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PAPERS FROM THE MANCHESTER SYMPOSIUM

Emulsion paint properties and structure—mechanism of film formation

The influence of comonomers, plasticisers and coalescing solvents on the minimum film forming temperature and film hardness of polymer dispersions

The role of surfactants in emulsion paints polymerisation and emulsion paints

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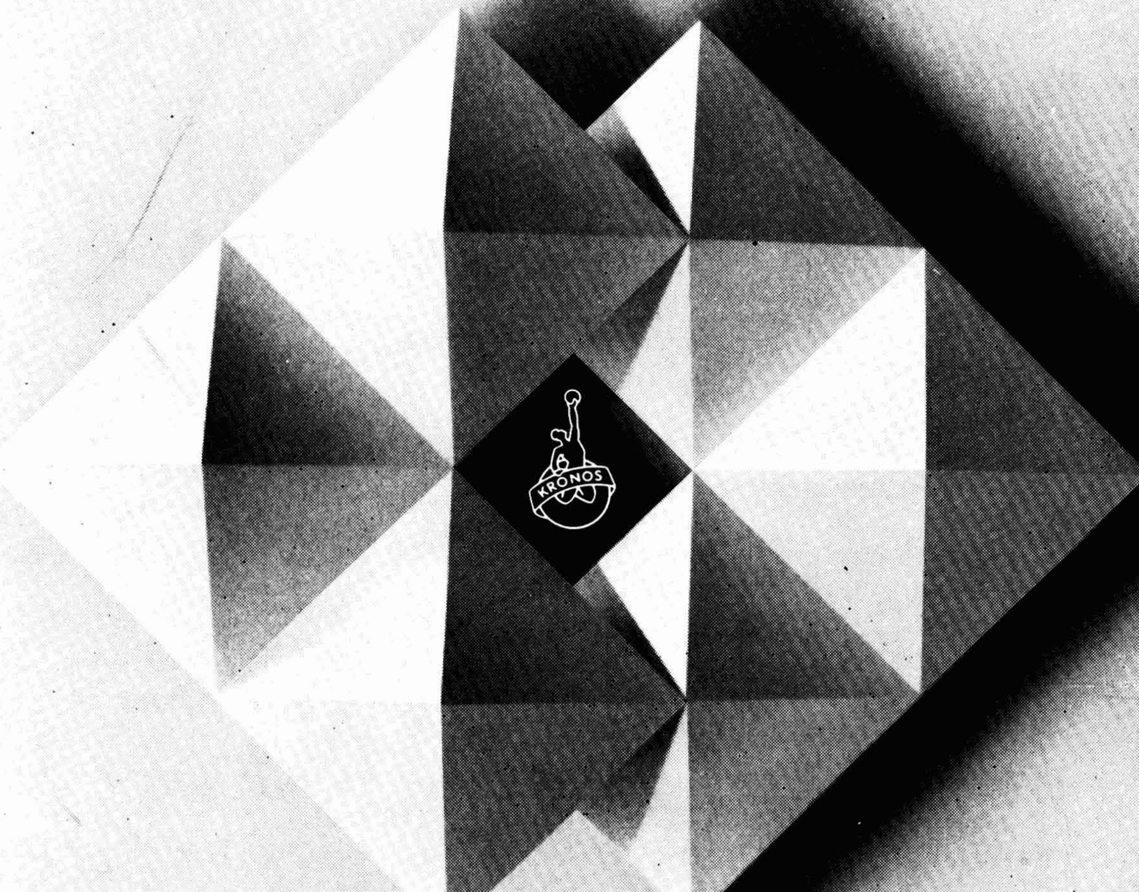
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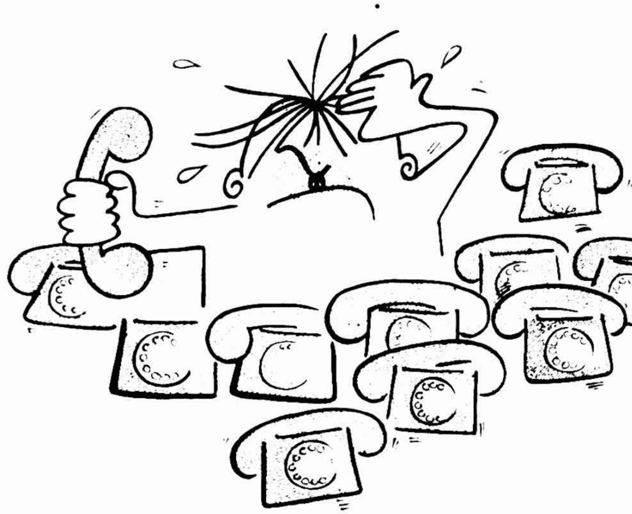

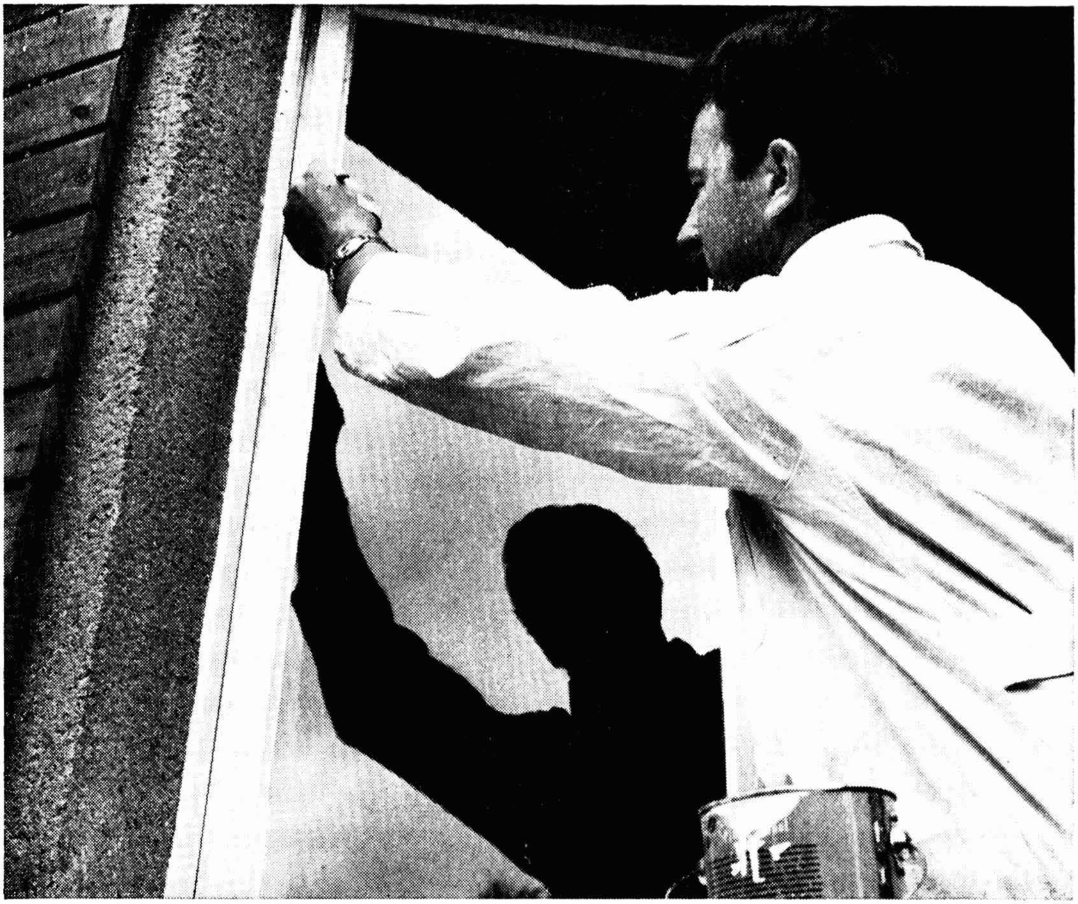

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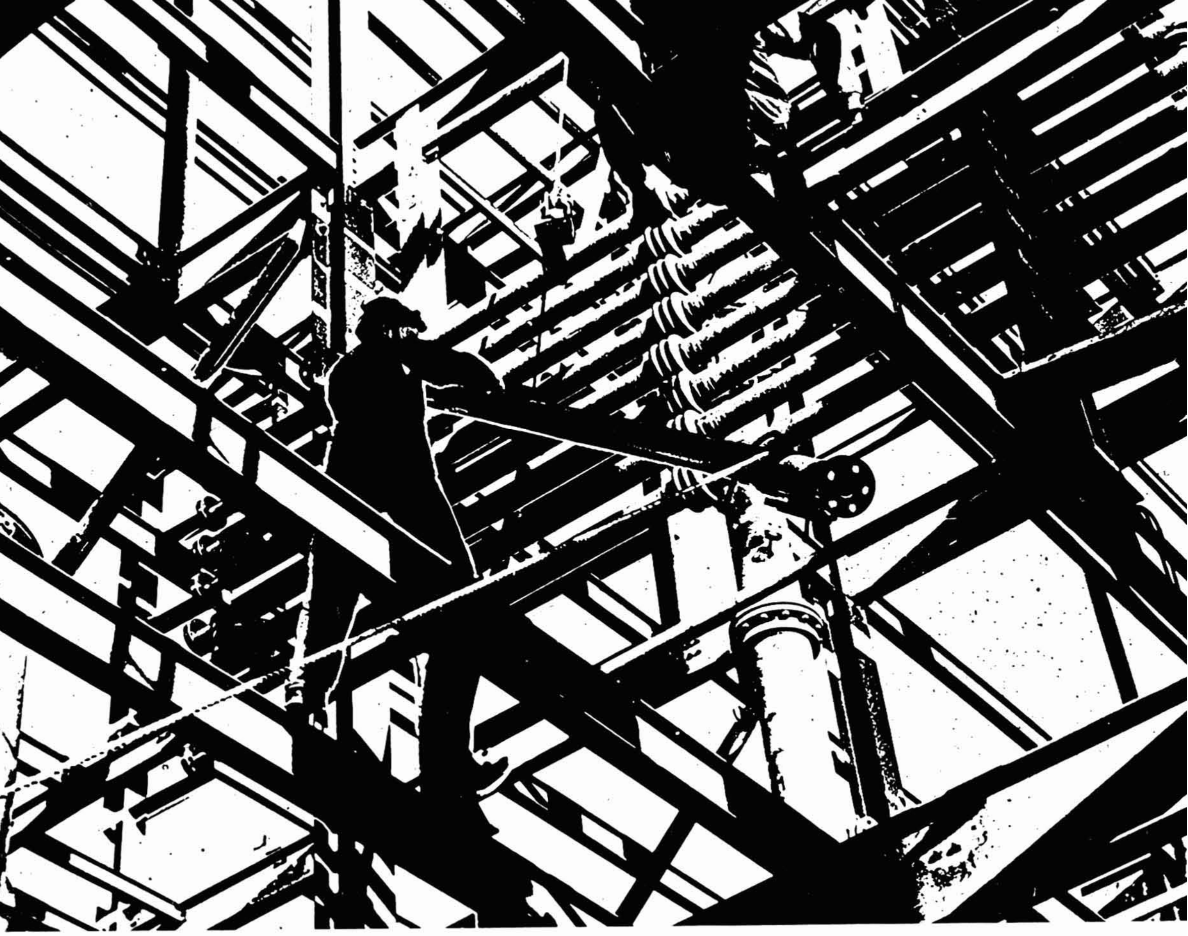

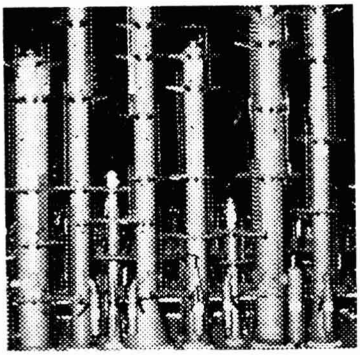

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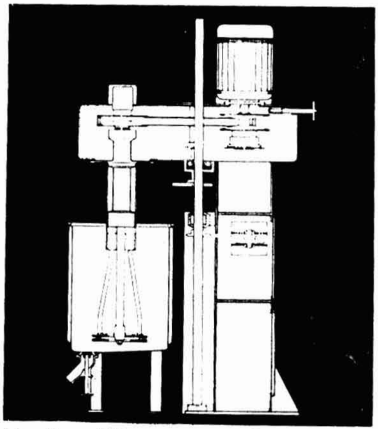

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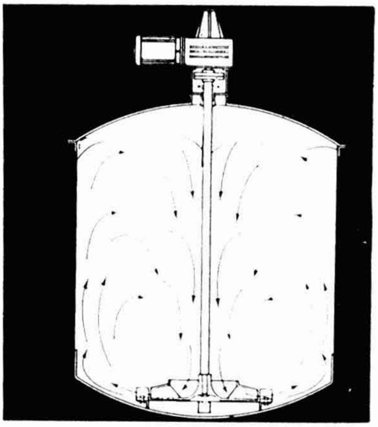

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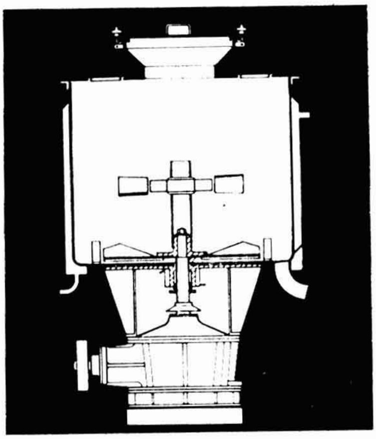

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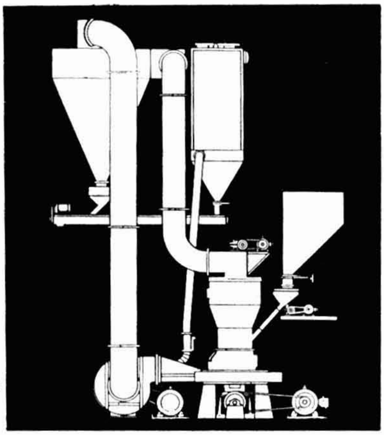

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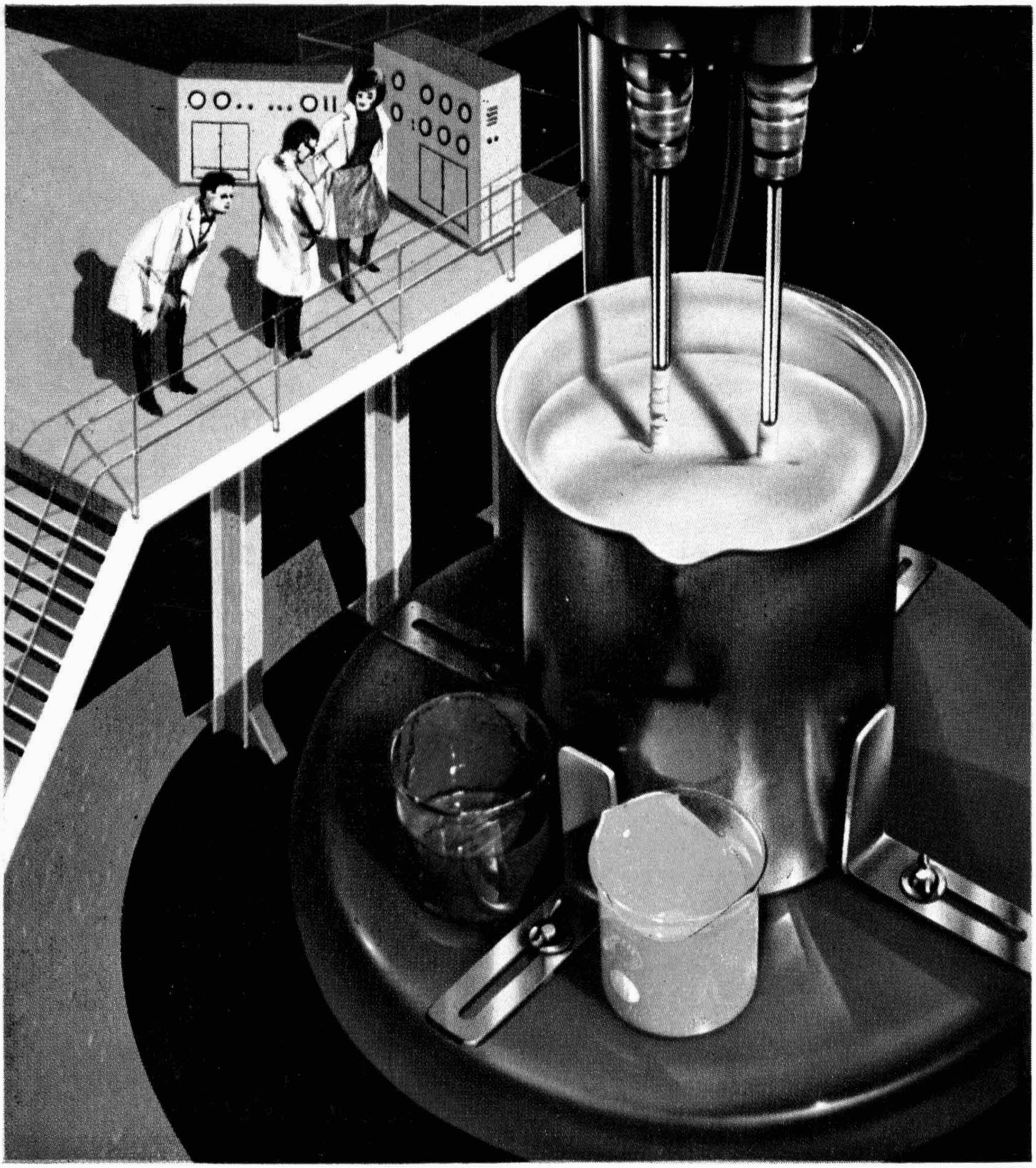


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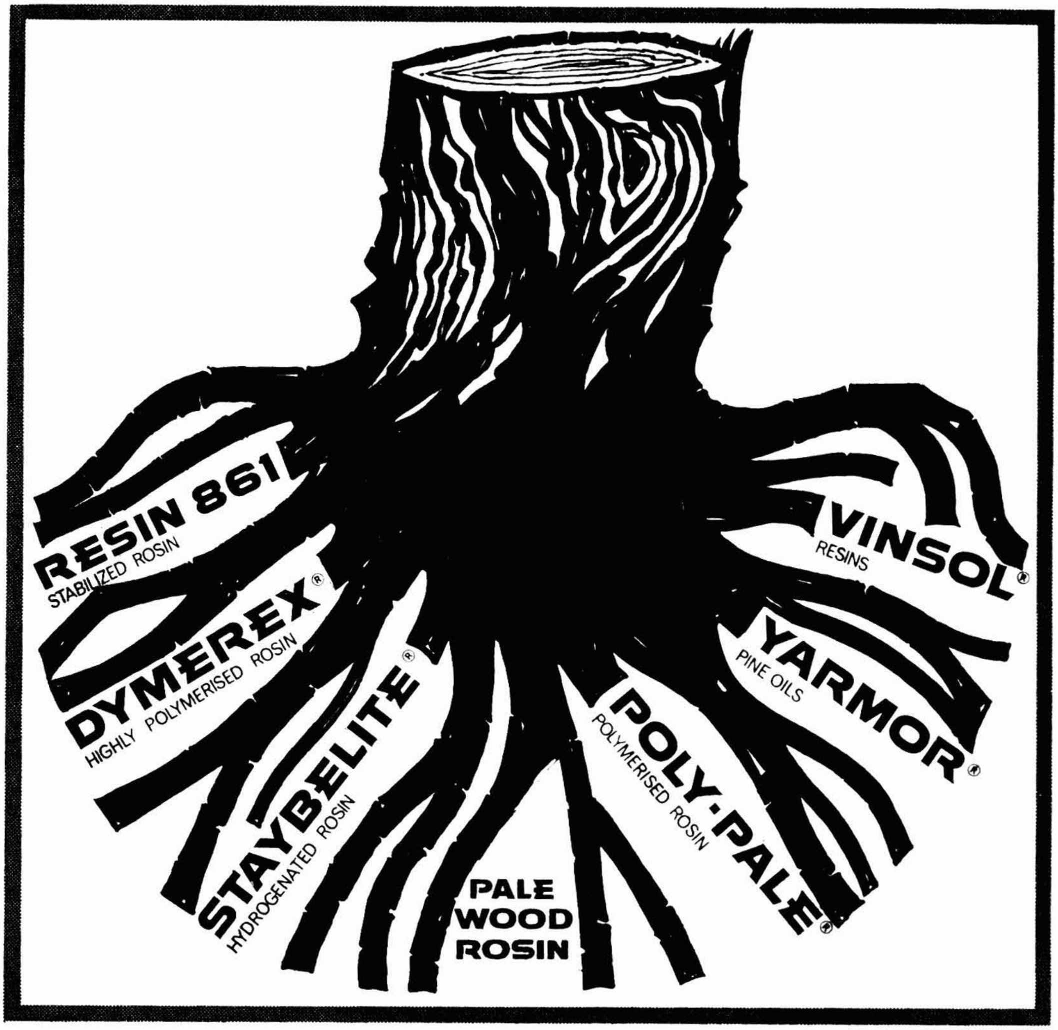
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Transactions and Communications

Emulsion paint properties and structure—mechanism of film formation*

By E. F. Redknap

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Summary

Suggested mechanisms for film formation from emulsions are outlined to emphasise the important role of the aqueous phase during drying of the film. It has been shown that appreciable polymer particle coalescence occurs only during the relatively late stages of drying, when capillary and possibly other forces would be operating. Exposure of poorly coalesced film to high humidity can effect substantial improvement in film integration, and high surface tension of the aqueous phase can also be beneficial.

A particular aspect of film formation, *viz.* that relating to gloss emulsion paints, has been studied by electron microscopy in terms of the effects of certain hydrophilic colloids, coalescing agents and pigments.

Propriétés de peintures—émulsions et le mécanisme structural de la formation de leurs feuils

Résumé

On trace quelques mécanismes proposés à l'égard de la formation des feuils à partir des émulsions afin de faire ressortir le rôle important de la phase aqueuse pendant le séchage du feuil. Il fut démontré qu'une coalescence appréciable arrive seulement pendant les étapes relativement avancées de séchage, lorsque la force capillaire et peut-être des autres forces entreraient en vigueur. L'exposition à haute humidité des feuils mal-coalescents peut effectuer une amélioration matérielle du complètement de feuil. Une phase aqueuse d'une haute tension superficielle peut être également avantageuse.

Un certain aspect de formation de feuil, c.-à-d. ce qui concerne le brillant de peintures-émulsions fut étudié, à l'aide de microscopie électronique, au point de vue des effets de certains colloïdes hydrophobiques, agents de coalescence, et pigments.

Die Eigenschaften von Emulsionsfarben und der Struktur—Mechanismus ihrer Filmbildung

Zusammenfassung

Um die bedeutende Rolle, die die wässrige Phase bei der Trocknung des Films spielt, zu unterstreichen, werden die für die Bildung von Filmen aus Emulsionen vorgeschlagenen Mechanismen skizziert. Es wurde aufgezeigt, dass erst während der verhältnismässig späten Trockenstadien, wenn Kapillar- und möglicherweise noch andere Kräfte am Werke sein könnten, ein merkliches koaleszieren der polymeren Partikel stattfindet. Werden schlecht zusammengeflossene Filme hoher Luftfeuchtigkeit ausgesetzt, so kann dies die Integration des Filmes wesentlich verbessern ; auch hohe Oberflächenspannung der wässrigen Phase kann von Nutzen sein.

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*Presented to the Manchester Section Symposium held on 19 April 1966.

Ein besonderer Gesichtspunkt der Filmbildung, nämlich der, welcher mit dem Glanz von Emulsionsfarben in Zusammenhang steht, wurde mit Hilfe des Elektronmikroskopes in Bezug auf die Einwirkung gewisser hydrophiler Kolloide, koaleszierender Agenzien und Pigmente untersucht.

Свойства эмульсионных красок и структурный механизм образования пленки

Резюме

Предлагаются в общих чертах механизмы пленочного образования из эмульсий с целью обратить внимание на важную роль водяной фазы во время сушки пленки. Показано что имеется заметное соединение полимерных частиц только в сравнительно конечных стадиях сушки, когда присутствуют капиллярные и может быть другие силы. Подвергание слабо сращенной пленки высокой влажности может вызвать значительное улучшение пленочного интегрирования и высокое поверхностное натяжение водяной фазы может оказать благоприятное действие.

Изучался особый вид пленочного образования — связанный с блестящими эмульсионными красками — с помощью электронной микроскопии относительно действия некоторых гидрофильных коллоидов, сращивающих веществ и грунтовых красок.

Introduction

The mechanism by which an emulsion or synthetic polymer dispersion produces a substantially continuous film has been the subject of various hypotheses, aimed primarily at explaining how the forces tending to produce particle coalescence are produced.

The suggested mechanisms may be broadly sub-divided into two main groups, one of which attempted to draw an analogy between the coalescence of emulsion polymer particles and the sintering of metal or glass spheres at high temperatures[1] ; the other explained coalescence mainly in terms of the generation of capillary forces during evaporation of the water[2].

In the " sintering " mechanism it was supposed that the water evaporated from the freshly applied film, leaving the particles in close contact, after which the driving force tending to produce fusion was provided by the air/polymer interfacial tension, which would tend to minimise the total surface area of the polymer.

Although this type of mechanism may contribute to film formation, it is open to a number of objections when regarded as a major factor, including failure to take into account the general observation that film formation in conventional paint emulsions proceeds concurrently with the evaporation of the water and is substantially complete by the time the emulsion is touch dry.

The sintering hypothesis was subsequently modified to bring in the aqueous phase, the fusion forces now being considered in terms of interfacial tension between polymer and aqueous phase rather than between polymer and air[3], in what may be regarded as a wet sintering process. For various reasons, one of which was the relatively low interfacial tension which would be involved in the presence of surfactant, this mechanism was allotted no more than minor significance by other workers, and the capillary hypothesis was put forward as explaining most of the observed features of film formation.

This hypothesis, which has since been supported[4], gives major significance to the part played by the aqueous phase. It proposes that the forces making for coalescence derive from the formation of liquid capillaries between the polymer particles during drying, and the consequent pressure differences across the negative curvature of the air/liquid interface.

