JOURNAL

OF THE

OIL AND COLOUR CHEMISTS' ASSOCIATION

Vol. 50 No. 1 **January 1967**

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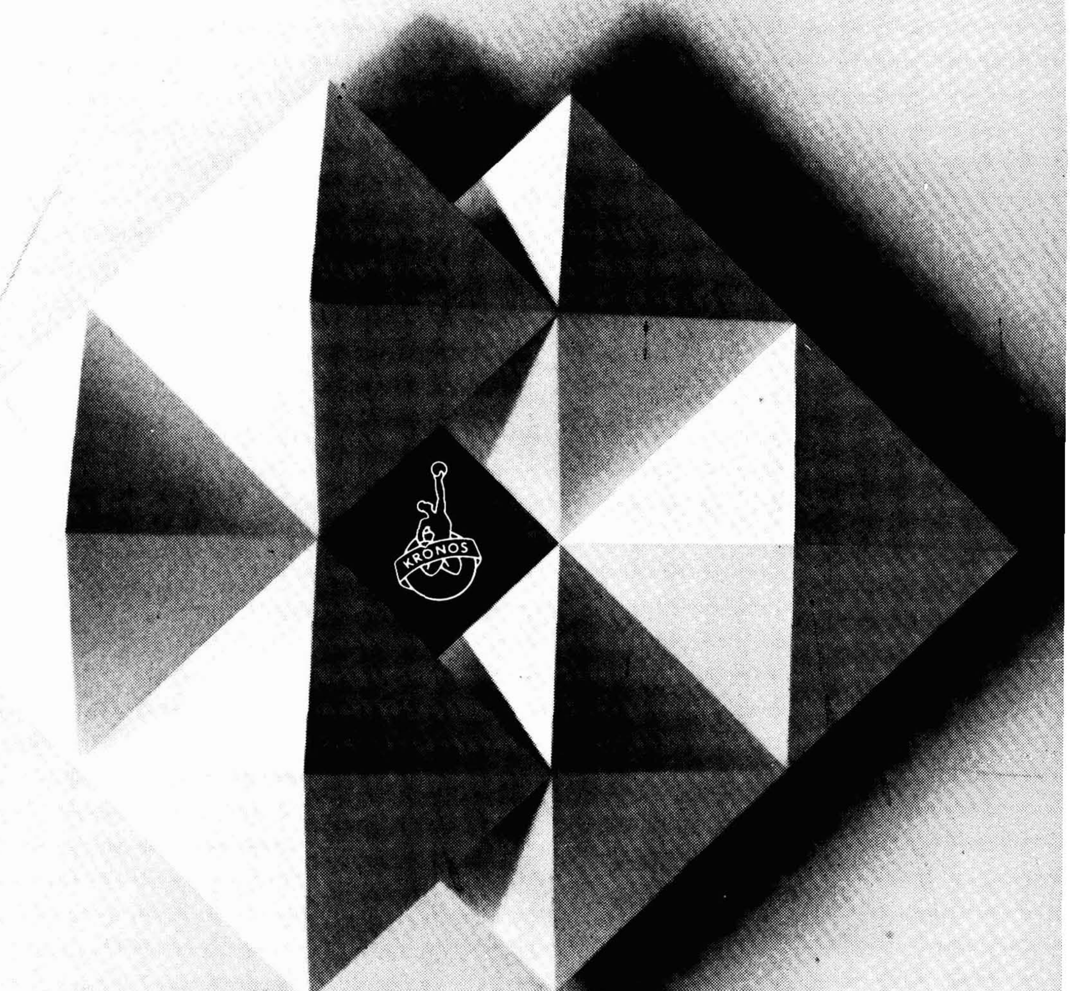
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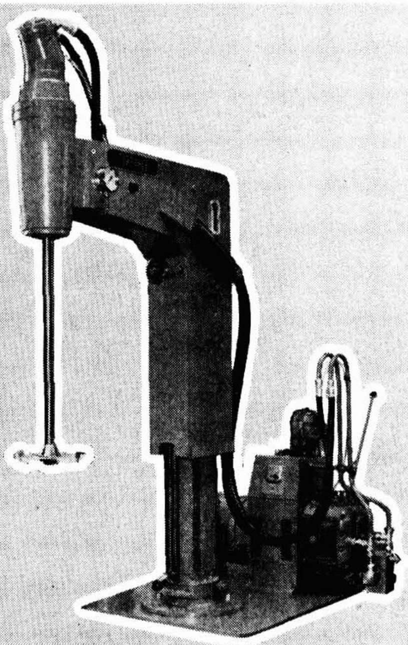

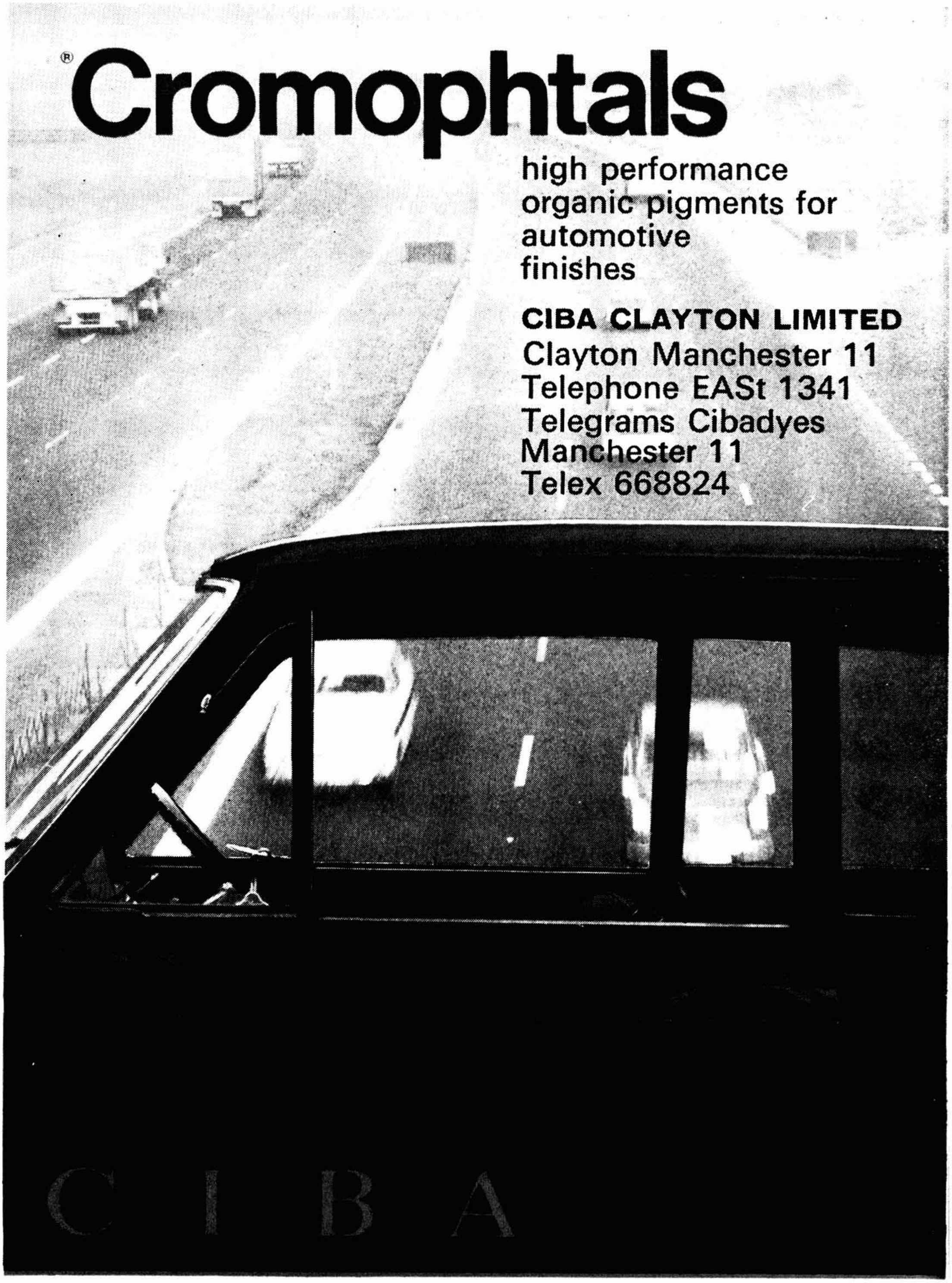

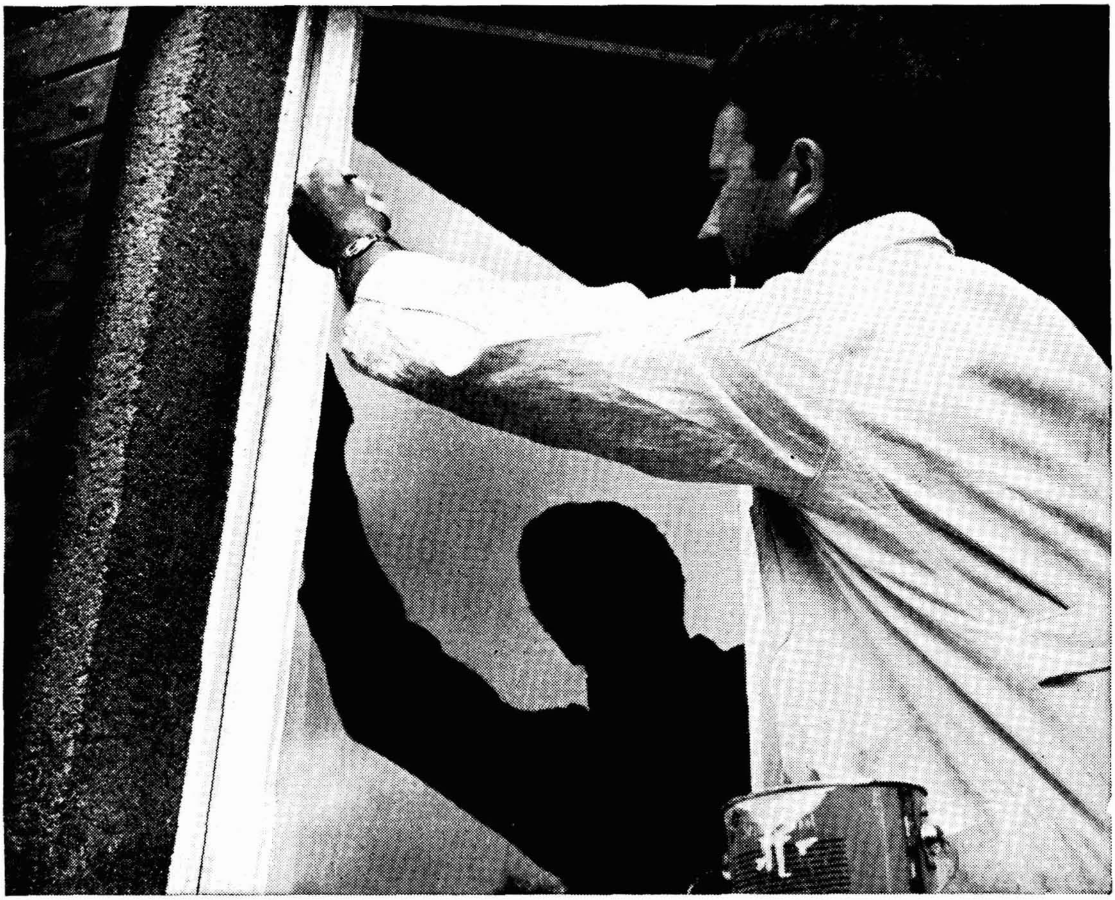

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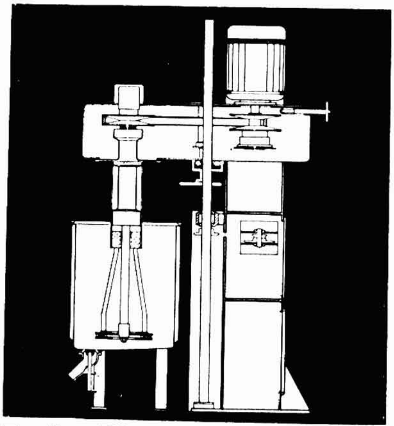

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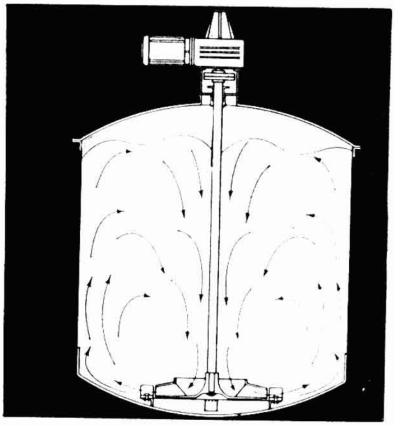

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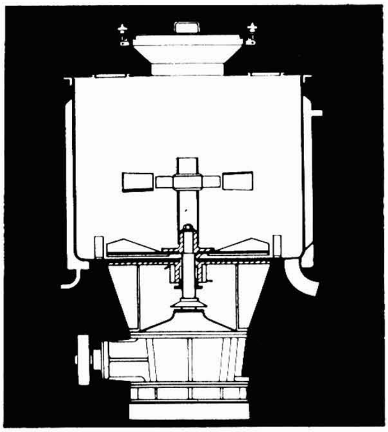

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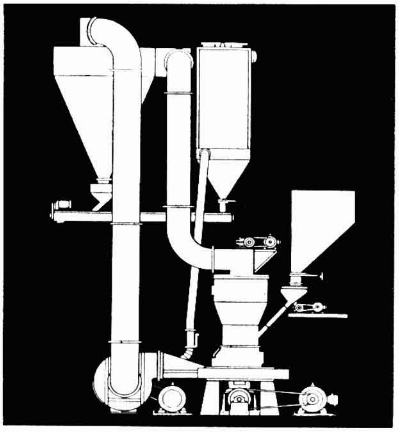

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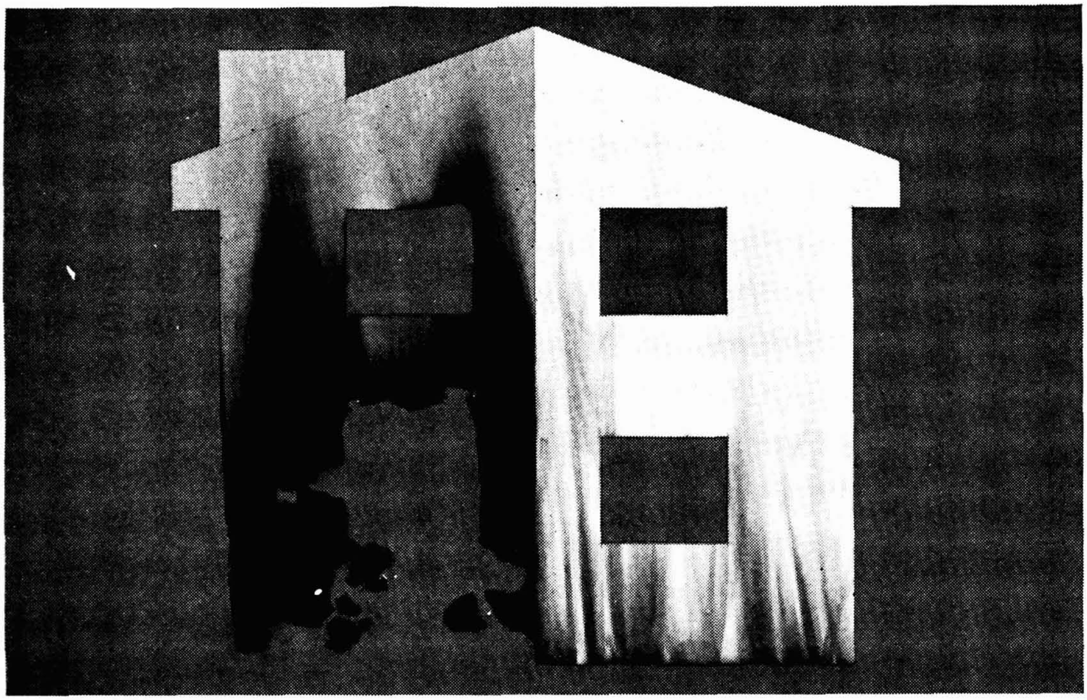

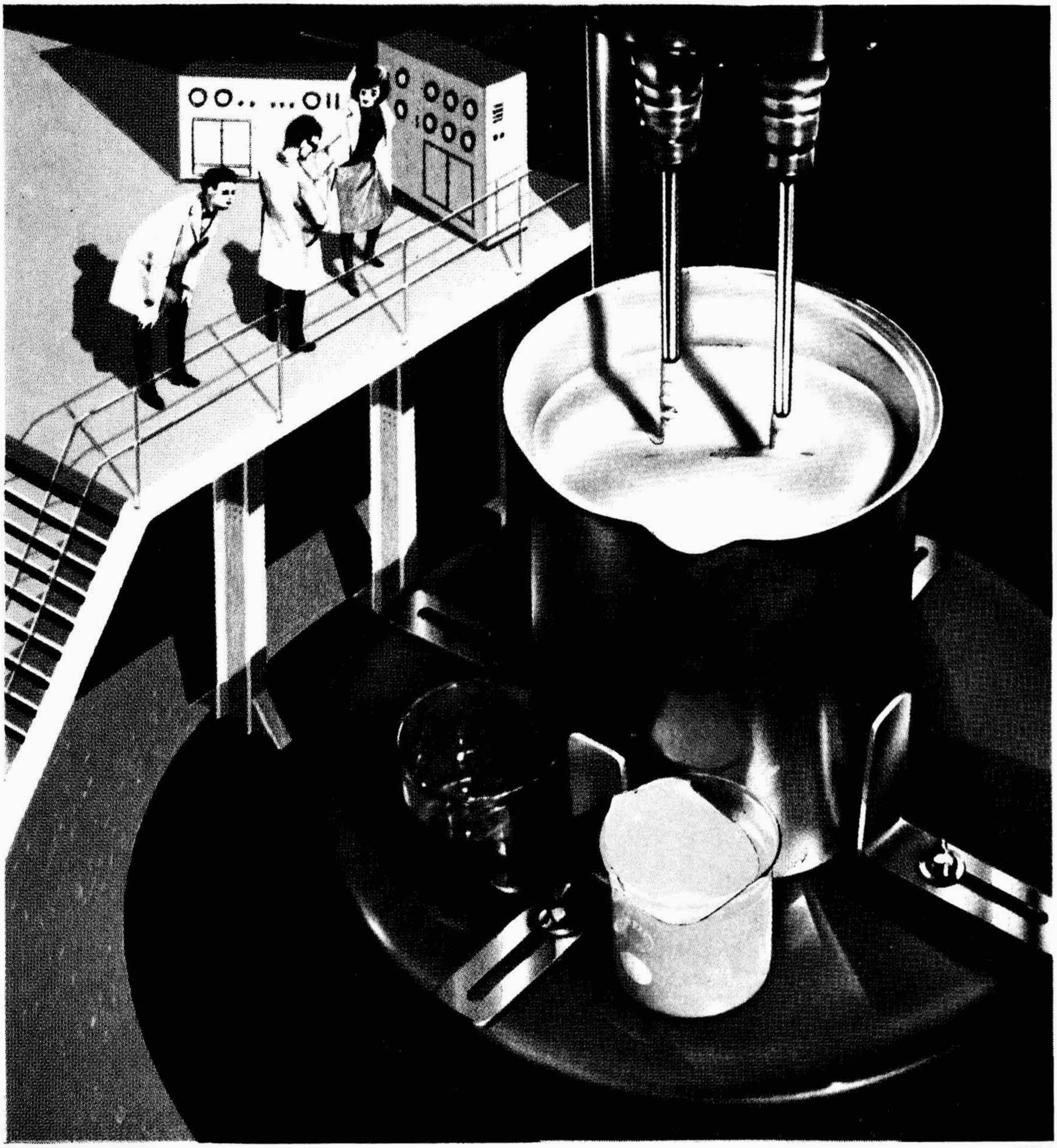


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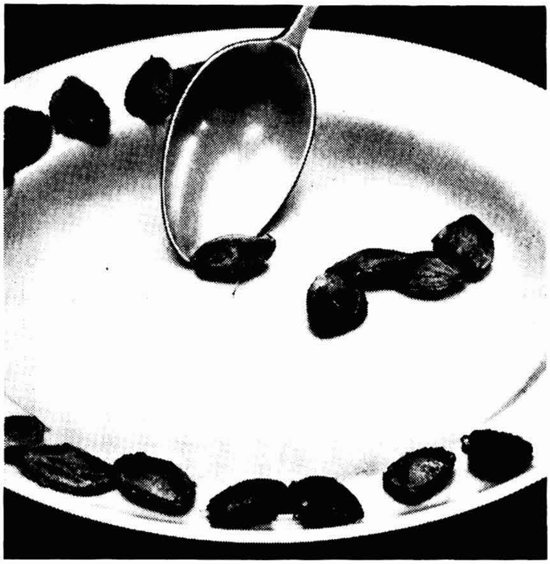

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Hon. Auditor : J. Smith, B.SC., Mengham Farm House, Selsmore Road, Hayling Island, Hants.

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R. A. Brown, B.SC., D. H. Wilson & Co. (Paints) Ltd., Cranleigh Road, Portchester, Hants.
J. K. B. Burke, M.A., " Avoca," 190 Pampisford Road, South Croydon, Surrey.
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J. R. Green, BIP Chemicals Ltd., Popes Lane, Oldbury, Birmingham.
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Co-ordinating Officer for Technical Education : P. C. Edbrooke, B.SC., A.R.I.C., 23 Tollgate Road, Hamsterley Mill, Rowlands Gill, Co. Durham.
Secretary, Junior Activities Sub-Committee : K. F. Baxter, 5 Greybourne Gardens, Sunderland, Co. Durham.
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K. V. Hodgson, 98 Alston Crescent, Seaburn, Sunderland.
J. A. Willey, B.SC., A.R.I.C., 40 Broxholm Road, Newcastle upon Tyne, 6.
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P. A. York, Esso Standard Oil (Aust.) Pty. Ltd., AMP Building, Circular Quay, Sydney, New South Wales, Australia.
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Hon. Research Liaison and Hon. Programme Officer : A. McGuire, 6 Cheviot Road, Newlands, Glasgow, S.3.

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A. Pisacane, c/o John S. Craig & Co. Ltd., 12-40 Bogmoor Road, Glasgow, S.W.1.

A. H. Smith, 102 Cartside Street, Glasgow, S.2.

J. D. Easton, B.SC., PH.D., A.R.I.C., 19 Craiglaw Avenue, Waterfoot, Eaglesham, Glasgow.

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Hon. Treasurer : R. Harvie, 8 Dean Park Crescent, Edinburgh, 4.

Hon. Publications Secretary : P. A. Gower, c/o Lorilleux & Bolton, Eclipse Works, Sighthill, Edinburgh, 11.

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Committee :

R. W. Miles, M.A., A.R.I.C., 22 Wester Broom Terrace, Edinburgh 12.

D. I. Muirhead, 73 Bonnyrigg Road, Eskbank, Midlothian.

P. R. Phillips, 10 Craigcrook Park, Blackhall, Edinburgh, 4.

J. H. Stewart, 49 Dreghorn Loan, Colinton, Edinburgh, 4.

T. P. Winter, 13 Belmont Road, Juniper Green, Edinburgh, 13.

A. Wood, 6 Lovedale Avenue, Balerno, Midlothian.

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Committee :

P. A. J. Gate, B.SC., A.R.I.C., c/o ICI (SA) Ltd., P.O. Box 11270, Johannesburg, South Africa.

D. C. Clemes, B.SC., P.O. Box 65, Paarden, Eiland, Cape Province, South Africa.

P. J. Mackenzie Gibb, B.SC., c/o G. J. Wevell (Pty.) Ltd., P.O. Box 1240, Durban, South Africa.

F. Schollick, B.SC., F.R.I.C., c/o British Industrial Plastics (SA) (Pty.) Ltd., P.O. Box 12, Pinetown, Natal, South Africa.

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J. Anneveldt, P.O. Box 46, Kuilsrivier (CP), South Africa.

W. J. de Beer Hoffman, Master Paint Industries (Pty.) Ltd., 18b Coronation Road, Maitland, CP, South Africa.

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This Branch is administered by the Section Committee acting as the Branch Committee.

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P. A. Draper, P.O. Box 44, Jacobs, Natal, South Africa.

K. Brennan, c/o Herbert Evans, P.O. Box 1386, Durban, South Africa.

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Additional Members :

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T. G. Edwards, B.SC., c/o Dulux Paints, P.O. Box 704, Alrode, Transvaal, South Africa.

J. E. Fullard, B.SC., M.B.A., M.S.A., CHEM.I., Organic Coatings Division, South African Bureau of Standards, Private Bag 191, Pretoria, South Africa.

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S. J. Hunt, CSR Chemicals (Pty.) Ltd., 172 Flinders Street, Adelaide, South Australia.

K. A. Metcalfe, B.MET.E., 1 Corona Venue, Fulham, South Australia.

R. G. Moon, 71 Finniss Street, Marion, South Australia.

I. D. Pike, 32 Arthur Street, Seacliff, South Australia.

T. G. Smith, B.SC., Flat 4, Armida Court, Jervois Street, North Glenelg, South Australia.

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J. S. Herron, 31 Hilltop Crescent, East Burwood, Melbourne, Victoria, Australia.

W. D. Lem, 2 Quentin Street, Forest Hill, Victoria, Australia.

F. D. Funnell, S. Smith & Co. Pty. Ltd., 1 Dynon Road, South Kensington, Victoria, Australia.

B. A. Wilcher, B.SC., A.R.A.C.I., ICIANZ Central Research Labs., Newson Street, Ascot Vale, W.2, Victoria, Australia.

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W. Braun, B.SC., ICIANZ Pigments Plant, Leeks Road, Laverton, Victoria, Australia.

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A. S. Jessop, B.SC., 35 Titiro Moana Road, Korokoro, Petone, New Zealand.
M. D. Thomson, 5 Burrows Avenue, Karore, Wellington, New Zealand.
D. J. Wilson, 19 Lower Tory Street, P.O. Box 3747, Wellington, New Zealand.
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A. J. F. Long, 41 Ravenswood Drive, Nollamara, Western Australia.
J. Horton, c/o Esso Standard Oil Aust. Pty. Ltd., B. Parliament Place, West Perth, Western Australia.
N. G. Alchin, c/o Esso Standard Oil Aust. Pty. Ltd., 8 Parliament Place, West Perth, Western Australia.
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Representative on the Council : L. Silver, SPL Paint Centre, 503 Bradford Road, Batley, Yorks.
Social Secretary: H. J. Cochrane, 4a Almsford Drive, Harrogate, Yorks.
Hon, Auditor : P. M. Haigh, A.M.C.T., " Newlands," 41 Borrage Lane, Ripon, Yorks.

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Mrs. K. Driver, John Hargreaves & Son (Bradford) Ltd., 1 Harris Street, Bradford 1.
D. T. Young, Sandoz Products Ltd., P.O. Box Horsforth No. 4, Calverley Lane, Horsforth, Leeds.
C. Allsop, 148 Hookstone Drive, Harrogate, Yorks.
D. Morris, 45 St. Leonards Oval, Harrogate, Yorks.
F. J. Moreham, 40 Princess Road, Ripon, Yorks.
D. R. Gray, 8 Marlborough Grove, Ripon, Yorks.

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Transactions and Communications

Water soluble colloids in emulsion paints with special reference to cellulose ethers*

By A. Reveley and H. Bates

British Celanese Limited, 345 Foleshill Road, Coventry

Summary

This paper discusses some of the conclusions that can be drawn empirically from experience in the use of a variety of colloids in emulsion paints. It is considered that the class of products offering the best balance of properties is that of water soluble cellulose ethers and the paper draws attention to the characteristics of these materials which are significant when selecting suitable grades or types for specific emulsion paint formulations. Reference is also made to the principal advantages and disadvantages of colloids other than cellulose ethers.

The solubility of cellulose derivatives is then discussed with an indication of the probable effect of different environments encountered in emulsion paint systems. A summary is made of the main paint properties which can be affected by colloid additions.

Although emulsion paints are easy to manufacture they are complex mixtures and too little is known of the basic physical chemistry to predict with any accuracy the interactions between the various components.

Le comportement en peintures-émulsions des colloïdes solubles dans l'eau par rapport particulier aux éthers cellulosiques

Résumé

Cet article discute certaines conclusions que l'on peut tirer empiriquement des expériences de l'utilisation en peintures-émulsions d'une gamme de colloïdes. On considère que la catégorie de produits offrant le meilleur bilan de propriétés c'est des éthers cellulosiques solubles dans l'eau. L'article fait remarquer les traits caractéristiques de ces matériaux qui sont d'une importance lors de la sélection des types convenables à la mise au point de formules spécifiques de peintures-émulsions. D'ailleurs on se rapporte aux avantages et inconvénients principaux des colloïdes autre que les éthers cellulosiques.

Ensuite on discute la solubilité des dérivés cellulosiques au point de vue de l'effet probable des environnements que l'on doit attendre aux systèmes de peintures-émulsions. On fait un résumé des propriétés principaux de peinture susceptibles aux additions de colloïde.

Bien que la préparation de peintures-émulsions soit facile, les peintures elles-mêmes sont des mélanges complexes dont la physico-chimie de base est trop peu comprise pour assurer la prédiction exacte des réactions entre les composants divers.

Wasserlösliche Kolloide in Emulsionsfarben mit besonderem Bezug auf Zelluloseäther

Zusammenfassung

In dieser Abhandlung werden einige der Schlussfolgerungen, die empirisch aus der bei der Anwendung verschiedenster Kolloide in Emulsionsfarben gesammelten Erfahrung gezogen werden können, behandelt. Es wird die Ansicht vertreten, dass die Gruppe der wasserlöslichen Zelluloseäther sich im grossen und ganzen am besten eignet, und die Abhandlung weist auf die

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* Presented to the Manchester Section on 18 April 1966

charakteristischen Eigenschaften dieser Stoffe, die für die Wahl der brauchbarsten Sorten oder Gruppen für spezifische Formulierungen der Emulsionsfarben von Bedeutung sind, hin. Auch die hauptsächlichsten Vor- und Nachteile anderer Kolloide, die also keine Zelluloseäther sind, werden erwähnt.

Anschliessend wird die Löslichkeit von Zelluloseabkömmlingen besprochen unter Hinweis auf die Folgen verschiedener äusserer Enflüsse, die bei Emulsionsfarbsystemen zu erwarten sind. Die wichtigsten Eigenschaften von Emulsionsfarben, die durch Zusätze von Kolloiden beeinflusst werden können, werden zusammengefasst.

Obwohl die Herstellung von Emulsionsfarben einfach ist, so ist zu bedenken, dass diese aus komplexen Mischungen bestehen. Man weiss zu wenig von der ihr zugrunde liegenden physikalischen Chemie, um mit Sicherheit die zwischen den verschiedenen Komponenten stattfindenden Reaktionen voraussagen zu können.

Растворимые в воде коллоиды в эмульсионных красках, особенно в отношении эфиров целлюлоза

Резюме

В статье обсуждаются некоторые выводы эмпирически полученные вследствии опытов с употреблением разных коллоидов в эмульсионных красках. Полагается что класс продуктов дающий наилучший баланс свойств найден в растворимых в воде целлюлозных эфирах и в статье обращается внимание на характеристики этих материалов имеющих значение при отборе подходящих сортов или типов для специфических формуловок эмульсионных красок. Обращается также внимание на главные преимущества и недостатки коллоидов, за исключением целлюлозных производных с указанием вероятностного эффекта различных окружающих обстановок которые встречаются в системах эмульсионных красок. Дается резюме главных красочных свойств на которые могут влиять добавки коллоидов. Хотя в производстве эмульсионных красок нет затруднений, всётаки они являются комплексными смесями и о их основной физической химии еще недостаточно известно для предсказания с удовлетворительной точностью взаимодействия между различными компонентами.

Emulsion paints have enjoyed increasing popularity particularly since World War II. This popularity is due to the absence of solvent smell, their ease of application, even on damp and porous surfaces, their resistance to intermittent condensation, and good washability.

The main advantage of having a binder in the form of an emulsion is that its high molecular weight has little effect on the emulsion viscosity. A satisfactory paint, however, with suitable performance in both storage and application, must contain a variety of additives including agents which function both as thickeners and protective colloids.

Recent developments

Developments of the principal parts of an emulsion paint, namely the binder and pigment/extender, to give, on the one hand, improvements in performance and, on the other hand, increased and easier processing, have resulted in the need for an even larger number of special additives. The present trend to the use of fine particle size emulsions of polyvinyl acetate co-polymers which are internally plasticised leads to higher surfactant demands. Some of the new pigments and extenders have special surface coatings to improve their performance and these coatings can have a considerable bearing on the rheological properties of the final paint.

Modern emulsion paints are very easy to make, but they are in fact very complex mixtures. It is, therefore, extremely difficult to establish the principal factors contributing to storage and subsequent application properties, since they cannot be separated and studied individually.

Colloids in emulsion paints

A wide range of high molecular weight water-soluble and alkali-soluble colloids may be used to produce satisfactory emulsion paints. The principal types which have been used include :

Casein
Gums
Polyacrylates
Polyvinyl alcohol
Cellulose derivatives
Starches and starch ethers
Alginates
Seaweed extracts
Polyethylene oxide

Experience over many years has confirmed that, whilst, in certain cases, each of the above types may show either technical or economic advantages, there is no doubt that the class giving the best all-round combination of properties is that of cellulose ethers. The commercial materials now offered, for example, under the trade names " Celacol " and " Courlose " give a wide choice of viscosity grade, type and physical form to suit individual formulation and processing requirements.

Colloids other than cellulose ethers

The principal advantages and disadvantages of colloids other than cellulose ethers which can be used in emulsion paints are summarised as follows. The significance of any particular characteristic may vary considerably from formulation to formulation.

	Advantage	*Disadvantage*
Casein	Promotes good flow	Basically variable, susceptible to bacteriological attack and large changes of pH
Gums	Good flow	,,
Polyacrylates	Very good flow	Viscosity changes at low pH Brush marking Tendency to pigment flocculation
Polyvinyl alcohol	Good protective colloid	Lacking in thickening properties
Starches/starch ethers	Low cost	Variable, susceptible to bacteriological attack
Alginates	Good flow	Susceptible to heavy metal ions and low pH
Seaweed extracts	Good stability	Considerable variation, susceptible to bacteriological attack
Polyethylene oxide	Efficient thickeners	Pigment flocculant

Cellulose ethers as colloids and thickeners

The main commercial water-soluble cellulose ethers used today in emulsion paint production as well as in a wide range of applications in both the surface coatings and other industries are :

1. MC	e.g.	Celacol M	Methofas M		
2. HEMC		Celacol HEM			
3. HPMC		Celacol HPM	Methofas HPM		
4. EHEC				Modocoll E	
5. HEC		Celacol HE			Natrasol
6. SCMC		Courlose F	Cellofas B		
7. ALCMC					

The principal differences between these various types are illustrated by their ionic characteristics and by the effect on heat of aqueous solutions. For example, types 1-5 in the above table are non-ionic ethers, whereas types 6 and 7 are ionic.

