelated by 2,2'-bipyridyl, as shown in Fig. 4.

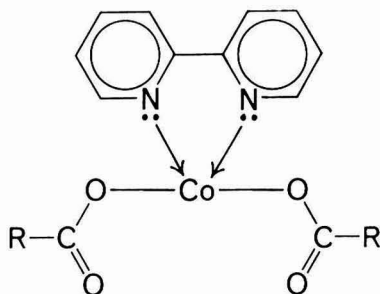
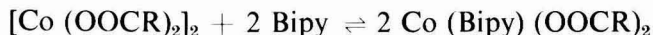


Fig. 4. Complex (III) formed by addition of two moles of 2,2'-bipyridyl to (I)

It may be complex (III) which is responsible for the initial high activity found when complex B is added to the polyol/isocyanate mixture. Complex (III) is smaller than the complexes represented by structures (I) and (II), so that steric hindrance is less. Also, in the case of (III) 2,2'-bipyridyl energises the cobalt, probably facilitating interaction with isocyanates and polyols. After only one month the activity of complex B was lost. It was even less active than cobalt 2-ethylhexanoate. It appeared that complex B could no longer have structure (III).

An analogous result was obtained in work carried out in unsaturated polyesters. The drastic change in storage stability was attributed to the weak interaction of 2,2'-bipyridyl with the polyester, so that the equilibrium below was weighted to the left:



Each bipyridyl ligand then interacted with the d_z^2 orbitals on each cobalt atom in the dimer (I) giving the dimer complex (IV) (see Fig. 5).

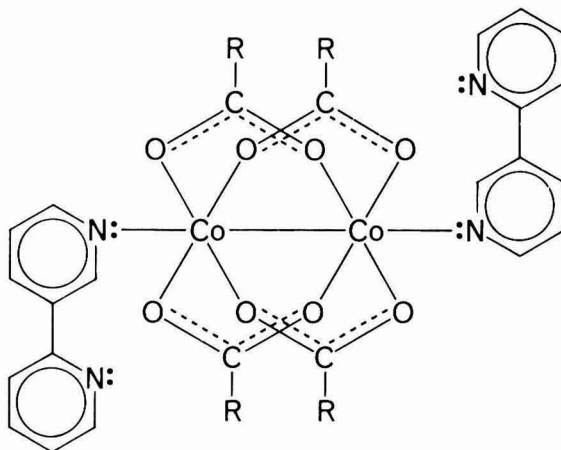
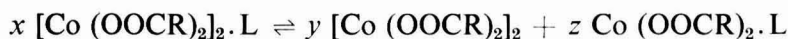


Fig. 5. Complex (IV)

Complex (IV) is not an accelerator for unsaturated polyester resins, because the same orbital responsible for interaction with organic peroxides is taken up in co-ordinate bonding with a nitrogen atom.

If 2,2'-bipyridyl interacts in a similar way with isocyanate or polyol then the equilibrium above will again lie to the left, resulting in formation of complex IV. If this is the case, it would again appear that the condition for accelerator activity is that d_z^2 orbitals in the dimer structure (I) must be empty to allow interaction with isocyanate and polyols. If both orbitals on a dimer structure are blocked by a ligand, such as 2,2'-bipyridyl, then the complex cannot behave as an accelerator. This is observed to happen in practice.

The behaviour of complex A (represented by structure II) is anomalous. As one d_z^2 orbital in the dimer structure is blocked by a ligand, it would be expected that complex A would be half as active as cobalt 2-ethylhexanoate. In fact it is more reactive. In addition it has good storage stability. It may be possible that complex A stored in a polyol solution consists of an equilibrium mixture of dimer (I), dimer (II) and monomer (III), so that its higher than expected activity comes from the chelated monomer component.



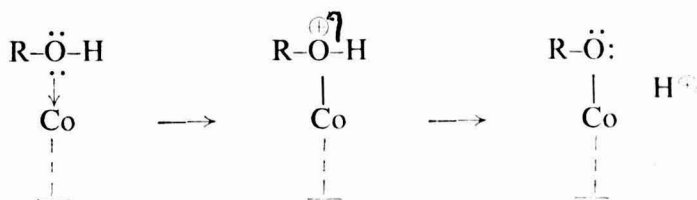
This behaviour is not found to occur in unsaturated polyester resins. Complex A is half as reactive as cobalt 2-ethylhexanoate.

Postulated mechanism of acceleration of the urethane reaction by cobalt systems in two-pack polyurethanes

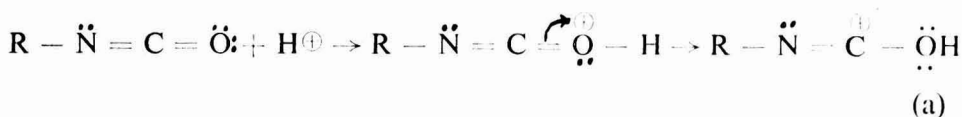
Pronina⁵ has already shown that cobalt octanoate forms complexes with butanol and phenyl isocyanate which interact to form a urethane. Britain and Gemeinhardt² and also Smith³ explain activity of organometallic compounds as accelerators by co-ordination of metal with isocyanate and alcohol. The results of this work also indicate that metals co-ordinate with isocyanate and polyol, facilitating the urethane reaction.

Proposed mechanisms

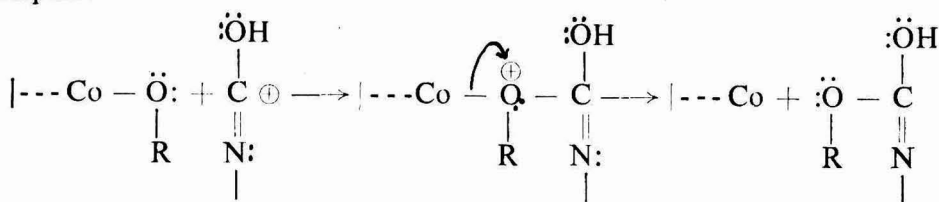
Alcohol as donor: Only one cobalt atom of the dimer is considered at a time and if the dimer is represented by $\text{Co} \text{---} \text{---} |$, then



The oxygen atom in a hydroxyl group donates an electron pair into an empty d_z^2 orbital of cobalt 2-ethylhexanoate, followed by the release of a proton which immediately reacts with isocyanate:

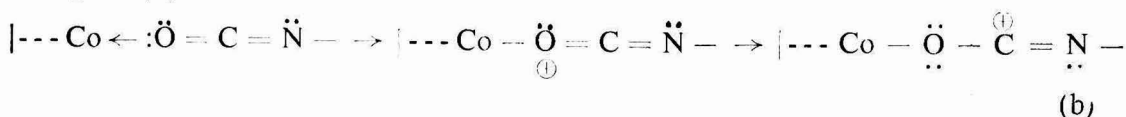


The electrophile (a) generated immediately interacts with the alkoxy cobalt complex:

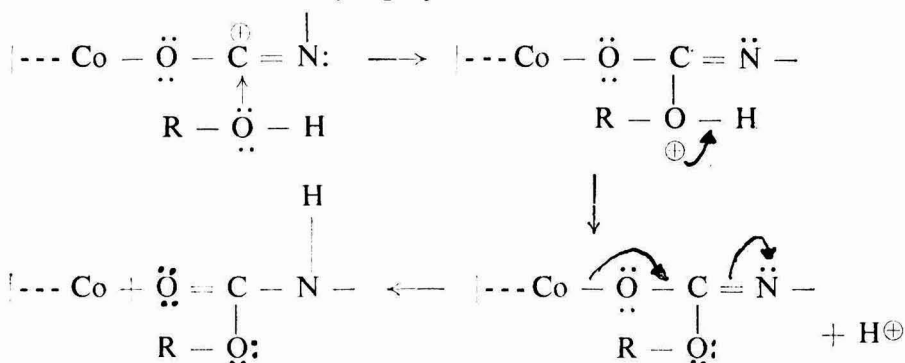


resulting in production of the "enol" form of a urethane.

Isocyanate as donor: Isocyanate interacts with a cobalt atom generating electrophile (b).



This offers a site for attack by a polyol.



The polyol oxygen probably interacts with the electrophile (b) generating a proton as shown. This attaches itself to the charged nitrogen atom produced as a result of the cobalt species dissociating itself from the adjacent oxygen atom. The result is a urethane.

The mechanisms postulated above indicate that in the case of cobalt 2-ethylhexanoate only one empty orbital on each cobalt atom is available for interaction with either polyol or isocyanate. If these orbitals are blocked by a ligand such as 2,2'-bipyridyl, cobalt 2-ethylhexanoate can no longer act as an accelerator. Evidence for this is that, on storage, complex B is less active than cobalt 2-ethylhexanoate owing to possible presence of structure IV.

Initially, complex B is probably monomeric with respect to cobalt (structure III). Gelation and drying times for a two-pack polyurethane containing monomeric complex B are shorter than for cobalt 2-ethylhexanoate, the reason being that the cobalt atom is activated towards isocyanate and polyol. As the dimer/monomer equilibrium shifts to the left with storage, so activity is lost completely.

Conclusion

It would appear that cobalt 2-ethylhexanoate systems behave in a similar way in both unsaturated polyesters and two-pack polyurethanes. A chelating agent such as 2,2'-bipyridyl will only initially chelate cobalt, thus activating it with respect to the urethane reaction. After only three weeks' storage the activity will be lost, probably owing to the cobalt 2-ethylhexanoate/bipyridyl complex taking up a structure which is dimeric and in which the orbitals responsible for interaction with polyols and isocyanates are blocked.

Acknowledgments

The authors would like to thank the Department of Chemistry and Polymer Technology, Polytechnic of the South Bank, for the provision of facilities to perform this work, and also the Science Research Council, which supplied a grant enabling the work to be carried out.

In addition, thanks are due to Dr W. M. Morgans who read and corrected this manuscript with such patience and also to Dr A. Lowe of ICI who offered technical advice.

[Received 1 March 1972]

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Next month's issue

The Honorary Editor has accepted the following papers for publication, and they are expected to appear in the October issue of the *Journal*.

"Some effects of the composition of lithographic printing inks," by J. R. Groom and K. Atkinson

"Investigations into coatings for weathered galvanised steel roofing," by C. Low and C. C. Vorster

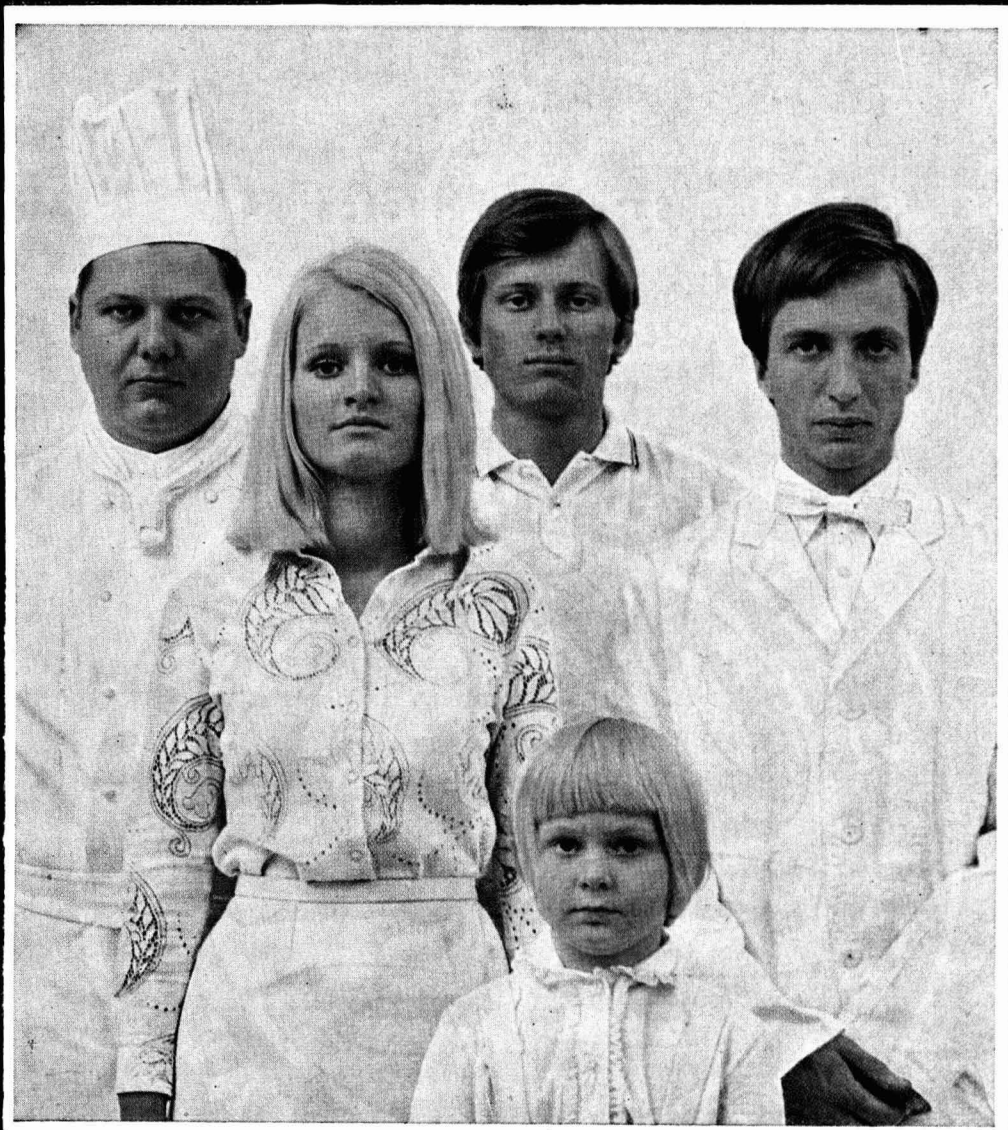
"The levelling of paint films," by M. Camina and D. M. Howell

"A new approach to the preparation of polyesters based on the glycidyl ester of a branched-chain acid," by G. Rossa

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Printex® 400	84	1,01	330	25	95	for decorative paints, carbon paper, gravure, flexo and rotary news inks
Printex® 30 *	90	0,91	400	27	78	for letterpress and offset inks of good colour
Printex® 300 ***	90	1,00	360	27	78	for rotary news inks
Printex® A *	94	0,73	300	41	46	for gravure and inexpensive letterpress and offset inks
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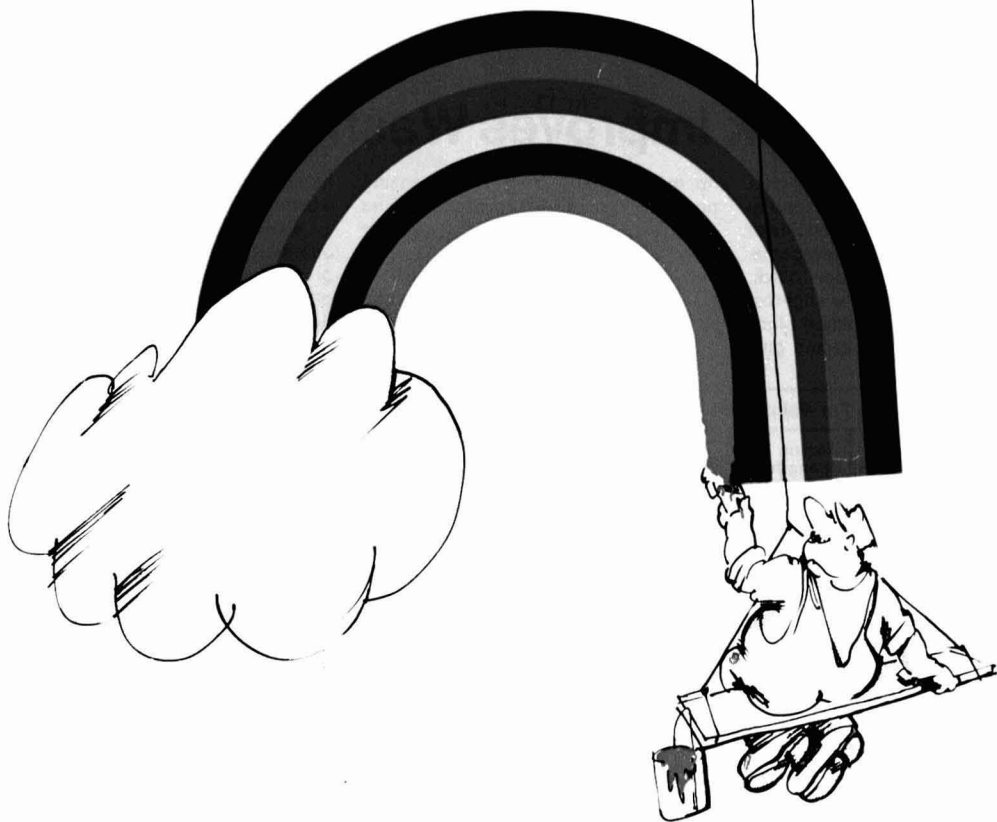
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Editorial

JOCCA to change size to A4

At a meeting of the Publications Committee in July, it was decided that, as from January 1973, the *Journal* will change its dimensions and format to the A4 size specified in the range of international paper sizes laid down by the International Organisation for Standardisation (ISO).