These pressure differences, which are directly proportional to the air/liquid interfacial tension and inversely proportional to the radius of curvature of the interface, can be of considerable magnitude. For example, pressures of 80 atmospheres have been calculated[2] for polymer particles of 1 micron particle size in the presence of an aqueous phase of surface tension 30 dynes/cm., such as is likely to be present in many emulsion paint media. Decreasing the particle size or increasing the surface tension gives rise to proportionate increases in the pressure generated. In normal circumstances such pressures will be sufficient to overcome the resistance of the polymer particles to deformation, and where the polymer has appropriate flow properties will lead to coalescence.

The contributions of wet sintering and capillarity to the film forming process have recently been analysed and another possible factor has been suggested. This factor relates to the diffusion of water through the polymer particles themselves and its evaporation from the surface, leading to the production of compressive forces which are regarded as playing a dominant role in the later stages of film formation[5].

The effects, in varying degrees, of the forces generated during the drying of the emulsion on the polymer particles have been demonstrated by electron microscopy at the Paint Research Station and elsewhere. Thus, many unplasticised emulsion films present a surface comprised of closely packed particles which are still substantially spherical in form. In other films, particularly where small amounts of plasticiser are present, the polymer particles appear as polyhedra. With increasing plasticisation or on ageing the original outlines of the particles may become barely or no longer visible.

In the present context the term coalescence has been taken to include these various degrees of film integration in so far as they lead to the production of a film with significant coherence and clarity.

Water content at coalescence

Against this background, further work has been carried out at the Paint Research Station. One aspect considered was the extent to which the water content of a drying emulsion film would fall before a substantial degree of particle coalescence occurred.

For this purpose use was first made of a polyvinyl acetate homopolymer emulsion of even particle size, approximately 0.5μ. The emulsion produced coherent, almost clear films when allowed to dry at room temperature (21°C.), indicative of a fair measure of particle coalescence, whereas at a lower temperature (6°C.) only an opaque, powdery deposit showing negligible cohesive properties was produced. At the lower temperature particle coalescence manifestly had not occurred, the polymer being too hard to respond to the film-forming forces.

These differences were used to follow the process of film formation in the following manner.

A number of comparable films were spread on glass panels. The first film was placed immediately in the refrigerator and allowed to dry at 6°C., whereby coalescence was entirely prevented. Subsequent films were allowed to stand for progressively increasing periods at 21°C.—at which coalescence was possible—before placing in the refrigerator to prevent further coalescence. The proportions of coalesced and non-coalesced film were then assessed in terms of the relative areas, readily distinguishable, of coherent and powdery material. Concurrently, the rate of loss of water from the films, while drying at 21°C., was followed gravimetrically by means of controls. In this way the relationship at a given time between extent of particle coalescence and water content of the films, while drying at 21°C., could be determined.

The results are summarised in Table 1, below—

Table 1

Coalescence of polyvinyl acetate emulsion film

Time of drying at 21°C. (mins)	Percent of original water lost	Wt. composition of drying film		Percent of film non-coalesced
		percent water	percent non-volatile	
0	0	65.1	34.9	100
2	2.9	64.4	35.6	99
17	25.2	58.3	41.7	96
34	49.0	48.8	51.2	91
53	70.8	35.3	64.7	83
70	87.8	18.6	81.4	79
92	97.2	5.7	94.3	60
111	97.3	4.9	95.1	12
112	97.3	4.9	95.1	0
139	97.3	4.8	95.2	0

Table 1 indicates that at 21°C substantial coalescence of the polymer particles did not occur until approximately 97 per cent of the original water content of the films had evaporated, corresponding to a film composition of approximately 5 per cent by weight of water and 95 per cent non-volatile matter, i.e., quite late in the drying process and at a stage at which capillary forces, together with possible contributions from the other mechanisms mentioned earlier, would be expected to be active.

The simple technique described above would appear to be open to some criticism, since it is a matter of common observation that emulsion films, after application, dry from the outer edges inwards, giving a higher water concentration in the central wet area than at the boundaries of the film. Measurement of the overall water content would thus give a lower figure than actually exists in the still wet areas. In the example just given the error does not appear to be of great significance. If, for example, the water content of the outer dried area of the film is taken as the final figure shown in the table, as seems not unreasonable, the overall water content of the film being known, the water content of the inner wet zone at the various stages of drying can be calculated. When this is done the water contents of the still wet areas during the significant later periods of drying (i.e., when the film is changing significantly from non-coalesced to coalesced form) become, from 70 minutes onwards, 22.3, 6.4, 5.7, 4.9 and 4.8 per cent. These figures are little greater than those shown in Table 1. However, the differences could well be greater in other (e.g., plasticised) systems and in subsequent experiments allowance was made for preferential boundary drying in the manner indicated.

The emulsion so far examined was of nominally unplasticised type, although in such cases there is probably some temporary plasticising effect on the polymer particles by the aqueous phase. Since in normal emulsion paint practice some degree of more permanent plasticisation would always be used, the experiments described above were extended to an externally plasticised (5 per cent dibutyl phthalate) sample of the polyvinyl acetate emulsion already described and to an internally plasticised vinyl acetate/acrylate polymer (plasticisation equivalent to 5-7 per cent dibutyl phthalate) of similar particle size.

With these plasticised emulsions the water contents of drying films at particle coalescence, allowing for preferential boundary drying, were 11 and 15 per cent respectively. This tendency for coalescence to occur at a rather earlier stage for the plasticised compared with the unplasticised emulsion would be anticipated on general theoretical grounds. Thus, relatively less capillary pressure would be acquired to coalesce the softer polymer particles, corresponding to a greater radius of curvature at the air/water interface and a greater water content in the film.

Effect of humidity on coalescence

It is fairly well known that the coalescence of a poorly-coalesced film, e.g., one dried at low temperature, can usually be substantially improved by re-wetting the film and allowing it to dry at room temperature. In view, however, of the relatively small amounts of water necessary for the generation of the appropriate forces, the effect of humid atmospheres rather than re-wetting as such has been examined.

A non-coalesced film of the unplasticised polyvinyl acetate mentioned above, obtained by drying the film at 6°C and subsequently in a desiccator at 25°C, was exposed in a closed vessel to an atmosphere of 90 per cent RH at the higher temperature. Over a period of 90 minutes the opaque, powdery film became virtually clear and developed a substantial degree of cohesion. The water absorbed amounted to 3.0 per cent of the original dry film weight and subsequently increased to 3.4 per cent after 16 hours. A comparable film kept in a desiccator ($CaCl_2$) at 25°C for several weeks showed no signs of coalescing.

Lower humidity—80 per cent RH—was much less effective in promoting coalescence of the unplasticised film but was quite effective with a lightly plasticised (5 per cent dibutyl phthalate) film. At 60 per cent RH the non-coalesced unplasticised film showed no significant improvement over ten days, while the plasticised film improved only slightly. Here the amount of water absorbed by the films was less than 1 per cent.

It would appear, therefore, that a poorly coalesced film, subsequently exposed to a sufficiently humid atmosphere, can undergo further significant coalescence and develop a useful degree of cohesion. This observation probably bears some relation to the familiar experience that emulsion paint films can show appreciable improvement in general film properties during their early life.

Another factor relating to the atmospheric humidity under which an emulsion film dries is the rate at which water is lost from the film. Thus an emulsion which is a marginal film former can be shown to be appreciably inferior in terms of film clarity and cohesion when dried at low humidity, when rate of evaporation will be high, than at high humidity when evaporation rate is low. This can be explained in terms of the relative times for which the forces making for coalescence are acting on the polymer particles. Similar effects would be expected if films were dried on substrates varying in porosity.

Effect of surface tension on coalescence

On the basis of the capillary hypothesis, a proportionate increase in the magnitude of the coalescing forces produced in the drying film would be expected with increase in surface tension of the aqueous phase, leading to a general improvement in film properties. That this is in fact so has been demonstrated in the following way.

Films of the plasticised polyvinyl acetate emulsion mentioned earlier were dried at 6°C to the powdery non-coalesced state and exhaustively extracted with water, to remove surfactant, until the washings were virtually water (70 dynes/cm. as determined by a Du Noüy tensiometer).

The still wet films were then re-dried at 6°C to preserve their non-coalesced condition and were divided into two sets. One set was re-wetted with 1 per cent surfactant solution (26 dynes/cm)., the other with water (70 dynes/cm), and both were then allowed to dry at room temperature (21°C).

The films dried from water were significantly tougher and less brittle than those dried from the surfactant solution, and the former also showed better gloss and clarity. Although other factors may also be involved, it appeared that improved coalescence resulting from the higher surface tension was largely responsible for the properties of the film dried from water. This may well have practical implications when a selection of surfactants for emulsion systems is being made.

Film formation and gloss of emulsion paints

One special field of studies of film formation from emulsions relates to the factors influencing the gloss of emulsion paints[6, 7].

Broadly, gloss may be considered as a composite phenomenon influenced mainly by the surface structure of the film and its refractive index. The refractive index will be decided largely by the type of polymer used, but the surface structure is likely to result from a number of inter-related factors presenting considerable complexity. However, it is apparent that a smooth surface is desirable and one contribution to this would be efficient coalescence of the polymer particles.

It is well known that one way of increasing the gloss obtainable from a given polymer type is to reduce the particle size of the emulsion. This, in itself, will tend to reduce the magnitude of any surface irregularities left in the film surface by the original polymer particles, but it would also be expected that the smaller particle size would favour the generation of greater coalescing forces during drying and hence more efficient coalescence.

In considering gloss it is necessary, however, to take into account the influence of other components of the emulsion paint, and the structural effects of various constituents, particularly hydrophilic colloids, coalescing agents and pigments, have been studied at the Paint Research Station, largely by electron microscopy.

It is generally acknowledged that a number of hydrophilic colloids such as cellulosic thickeners have an adverse effect on gloss. This effect has been examined using a polyvinyl acetate emulsion of very even particle size (0.25μ), prepared with an anionic/non-ionic surfactant system in the absence of conventional colloids.

This emulsion gave clear, glossy and fairly flexible films even in the absence of plasticisers. On the addition of small amounts of certain colloid solutions—hydroxyethyl cellulose, methyl cellulose and sodium carboxymethyl cellulose—the emulsion deposited films which were now cloudy and with very low gloss.

Preliminary examination of the bulk emulsion with an optical microscope showed an apparent increase in particle size to approximately 0.5—1μ, the particles presenting an elongated appearance. At higher magnification the microscope showed that these elongated particles were in fact short chains comprising mainly two or three of the original particles.

Subsequent electron microscopy of the surfaces of films deposited from the colloid-free emulsion showed that these presented an homogeneous appearance such as would be expected from the packing of evenly distributed individual spheres. In films deposited in the presence of colloid, however, the aggregates previously observed in the bulk emulsion had evidently persisted during the drying of the film, which now presented a much more heterogeneous surface structure.

This would account for the marked loss of clarity and gloss noted earlier. Apart from the direct effects of the virtually larger particles present, these would be expected to be less susceptible to coalescence during drying than the smaller individual particles. Evidence that this was so was provided by the technique for measuring water content of films at coalescence described earlier. In the absence of colloid, coalescence occurred at a water content of approximately 11 per cent, whereas in the presence of colloid the corresponding figure was 6 per cent, indicating that greater coalescing forces were required in the latter instance.

Small amounts of coalescing agents, such as certain aliphatic glycols, alcohol ethers and alcohol ether esters, can be used not only to improve the general film properties (e.g. scrub-resistance) of conventional emulsion paints but also to increase gloss. These effects, as terminology suggests, are primarily a matter of improved polymer particle coalescence, as has been confirmed by the electron microscopy of film surfaces. In the presence of coalescing agents it has, for example, been shown that an emulsion film presents a very much more even surface early in its life, with elimination of the outlines of the individual particles.

The question of the effect of pigmentation on the structure of glossy emulsion films, i.e., what happens to the pigment, is one of continued investigation.

Electron microscopy of film sections has shown that in general pigment dispersion is poorer in emulsion than in solution type media. In particular, this has been demonstrated for a given acrylic resin prepared as an emulsion but also capable of conversion, through carboxyl groups present, to solution form. However, current indications are that pigment dispersion is better in glossy emulsion films than in non-glossy.

This, in itself, might be expected to influence the surface texture of such films. In simple emulsion paints there is some evidence that the glossy films have a more even surface structure in terms of protruding pigment than the non-glossy, but the differences so far observed have not been very marked.

Much greater differences have been noted between the surface replicas of simple emulsion paints of only moderate gloss and similar paints modified with minor amounts of water-soluble acrylic resin and giving high gloss. In the former, surface replicas clearly showed the presence of pigment particles in the surface and also traces of the original polymer particles. In the latter, pigment particles were not in evidence and the overall texture was more uniform.

Probably at least two factors contributed to the improved surface structure—and gloss—of the solution modified emulsion paint, one being better pigment dispersion obtained by the grinding of the pigment with the solution before incorporation of the latter into the emulsion, and the other the ability of the solution resin to fill any depressions in the surface round the boundaries of the original emulsion particles.

The pigment to binder ratio of glossy emulsion paints is usually quite low, not more than 1 : 1 by weight, and small increases in the amount of pigment markedly decrease gloss. It was of considerable interest, therefore, to find in the course of pigment packing studies at the Paint Research Station that certain pigment cakes, in the virtual absence of binder but depending on the packing, were surprisingly glossy. Addition of a polymer emulsion disturbed the packing and reduced the gloss. This observation served to emphasise the part played by surface arrangement in influencing gloss, irrespective of the chemical constitutions of the components concerned.

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Discussion at Manchester Symposium

A VISITOR cited a case of an emulsion paint applied to steel which initially had poor adhesion but in a humid atmosphere achieved better adhesion. In view of comments on the effect of humidity on coalescence, was it possible that this in turn gave improved adhesion to metal?

MR. REDKNAP said that emulsion films usually lost adhesion during exposure to a humid atmosphere, possibly because of the presence of water-sensitive material adjacent to the substrate. Adhesion was largely but not entirely recovered on drying out. However, with a poorly coalesced film, a more important result of exposure to high humidity could well be improved coalescence of the polymer particles, leading to more intimate contact between the film and the substrate and hence to the improved adhesion observed.

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The influence of comonomers, plasticisers and coalescing solvents on the minimum film forming temperature and film hardness of polymer dispersions*

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Summary

The relative efficiency of a number of acrylate esters in imparting flexibility to vinyl acetate copolymers is assessed by measuring the film hardness of the copolymers and the minimum film-forming temperature of their aqueous dispersions. The influence of chain length and branching is demonstrated. Data obtained with the vinyl ester of the highly branched " Versatic acid 911 " provides additional evidence of the reduction in flexibility due to chain branching.

The efficiencies of 12 solvents commonly recommended as plasticisers or coalescing solvents are compared by examining their effect on the properties of a vinyl acetate copolymer containing 19 per cent butyl acrylate.

The variation of film hardness with temperature is also demonstrated and the different gradients of film hardness versus temperature obtained with internal and external plasticisers are discussed.

L'influence excercée par comonomères, plastifiants et solvants coalescants sur la température filmogène minimum et sur la dureté de film de dispersions polymères

Résumé

Le rendement rélatif d'une série d'esters acryliques en donnant la flexibilité aux copolymères d'acétate de vinyle est constaté par le mesurage de la dureté de film des copolymères et par la détermination de la température filmogène minimum de leurs dispersions aqueuses. On démontre l'influence également de longueur et de ramification de chaîne.

Les rendements de douze solvents souvent recommandés en tant que plastifiants ou solvants coalescants sont comparés par leurs effets sur les propriétés d'un copolymère d'acétate de vinyle contenant 19% d'acrylate de butyle.

La variation de dureté de film selon la température est démontrée, et l'on discute les courbes différentes de dureté de film contre température qui se rendent par plastifiants intérieurs et extérieurs respectivement.

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*Presented to the Manchester Section Symposium on 19 April 1966.

Der Einfluss von Mischmonomeren, Weichmachern und koaleszierenden Lösungsmitteln auf die für die Filmbildung notwendige Mindesttemperatur und die Filmhärte polymerer Dispersionen

Zusammenfassung :

Die relative Fähigkeit, einer Anzahl von Akrylsäure-estern den Vinylazetatmischpolymeren Geschmeidigkeit zu verleihen, wird durch Messung von Filmhärte des Mischpolymers und der Filmbildungsmindesttemperatur ihrer wässrigen Dispersionen bewertet. Der Einfluss der Kettenlänge und-verzweigung wird auseinandergesetzt. Werte, die für die Vinylester der stark verzweigten "Versaticsäure 911" erhalten wurden, ergeben den zusätzlichen Beweis, dass Kettenverzweigung die Geschmeidigkeit herabsetzt.

Die Wirkungsweise von 12 Lösungsmitteln, die gewöhnlich als Weichmacher oder koaleszierende Lösungsmittel empfohlen werden, wird durch Untersuchung ihres Einflusses auf die Eigenschaften eines 19% Butylakrylat enthaltenden Vinylazetat- Mischpolymers verglichen.

Die sich mit der Temperatur ändernde Filmhärte wird gleichfalls aufgezeigt, und die durch Einsatz innerlich oder äusserlich gebundener Weichmachungsmittel je nach Temperatur erhaltenen verschiedenen Abstufungen in der Filmhärte werden besprochen.

Влияние комономеров, пластификаторов и срастающих растворителей на минимальную температуру формации и твердость пленок полимерных дисперсий

Резюме

Дается оценка относительной эффективности ряда акрилатовых эфиров в сообщении податливости кополимерам винилового ацетата, посредством измерений твердости пленок кополимеров и минимальной температуры формации пленок их водяных дисперсий. Доказывается влияние длины цепи и разветвления структуры. Полученные данные винилового эфира синтетической весьма разветвленной цепной жирной кислоты 911 снабжают добавочное доказательство снижения податливости из-за цепного разветвления структуры. Сравнивается эффективность двенадцати растворителей обычно рекомендованных в качестве пластификаторов или срастающих растворителей, по исследованию их эффекта на свойства кополимера винилового ацетата содержащего 19% бутилого акрилата. Доказывается также изменение твердости пленок с температурой и обсуждаются различных кдассы пленочной твердости в сопоставлении с температурой, подученные с внутренними и внешними пластификаторами.

Introduction

The emulsion chemist is constantly faced with the problem of selecting the most attractive polymer system from the materials which are commercially available, striving to produce the best technical product within the limits set by economic circumstances. In the surface coating emulsion field, vinyl acetate has long been the cheapest acceptable monomer available, bearing in mind the poor colour stability of the styrene-butadiene copolymers. One of the main limitations of polyvinyl acetate is its brittleness and relatively high film forming temperature ; therefore it has been copolymerised with a variety of other monomers which impart flexibility to the polymer in order to avoid the use of external plasticisers with their attendant disadvantages.

The work which is described in this paper constitutes an attempt to assess the relative efficiency of a number of monomers as internal plasticisers in vinyl acetate copolymers, and to study the effect of supplementary plasticisers and coalescing solvents on their performance. Two properties were chosen to form the basis of the assessment, namely the minimum film forming temperature of the polymer dispersion, and the hardness of polymer film.

One might aspire to a more fundamental approach to the subject and seek to measure the 2nd order or glass transition temperature (Tg) of the polymer, and also to determine in detail its stress-strain relationships. However, in the case of film formation, measurement of the minimum film forming temperature (MFT) of a dispersion gives a direct indication of its practical performance, whereas the Tg of the polymer would be only one of several factors governing this property. It is well known that particle size and the composition of the emulsifying system exert a significant effect on the MFT of a polymer dispersion.

Characterisation of the general mechanical properties of copolymer films is a more formidable task which can entail difficult and laborious techniques. Reference to the literature will show that many different parameters have been measured in order to assess mechanical performance. The Clash and Berg Elastometer has been used to measure the flexibility of polyvinyl acetate films[1], and the Instron Tensometer to measure the tensile strength and modulus of elasticity of vinyl acetate copolymers[2]. Other workers have used a Torsion pendulum[3, 4] and various hardness testers such as the Koenig pendulum. Zorll reports good agreement between comparisons made with the Torsion pendulum and the Koenig pendulum[4].

Several reasons caused the authors to base their work on the Koenig pendulum hardness tester. They were interested in comparing relatively soft polymer films ; therefore techniques involving the handling of detached films were avoided. The Clash and Berg, and Instron testers were thus excluded.

Another object was to compare polymer properties at various temperatures and humidities. This again excluded some of the instruments available, and it was finally decided to use either the Sward rocker hardness tester or the Koenig pendulum. The former was used for some of the earlier work, but it was later decided that the pendulum was the more convenient instrument. Recently the ICI pneumatic micro-indentation apparatus has become available, and this promises to be a more versatile instrument[5], particularly when data on the temperature coefficients of plasticity of films are needed.

Experimental

1. Apparatus for the measurement of minimum film-forming temperatures

This apparatus is a development of the Parr Bar, and its modification for the purpose of measuring the minimum film forming temperature of dispersions is based on a design described by Protzman and Brown[6]. Many differences in detail will be apparent to those familiar with the Protzman apparatus (see Fig. 1). A temperature gradient is maintained in an 18 in long steel block with a planar upper surface which is chromium plated. One end of the block is drilled to receive a cylindrical 180W heater (H), and the other contains a channel (C) through which a cooling fluid is circulated. The heat input is adjusted by means of a " Variac " auto-transformer (V), and the rate of cooling is controlled by varying the speed of the circulating pump (M). The speed of the pump is adjusted by means of the rheostat r_2 to achieve the required temperature gradient along the block, and a thermostat (T) actuates a relay switch (S) which introduces an extra resistance r_1 to provide a fine control. The thermostat is

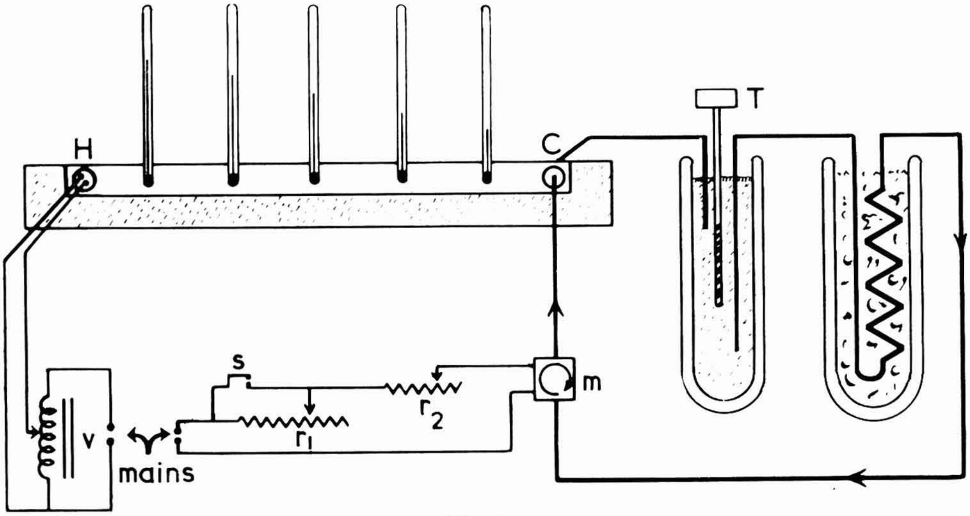

Fig. 1a

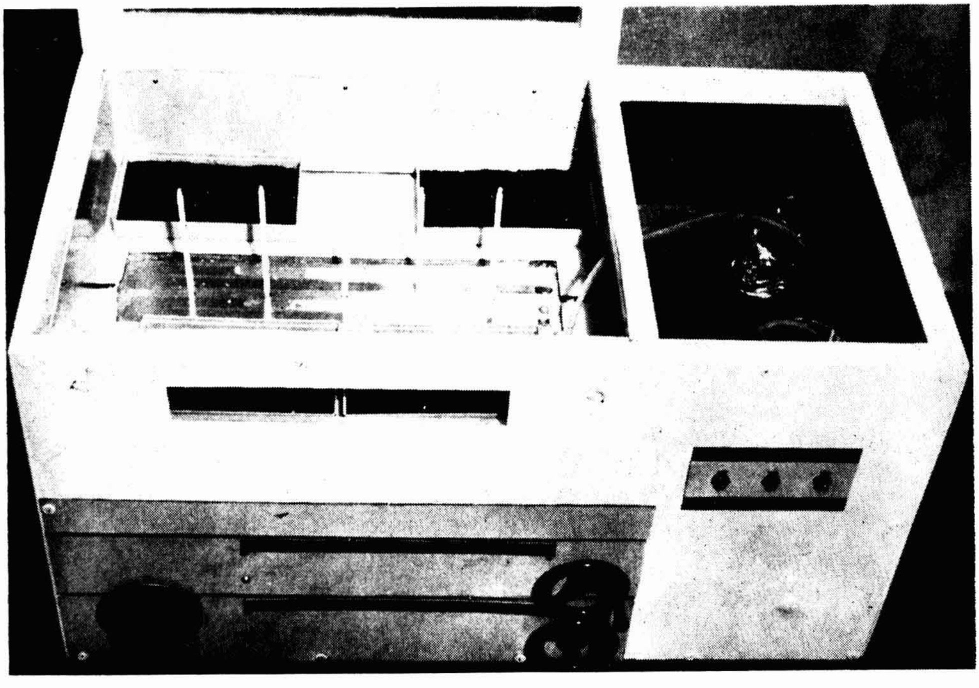

Fig. 1b. M.F.T. apparatus

situated in a reservoir of the circulating coolant which is drawn through a coil cooled by a mixture of " Cardice " and ethanol. The block normally operates with a temperature gradient of approximately 2°C per inch along its length.

When steady conditions have been achieved, an applicator is used to draw four $\frac{1}{2}$ in. strips of film of 0.006 in wet thickness from the hot end to the cold end of the block. The lid of the enclosure is then secured, and with the aid of silica gel desiccant the films dry within 30-60 minutes. A sharp division between a clear continuous film and a white, opaque, discontinuous film marks the MFT of the dispersion. This temperature may be determined to ± 1°C with confidence.