Types 1-4 have a definite gel point when their solutions are heated, whereas types 5-6 have no gel point. These effects are characteristic of properties which are particularly important for the way in which the various types exhibit their protective colloid, stabilising and thickening functions.

Solubility of cellulose ethers

The starting point for the manufacture of these types is cellulose which is a partly amorphous, partly crystalline solid insoluble in water. It consists of long chains of anhydroglucose units. Its insolubility is accounted for by the strong hydrogen bonding between molecular chains within the fibrous structure and it is the reduction of this bonding, amongst other things, during etherification which results in a water-soluble product. Detailed investigations have shown that there are three distinct boundaries in the structure of crystalline cellulose.

(*a*) Fibre with a diameter of approximately 100,000 Å.

(*b*) A surface fibril with a diameter of approximately 100 Å.

(*c*) The cellulose molecule with an approximate diameter of 10 Å.

The detailed physical chemical reasons why water-soluble macromolecules such as cellulose ethers do dissolve in water are not fully understood, but it is generally considered that the ionisation of the associated water plays an important part.

In aqueous solution, it is suggested, e.g. by Jirgensons and Straumanis, that the water associates with the cellulose ether molecules in three ways :

(*a*) Water tightly bound by hydrogen bonds especially to polar groups. Here the ionic SCMC differs from the non-ionic ethers.

(*b*) Layers of water molecules associated by hydrogen bonding to the first layer.

(*c*) Slightly associated water immobilised by the geometry of the large cellulose molecule.

These factors too are significant when bonds are formed between solid particles of binder, pigment or extender in an emulsion paint system and the colloid. The redistribution of associated water in long-term storage will be related to such phenomena as syneresis and gel structure development.

Effect of heat and additives

In a simple aqueous solution the effect of heat or the addition of electrolytes will have a more or less significant effect particularly on loosely bound water. The thermogelling ethers have a greater proportion of water which can disassociate as its temperature increases, while the presence of polar groups or more active OH groups, as in HEC, accounts for the less marked effect of heat and electrolytes on non-thermogelling ethers.

Addition of polar agents, such as wetting agents and chlorinated phenols, to cellulose ether solutions may give some redistribution of water and cross-linking of the macromolecules, resulting in a viscosity increase. Similar effects could also occur, say, on pigment surfaces where more or less " reactive sites " would preferentially associate with active groupings, whether polar COO^- groups or less reactive hydroxyls.

The gel point of a thermogelling ether is dependent on viscosity grade and concentration. At relatively low concentrations, discrete particles will precipitate from solutions, while at high concentrations, say, greater than 2-3 per cent, particularly for high viscosity grades, gels of various textures will be formed. These effects are fully reversible. Some additions, such as alcohol and thiocyanates, increase the gel point, while others, such as phenols and tannins, decrease it.

Other important characteristics of cellulose ethers

Three important characteristics of cellulose ethers are :

(*a*) DP (degree of polymerisation).
(*b*) DS (degree of substitution).
(*c*) MS (molar substitution).

(*a*) The degree of polymerisation is the number of units in the cellulose chain, and it is this factor which very largely controls solution viscosity. For commercial products, the DP may range from 50 (molecular weight about 10,000) for low viscosity grades, to 1,500-2,000 (molecular weight 180,000-250,000) for high viscosity grades.

(*b*) The degree of substitution (DS) is the number of hydroxyl groups chemically reacted per anhydroglucose unit. The maximum is 3.

To achieve water solubility the following DS levels are normally used :

Type	*Level of substitution*
SCMC	0.4-1.2 (particularly 0.5-0.8)
MC	1.2-1.9 (,, 1.6-1.9)
HPMC	1.2-1.7 methoxyl 0.2-0.3 hydroxypropoxyl
EHEC	1.0 ethoxyl 0.6-0.8 hydroxyethyl

In the case of hydroxyethyl cellulose the MS is always higher than DS, since there is a marked tendency for the second ethylene oxide molecule to substitute on the new OH formed by the first, rather than to take up another OH on the anhydroglucose ring. Commercial materials have MS in the range 1.8-2.5 corresponding to DS of 1.0-1.6.

The relative reactivities instanced below also have a bearing on the evenness of substitution for particular types, as also does the production method used. Quality of the cellulose ether solutions depends largely on this factor, as do such properties as resistance to bacteriological (enzymatic) attack and degradative oxidation. A more evenly substituted product will have a higher solution quality and greater resistance to depolymerisation than a less evenly substituted product.

The relative reactivities of the three cellulose OH groups are :

	2 : 3 : 6	end OH after first OH substitutes
Methylation	4.5 : 1 : 1.5	—
Hydroxyethylation	3 : 1 : 10	20
Carboxymethylation	2 : 1 : 2.5	—

The main factors which distinguish between the cellulose ethers may be summarised as follows :

Solid	SCMC	MC	EHEC HPMC HEMC	HEC
Solubility in water	Soluble up to 100°C	Thermo-gelling temp. 50°C	Thermo-gelling temp. 65-85°C	Soluble up to 100°C
Solubility in polar organic solvents	Insoluble	Highly substituted grades have limited solubility	Highly substituted grades have limited solubility	Insoluble
Aqueous solution				
Effect of heating (these are reversible)	Viscosity decreases	Viscosity decreases until gel pt./pptn. pt. reached		Viscosity decreases
pH stability	5.0-11.0	———	2.0-12.0	———
Effect of heavy metal (HM) salts	pptn. of (HM) CMC	unaffected until " salted out "		
Tolerance of electrolytes	—	MC	$<$HPMC	$<$HEC
Effect of electrolysis	Migrates	No migration		
Surface tension dynes/cm	70	54	60	63
Bacteriological resistance, most resistance No. 1	4	2	1	3

Paint properties affected by colloid

The following examples illustrate the different effects which can be obtained by using the various ethers :

1. *Variation of pH and presence of heavy metal ions*

When pva homopolymers were first introduced they tended to hydrolyse, resulting in localised reductions of pH. To offset this, additions of buffers such as $CaCO_3$ were made giving an increase in Ca^{++} concentration. When SCMC was used as colloid, the effect of low pH and Ca^{++} gave free CMC and Ca CMC, both of which are water insoluble. This effect was superimposed on the loss of viscosity by bacteriological degradation, and resulted in preference for non-ionic derivatives.

Current emulsions do not suffer from these disadvantages, and many systems can now incorporate SCMC because it does, in general, improve flow properties.

In the USA, where Ti Cal is the main pigment used, ionic colloids are a disadvantage owing to the chemical interaction which takes place with the Ca^{++} ions. These effects can be offset by using a more highly substituted SCMC, but even this is not widely favoured.

2. *Temperature increase*

This may arise during processing or in subsequent storage. While paints with satisfactory tropical storage can be made from MC, the non-ionic with the lowest solution gel point, the trend is to use higher gelling mixed ethers such as HPMC or non-gelling HEC or SCMC.

3. *Flow and brushability*

Since SCMC is ionic, its interaction with pigment/emulsion is of a higher order, and less time-dependent than with the non-ionics. Structure development is less as the surface rearrangements are fewer. Good flow is obtained, as the shear during brushing or rolling easily breaks any bonded matrix which forms. Bonds are, however, relatively slow to reform and, while sagging is prevented, brush marks do flow out satisfactorily.

The non-ionic colloids form bonds of a lower order than SCMC, and this formation is more time-dependent. Surface rearrangements occur over a larger period and structure is more likely to develop. Depending on the nature of other ions and additives in the aqueous phase, cross-linking may occur between colloid molecules, and this supports the development of a matrix between the solid particles in the system. The form of the matrix and the viscosity of the aqueous phase both contribute to satisfactory application properties.

Low molecular weight colloids may be better for flow and for improving wet edge time than high molecular weight types, although the latter are more economical thickeners.

4. *Stability on storage*

Although the interaction of SCMC is of a higher order than that of non-ionics, SCMC is susceptible to heavy metal ions present either on the pigment surface or in the aqueous phase. The result of replacing sodium by, say, calcium will be redistribution of water, resulting in a possible loss in viscosity, but this can be offset by using material of suitable degree of substitution. In modern paints, reactive ions present on pigment surfaces are more relevant than those in the aqueous phase.

Low molecular weight colloids, such as PV alcohol and low viscosity cellulose ethers, give good stability. It is not necessarily economically sound to use less of a high viscosity colloid to give satisfactory paint consistency, as the actual amount of colloid present may be of greater importance. It may be an advantage to use a mixture of molecular weights (i.e. high and low viscosity grades), or even types, e.g. low viscosity SCMC and high viscosity HPMC or HEC, to get best stability and consistency.

Satisfactory thixotropic emulsion paints can be made using all the main cellulose ethers. pH conditions may be selected to give the desired results with combinations of colloids and complexing agents.

Alkali-soluble cellulose ethers, such as Al CMC, can also be used. These types are more likely to give intermolecular cross-linking to form a thixotropic matrix, but their effect is somewhat pH dependent.

It seems that emulsion paint systems require a certain minimum amount of colloid for satisfactory stability. Thus, when colloid-free emulsions are used, the amount of colloid added to the paint must be increased. The use of cellulose ethers as polymerisation colloids can improve paint stability because of their low molecular weight (after degradation in the polymerisation process) and their close association with the emulsion before mixing with other paint components.

Other paint properties where colloid may be important

Some of these can depend very much on formulation.

(*a*) HEC can give more pigment flocculation than other non-ionics.

(*b*) Bacteriological resistance. The most resistant are the mixed ethers, e.g. HPMC, closely followed by MC. Less resistant are HEC and SCMC in that order.

It is important in paint formulations to avoid the presence of enzymes and not merely to kill off enzyme-producing bacteria.

(*c*) Wet rub resistance. There are smaller differences now between the effects of cellulose ether types on wet scrub resistance mainly due to improvements in emulsion and extenders.

(*d*) Some preserving agents and surfactants can have a significant effect on solution viscosity of the colloids. This effect can usually be restrained by adding the cellulose ether separately from the reactive component and at a stage where some dilution takes place.

(*e*) While certain emulsions give the best performance with a limited number of colloids, many of the newer products can give satisfactory paints with most of the available cellulose ethers.

Conclusion

Steady improvements in solution quality of cellulose ethers, and the availability of a wide range of viscosity grades, in physical forms for quick and easy solubility, has allowed these colloids to keep pace with improvements being made to other components of the complex mixture called an emulsion paint.

[*Received 6 June 1966*

Discussion at the Manchester Symposium

Mr. Nation believed that manufacturers of colloidal stabilising materials now offered grades treated with surfactant to promote rapid solubility. He asked if this practice was desirable, bearing in mind the influence of surfactants on the stability of the complete emulsion paint system.

Mr. Reveley thought that this influence could be disregarded. The ratio of surfactant added to colloids was very small, the types were largely non-ionic and, at the colloid concentration used in the final paint, he considered the extent of interference to be infinitesimal.

Dr. O'Neill said that colloids could be placed in order of resistance to bacterial degradation, and asked if the same order would be obtained for resistance to enzymatic degradation.

Mr. Bates replied that solutions of cellulose ethers showed different viscosity stability to bacterial attack arising from enzymatic degradation. There is little difference in the order of magnitude of effect on the various ethers, but their resistance to degradation is in the order HPMC greater than MC, much greater than HEC, greater than SMC.

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Some recent advances in thermosetting acrylic resins*

By P. V. Robinson and K. Winter

Styrene Co-Polymers Ltd., Cheadle, Cheshire

Summary

A brief review of the various types of thermosetting acrylic resin is given. The work carried out by the authors to develop thermosetting acrylic resins with low temperature cure properties for specific application is described, including a discussion of why many thermosetting acrylic resins do not cure until temperatures of 150°C are reached. The performance of the polymer systems for specific application is described in terms of paint evaluation and further areas of research are suggested.

Quelques récents développements dans le domaine des résines acryliques thermodurcissables

Résumé

On passe brièvement en revue les divers types des résines acryliques thermodurcissables. On décrit les recherches effectuées par les auteurs dont le but était la mise au point des résines acryliques destinées à l'usage particulier qui se durcissent à des températures basses. On considère pourquoi beaucoup de résines acryliques thermodurcissables ne se durcissent pas jusqu'on arrive aux températures près de 150°C. On décrit le comportement des systèmes polymères destinés à l'usage particulier relatif à l'evaluation des peintures applicables.

Neue Fortschritte auf dem Gebiete Wärmehärtbarer Akrylsäureharze

Zusammenfassung

Es wird über die verschiedenen Arten von wärmehärtbaren Akrylsäureharzen eine kurze Übersicht gegeben. Die von den Autoren zwecks Entwicklung für spezifische Zwecke bei niedriger Temperatur wärmehärtender Akrylsäureharze durchgeführten Arbeiten werden beschrieben. Ausserdem wird ausgeführt, warum zahlreiche wärmehärtbare Akrylsäureharze nicht unlöslich werden, ehe eine Temperatur von 150°C erreicht ist. Der Grad der Leistungsfähigkeit des für spezielle Zwecke geschaffenen Polymersystems wird mittels Bewertung von Anstrichmitteln klargemacht. Weitere Forschungsgebiete werden vorgeschlagen.

Некоторые новейшие успехи в исследовании термозатвердевающих акриловых смол

Резюме

Дается краткий обзор различных типов термозатвердевающих акриловых смол. Описывается работа выполненная авторами для развития термозатвердевающих акриловых смол с свойством низкой затвердевающей температуры, применяемые в определенных случаях, в этой работе включается также обсуждение вопроса о причине многих акриловых смол не затвердевающих ниже температуры 150°C. Описывается также действие полимерных систем с специфическими применениями относительно оценки красок и предлагаются дальнейшие развития исследований.

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*Presented to the Newcastle Section on 7 January 1965.

Introduction

The chemistry and properties of thermosetting acrylic resins have been reviewed in the past and particular mention might be made of K. E. Piggott's paper published in this *Journal* some time ago[1]. That paper covers comprehensively the chemistry of polymerisation and cross-linking of the various types of thermosetting acrylics whether commercial or not. The present paper deals with certain aspects of thermosetting acrylic resins which have been carried out in the authors' laboratories.

When thermosetting acrylic resins were introduced, they constituted a new family of polymers of extensive usefulness in the paint industry and, up to three or four years ago, the variety of paint systems offered was governed by the range of different polymer systems which became available. In the last few years there have not been any technically significant additions to the range of polymers available from various manufacturers but rather the emphasis has been placed on the end use. Of course, this has meant that existing polymer systems have had to be modified to fit them more suitably for their particular application, but basically the polymer systems are still the same. For example, there has been an increasing demand for water soluble resins suitable for application by the revived technique of electrodeposition, solid resins for electrostatic and fluidised bed applications, together with large-scale applications in which the means of depositing the film are conventional, but where there has been a major bid by the acrylic system for business held by the widely used alkyd/melamine formulations. Typical of this latter development is the interest of certain motor companies in the use of thermosetting acrylics in motor car top coats.

Definition

For the purpose of this paper a thermosetting acrylic resin is regarded as one in which the carbon-to-carbon polymeric chain is cross-linked in the film and at least part of the active cross-linking agent is acrylic derived. Accordingly, this does not exclude such typical thermosetting acrylic materials[2] as Resin (1) in Table 1 which is predominantly non-acrylic although it does cross-link by

Table 1

Typical formulations of acrylamide—containing interpolymers

	Resin (1)	Resin (2)	Resin (3)
Styrene	82.5	37.5	25.0
Ethyl acrylate	—	45.0	64.0
Acrylamide	15.0	15.0	10.0
Methacrylic acid	2.5	2.5	1.0
Xylene	50.0	50.0	—
Butanol	50.0	50.0	33.0
Shellsol A.B.	—	—	33.0

way of its acrylamide component. On the basis of this definition, it is intended to discuss, very briefly, the elementary chemistry of thermosetting acrylic resins in general. It is then intended to describe some of the problems which have been of interest recently, including work directed towards systems which bake at temperatures below 175°C. Finally, the latest polymer systems developed in the authors' laboratories will be described and the relationship of the new polymers to laboratory work will be evident.

Vinyl polymerisation

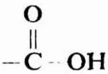
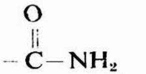
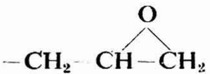
Vinyl monomers are characterised by the formula $CH_2{=}CHR$ where R can be almost any group. Polymerisation of such monomers is additive and can be described by four distinct steps, termed Initiation, Propagation, Transfer and Termination[3]. Vinyl copolymerisation involves two or more monomers and the monomers are seldom used up randomly. The manner in which the monomers are used can be described by reactivity ratios which are characteristic of the monomers in question[4]. A number of reactivity ratios for various monomer pairs have been determined experimentally and the relationship of reactivity ratio and monomer structure has been shown semi-quantitatively[5]. Consideration of published data relating to reactivity ratio is of the utmost importance in the preparation of TSA resins, since without suitable precautions heterogeneous copolymers may be obtained[6].

The use of reactivity ratio data becomes more difficult as the number of components in a system increases due to unwieldy arithmetic, although the general case has been stated[7]. An interesting solution to this problem involves the use of a three-component graph and the relevant patents claim that only those compositions of a three-component monomer system which fall into a certain area on the graph are homogeneous[8].

Cross-link chemistry

The chemistry involved during cross-linking reactions is well known from classical organic chemistry and the exact cross-linking mechanism depends on the type of monomer used to introduce cross-linking potential (see Table 2). Hence, if a copolymer contains carboxyl groups derived from such monomers as methacrylic acid, acrylic acid, etc., then this can be cross-linked with polyepoxides[9], the chemistry of this reaction being well known from the use of epoxy resins cross-linked with diacids. Such an acid-containing polymer may also be cross-linked with an aminoplast to form interesting coatings products[10]. Hydroxyl groups may be incorporated in the copolymer either by the use of monomers, such as hydroxyethyl or hydroxypropyl acrylates or methacrylates[11], or by the hydroxyethylation or hydroxypropylation of carboxyl containing copolymers[12]. Such hydroxyl containing copolymers are particularly well suited to cross-linking with aminoplast condensates[13] and di-isocyanates (cold cure)[14]. In some cases the acrylic resin can contain both carboxyl and hydroxyl groups[15] and as such could be regarded as taking the place of non-drying alkyds in alkyd/melamine systems. Obviously, there are many other chemical reactions which could be used to cross-link vinyl copolymers. Such monomers as methylol acrylamides[16], N-butoxymethyl acrylamide[17] and monomers containing the groups glycidyl[18], amine[19], allyl ether[20], isocyanate[21], etc. are examples of specific means of obtaining copolymers with different functional groups which

Table 2
Typical cross-linking monomers

Pendant groups	Typical monomer	Cross-linking reagent	Catalyst
(A)  $-\overset{\overset{O}{\parallel}}{C}-OH$ Carboxyl	Methacrylic acid	Epoxy resins Aminoplasts Phenoplasts	Basic
(B) $-CH_2-CH_2-OH$ Hydroxyl	Hydroxyethyl methacrylate	Aminoplasts Di-isocyanates Phenoplasts	Acidic Zn. octoate
(C) $-NCO$ Isocyanate	Vinyl isocyanate	Polyhydroxies Polyamides Polyamines	Zn. octoate Zn. octoate Zn. octoate
(D)  $-\overset{\overset{O}{\parallel}}{C}-NH_2$ Amide	Acrylamide	Dialdehydes (glyoxal)	Basic
(E)  $-\overset{\overset{O}{\parallel}}{C}-NH-CH_2-OH$ Methylolamide	Methylolacrylamide	Not required (epoxy resins, aminoplasts etc.)	Acidic
(F)  $-\overset{\overset{O}{\parallel}}{C}-NH-CH_2-O-R$ N-alkoxymethyl Amide	N-butoxymethyl acrylamide	Not required (epoxy resins, aminoplasts, etc.)	Acidic
(G)  Glycidyl	Glycidyl methacrylate	Not required (polycarboxyls, polyamines, polyamides, etc.)	Basic Basic — —
(H) $-CH_2-NH_2$ Amine	Allyl amine (Vinyl pyridine)	Epoxy resins Di-isocyanates	— Zn, Sn salts
(I) $-O-CH_2-CH=CH_2$ Allyl ether	TMP diallyl ether methacrylate	Not reqd. (O_2) (polyhydroxyls)	Co. salts

can then be cross-linked in some suitable manner. Cross-linking systems can be divided into two groups, one group being self-reactive, the other group being potentially co-reactive. In the self-reactive group one might consider methylol acrylamide copolymers which will cure without a cross-linking agent, whilst an example of the potentially co-reactive type of system would be the carboxyl containing polymer which is thermoplastic in its own right but which can be thermoset by use of such cross-linking agents as polyepoxides or aminoplast condensates.

Standard acrylamide vehicles

As a class of polymers these can be regarded as being self-reactive, but this does not mean that reactive cross-linking agents may not be used as well.

For example, several commercially successful products contain both self-reactive methylolamide groups which are sometimes etherified (see Table 1) and carboxyl groups. The resultant resin is blended with a polyepoxide and the carboxyl group fulfils the dual role of catalysing the self-cross-linking of the substituted amide group and of entering into cross-linking reactions with the epoxy groups of the polyepoxide. The technique of preparing acrylamide and other interpolymers is relatively simple, although there are obviously many points of detail which must come under the heading of " know how."

Recent work

The authors' recent activity in the field of thermosetting acrylics has covered a wide spectrum of industrial uses and for the purpose of this paper " recent " activity is regarded as being not more than two or three years old. Some of this work is obviously at an intermediate stage and has yet to be completed, whilst other work has resulted in patents being applied for and granted.

Clarity stability

In the early days of thermosetting acrylic resin production based on acrylamide, polymer solutions were prepared which, although clear and bright initially, gradually developed a hazy appearance on prolonged storage. Detailed investigation showed quite conclusively that this haze development had no deleterious effects on performance in paint. It was established that the cause of the haze development was the reaction of ammonia, produced as a by-product during polymerisation, with the epoxy resin added at the end of the reaction. Two methods of overcoming this haze formation were developed. One involved the removal of the epoxy group of the epoxy resin prior to its addition to the copolymer solution ; the second involved the protection of the amide group of acrylamide (shown to be the source of the ammonia) during the polymerisation so that breakdown could not occur.

Low temperature cure

Concurrent with the problem of haze was the problem of stoving temperature. Standard acrylamide based resins must be given a curing schedule of 30 minutes at 170°-180°C or equivalent, and it was evident that sales resistance was being met because of this high temperature schedule. A programme of work was therefore adopted to investigate ways and means of reducing the curing temperature and yet maintain the same performance and price. Several techniques of producing lower curing temperature products were examined. External catalysis in the form of stronger acids or other catalysts to promote the methylolamide cross-linking reaction were tried ; more active cross-linking agents were developed and one of special interest involved the preparation of a more active form of epoxy resin for use in blends with standard acrylics. Internal catalysis in the form of higher copolymerised acid content and copolymerised catalysts for the carboxyl/epoxy reaction were also investigated.

The result of this investigation was the development of two products which would bake at a lower temperature, but it was established that if no concessions were made in respect of film performance, then the absolute lower limit of stoving temperature when baked for 30 minutes was 145°C. The reasons for this lower limit are a little difficult to understand, because if one considers the catalysed curing of aminoplasts, a reaction which is chemically similar to the cure reaction of acrylamide interpolymers, then cure temperatures much lower than 145°C are obtainable. It was suggested that the relevant activation energies were being attained, especially in the catalysed systems, for self-cross-linking to take place at temperatures below 145°C, but the reactive groups were not close enough to each other. The higher temperatures (i.e. greater activation energies) were thought to be necessary in order to move the vinyl polymer chains around sufficiently for cross-linking to become probable. This additional activation energy can only be obtained at temperatures approaching 150°C. This feeling was strengthened when it was discovered that all techniques aimed at reducing curing temperatures were successful only to 145°C and this was, in many respects, independent of the cross-linking mechanism ; hence polymers cross-linked according to the carboxyl/epoxy reaction also appeared to have this minimum curing temperature.

The performance of acrylamide-containing polymers modified with increased levels of combined acid is shown in Table 3. Generally, the performance of Resin (2), which contains more copolymerised acid than Resin (1), is equivalent when baked for 30 minutes at 150°C to that of Resin (1) baked for 30 minutes at 175°C.

Table 3

Performance of low bake acrylic—acrylamide type

	Resin (1)	Resin (2)
Cured	30 mins. 175°C	30 mins. 150°C
Erichsen	2.0	1.5
Bend	Pass 1″	Pass 1″
Adhesion	Fair	Fair
Impact	Fail 15″	Fail 15″
Scratch hardness	>3100	>3100
Pencil hardness	5H	4H
Lipstick stain 24 hrs.	Unaffected	Unaffected
Humidity 14 days	Isolated fine blis.	Isolated fine blis.
Salt spray 21 days	$\frac{1}{8}$″ Creep	$\frac{1}{8}$″ Creep
Boiling detergent	Fine blisters	Fine blisters
50% H_2SO_4	Unattacked	Unattacked
40% NaOH	Unattacked	Unattacked

The use of highly functional cross-linking materials such as aminoplasts and alkyds in association with functional thermosetting acrylic resins, permit lower curing temperatures—in some cases down to 120°C. or less—and it was felt that this also strengthened these views on the nature of curing reactions that the high functionality of the cross-linking additive (aminoplast or alkyd) would ensure adequate cross-linking in the absence of the energy required to activate the vinyl polymer chains into suitable cure positions. The properties of such cured systems, whilst being of a high order are not, unfortunately, of the highest quality that can be attained from the original resins cured at 150-175°C.

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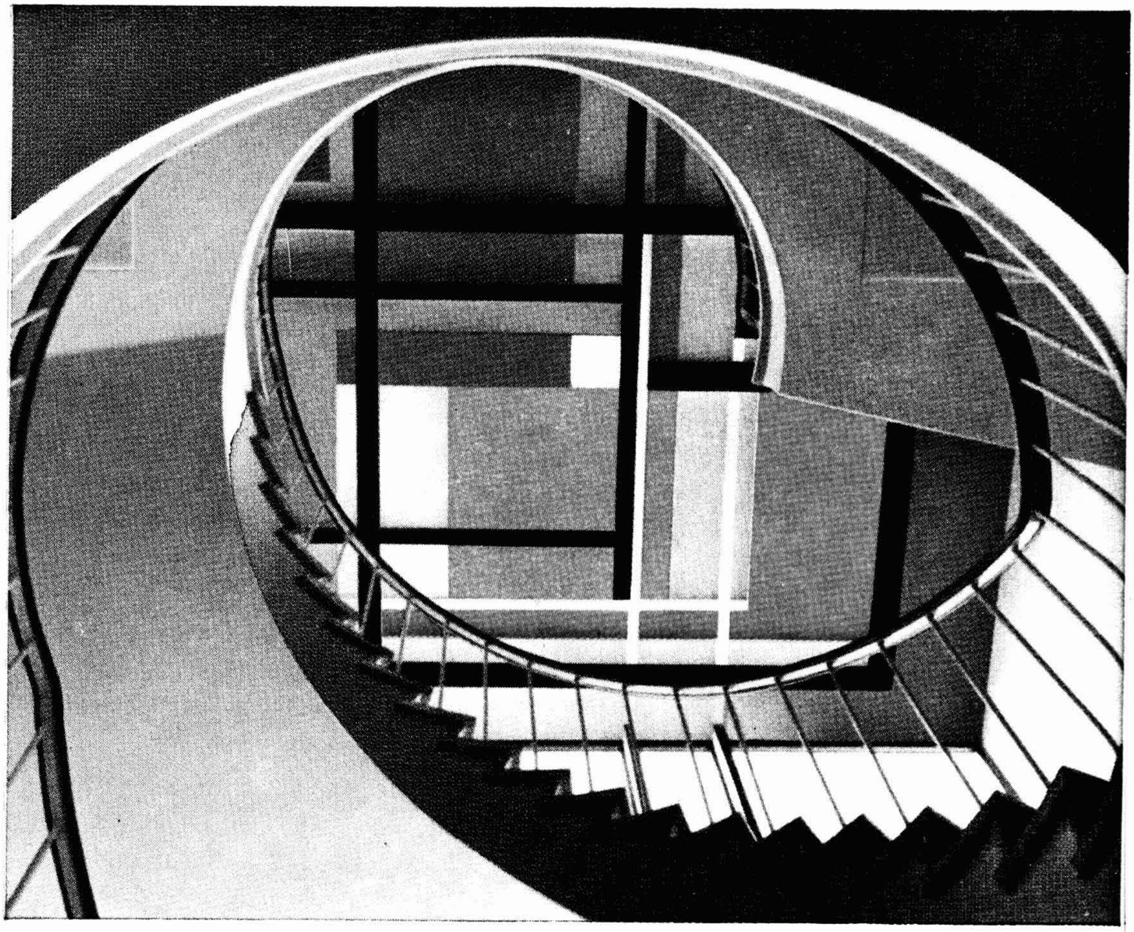

This observation was confirmed by carrying out simple solvent inextractible tests, where poorer cure was found in systems baking below 150°C. The results obtained from these tests, however, were used as a starting point in the choice of systems for different applications. Fig. 1 shows the solvent inextractible content of four different polymer systems cured over a wide range of temperatures.

System 1 is a typical acrylamide containing vehicle.

System 2 is a modified version of this, in which the acid level is significantly higher, prepared as a result of the investigation into curing mechanisms described previously.

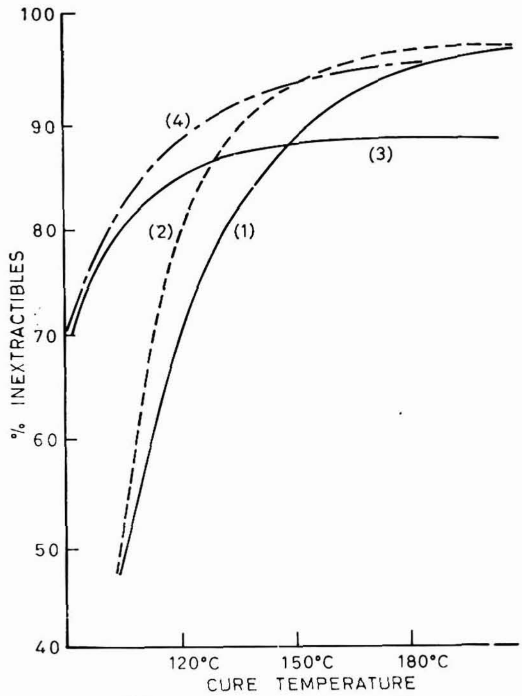

Fig. 1. Solvent inextractibles of different thermosetting acrylics.

System 3 is a carboxyl/hydroxyl-containing copolymer, cross-linked with a melamine formaldehyde resin, whilst System 4 is a polymer system which has been developed very recently, cured by a cross-linking mechanism which is a combination of the first three systems.

System 1 has a very low level of cure at 120°C and only attains a reasonable degree of cure at 150°C with full cure of 96 per cent inextractibles or better being obtained at 180°C. The modified version of this is shown as System 2, and attains acceptable degrees of cure at 150°C but below 150°C there is a sharp fall off in inextractible resin content of the cured film.

System 3 demonstrates a very high level of cure at 120°C but with no further significant increase in cure even up to 180°C, whilst System 4 shows an even higher degree of cure than System 3 at 120°C and rises to the same degree of cure as Systems 1 and 2 at their respective optimum cure temperatures.

From these results it is apparent that System 1 can only be cured at temperatures around 175°C, whilst System 2 has a minimum curing temperature of around 145°-150°C. Neither of these systems holds out promise for subsequent modification that would permit acceptable degrees of cure at 120°C. The performance, however, of these two systems at their optimum cure temperatures is extremely high, as shown previously. System 3, on the other hand, obviously cannot be considered for highly chemical resistant coatings because of its inability to reach a high level of cure, but it does hold out promise for applications which do not involve such high levels of chemical resistance. System 4 cannot be considered for finishes where high durability is required on account of the monomer and additive composition which is not suitable for exterior durability applications and which is a two-pot system anyway. The performance of this system, however, in its chemical resistance characteristics is outstanding, being a significant improvement over conventional alkyd/melamine when baked at 120°C with the cost being somewhere between a conventional alkyd/melamine and the kind of resin typified by System 1.

Motor car finishes

Since the motor car industry has, over the last few years, started to evaluate thermosetting acrylic resins as the basis of motor car finishes, it was decided to base the preliminary investigation on System 3 because of the encouraging cure results obtained. The reasons for this interest are varied and differ from manufacturer to manufacturer, but in brief they are concerned with difficulties in application associated with conventional systems, along with difficulties in certain types of pigmentations. It has been stated[22] that, after application and cure of the conventional alkyd/melamine paint, as many as 30-40 per cent of the finished cars are rejected by Inspection as requiring further treatment. Furthermore, one of the most salesworthy motor car enamels is the so-called polychromatic finish and, as is well known, this is difficult to attain with a conventional alkyd/melamine formulation. It has been amply demonstrated that polychromatic finishes based on acrylic systems have excellent gloss and brightness, whilst the whole point about the use of thermosetting acrylics in standard colours is that the enamel may be abraded and re-polished after baking whilst still retaining the other desirable properties of an alkyd/melamine formaldehyde formulation.

The requirements for a motor car enamel are varied, and a few of these are : film hardness, flexibility, gloss and gloss retention, colour and colour retention, mar resistance, polishability, corrosion resistance, durability, petrol and stain resistance, acid cure capability, impact resistance, chip resistance, adequate film build in one application—all combined with a baking temperature of 120°C for half-an-hour.

Many of these requirements are inter-related ; thus, mar resistance and polishability are difficult factors to reconcile and a great deal of work has been carried out in America, this country and Europe to develop a workable system. As presently foreseen, thermosetting acrylics will cost more than conventional alkyd/melamines and the general technique seems to be that the alkyd component of an alkyd/melamine system is replaced by a suitable acrylic component. There are many organisations working according to this idea and at the moment the patent situation is very confused. There are at least four American systems available, either directly or under licence, and several British and European manufacturers are developing their own.

From the patents mentioned all the systems appear to be very similar in that they consist of copolymers containing carboxyl and/or hydroxyl groups cross-linked with a suitable melamine formaldehyde resin. The kind of results which can be obtained from this type of system has been mentioned briefly during the description of the work on comparison of the degree of cure of various polymer types. As has also previously been pointed out, there are other factors which need to be taken into account when a motor car finish is formulated and in order to obtain the required degree of flexibility, hardness, mar resistance and polishability, such monomers as ethyl, isobutyl, butyl acrylate and styrene, methyl methacrylate and acrylonitrile may all be used as the basis of a copolymer containing hydroxyl and carboxyl groups. The choice of these monomers is further complicated by considerations of reactivity ratio, transferability and solubility parameter of the completed polymer. The use of some monomers is further restricted by such factors as durability, alkali resistance, etc. an obvious example in the case of durability being styrene which is generally absent or only present in small quantities in motor car systems.