The *Journal* has retained its present size since its inception in 1918, and the decision of the Publications Committee to break with this long tradition was not made without a great deal of consideration. However, as a scientific publication recognised as one of the foremost in its field in the world, it seemed logical to the Committee that the *Journal* should support a scientifically based international standard such as the ISO paper system, particularly in the light of two important developments: its own recent decision to encourage, and eventually insist upon, the use of the ISO-approved system of units and nomenclature in all technical papers published in the *Journal* (see below), and the proposed entry of Great Britain into the European Economic Community, where the ISO paper sizes are used extensively.

The Committee decided to adopt A4 as opposed to the smaller A5 size because the larger format was considered to offer a cleaner, more readable layout with the maximum design flexibility.

The Publications Committee has taken this step believing it to be mutually beneficial to the author, the reader, and the advertiser; it should be emphasised that no change in editorial policy is envisaged.

SI Units

Readers are reminded that, as announced in the January 1972 issue, the Publications Committee has decided that SI Units will be used exclusively in the *Journal* as from January 1975. As explained in the April 1971 issue, SI Units have become recommended units in the *Journal*, but it was not felt appropriate to insist upon their use at that stage. As these units are being increasingly accepted, it is felt that by 1975 there will be little difficulty in taking this step, and authors are recommended to use SI Units where possible in all papers during the coming two-year period, so that a gradual phasing-in of the system can take place.

Correspondence

The theory and practice of dispersion

SIR—Dr Crowl has written an exceptionally fine article on dispersion in your May issue (*JOCCA*, 1972, 55, 388). I do not agree, however, with some of the conclusions reached in respect to the efficiency of utilisation of titanium dioxide in a series of commercial gloss paints and undercoats.

The light-scattering ability of titanium dioxide is a function of its volume concentration in the paint film. Consequently, the most "efficient" use of titanium dioxide possible, from a purely optical point of view, would be at an impractically low PVC for either of the types of finishes surveyed.

Cost is also generally a function of PVC, if total solids by volume are considered to be relatively constant. As a result, if efficiency were to be expressed in terms of the cost to develop a contrast ratio of 0.90, Dr Crowl might arrive at a different opinion as to the relative efficiency of these commercial coatings.

While titanium dioxide is the most expensive ingredient of a paint film on a volume basis, vehicle solids are the next most expensive, and extenders are the cheapest. Consequently, it is quite possible to replace vehicle solids with a combination of titanium dioxide and extender and to reduce cost while increasing titanium dioxide content. The result is of course an increase in PVC and a loss of efficiency in terms of hiding power per mg of pigment—but a gain in efficiency in terms of hiding power per unit of total cost.

I recently had occasion to compare a short series of gloss paints formulated at equal opacity, and found that the highest PVC formulation contained 27 per cent more titanium dioxide (at no increase in opacity!) but cost 11 per cent less, as compared to the lowest PVC in the series.

Perhaps, as an American, I place too high a value on relative cost, but I believe there would be small comfort anywhere in realising that one's product was performing at peak optical efficiency if it were also being undersold by a competitor.

It seems quite probable that composition, in terms of PVC and the amount of extender present, may have had more to do with the observed variations in titanium pigment "efficiency of utilisation" than dispersion.

Yours faithfully,

F. B. STIEG

*NL Industries Inc.,
Titanium Pigment Division,
100 Chevalier Avenue,
South Amboy,
NJ 08879, USA.
20 June 1972.*

SIR—In reply to Mr Stieg's comments on the inter-firm comparison of the utilisation efficiency of titanium dioxide pigments described in my paper, I appreciate his point that cost is more important than optical efficiency.

However, in UK practice there is not a large usage of extenders in gloss finishes, so that their cost is not a significant factor. With the undercoats, Mr Stieg's argument is more relevant. Unfortunately it was not considered economical to analyse the paints for their extender contents, and naturally this information was not disclosed by the manufacturers. To take an example, undercoats nos. 21 and 22 in Table 5 (p. 406) both had high non-volatile contents and lower TiO_2 contents, indicating a considerable usage of extenders; yet no. 21 showed up well in Table 7 (p. 407), while no. 22 was in fact the worst.

I find myself in partial agreement with Mr Stieg; unfortunately we had insufficient data to draw firm conclusions. It may be that Mr Stieg himself has data which could be published which would clarify this point.

Yours faithfully,

V. T. CROWL

*Paint Research Association,
Teddington, Middx.*

Reviews

THE APPLICATIONS OF SYNTHETIC RESIN EMULSIONS

BY H. WARSON. London: Ernest Benn Ltd., 1972, pp. xxiii + 1078. Price £20.00

The purpose of this far from inconsiderable volume of 1078 pages is threefold in that it is designed, within the field of polymer emulsions, to serve research chemists, technical personnel concerned with potential uses and, finally, technologists in the various applications industries. The objective is achieved by making free and extensive reference to technical, patent and trade literature and it would not be inaccurate to describe the book as a vast and certainly comprehensive review of the literature on the subject. One possible danger of this method of presentation lies in the fact that not all patents, not all technical papers and, dare it be suggested, not all trade formulations represent ideas which ultimately achieve commercial practicability. From this point of view, therefore, it is conceivable that an uncritical perusal of a section of unfamiliar technology could be somewhat misleading.

However, the author appears to be well enough aware of this situation. Not only does he make it clear that he is, in a sense, less concerned with practical processes than with how technologists have been thinking, but he also makes the understandable point that, in describing process requirements, he has not attempted to be authoritative on the grounds that it would be impossible for any one person to know sufficient of some twenty different industries to achieve anything like this status. At a quick check, the bulk of the references appear to be in the region of the 1960's. That few are later than 1968-69 is, no doubt, due to the fact that a book of this size must have been in print for some time, while a number of very early ones merit inclusion on historical grounds.

There are sixteen chapters in the book, the first six of these covering the more theoretical aspects of fundamental polymer chemistry, emulsions and emulsion polymerisation, polymer emulsion applications, polyester emulsions and non-vinyl emulsions. This section accounts for some 25 per cent of the text.

The remaining chapters deal with the more practical aspects of emulsions in the fields of adhesives, surface coatings generally, the formulation of emulsion paints, cross-linking and industrial finishes, textiles, paper, leather, polishes, the building industry and a variety of miscellaneous applications, concluding with a review of some newer developments, such as hydrosols and non-aqueous dispersions. Each subject is treated very thoroughly and there can be very little relevant published information which has not been incorporated.

Some indication of the detail with which the subject matter is treated is given by the fact that the list of contents alone runs to some ten pages. Those chapters dealing with surface coatings in general and with the formulation of emulsion paints and industrial finishes occupy fully 25 per cent of the volume—a fair indication not only of the thoroughness of their treatment, but also that of the subject matter in general. Full use is made of tables, diagrams and other illustrations and a number of chapters conclude with lists of relevant specifications and test methods, together with glossaries of terms used in the

respective industries. Oddly enough, for some of these latter definitions the reader is referred back to the preceding text.

Profuse use is made of cross-references within the text, a valuable feature which makes for easy amplification of information on specific points of interest without unnecessary searching in the index. The latter, running to some sixty pages, is as extensive as this part of a work of reference must be if it is to be exploited to the full. In this case, it appears to be fully adequate in scope and detail.

The technique of quoting from trade literature, with the inevitable use of ambiguous brand names, is always open to argument. As the author suggests, it can often prove to be a mine of information; but, on the other hand, it can involve reference to raw materials which are no longer available. Not infrequently, the method unavoidably fails to pinpoint accurately the fundamental principles involved. Reference to prices, particularly comparative US/UK ones, seem of doubtful value, although the intention is understandable. The fact is that those quoted are already out of date and will be even further so before a work of this magnitude is reprinted. In any case, in 1972 the UK prices really ought to have been decimalised.

A number of inconsistencies occur which are, perhaps, rather more annoying than serious. For example, both US and Imperial gallons are used as measures of volume; both microns and Å are used as units for the measurement of particle size; stokes and poises are used as units of viscosity; temperatures are quoted both in deg C and deg F, while occasionally, neither scale is indicated specifically.

Unhappily, the text is marred by a significant number of irritating minor errors. While many of these are typographical, some of them do tend to make for confusion or inaccuracy. For instance, the last two lines of p. 516 suggest that ". . . solvent is stripped off until pressure is reduced to a solids content of 30-35 per cent . . ."; on p. 54 there seems to be some uncertainty in reference to the HLB Value; the formula for polystyrene towards the bottom of p. 26 contains what is suspiciously like a trivalent carbon. The inclusion of a list of errata does something to adjust matters; but there does appear to be an error within this list itself for, although the correction indicated for line 31 of p. 426 is valid enough, the one for the following line 32 does not appear to have any relevance at all. It is most unfortunate that such errors should occur and, perhaps, even more surprising that they were not picked up in proof.

There is no doubt that this book is a massive achievement on the part of the author and that it represents many years of work. In its scope and detail it is not likely to be superseded for a long time and it is in this aspect that a great deal of its value lies. It is a valuable source of information in fields which are outwith the technologist's own sphere of operation and to this extent it is a reference book to which many will, no doubt, have recourse over the years. It is also massive in the strictly physical sense, to the degree that it would be permissible to speculate on just how well it may stand up to constant handling. When this size is considered in relation to a cost of £20.00, the book is not, however, likely to figure largely in the holiday reading lists of many technologists.

THE BOOK OF THE XI FATIPEC CONGRESS

Milan: Edizioni Ariminum Srl, 1972, pp. 682 + LX + 114. Price 25,000 lira. A report of the XI FATIPEC Congress appears elsewhere in this issue of the *Journal* and, other than to say that it contains, in full, the 10 plenary lectures and 76 general lectures presented at the Congress, there is little that can be added about this book. The Congress papers are contained in the first 682-page section, followed by advertisements, and the FATIPEC official yearbook for 1972, which is bound in as a 114-page supplement.

Originally prepared for delegates to Florence, the book is now available direct from the publishers, Edizioni Ariminum, Via Negroli 15, Milan, Italy.

Student Review

Paint Technology Manuals. Part Seven: Works Practice

Chapter IV. Paint manufacture

(Part III)

Tinting, filling, warehouse layout and maintenance

Tinting

It is seldom that a paint can be formulated and manufactured to produce precisely the required shade, without some final adjustment of the colour. This process of adjustment is generally known as tinting. The accuracy of colour matching required will depend upon the use to which the paint will be put and is most critical in the industrial field where articles are assembled from components made at different places and at different times. It is essential that the matching is accurately to the standard and there is no batch to batch variation.

The appearance of colour in a paint is due to the light which is reflected from its surfaces, from various levels within the film and sometimes from the substrate to which the film is attached. It is evident that only light which falls on the film can be reflected, for instance suppose a paint appears green when observed in natural daylight, it has this apparent colour because it is able to absorb any red light falling on it but does not absorb yellow and blue light to the same extent; light of these colours is reflected and the pattern appears green because the eye is able to integrate to a greater or lesser extent and average the light it receives from an observed object. If this same paint is illuminated by a pure red light, which contains no yellow or blue, these latter colours cannot be reflected and, since the red will be absorbed, the paint must appear to be black, or nearly so. This is, of course, an extreme example but it serves to illustrate the importance of the light source on the observed colour and consequently the necessity of standard lighting conditions for colour matching purposes. Where possible, natural north daylight is the preferred illumination and it should be realised that this can be influenced by neighbouring coloured surfaces from which reflection can occur, e.g. a bright red brick wall.

This brings up another problem; let it be supposed that two green paints have been prepared that are acceptable matches to each other under standard conditions of illumination. Let it also be assumed that the paints have each been prepared from two different sets of yellow and blue pigments. They appear to be the same colour with this illumination because the eye gives the same integrated average response to the two paints. Suppose that the two paints are now viewed in a different light, it is very unlikely that both yellow and both blue pigments will have similar curves of reflectance against wavelength, so that under the new lighting the eye will receive different distributions of wavelength of light from the two samples and the integrated average responses will differ. That is, the two paints will not only both differ in colour from the previous appearance, but they will no longer match each other. This effect is known as "metamerism."

A colour match to a standard under a given illumination may often be possible with a number of different pigment combinations but, in general, a non-metameric match to a standard, that is to say a match under varied lighting conditions, can only be obtained when identical pigments are present in the two samples. Thus, the formulation of a coloured paint must be laid down and maintained strictly if successive batches of it are to be non-metameric matches. This is important in articles such as filing cabinets, where the cabinet and the drawers may be painted at different times and with different batches of paint. A metameric match may give the same colours when illuminated with light equal to that in which the match was made, e.g. north daylight, but the colours of the two paints may appear very different at night under artificial light. The general subject of colour is discussed in Part 6 of these Manuals, "Pigments, dyestuffs and lakes" in Chapter 2, p. 30 and metamerism on p. 79 of the same part. Colour matching and metamerism are considered from the point of view of quality control in Part 5 "The testing of paints" pp. 52-60.

Slight differences in the degree of dispersion of the pigment and slight batch to batch differences in the colour strength of pigments make it difficult to manufacture paint to a close colour tolerance without some final adjustment of the shade.

Basically there is the choice of preparing a mill base whose colour is near to that required or to start with a base paint, say white, and to obtain an approximate match by the addition of suitable "tinters." These tinters may vary from concentrated pigment pastes to finished paints. The decision regarding whether to prepare the paint as a "self colour" or from a base by tinting generally depends on the quantity required, the particular colour and perhaps the urgency, since manufacture from tinters commences with already dispersed pigments. In general terms, it could be said that pastel shades and light colours are most conveniently made from a white base and tinters, whilst the darker colours are best made by dispersing a suitable blend of pigments.

Whichever method is used to prepare paint of the approximately correct colour, the basic formulation should be slightly deficient in strong pigments or pastes present in small quantities. Suppose some paint theoretically requires 95 per cent white and 5 per cent of say a blue pigment. If the original formula contains, say, 4.5 per cent of the blue, then only an addition of about 0.5 per cent blue would be needed in the final tinting. However, if the original formulation for some reason contained effectively 5.5 per cent of blue, an addition to increase the white to 104.5 per cent or an addition of 9.5 per cent white would be required to obtain the correct colour. Such an addition might involve a change to a larger container or the manufacture of more paint than required. The same consideration applies to the final tinting, or "shading" to bring the colour within the required degree of matching. If the colour is overshot by the addition of too much of a strong colour, large additions of the base colour will be required to reduce the shade. For the reasons explained under metamerism, the composition of a tinted paint must be laid down and the same tinters must be used for the final colour adjustment. There is a great temptation for even experienced colour matchers to add tinters which are not present in the basic formulation when making the final adjustments; such a

practice may have disastrous results with non-metameric matches and in some cases may adversely affect the light fastness of the paint on exposure.

The final colour matching stage may often take some time because more than one adjustment may have to be made and because possible flotation, flooding, discoloration due to driers etc. and possibly gloss effects when wet, require that a sample should be dry or stoved before its final colour can be judged. It is, therefore, generally advisable to discharge any mill in which the paint was prepared into a simple tank or container whilst the final colour adjustment is being made, so as not to hold up valuable equipment. Since small quantities of paste or liquid tinters may have to be added, thorough mixing is necessary, and it is practically essential that the tank or container should either be fitted with a mechanical stirrer or be used with a portable stirrer.

The mixing of finished paints with final adjustment made by tinter addition, probably gives the most convenient and flexible method of colour matching. However, as relatively large additions may have to be made, such tinting paints must contain driers where necessary. This introduces difficulties if skinning or other contamination during storage and continued use can occur, since the final paint being made will also become contaminated. Paste pigments contain only small amount of medium, and if only small amounts are used they can be prepared without driers and used as such without upsetting the drier balance of the paint to which they are added.

Straining and filling

Most of the products manufactured by the paint industry are sold by volume. There are, however, some which are sold by weight. Container sizes vary from 250ml to 205 litre drums. For industrial purposes there is also a demand for supply in bulk i.e. by road tanker and returnable tanks.

Supplies of paint to be containerised are housed in mobile vessels of from 100 to 1,000 litre capacity, or in static vessels, sometimes as large as 20,000 litres.

Immediately before it is to be tinned, the paint must be strained to eliminate foreign matter, gelatinous particles and skins. The latter cause the most trouble, and straining is much simplified if care is taken to prevent their formation during temporary storage and tinting processes. Various grades of fabric, such as muslin, mutton cloth, felt, nylon gauze, or wire sieves of different mesh made of copper, bronze or stainless steel, are used. The mesh may vary from 40 to 300. (300 mesh = 0.002 inch opening = 50 micron). Such materials, fitted to a ring and supported inside a funnel, are used for hand straining small batches of paint. The gauze, however, quickly becomes clogged with accumulated residues and throughput falls off; too vigorous scraping of the gauze can force unwanted material through or rupture the fabric.

Ideally the "cleaning up" should be mechanically linked to a filling machine, making the operation semi-, or fully, automatic.