2. The Koenig pendulum hardness tester

This apparatus is probably familiar to most people. The pendulum was enclosed in a case to eliminate draughts and facilitate control of humidity (Fig. 2). The release mechanisms which lower the pendulum on to the specimen and start its oscillation were operated from outside the case. The apparatus was standardised by adjusting the centre of gravity of the pendulum to give a reading of 250 seconds on plate glass. This represents the time taken for the amplitude of oscillation to decrease from 6° to 3° from the vertical.

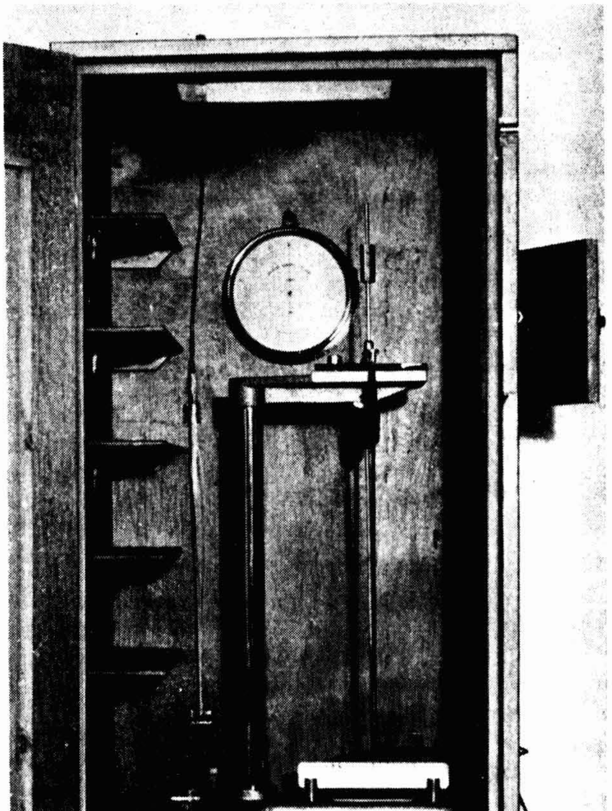

Fig. 2. Koenig pendulum in enclosure

As will be shown later, data obtained with the Sward rocker hardness tester indicate that the effect of humidity on the hardness of a polyvinyl acetate film is slight below 30 per cent RH. All measurements were therefore made at 20-30 per cent R.H. This level was maintained by placing trays of silica gel inside the cabinet.

3. Preparation of films for the hardness test

Films were drawn down on 4 in square panels of $\frac{1}{4}$ in plate glass with an applicator set at 0.006 in. These were dried for 60 minutes in an oven at 40°C, then conditioned for 24 hours at constant temperature in a desiccator containing silica gel. In practice the desiccator reached an equilibrium of about 10-15 per cent RH. The films were stored in desiccators and transferred to the pendulum cabinet immediately before performing the test. Due to its large size it was not convenient to maintain such a low humidity level in the cabinet as in the desiccators, but all readings were made in an environment at less than 30 per cent RH. This condition was achieved easily at 25°C, but it was more tedious at 5°C. A maximum error of ±6.7 per cent of the measured value was incurred with the Koenig pendulum.

4. The effect of humidity on film hardness

The Sward rocker hardness tester was used to determine the effect of humidity because it was a rapid test which could be performed under normal humidity conditions on films which had been conditioned over suitable salts in a desiccator. The acceptability of such a procedure was demonstrated by the fact that successive readings obtained on a film showed no deviation in one direction.

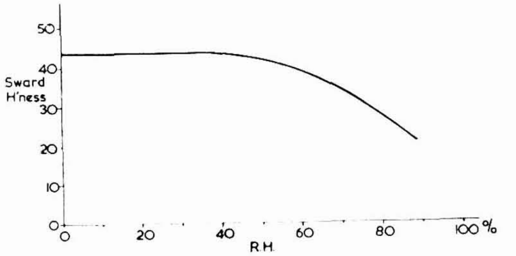

Fig. 3.

Polyvinyl acetate was chosen as the polymer likely to be most affected by humidity, and Fig. 3 illustrates the results which were obtained at 25°C. This shows a marked softening of the polymer under conditions more humid than 40 per cent RH, but a negligible effect over the range 10-30 per cent RH. It was, therefore, concluded that hardness values of vinyl acetate copolymers would be constant at humidity levels in this range.

Comparisons of vinyl acetate copolymers

The polymers studied in this exercise were all produced under identical polymerisation conditions using the same emulsion surfactant system. The effect of extraneous factors on a comparison of the various copolymers was therefore minimised, it being appreciated that variations in composition of the emulsifiers and particle size of the polymer would have marked effects on the MFT of a dispersion.

1. MFT related to per cent acrylate ester

Fig. 4 shows the effect of a number of acrylate ester comonomers on the MFT of a vinyl acetate copolymer. Alphanol 79 acrylate and Alfol 8-10 acrylate are development products derived from narrow cut alcohol mixtures. Alfol 8-10 is a mixture containing approximately 43 per cent n-octyl alcohol and 55 per cent n-decyl alcohol, whereas Alphanol 79 is a mixture of normal, cyclic, and branch chained alcohols containing 7-9 carbon atoms. Higher members of the homologous series can be seen to have a greater effect on the MFT, but 2-ethylhexyl acrylate and Alphanol 79 acrylate are less effective than n-heptyl acrylate by virtue of their branched chains.

Fig. 5 shows the greater effect on MFT of an external plasticiser, such as dibutyl phthalate, than of the copolymerised butyl acrylate or 2-ethylhexyl acrylate. The fourth curve on this graph is that of " Veova 911." This monomer is the vinyl ester of a synthetic tertiary acid containing 9-11 carbon atoms. Chain branching makes it less effective than butyl acrylate.

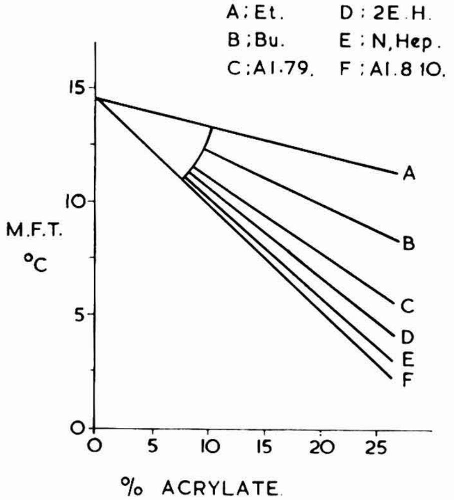

Fig. 4.

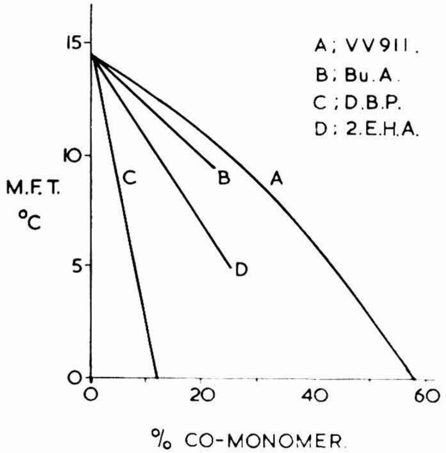

Fig. 5.

2. Hardness related to per cent acrylate ester

Figs. 6 and 7 show a similar comparison of the hardness of the copolymer films measured at 25°C. Hardness is related to comonomer structure in the same way as the MFT. The difference between adjacent curves from B to F in Fig. 6 is barely significant, but it can be seen that of the commercially available acrylate esters, 2-ethylhexyl acrylate is the most efficient weight for weight. On the other hand, price differences between 2-ethylhexyl acrylate and butyl acrylate make the latter an equally attractive candidate. Use of a higher percentage of acrylate monomer will also contribute marginal improvements in other properties, such as hydrolytic stability.

Fig. 7 demonstrates the greater plasticising effect of butyl acrylate and 2-ethylhexyl acrylate compared with the " Versatic " ester, and again highlights the difference between the plasticising comonomers and an external plasticiser such as DBP.

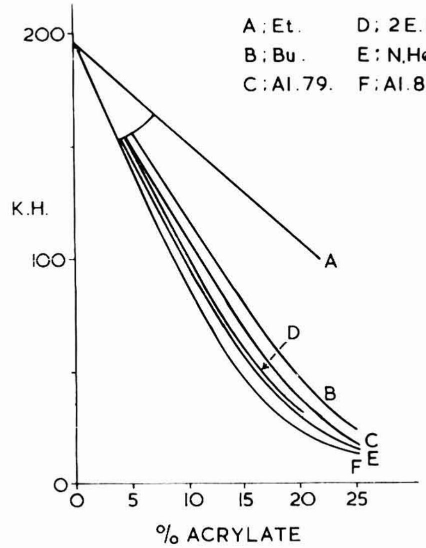

Fig. 6.

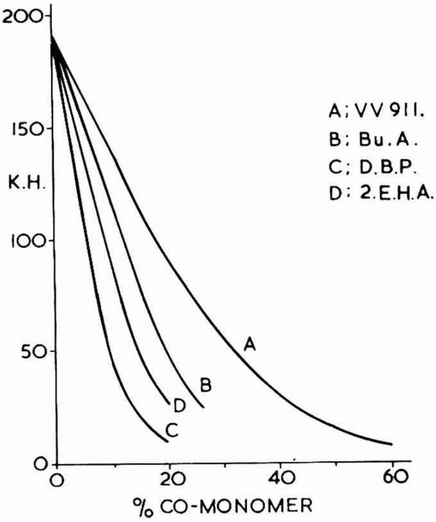

Fig. 7.

3. The addition of plasticisers and coalescing solvents to a copolymer

The marked effect of DBP on the MFT of a PVA homopolymer was demonstrated in Fig. 5. This gives an indication of why additions of coalescing solvents are so effective in improving the low temperature coalescence of emulsion paints.

The efficiencies of 12 solvents were compared in tests performed on a typical copolymer containing 19 per cent butyl acrylate. Two levels of solvent addition were examined, namely 3 per cent and 6 per cent by weight on the polymer. The range of solvents comprised :

Benzyl alcohol
Xylol
Ethylene glycol
Hexylene glycol
Dibutyl phthalate (DBP)
Dibutyl glycol phthalate (DBGP)

Cellosolve
Carbitol
Butyl Carbitol acetate (BCA)
Di isopropyl succinate (Bisol DPS)
Dalpad A (manufactured by Dow Chem. Co.)
Pycal 94 (manufactured by Atlas Chemical Industries)

Fig. 8 shows the effect of these additions on the MFT of the copolymer, and Fig. 9 refers to their effect on hardness measured at 25°C. The first significant fact which is observed is the ineffectiveness of ethylene glycol as a coalescing solvent. Its presence to improve freeze-thaw resistance contributes nothing to ease of coalescence. Butyl Carbitol acetate is clearly the most effective solvent and its popularity is justified. On the other hand, if a decrease in hardness is also sought, Dalpad A might prove to be a more attractive prospect. As will be seen from Figs. 8 and 9, there is no direct correlation between the effects on MFT and hardness. In some cases it is believed that this may be explained by

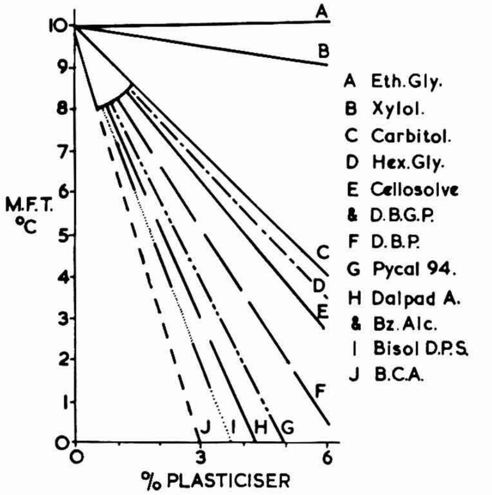

Fig. 8.

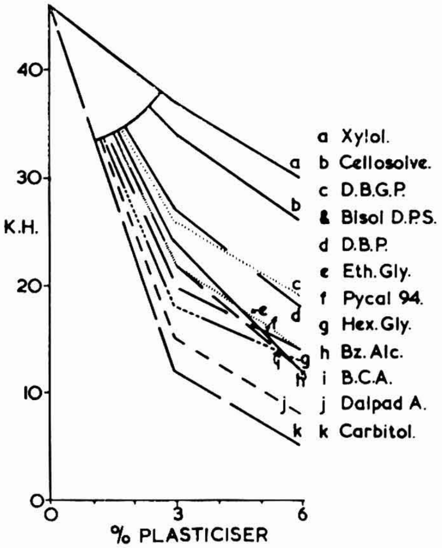

Fig. 9.

the miscibility of the solvent with water. Thus, in the case of ethylene glycol, failure to depress the MFT may be due to non-migration of the glycol into the polymer while the aqueous phase is present. Once this is removed the solvent is absorbed into the polymer and acts as a plasticiser. The effect is obviously controlled by the basic plasticising efficiency of the solvent, as well as its partition coefficient between the polymer and aqueous phase. Xylol, for example, is clearly a poor plasticiser for PVA copolymers.

4. The effect of temperature on the hardness of a copolymer

In order to compare the relative efficiencies of the plasticisers at low temperatures with the results obtained at 25°C, the hardness of the samples containing 6 per cent plasticiser was measured again at 5°C. Reference to Fig. 10 shows that there is surprisingly little change in their relative efficiencies at the two temperatures. An exception is the case of xylol and Cellosolve where the curves actually cross.

A similar study of the effect of temperature on hardness was made with a selection of copolymers. Three samples of a PVA homopolymer plasticised with different amounts of DBP were included in the series as standards for comparison.

Fig. 11 records the results obtained. The most interesting point which emerged from this study was the more favourable gradient of hardness versus temperature possessed by the copolymers compared to the external plasticiser, i.e. the acrylate copolymers harden less than the externally plasticised homopolymer as the temperature falls. This trend is contrary to what one would expect from the MFT's. For example, Fig. 5 shows that, in the type of emulsion used for this investigation, 20 per cent butyl acrylate is required to achieve an MFT of 10°C. From Fig. 11 one would infer that the 20 per cent butyl acrylate copolymer would have a similar hardness at 10°C to that of the homopolymer plasticised with 15 per cent dibutyl phthalate. However, it is known that the MFT of the latter is less than 0°C. There is, therefore, no direct correlation between the two properties.

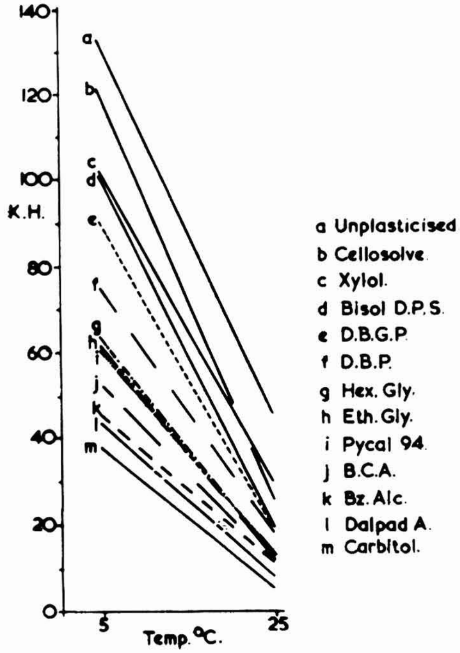

Fig. 10

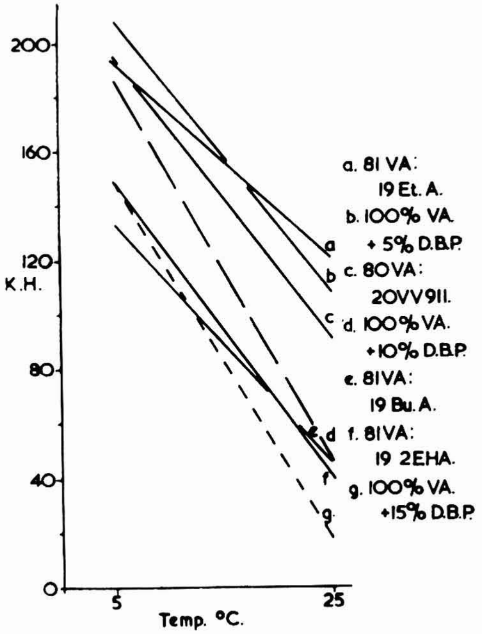

Fig. 11

The difference between the hardening of copolymers and the hardening of the externally plasticised homopolymer with fall of temperature is contrary to expectations. However, it must be remembered that measurements made with the Koenig pendulum depend, to some extent, on the tackiness of the polymer. This naturally complicates the interpretation of the results, and the authors feel that the subject requires further investigation before any firm conclusions can be drawn. If the results are a genuine reflection of changes in flexibility of the polymer films, they could have an important bearing on the choice of medium for low temperature performance.

5. Additional data on the efficiency of butyl Carbitol acetate

Since butyl Carbitol acetate was the most effective coalescing solvent evaluated in the programme, it was chosen as the agent used in a brief comparison of two commercial monomers. These were butyl acrylate, which enjoys wide popularity as a comonomer for vinyl acetate, and " Veova 911," which is one of the newer monomers attracting attention. Fig. 12 presents data on MFT and Fig. 13 refers to the hardness values obtained. The main fact that emerges from these data is that 20 per cent butyl acrylate is roughly equivalent to 30 per cent " Veova 911."

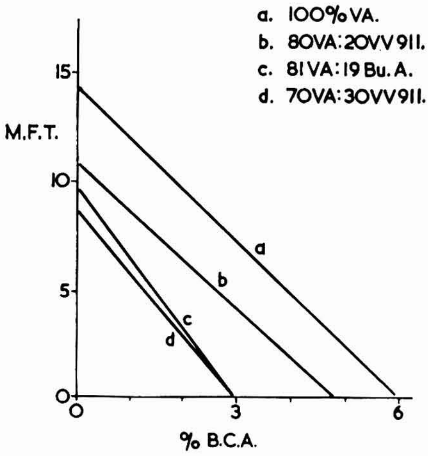

Fig. 12

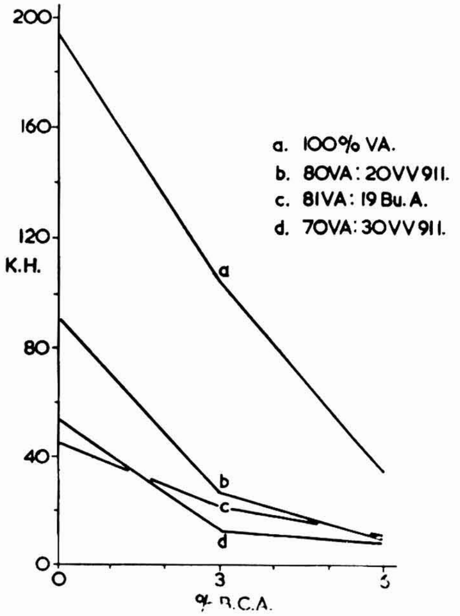

Fig. 13

Conclusion

It must be stressed that values quoted in this paper for the MFT's of various copolymers are specific to the emulsion formula which was used, and cannot be compared with those obtained by other workers. Nevertheless, they provide a valid comparison of the copolymers and coalescing solvents described. For this reason alone, the data should interest all users of polymer dispersions, whether they be paint manufacturers or not.

The hardness values also provide a useful means of comparing the various copolymers, and assessing their economic merits. Reference has been made to the comparison of 2-ethylhexyl acrylate with butyl acrylate. Hardness measurements made at 25°C indicate that equivalent results can be obtained at the same cost with the two co-monomers, whereas examination of hardness at 5°C favours butyl acrylate. However, if consideration of MFT's is included in the assessment, use of 2-ethylhexyl acrylate might well be justified because it would require less coalescing solvent than butyl acrylate.

The relative emphasis placed on the two properties will obviously depend on the application under consideration. MFT's will be of prime importance when dispersions are intended for use under varying climatic conditions, as is the case with emulsion paints. When the product is intended for factory applications at temperatures exceeding 15°C, its MFT will not be significant.

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Acknowledgment

The authors wish to express their thanks to the directors of British Resin Products Limited for permission to present the data given in this paper.

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Discussion at Manchester Symposium

MR. RANKIN asked why film hardness had been determined by the Koenig pendulum in preference to the Sward rocker.

MR. LLEWELLYN replied that, provided surface defects were absent from the film, either test was satisfactory. However, when minor imperfections were present, these could be more easily avoided with the Koenig pendulum because this rocked on one point, whereas the Sward rocker traversed a path on the surface.

MR. RANKIN asked if the ultimate film hardness had been determined, i.e. the hardness when the coalescing solvent had been removed.

MR. LLEWELLYN replied that no attempt had been made to do this ; testing was carried out 24 hours after film preparation.

MR. SECKERT pointed out that low relative humidity conditions were used for measuring minimum film forming temperature, but that it was known that MFT was dependent on relative humidity. He asked what MFT results were obtained at normal humidity, e.g. 65 per cent or higher.

MR. LLEWELLYN agreed that MFT was affected by humidity, but stated that the particular apparatus used operated at low humidity only. The film was dried in still air, and silica gel was placed in the cabinet in order to obtain a reasonable rate of drying.

MR. OOSTERHOF said that good coalescence required a soft polymer, resistance to dirt pick-up, a hard one, and doubted whether film hardness was an adequate means of defining polymer properties.

MR. LLEWELLYN pointed out the difficulty in choosing a parameter by which copolymers could be compared and claimed that film hardness was a valid property to measure when comparing a series of related components, such as esters of acrylic acid. There could be some criticism of the use of film hardness if it were used to compare dissimilar components.

MR. MILES asked if there was information relating the age of the emulsion with MFT when using external plasticisers.

MR. LLEWELLYN replied that no information was available relating to the rate of migration of external plasticisers. The measurements were made a few days after preparation of the samples and the same values were obtained when the MFT was re-determined after several months' storage.

MR. FLETCHER doubted the validity of correlating MFT with film hardness since each measurement was made under different temperature conditions and large differences were likely to exist between the physical state of the films on the block at MFT and when cast at room temperature.

MR. LLEWELLYN replied that the figures showed variations in the hardness of films formed at temperatures higher than the MFT, and there was no inference that the hardness values obtained at temperatures below the MFT were related to films dried at such temperatures. He agreed that a film cast at MFT would not be integrated sufficiently to give its full hardness or flexibility.

Mr. Woodbridge pointed out that conditions for determining MFT were far removed from emulsion paint application conditions ; a non-porous substrate and drying times of one hour were used. He suggested that coalescence problems were far greater when films dried quickly, e.g. in less than five minutes, and that the degree of water solubility of the coalescing solvent would determine how much remained in the film after a proportion had been absorbed by the substrate along with water. Because of these differences he had grave doubts on the validity of the MFT method in terms of emulsion paint performance.

Mr. Llewellyn agreed with these comments to a large degree, but pointed out that a standardised substrate capable of attaining the requisite temperature gradient must be used. He recommended that Mr. Woodbridge's comments should be considered when the data presented in the paper was actually applied to emulsion paint problems.

Mr. Walter commented that, in his view, such tests should be used as an initial sorting process, the results from which should be confirmed by practical testing.

Mr. Llewellyn agreed, saying that the tests described could be used to place coalescing solvents and plasticisers in order of efficiency with relation to a given polymer.

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The role of surfactants in emulsion polymerisation and emulsion paints*

By C. Bondy

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Summary

The behaviour of surfactants in aqueous solutions is described with particular reference to oriented adsorption and micelle formation. Monomer solubilisation in surfactant micelles and its significance for emulsion polymerisation processes is described. The influence of surfactants on the stability of polymer dispersions and emulsion paints is examined, and the importance of hydrophilic-lipophilic balances is underlined. Attention is drawn to the effects which may result from the interaction of surfactants with colloids, pigments and other paint ingredients.

Le rôle de surfactifs en polymérisation dans la phase discontinue et en peintures-émulsions

Résumé

On décrit le comportement de surfactifs en solution aqueuse par rapport particulier à l'adsorption orientée et à la formation de micelles. Egalement on décrit la solubilisation du monomère dans les micelles de surfactif et son importance en ce qui concerne les procédés de polymérisation dans la phase discontinue. L'influence exercée par surfactifs sur la stabilité de dispersions polymères et de peintures-émulsions est considérée et l'on souligne l'importance des équilibres hydrophiliques/lipophiliques. On fait remarquer les effets qui peuvent se produire par l'entr'action de surfactifs, colloïdes, pigments, et autres composants de peinture.

Die Rolle oberflächenaktiver Mittel in der Emulsionspolymerisation und in Dispersionsfarben

Zusammenfassung

Das Verhalten oberflächenaktiver Mittel in wässrigen Lösungen wird mit besonderer Berücksichtigung orientierter Adsorption und Mizellenbildung besprochen. Es wird die Solubilisation von monomeren in oberflächenaktiven Mizellen und ihre Wichtigkeit für die Vorgänge bei der Emulsions-polymerisation dargelegt. Der Einfluss oberflächenaktiver Agenzien auf die Beständigkeit polymerer Dispersionen und von Dispersionsfarben wird geprüft, und die Bedeutung des hydrophilen-lipophilen Gleichgewichts betont. Auf die Folgen, die auf Reaktionen zwischen oberflächenaktiven Agenzien und Kolloiden, Pigmenten und anderen Bestandteilen des Anstrichmittels beruhen könnten, wird hingewiesen.

Роль поверхностно-активных веществ в полимеризационно-змульсионных и змульсионных красках

Резюме

Описывается поведение поверхностно-активных веществ в водяных растворах, в частности их ориентированной адсорбции и формации мицелл. Также описывается растворимость мономеров в поверхностно-активных мицеллах и ее значение в полимеризационно-эмульсионных процессах. Исследуется влияние поверхностно активных веществ на устойчивость полимерных дисперсий и эмульсионных красок и подчеркивается важность присутствия гидрофильно-липофильных равновесий. Привлекается внимание на возможные эффекты взаимодействия поверхностно-активных веществ с коддоидами, грунтовыми красками и другими компонентами красок.

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*Presented to the Manchester Section Symposium held on 19 April 1966.