Earlier it was pointed out that the extremely low level of cure developed by Systems 1 and 2 at 120°C did not hold out much promise for any modified version being capable of curing at 120°C. System 3, however, did hold promise in this direction and it was decided to evaluate the effect of carboxyl and hydroxyl content of the acrylic copolymer and, in addition, the effect of different melamine contents on the degree of cure and film performance of enamels derived from them.

Fig. 2. shows the results obtained when a series of resins of different hydroxyl and carboxyl contents was cured at 120°C in the presence of 30 per cent melamine formaldehyde resin. The first obvious conclusion is that a copolymer containing high levels of carboxyl groups but low levels of hydroxyl groups does not cure at all well with the melamine resin used in these experiments and it is only at a hydroxyl number of around 25 that adequate levels of cure are obtained. The second conclusion is that there appears to be an increase in performance with a lowering of acid number at the same hydroxyl content and, although the results are not unambiguous here, it was decided to concentrate on the lower acid number materials because of the poorer water resistance properties of resins containing high levels of carboxyl groups. What can be said is that there is no improvement to be gained by increasing the acid number beyond a level demonstrated by Curve " B." Another point worth mentioning is that, similarly, there is little to be gained from increasing the hydroxyl number above a certain level since this does not result in any further significant increase in inextractibles. It is felt that this factor is related to reactivity ratio considerations ; it is envisaged that copolymer molecules exist which do not contain any cross-linking active centres.

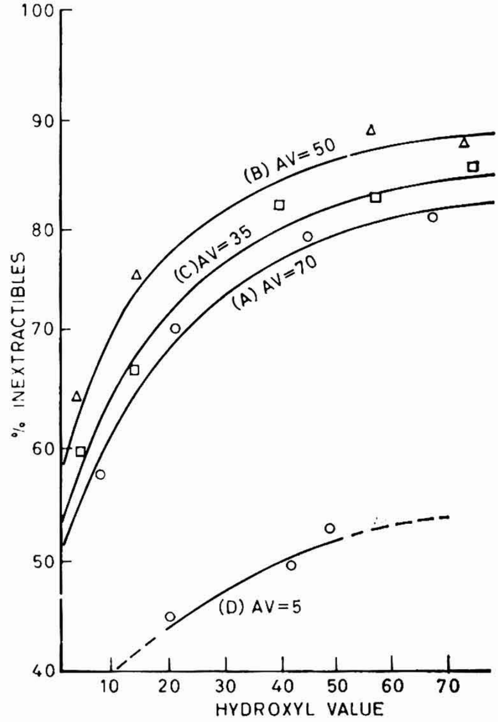

Fig. 2. Inextractible contents. Effect of OH and COOH level

From these results, it would obviously be interesting to find out what would happen if, while maintaining hydroxyl numbers in excess of about 20, acid values lower than 35 were tried. Unfortunately, when the particular melamine resin used in the experimental work so far was tried, incompatibility problems arose and this point could not be checked directly. A modified melamine formaldehyde resin was prepared, therefore, which was compatible with such low acid value copolymers, and the extractability results obtained showed that, where the acid level was very low, then, even though high levels of hydroxyl content were present, low degrees of cure were obtained. This would suggest that the carboxyl group has at least a dual function in that it can act as a catalyst for the hydroxyl/aminoplast reaction as well as taking part in cross-linking reactions directly. Similar conclusions have also been arrived at by workers at the Paint Research Station working with certain alkyd/melamine systems[23].

A further investigation involved the use of different levels of melamine resin in blend with a copolymer of the optimum carboxyl/hydroxyl contents. Fig. 3 shows that increasing cure with increasing melamine formaldehyde content is obtained. This effect is a true inter-cross-linking effect, but, at high levels of melamine formaldehyde resin, is also strongly related to the increasing proportion of self-crosslinkable component. In this case, the choice of melamine level must obviously be decided upon as a result of film performance data.

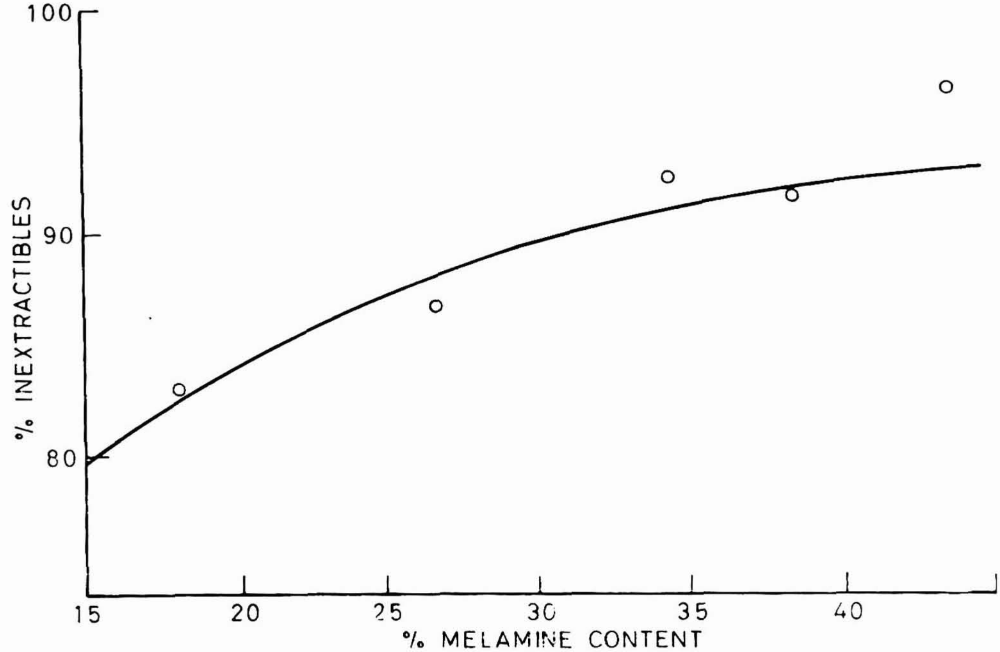

Fig. 3. Inextractible contents—effect of varying melamine content

Table 4 shows the film performance obtained with four different melamine modifications of the copolymer used in these experiments and from these results a 30 per cent melamine level was thought to offer optimum performance,

Table 4

Effect of varying melamine content

Cured 30 minutes 120°C

	15% Melamine formaldehyde	22% Melamine formaldehyde	30% Melamine formaldehyde	35% Melamine formaldehyde
Erichsen	3.5 m.m.	2.2 m.m.	1.5 m.m.	1.0 m.m.
Impact ″/lbs	Fail 15	Fail 15	Fail 15	Fail 15
Reverse impact ″/lbs	Pass 15	Pass 15	Pass 15	Pass 15
Bend	Fail 1″	Fail 1″	Fail 1″	Fail 1″
Cross hatch adhesion	Excellent	Excellent	Excellent	Excellent
Gloss	97%	96%	102%	93%
Salt spray 240 hrs.	$\frac{1}{32}$″ × creep	$\frac{1}{16}$″ × creep	$\frac{3}{64}$″ × creep	$\frac{1}{32}$″ × creep
Water soak 32 C 240 hrs.	Unaffected	Unaffected	Unaffected	Unaffected
Humidity 240 hrs.	Overall micro blis.	Overall micro and isol. $\frac{1}{32}$″ blis.	Micro blis. and isol. $\frac{1}{16}$″ blis.	$\frac{1}{32}$″ × creep and isol. $\frac{3}{32}$″ blis.
Mar resistance	Moderate	Moderate/good	V. good	V. good
Polishing properties	Good	Good	Good	Moderate/good

especially when the properties of mar resistance and polishability were considered.

In Table 5 can be seen the kind of performance which can be obtained from thermosetting acrylic resins of the types described in comparison with typical alkyd/melamine resin as used for motor car enamels. As can be seen, the main improvements obtained are in respect of polishing properties at the expense of a slight reduction in mar resistance. Generally, other properties are of a similar order, but the poor flexibility characteristics of thermosetting acrylic Resin (1) gave some cause for concern. Accordingly, thermosetting acrylic Resin (2) was prepared, which was designed to have properties as close as possible to those of the first resin, but with improved flexibility characteristics.

One of the major requirements of the motor-car industry is that paint systems should be capable of undergoing cure under low temperature, catalysed conditions. Table 6 shows the kind of performance obtained when thermosetting acrylic resins are acid catalysed and baked at a number of schedules below 120°C. There appears to be an increase in flexibility and some loss of gloss with evidence of under-cure where the stoving schedule coupled a short stoving cycle with a low temperature.

Motor-car enamels obviously have to be highly durable and Table 7 shows that the two resins being discussed here have a comparable performance to that of a standard alkyd/melamine. The trials on durability are obviously not complete and further results are continually coming to hand.

General finishing

Reference to Fig. 1 shows that System 4 has a high inextractible resin content, and although its formulation is such that it will not perform well in exterior applications, the system was evaluated for its level of performance as a general purpose appliance enamel. An enamel prepared from this polymer system was used as the basis of a one-coat system applied to bare untreated steel and baked at two schedules (see Table 8). The first was for 30 minutes at 120°C, whilst the second was for 30 minutes at 150°C. The system was compared against a standard alkyd/melamine baked for 30 minutes at 120°C and an acrylamide containing copolymer baked for 30 minutes at 150°C. The properties of this system, especially when cured for 30 minutes at 120°C, are very encouraging since the performance is very close to that of an acrylamide containing copolymer and is a significant advance in performance over an alkyd/melamine baked at 30 minutes at 120°C ; in particular an improvement in properties is obtained in hardness, stain resistance, chemical resistance and water soak resistance. The acrylic composition is a one-coat system in distinction to the alkyd/melamine formaldehyde which is over a primer.

Water dilutable resins

In recent years there has been a very large development of interest in water dilutable polymeric systems for use in surface coatings.

Table 5

Comparison of two thermosetting acrylic systems with alkyd/melamine

	Thermosetting acrylic (1)	Thermosetting acrylic (2)	Alkyd/melamine
Cure	30 mins. 120°C	30 mins. 120°C	30 mins. 120°C
Erichsen	1.5 m.m.	4.0 m.m.	7.0 m.m.
Impact ″/lbs	Fail 15	Fail 15	Fail 15
Reverse impact ″/lbs	Pass 15	Pass 60	Pass 60
Bend	Fail 1″	Pass $\frac{3}{8}''$	Pass $\frac{1}{4}''$
Cross hatch adhesion	Excellent	Excellent	Fair
Gloss	102%	97%	100%
Salt spray 240 hrs.	$\frac{3}{64}''$ × creep	$\frac{1}{16}''$ × creep	$\frac{1}{16}''$ × creep
Water soak 32°C 240 hrs.	Unaffected	$\frac{1}{32}''$ × creep	$\frac{1}{32}''$ × creep
Humidity 240 hrs.	$\frac{1}{16}''$ creep $\frac{1}{16}''$ blis.	Isol. $\frac{1}{16}''$ blis.	Loss of gloss Isol. micro blis. soft
Mar resistance	V. good	V. good	Excellent
Polishing properties	Good	Good	Poor

Table 6

Effect of stoving schedule on acid cure—2½% catalyst

Normal enamel cure 30 mins. 120°C

Cure	30 mins. 80°C	45 mins. 80°C	60 mins. 80°C	20 mins. 99°C
Erichsen	4.0 m.m.	3.9 m.m.	4.0 m.m.	3.0 m.m.
Impact ″/lbs	Fail 15	Fail 15	Fail 15	Fail 15
Reverse impact ″/lbs	Pass 15	Pass 15	Pass 15	Pass 15
Bend	Fail 1″	Fail 1″	Fail 1″	Fail 1″
Cross hatch adhesion	V. good	V. good	V. good	V. good
Gloss	105%	104%	103%	99%
Salt spray 240 hrs.	$\frac{1}{16}$″ × creep	$\frac{1}{16}$″ × creep	$\frac{3}{32}$″ × creep	$\frac{1}{16}$″ × creep
Water soak 32°C 240 hrs.	Loss of gloss Soft	Sl. loss of gloss Soft	Sl. loss of gloss $\frac{1}{64}$″ × creep	Unaffected
Humidity 240 hrs.	Loss of gloss Film completely broke down	Loss of gloss Film chalky blis. to $\frac{1}{16}$″	Loss of gloss Soft, sl. chalky film $\frac{1}{16}$″blis.	Loss of gloss $\frac{1}{16}$″ creep $\frac{1}{16}$″ blis.
Mar resistance	Poor	Poor/moderate	Moderate/good	Good
Polishing properties	Good	Good	Good	Good

Table 7

Florida exposure—direct inland, 45° south

Product	60° Gloss Original	60° Gloss Present	Chalk, bronze and scum	Colour change	Dirt retention	Mildew
Auto finish ' A '	92	80	None	Sl. fad.	Sl.	Sl.
Auto finish ' B '	90	78	None	Sl. fad.	Sl.	Sl.
Alkyd/melamine	99	78	None	None	Sl.	Sl.

Table 8

New thermosetting acrylic

Cure	30′ 120°C	30′ 150°C	Alkyd melamine 30′ 120°C	Acrylamide containing co-polymer 30′ 150°C
Erichsen m.m.	3.0	0.5	7.0	3.0
Impact ″/lbs.	F.15	F.15	F.15	P.30
Cross hatch	Fair	Fair-Poor	Fair	V. good
Scratch hardness	3100+	3100+	1800	3100+
O'Stove 20 hrs./120°C	No discoloration			Sl. discol'n
	← Sl. loss of gloss →			No loss of gloss
Lipstick $2\frac{1}{2}$ hrs.	Unaff.	Unaff.	Severe	Unaff.
36 hrs.	V. sl.	V. sl.	Severe	Unaff.
40% NaOH 7 days	Unaff.	Unaff.	Loss of gloss Film pitting	Unaff.
50% H_2SO_4 3 days	← Loss of adhesion →			Unaff.
1% Tide 20°C 7 days	← Unaff. →		Isol. $\frac{1}{8}$″-$\frac{1}{4}$″ blis.	Unaff.
28 days	← Isol. $\frac{1}{16}$″-$\frac{1}{4}$″ → blis.		Isol. $\frac{1}{4}$″-$\frac{1}{2}$″ blis.	Isol. $\frac{1}{32}$″-$\frac{1}{16}$″ blis.
1% Tide 98°C 6 hrs.	O'all $\frac{1}{16}$″-$\frac{1}{8}$″ blis. ← with no difference → between cure temp.		O'all $\frac{1}{8}$″ blis.	$\frac{1}{4}$ area covered in micro blis.
Water soak 32°C 1000 hrs.	$\frac{1}{4}$″ × creep and blis.	$\frac{3}{16}$″ × creep and blis.	O'all micro blis. $\frac{1}{32}$″ creep	Isol. × blis.
Water soak 20°C 1000 hrs.	O'all $\frac{1}{32}$″ blis. × creep	$\frac{1}{32}$″ × blis. and creep	Isol. micro blis. $\frac{1}{32}$″ × blis. and $\frac{1}{16}$″ × creep	Isol. × blis.

Some 30 years ago the Crosse and Blackwell patents on " electrophoresis " were taken out and it is widely accepted that one of the main reasons for their ultimate lack of commercial exploitation was that a water dilutable resin of adequate film performance was not available. Since that time there has been considerable work carried out to develop water dilutable systems with the necessary standards of film performance and this has been aided to a very large extent by the commercial availability of a wide range of new raw materials.

Methods

One of the most widely used methods of obtaining a water soluble resinous system is to provide the polymer with sufficient carboxyl groups such that subsequent neutralisation with a volatile base will cause the polymer to become water soluble. Obviously, if the carboxyl content of a polymer is taken too high, then, although improved water solubility may be achieved, there is a falling-off in film properties, especially in respect of water resistances. The other most popular method of obtaining water dilutable systems is to produce a polymer in emulsion or suspension form and both methods have points for and against them.

Water soluble alkyds are well known in which the alkyd is cooked to a suitable viscosity at an acid value of approximately 50. A solubilising base such as ammonia or triethylamine is then added and the resulting alkyd is water soluble. Vinyl polymerisation, however, in the presence of a suitable acid such as methacrylic acid is not so easy in the mass, and hence polymerisations are usually carried out in a water soluble solvent such as isopropanol, ethanol, dioxan, etc., followed in some cases by distillation to remove at least a part of the water soluble solvent[24].

A volatile base is then added and the resultant polymer salt can be diluted indefinitely in water. In some cases it is preferable to prepare a suitable polymer by emulsion polymerisation followed by the addition of volatile base upon which the polymer emulsion passes into a water solution. In other cases it is preferable to use the polymer emulsion for paint making in the emulsion form.

Generally, preparation of vinyl copolymers in water soluble solvents can be carried out very easily and all the subsidiary reactions necessary for the ultimate preparation of the polymer, such as the addition of formaldehyde followed by some etherification in the case of acrylamide interpolymers, or hydroxyalkylation of carboxyl containing polymers, are feasible. One of the major disadvantages of this method of preparation is that, usually, it is not possible to remove all the solvent, especially in the case of some self-reactive polymers, and accordingly the final water soluble resin will contain solvent. This is particularly a disadvantage when high flash point solutions are essential. On the other hand the presence of organic solvents can be an advantage as far as solvent release, gloss, flow, can-stability and electrodeposition properties, etc., are concerned.

Emulsion polymers are prepared by causing the polymerisation to take place in the surfactant micelles of a water/surfactant mixture. This is usually carried out by first emulsifying a portion of the appropriate monomer mixture with suitable surfactants, followed by the addition of water soluble catalyst and activator. When the reaction commences further monomer mixture is added together with further surfactant, water and catalyst, until copolymerisation is complete. This is by no means the only method of emulsion polymerisation and there are a great many different and equally effective procedures. A disadvantage with the emulsion polymerisation technique is that reactions on the completed polymer chains are more difficult than is the case with a solution polymer. In the case of acrylamide interpolymers, a suitable modified monomer has to be prepared prior to emulsification and polymerisation. The reason for this is that acrylamide is water soluble and hence polymerises mainly in the continuous phase, even though it is found possible to dissolve some of the acrylamide in the monomer phase prior to emulsification. A further complication is that subsequent reaction with formaldehyde is difficult, if not impossible, and this is certainly the case if etherification is attempted. The technique adopted here is to react acrylamide with formaldehyde to form methylol acrylamide, followed by etherification with a suitable alcohol to obtain an N-alkoxy methyl acrylamide[25]. This monomer is usually liquid and is fairly insoluble in water, depending on the nature of the alkyl group, the methoxymethyl acrylamide, however, being quite water soluble. Having prepared the modified acrylamide monomer, a monomer mixture can be made up and a polymer prepared in the usual way utilising one of the normal techniques of emulsion polymerisation. As pointed out previously, a further modification is that an appreciable proportion of carboxyl-containing monomer may be incorporated in the monomer mixture such that the resultant polymer dispersion will pass into solution on the addition of a base. Whether the emulsion is to be used as an emulsion or, after treatment with a base, as a solution, the most serious disadvantage of emulsion systems is that the final product always contains surfactant.

The presence of this surfactant leads to poor performance when compared to a similar system prepared by the water soluble solvent technique and this is especially noticeable in tests involving the use of water. Generally, the water soluble solvent method of preparation has been adopted because of the belief that the disadvantages of the emulsion process and products outweigh those of the solution type. At present, two solution types are being studied, one of which is an acrylamide interpolymer, whilst the other is a carboxyl copolymer which also contains hydroxyl groups. In each case the polymer is cured in the presence of a water-soluble melamine formaldehyde compound of the hexamethoxymethyl melamine type. In general, the considerations of formulation as applied to solvent based acrylamide and carboxyl/hydroxyl copolymers can be applied to water soluble copolymers with the exception that the water-soluble copolymers obviously require extra combined acid.

On neutralisation of the type of polymers described by a suitable volatile base followed by dilution with water, there is an initial rise in viscosity and it is interesting to note that this effect is common to both the acrylamide copolymer and the hydroxyl/carboxyl copolymer even though they are chemically dissimilar. As dilution progresses a peak in the viscosity dilution curve is obtained and thereafter there is a rapid fall in viscosity. The development of the peak is associated in both cases with a change in appearance from a true solution to a fine emulsion or suspension. It is felt that the initial sharp rise in viscosity is a hydrogen bonding effect developed by the addition of the water diluent. The subsequent rapid fall in viscosity is associated with increasing levels of emulsion or suspension formation. The stability of such an emulsion, or of a paint made from it, is very good. As with most water dilutable systems which are dilutable because of a definite pH environment, there is a drift in pH during storage, processing and use, and appropriate adjustments must be made.

The performance of such acrylic copolymers is shown in Table 9.

Five systems were compared, in each case adopting the curing schedule most appropriate to the individual resin. The resins were a water soluble acrylamide-containing copolymer, a water soluble carboxyl/hydroxyl-containing copolymer, a water soluble trimellitic anhydride alkyd/melamine formaldehyde blend, a solvent based alkyd/melamine formaldehyde composition, and a solvent based acrylamide-containing copolymer. It can be seen that both water soluble acrylics have a standard of performance which is greatly superior to that of the alkyd/melamine systems, and, in fact, the performance approaches

Table 9

Comparison of water soluble acrylic performances with conventional systems

	Water sol. acrylamide-containing copolymer	Water sol. carboxyl/hydroxyl-containing copolymer	Water sol. alkyd/melamine formaldehyde	Solvent sol. alkyd/melamine formaldehyde	Solvent sol. acrylamide-containing copolymer
Stoving schedule	½ hr. 175 C	½ hr. 175°C	½ hr. 150°C	½ hr. 120°C	½ hr. 175°C
Erichsen	1 m.m.	5 m.m.	Pass 8 m.m.	7.0 m.m.	2 m.m.
Bend	Fail ½"	Pass ¼"	Pass ¼"	Pass ¼"	Fail ¾"
Scratch hardness	3100 gm.	>3100 gm.	1800 gm.	1800 gm.	>3100 gm.
Pencil hardness	H	3H	B	B	5H
Stain (lipstick)	2 hrs.	Unaffected	Severe	Severe	Unaffected
Detergent resist. 8 hrs. (3% cold)	Unaffected	Unaffected	Disintegration	$\frac{1}{16}$" micro blis.	Unaffected
Humidity resist. 500 hrs. ..	Unaffected	Sl. creep at X	Sl. creep at X	Sl. creep at X	Sl. creep micro blis.
Salt spray resist. 500 hrs. ..	Unaffected	Sl. creep at X micro blis.	Sl. creep at X	Sl. creep at X	Sl. creep micro blis.

that of the solvent based acrylamide interpolymer. At this stage, water soluble acrylics are expensive and a great deal of work is taking place to reduce the cost.

Electrodeposition

An investigation has recently been carried out into the performance of a pigmented water soluble acrylic resin when deposited under electrodeposition conditions. Generally the resin, which was an acrylamide based material, performed in a manner similar to other resinous media which have been reported from time to time in the technical press. Measurements of pH, pH drift, behaviour under conditions of constant current, constant voltage and coulombic yield have been made. Since the details of application are so similar to the conditions already described by other workers, it is not intended to discuss them in detail here. Suffice it to say that the profile voltage technique has been found to be very effective with this system with an upper limit in voltage of 150 volts being used. Film thicknesses of approximately 1 thou are obtained under these conditions at a pigment : binder of 0.5 : 1. Since an acrylic resin of known good colour retention characteristics was being dealt with it was decided to examine immediately the properties of the resin as the basis of an electrodeposition white system. Under suitable conditions of voltage, paint concentration, pH, etc., very good electrodeposited white coatings were obtained with no evidence of metallic staining on the surface, even when the substrate was mild steel. It is not certain if this effect is due to there being little or no migration of metallic ions into the film under these conditions, or whether there is appreciable diffusion of metallic ions, but that the resin/ion complex is colourless. This point is under investigation at present and subsequent to the presentation of this paper it has been found that ion migration does take place and is coloured, but that migration is localised at the resin/metal interface. The performance of such electrodeposited films is of a very high order, being if anything higher than that shown in Column 1 of Table 9.

Hardin process

A further development which has taken place in the last few years and in which again the emphasis has been shifted on to application technique is that of dipping objects to be painted into a trichlorethylene based paint followed by some form of curing. The advantages of this method of application have been stated comprehensively elsewhere, but briefly include uniform application especially at edges, absence of thick edges in most cases, no necessity to degrease in many cases, non-inflammability, theoretically no solvent loss, reduced heat losses, etc.

The difficulties, however, of preparing and maintaining trichlorethylene based paints are more serious and directly connected with the special nature of the solvents. For example, if it is desired to prepare an acrylamide interpolymer in trichlorethylene, then obviously there must be sufficient alcohol present to enable etherification to take place. In practice, a considerable molar excess of alcohol has to be used if premature gelation is to be avoided in the resin preparation, and hence the resulting solvent blend in the finished resin will contain an appreciable quantity of alcohol in addition to the trichlorethylene. Similarly, it may be desired to prepare a carboxyl/hydroxyl copolymer in trichlorethylene for use in blend with an appropriate melamine resin. Under these conditions a very small amount of esterification can take place, leading, in some cases, to premature gelation. A convenient way of suppressing these gelation tendencies is to incorporate alcohol in the solvent blend.

Another consideration which has to be borne in mind is that of solvency. It may be quite possible to start the preparation of a polymer in a chlorinated solvent, but the final polymer might be found to be at least partially insoluble in the solvent and hence a suitable solvent needs to be added in order to attain complete solubility. Resin stability must also be taken into account, especially where a preformed resin additive is used in conjunction with the trichlorethylene based acrylic. For example, a carboxyl/hydroxyl copolymer would, in practice, be blended with a melamine/formaldehyde resin, and if the alcohol concentration of the combined solvent was not high enough, precipitation of the melamine formaldehyde would occur on standing. The most convenient technique of preparing vinyl copolymers in solution in trichlorethylene is to carry out the polymerisation in this solvent rather than first preforming the polymer and then dissolving it in trichlorethylene. This technique, however, involves some difficulty since trichlorethylene is a particularly good chain transfer agent, and hence low molecular weights are generally obtained. Following work carried out in the authors' laboratories, it is felt that the best approach to the various problems involving solvent is to make use of azeotrope compositions. In this case, the appropriate solvent for the resin system being considered is chosen and its azeotrope composition with trichlorethylene as second component is determined if such an azeotrope exists. Wherever possible this azeotrope composition is then utilised as the solvent for the final resin, so that the ratio of trichlorethylene and other solvent in the subsequent paint bath always remains the same. By this technique problems of solvent variability following evaporation are much reduced and it is fairly simple to top up with the appropriate blend. Similarly, stability problems can also be minimised.

Table 10 shows the azeotrope compositions of trichlorethylene with a range of different solvents ; each composition can obviously be used for different applications. A number of resins have been prepared in trichlorethylene, either alone or in blend with an appropriate co-solvent, and a few examples are :

> an epoxy ester, a styrenated epoxy ester, an acrylamide based interpolymer in blend with an epoxy resin, and a carboxyl/hydroxyl interpolymer in blend with a melamine/formaldehyde resin.

Table 10

Azeotrope compositions of trichlorethylene

Trichlorethylene % W/W	Secondary component	% W/W
70	Iso-propanol	30
97.5	n-Butanol	2.5
79.6	Methyl iso-butyl ketone	20.4
87.2	Xylene	12.8
85.1	Butyl acrylate	14.9
66	Cyclohexanol	34.0

Future developments

The authors' recent activities in the field of thermosetting acrylics have been described and it is felt that there are a number of sketchily explored areas which are of interest to paint resin manufacturers and end users alike, and it is proposed to mention just a few of these fields.

The use of powder coatings has become of major importance recently and thermosetting acrylic resins could find application here. The problems, however, of producing a dry, thermosetting acrylic resin, which will flow sufficiently before cross-linking takes place, allow products of cure to leave the film, and even more, of pigmenting it, are formidable.

Obviously, any technique of removal of solvent which was used as a carrying solvent during polymerisation is not an easy matter. Spray-drying, drum-drying and thin film evaporators are obvious possibilities, but problems of flash point and explosion limits must be considered. If these problems can be overcome, then these techniques of drying can also be applied to the paint with the result that colour control and matching can be made very much easier than is normally the case with thermosettable dried paints. Another advantage is that blending of two or more polymer systems becomes a relatively simple matter, while yet another advantage is that the re-use of fines rejected by particle size grading becomes simple. Suitable polymers can also be made by pearl or bead polymerisation techniques, but here problems of molecular weight become extremely difficult. Such polymers, however, can be filtered and dried quite easily, but resin blending and paint preparation is still a problem.

Cold cure

The trend towards lower curing temperatures obviously has its ultimate point of development in the preparation of acrylic copolymers which will either cold-set or air-dry by oxidation ; the necessary chemistry for such systems being well known already. The preparation of hydroxyl containing copolymers cross-linked with polyisocyanate can be regarded as an improvement over alkyd/isocyanate systems in that the polymer backbone is made up of carbon-to-carbon chains and hence is unsaponifiable. One can consider other cold cure systems by reference to Table 2, in which it can be seen that one merely has to introduce the relevant reactive group for cold cure reactions to take place, e.g. by the addition of a co-reactant, moisture curing or air oxidation.

Stereoregular polymers

In the early 1950s the development of polymers exhibiting a degree of stereoregularity of the asymmetric carbon atoms on the polymer chain took place. The properties obtained from such stereoisomers were a distinct improvement over those of existing random polymers of the same constitution and, until recently, stereospecific polymerisation seems to have been limited to the hydrocarbon polymers. Recently there has been an increase in the disclosure of stereospecific polymers using acrylic monomers, but the inclusion of a reactive group into the polymer chain is still fairly difficult. The reason for this is that the ionic catalysts used to produce the stereoregular polymers are themselves highly reactive. A recent patent[26] mentions the use of Grignard reagents, and the reactivity of these materials for the functional groups of the monomers which have been discussed in this paper is a matter of classical organic chemistry. The improvements to be gained, however, from stereoregular polymers are such that a thermosettable type should be a distinct advance over randomly polymerised types currently available. A point that should be borne in mind, however, is that, with the change in the reaction mechanism of the propagation step of polymerisation, there will obviously be a change in the relative reactivity ratios. A pair of monomers which may well copolymerise satisfactorily by free radical polymerisation could be completely unsuitable if ionic polymerisation is attempted, and vice versa.

New cross-link mechanisms

It has been said elsewhere[27] that the amount of effort devoted to developing new cross-linking reactions is immensely greater in other industries than it is in the paint industry and the specific example given was that of the textile industry. Furthermore, by making use of the " other man's technology " significant advances in paint polymer technology could result. For example, the recent introduction of vinyl sulphone-based finishing treatments for cellulosic material in the textile industry could be applicable to the paint industry. This would depend on the development of a suitable monomer prior to polymerisation or the grafting on to a preformed polymer chain of a suitable reactive group. A further point of interest is the development of pigment and metal reactive polymers, such that cured paint systems would have improved cohesion and adhesion properties.

Conclusions

An attempt has been made to describe the kind of work which has taken place in the authors' laboratories over the last few years and of the products and properties to which the work has led. At the beginning it was pointed out that the first thermosetting acrylic resins could be regarded as being a new class of polymers useful to the paint industry. The next step, in the authors' view, was the development of new processes which used these and other polymers. As far as thermosetting acrylic resins are concerned, it is believed that the next step is the responsibility of the resin manufacturer, in that new polymer systems which could be cold cure types, stereoregular or displaying more chemically stable cross-links must be developed. The ultimate stage in this kind of investigation is the development of a carbon-to-carbon cross-link, a problem which interests and occupies all of those who work in this sector of the synthetic resin industry.

Acknowledgment

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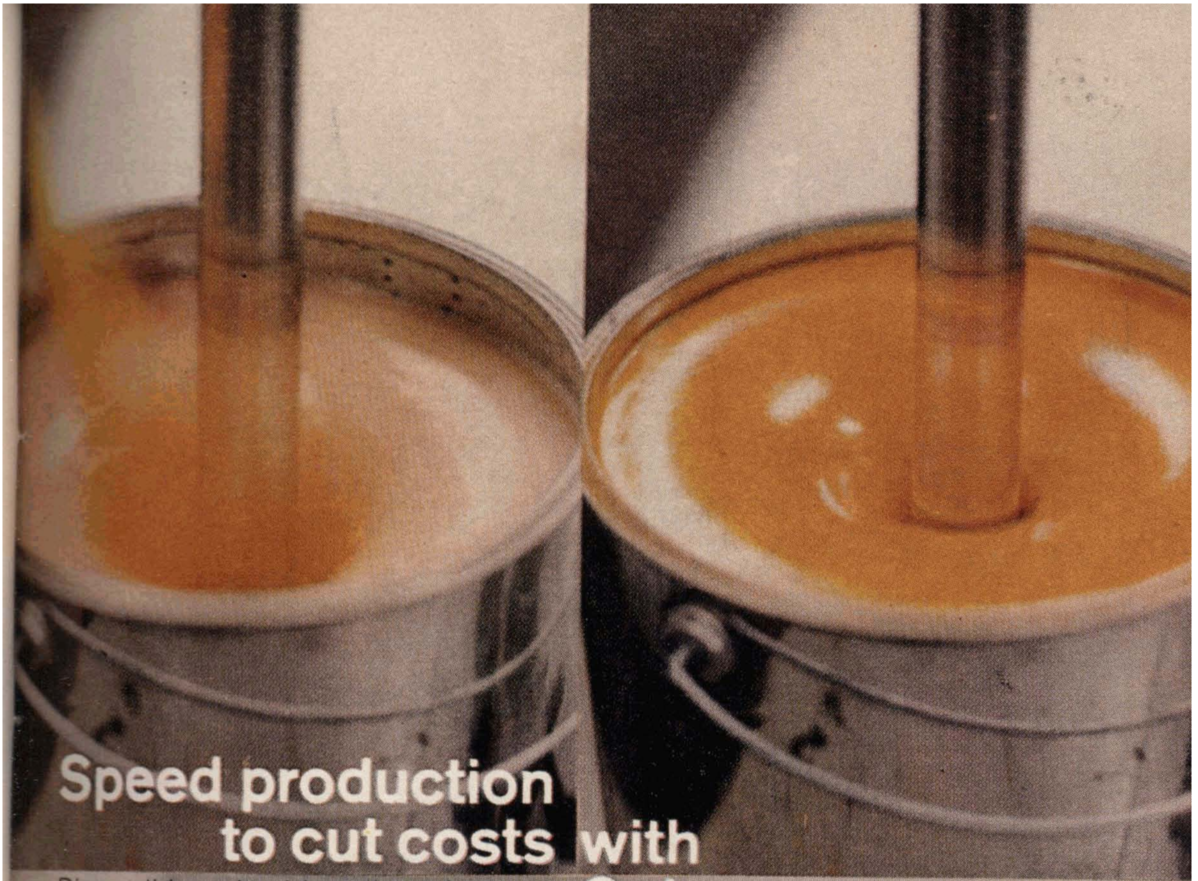

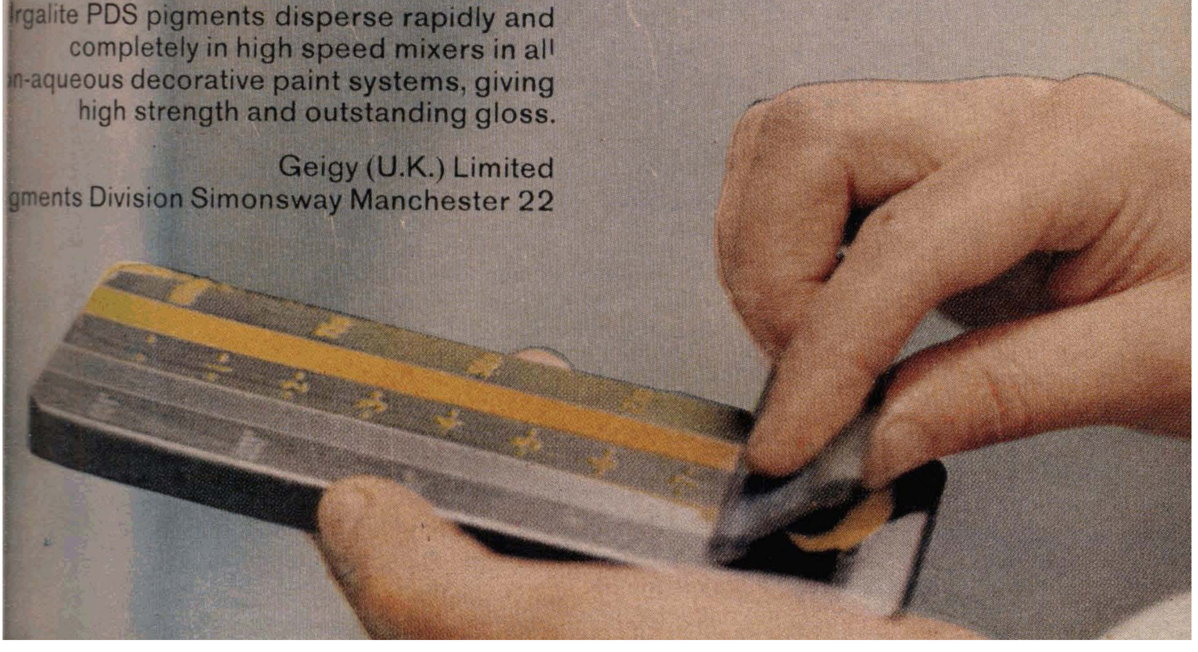

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*Since this paper was presented BP 980, 386 has been published.