There are many variations of filtering and straining and the main methods are given below.

Cartridge filters

For high quality industrial and domestic equipment and for automotive finishes, a cartridge type of filter is employed, giving filtration to 1 micron or below. The filter consists of phenol or urea bonded wool or polypropylene wound cylinders graded into various densities, see Fig. 33. The product is pumped through the cartridges with a bypass system and pressure gauge between the pump and filter. The pressure gauge indicates when the cartridge is blocked.

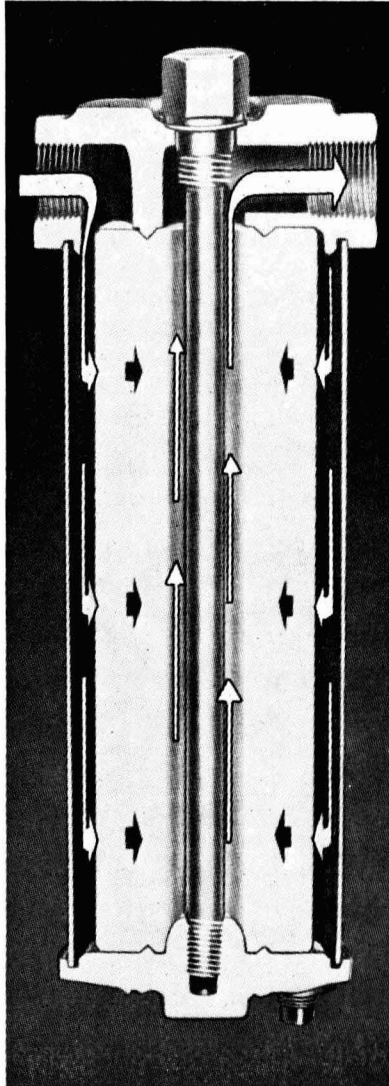


Fig. 33. Disposable cartridge filter (courtesy of AMF International Ltd.)

Rotary machines

Rotary, self cleaning, back washing, straining machines. This type of machine consists of a pumping unit which forces the product through nylon or metal

mesh sandwiched between two perforated strainer plates. A predetermined percentage of the cleaned up product is by-passed back through the strainer plates by means of a slowly rotating sector arm to keep the contaminated side of the mesh free of skins and other matter. The pumping unit is linked to the filling machine by float switch mechanism to enable a constant level in the hopper of the filling machine.

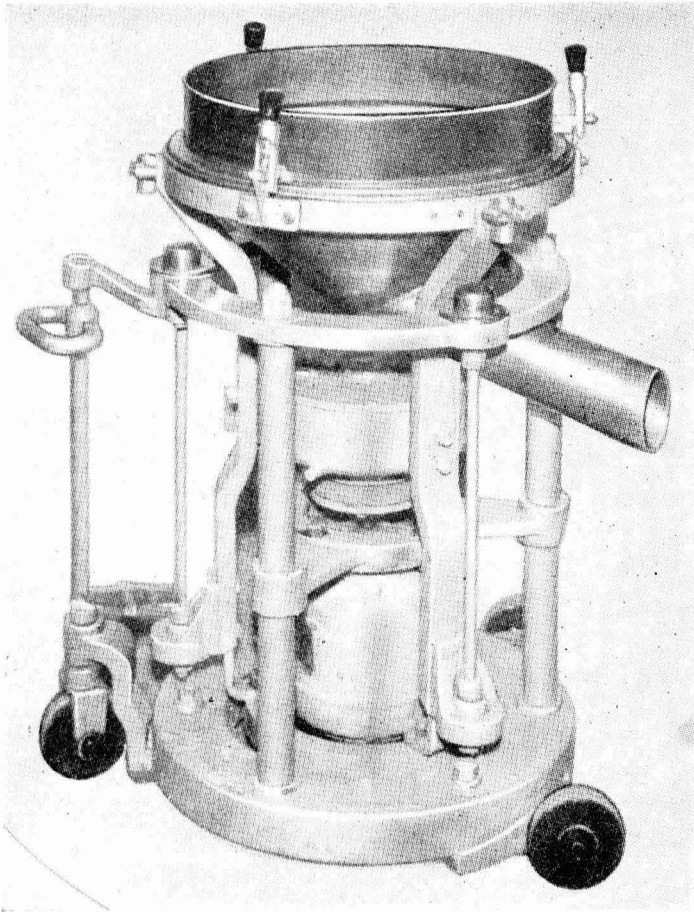


Fig. 34. Vibratory filter unit (courtesy of Russell Constructions Ltd.)

Vibratory sieves

Vibratory sieves consist of a funnel type feed hopper on which is mounted a relatively shallow tray with nylon or other mesh forming the bottom of the tray. The whole unit is constantly vibrated to ensure free movement of the product through the mesh into the hopper of the filling machine. The rapid vibratory action induces a turbulent action in the paint above the sieve with the result that contaminants are kept in suspension clear of the mesh. A typical machine of this type is shown in Fig. 34. This particular machine uses a variable speed vibratory sieve operating at frequencies from 1,000 to 3,000 per minute.

The sieves are made of nylon or metal, a mesh of 120 being considered suitable for undercoats and 300 for enamel paint. The vibrating sieve of the machine is built into a rigid structure mounted on trolley wheels; an electric motor attached to the frame drives the vibration generator unit through a flexible coupling. The sieving element is retained in the unit by manually operated quick release toggle clips and is quickly detachable for cleaning or exchange. Another machine of this type is shown in Fig. 35.

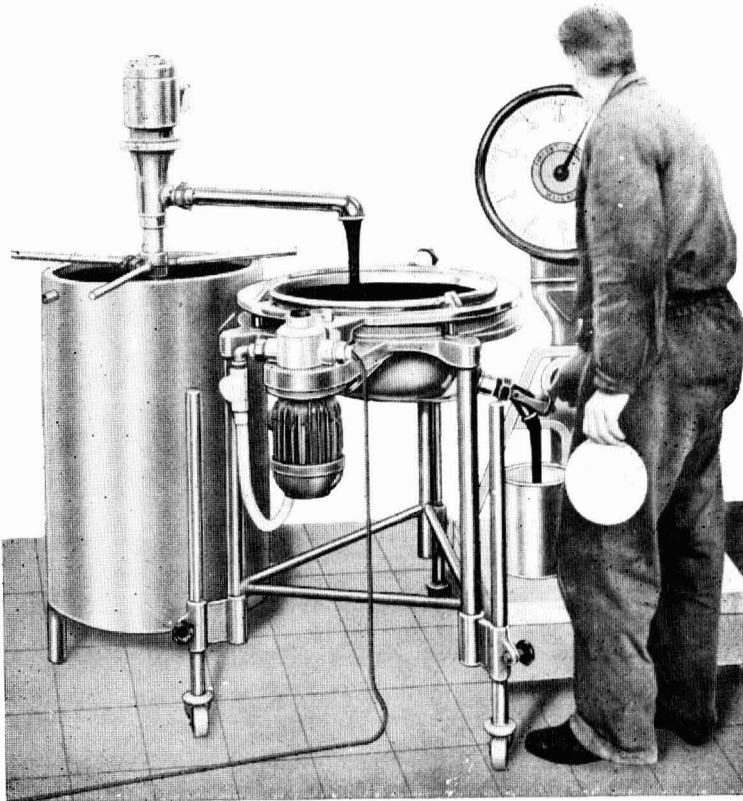


Fig. 35. "Vibrofiltro" vibratory filter unit (courtesy of G. J. Erlich Ltd.)

Strainer bags

For very small batches (100 litres and below) nylon, muslin or metal meshes can be fitted to funnels or small hoppers through which the contaminated product flows by gravity. A convenient method for this type of application is provided by the use of strainer bags fitted over the end of the paint delivery pipe through which the paint is gravity fed or pumped. The availability of synthetic fibres of considerable strength has extended the use of strainer bags, which are available to retain particles within the range of 5 to 100 microns. Fig. 36 shows an AFCO "snap ring" strainer bag. This type of strainer bag is fitted with a built-in flexible snap ring at the top, which holds the bag to an adapter head attached to the discharge pipe and will withstand pressure up to

1.25kg m⁻² (18 psi). Still higher pressures can be used if the strainer bag is supported by a stainless steel “restrainer.”

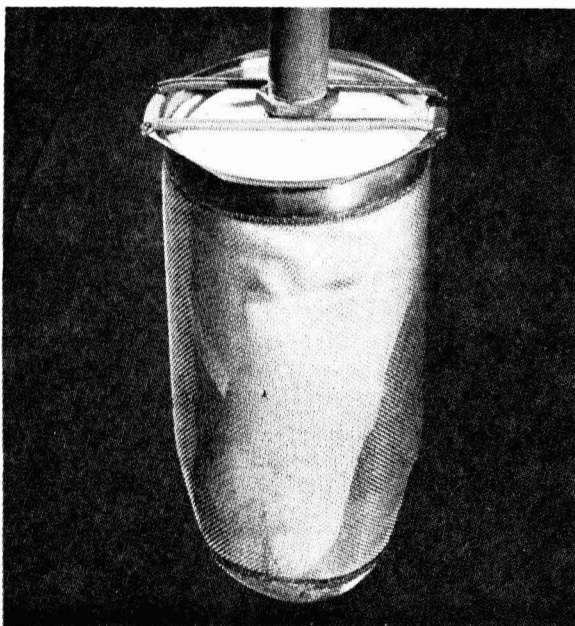


Fig. 36. Snap-ring strainer bag (courtesy of GAF Corporation)

Filling

Depending on the size and number of containers to be filled at any one time, it must be decided whether hand or machine filling will be employed; a generally accepted minimum for small semi-automatic filling is 100 litres in small packs or 200 litres in 5 litre containers.

Filling machines should always be easy to clean; hoppers must have radiused corners, pipelines should be as short as possible and with the minimum of elbows and unions. The various methods of filling are shown below.

Manual measurement

With liquids of low viscosity, the packages can be filled manually by using standard measures, which are supplied in various sizes. Before use they must be certified by the local Weights and Measures Inspectorate, and bear the appropriate approval stamp. The volume of liquid for which the measure is designed must also be stamped on it.

These measures generally have a truncated conical form, and are fitted at the upper end with a spill guard, so shaped as to act as a spout. A handle (or handles) is fitted to the side. The volume for which the instrument is designed is accurately measured when the liquid in it just reaches the upper rim. It must not be used at above normal atmospheric temperatures and must be cleaned and stored under good conditions. To maintain its accuracy, it must not be subjected to any treatment which may produce dents or leaks. If for any reason the measure loses its shape, it must be re-tested immediately. The volume which

it contains is that quantity of water which it would deliver, after having been filled from the dry condition to the upper rim and allowed to drain. Any liquid which has such a viscosity that it does not readily drain out of the vessel will not, therefore, be delivered in the stated quantity, so that the instrument is limited to liquids which drain quickly. Once the quantity is measured, no splashing may occur when introducing the liquid into the package and the measure must be drained. A funnel is necessary and it also must be allowed to drain.

Meters

An automatic method of rapidly filling containers to the required accuracy is by use of the type of meter adopted for the sale of petrol. Feed to the meter can be by gravity or by pump. In the latter case the pump must be arranged to have a spring-loaded by-pass valve of such dimensions as to ensure that high pressures are not developed when the valve is closed. Pump glands, delivery hose, if used, and any other fittings must be resistant to the solvent being delivered. Inspection and certification by the Weights and Measures authority are again required. In general, the equipment is satisfactory only for thinners; pigmented materials and varnishes would gradually produce deposits in the meter and so give rise to inaccurate delivery.

Volume measurement filling machines

For the filling of large numbers of packages with a product, either pigmented or varnish, filling machines are available which deliver an accurate quantity; usually they are limited to quantities of up to 5 litres. They are in the form of a cylinder and piston. Measurement takes place in the horizontal cylinder, the stroke of the piston and the diameter of the bore of the cylinder being such that the required quantity is delivered once the cylinder is completely filled. To vary the quantity delivered, the stroke of the piston is varied. The suction stroke refills the cylinder, and to ensure that this occurs at every stroke, the suction connection is taken from a delivery tank, the lowest point of which is at least three feet above the cylinder of the machine. On the upper surface of the cylinder, a slide valve is mounted. This changes suction to delivery and vice versa instantaneously at the end of each stroke. The product passes to a valve-head mounted over a conveyor on which the containers are moved into the filling position, delayed while the filling takes place, and then passed on to be fitted with lids. The valve head contains a flat valve plate controlled by a solenoid and spring. The solenoid is arranged to lift the plate during delivery of the product, and it is returned to the closed position by the spring immediately at the end of the pump stroke. The flat plate stops the flow by being pressed on to a seating, which consists of a flat disc containing a number of tapered holes. The small diameter of the holes is on the lower side, and the surface tension of the product is sufficient to prevent any drips forming during the closed period of the valve. Various seating discs are used, depending on the quantity to be filled; that for 2 to 5 litre deliveries has a large number of holes, and for small quantities (100 to 250ml) only a small number. Safety devices are incorporated to prevent the filling operation taking place when no tin is present, and to obviate damage if the several movements of the machine should not occur in correct sequence.

In operation, the machine is best fitted into a conveyor system for the supply of empty packages and, if possible, for the removal of filled ones. The product either flows or is pumped to the delivery tank, passing through a mesh or fabric filter to hold up any traces of skins or other contamination. The machine is operated with tins in position until all the air in the system has been removed. At this stage the amount of product in the packages is checked to see that the correct volume is being filled. If not, adjustments are made to the cylinder stroke. During the run, periodic checks must be made to see that no variations arise. The method of checking the volume delivered is important and is best carried out by introducing a container having known weight and of sufficient volume. When it has been filled, it is re-weighed. Using the specific gravity of the product, calculation will rapidly check the volume delivered.

It should be noted that this machine cannot be approved by the Weights and Measures Inspector as its delivery can be varied, but the weighing machine used for checking may be approved. The onus of correct volume, therefore, is in the hands of the company producing the material, but the advice of the Weights and Measures Inspectorate will be found most helpful.

Measurement by weight

To fill a given volume by weight, the specific gravity of the product must be known. From this, the weight of any volume can be calculated. The weight of an empty container is first ascertained and then the total weight involved can be fixed. The filling process is under manual or mechanically automatic control.

Manual method: This simple method involves the empty container being placed on an appropriate type of weighing machine. The weight of the empty container should be checked and the product is then allowed to flow into the package, the flow being slowed somewhat as the desired weight is approached. A spring-loaded valve for the control of the flow is extremely valuable. It is necessary to check the weight of the empty container because the weight of containers of the same capacity may vary, owing to variations in the gauge of metal used and the dimensions of the container itself. Certification of the weighing machine and weights for use with it are required by the Weights and Measures Inspectorate. The maintenance and cleanliness of the weighing machine and, in the case of counterweight machines of the set of weights belonging to the machine, are of the utmost importance. The material to be used can be supplied by gravity or pumped from the storage tanks; care should be taken that all components are resistant to the solvents being delivered, and if a pump is used, that it is fitted with an efficient relief valve.

Mechanical methods: The operations described above can be carried out mechanically if the weighing machine is fitted with a means of tripping the supply valve when the desired weight has been poured into the container. The tripping of the valve may be carried out by mechanical linkages or by an electrical device that uses a solenoid to hold the valve in the open position. In either case, the tank on the machine containing the material must be maintained at a constant level by means of a float valve. By this device the quantity of liquid that is flowing between the valve and the container, but which has not yet reached the container, is constant for each package. It follows that if, say,

1 kilo of material is to be poured into the package, the weights on the machine will not be 1 kilo plus the weight of the empty container, as a quantity will, in fact, flow between the valve and the surface of the material in the package, after the valve is shut, and allowance will be made for this. By this means an accurate quantity can be delivered.

Mechanical linkage: The valve in this case consists of a length of steel shaft, the lower end tapered to mate with a seating in the bottom of the machine tank. By means of a hand-operated ball-crank lever, the valve shaft can be raised from the seating and thus allow the liquid to flow into the package. The package is placed on one pan of a weighing system consisting of a series of levers, on one of which adjustable weights can slide and be fixed when adjusted to their correct position. On one of these levers, a trigger mechanism that releases the ball-crank lever controlling the valve shaft is mounted. When the correct weight of container and contents has been reached, the trigger mechanism allows the valve shaft to fall and thus cut off the flow of product. A further package is then placed on the pan, the valve raised and the operation repeated. By modifications in the design, two patterns are available; these fill either 5 litre or 5 to 25 litre drums. These machines, whilst extremely robust, are equipped with knife-edges, so that care must be taken in their operation, cleaning and maintenance. Certification is again not possible, and the onus is on the operating company to see that the contents are as stated; the advice of the local Inspectorate of Weights and Measures should be sought.