I. Introduction

In this brief discussion of the role played by surfactants in the preparation of polymer emulsions and the performance of emulsion paints, it is not intended to do more than to pin-point the most salient features of a very complex subject. Some over-simplifications are, therefore, unavoidable and the reader is asked for his indulgence in advance. Attention will be focused chiefly on three topics: the effect of surfactants on the polymerisation and copolymerisation of more or less water insoluble monomers in an aqueous medium ; the stabilisation and size control of polymer particles ; the hydrophilic—lipophilic balance of emulsifiers and its effect on emulsion polymerisation and emulsion paint systems.

II. The nature and behaviour of surfactants :

(*a*) *Surface activity and chemical make-up of surfactants :*

Surfactants, by definition, are substances which lower the surface tension of liquids in which they are dissolved or the interfacial tension between two or more mutually immiscible phases. Energy considerations demand that interfacial tension depressants must be enriched or adsorbed at the phase boundary. A quantitative expression for the amount of a surface active material adsorbed at an interface was first derived by Gibbs[1] for idealised conditions :

$$a = -\frac{c}{RT}\left(\frac{\delta_\gamma}{\delta_c}\right) T$$

a = quantity adsorbed (moles/unit area)
c = surfactant concentration
γ = interfacial tension
T = absolute temperature
R = Gas constant

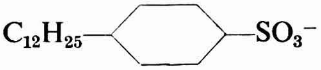
It has long been recognised that the most effective surface tension depressants contain highly water-attracting (hydrophilic) and highly water-repellent (hydrophobic) groups, joined together in the same molecule. They have, therefore, been called "amphiphilic " or " amphipathic "[2], i.e. substances with an affinity for two different phases.

The most important hydrophilic (polar) groups found in surfactants are, for anionics : ionised sulphonate, sulphate, phosphate and carboxyl groups ; for non-ionics : polyoxyethylene chains and polyols and, for cationics : ionised tertiary or quaternary ammonium groups. The somewhat rarer amphoteric surfactants contain both anionic and cationic hydrophilic groups. The hydrophobic portion of the surfactant molecule usually consists of hydrocarbon radicals with more than eight carbon atoms, i.e. alkyl-aryl or long chain alkyl. Since the hydrophobic hydrocarbon groups have considerable affinity for oils and fats they have also been termed lipophilic or fat-loving. Long polyoxypropylene chains, though less hydrophobic than hydrocarbons, possess, nevertheless, sufficient water repellency to confer strong surface activity to compounds wherein they are linked to hydrophilic groupings such as polyoxyethylene chains. Thus a very versatile range of surfactants consists of block copolymers of ethylene oxide and propylene oxide in which the ratios and the molecular weights of the two different types of polyether chains are varied over a wide range. The following examples illustrate the chemical make-up found in typical commercial surfactants :

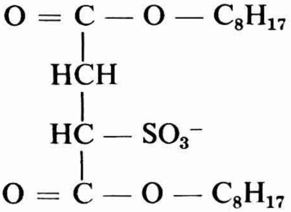
Anionics

$C_{17}H_{35}COO^-$
Stearate soap

$C_{12}H_{25}{-}O{-}SO_3^-$
Dodecyl sulphate

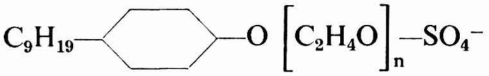


Dodecylbenzene sulphonate



$$\begin{array}{l} O = C - O - C_8H_{17} \\ \quad\;\; | \\ \quad HCH \\ \quad\;\; | \\ \quad HC - SO_3^- \\ \quad\;\; | \\ O = C - O - C_8H_{17} \end{array}$$

Dioctyl sulphosuccinate



Nonylphenol polyether sulphate

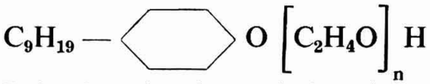
$C_{12}H_{25}{-}O\left[C_2H_4O\right]_n{-}PO_4^{--}$
Dodecyl polyether phosphate

Nonionics

$C_{17}H_{33}\,COO\left[C_2H_4O\right]_n H$
Polyethoxylated oleic acid

$C_{17}H_{35}\,CONH\left[C_2H_4O\right]_n H$
Polyethoxylated stearamide

$C_nH_{2n+1}{-}O\left[C_2H_4O\right]_n H$
Polyethoxylated alkanol



Polyethoxylated nonyl phenol

$$OH\left[C_2H_4O\right]_l - \left[C_3H_6O\right]_m - \left[C_2H_4O\right]_n H$$

Polyethoxylated polypropylene glycol
(Pluronic)

$C_3H_7O_3 - CO\,C_{11}H_{23}$
Glyceryl monolaurate

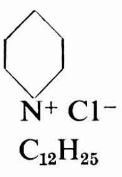
Cationics

$\left[(CH_3)_3N{-}C_{18}H_{37}\right]^+Br^-$

Cetyltrimethyl ammonium bromide
(Cetrimide)

$\left[(CH_3)_3\,N{-}CH_2{-}COOC_{18}H_{37}\right]^+Cl^-$

Trimethyl carboxymethylcetyl
ammonium chloride



Lauryl pyridinium chloride

(*b*) *Orientated adsorption:*

The behaviour of amphiphilic compounds in either aqueous or non-aqueous media is determined by the relative effectiveness of their hydrophilic and hydrophobic groups. In aqueous media the hydrophilic groups are strongly associated with the water molecules whilst the hydrophobic groups are repelled and tend to concentrate at the air-water interface. In the presence of both aqueous and oily phases the affinities of both groups can be satisfied by concentration of the surfactant molecules at the oil-water interface. In either case the phase boundary will be enriched in surfactant in accordance with Gibbs' equation and the surfactant molecules will be orientated[3] in such a way that the hydrophobic groups are associated with the non-aqueous phase while the hydrophilic groups are firmly anchored in the water layer.

(*c*) *Micelle formation*

If the interfacial area is small, it can only accommodate a small number of molecules. When, as is usual, many more surfactant molecules than this are present, the majority cannot escape from the bulk liquid to the interface and the affinities of the hydrophilic and lipophilic groups must be satisfied by other means if thermodynamic stability is to be achieved. This again occurs by a process of orientation ; in an aqueous medium the hydrophobic groups turn towards and associate with one another, forming in effect their own oil phase, surrounded by the hydrophilic groups turned outwards and anchored in the water. This type of internal association and orientation has been termed micelle formation. Micelles may assume many different shapes. There is experimental evidence for the existence of both spherical and lamellar shapes[4] as illustrated in cross section in Fig. 1.

In both types the dimensions are dictated by the spatial requirements of the amphipathic molecules. As a rough approximation, it may be assumed that the lipophilic portion has a diameter (spherical micelle) or thickness (lamellar micelle) comparable in size to just over twice the length of the hydrocarbon tail. Each micelle may contain from about 50 to about 400 molecules depending on the nature of the surfactant.

The " escape mechanism " of micelle formation only becomes operative above a certain minimum surfactant concentration. This concentration has been termed the critical micelle concentration (CMC). CMCs vary from about 5×10^{-2} moles per litre for the most hydrophilic to about 5×10^{-4} moles per litre for the most hydrophobic types of surfactant. They are influenced by electrolytes, especially in the case of ionic surfactants, and also by other polar/non-polar chemical compounds such as alcohols, amides and, of course, other surfactants.

(*d*) *Solubilisation :*

The most important consequence of micelle formation in the process of emulsion polymerisation is the solubilisation[5] of organic compounds in aqueous media. Since the association of lipophilic groups inside a micelle leads to a formation of centres of attraction for organic compounds it is possible to dissolve appreciably higher portions of sparingly water-soluble monomers in micellar solutions than in water alone. Monomers which are essentially non-polar in

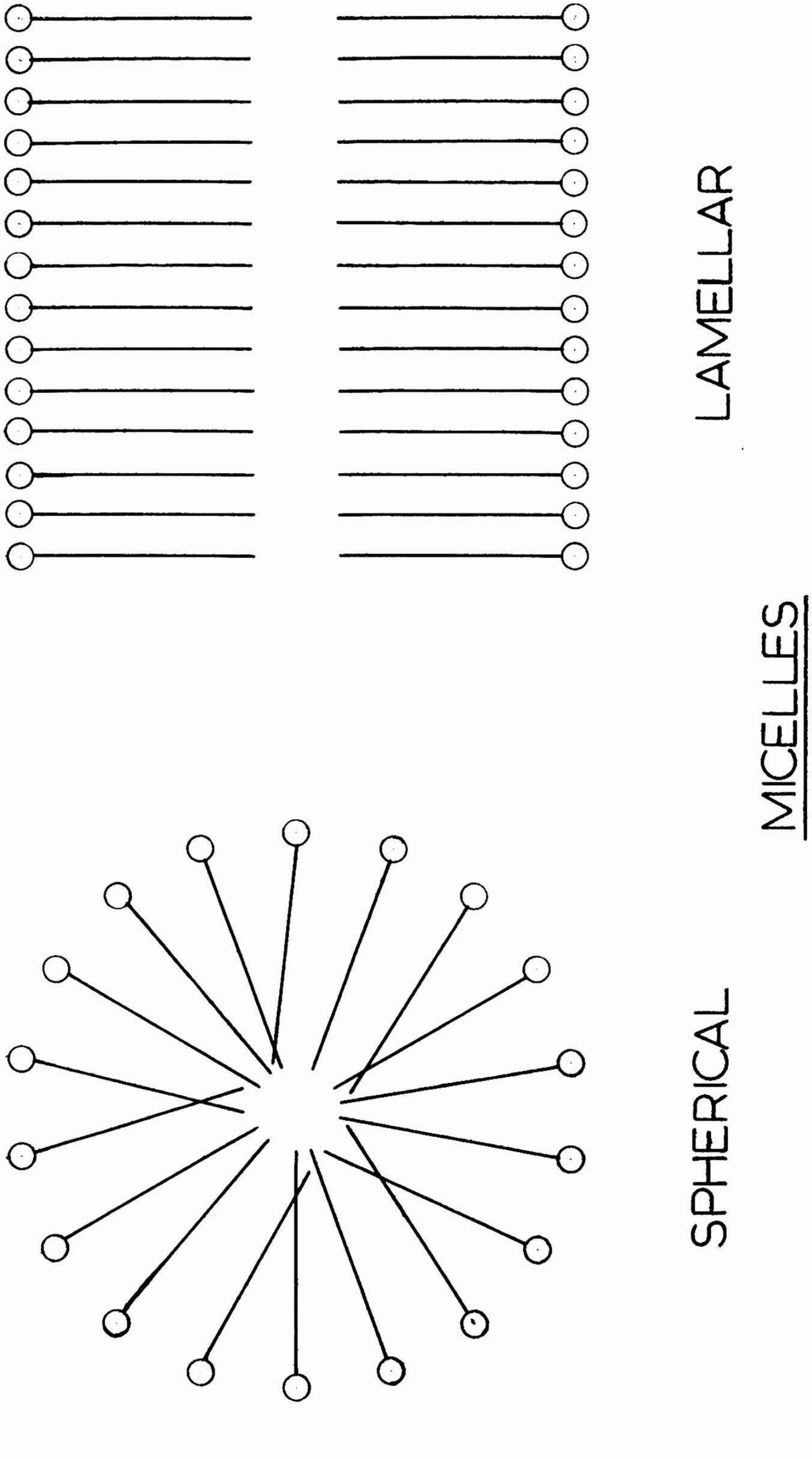


Fig. 1

character may be expected to dissolve only inside the *hydrocarbon* portion of the micelle. Their molecular dimensions must, therefore, be such that they can be accommodated in the centre of the micelle. Large molecules consequently require surfactants with longer lipophilic chains than do small molecules.

Compounds with polar groups can at least partially be accommodated in the water phase or at the micelle surface so that the requirements for the micelle dimensions are less critical. Table 1 illustrates the effect of lipophilic chain length and type of surfactant on the solubilisation of semi-polar as well as non-polar compounds[6].

Table 1

	Moles solubilised per mole of surfactant							
Surfactant	n-Hexane	n-Heptane	n-Octane	Oleic acid	Dodecanol	Styrene at 50°C	n-Heptyl mercaptan	Dimethyl-amino Azo-benzene at 50°C
(*a*) *Alkali metal soaps*								
Laurate	0.18	0.14	0.08	0.02	0.03	—	0.13	0.011
Myristate	—	—	—	—	—	—	0.30	0.018
Palmitate	—	0.31	—	—	—	1.4	—	0.026
Stearate	0.46	—	0.18	0.05	0.13	—	—	0.035
Oleate	—	—	—	—	—	—	—	0.025
(*b*) *Sulphates*								
Decyl	—	0.17	—	—	—	—	—	—
Undecyl	—	0.25	—	—	—	—	—	—
Dodecyl	—	0.34	—	—	—	—	0.31	0.025
(*c*) *Quaternary ammonium salts*								
Dodecylamine hydrochloride ..	—	—	0.29	—	—	0.95	—	—

(*e*) *The hydrophilic-lipophilic balance* (*HLB*) *of surfactants*

We have already seen that surfactants are made up of—usually localised—hydrophilic and lipophilic (hydrophobic) groupings. It has long been recognised that in many applications such as emulsion stabilisation, detergency, foaming, surface wetting, etc., an appropriate balance between the hydrophilic and lipophilic functions must be sought for optimum performance. More recently this has been established in a more quantitative way by research workers of the Atlas Powder Company, who introduced the concept of HLB to the world at large[7].

In certain non-ionic surfactants, where hydrocarbon radicals are attached by ester, ether or amide linkages to polyethylene glycol chains of varying molecular weight, approximate HLB values can be calculated by the following expression :

$$\text{HLB} = \frac{\text{Molecular weight of hydrophilic portion}}{\text{Molecular weight of surfactant}} \times 20$$

The hydrophilic portion is essentially the polyether chain, but other polar segments of the molecule, e.g. polyol configurations, should be included. The factor 20 was chosen arbitrarily to define the hydrophilicity of polyether and related water attracting groupings. For the computation of HLBs in ionogenic surfactants, sulphonate, sulphate, phosphate, carboxyl or quaternary ammonium groups would have to be assigned different—much higher—

hydrophile factors. Special factors will also have to be established for different lipophilic groupings such as fluorinated hydrocarbon, polyoxypropylene, etc. In practice it is easier to assign HLB numbers to surfactants of widely differing types by comparing their effects on the mutual spreading properties and interfacial tensions between water and organic liquids[8]. The value of the HLB concept lies chiefly in its application to the selection of appropriately balanced emulsifiers or emulsifier blends for the formation and stabilisation of disperse systems.

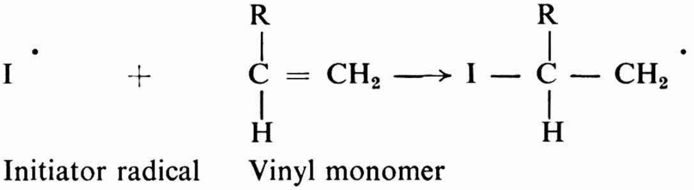
III. Surfactants in emulsion polymerisation

(*a*) *The mechanism*

The role played by surfactants in emulsion polymerisation can best be demonstrated in a simple recipe involving only water, surfactant, monomer(s) and polymerisation initiator. When a sparingly water-soluble monomer is stirred into an aqueous surfactant solution it will be broken up into droplets of varying size and give a more or less stable emulsion depending on the choice and quantity of surfactant present. If the surfactant concentration exceeds the CMC, some of the monomer will be solubilised in micelles. On the addition of a polymerisation initiator—and this almost invariably means a substance capable of producing free radicals—polymerisation will begin as soon as the initiator has been activated either thermally or chemically to yield free radicals.

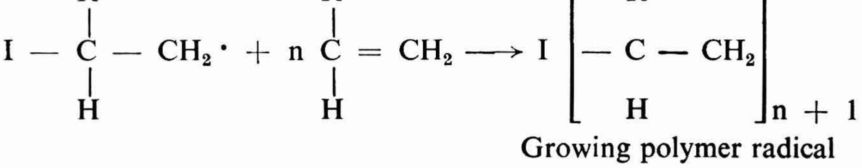
Originally it was presumed that polymerisation only occurred in the droplets of emulsified monomer. It was only after Fikentscher[9] had observed rapid polymer formation in saturated aqueous solutions of hydrocarbon monomers that attention was focused on the water phase as a polymerisation site. Harkins and his collaborators were the first to recognise clearly the significance of solubilising micelles as loci for the fast initial polymerisation of water insoluble monomers[10]. The mechanism postulated by Harkins for the emulsion polymerisation and essentially confirmed by a great volume of subsequent investigations may be summarised as follows.

Radicals derived from the—usually water soluble—polymerisation initiator enter the monomer-saturated micelles where they find a sufficient number of solubilised molecules to start a rapid chain reaction.



$$\mathrm{I}^{\bullet} + \underset{\mathrm{H}}{\overset{\mathrm{R}}{\mathrm{C}}} = \mathrm{CH_2} \longrightarrow \mathrm{I} - \underset{\mathrm{H}}{\overset{\mathrm{R}}{\mathrm{C}}} - \mathrm{CH_2}^{\bullet}$$

Initiator radical Vinyl monomer



$$\mathrm{I} - \underset{\mathrm{H}}{\overset{\mathrm{R}}{\mathrm{C}}} - \mathrm{CH_2}^{\bullet} + \mathrm{n}\ \underset{\mathrm{H}}{\overset{\mathrm{R}}{\mathrm{C}}} = \mathrm{CH_2} \longrightarrow \mathrm{I}\left[- \underset{\mathrm{H}}{\overset{\mathrm{R}}{\mathrm{C}}} - \mathrm{CH_2} \right]^{\bullet}_{\mathrm{n}+1}$$

Growing polymer radical

Each polymer radical first exhausts the monomer contained in the micelle it is growing in and then captures additional supplies from 50 or more other micelles before the chain reaction is terminated. Some of the depleted micelles then break up and the released emulsifier molecules are adsorbed at the surface of the newly-formed primary polymer particles. The remainder are replenished by diffusion from the emulsified monomer droplets which act essentially as reservoirs.

The formation of fresh polymer particles continues until all the emulsifier originally contained in the micelles is adsorbed at the large polymer/water interface and the surfactant concentration has dropped below the CMC. A new and different situation is thus created for the polymerisation which would come to a halt if it could only proceed inside surfactant micelles. The growing polymer particle is, however, still very similar in general characteristics to a true (spherical) micelle. The chief difference is the composition and size of its lipophilic centre. On the outside there is still the layer of oriented surfactant molecules with their hydrophilic groups pointed towards the external water phase while their lipophilic groups are now associated, not with each other, but with the dispersed internal polymer phase. The conditions for monomer solubilisation are in fact greatly improved. Quite apart from the fact that the polymer particles have a far greater affinity for monomer molecules than the micelles ever had, there is now a very considerable interfacial area available where interface solubilisation—akin to intramicellar solubilisation—can take place. It is this interface solubility of monomers with which one is chiefly concerned in the second phase of polymerisation, i.e. after the disappearance of micelles. The loci of polymerisation have then shifted from the micelles to the polymer particles to which all the emulsified monomer is gradually transferred.

It is instructive to examine the implications of this statement. If it is true that polymerisation can now only proceed inside or, more probably, at the surface of pre-formed polymer/monomer particles then *their number must henceforth remain unchanged* and only their size can increase with increasing monomer conversion. Now this is just what happens in practice provided subsequent additions do not raise the surfactant concentration above the CMC and provided the adsorbed layer can impart sufficient stability to the polymer dispersion to prevent the agglomeration of seed particles. It can, therefore, be stated that in the emulsion polymerisation of sparingly water soluble monomers the particle number, and hence the particle size, of surfactant stabilised dispersions can be predetermined at an early stage, namely at the time when the surfactant micelles disappear. At the initial surfactant concentrations normally employed in the preparation of approximately 50 per cent polymer dispersion this occurs usually when between 10 and 20 per cent of the total monomer is converted to polymer.

Now consider the case of the polymerisation of monomers with an appeciable water solubility and their copolymerisation with less soluble co-monomers. Monomers such as vinyl acetate or methyl acrylate have sufficient water solubility to permit their rapid polymerisation in the water phase even in the absence or after the disappearance of surfactant micelles. New polymer particles can be formed as long as the monomer concentration in the water phase remains high enough. In most cases, there is strong monomer/polymer affinity so that more and more monomer will be extracted from the water phase. As polymer concentrations increase, polymerisation in the water phase will finally cease and with it the formation of new particles. Henceforth, conversion will proceed at the surface of the polymer/monomer particles in much the same way as in the case of water-insoluble monomers after the disappearance of the surfactant micelle. However, before this state of affairs can be reached a heterodisperse emulsion will have been formed because new particles will have continued to appear long after the first-comers had started to grow.

The copolymerisation of a relatively water-soluble monomer like vinyl acetate with a relatively water-insoluble monomer like 2-ethylhexyl acrylate presents special problems. Here again the micelle-forming surfactant plays a vital role. While micellar solubilisation may increase the water solubility of sparingly soluble substances by a factor 100 or more, its effect on already fairly soluble materials is relatively insignificant. This means in fact that surfactants help to even out differences in solubility and thus provide equally favourable polymerisation conditions for monomers of widely different solubility. After the disappearance of the micelles, copolymerisation can proceed in the surfactant layer adsorbed on the polymer/monomer particles.

Owing to the relatively high water solubility of vinyl acetate, it is possible to make homopolymer emulsions with little or no surfactant, while copolymerisation with a much less soluble co-monomer requires the presence of micelle-forming materials, notably surfactants. These, in the absence of suitable anti-foams, tend to aggravate foaming tendencies. It is, therefore, perhaps not surprising that paint makers have at times commented that foam control with copolymer emulsions was more difficult than with the "old homopolymers."

(b) Particle size control :

It has already been pointed out that, in the case of sparingly water-soluble monomers, the number of particles may be kept constant after the " seed stage," i.e. after the disappearance of the original micelles. Two conditions must be met to achieve this : (1) sufficient stability must be maintained to prevent the agglomeration of primary particles, and (2) surfactant concentrations must be maintained below the CMC during subsequent operations.

Maintenance of stability may not always be easy without the addition of, extra surfactant during the progress of the polymerisation. However, as long as the concentration is maintained below the CMC no change in particle number need occur. The risk of agglomeration may be further reduced by keeping free monomer concentrations in the polymerisation charge at relatively low levels, e.g. by incremental addition. The particle size of the seed becomes, therefore, of primary importance. Control may be exercised by a number of means : variation of initial monomer concentration, variation of surfactant concentration choice of surfactant, especially with regard to its HLB, and variation of initiator concentration.

The effect of surfactant and initiator concentration on particle size was studied by Smith and Ewart[11], whose conclusions may be summarised in the following equation :

$$N = K \cdot I^{2/5} \cdot S^{3/5}$$

or, simplified roughly in accordance with experiment :

$$N = K \sqrt{I \cdot S}$$

Since the total volume V of polymer particles can be expressed as :

$$V = N \cdot \tfrac{4}{3} \pi r^3$$

it follows that, for constant polymer volume

$$r = \frac{K_1}{I^{1/6} \cdot S^{1/6}}$$

where N = number of polymer particles
I = initiator concentration during the seed stage
S = surfactant concentration during the seed stage
r = particle radius
K and K_1 are constants

A fourfold increase in initial surfactant concentration or initiator concentration should thus lead to an approximately 20 per cent reduction in particle size. This may apply in those cases where surfactant concentrations are fairly high[12] but, in practice, it is often found that the particle size decreases much more sharply with increasing emulsifier concentrations[13]. Figs. 2a and 2b illustrate the order of effect one might expect to find in actual polymerisation recipes involving typical monomer compositions. Fig. 2a refers to the polymerisation of acrylic monomers in the presence of an anionic emulsifier while, in Fig. 2, the polymerisation of styrene with an anionic-nonionic blend is described.

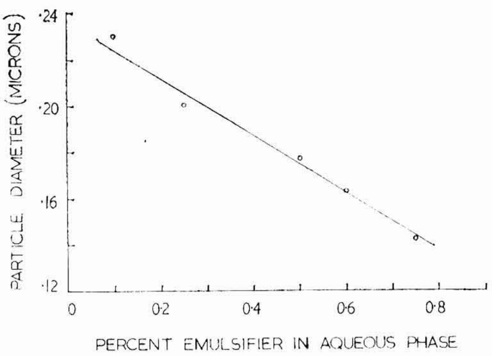


Fig. 2a.