In the case of many of the patents cited above the example given is purely representative of a number of similar patents dealing with that particular subject.

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Paint storage stability in relation to pigment surface characteristics*

By J. Taylor

Laporte Titanium Ltd., Stallingborough, Lincolnshire

Summary

Methods of determining the sequestering/dispersing agent demand of a pigment/extender dispersion or of the complete emulsion paint system are described. Stability of emulsion paints at varying levels of sequestering agent concentration are determined after storage for eight weeks at 40°C. The level of agent required for maximum stability in the systems studied is shown to be twice that required to achieve dispersion of the pigment/extender. Increase in the after-treatment of the titanium oxide does not decrease the stability of the paint.

La stabilité au stockage de peintures-émulsions en rélation aux caractéristiques superficielles pigmentaires

Résumé

On décrit des méthodes pour déterminer la demande d'agent de dispersion ou de séquestration qu'exige soit une dispersion d'un mélange de pigment et de matière de charge, soit une peinture-émulsion entière. On détermine les stabilités, après une durée de stockage de huit semaines à 40°C, manifestées par des peintures-émulsions aux teneurs divers d'agent de séquestration. Dans les systèmes considérées la teneur de l'agent nécessaire pour donner la stabilité maximum se démontre deux fois autant que celle qui est nécessaire pour achever la dispersion du mélange de pigment et de matière de charge. L'augmentation du post-traitement de l'oxyde de titane ne diminue pas la stabilité de la peinture.

Die Lagerstabilität von Anstrichfarben im Verhältnis zu den Oberflächencharakteristika des Pigmentanteils

Zusammenfassung

Methoden zur Bestimmung des Bedarfes an Abscheide/Dispersionsmitteln einer Pigment/Streckmittel Dispersion oder des vollständigen Emulsionsfarbsystems wird beschrieben. Die Stabilität von Dispersionsfarben mit verschiedenen Gehalten an Abscheidemittel wird nach achtwöchiger Lagerung bei 40°C bestimmt. Es wird aufgezeigt, dass der Gehalt an für maximale Stabilität in den untersuchten Systemen notwendigem Agens doppelt so hoch sein muss als für die Dispersion von Pigment/Streckmittel. Verstärkte Nachbehandlung des Titanoxides verringert die Stabilität der Anstrichfarbe nicht.

Устойчивость хранения красок в зависимости от характеристик грунтовых красочных поверхностей

Резюме

Описываются методы определения требования грунтовой красочно/расширительной дисперсии для изоляционно/дисперсионного агента или полной эмульсированной красочной системы. Определяется устойчивость эмульсированных красок при разных уровнях концентрации изоляционного агента после хранения в течение восьми недель при 40°C. Требуемый уровень агента для обеспечения максимума устойчивости в изученных системах оказывается два раза больше чем нужно для достижения грунтовой красочно/расширительной дисперсии. Увеличение последюшей обработки окиси титана не уменьшает устойчивость краски.

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*Presented to Manchester Section on 18 April 1966.

Introduction

It has been shown that the hiding power of emulsion paints is hardly affected by the amount of sequestering agent present in the system except at very low PVCs, which are outside the normal range of use. Therefore, in considering how much sequestering/dispersing agent to use, one can ignore their effect on hiding power and concentrate on the effect on pigment/extender dispersion during manufacture and on stability of the emulsion paint during storage. It has been necessary to limit the study by choosing only three sequestering systems, namely Calgon, Tetron, and a mixture of equal parts Calgon and Orotan 731*. Three concentrations of agent were used with paints based on mixtures of Runa RE30 Whiting and a standard grade/Whiting, maintaining the titanium oxide PVC at 19.7 per cent throughout and varying the total PVC from 25-75 per cent.

Determination of sequestering agent demand

Several methods are available in order to predetermine the concentration of agent to give the optimum degree of dispersion. Three methods are outlined using, as illustration, titanium oxide only.

In Method 1 a 50 per cent by weight slurry of the titanium oxide in a 0.625 per cent thickener solution in demineralised water is made and this is titrated on a Rotothinner with a 5 per cent solution of the agent under test. The viscosity is recorded and plotted against the percentage agent calculated on the pigment. The agent demand is taken at the point when the curve flattens out. See Fig. 1. This method suffers in interpretation from the defect of dilution with water.

Method 2 involves the preparation of pigment slurries at 50 per cent concentration in thickener solution in demineralised water with varying percentages of agent. Each slurry is then adjusted to 4 poise viscosity and the amount of water required is plotted against agent concentration. See Fig. 2. The minimum point on the curve is taken as the agent demand.

Method 3 consists of preparing a 20 per cent volume solids pigment dispersion in thickener solution and titrating with agent by solid increments until the point is reached when the dispersion begins to increase in viscosity due to the onset of flocculation. See Fig. 3. The minimum value extends over a wider range.

None of these methods is completely satisfactory from the point of view of determining the agent demand for the whole emulsion paint system, but, by modifying the last method, using the titanium oxide/extender mixtures in the proportions in which they will be used in the final paint, one can determine what proportion of agent to use for the most efficient dispersion/wetting of the pigment. In order to take into account the effect of the emulsion on the viscosity of the system, the test can be carried out with all the ingredients of the emulsion paint present. This gives a picture of the effect of sequestering agent on the final paint viscosity. See Fig. 4.

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*Calgon, sodium hexametaphosphate, Albright & Wilson Ltd. Orotan 731, sodium salt of polycarboxylic electrolyte, Rohm & Haas. Tetron, tetra sodium pyrophosphate, Albright & Wilson Ltd.

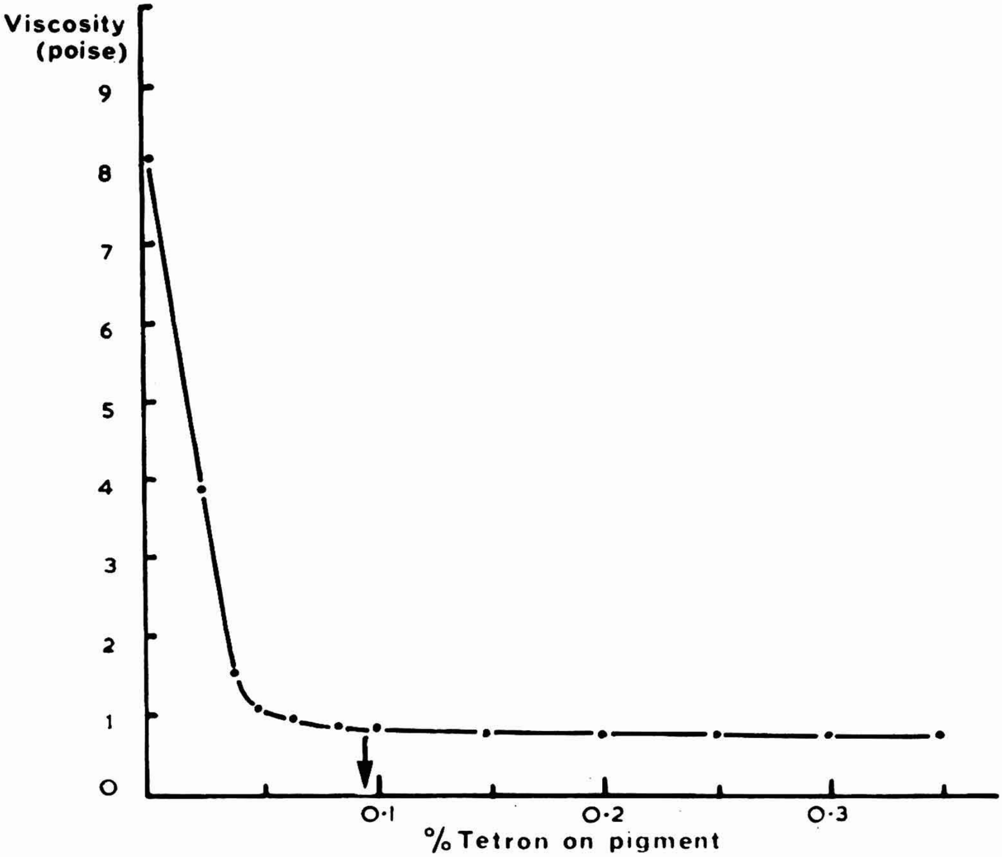

Fig. 1. Dispersant demand—Method 1

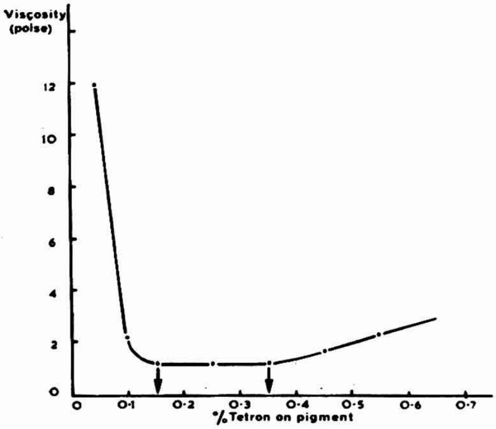

Fig. 2. Dispersant demand—Method 2

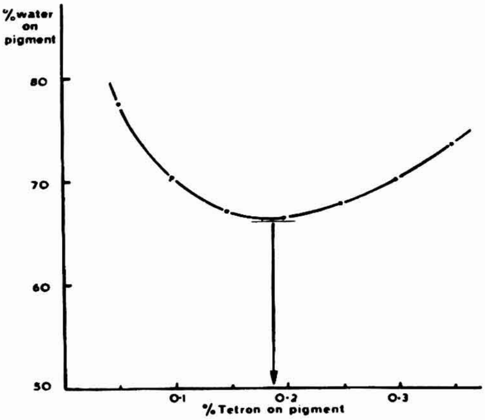

Fig. 3. Dispersant demand—Method 3

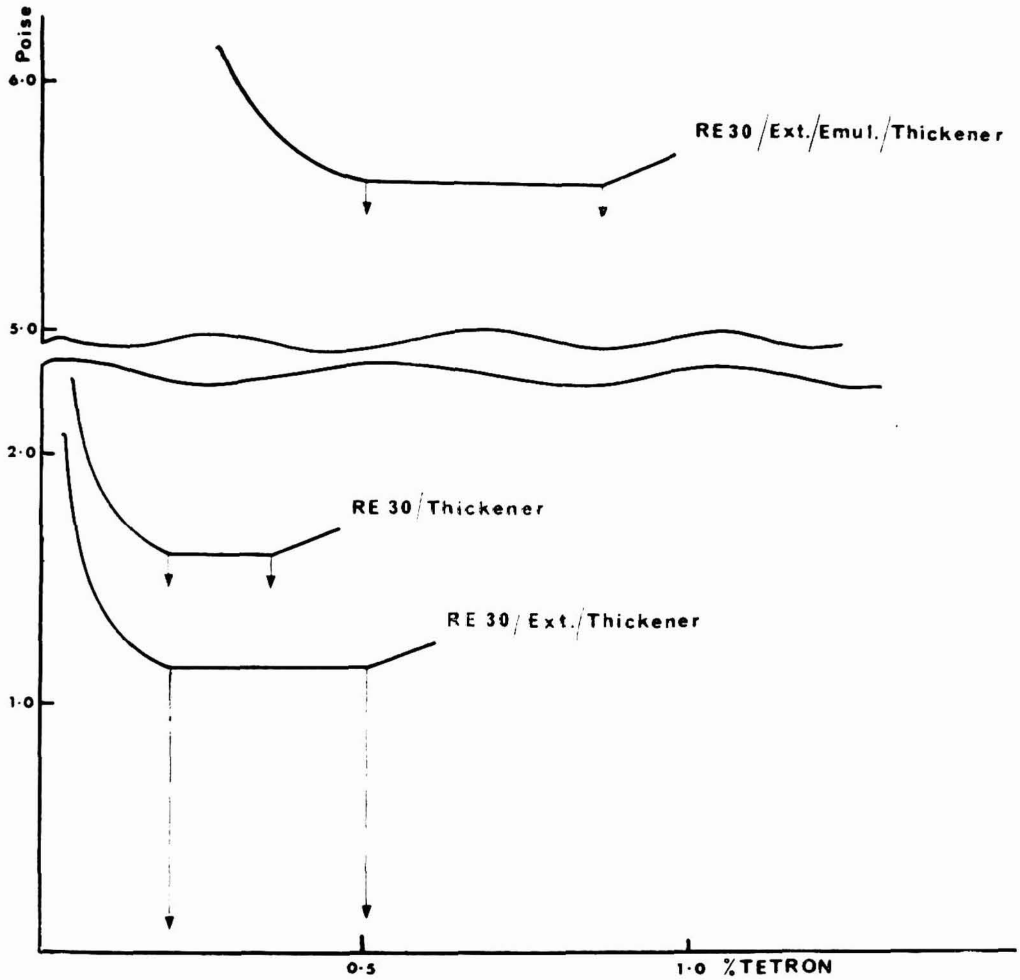

Fig. 4. Effect of ingredients on dispersant demand

Storage trials

Agent demand by Method 3 was determined on the pigment/extender/thickener/emulsion mixtures covering the range of PVCs used in the stability experiment. It was found that, despite the change in proportions of pigments and extender, the agent demand over the whole range varies very little from that of the 45 per cent PVC mixture and this justifies the choice of this level for the formulations throughout the whole range. See Fig. 5 and Table 1. The wave form of the curve of PVC against Tetron requirement illustrated in Fig. 5 cannot be explained, although it should be emphasised that these results are reproducible using constant techniques of mixing the ingredients. This amount is referred to as the normal amount and, in addition, paints were made with half and twice this amount of agent. Actual formulations are given in Table 2.

Table 1

Tetron requirements for the pigment mixtures used in formulations

PVC of paint	Tetron requirement	
	Standard grade	RE30
25%	0.65-1.05	0.40-0.70
35%	0.70-1.15	0.60-0.85
45%	0.50-1.05	0.45-0.75
65%	0.40-0.85	0.35-0.70
75%	0.45-0.90	0.45-0.75

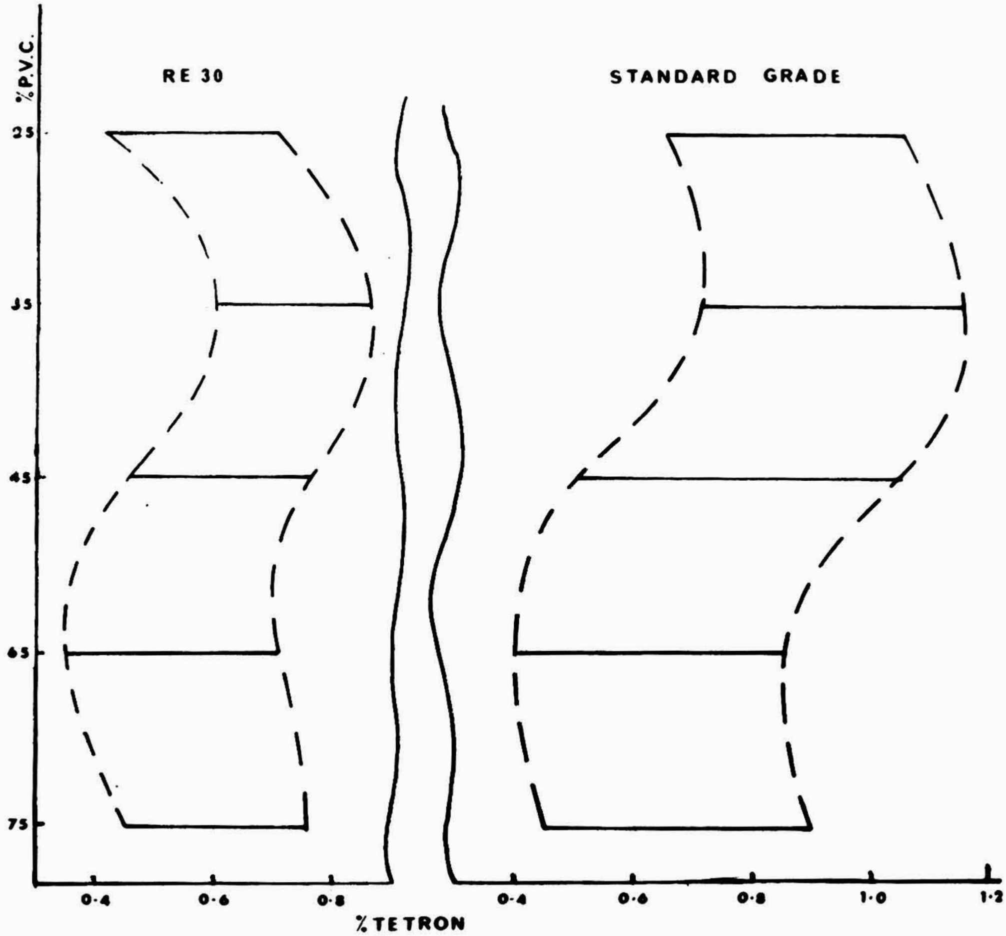

Fig. 5. Relation of agent demand to PVC

Table 2
Formulae used in storage trials

Raw material	Paint formulation				
	I	II	III	IV	V
Titanium dioxide	22.5	22.5	21.0	18.0	17.0
Snowcal 6ML (Cement Marketing Co. Ltd.)	1.2	12.5	19.0	28.9	33.2
Natrosol 250MR (Hercules Powder Co. Ltd.)	0.3	0.3	0.3	0.3	0.3
Fomescol U50 (Glover Chemicals Ltd.)	0.1	0.1	0.1	0.1	0.1
Dispersant Nuodex 321 (Nuodex Ltd.)	0.3	0.3	0.3	0.3	0.3
Vinamul N.6815 (Vinyl Products Ltd.)	40.0	40.0	31.8	17.3	12.2
Demin. water	18.0	16.8	17.3	19.4	20.2
PVC %	25	35	45	65	75
PVC TiO_2 %	19.7	19.7	19.7	19.7	19.7
Theoretical dry film density	1.85	1.98	2.12	2.40	2.54
Volume solids %	72	64	55	60	62
Weight solids %	56.2	62.2	64.5	67.6	69.0

Dispersant amount (% by wt. on pigment mixture)

Titanium dioxide	Standard grade			Runa RE30		
	0.5	1.0	2.0	0.5	1.0	2.0
Tetron	0.3	0.7	1.5	0.3	0.7	1.5
Calgon	0.4	1.0	2.0	0.6	1.6	3.0
Calgon/Orotan 731	0.6	1.4	2.8	0.6	1.4	2.8

Observations on the stability of these paints were made by measurements of viscosity on a Rotothinner 16-24 hours after manufacture and after storing at 40°C for increasing periods of time. The drift in pH was also recorded. The changes up to eight weeks are recorded in Tables 3 and 4. Initial pH was adjusted where possible to lie between 8.0 and 9.0 In some cases, where the sequestering agent content was high and the PVC high, the pH figure sometimes rose above 9.

The changes in viscosity for the three sequestering agents used at increasing PVC are shown graphically in Figs. 6, 7 and 8. It will be seen that Tetron gives the most regular pattern, suggesting the greatest stability. Calgon gives a non-predictable performance, which is improved by mixture with Orotan 731.

Conclusions

The following conclusions can be drawn from this limited study.

1. The use of whiting as an extender in increasing amounts gives greater stability to the emulsion paint.
2. The dispersant concentration giving the best stability in the system is twice the optimum required for dispersion of the pigment and extender in the presence of thickener and emulsion.
3. Of the three dispersants studied, Tetron gives results closest to those which would be forecasted from the known composition.

4. The mixture of Calgon and Orotan 731 gives least viscosity change over the whole range of PVC.
5. The pigment with the higher treatment, Runa RE30, gives somewhat greater stability.

Table 3

Change in viscosity on storage at 40°C (Poise)

Standard grade

% PVC	Disp. Amt. × normal	Calgon		Tetron		Calgon/Orotan	
		2 wk.	8 wk.	2 wk.	8 wk.	2 wk.	8 wk.
25	0.5	2.6	4.0	3.9	7.2	1.6	3.5
	1.0	1.8	4.3	1.1	4.2	1.3	1.1
	2.0	1.2	0.8	0.5	0.2	0.3	1.3
35	0.5	2.7	5.2	3.4	6.4	0.1	2.4
	1.0	1.4	2.0	1.0	3.1	0.3	0.8
	2.0	2.2	1.9	0.7	0.3	1.3	0.9
45	0.5	1.9	3.7	1.8	4.9	1.2	2.9
	1.0	1.7	2.4	0.4	1.4	0.4	0.1
	2.0	2.5	1.8	0.3	−0.4	0.7	0.2
65	0.5	1.6	1.9	1.1	2.4	0.3	−0.3
	1.0	1.7	1.6	0.2	0.3	0.8	0.1
	2.0	3.6	2.8	−1.5	−2.0	1.8	0.7
75	0.5	1.9	2.1	0.1	1.9	0.1	−0.5
	1.0	1.0	0.5	−0.5	−0.2	1.0	0.3
	2.0	3.6	2.5	−1.2	−1.6	2.3	2.0

Runa RE30

25	0.5	1.6	4.1	3.0	6.3	2.0	4.5
	1.0	0.7	4.0	1.1	1.8	0.2	0.5
	2.0	0.0	—0.1	−0.3	0.3	0.4	1.1
35	0.5	0.9	4.0	2.4	4.4	0.4	2.7
	1.0	0.7	1.1	0.7	1.7	0.7	0.9
	2.0	0.8	0.8	0.6	0.3	0.8	0.9
45	0.5	1.3	2.5	2.0	3.2	0.3	3.2
	1.0	0.9	2.3	0.5	0.7	0.6	1.5
	2.0	1.9	1.3	−0.1	−0.6	0.4	0.4
65	0.5	0.8	1.1	1.2	2.1	−0.1	−0.1
	1.0	0.4	1.1	−0.6	−0.5	0.8	0.5
	2.0	1.3	1.9	−0.6	−1.0	1.4	1.2
75	0.5	0.4	1.4	0.7	1.8	−0.2	−0.1
	1.0	0.6	1.3	−0.6	−0.7	0.4	0.9
	2.0	1.7	3.2	−0.7	−0.9	1.2	1.7

Table 4

Change in pH on storage at 40°C

Standard grade

% PVC	Disp. Amt. × normal	Calgon		Tetron		Calgon/Orotan	
		2 wk.	8 wk.	2 wk.	8 wk.	2 wk.	8 wk.
25	0.5	−2.35	−2.40	−1.55	−1.60	−1.30	−1.75
	1.0	−1.85	−1.75	−1.60	−1.75	−1.45	−1.75
	2.0	−1.45	−1.45	−1.20	−1.50	−1.50	−1.65
35	0.5	−1.60	−1.20	−1.65	−1.80	−1.65	−1.40
	1.0	−1.50	−1.35	−1.20	−1.25	−1.40	−1.45
	2.0	−1.60	−1.40	−1.10	−1.55	−1.35	−1.15
45	0.5	−1.85	−1.60	−1.40	−1.50	−1.40	−1.45
	1.0	−1.25	−0.90	−1.20	−1.40	−1.50	−1.40
	2.0	−1.50	−1.40	−0.90	−1.20	−1.15	−0.85
65	0.5	−1.40	−1.10	−1.10	−1.10	−1.30	−0.90
	1.0	−1.00	−0.60	−0.95	−1.30	−1.00	−0.60
	2.0	−1.40	−1.25	−0.90	−1.35	−1.10	−1.10
75	0.5	−1.35	−0.90	−1.00	−1.15	−0.75	−0.45
	1.0	−1.15	−1.00	−0.90	−1.25	−0.75	−0.55
	2.0	−1.45	−1.15	−0.70	−1.25	−1.15	−1.20
Runa RE30							
25	0.5	−1.40	−1.40	−1.15	−1.10	−1.60	−1.55
	1.0	−1.25	−1.35	−1.10	−1.30	−1.35	−1.50
	2.0	−1.15	−1.20	−0.80	−1.00	−1.20	−1.45
35	0.5	−1.35	−1.35	−1.20	−1.25	−1.40	−1.55
	1.0	−1.25	−1.35	−1.05	−1.00	−1.30	−1.50
	2.0	−1.20	−1.10	−0.95	−1.10	−1.20	−1.30
45	0.5	−1.30	−1.30	−1.35	−1.20	−1.50	−1.65
	1.0	−1.20	−0.80	−0.85	−0.90	−1.30	−1.30
	2.0	−1.05	−1.00	−0.95	−1.30	−1.05	−1.10
65	0.5	−1.10	−0.80	−1.70	−0.75	−1.10	−1.15
	1.0	−1.25	−1.20	−0.90	−1.20	−0.95	−0.90
	2.0	−1.10	−0.90	−0.95	−1.25	−0.80	−0.80
75	0.5	−1.20	−1.10	−0.75	−0.80	−1.10	−1.35
	1.0	−0.70	−0.40	−0.85	−1.15	−0.75	−0.60
	2.0	−1.20	−1.00	−0.70	−1.10	−1.25	−1.10

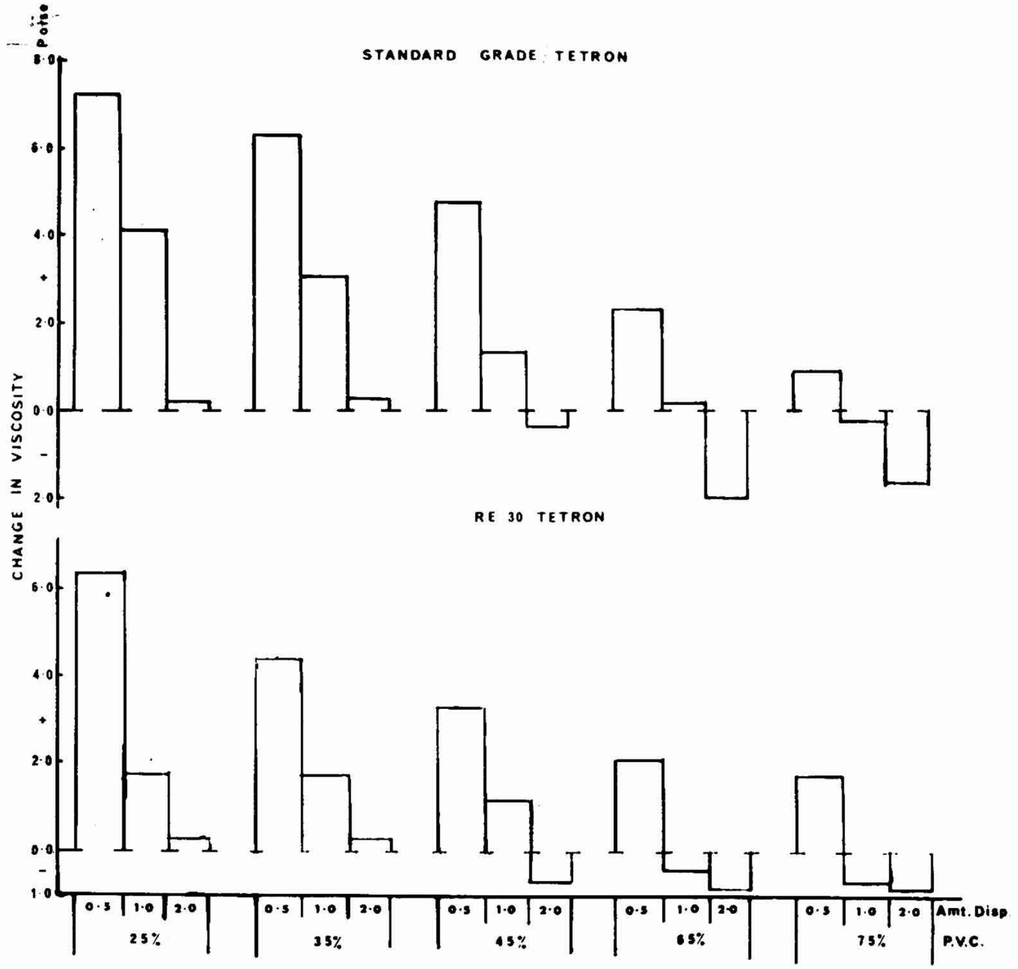

Fig. 6. Change in viscosity on storage for eight weeks using Tetron

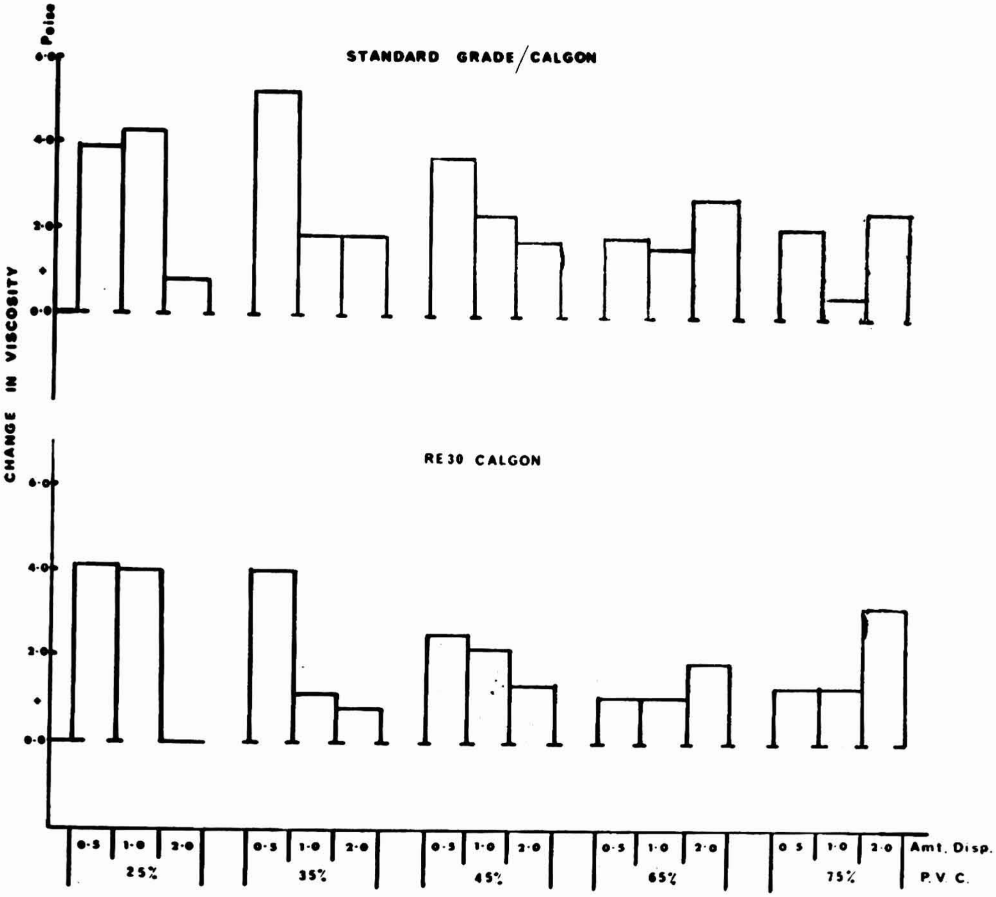

Fig. 7 Change in viscosity on storage for eight weeks using Calgon

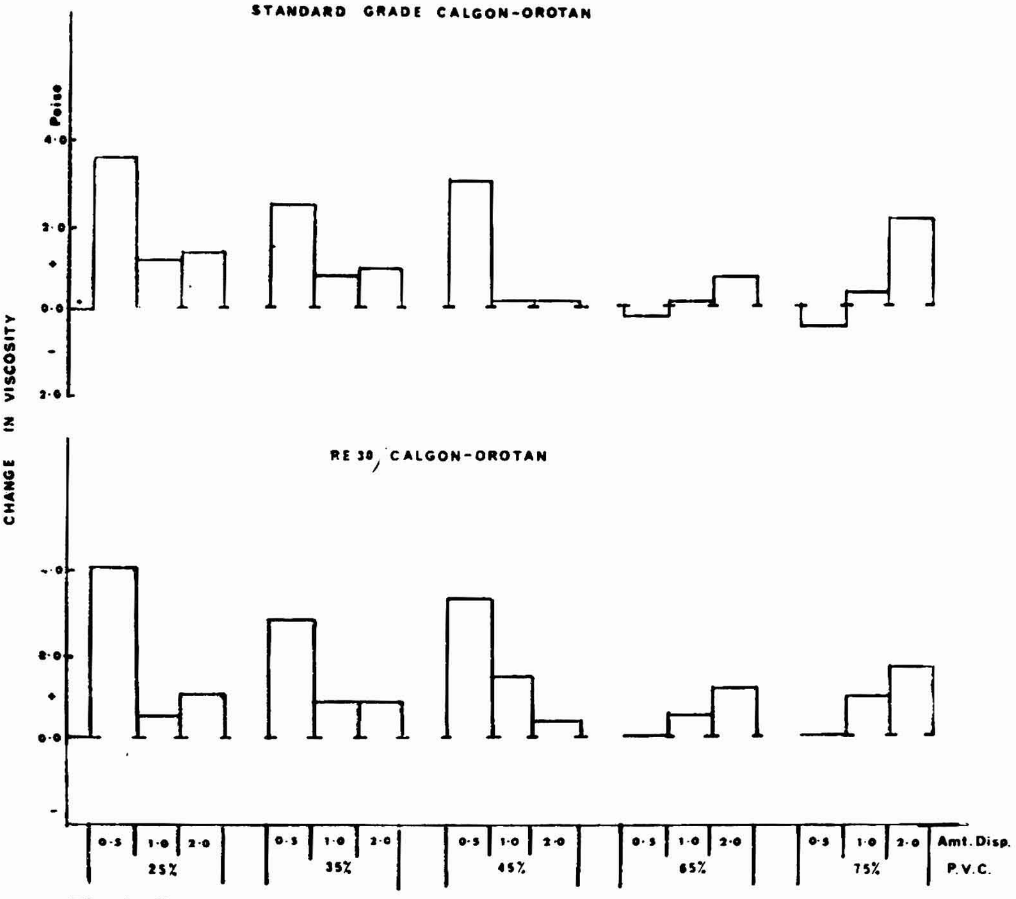

Fig. 8. Change in viscosity on storage for eight weeks using Calgon/Orotan

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The accuracy of colour measurement

By J. M. Adams

Printing, Packaging & Allied Trades Research Association, Leatherhead, Surrey

Summary

A general account is given of the factors which affect the accuracy of measurement and computation of CIE tristimulus values of reflecting and transmitting materials. Inaccuracy due to errors in measurement of reflection or transmission factors is distinguished from inaccurate computation. Reference is made to past investigations.