Electrical linkage: If the weighing mechanism is made to operate an electrical switch rather than a trigger mechanism, and the valve is held open by a solenoid, then the same cycles as described under mechanical linkage can take place. Two types of solenoid and valve systems are in use: the valve is opened against a spring by hand, is held open by a solenoid while the package is being filled, and is closed by the spring when the electrical circuit is broken by the switch on the weighing apparatus; or the solenoid opens the valve when the scale pan rises and allows it to close by a spring return when the scale pan falls. Whilst the second arrangement is faster than the first, some care is necessary, since once the electrical system is switched on, the scale pan must not be allowed to rise unless an empty package is in position on the pan. Manually, this can be achieved by pushing the filled container off the scale pan by one hand, at the same time exerting a downward force. Once a fresh empty container is in its correct position, the grip can be released, allowing the scale to rise and filling to commence. This method is more useful than the other for small packages. Certification is again not possible, but since the weighing system uses weights and itself is of normal construction, these parts of the mechanism can be inspected and checked.

The filling system can be made completely automatic, by fitting the machine into a conveyor system which allows the empty package to push the filled package from the scale pan, and makes allowance for the delay time in filling and then proceeds to repeat the operation.

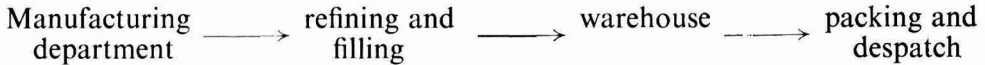
Variation in the weights of empty containers must be borne in mind. When carrying out the method manually, checking of the tare weight is possible, but when either of the two mechanical methods is adopted the only safe tare weight is the maximum weight of the containers. This can be obtained from

the package makers, or by carefully weighing a large number of the packages from several deliveries and ascertaining the maximum weight.

Warehouse, packing and despatch departments

Warehouse

The warehouse operates in close conjunction with the filling departments, most factories utilising a layout something like:



The function of the warehouse varies from factory to factory and may include: bulk storage; storage of filled containers or mixtures of these; decorative and/or industrial finishes.

Its general functions are summarised below.

It permits the prompt execution of orders, assembly of a mixed order and, in some instances, control of progress chasing.

The production units are allowed to plan their output in a manner which is economic and largely independent of day to day orders.

Control can be kept on stocks; lines which are not moving can be noted and the manufacturing departments' work planned accordingly.

In factories where a cost control system operates that is based on actual packed yield from batches, the receipts into stock provide an important part of the efficient running of such a system.

Finished products are not left in manufacturing departments, (after receiving laboratory clearance) since they move straight into the warehouse in bulk or in tins. This reduces risk of deterioration owing to skinning, evaporation, contamination or pilferage, and also helps to keep bulk containers in circulation. (In some factories bulk storage of finished material is by means of sealed tanks, the surface of the paint being covered with carbon dioxide).

The warehouse acts as a buffer between the occasional direct purchaser and the factory in some circumstances. Such purchases can constitute a problem, since in isolated areas local merchants, users and so on are liable to call in for some particular requirement with the intention of paying cash. Such service can be time consuming for production personnel and the warehouse staff can cope more readily with such requests, acting almost like a retail counter.

The actual cans or drums of materials stocked can be checked for such faults as leaking (owing to faulty soldering), badly fitting lids, rusting, and so on.

A separate section of the warehouse often looks after new unfilled containers, as some manufacturers find that this facilitates stocking and so on; however, this particular point depends mainly on the factory in question.

Sectional metal shelving with wood facing is about the simplest and most efficient method of storing packed goods and, if the turnover is fairly large, then the warehouse needs equipping with its own materials handling plant, e.g. box type barrows or stillage trucks (the flat, open type can cause havoc owing to cans falling off when being moved), roller conveyors leading to despatch, or power operated trucks to perform the same task. A recent development

is the installation of sectional shelving fitted with rollers, the idea being to load on trays from one side and, as fresh trays are put on to the rack, they automatically push the previous tray forward, eliminating "dead" storage. If upwards storage is employed, safe and efficient means of reaching the highest point must be installed, and adequate lighting to enable easy vision is essential. The temperature of the warehouse should also receive some attention, since there are many products likely to be in store which can suffer damage if allowed to fluctuate too widely in temperature. Finally, a properly equipped office is necessary, since much of the warehouse keeper's task is clerical in nature.

Packing department

The function of this department is to pack orders in suitable outer containers ready for despatch either to depots or customers.

Small items such as tubes, tinlets etc. may be packed in cartons by the filling department into standard numbers (e.g. dozens) and it will be these cartons which count as units when packed. An order will be assembled by the warehouse and passed with the relevant documents to the packing department, so that a heterogeneous group of containers will arrive there; the packer will probably sort these into groups so that the maximum protection is given by the outer packaging with the minimum number of packages (crates, cartons, boxes etc.)

Obviously, it will be necessary for the despatch department to carry adequate stocks of all types of outer container, and sawdust, woodwool, paper shred or other types of absorbent packaging material. These two items constitute a space-consuming problem and a relatively high-fire risk. Machines for stapling cartons (which may well be power operated), for banding or wiring the outer containers with strapping material, and for stapling on labels etc. are three additional items of equipment which will be required. There may also be a small stencilling section where the outers are marked, and this could necessitate spray equipment, so it is clear that the packing department constitutes a "factory" in its own right. Adequate, easily cleaned benches of comfortable working height will be required, together with some sort of "holding" bay where an operator can keep a complete order whilst it is being packed. Handling equipment will also be necessary and this may comprise anything from the ubiquitous sack barrow or fork-lift truck to conveyors of the gravity or power-operated type; this apparatus will take the packages on into the despatch department. Hammers, nails, pincers, saws etc. will be required if wooden cases are employed, as well as various sizes and types of brown paper for case lining (e.g. export packing generally employs bituminised brown paper).

Reference has been made to the probable use of sawdust as the outer absorbent packing material, and it is worth noting that this can cause quite a problem to the customer—it gets into the rim round the top of a tin, is extremely difficult to remove and results in complaints about "bits" in the product. Putting the tins into bags (paper, polythene, pvc) and twisting the neck of the bag tightly will practically eliminate the "bits" problem, but it does introduce an extra packing operation and necessitates carrying an adequate stock of various-sized bags.

Despatch department

Working in close conjunction with the warehouse, this department merits extra care, since it is here that a factory's reputation is often assessed by a customer.

The department's tasks are:

despatch of goods,

packing of these in a suitable manner,

loading of transport with the packed goods, and

recording of all despatches.

Examination of these sub-headings reveals quite a complex story.

Despatch: This necessitates an intimate knowledge of the best method of sending goods to their destination; it may be by direct (i.e. factory's own) road transport, sub-contracting road transport, rail, or water, if consignment is to the home country. If goods are for export, it is necessary to decide which route is the quickest and most economic to the country involved, including the best port for shipping, the best route to that port, the necessary documentation for the ship's master to accept the goods, the date of sailing and so on. The order office will be involved in this system, but the despatch department must be familiar with these points.

Packing: The department has to decide whether the goods will be packed in cartons, open trays or sealed cases; how many tins (or how much weight) for each parcel, what protective packing is called for inside a sealed case or carton and what markings have to be stencilled on these so that customers (or customs in case of export) can identify the goods quickly against the documents referred to above. Also, it must calculate how many packages are needed to complete an order and, from this, what total volume of shipping space or tonnage has to be booked for that order, as well as what type of transport is needed directly at the factory for taking the order away. From this latter the number of cases needed from case stores or case suppliers must be calculated so that the order is not delayed whilst these have to be made. One other point to be remembered here is that of labelling the cases; has the information for proper markings been obtained from the shippers (these are the means for easily identifying goods at port of arrival) and has time been allowed for the time-consuming task of putting the markings on?

Loading: Loading of packed goods on site does not present a great problem, the main consideration being a physical one. Cartons and cases may need lifting on to lorries, and this could require hoisting apparatus or fork-lift trucks to move to the point of loading. The ideal method is to design the despatch department with a loading bay, the level of which allows a lorry to back up to it so that the tail board just falls in line with the loading floor. If sealed railway trucks in railway sidings are employed, then the loading platform should be level with the opening on the truck side, thereby eliminating any need for lifting. The modern "freight liner" is very convenient for large loads to suitable destinations.

Typical factory lay-outs

Grouping of machines

Where many machines are employed, consideration must be given to their grouping and method of drive.

Modern machines, e.g. high-speed stirrers, sand mills etc. invariably have self-contained motors and, in consequence, line shafting is disappearing. Nevertheless, batches of roller mills or horizontal mixers may still be driven by the line shaft method and there is an obvious advantage in its use in areas where there are fire risks.

Table 5 summarises the advantages and disadvantages of the two methods.

Table 5

Advantages and disadvantages of line shaft and direct drive

	<i>Line shaft drive</i>	
<i>Advantages</i>		<i>Disadvantages</i>
One motor only needed for several machines. If flameproof conditions are required, can be situated outside danger zone. One set of starting devices. Capital outlay usually lower. The inertia of other machines sometimes helps to smooth the load when starting.		Shafting, striking gear, supports needed. Machines can only run parallel to shaft. Many different pulleys needed to obtain the various machine speeds required. Careless starting of the big motor can cause an overload charge. If motor burns out everything stops. A change in the layout is usually impossible. Inflexible—for overtime working of individual machines.
	<i>Direct drive</i>	
<i>Advantages</i>		<i>Disadvantages</i>
Neat layout, machines placed where and how required. Power to a machine only on when needed. Machines can be moved for layout rearrangement.		Capital outlay may be greater (individual switches, starters, and flameproof motors may be essential). Each motor is always rated above maximum load likely, therefore total load is higher. Geared motors necessary for low speeds. Some risk of damage to motors by knocks, spillage, etc.

Unit motorisation generally employs a multi vee-belt drive and this readily transfers nearly all the available power with very little "belt-slip." Flat belting is affected by weather changes (it stretches or shrinks) and this can prove a time-wasting factor in several ways—belts breaking, belts slipping badly, and belts riding off the drive pulley; rubberised flat belting is more satisfactory than flat leather belting with respect to its resistance to climatic changes, and although it is more expensive to install, the additional cost is soon recovered by time saved in avoiding the difficulties described above. The power transmission factor of belting is worth mentioning; belts of the same width but of different materials will transmit quite different amounts of power from a master drive, and this is a point worth bearing in mind when long lengths of flat belt are used.

Having decided on the individual machines to be used in a given production department, the next step is to set them out in groups, e.g. premixing, grinding, thinning, tinting, so as to give ready access to raw materials and easy disposal of the finished paint. Machine capacity, i.e. size and output, should be considered in the light of the desired volume of production; the inter-relationships of machine capacities of premixers, grinding machines and the sizes of finishing, tinting and storage tanks must be carefully estimated.

The output yield of the grinding machine is a vital factor in the calculations; this varies widely for different products and in the initial planning it is advisable to allow some surplus capacity. Table 6, gives an approximate range of output for some different dispersing machines.

Table 6
Broad comparison of output from different dispersing machines

	Decorative undercoat finished Litres	Decorative gloss coat finished Litres	Industrial enamel finished Litres
3-roll 13in × 32in, per hour	300—720	80—100	140—240
Pebble mill 1000 litres, per shift	600—1,000	800—2,000	600—1,700
Ball mill, steel 1200 litres, per shift	1,200—1,400	1,600—2,200	1,200—1,900
Sand mill No. 8, per hour	320	180—300	200—300

Typical plant lay-out

Table 7 shows which machines are generally used to make specific paints; the layouts will vary from type to type.

Table 7
Typical machine usage

Product	Machines used	Ancillary machines required
Gloss finishes	Single-roll machine Ball mill Triple-roll machine Sand mill	Premixer and final mixer Final mixer Premixer and final mixer Premixer and final mixer
Undercoats	Single-roll machine Ball mill High-speed cavitation mixer	Premixer and final mixer Final mixer Probably none
Eggshell finishes	Single-roll machine Ball mill	Premixer and final mixer Final mixer

*Table 7—cont.**Typical machine usage*

Product	Machines used	Ancillary machines required
Industrial finishes	Ball mill Sand mill	Final mixer Premixer and final mixer
Cellulose and similar high volatility finishes	High-speed cavitation mixer (selected pigments) Ball mill Sealed sand mill	Probably none Final mixer Premixer and final mixer
Emulsion paints	Ball mill High-speed cavitation mixer Kady	Final mixer Probably none Probably none
Tinters in paste form	Triple-roll mill Single-roll mill Colloid mill	Premixer and final mixer Premixer and final mixer Probably none

Enamel paints and undercoats

(a) Utilising horizontal mixers and triple-roll mills. (see Fig. 37)

The horizontal mixers could be replaced by one change pan heavy duty mixer and the triple-roll mill by a single-roll mill.

(b) Utilising sand mill equipment on one floor. (see Fig. 38)

Temporary storage, tinting, straining and filling on floor below.

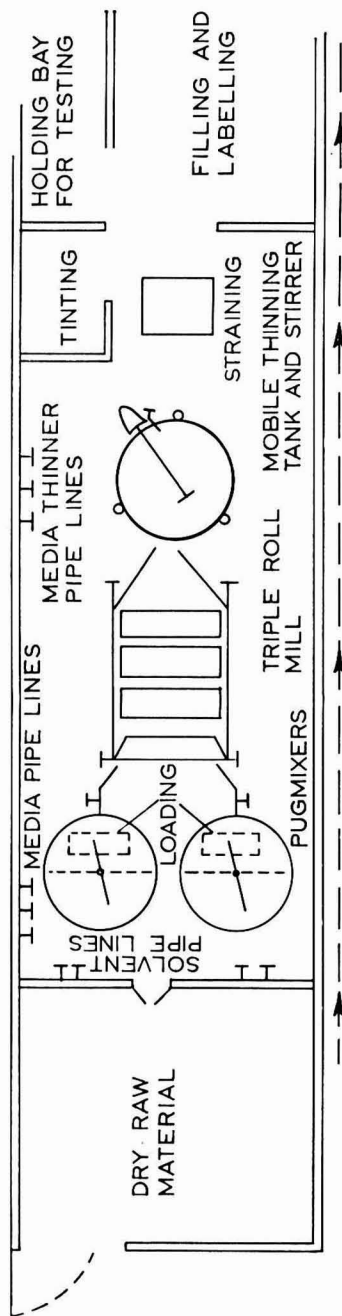


Fig. 37. Typical enamel paint plant using horizontal mixers and triple-roll mills. If a mezzanine floor or a multi-storey factory is employed, gravity discharge is utilised with stores/premixers at highest point

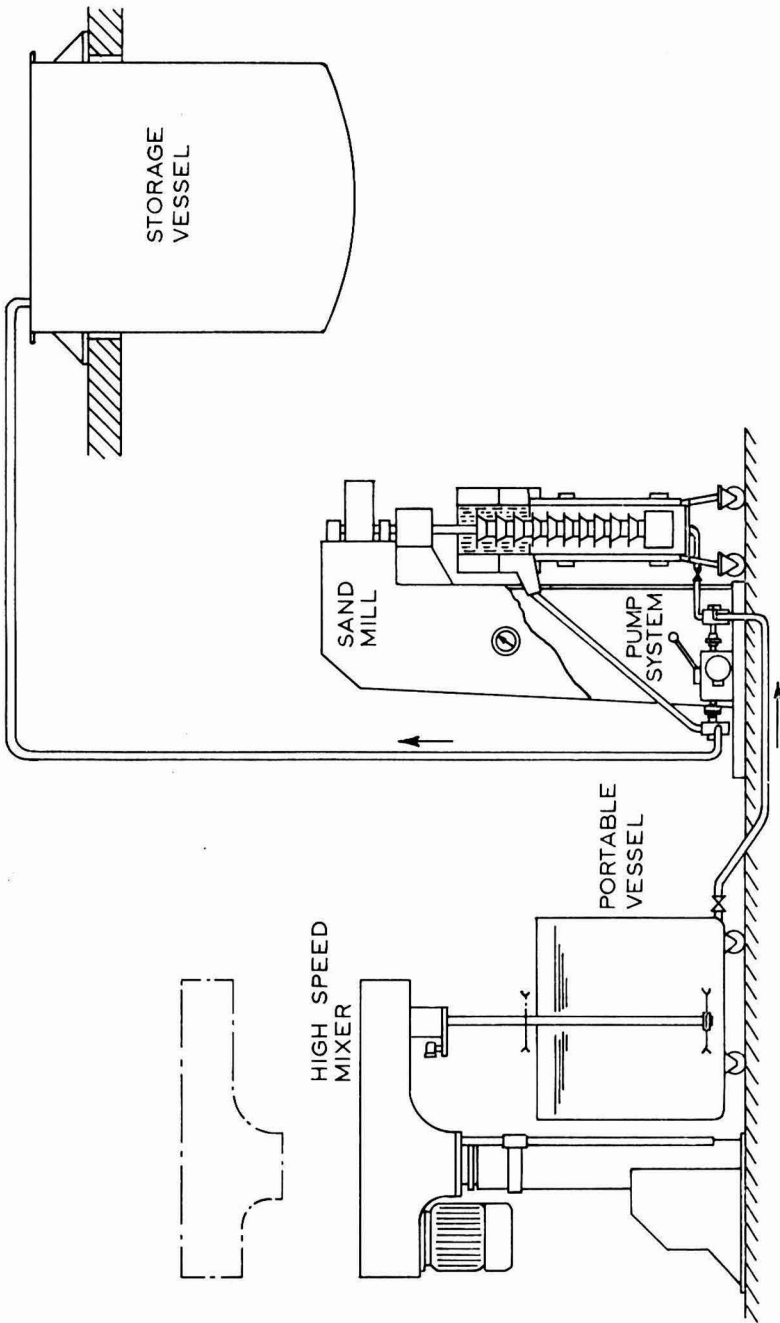


Fig. 38. Typical enclosed sand mill layout, pumping to storage tank on lower floor (courtesy of DH Industries Ltd.)