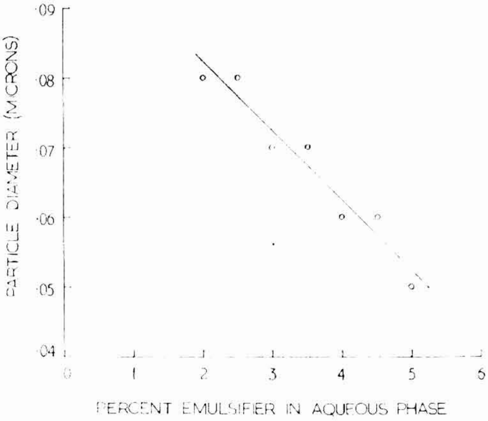
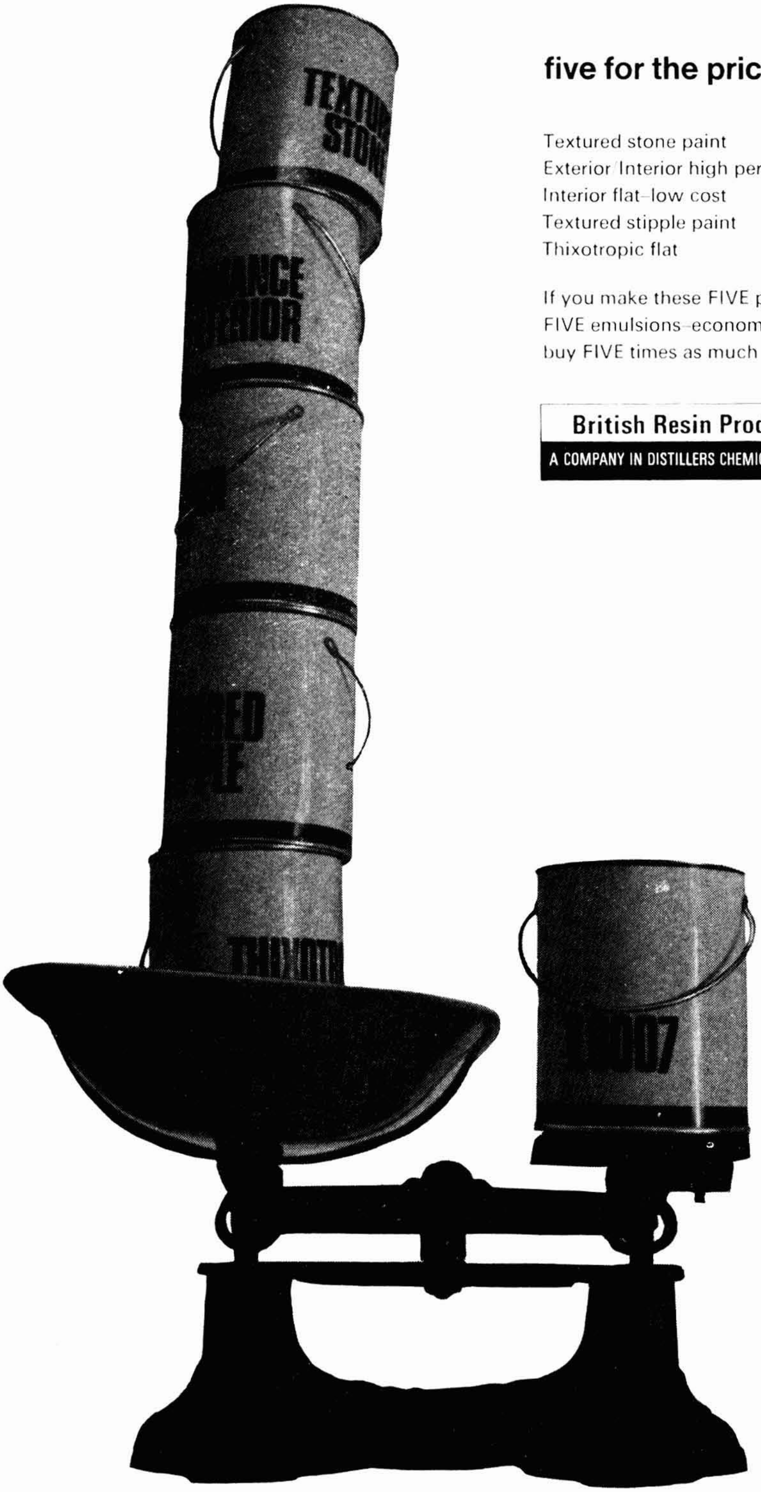


Fig. 2b.

These deviations from the original predictions give some food for thought. The most plausible explanation is to assume that the primary polymer particles postulated by, e.g. Smith and Ewart, are insufficiently stabilised to survive. They would, therefore, either before or immediately after the disappearance of micelles, tend to fuse to larger secondary seed particles with a much reduced total surface area. The fusion of polymer particles whose surface is too large



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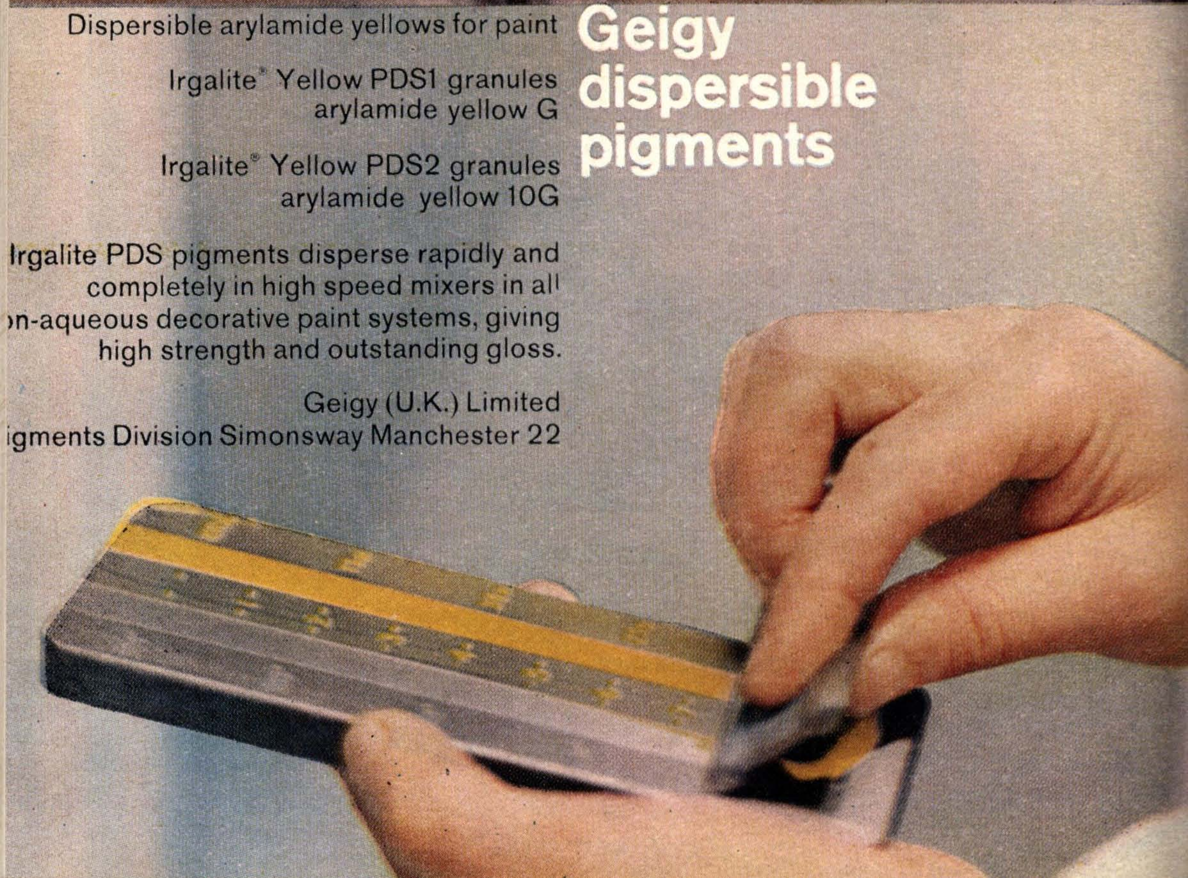

to be adequately protected by the available emulsifier is well known in other contexts and will be referred to later.

If, for any given emulsifier system, a minimum number of adsorbed molecules per unit area is necessary to afford stability, then it would follow that the total surface area surviving in the seed latex must be proportional to the amount of surfactant present.

Let V be the total volume of polymer in a seed latex containing N uniformly sized particles of radius r. Assuming the total interfacial area A to be proportional to the surfactant concentration S, we can write :

$$V = N^{\frac{4}{3}} \pi r^3 \qquad A = KS = N \,.\, 4 \pi r^2 \text{ and thus}$$

$$r = \frac{3V}{KS} \text{ which for constant polymer volume becomes } r = \frac{1}{K_1 S}$$

where K and K_1 are constants.

The important influence of particle stability on particle size is also emphasised in the work of Greth and Wilson[13] who studied the effect of HLB on polymerisation rates and particle size. Their findings reveal that, as the HLB approaches the optimum value the particle size goes through a well defined minimum rising sharply on either side. Fig. 3, reprinted from their paper refers to the polymerisation of styrene in solutions of blends of anionic and non-ionic emulsifiers.

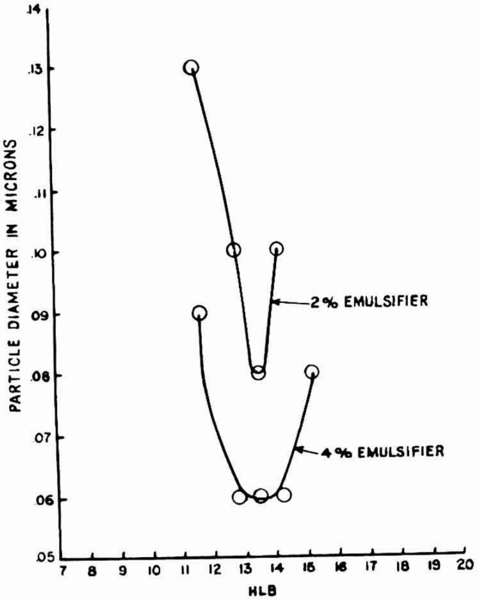

Fig. 3

The same authors report similar findings for the polymerisation of vinyl acetate, but here the picture is somewhat obscured by the conjoint use of colloid and surfactant stabilisers. Budewitz describes the use of the HLB concept for the copolymerisation of vinyl acetate with maleic and acrylic monomers)[14]. The recurrent theme is the predominant role played by surfactants in the stabilisation of the disperse phase, especially during the seed stage.

It is self-evident that the requirements for emulsion stability become increasingly more stringent the greater the surface area of the polymer particles, that is to say, the finer the emulsion is. While anionic surfactants usually give the highest micellar solubilisation and hence the fastest polymerisation rates, it may be difficult to obtain adequate emulsion stability when they are used to the exclusion of other types. One need not look too far for an explanation. The amount of highly charged molecules which can be adsorbed at the polymer water interface is of necessity restricted by the Coulomb repulsion forces exerted by the highly charged ionised groups. Non-ionic surfactants can fill the gaps left on the surface by the sparsely adsorbed anionics and thus reinforce the stabilising layer sufficiently to give the required stability.

Practical dispersions, especially vinyl acetate homo- and copolymer emulsions, are frequently stabilised with hydrophilic colloids as well as surfactants. If, as has previously been shown, even the relatively low-molecular surfactant molecules can only barely cover the enormous surface area of the fine polymer particles, how much more difficult must it be for colloids with molecular weights 100 or more times higher and used at comparable weight concentrations? Clearly, if colloid molecules are to stabilise the polymer particles they must be adsorbed at the surface and have an affinity for this surface. If the quantity of available colloid is insufficient to cover the entire surface area it would be improbable, under equilibrium conditions, for some particles to be saturated while others remain bare. There will, therefore, be a tendency for the colloid molecules to be shared evenly between all the polymer particles. This implies that water soluble polymers can " glue " large numbers of fine particles together until, after fusion of the agglomerates, the surface area is sufficiently reduced to permit saturation.

Since the originally formed particles do not survive, the final emulsion will be considerably coarsened. As the coarsening is due to a coagulation process, it is only to be expected that a wide spectrum of particle sizes will be present, and it is indeed a general observation that colloid stabilised emulsions have a much wider particle size distribution and contain, as a rule, much coarser particles than surfactant stabilised ones. Even so, the hydrophilic colloid has to occupy a fair proportion of the polymer water interface to be effective as a stabiliser and it will, therefore, be readily understood why low molecular weight colloids are preferred to high molecular weight ones. In those cases where high molecular weight colloids such as hydroxyethyl cellulose have been used successfully in the preparation of polymer emulsions, it could be demonstrated that the peroxidic polymerisation initiator had split the large molecules into many smaller fragments through oxidative breakdown.

IV. Emulsion stability

(*a*) *Surfactant stabilised emulsions*

Apart from the part played by hydrophilic centres built into the copolymer itself, the adsorbed layer of surfactant is mainly responsible for stability during the manufacture and subsequent use of the emulsions. Where only anionic emulsifiers are used, their adsorption on the phase boundary is limited by inter-molecular Coulomb repulsion forces. Surface coverage and hence stability may, therefore, be rather below the desired level. While maintaining the advantage of interparticle repulsion due to electrical charges, the adsorbed layer may be considerably reinforced by non-ionic emulsifiers which can be accommodated in the surface even when it is already saturated with regard to anionic surfactants. Highly stabilised emulsions may, of course, not always give the desired properties in final application.

It has already been seen how, in many emulsion polymerisation recipes, all the available emulsifier may be adsorbed on the " seed " particles. Their surfaces would become " under-saturated " during subsequent growth unless extra emulsifier were fed into the polymerisation charge. " Under-saturated " emulsions can often be recognised by their relatively high surface tension, i.e. > 35 dynes/cm. They are not uncommon, especially in synthetic rubber technology where their lack of stability may, in fact, be turned to good account in a process of freeze[15], shear[16] or colloid[17] aggregation. If a fine particled, under-saturated—e.g. styrene/butadiene copolymer—emulsion is subjected to freezing, high shear or the action of hydrophilic colloids, the polymer particles coalesce to larger droplets whose total surface area is just small enough to ensure complete emulsifier saturation. By these means it is possible to reap the benefit of fast polymerisation rates characteristic of fine particled emulsions without having to contend with their technological disadvantages in subsequent applications. This behaviour of under-saturated emulsions must obviously have a major bearing on the freeze-thaw and mechanical stability of emulsions and emulsion paints.

There is already considerable evidence to show that the stability of all dispersions is greatly influenced by the HLB of the stabilising system. While many details still remain to be elucidated, e.g. the influence of structure and chemical make-up of the emulsifiers, the mutual interaction of surfactants and colloids and the effect of electrical charges, some salient features are, nevertheless, now beginning to emerge in principle. The following broad generalisations may be used as a guide :

(1) The HLB required for optimum stability shifts from lower values to higher values as the polarity or hydrophilicity of the disperse phase increases. In the case of polymer emulsions this would mean that the required HLB for poly-2-ethylhexyl acrylate < polybutyl acrylate < polyethyl acrylate < polymethyl acrylate : similarly the required HLB for polystyrene < styrene/butyl acrylate copolymer < polybutyl acrylate < polyvinyl acetate.

(2) The HLB requirements of mixed dispersed phases are intermediate between those of the components and are proportionately additive in much the same way as HLB numbers of emulsifier blends.

(3) The more hydrophobic the disperse phase the more sensitive it will be to deviations from the optimum HLB.

(4) Blends of chemically dissimilar types of surfactants, e.g. anionic and non-ionic, give broader stability peaks than blends of chemically similar types.

(5) HLB values of surfactants, especially non-ionics, may undergo considerable shifts during polymerisation.

(*b*) *Colloid stabilised emulsions*

In the context of this paper it is intended to discuss only those emulsions which contain colloid as well as surfactant stabilisers. The composition and topography of the protective layer surrounding the polymer particles in such emulsions has not yet been fully investigated and many gaps in our knowledge remain to be filled. It would, however, appear reasonable to assume that the interface is occupied by a mixed adsorbate consisting of both surfactant and colloid molecules whose hydrophilic groups are instrumental in providing the emulsion droplets with their protective water envelopes. The relative proportions of the two species present in the adsorbed layer will depend on their adsorption potentials. Some colloids, like fully saponified polyvinyl alcohol, methyl cellulose, sodium alginate or even hydroxyethyl cellulose, have a rather low surface activity compared with most commercial surfactants. Provided they are not irreversibly adsorbed some displacement will occur if further surfactant is added to the emulsion, as may well happen when it is mixed with a pigment slurry. It would not always be possible to predict whether the partial displacement of colloid by surfactant would result in higher or in lower stability. The risk of serious destabilisation after a disturbance of the adsorption equilibrium must, however, always be borne in mind.

Surfactants are, as a rule, less powerful protective agents than colloids because of their higher mobility which enables them to move out of the way when particles with high kinetic energy collide. There may, also, be a strong competition for water of hydration between colloids and surfactants. This can be quite readily demonstrated, e.g. in the case of fatty acid soaps. If an ammonium oleate solution is mixed with a solution of methyl or hydroxyethyl cellulose, first a marked turbidity then a flocculant precipitate and finally complete separation of the soap is observed. In the presence of an organic pigment dispersion, a coloured surface scum is formed on top of an almost colourless clear liquid. The destabilisation and flocculation of emulsions by means of a similar mechanism is used commercially for the " creaming " of rubber latex. The particles in ammoniated natural rubber latex are covered with an adsorbed layer of protein and a small amount of soap. On the addition of methyl cellulose, ammonium alginate or ammonium polyacrylate, the adsorbed layer undergoes partial dehydration and destabilised particles join up to large agglomerates which rise rapidly to the top where they form a concentrated cream layer above an almost clear water phase[18]. With colloids of very low adsorption potential such as alginates the process may be repeated several times simply by mixing the cream with its own volume of a dilute colloid solution. If, on the other hand, the agglomerating hydrophilic polymer is fairly readily adsorbed on the particle surface like, e.g. pectin or ammonium polyacrylate, further quantities can redisperse the cream and protect the system against reagglomeration. However, as soon as more surfactant is added and the colloid displaced from the surface, creaming recommences. Similar phenomena are not uncommonly observed with the synthetic polymer dispersions used in the paint industry. The addition of a highly surface active emulsifier may cause pronounced thickening and even instability in many colloid stabilised emulsions. It is also frequently found that, contrary to expectation, sedimentation in dilute emulsions is accelerated by the addition of a thickener, such as high viscosity methyl or carboxymethyl cellulose. The increased sedimentation rate may be further accentuated by the addition of surfactants.

From the foregoing remarks it may be inferred that the correct balance of all ingredients used in emulsion and emulsion paint manufacture is of vital importance for successful product design.

V. Emulsion paints

(*a*) *The liquid paint*

Neither the polymer nor the organic pigment dispersions employed in emulsion paints are usually free from surfactants. Even if the paint formulator did not wish to incorporate any additional quantities, or types of his own choosing, he will have to provide a well balanced composition with the materials he is given. This can, indeed, be a formidable task, since even the simplest emulsion paint is a very complex system which has to conform to different and often divergent minimum requirements. Many of the properties required may almost be regarded as mutually exclusive. The following are some of the desired characteristics, paired to emphasise their apparent or real incompatibility. High storage and freeze/thaw stability—ready coalescence ; good flow—good sag resistance ; good wetting of substrates (low surface tension)—good levelling, low foaming (high surface tension) ; high stability—high water resistance ; deflocculation and stabilisation of hydrophilic pigments and extenders—deflocculation and stabilisation of hydrophobic organic colourants ; fast drying rate—good wet edge ; easy brushing—good single coat hiding ; reversible pigment and binder aggregation resulting in good body, thixotropy, easy brushing and freedom from sagging—complete deflocculation leading to good levelling and pigment utilisation, freedom from sheariness, streaking and brush marks.

Without a computer and in the absence of adequate experimental data it would be impossible to assess all the effects surfactants can have on the many components of an emulsion paint. A few only of the more obvious problems will therefore be considered.

The binder emulsion will contain an emulsifier or emulsifier combination with an HLB chosen for optimum stability and polymerisation rates. For vinyl acetate or ethyl acrylate homo- or copolymers this will lie around HLB values from 15 to 17, while styrene copolymers will require an HLB from 12.5 to 15, with higher acrylates and alkyds in an intermediate range. In a practical paint system, it would be necessary to accommodate titanium dioxide, extenders and, usually, organic tinters. The required HLBs for the different ingredients may vary over a considerable range. Many inorganic oxides, sulphates, carbonates and silicates are best served with a very hydrophilic stabilising system, the required HLBs being of the order of 18 to well over 20[19]. A number of important organic pigments, notably phthalocyanine blue, phthalocyanine green and Hansa Yellow, require an HLB round about 14, i.e. close to the optimum HLB of the binder dispersion, while other commonly used pigments, such as some toluidine and especially BON Reds, carbon blacks and red iron oxides, are best served with more hydrophobic surfactants having HLBs between 10 and 13. Even with surfactants or surfactant blends capable of giving broad stability peaks, it may at times be impossible to span the entire range of required HLBs so that destabilisation or partial flocculation is likely to occur. This divergence of requirements is almost certainly responsible for the difficulties experienced by paint formulators with some tints, especially deep shade tints, in paints where very hydrophobic colourants have to coexist with hydrophilic extenders. Not very much is known, so far, about the effect of dispersing agents like polyphosphates on the HLB requirements of the disperse phase. It appears, however, reasonably well established that amphiphilic water soluble polymers are able to bridge the gap of HLB requirements to quite some extent. This is not difficult to explain when one remembers that electrophoretic measurements have shown that, e.g. in a protein solution, disperse phases as different as mineral oil droplets and quartz particles, virtually have the same cataphoretic mobility which in turn is practically identical with that of the protein itself[20]. Absorbed polymer layers on particle surfaces should have similar HLB requirements irrespective of the nature of the adsorbent. Since, in an emulsion paint, the total surface of the disperse phases is very large, it is only to be expected that low molecular weight amphiphilic polymers perform more satisfactorily than high molecular weight ones whose relatively few molecules could not easily be spread over so large an area.

High molecular weight colloids, usually of only moderate adsorbability, are used as thickeners in emulsion paints. If they are incorporated in the pigment paste, they may be adsorbed on the surface of the titanium dioxide and extender particles. The extent of adsorption will depend very largely on the concentration of such ingredients as dispersing agents and surfactants, and also on the order of mixing[21]. Adsorption may be small, if dispersing agents are introduced before the colloid, and appreciable, if the mixing order is reversed. Owing to strong hydrogen bonding it may even become irreversible. It is thus possible to obtain pigment pastes of rather different behaviour depending solely on the method of manufacture. In the case of irreversible adsorption the subsequent addition of a surfactant may only have the effect of increasing the stability, provided the correct HLB is maintained. Pigment or extender dispersions, first stabilised by surfactants or dispersing agents, may, on the other hand, undergo flocculation if, at a later stage, they are subjected to the action of dissolved colloid. The effect would be similar to that discussed in the context of latex creaming.

Some paint formulators like to use very high molecular weight thickeners in order to obtain the maximum effect with minimum quantities. This can be a dangerous practice. If the thickener molecules have a strong affinity for the pigment or extender but are too few in number to cover the entire surface, they will tend to be shared by several particles at once. This may cause extensive pigment or pigment-resin aggregation which in turn could lead to syneresis, poor stability and application properties, as well as low opacity. The risk of unbalancing the paint system with colloids, surfactants, dispersing agents, etc., is reduced if the pigments and extenders are dispersed in an aqueous medium already containing a proportion of all water soluble ingredients it is intended to use. Preferably the binder dispersion, or at least part of it, should be included as well if subsequent pigment shock is to be minimised.

(*b*) *The paint film*

So far only the effect of surfactants and their balance on the behaviour and stability of the liquid paint has been considered. The formation and performance of the paint film is of equal if not greater importance. During drying the concentrations of all water solubles increases steadily and additional quantities of surfactants and, possibly, colloids are released into the dwindling water phase as coalescence and flocculation reduce the adsorptive surface area. There will consequently be a considerable disturbance of the balance of the system. While at moderate concentrations, stability can be maintained even if the required HLBs of the different disperse phases are fairly far apart, the demands for accurate balance become more selective as concentration increases. It is very probable that different species of dispersed particles reach critical instability at different stages of drying, thus favouring the formation of flocculant heaps of pigments or extenders embedded in clear binder whose particles have coalesced separately. The whole system will become " frozen " when the paint becomes touch dry and no further separation of the disperse phases can occur. In order to minimise the " pigment heap " and " resin window " formation described in many publications of the Paint Research Station[22] it might be thought that rapid freezing of the whole system by quick drying, e.g. on a porous substrate, could give the desired effect. Unfortunately, this is not so because under those conditions coalescence is greatly impaired and a film of insufficient coherence and adherence results. An alternative method also suggests itself, namely the gross overstabilisation of the whole system which would prevent selective flocculation until the paint is practically dry. In this case, however, the presence of large quantities of water-solubles trapped in the film and held at the surface of the binder and pigment particles would almost completely inhibit coalescence and thus lead to highly water sensitive and re-emulsifiable paint films.

A third approach might be contemplated in theory and is put forward here as food for thought. If all inorganic and organic pigments as well as extenders could be so treated or so chosen as to ensure that they would, within very narrow limits, have the same HLB requirements for optimum stability as the resin binder particles, more homogeneous paint films with better pigment utilisation might result. The resin emulsions themselves could be fairly readily adapted, by appropriate choice of co-monomers, to conform with a mutually agreeable choice of HLB requirements within the range of 12-18. The middle of the range would probably give the best all round performance.

Since high molecular weight hydrophilic colloids like cellulose ethers may exert selective or general flocculating and destabilising effects on the paint system, a search for alternative thickeners may prove necessary when designing improved emulsion paint systems. Mineral thickeners of the montmorillonite or hectorite type merit special attention.

A surfactant stabilised emulsion combined with a surfactant stabilised dispersion of specially treated pigments and a colloid free thickener might well be the model of an improved emulsion paint of the future.

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Discussion at Manchester Symposium

DR. WARSON said that colloid acceptance in emulsion polymerisation varied widely with different monomers ; with vinyl acetate, colloid acceptance was good, giving improved stability of emulsions and paints made from them ; with acrylics and styrene, colloid addition detracted from stability unless large excess was used. Could this be explained ?

DR. BONDY suggested that an important aspect was the behaviour of colloids under the influence of grafting. Vinyl acetate grafted cellulose derivatives usually retained their solubility and stabilising effect. Polyvinyl alcohol, when grafted with methyl methacrylate, would come out of solution at an early stage, giving an insoluble colloid which, presumably, had less stabilising effect. He agreed that styrene and acrylic ester systems were more sensitive to colloids than was vinyl acetate.

DR. WARSON asked if any quantitative work had been done on the transfer of colloids or emulsifying agents between latices and pigments.

DR. BONDY thought that transfer of colloid or surfactant from latex to pigment was less likely than the reverse, because the agents were closely integrated with the resin particles. This applied also to non-ionic surfactants, of which only about 10 per cent of the original concentration occurred in the free state after polymerisation.

DR. O'NEILL referred to the effect of colloids in reducing the gloss of emulsion systems, and asked if this could be avoided.

DR. BONDY felt that the optimum in gloss development would not be reached until the flocculating effect of colloid thickeners was eliminated, and thought that the use of built-in thickening systems or water insoluble thickeners might provide a solution.

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Surface treatment and optical properties of titanium dioxide pigments*

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Summary

The development of increased hiding power in emulsion paints by modification of the after treatment of the titanium oxide is discussed. Film density measurements show that the achievement of greater hiding power is dependent on the inclusion of air in the film at lower pigment volume concentrations due to a lowering of the critical pigment volume concentration of the system.