L'exactitude de colorimétrie

Résumé

On donne un exposé des facteurs qui affectent de l'exactitude de mesurage et de supputation des valeurs tristimulus de la CIE rendues par des matériaux réflecteurs ou transmetteurs. On distingue entre l'inexactitude due aux erreurs de mesurage des facteurs de réflection ou de transmission et celle due à la supputation inexacte. On fait rapport aux investigations précédentes.

Die Genauigkeit von Farbtonmessungen

Zusammenfassung

Über die Faktoren, welche die Messungs- und Berechnungsgenauigkeit von CIE Spektralwerten rückstrahlender oder durchlässiger Stoffe beeinflussen, wird ein allgemeiner Bericht erstattet. Es wird zwischen Ungenauigkeit zufolge Irrtums beim Messen von Reflexions- oder Durchlässigkeitsfaktoren und zufolge ungenauer Berechnung unterschieden. Auf früher vorgenommene Untersuchungen wird Bezug genommen.

Точность измерений красок

Резюме

Дается общий отчет факторов влияющих на точность измерений и исчислений C.I.E. трехвозбужденных значений отражающих и передаточных материалов. Отмечаются разницы между неточностями обусловленными ошибками в измерениях отражений или передаточных факторов и неточностями в исчислениях. Упоминаются предыдущие исследования.

Introduction

The CIE co-ordinates (tristimulus values) of a coloured material are defined as three integrals :

$$X = \int_{\lambda = 380\,\mathrm{m}\mu}^{780} R_\lambda\, E_\lambda\, \bar{x}_\lambda\, d\lambda$$

$$Y = \int_{\lambda = 380\,\mathrm{m}\mu}^{780} R_\lambda\, E_\lambda\, \bar{y}_\lambda\, d\lambda$$

$$Z = \int_{\lambda = 380\ m\mu}^{780} R_\lambda\ E_\lambda\ \bar{z}_\lambda\ d\ \lambda$$

where R_λ is the reflection factor (or transmission factor),
E is the energy of the illuminant,
$\bar{x}_\lambda$, $\bar{y}_\lambda$, $\bar{z}_\lambda$ are the CIE distribution coefficients, i.e. the tristimulus values of unit energy.

In practical situations the user of the CIE system measures R, the reflection (or transmission) factor, while the distributions of $E_\lambda\ \bar{x}_\lambda$, $E_\lambda\ \bar{y}_\lambda$ and $E_\lambda\ \bar{z}_\lambda$ are provided for him. When computing tristimulus values from spectrophotometric curves, these distributions are in the form of tables (allowing the integration to be performed as a summation), or of cams in the calculator attached to a recording spectrophotometer. In a colorimeter, the spectral emission of the lamp, transmissions of the filters and sensitivity of the photocell combine to give the required distributions.

It is important to distinguish between two sources of error : that due to inaccurate measurement and the error resulting from inaccurate computation.

Theoretical approach

This distinction was made very clearly in two papers by Nimeroff[8, 15]. The earlier paper was concerned with spectrophotometry and examined only the effect of errors in reflectance on the tristimulus values. This restriction was justified by the assumption that computational methods were free of error, although arguments against this will be presented below. The later paper recognised that errors in the weighted distribution coefficients, $E_\lambda\ \bar{x}_\lambda$, etc., were likely when using colorimeters, and examined the effect of these errors on the CIE values of the sample.

This purely theoretical approach appears to have been sterile. Ideally, it should be possible, from Nimeroff's later paper, to derive the accuracy of a colorimeter from the differences between its weighted distribution coefficients and true CIE coefficients. This appears never to have been done for an existing colorimeter. A graph showing these differences is often provided, but their effect is never stated—apart from a claim by the manufacturer that it is negligible.

Nimeroff's earlier paper might allow tolerances to be set to spectrophotometric curves that were meaningful in terms of colorimetric—and so, visual—values. This approach was taken further by Shipley and Walker[13], who divided errors into two classes : "constant errors" when all readings were true +x per cent, and " errors independent of wavelength." They pointed out the illogicality of specifying tolerances as limit curves. An error giving measurements close to one limit throughout the curve (Fig. 1a) will give a smaller error colorimetrically, and particularly a smaller hue error, than measurements which approach one limit at one end of the spectrum and the other limit near the other end (Fig. 1b).

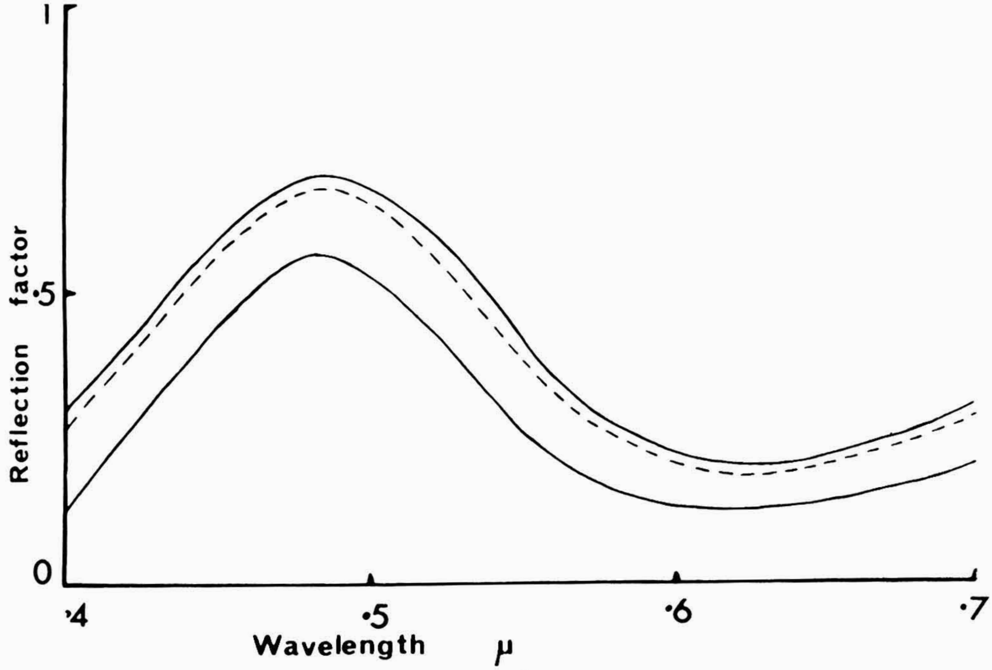

Fig. 1a

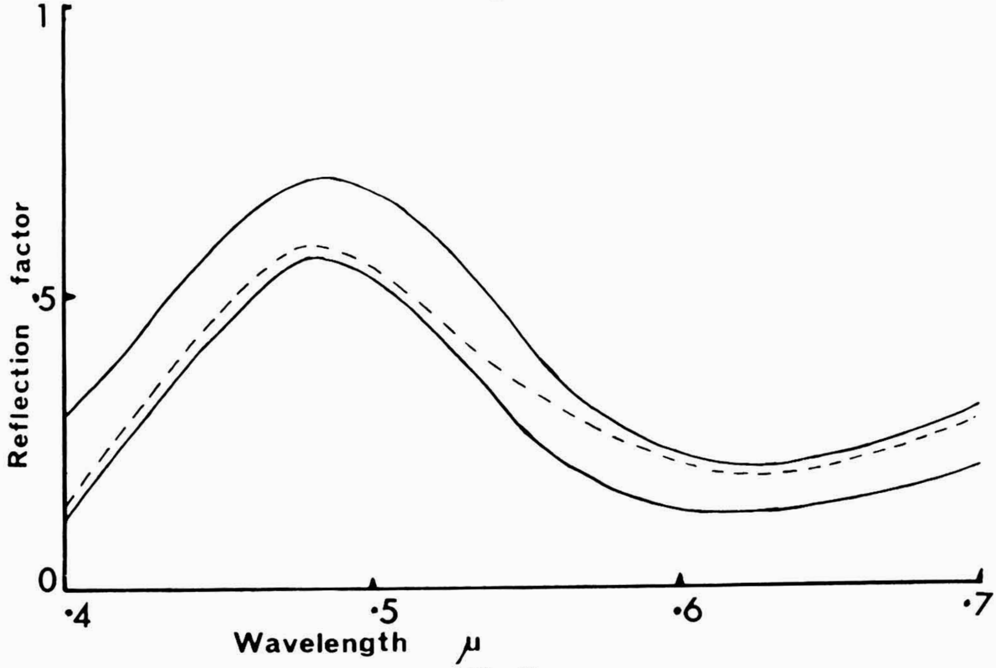

Fig. 1b

Fig. 1. Spectrophotometric curve, dashed line (a) lying close to one limit curve throughout spectrum, (b) approaching one limit at one end and the other limit at the other end of the spectrum

Computation

Basic data

The first assumption one makes when computing tristimulus values is that one's data relating to the CIE system are accurate. However, a report by the American Committee on Colorimetry[3] pointed out that their table of selected ordinates differed from that given in the earlier editions of the *Handbook of Colorimetry*[2]. These differences appear to be up to 0.2 mμ, and so are unlikely to worry most people taking 30 ordinates from graphs 30 cm long. They appear to have been due to errors in interpolation.

An associated problem is the validity of the basic data ; the correspondence of the weighted CIE distribution to the characteristics of human vision. One limitation that has always been recognised is the dependence of the data on the conditions under which the original 1931 determinations were made, and in particular the restriction of the field of view to 2°. This review is confined to work related to the 1931 CIE recommendations, and inaccuracies in the use of 10°, and other more recent data are not considered.

Another criticism of the CIE functions was made by Jacobsen[5], who found that samples of titanium dioxide having spectrophotometric reflectance curves with sharp cut-offs between 390 and 430 mμ were not separated by CIE measurements, although they appeared different to observers. He proposed that CIE functions should be modified to bring the measurements into line with the observations.

The problem was investigated by Judd[7], who claimed that the differences were small and varied between observers. But he later reported[16] that some American users had changed to a revised CIE $\bar{z}$ function intended to give better agreement with the visual observations.

Weighted and selected ordinates

In practice the integration of a spectrophotometric curve is carried out as a summation, and there have been several empirical investigations of the relative accuracies of the weighted and selected ordinate methods of calculating CIE values, and of the number of ordinates required to attain a given accuracy. Both Nickerson[1] and de Kerf[17] agree that, for a given number of ordinates, the weighted ordinate method is the more accurate. This is surprising when one considers that the curve is less well sampled when using the weighted ordinate method, particularly when computing the Z tristimulus value. Fig. 2a shows the ordinates for computing the Z value using ten selected ordinates. But, as shown in Fig. 2b, only five of the ten weighted ordinates come within the $\bar{z}$ distribution curve, if we ignore values of $E_c\bar{z}$ less than one-hundredth of the maximum value.

The uncertainty in the tristimulus values resulting from the use of a limited number of ordinates depends on the sharpness of the absorption bands of the colour. Nickerson used Munsell colours and found that 30 ordinates gave higher accuracy than disc colorimetry. De Kerf used a wider range of samples including didymium glass, and expressed his results as the number of samples accurate to within $\frac{1}{10}$ or $\frac{1}{2}$ NBS unit for each method of calculation.

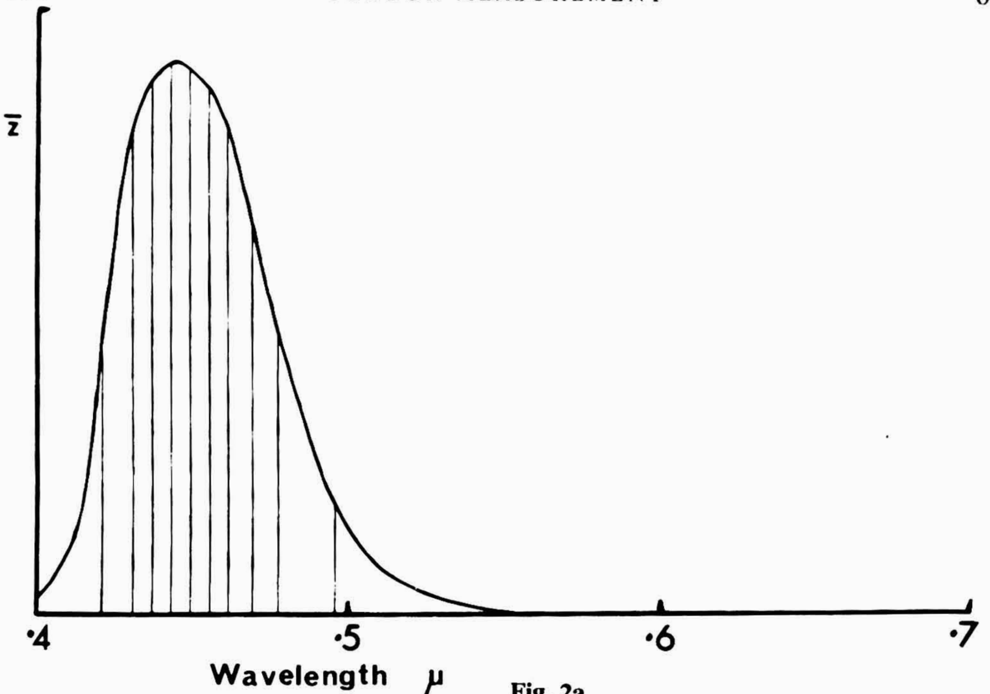

Fig. 2a

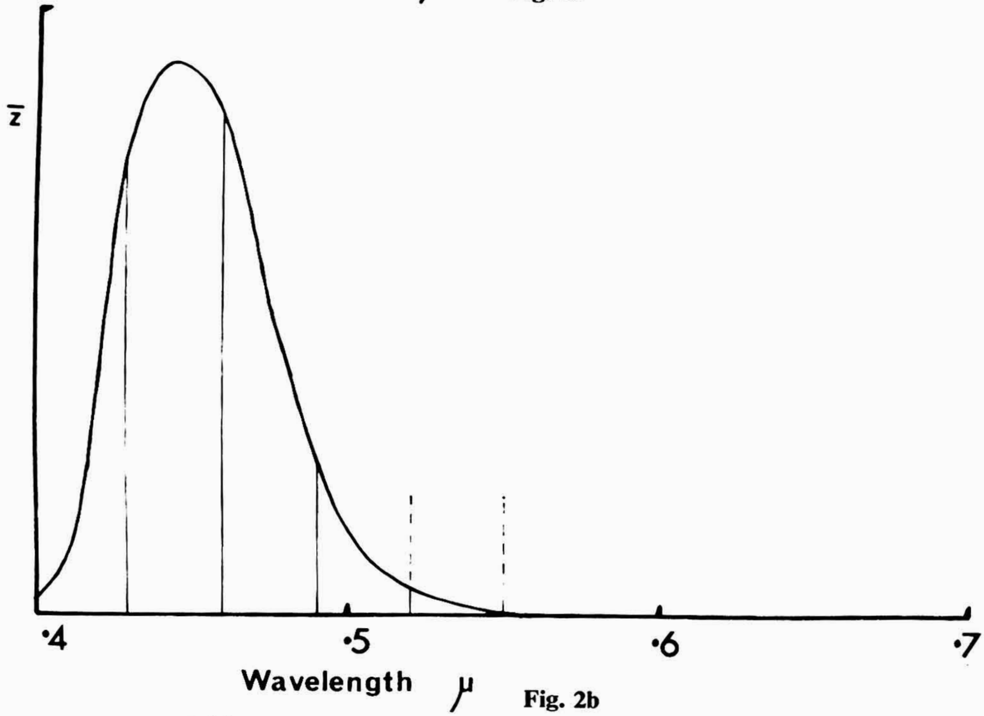

Fig. 2b

Fig. 2. Positions of (a) ten selected and (b) ten weighted ordinates for calculation of the Z tristimulus value

Recording spectrophotometers

There appear to be no data regarding the accuracy of the computers that can be attached to recording spectrophotometers. Some at least of the papers including results from such computers seem to assume that their accuracy is absolute.

Colorimeters

The combination of the spectral emission of the colorimeter lamp, the spectral transmissions of the filters and the spectral sensitivity of the photocell, forms effectively an analogue computer giving the tristimulus values from the reflectance readings. Owing to limitations of available components, the combination of spectral distribution is only an approximation to CIE requirements, and the departures from CIE requirements cause inaccuracy.

However, so long as the spectral distributions of the colorimeter components remain constant, the error will be constant. Thus, although it may be difficult to make a colorimeter which will give a correct result, it is possible to make one which will give its wrong answer with extreme consistency. It has been argued that for many applications this very high precision is adequate, and may be more important than fairly high accuracy[11].

Of the three factors affecting the agreement of a colorimeter with CIE requirements, that most likely to vary is the spectral energy curve of the lamp. The light from a filament bulb becomes yellower as the bulb ages, and in most colorimeters this can be compensated. Yellowing of a bulb does not, of course, affect spectrophotometric measurements, as the sensitivity is set for each wavelength individually.

Ultra-violet and infra-red

Colorimeter or abridged spectrophotometer filters having transmission bands in the ultra-violet or infra-red regions are likely to cause unsuspected errors if the photocells used are sensitive to these regions. This trouble is most likely to occur with abridged spectrophotometers having narrow band interference filters. These often have additional transmission peaks outside the visible spectrum, and the glass or gelatine filters, bound with the interference filters to suppress unwanted transmission peaks, must be effective over the whole range in which the photocell is sensitive. The error caused by such unwanted peaks in spectrophotometer filters should in fact be classed as a measurement error. The value of reflection or transmission factor of the sample will be an average of the values at the two or more wavelengths at which the filter transmits, instead of the measurement at the stated wavelength only.

Transmission by a colorimeter filter outside the visible spectrum would introduce an error into the " analogue computer," of which the filter is a part. This fault has not been recorded in colorimeters, but can affect results from densitometers[30] in which the transmission of the red tri-colour filter may extend into the infra-red.

Fluorescence

Normal colorimetry and spectrophotometry is based on the assumption that the wavelength of light is not changed during reflection or transmission by a sample. Effectively this is not true for fluorescent materials, and the light reaching the eye from such a material illuminated by " white " light is a mixture of light reflected (or transmitted) and radiation absorbed and re-emitted in the visible region of the spectrum. Thus a measurement on a fluorescent material that is to correspond with normal viewing conditions must be made with the sample illuminated with the white light under which it will be viewed. Tri-colour filters or a monochromator must be between the sample and the photocell.

The main practical problem in the measurement of fluorescent colours is that of obtaining a light source with an ultra-violet content similar to that of daylight[26]. The 1931 CIE illuminants have no ultra-violet content, and are not intended to be used with fluorescent materials. If a sample is fluorescent, a 1931 CIE measurement made on an instrument with the filters or monochromator between the sample and the photocell will give a measurement characteristic of the sample seen under the CIE illuminant. If the instrument used has the filters or monochromator between the lamp and the sample, the measurement will be meaningless, as the wavelength scale will not represent the light reaching the photocell.

Driancourt has considered this problem[24], but has also suggested that the measurement of non-fluorescent materials may be affected by the relative positions of lamp, sample, monochromator and photocell. He suggests that the scattering from a surface illuminated with white light will introduce a desaturating component, and that this will not occur with monochromatic illumination. This argument appears illogical, and it seems likely that the differences that Driancourt found on changing his narrow-band filters from the incident to the reflected beam of his reflectometer were due to either fluorescence or a change in the stray light in his instrument.

Reference white

All reflectometers give measurements relative to some standard, so the accuracy of the measurement will depend on the accuracy of the standard used. Traditionally, the ultimate standard is taken as a freshly smoked magnesium oxide layer, and this is assumed to have a reflectance of 100 per cent at all wavelengths. In fact, the reflectance of magnesium oxide depends on its method of preparation, and Robertson and Wright[37] give the likely variation as 2 or 3 per cent. A more particular result of this investigation was the finding that the National Bureau of Standards' magnesium oxide, against which many American laboratories calibrate their working standards, was lighter and bluer than the average of smoked surfaces produced elsewhere.

The effect of reference standards once again brings up the question of whether the requirement is for accuracy or precision. An incorrectly calibrated but stable reference standard will cause an error, but this error will be constant, and it is still possible to make colour difference measurements with a high degree of precision.

Optical geometry

Most coloured materials scatter light in all directions, but the extent to which the light is scattered and the direction in which it is scattered varies with the texture of the material. A practical colour measurement is a sampling of this distribution, with the angles of illumination and viewing being fixed by the construction of the instrument used. The variation in optical geometry between instruments appears to be the biggest single factor contributing to the disagreement between them.

Transmission measurements

Most instruments designed for measuring transmission colours are designed for use with solutions, glasses or clear plastics, and so measure direct transmission only. If one tries to examine translucent materials with such instruments, one obtains very low values, as most of the light transmitted is scattered and never reaches the photocell.

In some applications, such as photographic printing from negatives, the scattered light must be considered, and relevant standards[4] specify instruments which measure total transmission.

One or other of these conditions, direct or total transmission, is accepted for most transmission measurements, and the effect of optical geometry on disagreement between transmission measurements is relatively small.

Reflection measurements

So far inaccuracy has been considered as departure from CIE specifications. When we come to optical geometry, we are faced with imprecision in the CIE specifications themselves. The CIE recommendations are illumination at 45° with normal viewing, or normal illumination with viewing at 45°, and imply that these two conditions are equivalent. This is not necessarily so[33]. In any case, samples are in practice not illuminated by single rays of light and there is no mention by the CIE of the limiting angular dimensions of the incident and reflected beams (Fig. 3). Also, 45° implies illumination or viewing from one side of the sample as indicated in Fig. 3, but many instruments have symmetrical optical systems corresponding to these conditions. A measurement with an instrument having an asymmetrical optical system will depend on the orientation of the sample if the material has a marked grain direction, as have many papers.

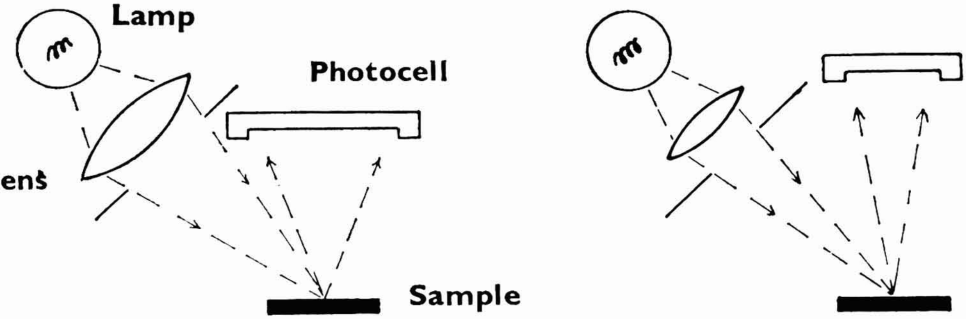

Fig. 3. CIE conditions of 45° incidence and normal viewing with (left) broad and (right) narrow cones of light

Many instruments depart entirely from CIE recommendations on optical geometry. Sometimes this is simply to allow a particular method of construction or design, but there are also more logical reasons for using alternative geometry.

The CIE conditions of illumination and viewing exclude completely the specular lobe of the light reflected from the sample, and it is sometimes advantageous to be able to include or exclude the specular component at will. This can be done using the conditions pioneered in the Hardy spectrophotometer, in which light is incident at 6°, and the light reflected is collected by an integrating sphere which has a removable segment where the specular component falls.

From the point of view of correlation with visual assessment of colour, it would be expected that the best conditions for instrumental measurements would be those which were closest to the conditions under which the visual assessments were carried out. Experimental work[19] has confirmed this.

Another reason for departing from CIE conditions is that the colour measurements may have to correlate with predictions by some theory. An example of this comes in the use of the Kubelka-Munk theory for the prediction of opacity and colour of papers. This theory assumes that the sample is illuminated diffusely, and it has been found[12] that agreement with the theoretical predictions is closest if the reflectometer used gives diffuse illumination with normal viewing. This recommendation has been incorporated into standards for reflectance of paper[27].

One problem has given rise to a proposal that the readings of a reflectometer should not be altered by a change of gloss of the sample being measured. When printing, and to some extent when painting, the wet film usually has a high gloss, and becomes less glossy during drying. This means that a measurement of the final colour cannot be made until the film is dry ; often after several hours. It has been claimed that the fitting of polarising filters in both the incident and reflected beams of a 45°-normal reflectometer[23] minimises the change of measured reflectance during drying, and so allows instrumental control of a freshly printed film without the necessity of predicting the change of gloss on drying.

Theoretically it must be possible to predict the change of measured colour with geometry[25]. The difficulty here is that of finding a sufficiently simple parameter that will allow a reading taken with one colorimeter to be converted to that appropriate to another without excessive calculation. One investigation that was started in the hope of finding such a parameter[35] concluded that the distribution of reflection from the samples tested—printed papers—was so complex that the complete solid polar diagram of the sample would have to be considered in such a conversion.

Obviously some tightening of the CIE specification of illuminating and viewing conditions is desirable. It is unlikely that any one set of conditions will be approved by all, but there are factors which allow general recommendations to be made. In most practical situations, the change of colour with orientation of a material is not important and this leads to the recommendation that the results given by a colour measuring instrument should not depend upon the orientation of the sample. This is achieved if a symmetrical optical system is used. Another factor is that, if the incident beam is anything but normal to the sample, the measured reflectance will depend on the state of polarisation of the incident beam[33]. These two factors could be incorporated in one form of the existing CIE conditions, in which the sample is illuminated normally and an annular receptor collects light at 45° elevation and at all azimuth angles. There are several alternative optical systems corresponding to these conditions (Fig. 4).

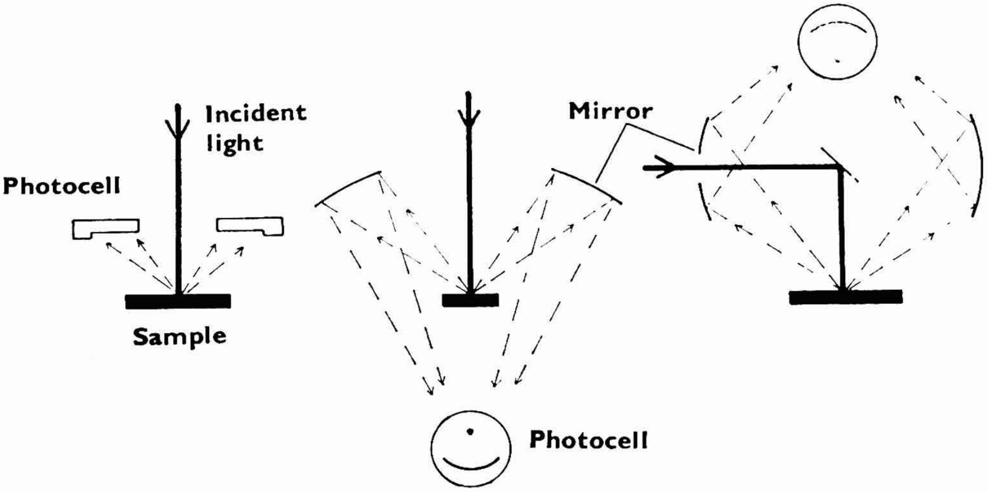

Fig. 4. Methods of obtaining normal viewing and 45° annular viewing

The measurement of fluorescent materials has not been of great importance in the past. As has already been pointed out, these must be illuminated directly by the lamp, and, with a spectrophotometer, this means that the light coming from the sample must be imaged on to the entrance slit of the monochromator. It would be difficult to do this and retain annular viewing at 45° as proposed above.

It may be argued that colours are usually illuminated diffusely and viewed normally, and that these should be standard conditions for colour measurements. Such conditions result in the specular component being included[34], but, in an instrument in which the illumination is via an integrating sphere, the specular component can be excluded by fitting a black annulus around the exit port. Unfortunately it is difficult to conceive an instrument giving diffuse illumination without an integrating sphere, and the maintenance of a matt neutral surface on the interior of the sphere may in practice give rise to difficulty. However, diffuse illumination and normal viewing should not give rise to any difficulties with regard to polarisation of light, and it would not be difficult to image the sample on to the entrance slit of a monochromator.

Overall accuracy

Most of the recent work on accuracy of colorimetry has taken the form of direct comparisons of existing colorimeters and spectrophotometers. This makes it difficult to sort out the individual factors contributing to the disagreements although, given an adequate analysis of a sufficient number of results, this can be done to some extent. Large differences occur between instruments used under normal commercial conditions[34]. Even the differences found by Robertson and Wright[37] are disturbing, particularly when one considers that all the organisations contributing results possessed laboratories specialising in colour measurement. In spite of this unsatisfactory position, colour measurement is widely used. Most users overcome the problem by quoting colour measurements within their organisation only. Under these circumstances they can ensure that all the instruments in use are of the same make and type, and it is possible to inter-calibrate them periodically, and so eliminate any differences that may occur. Such an inter-calibration is an effective way of ensuring that instruments agree, and has been used in the paper industry for many years. A very widely used American standard for blue reflectance of paper[6] was based on a particular instrument, and the manufacturers of this instrument circulated samples to users of the instruments periodically. These samples were near-white papers and only the reflection in the blue region was controlled, so they would not be applicable in the wider field of colour measurement. A similar service has been organised in connection with the more recent Swedish standard for reflectance of paper[27].

An industrial process which depends critically on interchange of colour measurements is the Instrumental Match Prediction service operated for textile dyers by Imperial Chemical Industries[32]. When using this service, a dyer sends to ICI by Telex the colour specification of the sample that he has to match. He also sends the dyeing conditions, type of fabric and so on. ICI then compute the dye recipe that will give the required colour, and send it to the dyer. Here the computation is based on the colour measurement sent in. The service was set up using the Colormaster colorimeter, but the message sent in by the dyer includes the type of colorimeter that he is using, and variations between colorimeters are allowed for. However, this service is limited to dyed textiles, which have a matt finish, and the allowance for the differences between colorimeters would probably be much more difficult if samples with a wide range of gloss were being measured.

Conclusions

The present position is that it is not difficult to make colour measurements of high precision, and that this is adequate when computing colour differences and when colour measurements are used entirely within one organisation. Interchange of colour specifications between organisations is still not generally practicable, and we are very far from the ideal situation in which colour measurements are able to replace coloured materials as samples. The biggest single factor appears to be the optical geometry of the instruments and, until this is more closely controlled, significant improvements in accuracy cannot be expected. The other factors are far from negligible, but it should be possible to eliminate variations between white standards by inter-comparisons between National Standards laboratories. There will always be departures from CIE functions ; these should be small with computed results, although they will probably always be present to a significant extent in filter colorimeters.

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Regulation of particle size of vinyl acetate/"VeoVa"* 911 copolymer latices†

By G. C. Vegter and E. P. Grommers

Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research N.V.)

Summary

To prepare paint latices based on copolymers of vinyl acetate and " VeoVa " 911, Koninklijke/Shell-Laboratorium, Amsterdam, have developed a delayed monomer emulsion addition procedure. The formulation contains a mixture of an anionic and nonionic emulsifiers. Besides, a small amount of acrylic acid is copolymerised into the resin.

An initial reactor charge, consisting of part of the water, anionic emulsifier, initiator and neutralising agent, is heated to the reaction temperature. A monomer feed emulsion, containing all the monomers and the nonionic emulsifier as well as the balance of the water, anionic emulsifier, initiator and neutralising agent is then gradually added. Finally a digestion period is applied.

It has been found that the distribution ratio of the anionic emulsifier between initial reactor charge and monomer feed emulsion greatly affects the particle size of the latex. A reproducible result is obtained only when a relatively large proportion of the anionic emulsifier is present in the initial reactor charge, but this eliminates the possibility of particle-size regulation via this method.

The particle size can be regulated in a reproducible way by varying the total amount of anionic, the type of anionic or by adding small amounts of electrolytes.

Le réglage de la grandeur particulaire des latices copolymères d'acétate de vinyle et de " VeoVa " 911

Résumé

Koninklijke/Shell-Laboratorium, Amsterdam a mis au point un procédé d'addition retardée de l'émulsion monomère pour la préparation des lattices à base de copolymères d'acétate de vinyle et de " VeoVa " 911. La formulation contient un mélange de deux émulsionnants, l'un anionique et l'autre nonionique. D'ailleurs on copolymèrise une petite quantité d'acide acrylique dans la résine.

La charge initiale de réaction consistant en des portions de l'eau, de l'émulsionnant anionique, de l'initiateur, et de l'agent neutrilisant est chauffée jusqu'a la température de réaction. Une émulsion monomère d'alimentation contenant la totalité de monomères et d'émulsionnant nonionique, ainsi que les restes de l'eau, de l'émulsionnant anionique, de l'initiateur et de l'agent neutrilisant s'introduisent graduellement. Enfin une période de digestion se met en vigueur.