Emulsion paint (see Fig. 39)

This scheme may be adapted to single-storey buildings but two or three storeys are preferable.

Pigment dispersion may be carried out in:
 high-speed cavitation mixer,
 Kady mill or
 ball mill.

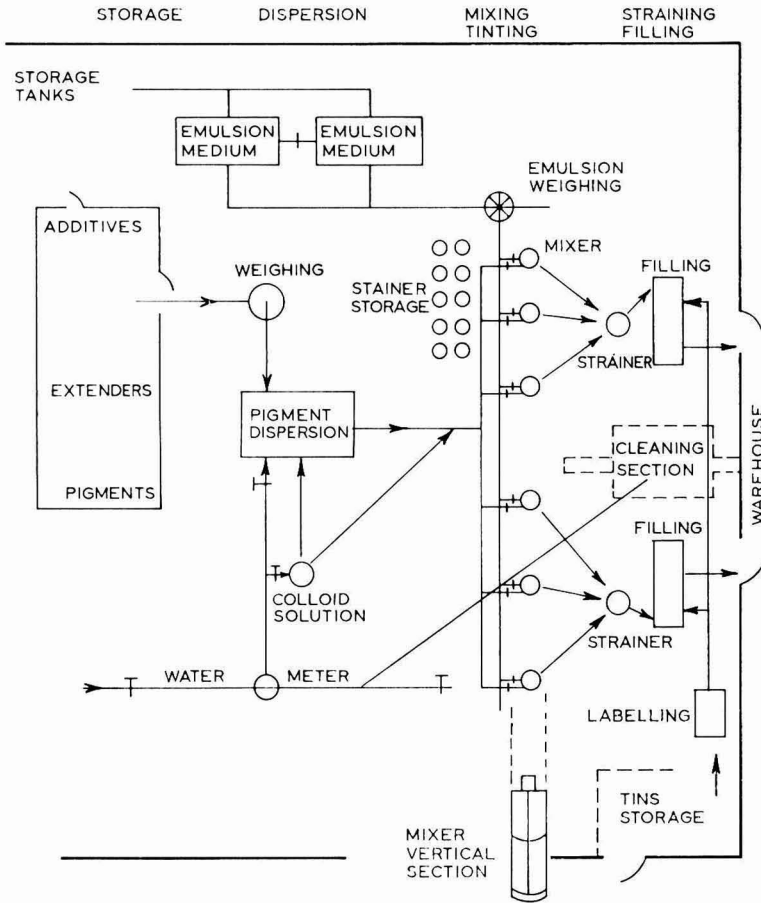


Fig. 39. Typical emulsion paint plant

It may be noted here that filling machines for emulsion paint must be of the weight-operated type, because foam may be present, which leads to a reduced volume of paint when the foam has broken.

The cleaning section should be provided with channels in the floor to permit flushing down and carrying the wash water to sumps outside the building, where the effluent must undergo settlement and other treatment before discharge into the sewers. (See also Chapter 1, *Paint Technology Manual Part 7. JOCCA, 1972, 55, 67.*)

Cellulose paints (see Fig. 40)

The plant is designed for the production of clear lacquers, pigmented lacquers, primers, primer-surfacers, stoppers and thinners. Owing to the highly inflammable nature of ingredients and products, a single-storey building is adopted. The materials throughout, with a roof of light construction in case of explosion. Provision of mezzanine floors in the manufacturing sections will assist in loading and discharge of mixers and ball mills.

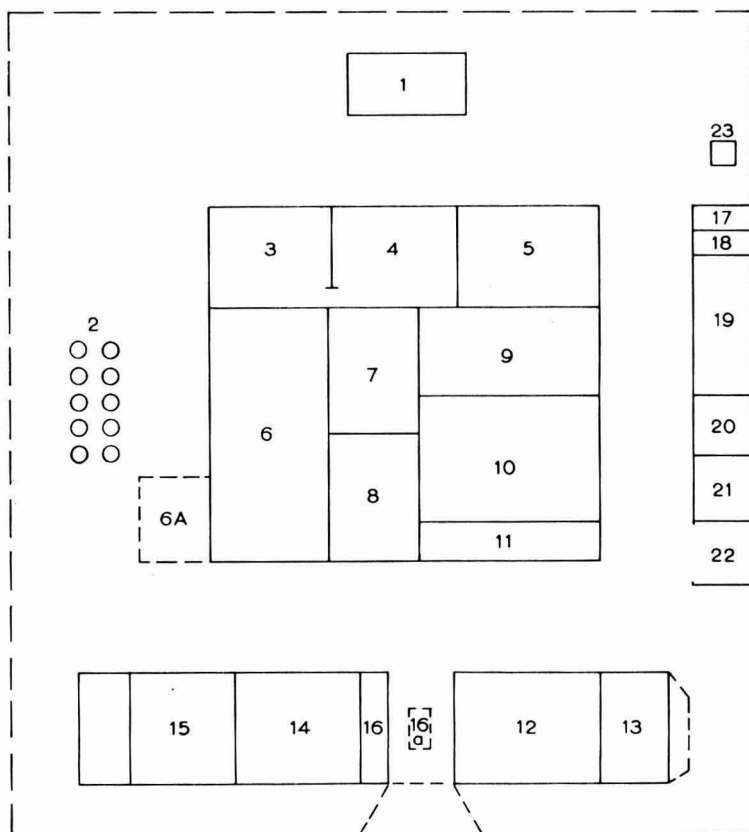


Fig. 40. Typical cellulose lacquer plant

(Adapted from *Paint, Oil and Colour Journal* "Answers to examination questions" 1954-55.)

KEY—1. Isolated building for storage of cellulose nitrate in original drums. 2. Bulk storage of solvents in underground tanks with pipelines to manufacturing sections 6, 7 and 10. 3. Storage of plasticisers and high-flash solvents in drums. 4. Storage of hard resins and alkyd resins in drums. 5. Pigment store with section for soluble dyes, if used. 6. Preparation of cellulose nitrate and resin-base solutions in paddle mixers or high-speed dissolvers. Mixers for preparation of clear lacquers and filter unit. Underground tanks for preparation of thinners. Filling of clear lacquers and thinners for warehouse. 6a. Alternative thinners bay. Where turnover of thinners is substantial, manufacture and filling in a separate bay is preferable to avoid interference with movement of materials in 6. 7. Storage of base media pumped from 6; alkyd resin solutions from resin plant or purchased. Pipelines to 6, 9 and 10. 8. Container store. 9. Milling section. Equipped with ball mills or sand mills for pigmented bases, primers, etc. Z-blade mixer for stoppers; triple-roll mill with premixer for pigment/plasticiser pastes, if required. 10. Enamel completion from pigmented bases prepared in 6. Alternatively, finishing enamels prepared in mixers from "chips" bought in or prepared in separate isolated building. Tinting. Section for "smalls". 11. Straining and filling. 12. Warehouse. 13. Packing and despatch with covered loading bay. 14. Offices. 15. Laboratories and spray booth. 16. Gate house. 16a. Weighbridge for tankers. 17. Toilets. 18. Boiler house. 19. Engineering shop. Vehicle maintenance. 20. Fire station. 21. First aid room. 22. Covered park for delivery vehicles. 23. Waste incinerator.

In the construction and running of the plant, the provisions of the Cellulose Regulations and the Petroleum Acts must be observed. (See Chapter 6, Legal Requirements)

The following safety precautions are emphasised.

All electrical equipment must be flameproof. Switches and fuse boxes are located outside manufacturing and storage sections.

All machines, tanks, mixers must be "earthed" to guard against build up of static charges.

All tools must be constructed of non-ferrous materials.

Provision must be made for forced ventilation in manufacturing sections to prevent build up of solvent vapour. High level and low level ventilation must be provided in the warehouse.

A safe form of heating is required, e.g. hot-water pipes from isolated boiler house. Alternatively, hot-air heating can be combined with forced ventilation.

Sections 6, 7, 9, 10, 11 and 12 require well floor construction.

Fire-fighting equipment capable of dealing with solvent fires must be available in all sections: either automatic sprinklers, or carbon dioxide equipment in more vulnerable sections.

Manufacturing and storage sections must have at least two independent exits.

Connecting doors between sections must be self closing and constructed of fire-resisting material.

Maintenance

Maintenance is an extremely important part of a works management's responsibility, and its object is threefold:

- to obtain maximum efficiency and life from machinery (ensures also minimal losses and delays in production);
- to assist in minimising accidents;
- to keep buildings and their purlieus in proper condition.

It can be seen from these points that the scope of maintenance is very wide and with labour/material costs rising rapidly over the last decade it has become a significant financial charge on the works cost. This fact has given rise to an attempt by many managers to operate a system of planned maintenance, and does not apply only to a large unit with full-time maintenance staff—even a small factory can usefully employ some form of maintenance planning.

The crux of the matter is a sensible approach to the whole problem, which requires a knowledge of the particular factory and its plant, together with a realistic appraisal of what will "pay off"; this means that to achieve maximum efficiency, some maintenance jobs will have to be carried out as frequently as every day (e.g. certain lubrications), whilst others may need only annual attention (e.g. examination of a gear box). Work specifically aimed at safety will be found in Chapter 7 and the following comments are directed at the other two factors only.

The keeping of maintenance records is well worth while; it is a little difficult to give a stereotyped form of card for this purpose but certain essential items can be recorded: machines and machine numbers in a register, with date installed; a brief summary of regular short-term jobs to be done; a report of any major examination with any replacements indicated and whether this work was done by the maker or maintenance staff. It should be realised that paint plant in general enjoys a long life when compared with that in, say, production engineering, so that information of this sort can prove extremely helpful at some future period.

Once the type of maintenance record has been decided, it will be necessary to consider exactly what will be involved in establishing a simple form of planned maintenance. The jobs to be tackled may be broken down into:

- inspection of building and equipment;
- servicing of buildings and equipment;
- repair of any obvious faults in both;
- elimination of any new risks which may arise;
- modification to improve factory efficiency.

These points depend upon one vital question: does the factory in question operate a system of "breakdown" maintenance or does it undertake scheduled maintenance? The difference between these two methods is simple; the former waits until something breaks down and then proceeds to put it right, whilst the latter aims at eliminating breakdown by regular overhaul.

It can be argued that no maintenance system will guarantee complete freedom from breakdown, even a brand new machine may well develop a serious fault, but it may safely be accepted that scheduled maintenance is a good investment; on the average, machines will suffer less from faults under such a system.

Scheduled maintenance on paint machinery presupposes that the machine will be available at the specified time and this may be achieved in one of three ways:

- examination and repair whilst a stand-by machine is used;
- performance of similar work during a holiday shut-down period;
- or
- during night time or during week-end.

Once again it becomes a question of deciding which method is best suited to the factory or department concerned. One point to remember is that week-end maintenance can prove expensive in labour costs since overtime rates will have to be paid.

To guide the student in these matters, Tables 8 and 9 are provided to give an idea of the factors to include when considering a planned maintenance programme; probably the most important thing is that management understands the requirements of the machinery involved; superficial knowledge can be very risky, and time spent studying a machine as it works and discussing it with the manufacturer will undoubtedly pay a high dividend in the ultimate success of the programme.

Table 8
Maintenance—general machinery checkpoints

Type of drive	Checkpoint
Lineshaft drive	<ol style="list-style-type: none"> 1. Drive pulleys are securely locked on shaft. 2. Loose pulleys are well lubricated. 3. Striking gear and safety locks function properly and quickly. 4. Driving belts centre on pulleys, fasteners are secure, belts are not slack, safety guards are in good order and in position. 5. Shaft plummet blocks are properly lubricated, drip feed oilers kept working. Any couplings in shaft are tight and supports remain firmly fixed.
Direct drive	<ol style="list-style-type: none"> 1. All electric wiring is as it should be (i.e. properly connected, encased, etc.). 2. Start and stop switches, automatic and hand rheostats, overload devices, working properly and showing no signs of overload. The fuse box covers, etc., are closed properly. 3. The motor itself is lubricated where necessary, and is firmly anchored; with ventilation holes clear of fluff, does not overheat when difficult job is being done. 4. Pulleys on armature shaft firmly fixed, no side slap on shaft, worn or slack vee belts.

Table 9
Maintenance—specific machines

Machine	Use	Power type	Speed type	Attend to
Heavy duty pug or Z blade mixer. May be h & c jacketed. May be variable speed	Mastics, adhesives, paste premixing pastes. Stoppers. High viscosity solutions	Heavy	Slow, c. 100rpm. Output fair	Tipping lock device. Crown wheel and pinion-gears bottom bearing; keying of blades. Outlet valve screw and seat
Portable stirrer	Premixing low viscosity bases and solution making. Blending and tinting low viscosity materials. Keeping such materials agitated	Usually driven by up to 1hp motor at high speed. Therefore low	1,400rpm, can be reduced to medium speed	Electrical connections and wire OK. Clamp OK. Tightness of shaft in bearing and impeller on shaft. Straightness of shaft. If impeller paddle removed it is replaced right way round
Heavy duty stirrer which moves up and down	As above but higher viscosities and large quantities. Aluminium paint	Medium—usually 2-5hp motor	As above	Counter weights and chain (or wire) suspending device is greased and OK and safety lock works. All fixing bolts and nuts are tight—as above except clamp

Table 9—cont.
Maintenance—specific machines

Machine	Use	Power type	Speed type	Attend to
Fixed, enclosed high speed mixer or emulsifier. May be h & c jacketed	Solutions of any viscosity. Emulsification. Paste and chip dispersion into media. Finishing off paint	50 gallon size needs 5hp	Impeller up to 7,000rpm	Driving belts (flat or vee) striking gear OK, i.e. slow advance works. Gland not weeping. Gearbox filled. Outlet valve not leaking. Impeller firm on shaft
Ball mill. Steel, porcelain or lined steel. Direct or cog driven. May be jacketed. Steel, pebble, or synthetic grinding balls	Volatile media grinding. Aqueous grinding. Low viscosity pastes and mill bases	Starting load high. Once running, low	Low	Driving belts not slipping. Cogs greased. Starting device 100%. Manhole clean and not leaking. Safety vent working. Ball charge is at right level. Lining not broken or badly worn
Roller mill. Triple, single	Pastes, mill bases, chips finishing after pugging. Occasionally refining after ball	High—about 3hp per 1ft of roller	Triple—slower than single. Output (dependent on viscosity) good	Cooling system is working. Scraper seats properly and is not worn or broken. Hopper clean and seats properly. All locking nuts, etc., are OK. Hydraulic system and gauges OK. Bars in multi are free. No belt slip
Edge runner	Water paints. Filler pastes	Low	Output may be low, dependent on size of trough	Wear on floor of trough checked by readjustment of roller. Scraper is tight fitting on wheel and also one on trough floor. Emptying gate is well greased. Wheel(s) tight on drive. Crown pinion OK
Colloid mill	Finishing premixed medium viscosity products and mill bases	Low	7,000rpm stone face. 12,000rpm stainless steel. Output good and can be varied at will	Stator plate and rotor are in good condition. All glands are liquid tight. Universal couplings are not worn or loose. Shaft bearings are in good order
Sand mill	As above	Low	Medium high, dependent on product, variable at will	Sieve is not perforated. Sand charge is at optimum. Pumps pumping OK. No leaky glands. Bearings oiled and in order

Table 9—cont.
Maintenance—specific machines

Machine	Use	Power type	Speed type	Attend to
Pumps	Movement of solvents, oils, solutions, paints, molten substances	Low	Wide range impeller, hydrovane, centrifugal, rotary, air-lift, piston, injection	Couplings and universal joints OK. Valves and glands do not weep. Inner parts and housing not pitted, scored, or worn. Stuffing boxes OK. <i>Pump not overworking</i>
Filter presses	Clarification varnishes, lacquers, solutions. Preparation pigment mash for drying	Pumps or compresses air and thus uses power, depending on: viscosity, type of filtrate, area of filtrant	Frame enclosed plate type, cartridge type	All seatings, pipework, clean, free from leaks. Plates assembled right way round. If filter aid used, right quantity, quality and mixture for job. Valves liquid tight, any pressure gauges accurate. Pumps as above
Centrifuge	Similar to above, omitting pigment manufacture. Some enamels	Starting load may be high. Low running costs	Machines are basically similar but speeds may vary 6,000-16,000 rpm. Output dependent on material viscosity, solids to be removed, size of machine	The centrifugal part is clean, properly balanced and suffering from no undue wear. Any gaskets washers inside not worn or broken. Lubricators not blocked. Fixing bolts all kept tight

No text has been printed on this page in order that reprints of the extracts from Part Seven of the Paint Technology Manuals may be run-on at the time of printing this issue of the Journal. It is intended at the end of the year to collate and bind these extracts and to offer them for sale. Registered students of the Association will be able to purchase one copy each at a considerably reduced rate.