The effect of a limited range of sequestering and dispersing agents on hiding power is examined and shown to be negligible.

Le traitement superficiel et les propriétés optiques des pigments du dioxyde de titane

Résumé

On discute la mise au point des peintures-émulsions d'un pouvoir couvrant augmenté grâce à la modification du post-traitement appliqué au dioxyde de titane. Des mesurages de la densité de feuil révèlent aux concentrations pigmentaires en volume peu élevées que la réalisation d'une augmentation en pouvoir couvrant se dépend d'une inclusion d'air dans le feuil à cause de la diminution de la concentration pigmentaire critique en volume du système.

On examine l'effet excercé par une gamme limitée d'agents de dispersion ou de séquestration sur le pouvoir couvrant et on le démontre négligeable.

Oberflächenbehandlung und optische Eigenschaften von Titandioxydpigmenten

Zusammenfassung

Das Verfahren, durch Modifikationen der Nachbehandlung des Titandioxydes die Deckkraft von Dispersionsfarben zu verbessern, wird einer Betrachtung unterzogen. Messungen der Filmdichte zeigen, dass grössere Deckkraft von der Einbettung von Luft bei niedrigen Pigment-Volumen-Konzentrationen als Folge der Erniedrigung der kritischen Pigment Volumen Konzentration des Systems abhängt.

Auch der Einfluss einer begrenzten Zahl von Trennungs-und Dispergierungsmitteln auf die Deckkraft wird untersucht und als unwichtig nachgewiesen.

Поверхностная обработка и оптические свойства грунтовых красок на базе двуокиси титана

Резюме

Обсуждается вопрос о развитии повышенной покрывающей способности в эмульсионных красках при видоизменении последующей обработки двуокиси титана. Измерения пленочной плотности показывают что достижение большей покрывающей способности

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*Presented to the Manchester Section Symposium on 19 April 1966.

зависит от включения воздуха в пленки при более низкой объемной концентрации краски за счет понижения критической объемной концентрации грунтовой краски в системе. Исследуется влияние ограниченного количества изолирующих и дисперсионных агентов на покрывающую способность и показано что это влияние незначительно.

Introduction

As long as titanium dioxide is completely immersed and fully dispersed in a continuous film, control of hiding power can be obtained by making changes in the mean particle size and particle size distribution of the pigment. It is known that the particle size of titanium oxide needed to give maximum opacity in a fully dispersed system varies with the pigment volume concentration. Advantage has been taken of this in the development of a pigment of a small mean particle diameter for use in plastics at PVCs of 1-2 per cent. It is known that the grades of titanium oxide of larger mean particle size are the more efficient at higher PVCs.

In emulsion paints, however, the situation is more complex. In the first place, the lower end of the range of PVCs used is approximately 35 per cent, much higher than is experienced in gloss finishes, and the particles of pigment and extender are much more likely to be in physical contact or in a flocculated state. As the PVC rises above this, there is an increasing certainty that pigment/air interfaces are introduced. Consequently, the approach to greater hiding in emulsion paint systems is quite different from that employed in developing pigments for gloss finishes. It is the purpose of this paper to discuss the techniques used and to demonstrate the achievement by comparison of standard and high opacity grades. The effect of other constituents of the emulsion paint, in particular sequestering and dispersing agents, on the opacity of the system also requires study.

Measurement of hiding power

Measurements of the hiding power of emulsion paints by contrast ratio methods using Morest charts is a tedious operation. Reproducible results can only be obtained by coating a number of charts and by taking several optical measurements of reflectance over most of the black and white squares on the charts. In a recent paper to the Hull section of OCCA, F. D. Robinson demonstrated that a hiding power method, based on determination of the scattering coefficient of the paint film, gives results which are extremely close to those obtained by contrast ratio methods. Although the determination of scattering coefficient requires more calculations to arrive at the hiding power figure, the practical steps in the method itself are far less tedious and less influenced by change of operator. An outline of the method is given below.

The emulsion paint is applied to a polyester film, Melinex Type O, gauge 150, by means of a spiral rod applicator depositing a sufficiently thick film to give a R_B (reflectance over black) of at least 75 per cent. In order to calculate the scattering coefficient, measurements of R_B and R_W are made. R_∞ can be determined by calculation from these figures or by measuring the reflectance of a very thick film of emulsion paint built up over several coats. The film thickness applied is determined by weighing a known area of film and using the theoretical density of the dried film to calculate the thickness. From the scattering coefficient the hiding power is calculated by using the formula given below, but in practice tables and nomographs relieve the tedium and save time.

W = Reflectance of white substrate.
R_W = Reflectance of dried paint film over white substrate.
R_B = Reflectance of dry paint film over black substrate.
R_∞ = Reflectance of infinitely thick film.
$= a - (a^2 - 1)^{\frac{1}{2}}$
X = Film thickness in mils.
K = Absorption coefficient.
S = Scattering coefficient.
$V_{0\cdot98}$ = Hiding power in square feet per gallon.

$$a = \tfrac{1}{2}\left[R_W + \left\{\frac{R_B - R_W + W}{R_B \quad W}\right\}\right]$$

$$b = (a - R_\infty)$$

$$K = S\,(a - 1)$$

$$S = \frac{1}{bX}\coth^{-1}\left\{\frac{1 - a\,R_B}{b\,R_B}\right\}$$

$$V_{0\cdot98} = \frac{1926.3\ b\ S}{\coth^{-1}\left(\dfrac{[(a + 0.0127551)^2 - 1.02040816]^{\frac{1}{2}} + 0.0127551}{b}\right)}$$

The film density may be determined directly by mercury displacement techniques, immersing the film in mercury whilst in a vacuum. Up to the critical pigment volume concentration the theoretical density and determined density are approximately the same, but above the critical pigment volume concentration the determined density falls below the theoretical, and gives a measure of the amount of air or vapour included in the film. This can be calculated from the ratio of determined and theoretical densities. Determination of the film density by this technique provides a check on the reproducibility of the film in regard to the amount of air included in it, and also confirms that no gross errors have occurred in the making up of the paints.

Critical pigment volume concentration

In considering the variation of opacity with level of pigmentation covering the range of pigment volume concentration from 35-75 per cent total (pigment/extender) PVC it is necessary to recognise that above a critical pigment volume concentration the presence of air/pigment interfaces makes an added contribution to the hiding power of the paint. As has already been indicated the degree of air inclusion in the film can be studied by plotting PVC against the film density determined by a mercury displacement method and comparing this with the plot of PVC against theoretical density (Fig. 1.). It will be seen that there is a sharp inflection in the theoretical density curve indicating the point at which the air begins to be included in the film, apart from the surface irregularities which are taken into account by the immersion in mercury under vacuum. By plotting the ratio of total pigment volume and total film volume against the PVC it should be possible to determine the critical PVC of the paint by noting the point of inflection. In paints where the binder is a solution, a very sharp break occurs in the curve and it is the PVC at this point which can be regarded as the critical pigment volume concentration (Fig. 2.). With emulsion paints, however, the transition from a substantially continuous film, where determined density approximates to theoretical density, to a film which contains air or vapour spaces, is more gradual as is illustrated by Fig. 3. However, by extrapolating two straight arms of the curve the critical pigment volume concentration can be determined.

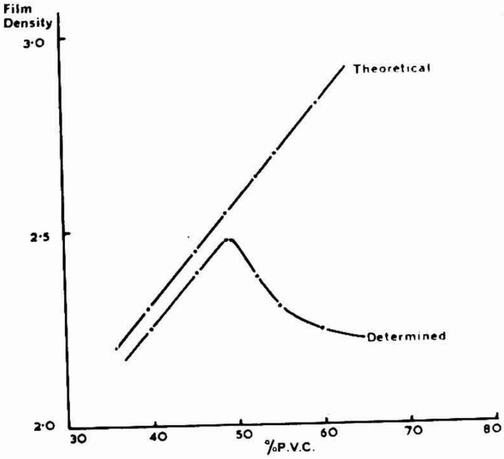

Fig. 1. Theoretical v determined density of emulsion paint film

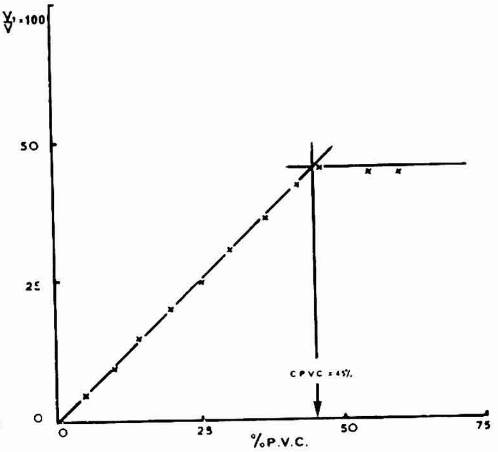

Fig. 2. Critical PVC—rutile titania in acrylic resin solution

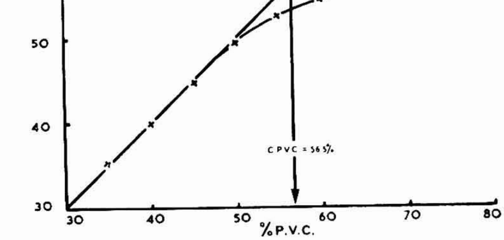

Fig. 3. Critical PVC—standard grade in acrylic emulsion

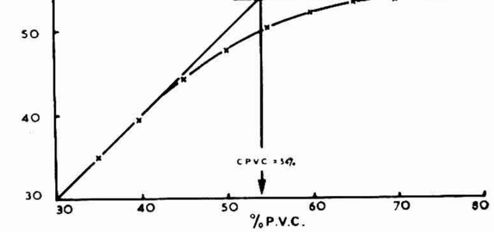

Fig. 4. Critical PVC—Runa RE30 in acrylic emulsion

Effect of surface area of the pigment

It is well known that the critical pigment volume concentration of a mixture of pigment and extenders can be altered by the choice of suitable combinations. Advantage was taken of this possibility in the development of titanium oxide grades especially designed for use in emulsion paints at higher pigment volume concentrations. By increasing the total hydrous oxides applied to the surface of the pigment in the after treatment process, a large increase in the total surface area of the pigment can be produced. This results in a lowering of the critical pigment volume concentration even in the presence of large proportions of extender of more normal particle size (Fig. 4). Using the technique outlined for measurements of critical pigment volume concentrations, four pigment samples were examined. The results shown in Table 1 were obtained.

Table 1

Critical pigment volume concentration
(TiO_2 19 per cent, extender varied)

	Total treatment	CPVC
(*a*) (Runa RH20)	4.1	56.5 per cent
(*b*) Experimental sample ..	5.8	56.0 per cent
(*c*) (Runa RE30)	7.5	54.0 per cent
(*d*) Experimental sample ..	8.1	53.5 per cent

The lowering of the critical pigment volume concentration results in air inclusion in the film at a lower PVC with the consequent increase in the hiding power of the film beginning with small increases just below the critical pigment volume concentration and becoming worthwhile at higher PVCs.

The level of after-treatment on Runa RE30 was finally chosen to take the maximum advantage of this property with the minimum disadvantageous effects that this increase in surface area might have on pigment properties and ease of production.

The scattering coefficient of emulsion paints pigmented with the two grades of titanium oxide only over the range of PVC from 25-75 per cent were measured (Fig. 5). The contribution to high dry hiding made by the higher level of after-treatment can be seen to particular advantage at the higher PVCs.

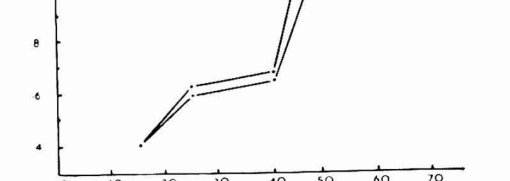

Fig. 5. Scattering coefficient of emulsion paints (titania only)

The same advantage persists when the titanium oxide is reduced with extender. A comparison was made of the standard grade and Runa RE30* at varying PVCs, maintaining the titanium oxide volume concentration at 19 per cent and adjusting the total PVC by increasing the extender content of the paint. The actual formulae used in these experiments are given in Table 2.

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*Runa RE30 is a high opacity treated TiO_2 for high PVCs (Laporte).

Table 2

Raw material	Paint formulation									
	I	II	III	IV	V	VI	VII	VIII	IX	X
Pigment	22.5	21.0	20.0	18.0	17.0	20.0	19.0	16.0	25.0	23.0
Snowcal	12.5	19.0	25.2	28.9	33.2	14.1	20.7	35.2	11.1	17.4
Natrosol M ..	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Fomescol U50 ..	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Tetron	0.05	0.05	0.05	0.1	0.1	0.05	0.05	0.1	0.05	0.05
Nuodex 321 ..	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Vinacryl 4000 ..	44.0	35.0	27.3	19.1	13.5	44.0	35.3	13.5	44.5	34.6
Water	20.35	24.35	26.85	33.3	35.6	21.25	24.35	34.65	19.2	14.8
PVC %	35	45	55	65	75	35	45	75	35	45
PVC TiO_2 ..	19	19	19	19	19	17	17	17	21	21
Theoretical dry density ..	1.93	2.08	2.23	2.40	2.51	1.90	2.05	2.5	1.94	2.11
Volume solids	40.7%	39.4%	38.0%	35.3%	34.0%	40.2%	39.6%	35.5%	41.7%	39.3%
Weight solids ..	57%	57.5%	58.9%	56.5%	57%	56.1%	57.4%	58%	58.4%	57.7%

The effect of slightly adjusting the titanium oxide volume concentration is also included in these experiments. Slight adjustments to sequestering agent level were found necessary to obtain suitable dispersions during manufacture.

The results of scattering coefficient measurements calculated by using the theoretical density of the film are plotted in Fig. 6 and these are converted to hiding power per gall. of dry paint in Fig. 7. The effect of varying the titanium oxide volume concentration is shown in Fig. 8.

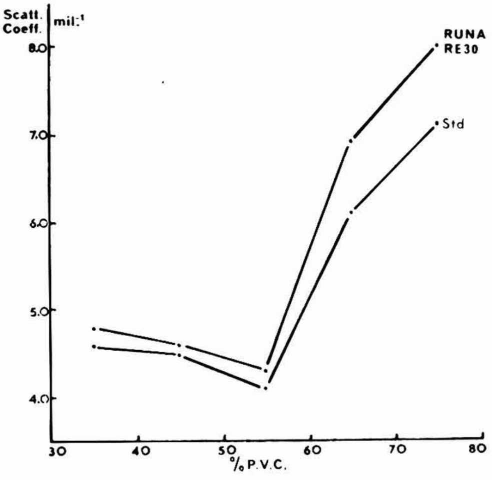

Fig. 6. Scattering coefficient of emulsion paints (19 per cent titania PVC)

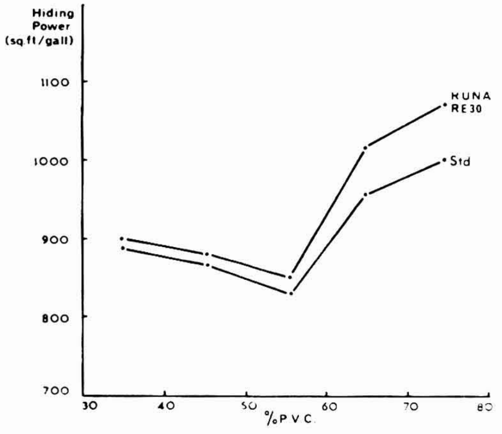

Fig. 7. Hiding power of emulsion paints (19 per cent titania PVC)

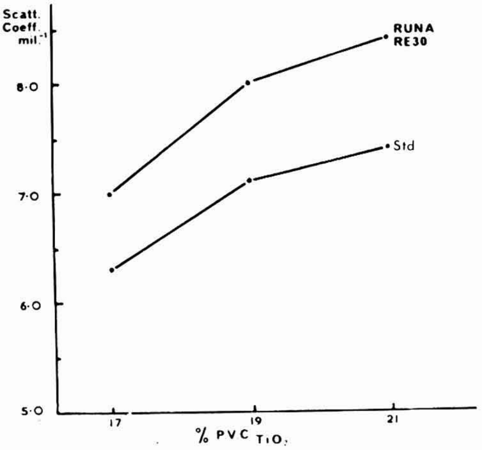

Fig. 8. Scattering coefficient of emulsion paints (75 per cent total PVC)

Effect of sequestering agent

So far, only the effect of the type of pigment on hiding power has been considered. Emulsion paints are such relatively complex systems that it would be surprising if the other ingredients did not also affect the results obtained. For example, very little is known of the state of flocculation of the pigment and extender from the time the film is applied to the point when, because of loss of water, the pigment particles are fixed in their final positions in the film. During this period the water soluble ingredients of the film which, at the concentration of the pigment and emulsion in the liquid paint, have a dispersing effect, might well become so concentrated as to cause flocculation. The effect of these water soluble ingredients on the properties of the pigmented system is therefore well worth studying at three distinct stages in the history of the emulsion paint.

(a) during manufacture.
(b) during storage.
(c) during film formation.

The first two stages can probably be studied fairly readily by viscosity measurements during the dispersion of the pigment and after incorporation of the emulsion, and a later paper will discuss the effect of these on the stability of the system. The proportion of sequestering/dispersing aids required to give optimum dispersion of the pigment/extender mixture can readily be determined. The final choice, however, must take into account the effect on paint stability and on properties such as hiding power.

A study of the effect of these agents on the scattering coefficient of emulsion paints of varying PVCs has been made. The choice has been limited to Tetron, Calgon and a 50/50 mixture of Calgon and Orotan 731.* The levels of additions were the optimum level for dispersion, as determined by methods outlined in the later paper, and amounts equal to 0.5 × optimum and 2.0 × optimum.

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*Calgon is sodium hexametaphosphate (Albright and Wilson Ltd.).
Tetron is tetra sodium pyrophosphate (Albright and Wilson Ltd.).
Orotan 731 is the sodium salt of a polycarboxylic electrolyte (Rohm and Haass).

Measurements of scattering coefficient initially and after storage at 40°C were made. The results are presented in Table 3.

Table 3

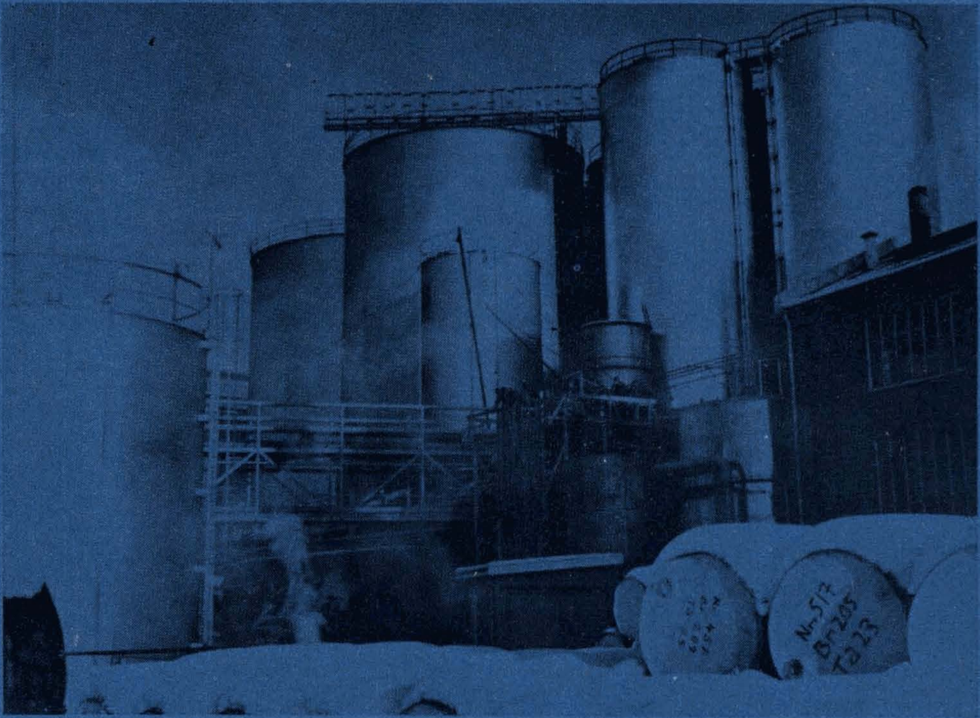
Effect of storage at 40°C on scattering coefficient

Standard grade

PVC %	Disp. Amt.	Calgon			Tetron			Calgon/Orotan		
		Init.	2 Wk.	4 Wk.	Init.	2 Wk.	4 Wk.	Init.	2 Wk.	4 Wk.
25	0.5	5.7	5.8	5.5	5.4	6.0	5.7	5.7	5.9	5.6
	1.0	5.2	5.4	5.2	5.3	5.3	5.3	5.5	5.8	5.5
	2.0	5.1	5.5	4.9	5.2	4.9	5.0	5.4	5.1	5.0
35	0.5	4.3	4.8	4.5	4.4	4.8	4.8	4.7	4.8	4.6
	1.0	4.5	4.6	4.3	4.4	4.5	4.5	4.3	4.5	4.4
	2.0	4.3	4.4	4.2	4.3	4.6	4.3	4.4	4.4	4.3
45	0.5	4.3	4.4	4.2	4.2	4.5	4.4	4.3	4.6	4.4
	1.0	4.4	4.6	4.1	4.3	4.8	4.4	4.1	4.7	4.2
	2.0	4.3	4.5	4.1	4.4	4.7	4.3	4.2	4.5	4.3
65	0.5	6.1	6.8	6.0	6.0	6.3	6.2	5.9	6.4	6.0
	1.0	6.1	7.0	6.1	6.0	6.5	6.3	6.1	6.8	6.2
	2.0	6.0	7.4	6.4	6.0	7.5	6.3	5.8	6.6	6.3
75	0.5	7.2	7.6	7.3	7.3	7.3	7.2	7.1	7.4	7.1
	1.0	7.3	7.7	7.6	7.1	7.6	7.3	7.3	7.6	7.4
	2.0	7.0	8.1	7.8	6.9	7.1	7.1	7.0	7.3	7.2

Runa RE30

PVC %	Disp. Amt.	Calgon			Tetron			Calgon/Orotan		
		Init.	2 Wk.	4 Wk.	Init.	2 Wk.	4 Wk.	Init.	2 Wk.	4 Wk.
25	0.5	6.2	6.5	6.2	6.3	6.4	6.6	6.4	6.5	6.2
	1.0	5.9	5.9	5.9	6.0	6.1	6.3	6.1	6.3	5.9
	2.0	5.7	5.6	5.6	5.8	5.7	5.9	6.0	5.8	5.7
35	0.5	4.8	4.9	5.0	4.8	5.3	5.1	5.1	5.2	5.0
	1.0	4.7	4.6	4.7	4.8	5.0	5.0	5.0	5.1	4.8
	2.0	4.7	4.7	4.8	4.6	4.8	5.0	4.8	4.9	4.8
45	0.5	4.8	4.6	4.7	4.5	4.9	4.8	4.9	5.2	4.9
	1.0	5.0	4.7	5.1	4.4	4.8	4.9	5.2	4.9	4.9
	2.0	4.8	4.8	5.1	4.5	4.9	5.0	5.1	4.8	4.9
65	0.5	6.7	6.9	6.9	6.8	6.9	7.1	7.2	7.0	7.3
	1.0	6.9	7.0	7.1	6.6	7.2	7.0	7.1	6.9	7.3
	2.0	7.0	7.2	7.2	6.8	7.0	6.8	6.9	6.9	7.1
75	0.5	7.9	8.1	8.1	7.9	8.2	7.9	8.2	8.1	8.2
	1.0	7.7	8.2	8.3	7.9	8.3	8.1	8.0	8.1	8,2
	2.0	7.7	8.0	8.3	7.8	8.2	7.7	7.9	7.9	8.0



It will be seen from Table 3

(a) that except at 25 per cent PVC the level of agent in the range chosen has little effect on the degree of hiding power of the paint.

(b) that at 25 per cent PVC increasing concentration of agent slightly reduces the hiding power obtained.

(c) that no significant change in hiding power has occurred after four weeks at 40°C except, in some cases, with Calgon only.

(d) that the three agents chosen give similar performance in respect of opacity.

(e) that at high PVCs the titanium oxide with the higher after-treatment level (Runa RE30) gives greater hiding power than the pigment with the lower after-treatment level.

The results obtained indicate that, when choosing the level of sequestering/wetting agents, one can leave out of consideration any effects on hiding power.

Acknowledgments

Acknowledgments are made to colleagues and the Technical Service Laboratories for most of the practical work and to the Directors of Laporte Titanium Ltd. for permission to publish this paper.

[*Received 6 June 1966*

Discussion at Manchester Symposium

MR. DAVIDSON suggested that the use of a specially treated TiO_2 at lower CPVC than a normally treated type was not necessarily an advantage. The normal type could be used with a greater proportion of extender, with the result that differences in formulation cost were minimised.

MR. TAYLOR pointed out that the specially treated TiO_2 had about 4 per cent extra surface area, i.e. about an extra 6 square metres per gram. He did not think that this type would be less economic in use at the higher PVC, since the increased surface area gave a large contribution to increased opacity.

DR. WAGENER asked what was the reproducibility, in terms of standard deviation, of the determinations of scattering coefficient and CPVC.

MR. TAYLOR could not quote standard deviations, but said that scattering coefficient was measurable to ± 0.1 on the figures quoted ; results within this bracket were regarded as being reliable.

DR. WAGENER then asked what order of film thickness was used in determining scattering coefficients.

MR. TAYLOR replied that it was important to have a sufficiently high film thickness to give a reflectance over black of >75 per cent.

DR. WAGENER finally asked if it had been found that the magnitude of the scattering coefficient was dependent on the paint film thickness used.

MR. TAYLOR had found a dependence of S on film thickness.

MR. DUSSELHOF commented that a hydrous oxide surface layer on TiO_2 pigments could cause paint thickening on storage. On the supposition that a thicker layer would have a greater effect on thickening, he asked if the specially treated grades were more reactive.

MR. TAYLOR said that increased after-treatment had been found not to reduce the stability of pigmented systems.