On a trouvé que le rapport de répartition de l'émulsionnant anionique entre la charge initiale de réaction et l'émulsion monomère d'alimentation excerce un effet important sur la grandeur particulaire du latex. On n'obtient qu'un résultat reproductible où la proportion d'émulsionnant anionique dans la charge initiale sera relativement éleveé. Evidemment cela élimine la possibilité de régler la grandeur particulaire au moyen de cette méthode.

On peut régler la grandeur particulaire dans une manière reproductible soit par la variation de quantité ou de type d'émulsionnant anionique soit par l'addition de petites quantités d'électrolytes.

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*Shell registered trade mark.

†Presented to the Manchester Section on 18 April 1966

Die Einstellung der Teilchengrösse von Vinylazetat/"VeoVa" 911 Mischpolymerlatexen

Zusammenfassung

Das Koninklijke Shell-Laboratorium Amsterdam hat ein Verfahren zur Darstellung von Latexen für Anstrichzwecke, die auf Mischpolymeren aus Vinylazetat und "VeoVa" 911 aufgebaut sind, entwickelt, dadurch gekennzeichnet, dass eine allmähliche Zugabe der monomeren Emulsion vorgenommen wird. Die Rezeptur enthält eine Mischung von anionischem mit nichtionisiertem Emulgator. Ausserdem wird eine kleine Menge Akrylsäure mit dem Harze mischpolymerisiert.

Eine erstmalige Beschickung des Reaktionsgefässes, die aus einem Teil des Wassers des anionischen Emulgators, des Initiators und des Neutralisierungsmittels besteht, wird auf die Reaktionstemperatur erhitzt. Dann wird allmählich eine alle Monomeren sowie den nichtionisierten Emulgator, als auch das restliche Wasser, den anionischen Emulgator, den Initiator und das Neutralisierungsmittel enthaltende monomere Emulsionscharge zugesetzt. Schliesslich wird genügend Zeit zum Digerieren vorgesehen.

Es stellte sich heraus, dass das Aufteilungsverhältnis des anionischen Emulgators zwischen der erstmaligen Charge in das Reaktionsgefäss und der monomeren Emulsionscharge die Teilchengrösse des Latexes stark beeinflusst. Nur, wenn ein verhältnismässig hoher Anteil von anionischem Emulgator in der anfänglichen Beschickung zugegen ist, erhält man ein reproduzierbares Produkt ; dies schliesst jedoch die Möglichkeit aus mit Hilfe dieser Methode die Teilchengrösse einzustellen.

Die Teilchengrösse kann durch Variation des Gesamtgehaltes an anionischen, Art der anionischen Emulgator oder durch Zusatz kleiner Mengen Electroligt reproduzierbar eingestellt werden.

Регулирование величины частиц винилового ацетата/'ВеоВа' 911 кополимерных латексов

Резюме

Усовершенствована Государственной-Шелл лабораторией в Амстердаме методика для изготовления красочных латексов на базе кополимеров винилового ацетата и 'ВеоВа' 911 из замедленной добавочной эмульсии мономера. Формуляция заключает в себе смесь анионного и неионного эмульсификатора. Кроме того небольшое количество акриловой кислоты кополимеризуется с смолой. Начальный заряд для реакции, состоящий из части воды, анионного эмульсификатора, начального и нейтрализирующего агента нагревается до температуры реакции. Потом производится постепенное добавление мономерной питательной эмульсии, содержащей все мономеры и неионный эмульсификатор также как и остатки воды, анионного эмульсификатора, начального и нейтрализирующего агента. Наконец применяется период варения. Установлено что зависимость распределения анионного эмульсификатора между начальным зарядом для реакции и мономерной питательной эмульсии сильно влияет на величину частиц в латексе. Такой результат можно воспроизводить только когда сравнительно большая часть анионного эмульсификатора присутствует в начальном заряде для реакции, но это исключает возможность регулировать величнины частиц по описанному методу.

Контроль величины частиц можно осуществлять воспроизводимым методом варируя суммарное количество аниона, типа аниона или добавляя небольшое количество электролитов.

Introduction

In the last few years various publications[1–10] have described surface coatings based on branched monocarboxylic acids, called "Versatic"* acids. These acids are prepared from olefins, carbon monoxide and water by means of an acid-catalysed reaction discovered by Dr. H. Koch, of the Max-Planck-Institut für Kohlenforschung at Mülheim, Germany.

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*Shell registered trade mark.

On the basis of this reaction, Koninklijke/Shell-Laboratorium, Amsterdam, have developed a process for the manufacture of " Versatic " acids, which have been produced commercially for some years past. The acid with 9 to 11 carbon atoms, " Versatic " 911, is used for the preparation of binders for surface coatings. It is incorporated via its glycidyl ester, " Cardura "* E, into alkyd resins[1-8] and via its vinyl ester, " VeoVa " 911, into paint latices[9, 10].

It has been established that, in stoving enamels as well as in latex paint applications, the surface coatings acquire some very desirable properties when they are based on resins in which branched " Versatic " structures are incorporated. The most important of these properties are a high resistance to degradation by outdoor weathering as well as to hydrolysis, and an excellent colour retention.

In the course of the investigations into the applicability of " VeoVa " 911, a delayed monomer emulsion addition procedure has been developed for the preparation of vinyl acetate/" VeoVa " 911 copolymer latices. As particle size is an important variable in paint latices, its regulation and reproducibility were studied in detail.

This paper describes the above-mentioned procedure, the reasons for the excellent reproducibility of particle size, as well as various methods for its regulation.

Recipe

The latex recipe used in this work was as follows :

Vinyl acetate (VA)	52.5 pbw
" VeoVa " 911	46.5 ,,
Acrylic acid	1.0 ,,
Water (deionised)	85 ,,
Fenopon SF 78 (85% act. mat.)†	1.0 ,,
Tergitol NP 40‡	2.5 ,,
Potassium persulphate	0.5 ,,
Borax	0.5 ,,

The small amount of acrylic acid is required to ensure freeze/thaw stability of the latex at a pH of 7 or higher, and contributes to its mechanical stability. The anionic emulsifier (Fenopon SF 78) influences the particle size and imparts adequate stability to the system during latex preparation. The nonionic emulsifier (Tergitol NP 40) is required to obtain sufficient electrolyte stability, and contributes to the mechanical and freeze/thaw stability of the latex. Borax is used as a neutralising agent.

Method of latex preparation

In the course of the investigations a method was selected for the preparation of the latices as illustrated by the following example. It is readily reproducible ; the reaction temperature is easy to control and the quantity of coagulum formed during the process is negligible.

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*Shell registered trade mark

†Sodium alkylbenzene sulfonate ex Antara Chemicals.

‡Nonylphenol condensed with on an average 20 moles of ethylene oxide per mole ; ex Union Carbide Chemical Company.

An initial reactor charge was prepared by dissolving 0.1 pbw of potassium persulphate, 0.05 pbw of borax and 0.6 pbw of Fenopon SF 78 in 25 pbw of deionised water. The balance of the ingredients was used as follows for the preparation of a monomer feed emulsion. In the 60 pbw of water left, were dissolved 2.5 pbw of Tergitol NP 40, 0.4 pbw of Fenopon SF 78, 0.4 pbw of potassium persulphate and 0.45 pbw of borax. To this solution 100 pbw of the monomer mixture was added with stirring. The monomer feed emulsion thus obtained was stable for about one day.

The reactor, a 750 ml conical glass flask provided with a stainless steel anchor-type stirrer, containing the initial charge, was then heated up to 80°C and the monomer feed emulsion was gradually added with stirring in about $2\frac{1}{2}$ hours. The temperature was kept at 80°C. After addition of the emulsion, stirring was continued, the temperature being kept at 80°C, for another two hours. Then the latex was cooled, with stirring, to room temperature.

The pH, which was about 4-4.5, was raised to 5 with 10 per cent w/w ammonia and then to above 7 with 0.5 pbw of ammonium carbonate as a 10 per cent w/w solution in water.

Influence of distribution ratio of anionic emulsifier between monomer feed emulsion and initial reactor charge on average particle size of the latex

One of the variables studied was the influence of the distribution ratio of the emulsifiers between monomer feed emulsion and initial reactor charge on the latex properties. It was found that small amounts of the nonionic emulsifier in the initial reactor charge caused coagulum formation during latex preparation. So the total amount of nonionic required had to be added with the monomer feed emulsion. Variation in the amount did not affect the particle size.

The distribution ratio of the anionic emulsifier, however, greatly affected this particle size, as is illustrated in Fig. 1. When the amount of anionic emulsifier in the initial reactor charge was very small, the average particle size increased considerably.

To gain a better understanding of this phenomenon, the number of particles in the reactor was followed with time during addition of the monomer emulsion for three different distribution ratios of this emulsifier. The ratios 40/60, 97/3 and 100/0 were chosen because they gave different particle sizes of the ultimate latex : the first on the flat part of the curve in Fig. 1, the second just in the bend and the third at the extreme left.

The results of these experiments are depicted in Fig. 2. It can be seen that the number of particles formed in the initial stages of latex preparation depends on the relative amount of anionic emulsifier present. When this amount was small, a relatively small number of particles was formed, which remained constant during further latex preparation. Thus, after initial particle formation, only growth of existing particles took place.

When a large amount of anionic was initially present in the reactor, a large number of particles was formed. In the course of the experiment this number decreased because not enough emulsifier was added with the monomer feed emulsion to keep the surface of the particles covered. Controlled agglomeration of polymer particles occurred to a stage where the total surface area of the particles had become so small that the amount of anionic present just provided the required stability.

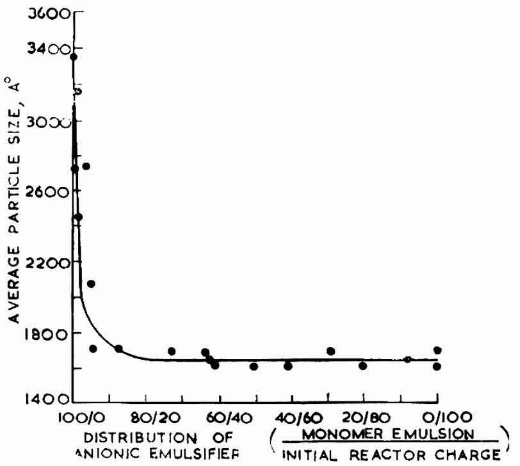

Fig. 1. Influence of distribution of anionic emulsifier on average particle size

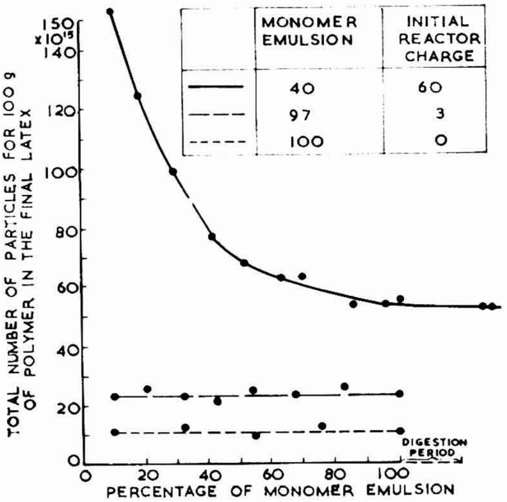

Fig. 2. Number of particles during the addition period for different partitions of the anionic emulsifier

Thus, when more particles are initially formed than can be stabilised by the amount of anionic present later on, the ultimate average particle size is determined by the total amount of anionic. When fewer particles are initially formed, the final average particle size is determined by the number of these particles. Fig. 1 shows that, when more than about 15 per cent of the anionic was originally present in the initial reactor charge, the average particle size was independent of the distribution ratio, indicating that it was only determined by the total amount of anionic present.

In actual fact, the average particle size of the latices proved readily reproducible under these conditions, whereas it had very poor reproducibility when less than 15 per cent of the anionic was present in the initial reactor charge.

It will be clear that the number of particles formed initially cannot be very reproducible. Small variations in induction period, for instance, will affect this number considerably because anionic is added also with the monomer feed emulsion.

Hence, although the distribution ratio of anionic emulsifier has a considerable influence on the average particle size of the latex, it cannot be used for reproducible particle-size regulation.

The particle-size distribution of the latices prepared by this procedure was invariably of the log-normal type as given in Fig. 3, independent of the way of particle formation. This illustrates that the agglomeration of particles during latex preparation when the initial reactor charge con-

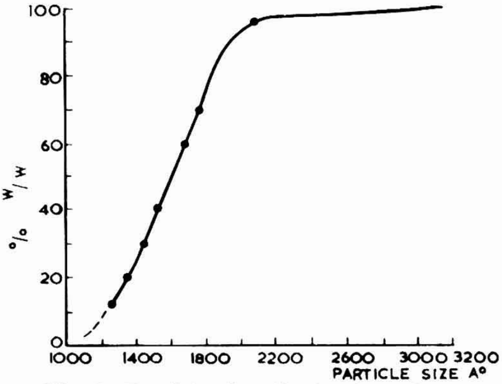

Fig. 3. Particle-size distribution of a latex prepared by the described process

tained more than 15 per cent of the anionic emulsifier is a random and not a selective process.

Regulation of particle size by changing amount and/or type of anionic emulsifier

The previous section indicates that, under reproducible conditions, the average particle size of the latex is determined by the total amount of anionic present. This has been verified by varying the total amount of anionic, the 40/60 distribution between monomer feed emulsion and initial reactor charge being kept constant. The results of these experiments are given in Fig. 4.

The above results are compared in Fig. 5 with those obtained by changing the distribution ratio of anionic emulsifier at constant total concentration. The essential difference between the two series of experiments is the amount of anionic in the monomer feed emulsion, indicated by the figures near the curve. Points of the two curves on the same vertical line through the graph relate to two experiments in which only the amount of anionic in the monomer feed emulsion differs. It can be seen that variation of this amount influences the average particle size considerably, which is in line with the previous statement that, in the region of controlled agglomeration, the average particle size is governed by the total amount of anionic.

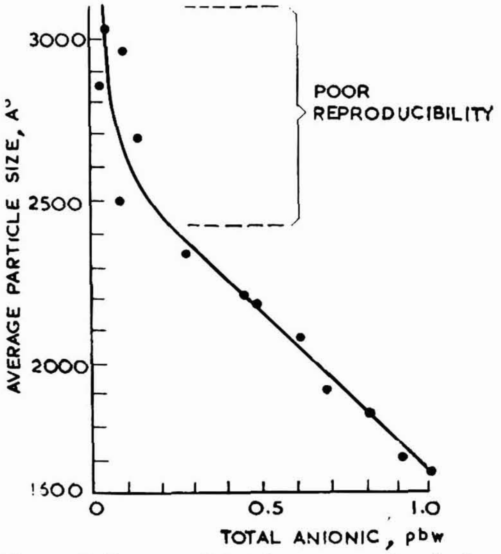

Fig. 4. Influence of total amount of anionic emulsifier on average particle size at a constant 40/60 distribution over monomer feed emulsion and initial reactor charge

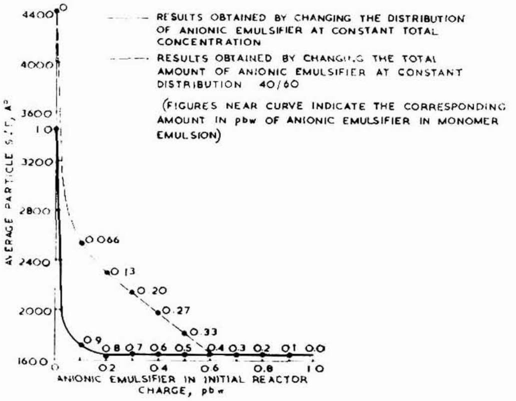

Fig. 5. Influence of distribution ratio and total amount of anionic emulsifier on average particle size

These results show that the particle size of the latices can be regulated reproducibly between about 1600 and 2400 Å by varying the amount of Fenopon SF 78 between 1 and 0.25 pbw at a constant 40/60 distribution ratio. At this ratio a total amount of anionic below about 0.20 pbw leads to irreproducibility due to the low concentration in the initial reactor charge. A change in ratio, e.g. to 0/100, would be expected to restore reproducibility, but the desired result is not obtained, because at such low total anionic concentrations considerable coagulation occurs, especially during the digestion period.

The type of anionic used also influences the particle size. This aspect has been investigated for a few other anionics. The results are given in Table I.

Table I

Influence of type and/or amount of anionic on latex properties

Anionic				
Name	Total amount pbw (active material)	Per cent of anionic in initial reactor charge	Particle size of latex Å	Overall latex stability
Fenopon SF 78	0.85	60	1650	Good
	0.26	60	2300	Good
Aerosol MA	0.85	60	1600	Insufficient
	0.26	60	3550	Good
Triton X 200	0.85	60	2150	Good
	0.26	60	2700	Good
" Teepol " 410	0.85	60	1400	Marginal

By varying the type and/or amount of anionic emulsifier, the average particle size of the latices can now be reproducibly regulated between about 1400 and 3550 Å.

Influence of VA/"VeoVa" 911 ratio on particle size

The work described so far was carried out at the monomer ratio given in the recipe, viz. VA/"VeoVa" 911/AA=52.5/46.5/1. The influence of varying polymer composition on particle size was also studied. The results, given in Fig. 6, show that the particle size increases with decreasing amount of " VeoVa " 911 in the copolymer.

Additional experiments showed that the number of particles formed in the initial stages of latex preparation does not fluctuate significantly with the monomer ratio. Therefore it must be assumed that there is more coalescence during the addition period of the monomer emulsion, which has obviously to be attributed to a decrease in stabilising power of the anionic emulsifier with decreasing " VeoVa " 911 content of the copolymer (increasing polarity).

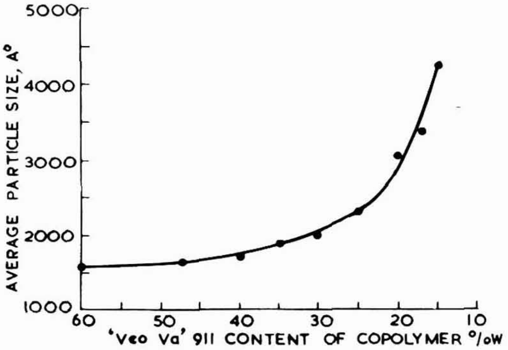

Fig. 6. Relation between "VeoVa" 911 content of copolymer and average particle size

The methods for particle size regulation discussed so far do not cover all the aspects involved. For instance, to eliminate a slight granularity* in latices with less than 35 per cent w/w of "VeoVa" 911 in the copolymer, it is sometimes advisable to reduce the solids content to about 51 per cent w/w by increasing the amount of water in the monomer feed emulsion from 60 to 75 pbw. The particle size, however, appears to be very sensitive to the amount of water. In latices with a monomer composition of e.g. VA/" VeoVa " 911/AA=79/20/1 a particle size of about 1300 Å was thus obtained, and the total amount of anionic had to be reduced to 0.25 pbw to obtain latices with an average particle size of about 2000 Å, which is considered practical in connection with the amount of nonionic required to ensure adequate stability (about 2.5 pbw).

It is clear that at this low concentration of anionic emulsifier particle size has to be regulated by means other than those indicated for latices with monomer ratio VA/" VeoVa " 911/AA=52.5/46.5/1.

Particle-size regulation with sodium chloride

It is a matter of common knowledge that addition of salts increases the particle size of latices prepared via an emulsion polymerisation procedure. This effect is generally attributed to interaction of the added ions with the electrical double layer around the particles.

The influence of adding sodium chloride to the monomer feed emulsion on the average particle size of the latices was investigated, using two different monomer ratios and two somewhat different recipes.

Latices with monomer ratios VA/" VeoVa " 911/AA=79/20/1 and 52.5/46.5/1 were prepared according to the normal recipe, viz. 0.25 and 1 pbw of Fenopon SF 78, 2.5 and 2 pbw of Tergitol NP 40 and 51 and 55 per cent w/w of solids, respectively. Sodium chloride was added to the monomer feed emulsion in amounts of up to 1.0 pbw.

In Fig. 7 the average particle size of these latices is depicted as a function of the amount of NaCl added. The results show that the recipe for 79/20/1 is more sensitive to NaCl than that for 52.5/46.5/1 latices. This can be ascribed to the lower amount of anionic emulsifier used.

The average particle size of latices with monomer ratio 79/20/1 can thus be regulated between 2100 and 4500 Å by adding up to 0.25 pbw of NaCl. More NaCl leads to severe coagulation during the latex preparation. In latices with a monomer ratio 52.5/46.5/1 the average particle size can be regulated between 1600 and

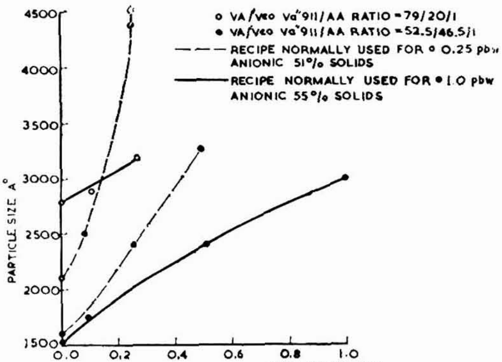

Fig. 7. Influence of sodium chloride concentration on particle size for different monomer ratios and recipes

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*Also the addition to 0.5 pbw of hydroxyethyl cellulose (e.g. Cellosize WP 09) to the monomer feed emulsion eliminates this granularity.

3000 Å by adding up to 1.0 pbw of NaCl; larger amounts again lead to severe coagulation.

The log-normal particle-size distributions referred to before are also found for the latices described here. The increase in particle size on addition of NaCl to the monomer feed emulsion must be ascribed to a further agglomeration of particles under the influence of the added ions. This is confirmed by the fact that the authors succeeded in enlarging the particles of a finished latex by heating it for one hour at 80°C in the presence of a small amount of salt ($K_2S_2O_8$), during which the log-normal distribution was maintained.

Influence of batch size on latex properties

As indicated before, the reactor used in the experiments described here was a 750 ml conical flask. On various occasions, however, larger batches of latex were required for evaluation purposes and experiments were performed in a 20 l round-bottomed glass flask and in a 250 l stainless steel reactor.

It was found that the scale of operation has no influence on the particle size or other latex properties when working under conditions indicated in the foregoing as being reproducible.

These large-scale experiments were in fact exact duplications of those carried out in the 750 ml reactor.

Conclusion

The delayed monomer emulsion addition procedure for the preparation of VA/" VeoVa " 911/AA latices, yields latices with excellently reproducible particle size when a relatively large amount of anionic emulsifier is present in the initial reactor charge. The average particle size is then governed by the total amount of anionic.

Reproducible regulation of particle size between 1400 and 3500 Å for latices with a monomer ratio VA/" VeoVa " 911/AA=52.5/46.5/1 and between 2000 and 4500 Å for latices with a 79/20/1 ratio can be effected by varying type and/or amount of anionic or by adding small amounts of sodium chloride to the monomer feed emulsion.

[*Received 25 August 1966*

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Discussion at the Manchester Symposium

DR. DE LA COURT asked Dr. Vegter if latex particle size distribution was measured microscopically, and if so, how the particles were prevented from flowing out of the observation zone.

DR. VEGTER stated that an ultra centrifuge method was used ; the question of flow out did not arise.

DR. DE LA COURT then asked if information could be given on the reactivity ratios of the monomers used.

DR. VEGTER replied that these parameters had been determined for " VeoVa " 911 and vinyl acetate, and had been found to be equal and unity, implying that from any monomer ratio at any time during polymerisation a completely random copolymer would be formed.

Finally, DR. DE LA COURT asked if the success in regulating particle size by varying the amount or type of anionic dispersant could be explained in terms of emulsion polymerisation theory.

DR. VEGTER said that the Smith-Ewart theory did not explain the effects found. The theory could be applied to the polymerisation of water insoluble monomers, but in the present case, with one of the monomers partially soluble in water, micelle formation was not necessary to induce polymerisation. With very low concentration of anionic surfactant the polymer particles formed initially coalesced. Micelles played a part at higher surfactant concentrations.

MR. HALL commented that in a copolymer system with low " VeoVa " 911 content, some granularity occurred in the emulsion which could be corrected by adding a colloid, and asked if this affected the particle size distribution to any extent.

DR. VEGTER stated that the particle size distribution was affected by the presence of colloids, but that he had no quantative information to present.

MR. HALL then asked if controlled particle size could be achieved if monomer and surfactant were added separately.

DR. VEGTER stated that the normal practice was to add monomer emulsion, that separate monomer addition tended to give small droplets which resulted in large particles of coagulum. The technique of using monomer feed emulsion gave greater freedom from coagulum formation.

MR. ARMITAGE inquired for the best proportion of vinyl acetate and " VeoVa " 911 for a good paint copolymer.

DR. VEGTER said that this depended on the criteria applied. The best copolymer was given by vinyl acetate 52.5, Vv 911 46.5, acrylic acid 1 ; the proportions of monomers to give the optimum performance/cost result depended on the cost of other materials ; a large improvement over PVA could already be obtained by using 15-20 parts by weight of " VeoVa " monomer in the final composition.

Next month's issue

The Honorary Editor has accepted the following papers from the Manchester Symposium for publication and these are expected to appear in the February issue :

" **The effect of pigment volume concentration and film thickness on the optical properties of surface coatings,**" *Craker and Robinson.*

" **The survey of the properties of thermosetting acrylic resins in automobile and domestic appliances,**" *J. R. Taylor and T. I. Price.*

" **Formulation of fungus resistant paints,**" *E. Hoffman.*

" **The effect of ethylenediaminetetracetic acid on the degradation of copper containing soaps,**" *S. A. Ramji and W. A. Hampson.*

Correspondence

" Texture of Pigments "

by W. Carr, *JOCCA*, 1966, **49**, 831-43.

SIR,—We were interested to read Dr. Carr's paper on the texture rating of pigments in which the relation between oil absorption and nitrogen adsorption surface area was examined. The useful collection of data for a range of types of pigments indicated that the "texture factor" S/Y approximated to unity in a number of cases. We were, however, unable to follow the theoretical treatment (pages 835-6). The equation for the " texture factor " is derived, assuming that a fraction of the oil, α, is present on the surface of the particles as a monomolecular layer, so that the remainder of the oil used in the oil absorption test, $1-\alpha$, is present in the voids between the coated particles.

$$\frac{S}{Y} = \frac{60.2\ \alpha\ D}{M}$$

where S=nitrogen adsorption surface area (m/²gram)
Y=oil absorption (grams oil/100 grams pigment)
D=cross sectional area of oil molecules (square Ångstroms)
M=molecular weight of oil

In making calculations for linseed oil (page 836), D is given as 30Å², while M is given as 873 or 879, the molecular weights of the triglycerides of linolenic and linoleic acids respectively. The literature quoted (reference 3) refers to the individual fatty acids having molecular areas of about 30Å², not the triglycerides, which would be expected to have molecular areas of about three times this value, assuming that the oil molecules were oriented with the polar ester groups on the polar pigment surface. There is little information in the literature on the monolayer behaviour of triglycerides, but we have made force-area measurements on the Langmuir trough of several samples of linseed oil and pure triglycerides. All the samples gave clearly defined reproducible force-area curves, and the areas quoted below are the means of four or five determinations in each case.

Linseed oil (acid refined)	90Å²
Linseed oil (bleached, alkali refined)	105Å²
Linseed oil (unbleached, alkali refined)	111Å²
Triolein (pure sample)	99Å²
Trilinolein (pure sample)	113Å²

These values confirm that the area for a triglyceride molecule is about 100Å², i.e. about three times the value for the individual unsaturated fatty acids. Gaines[1] also quotes a value of 100Å² for triolein. With this revised figure for D, then the equation for the "texture factor" becomes

$$\frac{S}{Y} = \frac{60.2\ \alpha\ 100}{873}$$
$$= 6.9\ \alpha$$

This relation can also be derived without making any assumptions about the molecular weight of the oil, by merely using the area occupied by a given weight of oil on the Langmuir trough to obtain the thickness of the monolayer. Taking the density of the oil in the monolayer to be that of the liquid, the thickness of the monolayer can be calculated to be 15.6 Ångstroms. If now the PVC of the oil absorption paste is P, then the area of pigment surface in 1 ml of oil absorption paste is

$$P \rho \mathrm{S} \times 10^{-2}\mathrm{m}^2$$

The volume of oil required to cover this area with a monolayer 15.6Å thick is

$$(P \rho \mathrm{S} \times 10^{-2}) \times 10^4 \times 15.6 \times 10^{-8}\mathrm{ml} = 1.56P \rho \mathrm{S} \times 10^{-5}\mathrm{ml}$$

The total oil in 1 ml of oil absorption paste is

$$(100—P) \times 10^{-2}\mathrm{ml}$$

$$\text{Hence } \alpha = \frac{1.56\ P \rho \mathrm{S}}{100—P} \times 10^{-3}$$

$$\text{or} \quad \mathrm{S} = \frac{(100—P)\ \alpha}{1.56P \rho} \times 10^{3}$$

Now the oil absorption Y, with linseed oil of density 0.93, is given by

$$\mathrm{Y} = \frac{(100—P) \times 0.93}{P \rho} \times 10^{2}$$

$$\text{Therefore } \frac{\mathrm{S}}{\mathrm{Y}} = \frac{\alpha}{1.56 \times 0.93} \times 10 = 6.9\ \alpha$$

How then does the experimentally determined value for S/Y approximate to unity in a number of cases? Dr. Carr indicates that α is of the order of 0.5 when the pigment is completely dispersed in the oil. We have not been able to find an indication of such a constant value in the literature quoted [4,5,6]. With a constant thickness of the adsorbed monolayer of oil, the value of α, the fraction of the total amount of oil in the monolayer will depend upon the particle size of the pigment and the type of packing in the oil absorption paste. Patton[2] listed the pigment volume concentrations calculated from oil absorption data of a range of pigments, and found that they varied appreciably. He showed that for many pigments the PVC approximated to that of cubic packing (52 per cent PVC), under oil absorption conditions, but that looser or tighter packings occured, up to tetrahedral (74 per cent PVC). The packing obtained will also depend upon the particle size distribution of the pigment, but it is possible to make calculations of α for ideal systems of spherical monosized particles, arranged in packings of varying PVC. In the calculation below the thickness of the monolayer of oil is taken as 15.6 Ångstroms, and the packing of 52 per cent PVC corresponds to cubic packing of the idealised pigment particles.

Diameter of particle (microns)	*Fraction of oil in monolayer, α*
1.0	0.010
0.8	0.012
0.6	0.016
0.4	0.024
0.2	0.047
0.1	0.087
0.08	0.105
0.06	0.133
0.04	0.179
0.03	0.218
0.02	0.277

Similar values for certain particle diameters were obtained by Lunkiewicz[3]. Tighter packings will give higher values of α, and looser packings lower values. It appears, therefore, that far from having a constant value of 0.5, α is very considerably lower for the range of sizes of most pigments and varies appreciably with particle size, only reaching values above 0.2 with the smallest sized particles.

Using the data presented by Dr. Carr in Tables 1-3, we have calculated the PVCs of the oil absorption pastes, using published values for the densities of the pigments, and from these obtained the appropriate values of α, assuming that in each case the pigment was broken down into ultimate particles, the size of which was obtained from the nitrogen adsorption surface area S. From these, calculated values of $S/Y = 6.9\ \alpha$ were obtained.

Table 1

$S/Y > 1$—High surface areas

Pigment	*PVC*	α	*Calculated S/Y*	*Experimental S/Y*	*Experimental S/Y / Calculated S/Y*
Bordeaux 2BS ..	57.1	0.275	1.90	1.78	0.94
Green DBN ..	54.0	0.251	1.73	1.62	0.94
Yellow 2GP ..	51.7	0.236	1.63	1.52	0.93
Red 4RH	60.8	0.201	1.39	1.33	0.96
Yellow G2T ..	41.1	0.209	1.44	1.30	0.90
Yellow BAW ..	62.5	0.197	1.36	1.30	0.96
Orange F2G ..	58.2	0.196	1.35	1.28	0.95
Yellow GTN ..	50.8	0.193	1.33	1.25	0.94
Red NBS	59.2	0.183	1.26	1.20	0.95
Blue GLS	57.0	0.180	1.24	1.20	0.97
Crimson 4BP ..	42.8	0.180	1.24	1.15	0.93
				Mean—	—0.94

Table 2

$S/Y \sim 1$—*Medium surface areas*

Pigment	*PVC*	α	*Calculated S/Y*	*Experimental S/Y*	*Experimental S/Y* / *Calculated S/Y*
Carmine FB ..	58.6	0.151	1.04	1.00	0.96
Rubine FBS ..	59.8	0.154	1.06	1.01	0.95
Red 4 RS ..	55.7	0.149	1.03	0.99	0.96
Red RLB	53.9	0.146	1.01	0.96	0.95
Red RLY	54.5	0.165	1.14	1.09	0.96
Yellow BAR ..	58.6	0.154	1.06	1.02	0.96
Yellow BAF ..	60.5	0.148	1.02	0.98	0.96
				Mean—	—0.96

Table 3

$S/Y < 1$—*Low surface areas*

Pigment	*PVC*	α	*Calculated S/Y*	*Experimental S/Y*	*Experimental S/Y* / *Calculated S/Y*
Maroon BN ..	48.5	0.130	0.90	0.86	0.96
Yellow BO ..	57.1	0.122	0.84	0.80	0.95
Orange P	56.7	0.117	0.81	0.78	0.96
Red FBS	58.8	0.104	0.72	0.70	0.97
Geranium RCP ..	53.6	0.100	0.69	0.67	0.97
Yellow CG ..	68.1	0.080	0.55	0.53	0.96
Yellow G	65.3	0.065	0.45	0.45	1.00
Red PRR	57.4	0.061	0.42	0.41	0.98
Bordeaux F2R ..	56.4	0.055	0.38	0.38	1.00
Scarlet RNP ..	62.9	0.042	0.29	0.28	0.97
Yellow VG ..	62.3	0.032	0.22	0.22	0.95
Red 2GM	51.7	0.025	0.17	0.17	1.00
				Mean—	—0.97

If the pigments were incompletely dispersed in the oil absorption paste, then the effective particle diameter would be greater, so that α would be smaller. Hence the experimentally determined value of S/Y would be lower than the calculated value. The ratios shown in the last columns of the tables indicate that with the high surface area pigments (Table 1) this is the case. With pigments of lower surface area (Tables 2 and 3) the mean ratio increases, and in three cases in Table 3 the ratio is 1, indicating complete dispersion of the larger sized pigment particles. A ratio lower than 1 could also be explained by the assumption that certain regions of the surface as measured by nitrogen adsorption, regions of " micro-roughness," were inaccessible to the monolayer of larger oil molecules. In no case does the ratio exceed 1, so that there is no evidence of disruption of the primary particles into smaller particles.