Courses available 1972-73

Details of full and part-time courses on surface coatings technology have been received from the technical colleges, and are shown below for the convenience of Students. Attention is drawn to the new structure of the City & Guilds of London Institute certificates. The Paint Technicians Certificate has been discontinued; those students wishing to specialise in paint would now normally take the Chemical Technician's Certificate, choosing the paint techniques option at Part II, and the paint technology route at Part III for the Full Technological Certificate. Some colleges are continuing the Paint Technician's Certificate for those who have already commenced the course; alternatively, students may transfer to the new courses.

Students are reminded that some of the courses offered at these colleges will satisfy part of the basic requirements for entrance to the Association's new Professional Grade of Licentiate (of OCCA) in the Technology of Surface Coatings (LTSC). Full details of entry requirements are included in the regulations printed in the September 1971 issue; further copies are available from the Association's offices on request.

City of Birmingham Polytechnic

Science and Technology North Centre, Department of Science, Franchise Street, Birmingham B42 2SU.

City & Guilds Chemical Technician's Certificate, Part II—Paint techniques.

Post HNC course to LRIC (Polymer Chemistry—Surface Coatings).

A one-year part time course which will have a core of polymer chemistry, and offer options in "Surface coatings technology," or "The Technology of plastics and rubbers."

Enrolment for these courses will take place at the college on Tuesday 12, Wednesday 13 and Thursday 14 September; those requiring further information should contact Mr M. V. Osborne, Principal Lecturer in Chemistry, at the above address.

East Ham College of Technology

Department of Science, High Street South, East Ham, London E6 4ER.

City & Guilds Chemical Technicians Certificate Part I.

City & Guilds Chemical Technicians Certificate Part II—Paint techniques.

City & Guilds Chemical Technicians Certificate Part III—Paint technology leading to Full Technological Certificate.

City & Guilds Paint Technicians Certificate.

For students who have already started this course, the final year will be offered.

Post HNC course to LRIC (Applied Chemistry—Surface Coatings).

City & Guilds Paintmakers Certificate.

Modern pigments for surface coatings.

A course of six weekly lectures of an advanced nature, arranged in conjunction with the London Section, and concerned with the development, control and specialised application of modern pigments for surface coatings.

Essentials of paint technology.

A one-year part time course intended to introduce the principles of paint technology to representatives, office staff and other such personnel concerned in the industries.

Enrolment for all courses except "Modern pigments for surface coatings" will take place on Monday 11, Tuesday 12 and Thursday 14 September from 9.00 a.m. until 12 noon on each day. Applications for admission to the modern pigments course, for which a reduced course fee is available to Members of the Association, should be made by post to Mr S. W. Stuart, Head of Department of Science, at the college, to whom all enquiries regarding all other courses should also be directed.

Manchester Polytechnic—John Dalton Faculty of Technology

Department of Polymer Technology, Chester Street, Manchester M1 5GD.

City & Guilds Chemical Technicians Certificate Part III—Paint technology, leading to Full Technological Certificate.

Students wishing to take the paint option at the Part II level should enrol initially at a local technical college operating the Chemical Technicians Certificate Part II; the local colleges and the Polytechnic are working in conjunction in this case.

Certificate in Paint Technology.

It is anticipated that students not having the formal qualifications for admission to the City & Guilds Part III course may be accepted, subject to an interview, for similar studies in paint technology leading to a college certificate.

Post-HNC endorsement "Chemical technology with special reference to polymers and surface coatings" leading to LRIC.

Associateship of the Society of Dyers and Colourists—including Branch 5 paints, lacquers and printing inks.

Enrolment for the courses, with the exception of Chemical Technicians Certificate Part II, as noted above, will take place at the college Monday 11, Tuesday 12 and Wednesday 13 September over the periods 10.00 a.m.—12 noon, 2.00—4.00 p.m., and 6.00—8.00 p.m. Those requiring further information should contact Dr V. G. Bashford, Head of Department, at the above address.

Slough College of Technology

Department of Science, Wellington Street, Slough SL1 1YG.

City & Guilds Chemical Technicians Certificate Part I.

City & Guilds Chemical Technicians Certificate Part II—Paint techniques.

City & Guilds Chemical Technicians Certificate Part III—Paint technology.

Graduate RIC for Part I and Part II (grouped scheme) examinations.

This course does not specifically deal with surface coatings, but may be of interest to some students.

Enrolment will take place on Thursday 14 and Friday 15 September between the hours 10.00 a.m. and 8.00 p.m. Those requiring further information should contact Mr H. Bray, Principal Lecturer in Surface Coatings, at the above address.

Polytechnic of the South Bank

Department of Chemistry and Polymer Technology, Borough Road, London SE1 0AA.

Post-HNC endorsement course leading to LRIC (Polymer chemistry—surface coatings).

This course is also open to students who may not wish to take the examination but have sufficient knowledge of chemistry to benefit from the course.

BSc in Chemical Technology, with specialisation in surface coatings.

A four-year sandwich course including two six-month periods working in industry. Students may either be college-based or works sponsored. Entry requirements are based on either: five GCE 'O' level subjects, including chemistry and one other science subject at 'A' level; or HNC in chemistry or science at a good standard. Students are recommended to obtain full details of the requirements from the college.

Certificate of the Polytechnic in Surface Coatings.

A three-year part time course. Entry requirements are GCE 'A' level chemistry with suitable 'O' level passes, or ONC in chemistry. Preliminary courses for students not possessing these qualifications are available at nearby colleges by arrangement.

The college points out that, as well as the LTSC, the Certificate enables students to proceed to Licentiate of the Institute of Metal Finishing (LIMF), by taking additional examinations in "corrosion and metal finishing," and "electrochemistry and metallurgy," and to Associate membership of the Institution of Corrosion Technology (AMI.Corr.T), either by completion of further studies after LIMF, or by a supplementary course following the Certificate.

Enrolment for the part-time courses will take place on Tuesday 19 September between the hours 9.30—12 noon and 5.30—8.00 p.m. Those interested in the degree course should contact Dr B. E. Weller, Head of the Department of Chemistry and Polymer Technology, from whom full details of all courses are also available.

Information Received

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

A reciprocal agreement has been concluded between **Russell Finex Limited** and **Fuji Paudal Co. Ltd.** of Japan under which Russell Finex will distribute the Japanese company's mixing, kneading, extruding, spheronising and drying process equipment to the UK, Eire, Western Europe and the Near East on an exclusive basis.

In return, Fuji Paudal will distribute the Russell Finex range of sieving, straining, lifting and tipping machines throughout Japan, Taiwan and Korea.

Allied Chemical International SA has now issued full technical data on *Quindo Violet ERV 8088* and *SP Quindo Violet ERV 8096*, the two new pigments on which advance announcements were available at 24 OCCA.

A new water-based dispersing agent, coded *TS 1109*, has been developed by **Cole Polymers Ltd.** Specially designed to perform efficiently on a wide range of pigments and extenders, *TS 1109* is claimed to give very fast wetting of pigments, and to offer emulsion paint manufacturers and paper convertors the facility to prepare low viscosity, high solids pigment dispersions on both medium and high shear mixers.

John & E. Sturge Limited, which produces precipitated calcium carbonate for the paint and allied industries, has received the Queens Award for Technology in respect of another of its activities, the development and commissioning of a deep fermentation plant for the production of citric acid.

The latest in the series of collections of infra-red reference spectra to be published by **Sadtler Research Laboratories Inc.**, deals with chemicals used in coatings. The collection contains 300 spectra, recorded on a grating instrument over the range 4,000—200 cm^{-1} , covering a wide range of materials used in coatings. Each spectrum is labelled with the trade name of the product, the chemical description, physical data (when available), the source of the sample, instrumentation, and method of sample preparation.

Dynamit Nobel AG has issued new booklets on its products. The first deals with *Dynasil H 500*, a modified silicic ester, and its use in zinc rich coatings for corrosion protection, while the other describes the range of *Dynamit* titanium esters, and their use as additives for paint and plastics, and in surface treatment.

Copies of these booklets are available in the UK from **Berk Limited**.

Improvements in application properties and a 17 per cent increase in gloss values are claimed by **Blundell-Permoglaze Ltd.** for its reformulated water-based *Permura Glossy Vinyl*. The new formulation is said to give better flow and longer wet-edge time without loss of brushability, and to impart better scrub, wash and yellowing resistance to the dry film. The new material is described as having a slightly thixotropic consistency in the tin, which is easily broken down by brushing.

The 13th edition of the Gardner-Sward paint testing manual "Physical and chemical examination, paints, varnishes, lacquers and colours," has been published by the ATSM. **Gardner Laboratories Inc.** has been authorised to sell the new edition of the manual, and Gardner's UK representatives, **Wentworth Instruments Ltd.**, can supply it in this country.

Bayer AG has added two new products to its range of *Helio Fast Fine Pastes*. *Helio Fast Red ERT Fine Paste* is based on an anthraquinone pigment, and is claimed to offer good light fastness, weather resistance, and fastness to recoating, as well as lime soap resistance. It is intended as a low-priced grade complementing the dearer high quality pigment preparations. *Helio Fast Red Violet EBFT Fine Paste* is intended for use in the paint, wallpaper and aqueous flexographic printing ink fields, having a clear red violet tone. Weathering tests have indicated that the pigment is suitable for outdoor use in full shade or medium reductions.

A new range of mills suitable for use in the paint and printing ink industries is now offered by **Glen Creston**. Manufactured by **Willy A. Bachofen** of Switzerland, *Dyno-Mills* operate by a system of grinding discs operating in a horizontal container; it is said that a uniform distribution of the grinding process over the container is obtained, giving a narrow particle size distribution. The grinding chamber, which is completely enclosed and airtight, is double walled, allowing cooling or heating during grinding; the inner wall is available in stainless steel, glass or other materials, and the grinding discs can be supplied in stainless steel, rubber or plastic.

Fytelson and Associates is a consulting body set up in the United States. It consists of a group of chemists with advanced degrees in science, engineering and business studies. The staff is drawn from a wide variety of industries, and can offer experience in colour manufacture, dispersion and application for automotive finishes, paint, printing inks, plastics, synthetic fibres, textiles, paper, rubber and floor coverings. Services in research and development programming, pilot plant scaling up to production, product and process development and engineering, plant construction and starting up, market surveys and analysis, and technical sales, are offered.

A £400,000 extension of its Carshalton, Surrey plant has been completed by **Vinyl Products Limited**. The new plant will give a major increase in the company's polymer emulsion capacity, being capable of producing a wide range of emulsion types.

The extension took place in two stages: a reactor of about 12 tons capacity came on stream in 1971, and the second stage was completed in May, centring round a reactor with a capacity of 30 tons. Both facilities can produce emulsions of high, medium or low viscosity, and the larger reactor is fitted with an automatic heat transfer process developed by Vinyl that enables it to be used for even strongly exothermic polymerisation processes.

Vinyl Products states that this is the last major extension possible on its Carshalton site. The company has an agreement to use land forming part of the site of **Joseph Crosfield & Sons Ltd.**, at Warrington, Lancs, and has options on further land for subsequent expansion; construction of a new factory at Warrington is claimed later in the year.

The latest techno-economic-marketing study from **Skeist Laboratories Inc.** is entitled "Adhesives and Sealants, II." The study, which runs to 800 pages, has a price of \$6,000; copies of an eight-page brochure giving a full description are available from Skeist on request.

A new pigmented polyester filler, *Jaxapol*, has been introduced by **Sonneborn & Rieck Ltd.** Designed to fill the need for a high build primer filler that would give good performance when applied by conventional methods, *Jaxapol* can be applied to give coats of 0.015 in dry thickness, and, it is claimed, can be built up by cross coat methods to $\frac{1}{8}$ inch on vertical surfaces without sagging. It is suitable for use on

most metal, plastics and wooden substrates, covering surface irregularities in one operation, and is available in red, yellow, blue, green and grey.

Barter Trading Corporation Ltd. has recently been appointed sole UK agent for two European companies: **Intermedios Organicos SA**, of Spain, and **SA Bleu d'Outremer et Couleurs de Mont St. Amand**, of Belgium.

The "UK Chemical Industries Statistics Handbook 1972," has now been published by the **Chemical Industries Association**. A new addition is a section giving selected major statistics of the chemical industries of the EEC countries. Copies are available from the CIA at a price of £2.00 per copy for CIA members, and £4.00 per copy for non-members.

Five new colours have been added to the *Plus Two Silk Finish* vinyl emulsion range introduced by **Crown Paints** earlier this year. The new colours are Soft White, Seagull, Bermuda Blue, Ice Blue and Wild Lilac; the range now comprises 17 colours in all.

A new, fast-acting foam destroyer, *Antifoam 27*, is now offered by **Tristar Chemical Company** of Texas. A synergistic blend of organic chemicals, the new product is a water-dispersible liquid, and can be used in a wide variety of systems both to prevent foam formation and to kill existing foam.

Two of the companies attached to the **Bayer AG** group have recently announced plant expansion. **Sumitomo Bayer Urethane Co. Ltd.**, the Japanese company owned jointly by Bayer and **Sumitomo Chemical Co. Ltd.**, has started up a new plant for polyethers with a capacity of 10,000 tons per year. A wide range of products can be produced, for flexible, rigid, semi-rigid and integral skin foams, elastomers and surface coatings.

Mobay Chemical Company of the USA, a division of Bayer's New York **Baychem Corp.**, has completed the first stage of a new factory in Texas. The new facility will have capacity to produce 45,000 tons of toluene di-isocyanate per year, increasing Mobay's total TDI capacity to 90,000 tons per year.

Two new specialist resins have been developed by **Scado NV**. *Scadonal 46-X-60* is an air-drying or stoving resin with quick drying properties, suitable for primers and enamels. *Scadoform L34* is an epoxy-phenolic pre-condensate, recommended as an ideal binder for gold lacquers, in which it gives an acceptable dark gold colour without modification.

These resins and all others in the Scado range, are available in the UK by **Synthetic Resins Ltd.**, Scado's associate company within the Unilever group.

The **Paint Research Association** has recently published a select bibliography on powder coatings. Containing nearly 300 references, including many to patent literature, the bibliography is available from the PRA library at a cost of £1.00 per copy.

A lightweight polymeric pigment has been developed by **Dow Chemical USA**. The pigment, which was described in a paper given to the recent TAPPI annual conference, is intended for paper coatings, and is claimed to have less than 50 per cent of the density of Kaolin clay, with equivalent, or better, properties in respect of blue-white brightness, opacity, glucability and calendered gloss development.

Stanhope-Seta Limited has issued the catalogue of its petroleum test equipment for 1972, and will supply copies on request.

Scottish Section

Eastern Branch

Development in ink technology

The 4th Ordinary Meeting of the session was held in the Carlton Hotel, Edinburgh, on Tuesday 11 January, when Mr G. H. Hutchinson of A. B. Fleming & Co. Ltd. lectured on "Development in ink technology". This was a joint meeting with the BPBMA.

Mr Hutchinson discussed the mechanisms of the major methods of ink drying under the headings:

- penetration—news inks, cold web offset inks;
- evaporation—gravure, flexographic and heat set web offset inks;
- oxidation—letterpress and lithographic inks;
- precipitation—letterpress and dry offset inks;
- new methods—all processes.

Each method was described in detail with reference to the four major printing processes and with molecular models to amplify the description. It was emphasised that many inks dried by a combination of methods. For example, the newer quick-setting lithographic and letterpress inks set initially by penetration and finally cross-linked by oxidation to a tough hard-dry film.

Under the heading "new methods", Mr Hutchinson described the use of microwave and radio frequency radiation, electron beam curing and ultra-violet radiation for drying inks.

Microwave and radio frequency radiation were really a sophisticated method of heating in depth. Materials with a dipole moment were excited by this radiation and internal friction between molecules caused the material to heat up. Substances with large dipole moments, such as water, were the most responsive and therefore water-based inks for gravure and flexographic printing seemed to be the most promising application.

Electron beam curing was very much for the future, but ultra-violet curing was generating a lot of interest at the moment in the offset litho and letterpress fields. Here entirely new ink systems were used, based on reactive monomers and pre-polymers coupled with ultra-violet initiators. This method opened up the possibility of instantaneous drying with no by-products, thereby eliminating any pollution problems.

J.H.S.

Aerosols, past, present and future

The 5th Ordinary Meeting of the session was held in the Carlton Hotel, Edinburgh, on Wednesday 26 January, with Mr R. Webster in the chair. Mr D. Lake of DH Industries Ltd. spoke on "Aerosols, past, present and future".