Editorial

111 + 11=1010

Few readers will fail to recognise this sum as the binary equivalent of 7+3=10. Binary arithmetic is particularly well suited to manipulation by electronic means and is hence the basis of all digital computer operations. Thus, a switch may be on or off, a spot on a magnetic drum may be magnetised or not, a condenser may be charged or not, and a conductor may be carrying a current or not, at any moment in time. In each case the numeral 1 may be made to correspond to one of these states, and 0 to the other. Coupling large numbers of such units yields an array capable of storing large numbers in binary expression, and manipulation of the array permits the manipulation of these numbers.

Computers have come a long way since the first commercial installation in the UK was built and operated by the Lyons Electronic Office (LEO). The modern machine is fully transistorised and tolerant of a wide range of ambient conditions ; the core store, the working heart of the computer, can accommodate 8,000 to 32,000 " words " of, say, 24 binary digits, and will respond to a repertoire of several hundred commands ; multiplication, addition and other simple operations are conducted in micro seconds, and results can be output on paper tape, on cards or by means of a line printer operating at up to 1,000 lines per minute. Numerous " peripherals " can be connected with the basic computer in addition to these output devices and it is now usual for these to be widely interchangeable through what is called " standard interface." Magnetic backing stores offer an almost unlimited capacity with 5-15 million characters carried on a single tape, whilst the laborious, albeit automatic, searching of tapes to find the right data, is being increasingly superseded by the rapid techniques of random access. Output need not be written or punched ; it can be displayed on a cathode ray tube or on an X-Y plotter and, if one does not approve of the plot, it can be altered by an electronic pen which will feed the correction back into the computer for future reference. Data processing, design and scientific calculations are joined by complete automation of complex operations by direct link, as growing areas of computer activity. A small basic machine will cost you £10,000-£30,000 and there is virtually no upper limit ; a fair sized installation with backing store, card handling and line printer facilities might run out at £150,000-£200,000. Both machines and time can, of course, be hired and at least one company offers computer time on a do-it-yourself basis for as little as £4 an hour.

Computers continue to grow in capacity and, other things being equal, would be expected to grow commensurately in physical size. This latter trend is being reversed by microminiaturisation (what word do we coin for the next step ?), and it is an interesting thought that the speed of the modern computer is now felt to be limited by its size, since even electromagnetic radiation takes a finite time to get from A to B. The computer of the future may well be no bigger than a cigarette packet ; not such a startling possibility to those of us who saw some of the little black boxes at Farnborough this year.

Reverting to binary arithmetic, the electronic manipulation of 0 and 1 is not limited by our concept of number. 0 and 1 can be identified with other concepts, provided simple duality is maintained. They may, for example, represent true and false, or yes and no. Then, given some set of operators corresponding to add, divide, etc., one can manipulate logical data on a computer in just the same way as one manipulates numbers. George Boole (1815-1864) was the pioneer of symbolic logic and his little book of 82 pages (*The Mathematical Analysis of Logic, being an essay towards a calculus of deductive reasoning ;* 1847) marked the beginnings from which sprang, eventually, such monumental works as Whitehead & Russell's *Principia Mathematica*. The work of Boole is immortalised in the name of the science used, *inter alia*, to computerise the operations of logic—Boolean Algebra. It is not a subject for bedtime reading—at least not for most of us—but its principles and precepts are well within the grasp of the technically trained man. It is a fascinating as well as a useful study, and one does not need a computer to use it.

All chemists are logical
All chemists are humans
Therefore all humans are logical

Boole would not have accepted the argument, even had he tolerated the major premise, but he could have *proved* it fallacious. Can you ?

Correspondence

SIR,—The publication (*JOCCA*, September 1966) of Chaplin and Fish's paper on the yellowing of white paints prompts us to write on this subject since we feel that this paper may tend to suppress interest in the ammonia test quite unjustifiably.

Our own work, which for reasons which are implicit in the discussion which follows has not yet arrived at results suitable for normal publication, has brought to light some of the reasons why the investigation of yellowing is one of the most difficult fields in our technology and why much of the published work must be discounted, including, we are afraid, that of Chaplin and Fish.

It is by now generally accepted that the yellowing of air-drying oil, alkyd and similar paints indoors is affected by the presence of ammonia or other nitrogenous bases (chemical yellowing) and by light (photo-yellowing). What does not appear to be sufficiently appreciated is that the sensitivity of a paint to either or both of these agents is very high and that neither phenomenon is simple. The joint operation of the two agents which generally occurs in practice is thus extremely complex and readily leads to contradictory or meaningless results in the unsophisticated types of investigation which have usually been reported.

Films which are rigorously protected from nitrogenous bases under conditions of very weak illumination show negligible yellowing. Further, the degree of yellowing produced by a definite time-limited exposure to ammonia is dependent on the age (oxidation state) of the film. Thus a film which receives a two-day ammonia exposure starting from the time when solvent is substantially lost will show negligible yellowing at the end of the exposure. A two-day exposure of a one-week-old film will produce considerable yellowing. A similar exposure at two weeks will probably show even more yellowing, while after one month the effect will probably be declining. We use the word " probably " since only a limited investigation of this kind has been done.

A similar paint without driers will probably be insensitive to ammonia during the first two weeks of its life and will reach maximum sensitivity much later. It thus appears that a very important factor is what may be termed the " oxidation age " of the film at the time of its exposure to ammonia.

The overall effect of light is also complex. Photo-yellowing is possibly a simple process in itself, although here again the oxidation age of the film might be expected to be significant. However, any chemical yellowing which has taken place, or which is taking place, during illumination is sensitive to light and more or less complete bleaching of some or all of the yellow colouring matters will occur. So far there appear to be no published results on photo-yellowing under conditions of rigorous exclusion of ammonia.

A consideration of these facts will show that no general correlation is to be expected between an ammonia test as conducted by Chaplin and yellowing under his " natural interior exposure " (read " unknown and irreproducible conditions ") particularly as he chose paints " to cover an expected wide range of yellowing properties." As would be expected from the above reasoning the ammonia test gave a very much greater spread, particularly at short exposure times, than was found in " natural exposure."

This does not mean that the ammonia test should be discarded as useless since it can clearly give useful information if properly conducted. For instance by applying the test to films of increasing age it is possible to establish the maximum chemical yellowing potential of a coating. It is also possible to compare paints of a *similar* type directly (at the same age) and to obtain a useful correlation with their practical behaviour under conditions where the effect of illumination may be neglected. We have found such correlations with panels exposed (*a*) in an office drawer, (*b*) in the darker areas of a factory kitchen and (*c*) in a lavatory with artificial lighting only. Since it is under conditions of this type that yellowing is most severe, even a simple ammonia test can be useful.

We should like also to question the relevance of the discussion of the ammonia content of the air of London. This discussion implicity assumes that free ammonia is the agent responsible for yellowing and further assumes that the ammonia will be irrevocably bound under the prevailing acid conditions. We have not seen any evidence for the former assumption, and even if this should be the case ammonium salts in general are well known for the ease with which they dissociate.

Unfortunately, the above discussion has by no means exhausted the pitfalls into which an investigator of yellowing may fall. We have found indications, from both experimental work and case histories, that yellowing (as measured by usual method described by Chaplin) is related to a large number of factors, many of which we have no means of defining at present. In glossy finishes, for example, the gloss is due to a thin surface layer which is either free from pigment or which has much lower pigment content than the bulk of the film. It is clear that the thickness of this layer, its pigment content and the degree of dispersion of the pigment will all affect the measured yellowness, even if the same binder is in question in a number of different cases. There are also indications that a paint which has dried slowly because of unfavourable drying conditions is more susceptible to yellowing. For reasons such as these we conclude that the intrinsic yellowing tendency of a binder cannot be directly related to the yellowing of pigmented finishes, and that while it may be *statistically* true that yellowing is associated with such factors as oil length and linolenic acid content, there are other factors which may easily outweigh the effect of such variables in any particular case.

The paper of Chaplin and Fish is a further indication of the increased awareness of paint yellowing amongst paint users, an awareness which is undoubtedly due to the new standards set by latex paints. Our " non-yellowing " paints of yesterday are clearly not good enough for today and it seems that some new fundamental work on oxidation drying processes will be necessary if they are not to be superseded to an even greater degree than at present.

Yours faithfully,

E. Wåhlin,
E. Sunderland,
T. Helmen.

Aktiebolaget Alfort and Cronholm,
Saltmätargatan 7,
Stockholm,
Sweden.

13 October 1966.

Sir,—Dr. Sunderland and his colleagues appear to have overlooked both the reason given for our little investigation and the conclusions drawn. The reason was clearly stated as " before adopting an ammonia test technique in the paint approval system of the Greater London Council it was, therefore, considered desirable to establish its validity for the purpose." The conclusion drawn was that " simple ammonia tests of the type described are not reliable for the prediction of the yellowing properties of alkyd based hard gloss white paints in normal London atmospheres."

We agree with much of what Dr. Sunderland writes, e.g. that " the joint operation of the two agents (ammonia and light) which generally occurs in practice is thus extremely complex " and that " natural interior exposure " could be written " unknown irreproducible conditions." Oxidation and other factors (some mentioned by Dr. Sunderland) almost certainly play a part.

Taking the matter further, we believe that neither ammonia alone nor light alone, nor indeed any other factor alone, is the sole cause of yellowing and that therefore a balanced assessment of the yellowing tendencies of a white paint under various conditions cannot be drawn from the results of one simple test. We were therefore not surprised to find that, contrary to what had been advocated, a simple ammonia test is not reliable for the prediction of yellowing in London (and we suspect other) atmospheres.

This is all we claim to have established, and since our results were factual, we reject the suggestion that the work " must be discounted."

Yours faithfully,

C. A. Chaplin.
R. A. Fish.

Scientific Branch,
Greater London Council,
County Hall,
London, S.E.1.

1 November 1966.

Reviews

PAINTING AND DECORATING DEFECTS : CAUSE AND CURE

By JOHN SNELLING. E. & F. N. Spon Ltd., London, 1966. Pp. 164, 16 illustrations. Price 25s.

This book, one of a series of Spon books for the building industries, is written " from a practical standpoint (no knowledge of chemistry required) " by an examiner for the City and Guilds of London Institute.

I read the book with a view to finding out its usefulness for education and training of personnel employed by the paint industry and especially considering the availability of the various OCCA training manuals.

The publishers rather ambitiously are recommending the book for use by consultants, foremen painters, teachers, managers, students in technical colleges, etc., etc.

Fifty-two different defects of decorative paintwork and wallpapering are described and grouped mainly according to their visual appearance under seven headings :

Broken Film Defects.
Irregular Plane Defects.
Colour Defects.
Soft Film Defects.
Sheen Defects.
Paint Defects.
Wallpapering Defects.

The author has restricted himself to defects on work with oil base, including synthetic resin paints and varnishes, emulsion paints, distempers and other water paints and to wallpapers (four pages only).

No use has apparently been made of the many excellent publications of the Ministry of Public Building and Works, not even of BS 2015, " Glossary of Paint Terms." Although the explanations are generally given with commonsense, if not always scientifically correct, the information is at times false as in the case of flooding, called " colour development," for which bad grinding is blamed. Dehydrated castor oil is described as non-drying, p. 112. Low flashpoint has been mixed up with high flashpoint, p. 144. A " clear formaldehyde " lacquer is mentioned on p. 11, etc. To recommend the use of a white lead sharp primer and to rub it down with glass paper is in my view not a hygienically up-to-date recommendation. Some sections, e.g. on blooming or erosion, are quite good ; perhaps the literature had been consulted in those cases.

Also some excellent practical advice is given repeatedly, as are good application hints.

Any decorator worth his salt should know his craft, including the contents of this book ; but his apprentices, or representatives, training for selling house paints could well benefit from reading it. The many repetitions may help to hammer the points into a beginner, but seem to be ballast for other readers, and, stripped of them, the handy 164-page volume shrinks considerably.

Whilst there may be a place for the book on the bookshelf of the sprouting decorator, its treatment is too primitive for that of a young paint technician.

MANFRED HESS.

ACETYLENE, ITS PROPERTIES, MANUFACTURE AND USES. VOLUME II

By S. A. MILLER. London : Ernest Benn Ltd., 1966. Pp. xvii+406. Price 126s.

The story of acetylene is a fascinating one. Part of this story was told in Volume I and was well received by reviewers. The story is brought up-to-date in Volume II. If this volume had been published as a separate work, divorced from Volume I, its title might well have been " The Manufacture, Properties and Uses of Vinyl Compounds." Whilst vinyl compounds can be obtained from acetylene and constitute the main commercial outlets for acetylene, other routes have been developed and used for economic reasons. Dr. Miller gives a comprehensive survey of manufacturing processes and evaluates their relative status with much less prejudice than the present title might suggest. In a four-page preface the author summarises the present position of acetylene and its competitors. This preface is a little masterpiece ; it presents a complex situation in a concise, unbiased and most readable manner.

The main chapter headings are : Hydrogenation and Halogenation, Hydrohalogenation, Acetaldehyde and Acrylonitrile, Vinyl Ethers, Vinyl Esters and finally Other Vinylation. Each main chapter comprises an appropriate number of sub-sections, and references and footnotes are printed beneath the text to which they refer, except where a reference has already been given in the sub-section. Properties and other data are presented in 44 tables, flow-diagrams are used to represent manufacturing processes and photographs illustrate some of the equipment and plant used in manufacture.

This book is outstandingly successful in combining depth with breadth. Aspects covered range from reaction mechanisms and physical properties to manufacturing processes, plant capacities throughout the world and commercial and projected end-uses. A wealth of data is presented concisely and particular attention is paid to correct usage of terms like emulsion polymerisation, latex, adiabatic polymerisation, etc. The subject matter is well arranged and is presented in a pleasantly readable style.

This volume is warmly recommended to users of vinyl compounds, not only as a well written and comprehensive source of background information, but as a reference book for scientific and industrial data, which are not readily available elsewhere.

L. R. SEABORNE.

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.)*

Cray Valley Products Ltd. announce that a new WATER SOLUBLE RESIN, RESYDROL E.474, has become generally available. They claim that this resin is the first to be developed specifically for electrodeposition. Although it is a new resin, it has been released only after extensive laboratory and works trials which have shown it to be especially able to overcome the problems associated with electrodeposition on to non-ferrous substrates, such as aluminium.

A. Revai & Co. (Chemicals) Limited, are pleased to announce that they have been appointed distributors for Buckman Laboratories Inc., of Memphis, Tennessee.

Johnson, Matthey & Co. Limited announce that their Blythe Colour Division and Transfers Division will operate from 1 October 1966 as separate subsidiary companies, with a considerable degree of autonomy, under the names Blythe Colours Limited, Matthey Printed Products Limited.

Victor Wolf Limited has issued a technical news sheet on the use of DEDICO/PENTAERYTHRITOL esters in white undercoats, which consists of a summary of work carried out by the company's research and development department.

An agreement has recently been finalised between British Resin Products Limited, of London, and Kyowa Gas Chemical Industry Co. Limited, Tokyo, for the range of BRP—developed HYDROXYLATED THERMOSETTING ACRYLIC RESINS, to be manufactured and sold in Japan.

An entirely new PAINT STRIPPER has been produced by Takdust Products Ltd., of Lye, Stourbridge—Takstripper 9/99 concentrate—which combines the desirable characteristics of both heated stripping solutions based on caustic soda and cold-dip processes, without any of their disadvantages. Like caustic soda-based strippers, Takstripper 9/99 is diluted with water, but does not require heat, yet it has the effectiveness of costly cold-dip compositions.

Stanhope-Seta Limited, sole agents for Gardner Laboratory Incorporated, of Bethesda, Maryland, USA, announce availability of the new model M-105-A WASHABILITY MACHINE, modified to conform to ASTM Method D2486-66T. The Gardner standard machine can now be furnished with five adjustable feet, a circular chrome water-proof level for levelling the test plane, and a spring-scale for adjusting cable tension.

Plans have been announced by Dow Chemical Company (UK) Limited to double LATEX PRODUCTION capacity at the company's King's Lynn, Norfolk site. Part of an 80-acre complex, the initial latex plant, which is still under construction, is due to be on stream by January 1967. The additional investment will bring Dow's total commitment at King's Lynn for latex and related facilities to more than £2.2 million.

A press reception was held at the new head office and laboratories of Styrene Co-Polymers Ltd., Cheadle Hulme, Cheshire, near Manchester. The company was formed under the leadership of the late Mr. E. A. Bevan in 1948 with the aim of pioneering at home and abroad the use of vinyl hydrocarbon modified alkyds. Production started at the Carrington factory in 1950 and research and development was carried out at Roebuck Lane, Sale, Cheshire.

A number of paint manufacturers, with strong marine connections, situated in different parts of the world have banded themselves together as a group working under the title of Pan Marine World Paints. On Thursday and Friday 29 and

30 September 1966 the first technical meeting of the group was held at the Speke factory of Goodlass Wall & Co. Ltd., Liverpool, where firms from England, Italy, Holland, Japan, Spain and France were represented.

A new Industrial Finishes Division has been set up by Walpamur. It integrates the existing industrial sales forces of the Walpamur Co. Limited and Wellington Industrial Finishes Limited.

Torrance & Sons Limited has announced the introduction of a production scale MICROFLOW MILL for the liquid ink industry, following the success of the 3½ in pilot machine. Designated the 15 in, the new microflow mill has been evolved round serviceability and cheap maintenance, coupled with good productivity performance.

ICI is to build a plant for the manufacture of " TPX " METHYLPENTENE POLYMERS, the new thermoplastics based on 4-methylpentene-l, which were first introduced in development quantities in March 1965 as a result of intensive research in the laboratories of the company's Plastics Division.

Berger, Jenson & Nicholson Ltd., the paint group, is to enter WALLPAPER MANUFACTURE. The company has announced that the group has acquired a majority share in W. S. MacGregor Ltd., wallpaper manufacturers and distributors, of Peterlee, Durham.

Rust-Oleum Nederland NV, Haarlem, announces the development and production of a new family of MOULD- AND FUNGUS-RESISTANT COATINGS that offer an easy method of painting to combat sanitation and food spoilage problems. Known as the 8400-series, these products have been especially formulated and tested to eliminate the formation and growth of harmful organisms on plant walls, ceilings, machinery and other surfaces.

Bristol

Trichlorethylene paints

The first technical session of the season was held at the Royal Hotel, Bristol, on Friday 30 September 1966, under the chairmanship of Mr. R. J. Woodbridge, when a paper entitled " Trichlorethylene Paints " was given by Mr. R. L. Godfrey, of Imperial Chemical Industries.

Mr. Godfrey commenced by describing the physical properties of trichlorethylene in comparison with a range of solvents commonly used in the paint industry. He elaborated on how the combination of non-inflammability, high volatility and high vapour density of the solvent was utilised to obtain the unique properties of trichlorethylene paints.

The low boiling point and narrow boiling range contributed to very fast drying systems, whilst the non-inflammable nature of the solvent gives distinct advantages when compared to the solvents used in other types of quick drying media.

Providing that the resins are wholly soluble in trichlorethylene no difficulties are encountered in the formulation of paints. Cold dip application techniques are highly suitable though it is of importance to ensure that correct plant design is utilised, both from a safety aspect and to obtain a satisfactory vapour blanket over the surface of the paint. The height of the " free board " above the liquid paint controls the depth of the vapour blanket, which must be sufficient to promote flow out and drainage after dipping.

Mr. Godfrey followed his paper with a film entitled " Paint Without Tears," in which the non-flammable characteristics of industrial trichlorethylene paints were shown.

During the lively discussion which took place afterwards the speaker more than adequately answered the many points raised, especially that of toxicity, when it was pointed out that the threshold limit value compared most favourably with many commonly used solvents.

A vote of thanks was proposed by Mr. Ruddick, which was heartily endorsed by all those present.

F. E. R.

Hull

Colour

The first technical meeting of the session was held at the Royal Station Hotel, Hull, on 3 October, with Mr. E. A. Brown in the chair, when Mr. W. B. Cork presented a paper entitled " Colour."

The scientific method of investigation involves observing the behaviour of the system concerned as closely as possible and the setting up of a mental model of the system. The behaviour of the system under a different set of conditions is predicted on the basis of the model ; these conditions are then set up and the behaviour of the system observed. When there is a discrepancy between the prediction and the observations, the model is refined and retested and the continuance of this process gradually leads to a model which approaches closer and closer to reality. Thus, a colour photograph is a closer approximation to reality than a monochromatic one, but it is still not a complete model since it is two-dimensional and does not represent wind, sound, etc.

The observation of colour involves the presence of light, its interaction with an object and most important an observer. Mr. Cork explained the implications of the fundamental equations : frequency × wave length = velocity of light, and frequency × Planck's Constant = Energy. Light energy is not continuous, but is emitted in discrete quantities known as quanta, whose magnitude is given by the above equation.

The energy connected with different states of rotation and vibration of molecules, atoms, electrons and nuclei is similarly quantised and energy can only be absorbed if the quantum concerned corresponds to some permissible change in the energy level of the absorbing molecule. Visible light is only a small proportion of the whole spectrum of electro-magnetic radiation and the energy band concerned corresponds to only a small proportion of the possible energy levels in an absorbing system. The band of visible light absorbed when light passes through a body will depend upon what levels of energy can be accepted by the absorbing molecules.

Taking into account the principle of the conservation of energy, the refractive indices of the pigment and the medium in which it is immersed, and the number of interfaces presented to the light, Mr. Cork explained the colour behaviour of many systems. He finally posed a number of questions which might be asked by an audience, such as " Why are there no organic whites ? ", " Why do colours fade ? ", " How can colours be made stronger ? ", " Why are glossy films richer than matt ones ? " and " Why do some blues look pink ? " Satisfactory answers were provided to them all.

Messrs. Taylor, Pierini, Read, Mell, Willis, Gilmore and Ford took part in an interesting discussion that followed. A vote of thanks to Mr. Cork was proposed by Mr. A. J. Ford and was passed with acclamation. Twenty-five members and five visitors were present.

S. R. F.

London

The behaviour of printing ink on rollers

The second technical meeting of the session was held on 20 October 1966 at Imperial College with Mr. R. N. Wheeler in the chair, when Mr. C. C. Mill, of PATRA, gave a paper on " The Behaviour of Printing Ink on Rollers." Before the meeting commenced the members present stood for a few minutes in memory of Mr. C. R. Pye, the Chairman of London Section.

Mr. Mill discussed the difficulty in relating the behaviour of ink on rollers to clearly defined physical properties. In operation, shear rates varied considerably, and there were major difficulties in attempting to measure rheological properties under conditions which would be realistic in terms of use. A theoretical analysis of the system was made, based on theories which had been developed for lubrication, and this had shown some success. Certain conclusions could be drawn from the theoretical analysis ; for example the negative pressures developed on the outgoing side of the nip would be expected to result in cavitation affects. More than 90 per cent of the pressure change in the ink on passing through the nip occurred within ± 2 mm.

Among the practical problems discussed was the relation between tack and viscosity. Tack was related to the apparent viscosity of the ink, but there was also an elastic component operating. Ribbing of ink on rollers could occur at quite low speeds, and it was frequently impossible to avoid its occurrence in the application of low viscosity varnishes and laminates. In such cases it was necessary to allow sufficient time for the coating to flow out before drying.

In the discussion various points were raised, including the occurrence of Moire patterns where an overall pattern resulted related to the original rib pattern. The various patterns of ribbing which could occur were discussed in relation to the types of ink and the operation of the rollers. Axial reciprocation of the rollers, preferably sinusoidal, could sometimes overcome ribbing. Those taking part in the discussion included Mr. P. Davies, Mr. A. R. H. Tawn, Mr. R. G. Kinsman, Mr. J. L. Hawkey, Mr. Haddon, Mr. I. Douglas and Dr. C. M. Wisbey. A vote of thanks to the speaker was proposed by Mr. R. S. Colbourne.

V. T. C.

Thames Valley Branch

Grinding

The first technical meeting of the Thames Valley Branch was held at the Royal White Hart Hotel, Beaconsfield, on 29 September, when Mr. A. C. B. Mathews spoke on " Grinding."

Mr. Mathews said that in his experience grinding had always been a fickle business and during a period in hospital in 1959, and subsequently, he had given considerable thought to the problems involved. In the old days grinding had really been necessary ; nowadays pigments were available with particles finer than the largest lumps acceptable, and dispersion was the "with-it" term. He preferred to call the process milling.

In his early thinking he had found it necessary to formulate his own definitions of terms and to stick to them strictly. Primary pigment particles, aggregates, agglomerates, flocculates, colloids, micelles, etc., had the meaning defined in the lecture, although not all authors using such terms attached quite the same meanings to them.

The point was argued that all effective milling was in fact internal shearing and therefore milling at the thickest consistency possible was the most effective. A mechanism explaining how air could be eliminated during milling was put forward, and the importance of a firmly adherent wetting layer on each pigment primary to give can stability and durability was pointed out. Mr. Mathews showed a slide classifying the full range of modern milling equipment in terms of thickness of paste handled, and their crushing or shearing action.

In 1927 his first job at Naylor Bros. had consisted of brushing out paints alongside the last batch and he had come to recognise good and bad paint. He produced a tin of paint made at that time and stored in his garage ; it was still in good condition. For good paint properties he believed that each primary particle needed to be surrounded by a thick adsorbed layer of the preferred polymer from the vehicle, and he could not believe that the familiar monolayer was thick enough. Then he thought, " why not several layers," and envisaged a sort of multilayer cocoon. Mixed pigment enamels raised problems as each pigment would not necessarily prefer the same first layer, but the vehicle could be made to provide a graded spectrum of polymers so that each pigment could make its own choice. His later views were that adhesion of the adsorbed layer to the primary pigment particles was of great importance for durability, and that for stability the pigment particles should be surrounded by multilayers of decreasing molecular weight, the outer layers of each cocoon being all the same and composed of short chain polymers from the vehicle. The existence of two adsorbed layers at least had recently been proved by Sherwood and Rybicka (*JOCCA*, 1966, **49**, 648). Mr. Mathews claimed his thesis provided explanations of paint stability, of flocculation, of the action of false body promoting pigments, and the beneficial effect of maturing, at least for oleo resinous varnishes.