It is clear that it is the ratio of the experimental to the calculated values of S/Y which should be termed the " texture factor," rather than the actual value of S/Y, which mainly depends on the particle size of the pigment.

Yours faithfully,

V. T. Crowl,
T. R. Bullett.

The Paint Research Station,
Teddington.

27 October 1966

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SIR,—In the above-mentioned most interesting paper the author states on page 832 that " The texture of pigments is a property, the significance of which is increasing greatly in the production of modern paints and inks but, as far as we know, there is no means of measuring it or giving it a numerical rating which is either comparative or absolute."

In contrary with this statement, I should like to remark that at least four quantitative methods of measuring texture or dispersibility have been described in literature.

D. von Pigenot, FATIPEC *7th*, Vichy, *1964*, 249-262, has given a mathematical description of the development of colour strength of a coloured pigment during its dispersion (on a triple roll mill) in a predispersed white pigment paste. From this quantitative rating of the texture of pigments have been deduced.

Simultaneously (FATIPEC *7th*, Vichy, *1964*, 313-319), the present author has described a reproducible method of dispersing a pigment in a vehicle. The curve obtained by plotting fineness of grind against time of dispersion can be transformed into a straight line. From the position and the slope of the straight line an absolute rating of the texture of a pigment can be obtained.

Optimisation of mill bases for ball mills as well as texture rating of organic and inorganic pigments have been described by H. G. Cook in this *Journal* (*JOCCA* **48**, 17-42 (1965)). In the relevant investigation a laboratory shaking machine was used to accelerate the rate of dispersion.

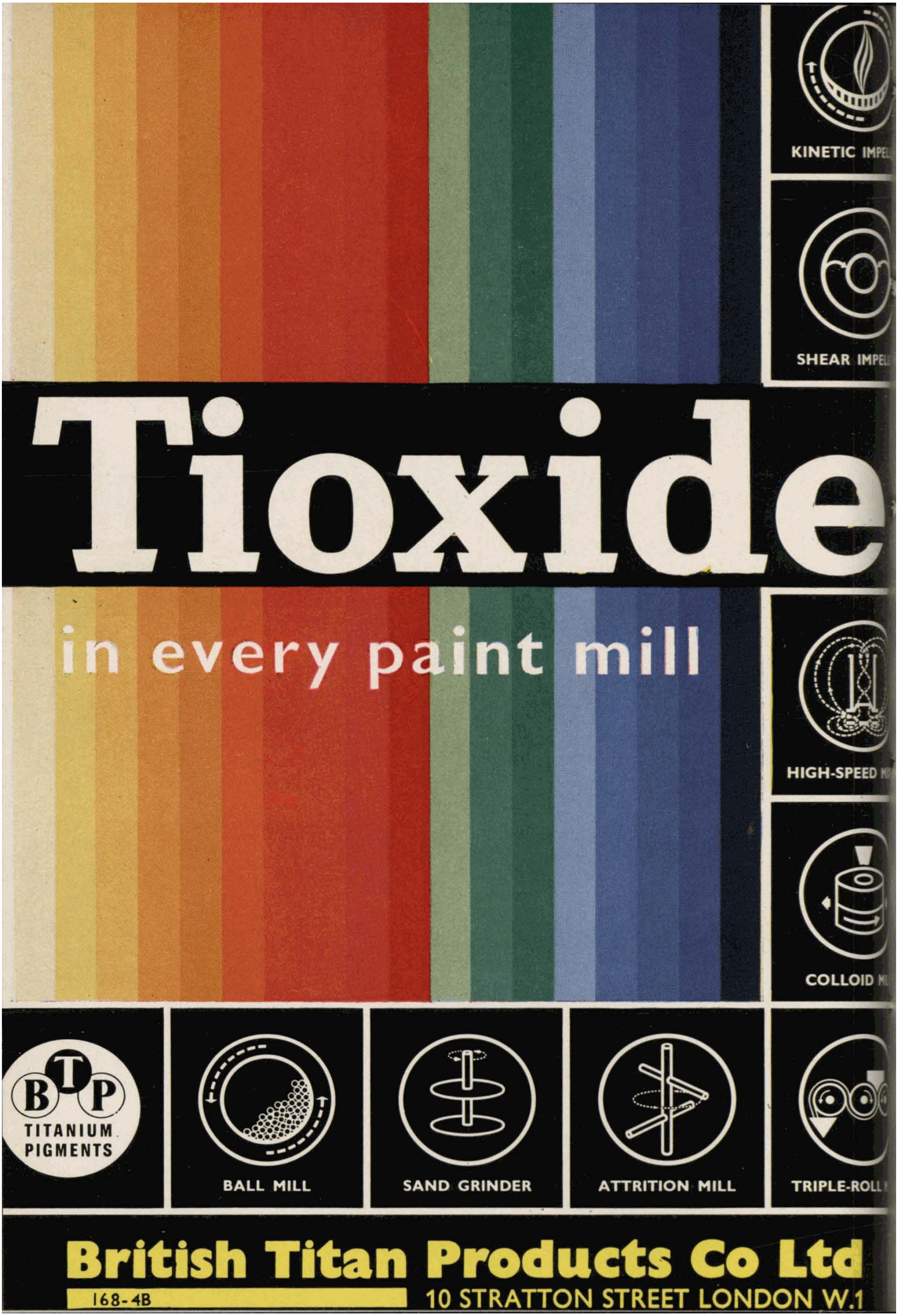
Recently, K. Reháček (Farbe u. Lack *72*, 27-35 (1966), ibid 201-5, ibid 333-9) described in detail a method by means of which a quantitative dispersibility rating of pigments can be obtained.

From this it is clear that the situation is not as bleak as Dr. Carr suggests.

Yours sincerely,

Dr. T. Doorgeest.
27 October 1966.

Verfinstituut TNO,
Schoemakerstraat 97,
Postbus 203,
Delft



Comments on letter from Dr. T. Doorgeest

SIR,—I am grateful to Dr. Doorgeest for his comments on my paper " Texture of Pigments " and would like to point out that the quotation includes the phrase " as far as we know."

I am familiar with his own paper and that by H. G. Cook, mainly because they are in English. His paper discusses the factors influencing the dispersbility of pigments ; Cook describes a method for the rapid determination of the optimum conditions for the dispersion of a pigment by ball milling. In both papers, dispersion is followed by measuring fineness of grind as a function of time. Neither paper mentions texture nor describes a method for measuring it nor gives any list of texture ratings.

The recent papers by K. Reháček have not yet come my way.

The paper by von Pigenot, from a quick survey, does appear to define a method for assessing texture and to give the results for a small number of pigments and I am grateful to Dr. Doorgeest for drawing my attention to it. I look forward to studying a translation of this paper in due course.

Yours faithfully,
W. Carr.

Geigy (UK) Ltd.,
Simonsway,
Manchester 22.

Reply to letter by Messrs. Crowl and Bullett

SIR,—I was very interested to read the comments of Dr. Crowl and Mr. Bullett on my paper " Texture of Pigments," which appeared in the October 1966 issue of *JOCCA*.

They have raised a number of very pertinent points which could be discussed at length, but I am reluctant to join in such a discussion in the *Journal* at the present time. This is because I have already submitted a paper (in September) for presentation at the OCCA Conference in June 1967, entitled " Texture and Dispersibility of Organic Pigments and Carbon Blacks." In this the texture theory is examined critically and more realistic values assigned to α and D, many of the points raised by Dr. Crowl and Mr. Bullett are discussed, and direct experimental evidence in support of the theory is presented. If this paper is accepted, I presume it will not be published until some time after the Conference, and I am uncertain of the propriety of releasing snippets or extracts of it in advance of publication. Some editorial guidance on this point would be appreciated.

For the record, I can state that in the Conference paper the value of D is taken as 100 $Å^2$ as the result of discussions with Dr. Crowl in June of this year, and due acknowledgment is made to Dr. Crowl and the PRS for determining this value experimentally.

Whilst certainly not agreeing with the conclusions of Dr. Crowl and Mr. Bullett, I am grateful that you have published their comments quickly, showing a more accurate value of D. This value is given in my Conference paper, but publication of this may be the best part of a year away.

W. Carr.

1 November 1966

We appreciate Dr. Carr's reluctance to anticipate his Conference paper. This will be available as a pre-print to those who register for the Conference, and will be published in this Journal *later in the year.—Ed.*

Information Received

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

ICI LTD are to increase their capacity for manufacture of " Melinex " polyester film from 6,000 to 13,000 tons a year, following the recent commissioning of two new plants, in Britain and Holland. The UK plant, at Dumfries, will increase ICI's UK capacity to 10,000 tons.

TITAN CO. AS Norway, a member of the Kronos group, recently timed the opening of their new factory in Fredrikstaat with the occasion of their 50th Anniversary, which also coincides with the 75th Anniversary of National Lead Company, New York, the parent company of the European group of Kronos producers.

The factory has a production capacity of 15,000 tons of titanium dioxide per annum.

An agreement has recently been completed between FEDERATED PAINTS LTD., of Glasgow, and BLUNDELL, SPENCE & COMPANY (AUSTRALIA) PTY LTD. to manufacture the paint PA-10 in Australia under licence.

PA-10 is a specialised etch primer which is used as a protective first coating on ferrous and non-ferrous metals.

Mr. Harold B. Gough, of FINNAREN & HALEY, INC., became the 45th President of the Federation of Societies for Paint Technology at the 44th Annual Meeting in Washington, DC.

Dr. Herbert L. Fenburr, of Hanna Paint Mfg. Co., Columbus, Ohio, was named President-Elect, and Martin E. Schleicher, of McDougall-Butler Co., Inc., was elected Treasurer.

DISTILLERS INDUSTRIAL SOLVENTS DIVISION can now make available comprehensive information on Isopropanol in their five-page *Technigram No. 302.*

An increase in morpholine production capacity is announced by JEFFERSON CHEMICAL COMPANY, INC., of Houston, Texas. The expanded facilities, with capacity almost double that of the present facilities, are at Jefferson's Conroe (Texas) plant, and will be completed in the first quarter of 1967.

The expansion will complement Jefferson's plans to build a new British morpholine plant, announced earlier this year.

A new " Chromato-Vue " portable fluorescence analysis cabinet designed for easy scanning of thin layer and paper chromatograms is announced by SHANDON SCIENTIFIC COMPANY LTD.

The " Chromato-Vue " incorporates a flexible lighting system providing long wave UV, short wave UV, or white light from above, reflecting from the sample, and long or short wave UV, from below, transmitted through the sample. This system is said to give greater resolution and stronger contrast of both paper and thin layer chromatograms, and to be ideal for other fluorescing and absorbing materials, such as dyes, textiles, etc.

TRUSTY MANUFACTURING CO. LTD., a member of the Cope Alman Group of companies, state that they have achieved an increase in production capacity, with a reduction of overall costs in the painting line, by the use of a new Ransburg electrostatic spray line, incorporating two Ransburg No. 2 process reciprocating discs.

A new Temperature Compensation Unit is announced by SANGAMO WESTON LIMITED, for use with their Sangamo Specific Gravity Meter. The unit measures the fluid temperature using a platinum resistance thermometer, and is arranged to modify the output signal from the Specific Gravity Meter, thus giving a constant measurement of density independent of fluid temperature.

A report has recently been issued by VICTOR WOLF LIMITED, on fatty acids in the manufacture of urethane oils. The report describes the manufacture of urethane oils of long oil length from soyabean fatty acids and from a dehydrated castor oil fatty acid containing 66 per cent of conjugated linoleic acid, and their evaluation by formulation into white paints and air drying varnishes.

BADISCHE ANILIN-& SODA-FABRIK AG has announced the publication of a booklet entitled *Colour in Building*, demonstrating the advantages of the Colanyl and Pigmosol pigments in exterior applications. The booklet will be available in English by the end of January 1967.

Following the merger of NV Koninklijke Zwanenberg Organon with Koninklijke Industrieele Maatschappij Noury & Van der Lande NV, it has been announced that their respective subsidiaries, the Industrial Chemicals Division of ORGANON LABORATORIES LTD. and NOVADEL LTD., will be integrated at the Novadel Ltd. premises in Wandsworth, London.

The International Conference and Exhibition for Surface Treatment was held in November in Basle, Switzerland. Of the 45 lectures, seven were presented by delegates from Great Britain, including one by the Honorary Editor, A. R. H. Tawn.

Bristol

The strip coating of steel with paint and plastic finishes

The 150th meeting of the Bristol Section took place on Friday 28 October at the Angel Hotel, Cardiff, under the chairmanship of Mr. R. J. Woodbridge, when a paper entitled " The strip coating of steel with paint and plastic finishes " was given by Mr. D. S. Newton, of Richard Thomas & Baldwins Ltd.

Mr. Newton's introductory remarks highlighted the rapid growth rate of strip coated metals in the USA, where the amount of coated strip steel had practically doubled in five years. Several types of steel were utilised in roller coating operations, including cold rolled and hot dipped galvanised steel, in metal thicknesses of up to 30 gauge and widths of up to 52 in.

In describing the general layout and capabilities of the RTB colour coated strip line at Gorseinon, Mr. Newton referred to the use of application speeds of up to 150 ft per minute. Initial surface preparation was critically controlled and a sophisticated phosphating process was employed to control the deposition weight within specification limits.

The anti-corrosive properties of the coating systems were continually under review. The use of two-pack self-etch primers had given satisfactory results on galvanised steel, but their pot life was a limiting factor, since all applied paints were recirculated and large volumes were in use at any one time. The replacement of inorganic chromates with organic chromates was giving interesting results, whilst the use of ion exchange resins showed promise.

The general requirements considered with organic coatings for strip metal were : (1) good appearance, (2) flexibility and extensibility, (3) abrasion and mar resistance, (4) colour stability, whilst the more specific requirements of (*i*) resistance to light and weathering, (*ii*) heat stability, (*iii*) resistance to stains and chemicals, and (*iv*) compatibility with mastics and adhesives were deciding factors.

To estimate the protective value of coatings which may be weathered for prolonged periods of 15 years, the performance on natural exposure tests after five years was considered, together with accelerated weathering tests. Micro indentation tests have also been developed to assess ultra-violet degradation of the coatings.

Mr. Newton concluded by indicating the possible future uses of different types of coating systems and variation in application techniques in this field. A lively discussion was opened by Mr. J. R. Taylor, in which Mr. Newton very adequately elaborated on the many points raised. In proposing a vote of thanks to Mr. Newton, Mr. D. M. Fidler commented on the interest shown in Mr. Newton's lecture by the presence of guests from South Africa and also the Midlands, Manchester and London Sections of the Association. The vote of thanks was warmly endorsed.

Hull

Recent developments in paints for naval ships

Mr. J. C. Kingcome gave a paper entitled " Recent developments in paints for naval ships " at the second technical meeting of the session on 7 November at the Royal Station Hotel, Hull. Mr. L. W. Wynn was in the chair.

Mr. Kingcome pointed out that the subject was too large to cover in a single lecture and proposed to describe some of the areas in which development had taken place since he last lectured on the subject in 1960.

In the field of surface preparation, shot or grit blasting was now widely accepted in HM dockyards, for both new construction and maintenance work. Numerous slides were shown illustrating the automatic process used. On new construction the extent of blasting is checked by observing the surface profile with the Talysurf. A replica technique has been developed using a dental moulding powder for use with existing ships.

The need for quick drying in shop or prefabrication primers was stressed and the other necessary requirements described. The primers may be divided into two classes : (1) epoxies and (2) reinforced etch primers. The former may be pigmented with zinc, aluminium or, more recently, iron oxide. The metallic pigments may lead to difficulties with respect to gassing in the tin, toxicity during welding and difficulties with cathodic protection or slow drying ; iron oxide pigmentation eliminates these difficulties, but so far testing has only been on a limited scale. The conditions of application, overcoating or removal were discussed.

Mr. Kingcome described the requirements for exterior weather work paints and discussed the problems caused in intercoat adhesion by the performance of sea trials before the top coat had been applied. The factors concerned in the retention of gloss and colour, and the difficulties caused by flotation in greys were discussed.

On the subject of interior paints, the problems caused by condensation, mould growth and the need for fire retardancy were described, and the corrosion problems due to the use of chlorinated compounds to reduce the fire hazard were stressed.

Under-water paints were briefly considered and a detailed description was given of the apparatus in use to assess these coatings in the laboratory.

The lecture was followed by an interesting discussion in which Messrs. Wynn, Pearson, Ford, Blythe and Rudram took part. A vote of thanks for a most interesting lecture was proposed by Mr. Rudram and passed in the usual manner. Thirty-two members and 30 visitors were present.

S. R. F.

London

Operational research methods in industry

The London Section held a half-day symposium on " Operational Research Methods in Industry " on 9 November 1966 at Imperial College. The Chairman, Mr. R. N. Wheeler, opened the symposium, and then handed over the chair to Mr. A. R. H. Tawn for the remainder of the proceedings.

Mr. H. R. Watkins, of Shell Mex and BP Ltd., spoke first on " The Purpose and Scope of Operational Research." A definition of operational research was " the application of scientific methods to complex problems involving human beings and machines." The essential stages were the definition of the problem, the collection of data, and the application of tests for accuracy, and the distinguishing feature of OR was the construction of a mathematical model of the problem. Due allowance was made for chance effects. In all the many diverse activities to which OR methods were applied, it was possible to distinguish eight basic types of problem. Firstly, inventory problems, where one was concerned with, say, the manufacture of a number of types of product in a limited plant, and the costs of stock holding at a sufficiently high level to meet expected fluctuations in demand. From the production aspect, long runs were required for efficiency ; this had to be balanced against the need for high stock levels, and by combining the two costs one could arrive at optimum batch size. There was generally a very steep rise in costs when batch sizes became too small.

A second type of problem was concerned with allocation, e.g. of plant operations, each of which would have certain restraints. Here linear programming was used. Distribution problems were of a similar nature. A third general type of problem was queuing, where some kind of service or facilities were provided, and it was necessary to determine the minimum size of the installation required to fulfil the tasks without excessive idle time. An explicit mathematical solution was possible only when the time for performance of the operation was independent of the number waiting ; in other cases simulation techniques had to be used, based on past experience of the operation. Sequencing formed a fourth type of problem, where one was dealing with an examination of all possible ways of achieving the desired production and minimising delays. This was an area where critical path planning techniques were used.

The fifth case was routing problems, where, for example, it was necessary to minimise the distance travelled by vehicles supplying customers spread over a large area. Computer solutions had been used in such cases, where every possible variation could be examined. This was a rather crude but effective method of solution. Replacement problems formed a fifth class ; these were of two main types, concerned with the replacement of capital equipment, and of small items which may suddenly fail at irregular times. In the latter case one could determine the saving obtained by replacement of all or some of them at fixed intervals of time. The seventh class of problem was the competitive situation ; here games theory had been developed, in which the interaction of various strategies by oneself and one's opponent (who could be, for example, the weather) could be studied. Finally, one came to search problems, such as might arise in quality control and inspection, accounting procedures, etc. The whole object of all these various techniques was to provide management with information on the consequences of various types of decision.

Mr. P. J. Harrison, of Imperial Chemical Industries Ltd., then spoke on " Short-Term Sales Forecasting." The objective of sales forecasting was to be able to satisfy the needs of one's customers in the most economical way ; long-term forecasting referred to periods of up to five years, while short-term forecasting covered periods of from a few days to a year. Two categories of information were available, past history, e.g. monthly sales or order statistics, and market intelligence. The relative importance of each source varied with the type of product. In the author's company systems were employed in which the existing data coming in each month was processed by computers to give sales forecasts ; these forecasts were used unless exceptional circumstances arose, e.g. further market information derived from the sales department. A control scheme had been introduced to look for forecasting errors. It was also possible to obtain figures for the random variations in customer demand, which could be used to show the required stock levels. Mr. Harrison outlined the requirements of a successful forecasting system, which would be able to cope with steady selling products, growth products, and seasonal products. One feature of forecasting was that the importance attached to sales or order figures fell off with the age of the statistics, and an exponentially weighted moving average was used, to take account of this factor. Similarly with growth products, a similarly exponentially weighted moving average of the trend was used. Seasonality could be introduced by the introduction of the appropriate factors derived from past experience.

After a period of discussion, the third paper was given by Mr. A. Kemp, of Geigy (UK) Ltd., who described " A Case Study in the Field of Stock Control/Production Planning in the Chemical Industry." In such tasks the problem was frequently ill-defined ; one was asked to provide a means of doing better than present practice, i.e. of minimising the cost of manufacture and stock holding. It was necessary for the OR man to have a complete understanding of the whole of the company's operations, and a considerable amount of time was spent in consultation with the departments concerned. The particular case described was a plant making some 30 kinds of textile chemicals, most of which involved separate stages of manufacture, in the one set of seven reaction vessels. Some of the products were made in large amounts regularly, while others were only required in smaller amounts. A sales forecasting system was developed to show the average demand and variability, which was high, e.g. sales in any month could be two to three times the average. It was assumed that the two main products would be made every campaign period, and for the remaining products it was necessary to determine the relations between the frequency of manufacture, and the necessary stock holding. The campaign length was also required, and eventually a period of three months was chosen. The results of 12 months' operation of the system were considered to be successful ; stock holding had been reduced by an average of 15 per cent, and was easily regulated by a stock control system ; a sales forecasting system was now available and used for many other aspects of management planning ; and a much closer co-operation existed between the various departments of the company.

Many points were raised in the discussions following the papers. Some speakers expressed concern at the fact that in OR work it was possible to tolerate an " out of stock " situation for a product, and calculate the loss of sales. In some industries, e.g. printing inks, this might result not merely in the loss of the particular sale, but the permanent loss of that customer's account. In reply, it was said that OR was merely providing information for management decisions ; if it was decided to operate with, say, a 1 per cent probability of " stockout," that was a conscious decision. There was considerable interest expressed as to how a small firm could initiate OR techniques, and whether one could get very far without computer facilities. In the beginning of OR, the advantages of having a team of mixed disciplines was stressed ; this appeared to be no longer necessary, and OR had become a separate subject, but one needed a statistician and someone who really understood the field of operations in the team. Other topics discussed were those relating to the supply of distribution depots and customers, and the possibility of the application of OR techniques to research and development projects. Those taking part in the discussions included Mr. G. W. Robinson, Mr. A. R. H. Tawn, Mr. C. C. Mell, Mr. M. R. Wilson, Dr. L. Valentine, Mr. D. S. Ford, Mr. J. S. Marsh, Mr. J. A. L. Hawkey, Mr. K. Pond, Mr. T. Jones, Dr. V. T. Crowl and Mr. K. D. C. Bruce.

In summing up the symposium, Mr. A. R. H. Tawn referred to the present era of professional management, which needed to be provided with the means for making the correct decisions. The recognition of the fact that there was only a limited range of types of problem was a great advance, and the fact that some of the apparent intangibles could be reduced to numerical data provided the means by which reasoned decisions could be made. In the final event, however, judgment and decision remained the province of management. Mr. J. Pooley proposed a vote of thanks to the speakers for what had been an extremely stimulating occasion, describing techniques which offered many possibilities of application to the paint and printing ink industries, with high raw material and stock holding costs.

V. T. C.

Southern Branch

Polyurethanes—progress in the surface coating industry

The first meeting of the 1966-67 session was held at the Royal Hotel, Southampton, on Monday 10 October, when Mr. G. Sutno read a paper on " Polyurethanes—Progress in the Surface Coating Industry."

Mr. Sutno introduced his subject with the observation that polyurethanes had been widely used in paints, lacquers, etc., only in the last five or six years. The discovery of polyurethanes was not accidental—Bayer in 1937 made it when they were seeking an alternative to Du Pont's polyamides (nylon) using isocyanates and hydroxyl containing materials. During the war the Germans used the new polymers in aircraft lacquers and for limited industrial use, but, later, in the 1950s, for wider industrial use. Outside Germany, polyurethanes made little impact until 1959 when one-pack systems were promoted in the USA. Even in 1965, polyurethane sales in the USA accounted for only 1 per cent of total coatings sales, the main outlet being in clear wood finishes. A similar percentage is obtained for the estimated UK polyurethane sales.

The high cost of polyurethanes relative to alternatives, such as alkyds, was referred to, and then the speaker discussed in detail the types of polyurethane systems available. These were convertible coatings—(1) urethane (oils) alkyds, (2) moisture cured isocyanate adducts or prepolymers, (3) heat cured blocked isocyanates, (4) two-pack isocyanate adduct and polyol, (5) prepolymer cured with catalyst or amine ; and non-convertible coatings—(1) urethane polymer solutions and (2) urethane emulsions.

The chemistry of the reactions in the convertible systems was outlined and the advantages of the various systems commented upon. In the moisture cured systems, problems due to traces of water in pigments had occurred, but stable systems of this type are in use, but not a commercial proposition for the retail market. It was interesting to note that in the two-pack systems, apart from the main reaction, water from the atmosphere and the polyol plays a significant part by reacting with up to 10 per cent of available-NCO groups.

Applications of the above systems were referred to : urethane oils in clear wood finishes, two-packs as rapid-dry sealers for furniture, and various systems, especially moisture cure type, in thick seamless flooring coatings reinforced with flakes of plastic. Panels of these flooring systems were displayed.

Questions and contributions then came from Mr. P. Targett, Mr. I. D. Sutherland, Mr. W. Morris, Mr. N. W. Morgan and Dr. Bailey. Mr. R. A. Brown concluded with a vote of thanks and expressed the appreciation of the audience for a most interesting lecture.

Members felt that the session had started well and the attendance of 25 members and guests, including visitors from Bristol Section and the USA, was very satisfactory.

J. K. B. B.

Grinding

The second meeting of the Branch took place at the Keppels Head Hotel, Portsmouth, on Monday 14 November, when Mr. A. C. B. Mathews presented his paper on "Grinding."

Many words had been spoken and written in years past to try to explain the physics and mechanics of paint and ink grinding, or milling as some preferred to term it. The speaker was not satisfied with much of the published literature on the subject and from his long practical experience and continual relevant thought had formulated his own picture of the *modus operandi* concerned in the making of the ideal paint and ink. He found that the phenomena associated with pigment dispersion fell into place on the basis of his theories.

The speaker emphasised the importance of air elimination in milling and described the mechanism by which air was removed from the pigment primary particles. Good wetting and adhesion were essential for good durability of the ultimate coating. A chart was shown indicating the relative performances of various types of milling machinery. The order of adding constituents was important and, other things being equal, the highest molecular weight materials were most strongly adsorbed. In maturing of varnish, micelle formation led to better flow, gloss and brushability.

Inactive sites on primaries (of pigment) were responsible for false body and the leafing of aluminium paint. The speaker advocated chip production which gave colour strength, transparency and gloss and, in general, noted that the key to good milling was by " very thick " working. During the lecture clear definitions were given for the various physical conditions of pigment such as agglomerates and aggregates.

The speaker's enthusiasm for his subject was obvious and his close observation of physical phenomena over the years and formulation of theories to embrace the facts was impressive. Further, simple experiments were used most effectively to illustrate some points.

Contributions were made by Mr. W. Morris, Mr. A. C. Edwards, Mr. A. R. H. Tawn, Mr. J. C. Kingcome and Mr. J. K. B. Burke, and a useful discussion took place. Mr. C. Carey thanked the speaker for giving us such an interesting talk.

The Chairman concluded the meeting, attended by 17 members and visitors, including two young ladies, by thanking Mr. A. R. H. Tawn, Hon. Editor of *JOCCA*, for paying a visit to Southern Branch.

J. K. B. B.

Manchester

Electrical methods of evaluating the corrosion resistance of paint specimens

A general meeting of the Section was held at the Manchester Literary and Philosophical Society on Friday 11 November to hear a lecture, " Electrical Methods of Evaluating the Corrosion Resistance of Paint Specimens," delivered by Mr. H. F. Clay (past Chairman, Manchester Section) to an audience of 61 members and guests.

The lecturer described original work on the polarisation testing of painted specimens, the method having been developed to facilitate the recording of performance testing. While much information is available on polarisation techniques applied to bare metal specimens, painted specimens require modified methods to avoid damage to the specimen during testing. Polarisation tests are made by immersing the specimen in the appropriate solution—sea water or salt spray—and observing the potential difference between the specimen and a reference half cell, whilst the panel is subjected to a polarising current from a platinum electrode also immersed in the solution.

In galvanostatic testing the polarising current is kept constant and the potential of the specimen is plotted against time. In potentiostatic testing the polarising current is adjusted so that the potential is charged through a predetermined range ; current is then plotted against potential.

The apparatus and the interpretation of the curves were dealt with in some detail. In general, galvanostatic and potentiostatic tests on painted specimens give similar pictures, the latter test being rather more informative. They give a correct indication of the weight of iron being corroded when scratched specimens are tested, but if the paint film is in good condition the test will indicate the condition at the scratch rather than under the paint film.

A good indication of the rate of corrosion of unscratched primed panels is given providing breakdown of the film has commenced. At the present stage of development, there is some promise that polarisation methods will extend the limited knowledge of the mechanism by which paint films control corrosion.

After a lively discussion period, at one stage between two members of the audience, the vote of thanks was proposed by Mr. W. G. Topham.

D. A. P./E. J. M.

Midlands

The printing of Bank of England notes

The Section met on 18 November at Wolverhampton and Staffordshire Technical College to hear Dr. A. C. Healey deliver a paper entitled " The Printing of Bank of England Notes."

Dr. Healey said that a bank note should be artistic, of convenient size and readily distinguishable from other denominations in the same series, be as simple and cheap to manufacture as possible and present maximum difficulty for counterfeiting. The paper was specially made, and incorporated security devices like watermarks, metal threads, blanchettes or coloured fibres. Generally more than one form of printing was used ; for example, the background could be printed by letterpress or lithography, whilst the main design used plate printing.

Plate printing owed its origins to silversmiths and goldsmiths making prints to test the nature of engraving. Subsequent use of plates made of copper gave the expression " copper-plate printing." Copper was no longer used for plates and plate printing was seldom used except for security printing of bonds, travellers' cheques, postage stamps and bank notes.

Plate printing was an intaglio process with the design engraved below the general level of the plate. The plate was covered with excess ink and the excess then removed by wiping. The paper was pressed against the plate and penetrated slightly into the engraving. This gave some embossing and a film of ink differing in thickness, according to the depth of engraving. The traditional use of damp paper to allow penetration into the engraving was discontinued by the Bank of England in 1947.

Because the ink film was above the general level of the paper, set-off was a particular problem. Formerly sheets of interleaving paper had to be inserted by hand and the prints were left several days to dry. The replacement of the traditional burnt linseed oil by synthetic resins gave inks which set much quicker and permitted automatic stacking. The notes were then placed in a heated safe overnight.

The ink, which was much thicker than that used in photogravure processes, was a compromise between a number of conflicting requirements and it had to have good rub-resistance, lightfastness and chemical resistance. Plate printing gave rise to a number of faults peculiar to the process. These were : smearing, tinting, starving, poor filling, wiping out, dragging out, spewing and feathering. A number of test methods, specific for plate printing, had been developed.

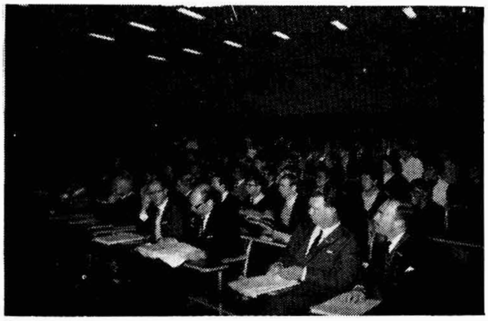
In 1956 the Bank of England had started research into printing by a web process. The first machine was installed in 1963 and four others had been ordered. The web process required fast drying inks. Moisture set inks were found to lack chemical resistance and special oxidising types were developed. Infra-red drying proved unsatisfactory and heated drums were cumbersome, so flame impingement was used for drying. It was found to be advantageous to reverse the order of printing and plate print before printing the background. The process was developed to give two offset prints on both sides of the paper at the same time. The numbers were added by letterpress using raised type.

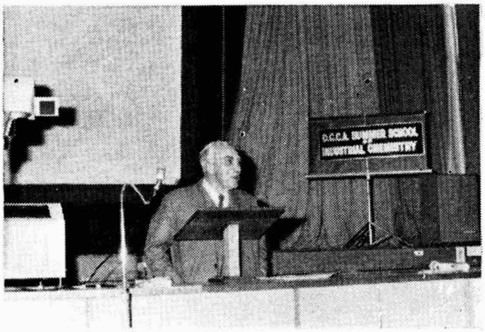
Possible future developments included the use of water soluble inks which could be wiped from plates more readily and electrostatic processes for printing.

The interest aroused by Dr. Healey's paper was reflected in the number of questions asked during the discussion period. Topics raised included the testing of paper, difficulties caused by the metal thread, the tendency for ink constituents to separate during printing, the average life of a bank note, magnetic inks, engraving depth, roller hardness and source of inks. Mr. W. Edwards proposed a vote of thanks to the lecturer.

L. R. S.

New South Wales





Top left : **Mr. W. Freeman giving the opening lecture**
Top right : **Front row, (*Left to right*) Mr. J. Samios, Mr. E. V. Collins, Mr. T. Willmott, Dr. K. B. James, Mr. A. C. Hatrick, Mr. J. Foxton, Mr. D. M. D. Stewart**
Centre left : **Miss. M. Haylock lecturing on Gas Chromotography and Infra-Red Spectroscopy**
Centre right : **Mr. E. T. Backous chairing the final session**
Bottom left : **General view of students during question time**
Bottom right : **Mr. L. J. Pearson during the final address**

Summer School of Industrial Chemistry

The New South Wales Section conducted a Summer School of Industrial Chemistry at the University of New South Wales, Kensington, on Friday and Saturday 26 and 27 August 1966.

More than 300 fifth year High School students devoted two days of their vacation period attending the " School " to obtain some idea of the role of the chemist in industry and were rewarded with some very fine entertaining lectures. Mr. W. Freeman, Chief Executive Officer of the Australian Chemical Industries Council, described the growth of the chemical industry in Australia, its complexities and its effect on the economy of the country. Mr. Freeman's lucidity and humour produced a sparkling 30-minute survey of the industry, which was warmly received by the students. Mr. Freeman spoke of the future development of the chemical industry and the growing demand for qualified chemists. He described the opportunities which await the ambitious chemist and particularly drew attention to the many leaders in the industry who began their careers in the laboratory.

This was followed by " The Chemistry of the Lemonade Bottle," which was to have been presented by Dr. Alan Draycott, of Australian Consolidated Industries. Unfortunately Alan was belatedly smitten by 'flu and his wife's hurried telephone calls gave Mr. J. De Teliga some 11 hours' notice of his " ordeal."