Mr Lake began his talk by outlining the history of aerosols from the first attempts in 1899 to the 300 million units sold in 1970. In the early days, carbon dioxide was used as a propellant, but this did not have sufficient expansion and it was not until the advent of fluorohydrocarbons in the 1930's that aerosols became viable. During the Second World War, the Americans used vast quantities of bacteriocidal sprays working at a pressure of 70 p.s.i. This pressure required very strong containers and

it was not until DuPont developed aerosols working at 35-40 p.s.i. that they came on to the domestic market.

Two systems were in normal use: the two-phase system, where one phase is propellant gas and the other gas plus product. This was the most common type. In the second system there were three phases, propellant gas, liquid propellant, and product. In this type, pure product only was discharged.

The normal aerosol can was made of 10 thou thick steel, but aluminium and glass could be used.

There were three methods of filling aerosols; cold filling, in which the liquid product was filled at -10°C and the propellant at -35°C , was the most common. The other methods were pressure filling and undercup filling.

Finally, Mr Lake described the vast array of aerosol types available and demonstrated the use of the many variations he had brought with him.

J.H.S.

Thames Valley

Powder coatings

The final meeting of the winter session of Thames Valley Section was held at the Beech Tree Hotel, Beaconsfield, on Thursday 23 March, when Dr Brussman of BASF, Ludwigshafen, gave a lecture on "Powder coatings".

He began by indicating some of the advantages of using powder coatings—reduction in atmospheric pollution and avoidance of unpleasant odours; reduced fire risk owing to absence of organic solvents; wide range of film thickness from single coat; controlled film weight. However, there were limitations to the process, such as expensive capital outlay for powder manufacturers; difficulty in reproducing a shade; risk of discontinuity at film weights lower than about 40μ ; high curing temperature; danger of inferior flow out giving orange peel; limited heat stability of the powder.

In Western Europe, 4,500 to 5,000 tons of powder coating were processed in 1971, and epoxy powders accounted for 90 per cent. The working economics were considered to be about the same as for a two-coat solution process, with an approximate plant cost, excluding buildings, of about £30,000 for an installation capable of a production rate of 100 kilos per hour.

Epoxy polymers had good mechanical properties and resistance to chemicals, but unfortunately gave very poor weathering resistance with high erosion rates. Much effort had therefore been put into devising thermosetting acrylic systems, though there was a wide range of powders available, including polyethylene, nylon 11-12, chlorinated polyesters, ethylene/vinyl acetate copolymers, and polyesters.

Dr Brussman dealt in some detail with the four cross-linking mechanisms available for acrylic systems, via methylol groups, hydroxyl groups, carboxyl groups, and epoxy groups.

Dealing with coating methods, the speaker said that the fluidised bed and electrostatic spray methods were almost universal. Surplus powder was recovered by cyclone filters and booth design involved consideration of the possibility of explosion.

The important factors affecting the charge and transportation of powder particles were the voltage and the polarity of the applied DC potential. The neutral electric equilibrium formed could be disturbed by: polarisation, i.e. electron polarisation if the electron paths within the atom were displaced, atomic polarisation if the existing dipoles were pushed apart, and orientation polarisation if the existing dipoles were orientated in one direction; or ionisation, if the particle assumed a negative or positive charge as a result of the removal or addition of electrons.

The forces caused by polarisation were so weak that they did not allow the coating to build up to a thickness that would be of any practical value. The function that polarisation can assume was to orientate the powder particles during their flight along the lines of force. In order to build up a coating from the powder on the substrate, forces of attraction were required, and these could be produced only by ionisation.

A major factor affecting the electrostatic charging and the adhesion of the powder coat to the substrate was the resistivity of the powder. A powder that was suitable for electrostatic spraying had a volume resistivity of the order of $10^{10} - 10^{16}$ ohm cm.

If the resistivity was less than 10^{10} ohm cm, the particles of powder released their charge too rapidly when in contact with the earthed substrate. Under these circumstances, the powder coating fell away from the substrate.

If the resistivity was greater than 10^{16} ohm cm, a back-spraying effect might occur after a slight layer of powder had formed. As a result of this, particles of powder that had already been deposited could be catapulted back explosively into the field of force as a result of dielectric breakdown.

The relationship of the charge on a spherical particle to the dielectric constant, the field strength, and the particle radius was illustrated by slides.

Dr Brussman described some aspects of powder manufacture. There were three distinct stages: premixing of raw materials, dispersion, and grinding and sieving. Organic pigments were satisfactory in full shades, but gave problems in tints. Continuous dispersion could be possible depending on the scorch resistance of the polymer to be used. The effect of pigment distribution on the powder flow out was all-important and slides demonstrated the point. Heterogeneities in the powder gave rise to differences in melt viscosity and surface tension during stoving, preventing uniform flow out.

Finally, Dr Brussman gave a straightforward comparison of the performance of an acrylic powder coating versus a typical acrylic solution coating. The solution gave better flow out, but in respect of mechanical and resistance properties, including salt spray, it was similar to the powder. The acrylic powder had given good weathering properties after three years.

In the ensuing discussion, there were numerous questions relating to minimum film thickness, relative epoxy and acrylic resin consumption, potential automotive applications and the possible use of powders in conjunction with electrodeposition paints.

Mr K. Chitty gave the vote of thanks which was endorsed by an appreciative audience.

R.E.G.



25th Technical Exhibition 21-24 May 1973

At the time of writing there were eight weeks remaining before the closing date for applications for stand space (2 October) and the Committee was very pleased with the response, both from United Kingdom and overseas companies, to the Invitation to Exhibit, which had been despatched eight weeks earlier.

As announced in the July issue of this *Journal*, the arrangements for the 25th (Silver Jubilee) Technical Exhibition have been modified to meet changing conditions and the Exhibition will open at 12 noon on the first day (Monday 21 May), and at 09.30 hrs on each of the three subsequent days. On each of the four days the Exhibition will close at 18.00 hrs. Instead of the customary Exhibition Luncheon on the opening day, it has been decided on this occasion to hold an Exhibition Dinner on the Monday evening at the Savoy Hotel, London WC2. Invitation to this important function will be extended as usual to the principal officers of other learned societies, trade associations, government establishments and research associations. Full information will be published at a later date in this *Journal* and also in the *Official Guide* to the Exhibition, each copy of which will contain a form of application for tickets.

The *Official Guide* will be prepared well in advance of the dates so that copies can be circulated widely, both to members and non-members, thus allowing visitors an opportunity to plan their itineraries. As well as maintaining the Exhibition's unique position as a purely technical display, manned by technical personnel, the Exhibition Committee has for many years followed the successful policy of encouraging visitors in this way, and by making no charge for admission, so that the maximum flow of communication between exhibitors and visitors can take place.

Indeed, the *raison d'être* of the Exhibition has frequently been stated as being "the forum for technical display and discussion", and to encourage the younger members of the Association to attend the Silver Jubilee Exhibition, the Council of the Association has asked the Section Committees to arrange visits by coach parties, wherever possible.

The list of exhibitors to whom space has been allocated will be published in the November issue of this *Journal* and any company wishing to be included in this list by applying for space should contact the Association's offices for copies of the Invitation to Exhibit and application form.

OCCA Biennial Conference

towards 2000

eastbourne 19-23 june 1973

Venue and dates

The outline programme of the Association's next biennial conference, to be held at the Grand Hotel, Eastbourne, from 19-23 June 1973, has now been arranged. As already announced, the theme of the conference is to be "Towards 2000", and it is intended that the papers presented will give delegates an insight into the future of the paint and allied industries, not only from a technical viewpoint, but also where economic and marketing aspects are concerned.

Structure of technical sessions

It is felt that, in the present climate of mushrooming technology, delegates to a conference require the maximum technical content, and thus the programme has been arranged so that there will be a session on each half-day of the conference, and there will be no parallel sessions. Technical sessions will be held on the mornings of the Wednesday, Thursday and Friday, and on Thursday afternoon; there will be a session concerned with techno-economic factors, including international relations, on the Wednesday afternoon, and three Workshop sessions will follow the Association's AGM on the Friday afternoon.

A further change from previous conferences will be in the structure of the Technical Sessions. It is planned that each session will have a broad sub-theme, and that each will be opened by a major paper on this sub-theme. The Hon. Research and Development Officer (Mr. A. R. H. Tawn) is pleased to announce that the following have agreed to present opening papers at three of the technical sessions:

Professor C. E. H. Bawn, CBE, FRS (Liverpool University): "Trends in polymer science".

Mr G. Isserlis (Polytechnic of the South Bank): "The challenge of metal finishing".

Dr H. Gysin (CIBA-GEIGY): "Environmental problems of the chemical industry."

The remainder of the session will be taken up with papers on more specialised topics within the sub-theme, amongst which it is hoped to include papers of a technological nature.

Programme

The programme of papers, to be presented by lecturers from the UK and overseas, has now been compiled, and it is hoped to publish it in full in the October issue. Summaries of the papers and short biographical notes on their authors will be published in subsequent issues.

Following the usual practice of the Association, papers will be preprinted and circulated to registrants a month before the conference; authors will only be required to outline their papers, highlighting points of particular interest, and it is thus particularly important that delegates are given the opportunity to read the full paper in advance, so that the maximum benefit may be obtained from the discussion period following each lecture.

Registration forms

Full details concerning registration fees, and a registration form, will be sent to all Members of the Association before the end of 1972. Non-members wishing to receive these items, when available, should apply in writing to the Director & Secretary, at the Association's offices, at the address shown at the front of this *Journal*.

Foundation Lecture 1972

Sir James Tait to present 1972 Lecture

The Council is honoured to announce that the 1972 Foundation Lecture will be given by the Vice-Chancellor of the City University, Sir James Tait, LLD, PhD, BSc, CEng, FIEE, FIMechE, who has chosen for his subject "The city—a technological university. Are tradition and technology compatible?".

The Lecture will be given at Painters' Hall, Little Trinity Lane, London EC4, on Tuesday 3 October 1972 at 7.15 p.m. and will be preceded by a short service

at St Vedast-alias-Foster, Foster Lane, London EC2, at 6.15 p.m. This is the church at which the commemorative service took place on the occasion of the Association's fiftieth anniversary celebrations in 1968.

Following the Association's usual custom, the Foundation Lecture will be followed by an informal dinner at the Painters' Hall.

The closing date for application for tickets is **22 September**.

Optional Professional Grade for Ordinary Members

After being successful in *viva voce* examinations, further members have been admitted to the Professional Grade. Their names and Sections to which they are attached are given below:

Associateship

Bolam, Ion Barrow (*Newcastle*)

Davis, Reginald Albert (*Bristol*)
Kenna, Frank William (*Manchester*)
Perry, Leonard C. (*Bristol*)

Licentiate

Boxall, John (*London*)
Downham, Stephen Airey
(*Thames Valley*)

Report of Meeting of Council

A Meeting of Council was held at Wax Chandlers' Hall, Gresham Street, London, on Wednesday 28 June, 1972, when the President, Mr A. W. Blenkinsop, was in the chair. There were 30 members present.

The President extended a welcome to members newly elected to Council, as President Designate, Elective Members, Vice-Presidents, Section Chairmen and Representatives.

It was reported that the Members attached to the South African Section had welcomed the conferment of Honorary Membership upon their Founder Chairman, Mr T. Howard. A report and photograph appeared in the July issue of the *Journal*.

The dates for Council Meetings for the forthcoming session were agreed and the appointment of Council Committees and Association representatives on other organisations was confirmed.

Reports were received on the Dinner Dance held at the Savoy Hotel in May 1972, the Annual General Meeting held at Wax Chandlers' Hall in June 1972 and the arrangements for the Foundation Lecture and Dinner to be held at the Painters' Hall in October, preceded by a short Commemorative Service at St. Vedast-alias-Foster. Reports were also received on the Exhibition held in April 1972 (24-OCCA) and the new arrangements for the Silver Jubilee Exhibition (OCCA-25 in May 1973), full details of

which have appeared in the *Journal*.

In accordance with Article 15 it was resolved to remove from the Register of Members the names of those members whose 1972 subscriptions were not received by 30 June. Council was pleased to note that the total in this category was considerably lower than in recent years.

The position concerning the availability of the Paint Technology Manuals was considered, since only Part VI was still in print. The second edition of Part III was scheduled to appear at the end of July and it was understood that the price per copy would be £2.80. The entire second editions of Parts I and II had now been sold and the second editions of Parts IV and V were not yet available for printing. Council was pleased to learn of the considerable interest which had been aroused by the publication of Part VII ("Works Practice") in part form in the *Journal* during 1972; bound reprints would be available early in 1973 with a special concessionary rate for Registered Students of the Association.

The arrangements for the sessions at the Association's Conference at Eastbourne in June 1973 under the general theme "Towards 2000" were reported and discussed. It was envisaged that there will be four technical sessions, together with a session devoted to a technoeconomic theme and workshop sessions. Each of the three days of the Conference will be fully occupied with sessions and full details will appear in the *Journal* before the end of the year.

The President reported that he hoped to attend the 50th Anniversary Meeting of the Federation of Societies for Paint Technology in Atlantic City in October and to present a commemorative scroll on behalf of the Association.

The Professional Grade Committee

report showed that, by the beginning of June, 300 applications had been received. Council was particularly pleased to learn that a number of candidates for Licentiatehip had now completed their dissertations and had been successful in *viva voce* examinations; others were awaiting examination. One dissertation had been forwarded to the Hon. Editor with the Committee's suggestion that it be considered for publication in the *Journal*.

As reported in the July issue of the *Journal*, Council was informed that the Association of Professional Scientists and Technologists had now confirmed that it would consider applications for membership on an individual basis from members of this Association and Council was naturally pleased to learn of this development.

Council was informed that it seemed unlikely that the lease at Wax Chandlers' Hall, where the Association's offices have been situated since January 1959, could be re-negotiated at a rental acceptable to the Association and discussion took place on the advisability of purchasing a property for a headquarters or moving to other premises.

Reports on Section activities were received and attention was drawn to the Manchester Section Symposium on "Paint performance and the microbiological environment" to be held 19 and 20 September 1972.

Council was pleased to learn of the award of the MBE in the Queen's Birthday Honours List to an Ordinary Member attached to the London Section, Miss D. L. Tilleard.

There being no other business, the President thanked the members for their attendance and declared the meeting closed.

FATIPEC Congress 1972

The 11th FATIPEC Congress was held in Florence from 11-18 June 1972. An extensive programme of lectures and social functions was very efficiently organised.

The theme of the congress was "Progress and evolution in the production and application of surface coatings and printing inks"—broad enough to cover any paper likely to be offered. There

were 10 plenary papers and 76 general lectures on this theme. In addition, there was a one-day symposium on "Interaction between pigments and media in liquid paints" comprising seven invited papers.

The plenary papers were mainly read as printed in the FATIPEC book (to assist simultaneous translation) and there was no discussion on them, in accordance with the usual FATIPEC tradition. Future organisers might consider whether it is desirable to maintain this rather inhibitive practice.

These papers included a very professional account of the new microvoid emulsion paints by Gerhart and Seiner (USA); a finely illustrated talk on pigment colour by McLaren & Plant (Great Britain); some unorthodox views on drying oil reactions by Petit (France) and on polycondensation by Bianchini (Italy); a realistic account of the present state of electron beam curing by Vrancken (Belgium); and examples of applications of instrumental analysis to paint problems by Raaschou Nielsen (Denmark). Sabbioni (Italy) discussed the particular problems of crystalline fluorocarbon polymers in coatings; van Steenis (Netherlands) described further developments with α - α branched carboxylic acids; Völz (Germany) discussed test methods for the optical properties of pigments, and Oesterle (Switzerland) gave a high-speed delivery on paint film structure.

The papers for the symposium on pigment/medium interaction were chosen so as to include one from each of seven countries. These papers were individually interesting but did not blend too well to provide a uniform picture—an expert summing up at the end was certainly required, but this would have been no easy task. The papers given were by Myers (USA) on mechanical properties, Reháček (Czechoslovakia) on adsorbed layers, Bleyser (Belgium) and Barcucci (Italy) on rheology, Schmitz (Germany) on heat of wetting, Donnet (France) on pigment/polymer interactions and O'Neill (Great Britain) on the use of

gel permeation chromatography to study the interaction.

The general papers covered a wide and representative field, including pigments, binders, additives, paint formulation and application, testing procedures etc. Notably absent however, were papers on printing inks and paint machinery; only two papers were offered on microbiology, one of which was withdrawn.

These papers were given concurrently in three rooms. More care could have been taken in the arrangement of the timetable to avoid clashing of lectures on related subjects. The level and amount of discussion following the papers was very variable.

The FATIPEC book is larger than ever, although the symposium is in a separate volume. Unfortunately it could not be sent out before the Congress so that it was difficult to read up many papers before their presentation.

Prizes were awarded for the papers by: Reháček & Schütte on the "Adsorption of binders on pigments," Bianchini on "Optimisation study on polycondensation" and Quiring & Wagner on "Branched systems with functional groups."