Mr. De Teliga's description of the many fields of chemistry involved in a simple bottle of lemonade and the manner in which he presented the paper earned the admiration of the students and of the OCCA members conducting the " School." Mr. De Teliga accurately and entertainingly described glass manufacture, soft drink processing, ceramic decoration of glass, cork processing, tinplate manufacture and processing, etc., and provided an introduction into the surface coating industry for later lecturers to develop.

" Paint—a Product of Many Chemical Industries " was the title of the next paper —the work of Ted Collins, of British Paints, John Samios, of Bayer Leverkusen, Australia, and John Hartley, of Lewis Berger. For his sins, John Samios was chosen to deliver the talk and, plagued by the ever present demon of speakers lower down the list, pressure of time, John proceeded to a definition of paint and its raw materials. Presentation in the form of a flow chart provided a simple picture of the use the paint industry makes of the product of other chemical industries. Strong reference was made to the number of chemists involved in the industry—approximately one in ten of the manufacturing staff.

The pattern of the lectures then was developed by Don Thompson, of Shell Chemicals, whose paper, " Solvents—Water to Petroleum," provoked a great deal of thought—silent and spoken—amongst the students, and produced some of the best questions of the " School." Don effectively described the action of a solvent, the reasons for the variety of solvents used in the paint industry, the difference between (and the need for) true solvents and latent solvents, the classes of solvents, and an illustration of the refining of hydrocarbon solvents.

" Water Dispersed Vehicles for Paint " was Tom Willmott's paper. Tom, who is Chief Chemist of Polymer Corporation Pty. Limited, presented this highly technical subject in a manner which provided a very attentive audience with some serious thinking. It was gratifying to see the number of students who devoted most of their " lunch-hour " to questioning Tom and the attention with which his rapidly drawn blackboard diagrams were received.

Dr. Bruce James, of Reichhold Chemicals, completed the first morning's session with a paper entitled " Resins—Reacted Oils and Chemicals." The printed notes of Bruce's paper provided a very erudite description of the subject, covering natural resins, phenolics, maleics, coumarone, petroleum, alkyd, amine, U-F, M-F, epoxide, polyurethane, and silicone resins. Again time permitted only a brief description of a few of these types. Emphasis was laid on manufacturing techniques and formulation problems.

The Friday afternoon session provided the students with the undoubted highlight of the " School." This was " Professor " Len Williamson's talk, " Colours for Surface Coatings." With the unobtrusive, but expert, help of Andy Wilson, Len demonstrated the production of colour—great masses of vivid, violent colour, whilst constantly challenging the intelligence of the students with a commentary which complemented the vibrancy of his colours.

OCCA 19

OCCA 1967 Technical Exhibition

Minister of State, Board of Trade, to open Exhibition

The Exhibition, which will take place in the Great Hall of Alexandra Palace, London, N.22, provides a focus for the technical display of advances made in raw materials, plant and equipment for the paint, printing ink and allied industries. In order to assist those visiting the Exhibition, a map showing the various ways in which Alexandra Palace can be reached from Central London will be reproduced in each copy of the *Official Guide*, which will be sent, without charge, to all members of the Association in January. Copies will also be sent individually to chemists and technologists in Western Europe and Scandinavia, to technical colleges and, through the courtesy of the trade associations, to companies in the paint, printing ink and pigment industries in the United Kingdom.

The map is also being reproduced separately in a folder which gives directions in six languages (French, German, Italian, Russian, Spanish and English) and copies of these will be sent with the *Official Guides* despatched to the Continent. Copies are also available to intending visitors and they will be despatched without charge upon application to the General Secretary of the Association. The six-language cards will also be sent to many paint and printing ink manufacturing companies on the Continent of Europe.

A free bus shuttle service will be operated by the Association from Wood Green Underground Station (Piccadilly Line) and there are ample free car parking facilities at Alexandra Palace.

The total number of stands allocated for the Exhibition is 107 and, of the companies showing, 12 have never shown at previous OCCA Technical Exhibitions, while 18 others did not show at the 1966 Exhibition. Amongst the overseas countries from which exhibits will be shown are Denmark, Finland, France, Germany, Holland, Italy, Norway, Sweden, Switzerland and the United States of America.

The Exhibition Luncheon will be held at the Savoy Hotel, London, W.C.2, on 13 March, and principal officers of other scientific bodies, industrial research associations and organisations representing both suppliers and consumers will be invited to attend. A form of application for tickets, which are priced at £2 12s. 6d. each, is enclosed in each copy of the *Official Guide*, or may be obtained from the General Secretary.

The Rt. Hon. George Darling, P.C., M.P.

All applications for tickets must be received by 1 March, since it will not be possible to accept late applications.

The Exhibition will again be open for five days. The hours of opening will be as follows :

Monday 13 March ..	15.00 to 18.30
Tuesday 14 March ..	10.00 to 18.00
Wednesday 15 March	10.00 to 18.00
Thursday 16 March ..	10.00 to 18.00
Friday 17 March ..	10.00 to 16.00

As in previous years, a stand will be devoted to Technical Education and this stand will adjoin the Association's Information Centre. Already many schools have accepted invitations to send parties of senior science students to the Exhibition on the mornings of 14, 15 and 16 March, when they will be given a short introductory talk by members of the Association in a separate Lecture Room before visiting the Exhibition. The Technical Education Stand will be staffed by representatives from the Association, technical colleges, and the trade organisations, and details will also be shown of the courses available in the technology of the industries.

Representatives from 26 overseas countries attended the 1966 Exhibition, and in order to assist the increasing number of both visitors and exhibiting companies, interpreters will again be in attendance, either at the Information Centre or at Stand 55. There will be no charge for admission to the Exhibition, or for copies of the *Official Guide*, which will be available from the Association's Information Centre or from the Association's offices prior to the Exhibition.

Amongst the facilities available at Alexandra Palace are two restaurants in the Palace Suite (the Edinburgh Room —reserved, and the Alexandra Room— unreserved) together with two cafeteria and several bars.

Any company or individual who wishes to receive copies of the *Official Guide* should write to the General Secretary, Oil & Colour Chemists' Association, Wax Chandlers' Hall, Gresham Street, London, E.C.2 (MONarch 1439, Ext. 3).

Alphabetical list of exhibitors

Allied Chemical Corporation
*AMF International Limited
Amoco International S/A
Anchor Chemical Co. Ltd.
*Applied Research Laboratories (GB) Ltd.
BASF United Kingdom Ltd.
Berk Ltd.
BIP Chemicals Ltd.
Blagden, Victor, & Co. Ltd.
Boehm, Fredk., Ltd.
Boulton, William, Ltd.
British Celanese Ltd.
British Oxygen Chemicals Ltd.
British Titan Products Co. Ltd.
Bush Beach & Segner Bayley Ltd.
Byk-Gulden Lomberg GmbH.
Campbell, Rex, & Co. Ltd.
Carless, Capel & Leonard Ltd.
Ciba (ARL) Ltd.
Ciba Clayton Ltd.
†Cole, R. H., Ltd.
Cornelius Chemical Co. Ltd.
Coulter Electronics Ltd.
†Cray Valley Products Ltd.
Crosfield, Joseph, & Sons Ltd.
Croxton & Garry Ltd.
*Daniel Products Co.
DH Industries Ltd.
Draiswerke GmbH.
Dunlop Chemical Products Div.
Durham Raw Materials Ltd.
Elcometer Instruments Ltd.
English China Clays
*Eutoplast Coatings
Farbenfabriken Bayer AG
Farbwerke Hoechst AG
Ferranti Ltd.
Geigy (UK) Ltd.
*Grace GmbH.
Grampian Press Ltd.
*Gunter Steirand KG
*Harlow Chemical Co. Ltd.
Hercules Powder Co. Ltd.
*Hibberd, Rockall & Craig Ltd.
Hoechst-Cassella Dyestuffs Ltd.

Hoechst Chemicals Ltd.
Imperial Chemical Industries Ltd.
Imperial Smelting Corporation (NSC) Ltd.
†Industrial Colours Ltd.
†Isopad Ltd.
†Kemisk Vaerk Køge A/S
Kingsley & Keith (Chemicals) Ltd.
Kronos Titanium Pigments Ltd.
Kunstharsfabriek Synthese NV
Lancashire Tar Distillers Ltd.
Laporte Industries Ltd.
Lennig Chemicals Ltd.
Little, J. H., & Co. Ltd.
Livingston Electronics Ltd.
Marchant Bros. Ltd.
*The Mastermix Engineering Co. Ltd.
*Meazzi, Dott. Edoardo
Meijer's, Rudolph, Inc.
*Microscal Ltd.
†Millroom Accessories and Chemicals Ltd.
†Mitchell, W. A., & Smith Ltd.
Molteni Off. Mecc.
†McKechnie Chemicals Ltd.
†Nederlandse Castor Oliefabriek Necof NV
†Norsk Spraengstofindustri A/S
†A/S Norwegian Talc
Novadel Ltd.
Paint, Oil & Colour Journal
Paint Research Station
†Pechiney-Saint-Gobain
Pfizer Ltd.
Plastanol Ltd.
†Pluess-Staufer
*Polyvinyl Chemie Holland NV
Premier Colloid Mills Ltd.
The Pyrene Co. Ltd.
Research Equipment (London) Ltd.
Rhone-Poulenc
Sangamo Controls Ltd.
Sawell Publications Ltd.
Scado Archer Daniels NV
Sericol Group Ltd.
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Shell Chemicals (UK) Ltd.
Silverson Machines Ltd.
Spelthorne Metals Ltd.
Steele & Cowlishaw Ltd.
Surface Coatings Synthetics Ltd.
Svenska Oljeslageri Aktiebolaget
†Swada (London) Ltd.
NV Tiofine
Titanium Intermediates Ltd.
Torrance & Sons Ltd.
†Translation & Technical Information Services
†United Coke & Chemicals Co. Ltd.
Vinyl Products Ltd.
Vuorikemia OY
Winkworth Machinery Ltd.
†Wolf, Victor, Ltd.
†Younghusband Stephens & Co. Ltd.

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† Denotes exhibitors who did not show at the 1966 exhibition.

*Denotes exhibitors who have not shown at previous exhibitions.

Scarborough Conference

20-24 June 1967

INTERFACIAL BEHAVIOUR

At the beginning of January copies of the 1967 Conference Brochure and Registration Form were sent to all Members in the United Kingdom and General Overseas Sections. Non-Members requiring copies should apply to the General Secretary at the address given on the front cover.

Biographies of the lecturers and synopses of the papers to be presented at the Conference were published in the October and November 1966 issues respectively and additional copies of the synopses are available from the General Secretary's office free of charge. Details of the programme of lectures, arranged by Mr. A. T. S. Rudram, the Association's Hon. Research and Development Officer, are set out below, together with the names of the Chairmen of Sessions.

Wednesday morning, 21 June

Chairmen : Mr. A. T. S. Rudram and Dr. G. D. Parfitt.

Speakers : Dr. G. D. Parfitt (University of Nottingham) " Dispersion."

Dr. R. H. Ottewill (University of Bristol) and Mr. J. M. Tiffany (University of Pennsylvania) " The Adsorption of Long Chain Acids on to Rutile from n-Heptane."

Dr. A. C. Zettlemoyer, Dr. R. H. Schiesser and Dr. W. D. Schaeffer (Lehigh University) " Adsorption of Polyamides-Infrared Measurements of the Interaction with Rutile and Carbon Black Surfaces."

Thursday morning, 22 June

Chairman : Dr. L. Valentine (Director, Paint Research Station).

Speakers : Dr. J. E. O. Mayne and Dr. A. J. Appleby (University of Cambridge) " Corrosion Inhibition by the Salts of the Long Chain Fatty Acids."

Dr. S. Wilska (Vuorikemia Oy) " Testing of Titanium Dioxide Pigments in Paint Film for Dispersion Weathering Resistance and Optical Properties."

Dr. W. Funke (Forschungsinstitut fur Pigmente und Lacke) " On the Relation between the Pigment-Vehicle Interaction and the Water Uptake of Solid Paint Films."

Thursday afternoon, 22 June

Chairman : Dr. G. D. Parfitt.

Speakers : Mr. D. F. Tunstall (British Titan Products Co. Ltd.) " Reflectance at Paint Substrate Boundaries."

Dr. D. Patterson and Mr. A. P. Gates (University of Leeds) " Some Effects of Media on the Lightfastness of Colouring Matters."

Friday morning, 23 June

Chairman : Dr. L. Valentine.

Speakers : Dr. V. T. Crowl (Paint Research Station) " Flocculation, Flotation and Flooding in Phthalocyanine/Titanium Dioxide Pigmented Paints."

Dr. T. Doorgeest (Verfinstituut TNO) "Adsorption of Water Vapour, Stearic Acid, Stearyl Alcohol and Alkyd Resins on to Rutile Titanium Dioxide Pigments."

Dr. W. Carr (Geigy UK Ltd.) " Texture and Dispersibility of Pigments."

On the Friday afternoon three Workshop Sessions will be held (at which attendance is restricted to ticket holders only) and the titles of these are :

Colour Terminology.

The Future of Electrodeposition.

Decorative Paint 1977.

The usual social programme of coach tours, sea trip, tournaments, theatre party and a hat show for the ladies has also been arranged, together with the Dinner and Dance at the Grand Hotel on the Friday evening when the Association will entertain the Mayor and Mayoress of Scarborough as well as other civic dignitaries. A Civic Reception will take place on the Wednesday.

Hull Section

(From left to right) Mrs. L. Wynn, L. Wynn (Chairman, Hull Section), Mrs. S. A. Reed, S. A. Reed (President, Hull Chemical and Engineering Society), Mrs. E. A. Armstrong, Dr. S. H. Bell (President), R. H. Hamblin (General Secretary)

Annual Dinner and Dance

The 1966 Annual Dinner and Dance of the Hull Section took place this year in the Garden Banqueting Suite of the Eden Hotel, Willerby, near Hull, on Friday 14 October.

This change of venue to a converted one-time manor house was a contributory factor to our having the highest attendance at this function for some few years.

The chief guest was the President, Dr. S. H. Bell, whose journey up from London, accompanied by Mr. R. H. Hamblin, General Secretary, was much appreciated. Other guests included, Mr. S. A. Reed, Chairman of the Hull Section the RIC, and Mrs. Reed. Mr. N. Cochrane, Chairman of the West Riding Section OCCA, and Mrs. Cochrane and Mr. C. H. Morris, Chairman of the Midland Section OCCA, and Mrs. Morris.

Following the dinner and three short speeches, the company of 150 enjoyed dancing to the music of the resident orchestra. The loyal toast was given by the Chairman, Mr. L. W. Wynn, who also proposed the toast to the Ladies and our Guests, to which the response was made by the President. The Toastmaster was Mr. E. Armstrong.

A Tombola, organised by Mr. E. A. Brown, was primarily intended to help meet expenses, but in so doing it also aroused considerable interest and contributed in no small measure to the general enjoyment of the evening.

In addition to the other Honorary Officers, the Hon. Social Secretary, Mr. T. A. Fillingham, was ably assisted by Mrs. Fillingham, Mr. S. J. Reed and Mr. C. G. Harrison in making the arrangements for what proved to be a most successful occasion.

Manchester Section

Annual Dinner-Dance

This event was held at the Midland Hotel, Manchester, on Friday 28 October, the Chairman, Mr. I. S. Moll, being present, together with Mrs. Moll and 370 members and guests. The principal guests were Dr. M. E. D. Jarrett (Chairman, Technical Division, WPM Limited) and Mrs. Jarrett ; the other guests were Dr. S. H. Bell (President, OCCA), Mr. I. S. Hutchison (Chairman, Scottish Section) and Mrs. Hutchison, Mr. C. H.

(Left to right) Dr. M. E. D. Jarrett, Mrs. Moll, Mr. I. S. Moll (Chairman, Manchester Section), Mrs. Jarrett, Dr. S. H. Bell (President)

Morris (Chairman, Midlands Section) and Mrs. Morris, Mr. L. W. Wynn (Chairman, Hull Section) and Mrs. Wynn, Mr. N. Cochrane (Chairman, West Riding Section) and Mrs. Cochrane, and Mr. R. H. Hamblin (General Secretary, OCCA) and Mrs. Hamblin.

The toast to the Manchester Section was proposed by Dr. Jarrett in an extremely witty speech delivered in the manner of a born raconteur. The Section apparently had geometrical origins, being composed neither of acute northerners, obtuse southerners, but comprising more Mancunian right angles. This, and other sallies, were greatly appreciated by the diners.

Mr. I. S. Moll then proposed the toasts to the guests and the ladies, and also referred to the work of the past Chairman (Mr. H. F. Clay) and of the Symposium Committee in organising a highly successful event.

After a short interval for reorganisation, dancing commenced and continued into the small hours until, towards the end, large balloon clusters deflocculated and were dispersed by the dancers.

D. A. P./E. J. M.

News of Members

Dr. S. R. W. Martin, an Ordinary Member attached to the London Section, of Mitchell & Smith Ltd., has been appointed by the Board of Ault & Wiborg Ltd., to the position of Associated Director.

Dr. Martin served on the OCCA Council from 1955-57 and from 1958-60, and was Treasurer of the London Section from 1959-60.

Mr. E. A. Greensitt, Associate member attached to the Newcastle Section, has been appointed Works Manager at International Paints main factory at Felling-on-Tyne.

Dr. J. B. Haley, an Ordinary Member attached to the London Section, has resigned from his position as Research Director of Chemical Building Products Ltd., and will take up a position as Senior Scientist in the Scientific Branch of the Greater London Council at the beginning of next year.

Obituary

Mr. T. Adamson

We are sorry to report the death on 17 November of Mr. T. Adamson, an Ordinary Member attached to the Newcastle Section since its inception in 1940. At the time of his death he was Joint Managing Director of Wailes Dove Bitumastic Limited, of Hebburn. Mr. Adamson will be greatly missed by his friends both within and outside the paint industry.

Register of Members

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

Ordinary Members

ADAMSON, DEREK W., B.SC., A.R.I.C., 31 Highfield Drive, Ickenham, Uxbridge, Middlesex. *(London)*

ASPINALL, WILLIAM DONALD, Glenside Printing Ink Co. Ltd., Palmerstown, Co. Dublin. *(Irish)*

AYED, ISSA SALEH, B.SC., PO Box 1833, Amman, Jordan. *(Overseas)*

BALDOCK, NORMAN WILLIAM, Morris Ashby Ltd., Queens Chambers, 61 Boldmere Road, Sutton Coldfield, Birmingham. *(Midlands)*

BARRETT, ROBERT MCDOWELL, B.SC., M.SC., 22 Drew Road, Wollescote, Stourbridge, Worcestershire. *(Midlands)*

BISHOP, JOHN HAROLD, M.SC., B.SC., Paints Group, Defence Standards Laboratories, PO Box 50, Ascot Vale, Melbourne, Victoria, Australia. *(Victorian)*

BLACK, ARCHIE LINDESAY, 9 Haros Avenue, Nunawading, Victoria, Australia. *(Victorian)*

CALDWELL-SMITH, PETER, A.S.T.C., A.R.A.C.I., Ampol Petroleum Co., Buchanan Street, Balmain, New South Wales, Australia. *(New South Wales)*

CLARKE, GEORGE LEONARD, BALM Paints Pty. Ltd., PO Box 4, Palmyra, Western Australia. *(West Australian)*

CRAIG, DEREK, 27 Greenvale Grove, Fairfield, Stockton-on-Tees. *(Newcastle)*

DAVIES, PAUL, PH.D., D.I.C., A.R.C.S., B.SC., 57 Woodland Rise, Welwyn Garden City, Hertfordshire. *(London)*

ELLERY, ERIC, B.SC., ICI Ltd., Queens Square, Bristol. *(Bristol)*

FEHERVARY, ALEXANDER, 5 Avery Street, Normanhurst, New South Wales, Australia. *(New South Wales)*

FURST, GERALD, 208 Kingshill Drive, Kenton, Harrow, Middlesex. *(London)*

HENDERSON, CHARLES NEIL, B.SC., 30 Churchill Drive, Bridge of Allan, Stirlingshire. *(Scottish—Eastern)*

HEPWORTH, JAMES ALWYN, B.SC., 6 Ganghill, Guildford, Surrey. *(London)*

HISLOP, DAVID WATSON, B.SC., Cherry Orchard, Stoke Poges. *(London—Thames Valley)*

HOLLAND, FREDERICK, Revertex (NZ) Ltd., Box 12077, Penrose, Auckland, New Zealand. *(Auckland)*

JOHNYS, DAVID LEONARD, 89 Larkhall Rise, Clapham, London, S.W.4. *(London)*

KERR, DAVID JOHN, 11 Gertz Avenue, Keon Park, Melbourne, Victoria, Australia. *(Victorian)*

LEES, JOHN MITCHELL, 162 Downham Crescent, Prestwich, Lancashire. *(Manchester)*

LEY, DAVID JOHN, 86 Marina Drive, Whitley Bay, Northumberland. *(Newcastle)*

LINEIRO DE ANTONISSEN, BEATRIZ, DR., SA Alba, Centenera 2750, Capital, Argentina. *(Overseas)*

MCGREISH, JOHN EDWARD LEE, 158 Beechwood Drive, Glasgow, W.1. *(Scottish)*

NORTON, DOUGLAS KENT, A.C.T., DIP. TECH., Gittings & Hills Ltd., Long Acre, Nechells, Birmingham, 6. *(Midlands)*
ROMY, GEORGE, B.SC., c/o Amoco International SA, 7 Rue Versonnex, Geneva, Switzerland. *(Overseas)*
SKINNER, CATHERINE ELIZABETH, 7 Spencer Road, East Molesey, Surrey. *(London)*
SMITH, JOHN WILLIAM, B.SC., A.S.T.C., A.MUS.A., 83a Harcourt Parade, Rosebery, New South Wales, Australia. *(New South Wales)*
SPENCER, ERIC, 14 Sierra Street, St. Heliers, Auckland, New Zealand. *(Auckland)*
TREUHERZ, RICHARD MANUEL, B.SC., Lewis Berger (GB) Ltd., Freshwater Road, Dagenham, Essex. *(London)*
TRIGGS, FRANCIS CYRIL, B.SC., Reeves & Sons Ltd., Lincoln Road, Enfield, Middlesex. *(London)*

Associate Members

CASTLEDINE, JOHN NORTON, Fidene Corporation Pty. Ltd., 300 George Street, Sydney, Australia. *(New South Wales)*
COOKE, CONOR J., 7 Woodlands Road, Johnstown Park, Dun Laoghaire, Co. Dublin. *(Irish)*
EDEH, AUGUSTINE NNEJIH, 84 King Edward Street, Chalvey, Slough, Buckinghamshire. *(London)*
ELLERINGTON, DAVID, 2 Southview Cottage, Broxhill Road, Havering, Romford, Essex. *(London)*
EVENNETT, CHRISTOPHER JOHN, c/o AC Hatrick Chemicals (Aust.) Pty. Ltd., 49-61 Stephen Road, Botany, New South Wales, Australia. *(New South Wales)*
HASTIE, JOHN RANKIN, 3 Hamilton Avenue, Harrogate, Yorkshire. *(Manchester)*
HAY, JAMES MARSHALL, 55 Hayes Way, Beckenham, Kent. *(London)*
JONES, FRANCIS WILLIAM, " The Oaklands," Denby Village, Derbyshire. *(Midlands)*
O'BEIRNE, ALBERT, B.COMM., D.P.A., ICI (Ireland) Ltd., 3 South Frederick Street, Dublin, 2. *(Irish)*
PATTINSON, MICHAEL GEORGE, 55 Crumpshall Lane, Manchester, 8. *(Manchester)*
PFEIFFER, REGINALD VERNE, Fidene Corporation Pty. Ltd., Box 1745, GPO, Sydney, Australia. *(New South Wales)*
RUDGE, WILLIAM LAW, 17 Allegra Avenue, Belmore, New South Wales, Australia. *(New South Wales)*
THOMAS, OTMAR, c/o J. McWade & Co., 28 Adelaide Road, Dublin. *(Irish)*
TURTILL, ARTHUR CHARLES, Forminex Pty. Ltd., 81-83 Old Pittwater Road, Brookvale, New South Wales, Australia. *(New South Wales)*

Junior Members

COOPER, MICHAEL CLIVE, 35 Pruden Avenue, Lansefield, Nr. Wolverhampton, Staffordshire. *(Midlands)*
COPE, WILLIAM JOHN, 67 Old Park Road, Dudley, Worcestershire. *(Midlands)*
FURNER, RAYMOND EDWIN, 26 Hazelbourne Road, London, S.W.12. *(London)*
KELLY, ALAN, 13 Glenby Avenue, Peel Hall, Wythenshawe, Manchester, 22. *(Manchester)*
MASON, JOHN OLIVER, 5 Courtenay Road, Penge, London, S.E.20. *(London)*
MCGILLIVRAY, PETER CARSWELL, 79a Lennard Road, Penge, London, S.E.20. *(London)*
MILNER, PETER JAMES, 10 York Road, Acton, London, W.3. *(London)*
NORTH, CHRISTOPHER ROBERT, 31 Dunkeld Road, Baguley, Wythenshawe, Manchester, 23. *(Manchester)*
PYLE, WILLIAM JOHN, " Nelledene," Old Mill Lane, Bray, Maidenhead, Berkshire. *(London—Thames Valley)*
WALMSLEY, TREVOR ALAN, 45 Cherry Tree Lane, Romiley, Cheshire. *(Manchester)*

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.

Monday 2 January

Hull Section. Hull Section Co-operative Research Programme, to be held at Royal Station Hotel, Hull, at 7 p.m.

Thursday 5 January

Midlands Section. Annual Ladies' Evening, to be held at George Hotel, Solihull, at 7 p.m.

Newcastle Section. " Newer Methods of Paint Application," by F. G. Dunkley, to be held at Royal Turk's Head Hotel, Grey Street, Newcastle upon Tyne, at 6.30 p.m.

Friday 6 January

Bristol Section. " Measurement of Colour by Instrumentation," by P. V. Foote, to be held at Royal Hotel, College Green, Bristol, 1, at 7.15 p.m.

Monday 9 January

London Section—Southern Branch. " Paint Test Methods," by T. R. Bullett, to be held at Keppels Head Hotel, The Hard, Portsmouth, at 7.30 p.m.

Tuesday 10 January

West Riding Section. " Plaster Type Paints from Plastic Emulsions," by Dr. Disselhoff, to be held at Great Northern Hotel, Leeds, at 7.30 p.m.

Thursday 12 January

Midlands Section—Trent Valley Branch. " Castor Oil Chemistry," by Dr. G. Silverstone, to be held at British Rail School of Transport, London Road, Derby, at 7.30 p.m.

Friday 13 January

Manchester Section. " What Kind of Staff Does the Paint Industry Need ? ", by M. H. M. Arnold, at Manchester Literary and Philosophical Society, at 6.30 p.m.

Scottish Section. Annual Dinner Dance at Central Hotel, Glasgow, at 6.30 p.m.

Saturday 14 January

Scottish Section—Student Group. " Forensic Medicine," by D. Jack, to be held at Lorne Hotel, Glasgow, at 10 a.m.

Wednesday 18 January

London Section. " Evaluation for Electrodeposition of Recently Developed Water Soluble Epoxy Esters," by L. A. Tysall and J. Van Westrenen, to be held at Physics Department, Imperial College of Science and Technology, South Kensington, London, S.W.7, at 6.30 p.m.

London Section—Thames Valley Branch. " The Use of Computers in Industry," by A. Davies, to be held at Royal White Hart Hotel, Beaconsfield, Bucks, at 7 p.m.

Thursday 19 January

Hull Section. Discussion Evening at Queens Hotel, George Street, Hull.

Scottish Section. " Some Industrial Applications of Water Based Paints," by a speaker from Vinyl Products Ltd., to be held at Lorne Hotel, Sauchiehall Street, Glasgow, at 6 p.m.

Friday 20 January

Midlands Section. " Surface Coatings in Nuclear Establishments," by W. J. Colclough, to be held at Chamber of Commerce House, 75 Harborne Road, Birmingham, 15, at 6.30 p.m.

Wednesday 25 January

Scottish Section—Eastern Branch. " Electrical Methods of Assessing the

Protection Provided by Paints Against Corrosion," by H. F. Clay, to be held at North British Hotel, Princes Street, Edinburgh, at 7.30 p.m.

Friday 27 January

Bristol Section. " The Use of a Computer to Control a Batch Reaction," by J. M. F. Drake, to be held at Royal Hotel, College Green, Bristol, 1, at 7.15 p.m.

Irish Section. Open Forum, to be held at Clarence Hotel, Wellington Quay, Dublin, at 8 p.m.

Thursday 2 February

Newcastle Section. " A Scientist Turns to Crime," by K. J. Kimber, to be held at Royal Turk's Head Hotel, Grey Street, Newcastle upon Tyne, at 6.30 p.m.

Monday 6 February

Hull Section. " Electronic Data Processing," by C. Campbell, to be held at Royal Station Hotel, Hull, at 7 p.m.

Tuesday 7 February

Newcastle Section. Evening visit to Northern Forensic Science Laboratory at Gosforth.

Wednesday 8 February

Irish Section. Works visit to Messrs. Lever Brothers, at 3 p.m.

Thursday 9 February

Scottish Section. " Aerosols," Metal Box Co. Ltd., to be held at Lorne Hotel, Sauchiehall Street, Glasgow, at 6.30 p.m.

Friday 10 February

Manchester Section. " The Restoration of Works of Art," by A. R. Ashton, to be held at Manchester Literary and Philosophical Society, at 6.30 p.m.

Saturday 11 February

Scottish Section—Student Group. " Discussion Morning—Annual General Meeting," to be held at Lorne Hotel, Sauchiehall Street, Glasgow, at 10 a.m.

Monday 13 February

Victorian Section. " Theoretical Approach to Contact Leaching of Anti-fouling Paints," by F. Marson.

London Section—Southern Branch. " Electrostatic Application of Powder Coating," by Dr. A. W. Bright, to be held at Royal Hotel, Southampton, at 7.30 p.m.

Tuesday 14 February

West Riding Section. " Plastics in Building," by J. R. Crowder, to be held at Great Northern Hotel, Leeds, at 7.30 p.m.

Thursday 16 February

New South Wales Section. Annual General Meeting.

London Section. " The Printing of Bank of England Notes," by Dr. A. C. Healey, to be held at Physics Department, Imperial College of Science and Technology, South Kensington, London, S.W.7, at 6.30 p.m.

Friday 17 February

Midlands Section. " Polymer Characterisation," by Dr. F. W. Peaker, to be held at Chamber of Commerce House, 75 Harborne Road, Birmingham, 15, at 6.30 p.m.

Tuesday 21 February

London Section—Thames Valley Branch. " Decorative Paints and Decoration," to be held at Royal White Hart Hotel, Beaconsfield, Bucks, at 7 p.m.

Wednesday 22 February

Scottish Section—Eastern Branch. " Applications of Computers in Industry," by C. T. Campbell, to be held at North British Hotel, Princes Street, Edinburgh, at 7.30 p.m.

Thursday 23 February

Midlands Section—Trent Valley Branch. "Electrical Methods of Assessing the Protection of Paints Against Corrosion," by H. F. Clay, to be held at British Rail School of Transport, London Road, Derby, at 7.30 p.m.

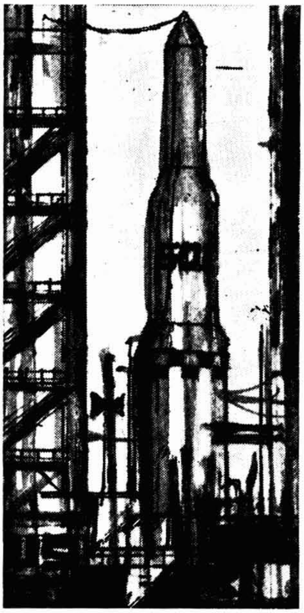
Friday 24 February

Bristol Section. "Solvents," by L. A. Tysall, to be held at Royal Hotel, College Green, Bristol, 1, at 7.15 p.m.

Newcastle Section. Ladies' Night at Five Bridges Hotel, Gateshead.

Thursday 16 March

New South Wales Section. "Contact Leaching Antifouling Paints," by F. Marson, Defence Standards Laboratories.

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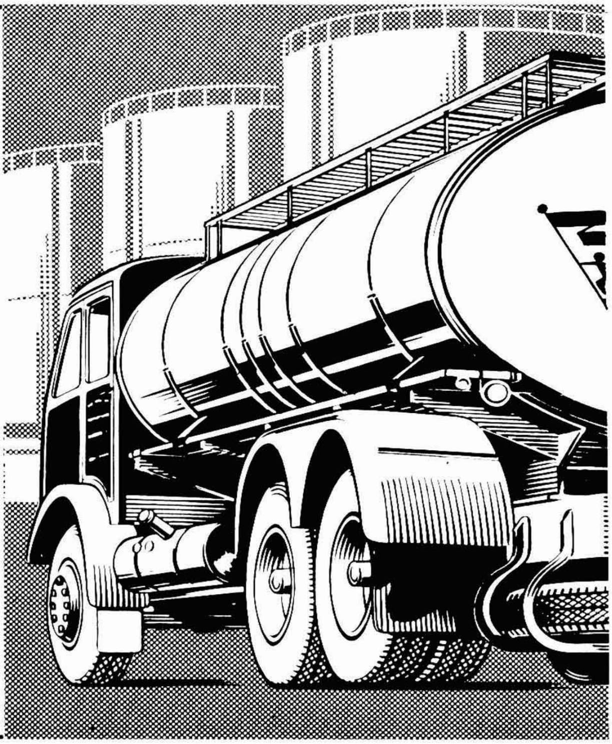

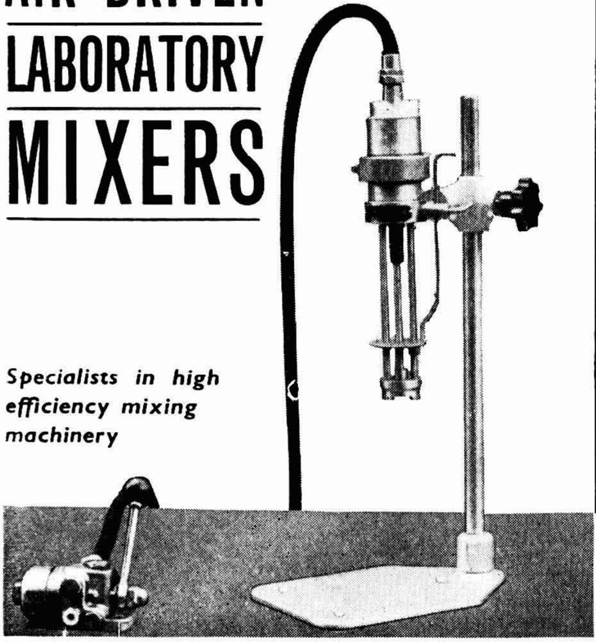

INTRODUCTION TO

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

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OCCA 19—Technical Exhibition

please turn to pages 100-102 for more information and an alphabetical list of exhibitors


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