The number of participants was over 500. About 30 were from Great Britain, but, as usual, only a few were from paint companies.

The social functions were very ambitious, including an event for each evening. These consisted of a reception, a Florentine feast, sampling of local food at a monastery, a concert of period music and a banquet. There was also a half-day excursion to Siena.

The next Congress is to take place in 1974 in Garmisch-Partenkirchen and the first notice is already available (from Dr H. Rechmann, D 5670 Opladen, Obere Strasse 16, West Germany).

Irish Section

Treasure Hunt

The annual car Treasure Hunt of the Irish Section was held on 20 May 1972.

At short notice, Mr S. Bull had arranged a route which covered 37 miles through the Dublin hills, and it proved to be a most interesting challenge to the navigators.

The winners were Mr D. Power and his navigator, with Mr and Mrs A. Richards taking the second prize, and Mr D. Sharp and Miss P. Magee the third.

The prizes were presented by Mr D. Sharp, as chairman, at the home of Mr and Mrs S. Bull, where an excellent selection of refreshments had been prepared.

A.R.

Golf outing

The annual golf outing was held on Friday 23 June, at the Clontarf Club. Regrettably, only 15 members and friends took part.

The result of the competition, played under Stapleford rules, is shown below, the player's handicap being shown in brackets.

Members

D. Godden (20)	42 pts.
K. O'Callaghan (24)	34 pts.
M. O'Hanlon (24)	24 pts.

Visitors

G. Eager (19)	34 pts.
P. Hayden (20)	31 pts.
P. Holmes (19)	27 pts.

A.R.

London Section

Section Officers and Committees

London (Southern Branch)

This committee list was received too late for inclusion in the August issue.

Chairman: J. R. E. F. Coates, Captains, Red Lane, Limpsfield, Oxted, Surrey.

Vice-Chairman: B. A. Richardson, BSc, Penarth Research Centre, Penarth House, Otterbourne Hill, Winchester, Hants.

Hon. Treasurer: R. A. Brown, BSc, Vanguard Paints Ltd., Cranleigh Road, Portchester, Hants.

Hon. Secretary: W. H. Morris, 4 Sandisplatt, Paul's Hill, Fareham, Hants.

Hon. Publications Officer: T. R. G. Cox, BSc, Penarth Research Centre, Penarth House, Otterbourne Hill, Winchester, Hants.

Hon. Auditor: J. R. Marchant, 19 Ash Close, South Merstham, Surrey.

Committee:

J. T. Tooke-Kirby, Fintry Lodge, 80 Arlington Avenue, Goring by Sea, Nr. Worthing, Sussex.

K. L. Bargrove, 18 Thornbury Avenue, Isleworth, Middx. TW7 4NQ.

D. L. Storer, 3 Blenheim Gardens, Denvilles, Havant, Hants. PO 92PN.

Southern Branch Programme

This programme was unfortunately received too late for insertion in the August issue.

All meetings will be held at the Pendragon Hotel, Southsea at 7.00 p.m.

1972

Tuesday 17 October

"Developments in clear finishes for timber" by Dr R. Laidlaw of the Princes Risborough Laboratories of the Building Research Establishment.

Tuesday 14 November

Details to be arranged.

Friday 1 December

Ladies' Evening with Buffet Supper.

"Protection or beauty" by Mr M. Hand of Max Factor.

1973

Tuesday 13 February

"Sealants" by Mr L. D. Hall of Ralli-Bondite Ltd.

Tuesday 13 March

"Medicines for coatings" by a speaker from Byk-Mallinckrodt.

Newcastle Section



Joint winners of the British Titan Cup, Mr A. J. Durdey (left), and Mr J. K. Rankin

The British Titan Cup

The eleventh annual tournament for the British Titan Cup was played for on Saturday 17 June 1972 over the Brancepeth Castle Golf Course. The competition, a four ball better ball against bogey, was won jointly by Messrs. A. J. Durdey of Camrex Ltd. and J. K. Rankin of Tioxide Inter-

national. The matches were played in blustery conditions and the winners score of "four up" was regarded as being creditable.

The cup was presented to the winners by the Section Chairman, Mr A. A. Duell, who also took part in the competition.

H.F.

South African Section

Powder Coatings Conference

The South African Section is to hold a conference on powder coatings on Friday 20 and Saturday 21 October 1972. The venue for the conference will be the Pine Lake Inn near White River, Eastern Transvaal, which is on the borders of the famous Kruger National Park, to which

a small bus tour has been arranged for the Sunday following the conference.

The conference itself will contain eleven papers, to be delivered by speakers from South Africa and overseas; full details are obtainable from Mr L. F. Saunders, the Hon. Publications Secretary of the Section, at PO Box 31, Durban, Natal, Republic of South Africa.

Paint Technology Manuals Part 3— Convertible Coatings

The second edition of the third part of the Paint Technology Manuals—"Convertible coatings," has now been published by Chapman & Hall Limited.

Since the book was first published, in 1962, a great deal of development and innovation has taken place in this field, and the collator of the volume, Dr H. W. Keenan, has given a great deal of consideration to the steps necessary in order to maintain the volume's position as a current reference work for students and others in the surface coatings

industries, consulting specialists in the various subjects covered where appropriate. As a result of this, three of the chapters—those dealing with epoxide resins, unsaturated polyester resins, and polyamide resins—have undergone extensive revision and expansion to bring in the latest developments, both in the chemistry of the resins themselves and in their use in coatings.

The second edition, which runs to 350 pages, including a revised index, is now available in limp covers at a price of £2.80.

News of Members

Mr P. D. Sutcliffe, an Associate Member attached to the West Riding Section, has been appointed to the executive board of Nopco Hess Limited. Mr Sutcliffe, who was previously sales manager of Nopco Hess's chemical division, is now director in charge of sales for this division.

with dispersed colours.

Mr W. S. Crisp, an Ordinary Member attached to the London Section, has been appointed industrial marketing manager of Berger Paints Limited. Mr Crisp was previously technical service manager, general industrial division.

Mr J. R. Groom, an Ordinary Member attached to the London Section, an Associate in the Professional Grade, and winner of the Jordan Award in 1971, has been appointed technical manager of a new technical service department set up by SCC Colours Limited to deal

Interlaboratory reference programme for colour and appearance test methods

The Manufacturers' Council on Colour and Appearance (MCCA), an American non-profit organisation, is sponsoring a collaborative reference programme on colour and appearance test methods, which is being administered by the

National Bureau of Standards. The immediate objectives of the programme are to provide a means whereby a participating company may periodically check the accuracy of its testing in comparison with that of other laboratories, and to improve the reliability of

test results both within and among laboratories.

Full details of the scheme may be obtained from Mr C. G. Leete, Executive Director, Manufacturers Council on Colour and Appearance, 9416 Gamba Court, Vienna, Virginia 22180, USA.

Register of Members

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

Ordinary Members

- ANGUS, COLIN WILLIAM, BSc, ANZIC, Polychem (NZ) Ltd., PO Box 9141, Wellington, New Zealand. *(Wellington)*
- CHARLTON, NORMAN VIVIAN GARTH, PO Box 57, Estcourt, Natal, South Africa. *(South African)*
- CHURNSIDE, MICHAEL JOHN, BSc, Berger Chemicals, Portland Road, Newcastle upon Tyne. *(Newcastle)*
- HARPER, BRUCE DOUGLAS, 3 Addis Place, Cockle Bay, Howick, Auckland, New Zealand. *(Auckland)*
- LANGFORD, GRAHAME ARTHUR, 26 Peter Buck Road, Avondale, New Zealand. *(Auckland)*
- OSWITCH, STANLEY, LRIC, Ferro Corporation, Technical Centre, 7500 E. Pleasant Valley Road, Independence, Ohio 44131, USA. *(General Overseas)*
- SAXON, BRIAN THOMAS, BSc, 19 Readhead Avenue, South Shields, Co. Durham NE33 3AW. *(Newcastle)*
- WHITAKER, DENNIS, ASDC, 281 Kohimarama Road, Auckland 5, New Zealand. *(Auckland)*
- WILLARD, RICHARD ERIC, Ados Chemical Co. Ltd., PO Box 38160, Petone, New Zealand. *(Wellington)*
- WINTER, THOMAS PEIRSON, CIBA-GEIGY (UK) Limited, Plastics Division, Simonsway, Manchester M22 5LB. *(Manchester)*

Associate Members

- ARMSTRONG, GRANT LAWRENCE, PO Box 5641, Auckland, New Zealand. *(Auckland)*
- CAMERON, MICHAEL PHILIP, BP Chemicals Division, Chemicals Manufacturing Co. Ltd., Box 1181, Wellington, New Zealand. *(Wellington)*
- CONGREVE, GEORGE DENNIS, British Aluminium Co. Limited, Latchford Locks Works, Warrington, Lancs. *(Manchester)*
- WILKINSON, RALPH ALBERT, 117 Dowse Drive, Lower Hutt, New Zealand. *(Wellington)*

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.

Tuesday 12 September

West Riding Section: "Micronised iron oxide pigments" by Mr W. Schleusser of Bayer AG. To be held at the Griffin Hotel, Leeds, at 7.30 p.m.

Friday 15 September

Midlands Section: Ladies' Evening. To be held at the Westbourne Suite, Botanical Gardens, at 7.00 p.m.

Irish Section: "The uses of carbon black in paint and printing ink" by Dr F. Muller-Focken of Degussa, to be held at the Clarence Hotel, Dublin, at 8.00 p.m.

Tuesday 19 — Wednesday 20 September

Manchester Section: Symposium "Paint performance and the microbiological environment". To be held at the University of Manchester Institute of Science and Technology.

Friday 22 September

Midlands Section: "Alpha-olefines—new monomers for surface coatings" by Mr K. B. Gilkes and Mr A. Laws of British Paints and Chemicals (Resinous Chemicals Division) to be held at the Birmingham Chamber of Commerce and Industry, 75 Harborne Road, Birmingham, at 6.30 p.m.

Thursday 28 September

Thames Valley Section: "Adhesives" by Dr Fletcher of Croda Polymers Ltd., to be held at the Beech Tree Hotel, Maxwell Road, Beaconsfield, Bucks, at 7.00 p.m.

Friday 29 September

Bristol Section: Ladies' Evening. "Design and colour in fabrics" by Mr I. W. Willis of Treforest Silk Printers Ltd., to be held at the Royal Hotel, Bristol, at 7.15 p.m.

Monday 2 October

Hull Section: "Plastic coated steel" by Mr J. Land of Dufay Plastics Ltd., to be held at the E. H. Bullock Lecture Theatre, Hull College of Technology at 7.00 p.m.

Tuesday 3 October

Oil and Colour Chemists' Association: Foundation Lecture and Dinner to be held at the Painters' Hall at 7.15 p.m. preceded by the Commemorative Service at St. Vedast-alias-Foster at 6.15 p.m.

Thursday 5 October

Newcastle Section: "The money game" by Mr S. M. Jennings of Thomas de la Rue & Co. Ltd., to be held at the Royal Turks Head Hotel, Grey Street, Newcastle-upon-Tyne at 6.30 p.m.

Thames Valley Section—Student Group: "Wood preservation" by Mr B. A. Richardson, to be held at the Slough College, Main Lecture Theatre, at 4.00 p.m.

Friday 6 October

London Section: "Ladies Night" to be held at the Cafe Royal, Regent Street, London W1, at 7.00 p.m. for 7.45 p.m.

Tuesday 10 October

West Riding Section: "Powder coatings" by Mr D. W. Brooker of Shell Research Ltd., to be held at the Griffin Hotel, Leeds, at 7.30 p.m.

Wednesday 11 October

London Section: "Permeability properties of surface coatings towards ions" by Dr J. D. Murray, of QAD (Mats.), to be held at the South Bank Polytechnic at 7.00 p.m.

Manchester Section—Student Group: "Corrosion theory for the paint technologist" by Dr J. Wolstenholme of Flintshire College of Technology, to be held at the Manchester Literary and Philosophical Society, 36 George Street, Manchester 1, at 4.30 p.m.

Scottish Section—Eastern Branch: "Leonardo da Vinci and his times" by Mr J. C. Patek of A. B. Fleming & Co. Ltd., to be held at the Carlton Hotel, North Bridge, Edinburgh at 7.30 p.m.

Thursday 12 October

Hull Section: Annual Dinner Dance, to be held at the Hotel Eden, Hull.

Midlands Section—Trent Valley Branch: "Powder coatings" by Mr M. Cotton of Shell Research Ltd., to be held at the British Rail School of Transport, London Road, Derby at 7.00 p.m.

Scottish Section: "A life-time in the chemical industry" by Mr J. Miller, to be held at the St. Enoch Hotel, Glasgow at 6.00 p.m.

Friday 13 October

Manchester Section: "New developments in clear coatings for exterior wood" by Dr R. Miller of Timber Laboratories, to be held at the Manchester Literary and Philosophical Society, 36 George Street, Manchester 1, at 6.30 p.m.

Saturday 14 October

Scottish Section—Student Group: "Corrosion and its costs" by Mr G. Scott of Federated Paints Ltd., to be held at the St. Enoch Hotel, Glasgow, at 10.00 a.m.

Tuesday 17 October

London Section—Southern Branch: "Developments in clear finishes for timber" by Dr R. Laidlaw of the

Building Research Establishment, to be held at the Pendragon Hotel, Southsea at 7.00 p.m.

Friday 20 October

Irish Section: Details to be announced.

Manchester Section: Annual Dinner Dance, to be held at the Piccadilly Hotel, Piccadilly Plaza, Manchester 1.

Midlands Section: "Colour passing—visual or instrumental?" by Mr K. McLaren of ICI Ltd., Dyestuffs Division, to be held at the Birmingham Chamber of Commerce and Industry, 75 Harborne Road, Birmingham at 6.30 p.m.

Saturday 21 October

Scottish Section—Eastern Branch: "Aqueous pigment dispersion" by Mr A. Gray and Mr J. T. Hunt of CIBA-GEIGY (UK) Ltd. Joint Meeting with the Scottish Section Student Group, Venue to be arranged.

Thursday 26 October

Thames Valley Section: "Colour measurement and control with the fibre optics colorimeter" by Mr D. Irish of the Paint Research Association, to be held at the Beech Tree Hotel, Maxwell Road, Beaconsfield, Bucks at 7.00 p.m.

Friday 27 October

Bristol Section: "Systems of appraisal" by Mr N. R. Felstead and Mr C. Sibley of Berger Jenson and Nicholson Ltd. Joint meeting with the Birmingham PVL Club to be held at the Hawthorne Hotel, Bristol at 7.15 p.m.

Saturday 28 October

Scottish Section—Student Group: Joint meeting and Skittles Match with the Eastern Branch, to be held at the St. Enoch Hotel, Glasgow at 10.00 a.m.

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The sales of this Association publication now exceed 13,000, and because of continuing high sales of the second edition, and the need for a work of reference to be constantly abreast of the latest developments in its field, the Council of the Oil and Colour Chemists' Association has authorised the addition of an eleventh chapter to the "Introduction to Paint Technology." Entitled "Recent Developments," the Chapter incorporates up-to-date information on the latest advances in the technology of the paint and allied industries.

This addition will help the "Introduction to Paint Technology" to maintain its position as an invaluable aid to young entrants into the industries and to marketing and other personnel requiring a basic knowledge of the principles and techniques of surface coating production and application.

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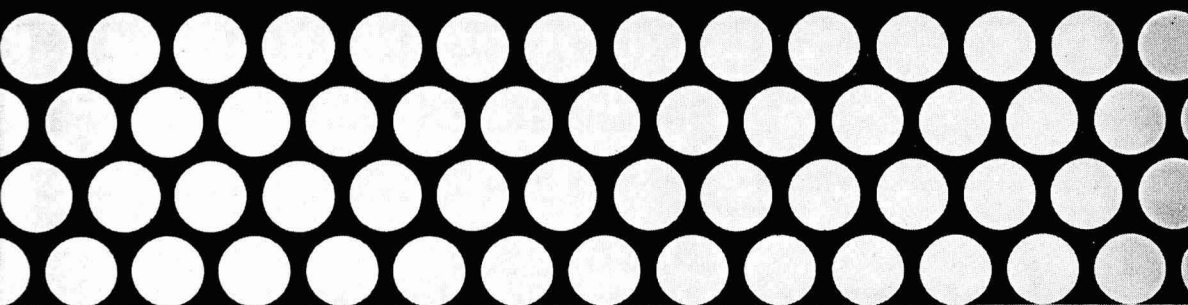
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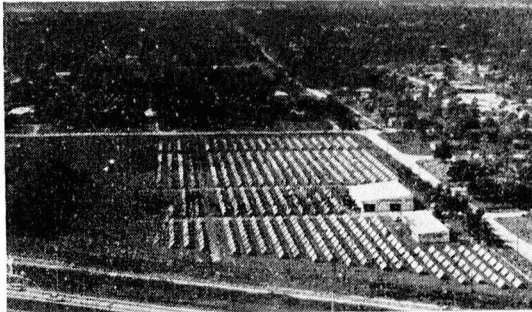
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