Mr. Mathews made the following recommendations for obtaining optimum paint properties :

1. Give the pigment the chance to make contact first with the highest molecular weight vehicle.
2. Exclude solvents if possible in the early stages of dispersion ; particularly those preferentially adsorbed on to pigments.

3. Get rid of the air entrapped between pigment particles as soon as possible.
4. Make additions in order of descending molecular weight.
5. Add thinners and driers last.
6. Give the paint a good opportunity to reach equilibrium conditions.

These recommendations were best met by the chip method of paint manufacture, but could be, and were, achieved by pug and roller mills. Ball mills, attritors, and high speed mixers were also-rans.

In the discussion which followed, Messrs. Holt, Moore and Davis and Drs. Henderson and Fuchs took part. The Chairman, Mr. Holt, thanked Mr. Mathews for a fascinating and stimulating, if provocative, talk. He particularly welcomed the innovation of lecture experiments.

V. T. C.

Manchester

Developments in the strip coating of steel with paint and plastic finishes

A joint meeting with the North-West Centre of the Institute of Metal Finishing was held at the Manchester Literary and Philosophical Society on 14 October. The lecturer, Mr. D. S. Newton, read a paper, " Developments in the Strip Coating of Steel with Paint and Plastic Finishes," to an audience of 115 members and guests.

In his introduction, Mr. Newton referred to the growth rate of strip coated materials in the US from 450,000 to 730,000 tons between 1962 and 1965, and pointed out that the process was applicable to thicknesses up to 30 gauge at speeds up to 150 ft per minute. An illustrated description of the layout of the coating line at Richard Thomas and Baldwin Ltd. then followed.

In discussing the pretreatment stage the lecturer stated that initial surface preparation was critical, and that the coating weight applied was an inadequate means of controlling a phosphating treatment. Two-pack etch primers gave good results on galvanised steel, but their pot life was a limiting feature since all applied liquids were recirculated from troughs to drums and a large volume was in use at one time. Organic chromates gave good results both on mild and galvanised steel, ion exchange resins showed promise ; here ionic iron released by the corrosion mechanism was sequestered.

In listing a number of performance requirements in use demanded for strip coated steel, Mr. Newton listed several which find their counterparts in paint testing, but also shared the need for compatibility with adhesives and mastics for jointing and filling. In trying to fulfil requirements for resistance to weathering which might be for a period of 15 years, the practice was to rely on direct experience of five years' exterior testing supplemented by weatherometer results. In order to detect quickly differences in weathering fastness, which might take 18 months before initial chalking was observed, the practice had been developed of using micro indentation tests to give an earlier detection of ultra violet degradation.

Technical assistance to customers was chiefly concerned with jointing methods employed in fabricating articles from sheet. By special techniques welds could be made in which a thermoplastic coating flowed and enclosed the weld. Two-pack epoxy and hot melt adhesives could be used, and bag sealing adhesives for polyethylene coatings. Induction heating occurring in 15-20 seconds utilised the coating itself to form the adhesive.

Finally in predicting the way ahead, Mr. Newton referred to fluorocarbons and silicones as new coating materials and pointed out that the use of water-based finishes could reduce the amount of heat required by the process by as much as two-thirds.

The vote of thanks proposed by Mr. W. F. McDonnell was received enthusiastically.

D. A. P.

Midlands

Trent Valley Branch

Versatic acids and their Derivatives

The first technical meeting of the session took place at the British Railways School of Transport, Derby, on 6 October 1966, with Mr. R. S. Law in the chair. Eighteen members and guests were present to listen to a talk by Mr. M. V. Moore entitled " Versatic Acids and their Derivatives."

Mr. Moore first described the use of the glycidyl ester of versatic 9-11 to upgrade the properties of various synthetic resins.

He particularly mentioned the use of this material to modify short oil alkyds to improve their adhesion and alkali resistance when used in stoving enamels. He emphasised that it was important to use versatic modified alkyds in conjunction with a slow reacting amino resin otherwise embrittlement would occur due to the amino resin cross-linking with itself in preference to the glycidyl ester.

The glycidyl ester of Versatic 9-11 can also be used to advantage for the modification of thermoset acrylic resins to provide excellent weathering overbake in alkali resistance with only a slight sacrifice of stain resistance.

Mr. Moore then went on to describe the use of vinyl ester of Versatic acid to produce latex emulsion paints with excellent durability and alkali resistance. He illustrated this with an interesting series of slides which showed these properties compared with conventional types of latices.

A very lively discussion period followed the talk. The vote of thanks was proposed by Mr. Guest.

J. R. B.

Newcastle

First meeting

The first meeting of the Newcastle upon Tyne Section in the 1966-67 season took place at the Royal Turks Head Hotel at 6.30 p.m. on Thursday 6 October. Approximately 50 members were in attendance.

Mr. R. N. Faulkner, of the Paint Research Station, gave an account of a research project devoted to metallo-organic primers, namely coatings which by virtue of having reactive groups built into the polymer structure react directly with the metallic substrate. The entire field of such coatings was briefly reviewed, mention being made of tannates and of media in which vegetable oils, alkyds and epoxy esters were combined with gallates, polyhydric phenols, phosphonic and sulphonic acids, acetoacetic ester and phthalocyanine type compounds, etc. The greatest promise had been shown by alkyd gallates made by alcoholysis of an alkyd with an ester of gallic acid. Conditions for its reaction with the steel substrate included the presence of oxygen and water, absence of too much rust on the surface, use of a water miscible and sufficiently volatile solvent and adequate concentration of the reactive material.

Specimens were shown in which this type of coating applied at ½ mil thickness had given good adhesion and better weathering resistance than a normal etch primer. Testing for use before welding it was shown to give some porosity in the weld but not to an unacceptable degree, satisfactory weld strength and the absence of toxic fumes beyond the maximum allowable concentration. The main impediments to its use as a prefabrication primer were insufficiently rapid drying time and costliness.

In the discussion period questions were posed by Messrs. Banfield, Boynton, Farrow, Hudson, Watson and Willey on aspects as diverse as prospects of electrodeposition and coating of razor blades. The vote of thanks was proposed by the Chairman.

F. R. B.

"Accelerated Weathering"

The second meeting of the Section was held on 3 November 1966, and was an Extraordinary Meeting. Two vacancies existed on the Committee, owing to the death of Mr. G. L. Lewis and the departure of Mr. P. B. Marsden from the industry. Messrs. D. Dixon and R. G. Carr were elected.

The lecture was given by Mr. T. M. Hipwood, of the DCI, Woolwich, and dealt with accelerated weathering with particular reference to BS 3900, Part F3. Mr. Hipwood paid tribute to M. W. Northway, who before his recent death was Chairman of the Joint Services Research Committee on Paints and Varnishes, and had contributed much to the work reported ; he was in fact to have collaborated with Mr. Hipwood in presenting the paper.

The work on seven paints which led to the modified DEF-1053 : Method 26 cycle, which is now BS 3900, Part F3, was reported in *JOCCA*, **47,** 73 (1964). The new cycle differs from the old in using a 1600 watt DC arc in place of a 900 watt AC arc, and introducing a two-hour " dry " period twice a day, together with some structural alterations. Mr. Hipwood went on to report further work on the same lines, using 14 paints, and comparing the results with outdoor exposures at four places in Britain, two in Australia (wet and dry) and one in Singapore. The results were illustrated by colour photographs. An interesting aspect was the difference between the wet and dry tropical sites : the dry site turned Brunswick Green paints yellow, not blue ; it caused a chlorinated rubber paint to chalk, which did not elsewhere ; and it failed to chalk an aromatic polyurethane, which did chalk at the other sites. In general the BS 3900, Part F3 test gave good correlation on a wide range of paints with exposures in Britain and in the " wet " tropical areas.

The second part of the lecture dealt with comparisons between this test and others. Out of 12 different tests mentioned by the ASTM one (Type E) was chosen for comparison: it was found to be more severe generally than the BS 3900 test but failed to produce blistering with a red oxide alkyd paint, which blistered outdoors and in the BS 3900 test. The Xenotest WL gave a more realistic discoloration of pigments, but did not blister the red oxide alkyd paint, and did not cause any deterioration of the high-quality alkyd paints at all. The effect of exposure to a low-pressure mercury arc lamp before exposure in the BS 3900 test was to accentuate the breakdown of alkyds, probably because of their high absorptivity for certain mercury UV lines. The Formica test, using fluorescent tubes, produced similar results to BS 3900 except for a weakness in its attack on rutile. Finally the accelerated natural sunlight machine EMMAQUA produced similar results to BS 3900, rather more quickly, except for a weakness in its attack on vinyl acetate emulsion paints.

There was a good audience and many questions, which Mr. Hipwood answered very competently. It is hoped that the material of this excellent lecture will be published in the *Journal.*

D. M. J.

Scottish

Fish oils, their composition, processing, and some industrial applications

The first technical meeting of the session was held in the Lorne Hotel, Sauchiehall Street, Glasgow, on Thursday 13 October at 6 p.m., when Mr. S. A. Reed delivered a lecture on " Fish Oils, their Composition, Processing, and Some Industrial Applications."

The amount of fish taken from the sea, said Mr. Reed, had more than doubled since 1948. The majority of this increase had been in the pelagic oily fish such as anchovy, herring, menhaden and pilchard, and had been accompanied, since 1959, by a significant reduction in the production of whale oil. Fish liver oils were also of interest, these coming mainly from cod and shark.

So far as composition was concerned, marine oils were characterised by C.20 and C.22 acids, the more highly unsaturated type containing four, five and six double bonds. Broadly, the components of these oils appeared to fall into two groups, i.e. saturates and monoenes at one end with, at the other, pentaenes and hexaenes, accompanied by small quantities of dienes, trienes and tetraenes.

Industrial application of these oils depended, in the main, on two alternative approaches—either by hydrogenation to eliminate unsaturation, as in the production of margarine, etc., or by the exploitation of the unsaturation itself. The latter field included outlets to the leather industry, the use of blown and sulphurised oils in lubrication, cutting oils and core oils. More recent potential developments lay in the direction of epoxidised fish oils as plasticisers and in combination with polyisocyanates. One of the most important outlets, however, was in the surface coatings and allied industries.

The traditional application of fish oils in surface coatings had been mainly as blown or stand oils, these having potential in industrial finishes, plasticisers for nitrocellulose, roof paints, cold cut enamels, rust proofing compounds, antifouling paints and low cost finishes. In the field of alkyd production, much work had previously been done on segregated pilchard oil. More recent investigation had, however, been concentrated on five specially refined grades of cod liver oil with free fatty acid levels below 0.2 per cent and iodine values in the range of 155 to 170.

Initial work on long oil pentaerythritol and medium oil glycerol alkyds indicated that they were, in many respects, comparable to the corresponding linseed resins, the main deficiencies being rather poorer colour on weathering, slightly lower hardness and poorer alkali resistance. Replacement of part of the phthalic anhydride by maleic anhydride resulted in improved hardness and drying time. The general indications were that alkyds based on cod liver oil could be of real interest, particularly in view of the favourable price differential which always prevailed in relation to linseed oil. The recognised weaknesses of cod liver oil alkyds, particularly slight residual surface drag and softness, might be tackled by such hardening media as rosin, phenolic or other resins ; by partial replacement with other fish oils ; and by improving the drying activity of the unsaturation present as, for instance, by conjugation.

Promising results had been obtained when using cod liver oils in the preparation of urethane oils. Such resins hardened, in the early stages, much more quickly than those based on linseed oil, but their ultimate hardness was lower, although they compared well with linseed pentaerythritol alkyds. Yellowing was more noticeable than for linseed-based urethane oils, while odour, although present, was generally not as great as that of some long oil soya alkyds.

Fish oils had been studied in styrene copolymer resins and in cyclopentadiene copolymers, the latter being favourably regarded in the USA.

After a discussion, in which Mr. McGuire, Mr. Hutchinson and Dr. Atherton participated, a vote of thanks was proposed by Mr. Burns.

Junior Section

Colour consciousness

The first meeting of the session took place in the Lorne Hotel, Glasgow, on 15 October.

Dr. F. M. Smith, of Geigy (UK) Ltd., delivered a lecture on " Colour Consciousness," which he extensively illustrated by slides. In this task he was ably supported by Mr. Malin, of Geigy (UK) Ltd., who acted as projectionist.

Dr. Smith showed how the source of light, the reflecting surface, and the eye and the brain play an important part in the interpretation of colour. He also managed to repeat the Land experiment when he produced a coloured print using only a black and white negative and a red filter.

R. F. H.

Reunion Dinner of Past Presidents, Past Honorary Officers, Founder Members and Council

The reunion dinner of Past Presidents, Past Honorary Officers, Founder Members and Council took place on 5 October at Wax Chandlers' Hall, London, preceded by a reception which enabled old friendships to be renewed. After proposing the loyal toast, the President welcomed the company and referred to those who could not attend, particularly to the Past Presidents, Dr. H. Houlston-Morgan, Mr. J. A. Frome Wilkinson and Mr. A. J. Gibson. In welcoming the Past Presidents present, he referred to Mr. W. E. Wornum as the most senior, and to Mr. L. O. Kekwick, Mr. C. W. A. Mundy, Mr. R. A. Bennett, Mr. P. J. Gay and Dr. J. E. Arnold.

Before reviewing the progress of the Association, he ventured some comments of a more personal nature about his own activities as President. During the last session he had attended all the Section annual dinners in this country, and he hoped to be present at the dinner of the newly-formed Irish Section in December. He had made many contacts and attended many meetings, but on some of the things he had wanted to do he had less to report than he had hoped ; in particular, he had been anxious to develop with the Officers a major consideration of Association activities, looking into the future with the conviction that the Association should be receptive when new challenges and new ideas came, as assuredly they would come, in a changing technical and industrial world. Other and more immediate problems had, however, claimed much attention, but the Officers had in fact made considerable progress in assembling views and comments. He was anxious to go much further with this " Forward Thinking " project, to which he had made reference on a number of occasions.

It was well known to those present that much thought, time and energy had been given to the Australian situation. It was a matter of considerable importance. He felt now, however, that with the Council's support that day for the Steering Committee's recommendations, a satisfactory procedure would emerge. There had been a valuable exchange of views with the Chairman of the Australian Federal Committee, Mr. Backous, on future developments ; indeed this was itself a part of " forward thinking " in changing circumstances.

The wide-ranging work of the Association demanded great activity by the permanent staff—the General Secretary, Mr. Hamblin, and his assistants, by whom the Association was so well served. But he stressed also the vital contribution made by voluntary work. " I can say," he said, " that through meetings, lengthy discussions, evening and week-end telephonings, and much else by way of personal contacts, the Officers have been worked very hard indeed, beyond their normal and specific duties ; and they have their daily work to do. I stress the contribution made by the Honorary Officers of OCCA, at home and abroad, which is very great and does not appear in the balance sheet."

Turning to the Progress Report on Association events, he recalled that last year the Chairmen of all Sections both in the UK and overseas and the Chairman of the Australian Federal Committee had received their badges of office, and there had been many indications of appreciation.

Top table (left to right) Mr. H. R. Wood (*Fdr. Mem.*), G. Copping (*Hon. Mem.*), Mr. W. E. Wornum (*Pres. 1940-44*), Dr. S. H. Bell (*Pres.*), Mr. F. Sowerbutts (*Pres. Des.*), Mr. R. P. L. Brittan (*Fdr. Mem.*), Mr. A. Z. Molteni (*Fdr. Mem.*)

Standing (left to right) Dr. J. E. Arnold (*Pres. 1963-65*), Mr. S. G. Tinsley (*Hon. Research and Dev. Officer*), Mr. A. R. H. Tawn (*Hon. Editor*), Mr. R. H. Hamblin (*Gen. Sec.*), Mr. R. P. Bell (*Assist. Sec.*), Dr. H. A. Hampton (*Pres. 1961-63*)

Seated facing camera right-hand table (left to right) Mr. L. O. Kekwick (*Pres.1951-53*), Mr. H. C. Worsdall (*El. Mem.*), Mr. A. Blenkinsop Mr. P. J. Gay (*Pres. 1959-61*), Mr. C. W. A. Mundy (*Pres. 1955-57*)

Seated right-hand table backs to camera (left to right) Mr. R. S. Law (*Hon. Sec. 1947-54*), Mr. D. J. Silsby (*Rep. Mid. Sec.*), Mr. J. A. L. Hawkey (*Rep. Wellington Sec.*), Mr. I. C. R. Bews (*Hon. Sec.*), Mr. N. H. Seymour (*El. Mem.*), Mr. C. H. Morris (*Chr. Midlands*), Mr. D. S. Newton (*Hon. Ed. 1962-65*)

Left-hand table facing camera (left to right) Mr. S. G. Clifford (*Hon. Treas., Hon. Sec. 1924-29*), Mr. T. Hedley-Barry (*Hon. Ed. 1924*), Mr. J. E. Pooley (*Rep. London*), Mr. L. A. Silver (*Rep. West Riding*), Mr. N. Cochrane (*Chr. West Riding*), Mr. L. W. Wynn (*Chr. Hull*), Mr. L. S. Fraser (*Hon. Treas.*), Mr. I. S. Hutchison (*Chr. Scottish*)

Left-hand side of left table (bottom to top) J. Lee (*Assist. Ed.*), Mr. A. A. Drummond (*Hon. Ed. 1929-31*), Dr. J. E. O. Cutter (*Hon. Res. and Dev. Off. 1941-43*), Mr. W. F. McDonnell (*Rep. Manchester*), Mr. I. S. Moll (*Chr. Manchester Section*), Mr. R. J. Woodbridge (*Chr. Bristol*), Mr. L. Tasker (*El. Mem.*)

Partly hidden Mr. V. C. Thompson (*Vice-Pres.*), Mr. N. A. Bennett (*Pres. 1957-59*)

During March 1966 the Association had held its Annual Exhibition at Alexandra Palace for the second time. This Exhibition had been opened by the Rt. Hon. the Earl of Kilmuir, President of the British Standards Institution and Chairman of the Plessey Co. Ltd. The Exhibition had been an unqualified success with an attendance of 11,500, many from overseas.

At the Annual General Meeting in June 1966, Mr. F. Sowerbutts was elected President Designate, after many years' service to the Association ; and Mr. A. S. Fraser, attached to the Scottish Section, was elected as the Honorary Treasurer.

An important decision, reached at the Annual General Meeting, was the confirmation of the resolution adopted at two earlier meetings of the Council regarding an increase in the membership subscription rates with effect from 1 January 1967. Following the Prime Minister's statement to the House of Commons in July on the Prices and Incomes Standstill for the remainder of 1966 and a period of restraint for the first half of 1967, the matter had been further considered by the Honorary Officers, and it had been recommended to, and agreed at, the Council meeting which preceded that evening's dinner that these increases in the membership subscription rates be postponed until 1 January 1968.

The AGM at the Hall of the Worshipful Company of Painter Stainers was followed by the Foundation Lecture by Dr. N. F. Astbury, Director of Research of the British Ceramic Research Association and Chairman of the Committee of Directors of Research Associations, under the title " Craft Against Craft Makes No Living," had proved very instructive and enjoyable. The Association had been pleased to welcome the Master and the Clerk of the Worshipful Company of Painter Stainers to the lecture and the dinner which followed, as well as five Past Presidents, three Founder Members and an Honorary Member. Dr. Houlston-Morgan (Senior Past President) had given the vote of thanks.

There had been considerable progress with the Paint Technology Manuals since the Past Presidents last met, and, by the time of the Exhibition in March, six volumes were available ; Volume IV (The Application of Surface Coatings) and Volume V (The Testing of Paints) became available last autumn, with Volume VI (Pigments, Dyestuffs and Lakes) being published early in 1966. It was hoped that Volume VII (Works Practice) would be published without undue delay.

The first OCCA Research Fellow (Dr. K. E. Lewis) had resigned from Nottingham University at the end of October 1965 and his successor (Mr. J. A. Wood) did not take up the project again until October 1966. In the meantime, however, a report on the work undertaken by Dr. Lewis, under the guidance of Dr. Parfitt, had appeared in the January issue of the *Journal*, and the first full paper in April. Dr. Parfitt would be presenting a further paper at the forthcoming Conference at Scarborough.

In conclusion, the President again referred to the future and matters which, he said, were so much in his mind. " I charge you all," he said, " to be forward looking for OCCA, and in your thinking, ingenious, in the best sense of that word." He stressed the importance of being always aware of the nation-wide and international character and responsibilities of OCCA, looking firmly into the future, receptive to new ideas, with readiness to meet new calls upon energies and resources ; being neither comfortable in very considerable past achievements nor parochial in attitudes. The aim must be to achieve to the full the aims and objects of the Association in a changing world.

Following the dinner, the President gave a highly informative and stimulating talk on Holland and its engineering activities in flood control and land reclamation. This was illustrated by slides prepared by the President, some of which had been obtained during a recent journey to that country for the VIIIth FATIPEC Congress at Scheviningen.

The senior Past President present, Mr. W. E. Wornum, proposed a vote of thanks, and in doing so paid tribute to the statesmanship, wide interests and broad thinking of the President which he had demonstrated that evening as throughout his term of office. He warmly welcomed the election of Mr. F. Sowerbutts as President Designate, a man who had those high qualities which the Association required of its Presidents.

Scarborough Conference, 20-24 June 1967

The Conference programme and application forms are now being prepared for despatch to members at the beginning of 1967, but non-members and visitors from abroad who would like to attend this important Conference (the biographies of the lecturers and details of the papers to be presented appeared in the October and November issues respectively) are asked to send their names to the General Secretary, at the address on the front cover, so that application forms may be despatched to them at the same time as they are sent to members.

At its meeting in October the Council fixed the registration fees at £8 for members, £5 for wives and £12 for non-members, and, once again, in order to encourage Junior Members, decided that they may attend on payment of half the fee for members.

There will be **four** technical sessions on this occasion under the general title " Interfacial Behaviour," and it is also planned to continue with the workshop sessions on the Friday afternoon, which were first introduced so successfully at the Torquay Conference in 1965.

Hull Section

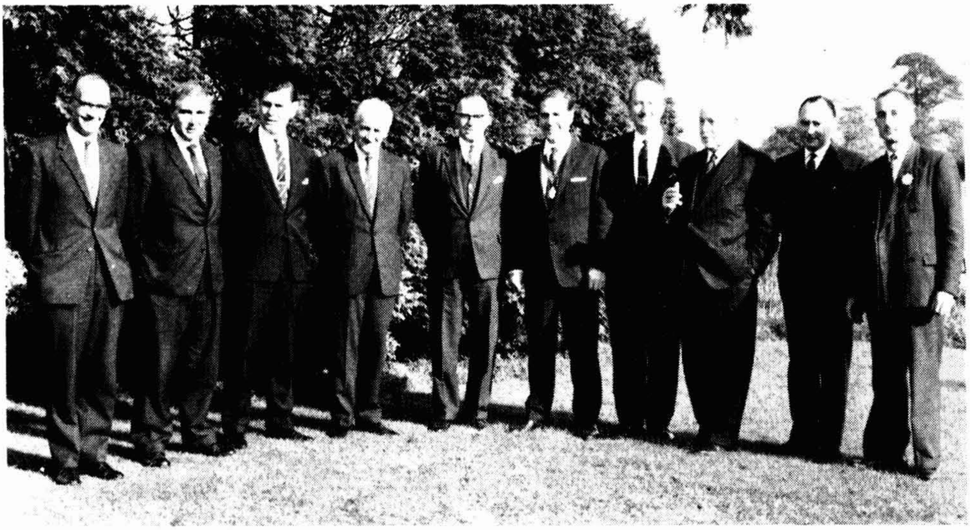
The Symposium which had been provisionally arranged for April 1967 has been postponed. It is now hoped that it will take place in the Spring of 1968 and further details will be given in later issues of the *Journal*.

Midlands Section

" Solvent or Solventless ? " Symposium

The Midlands Section of the Oil and Colour Chemists' Association held its second day Symposium on 20 October at The Regency Club, Solihull, Warwickshire. The Section Chairman, Mr. C. H. Morris welcomed the 120 delegates and said that the subject chosen for the symposium was a topical one which provided scope for much discussion. He then invited Mr. R. D. Calvert, the immediate past chairman of the section to preside at the morning session.

The first speaker, Mr. B. J. Wilmin of Rolls-Royce Ltd., said that paint requirements were influenced by the specialist nature of Rolls-Royce cars. The first stage in transforming the composite metal body shell involved rectification with lead solders. Solventless fillers had proved very useful in conjunction with solder but could not entirely replace



(Left to right) R. D. Calvert (Immediate Past Chairman, Midlands Section), J. Smith (M.O.D. Navy Department), V. A. Moore (Pinchin, Johnson & Associates), F. G. Dunkley (British Railways, Immediate Past Chairman, Trent Valley Branch, Midlands Section), Dr. S. H. Bell (President), C. H. Morris (Chairman, Midlands Section), B. J. Wilmin (Rolls-Royce Ltd.), F. Meyer (Sterling Varnish Co. Ltd.), N. H. Seymour (a Past Chairman of the Midlands Section), D. J. Silsby (Hon. Secretary, Midlands Section)

solders. The body was then cleaned, phosphatised, rinsed with deionised water and an acid etch primer was applied. It was then treated with a water soluble dip-primer. Rolls-Royce Ltd. had used water soluble primers for five years with very satisfactory results. The advantages were good tank stability, good thickness within boxed sections, less solvent wash and freedom from runs. The stoving temperature of 335°F was critical, giving an adequate cure below the flow point of lead solder. Water thinned fillers had been examined but they lacked good rubbing properties. Subsequent treatment with fillers, a nitro-cellulose primer-sealer, nitro-cellulose stoppers and colour coats of nitro-cellulose modified with alkyd or acrylic all made use of conventional solvent techniques. Some of the inadequacies of contemporary coatings were the amount of polishing required in service, sensitivity to intercoat adhesion, and colour matching. Future trends would have to develop in step with application methods. One promising method was the use of irradiation to polymerise without needing heat or catalysts.

The next speaker was Mr. F. G. Dunkley of British Rail. After classifying paints into emulsions, solvent thinned (using either water or organic solvents) and solventless he said that he thought that it would be many years before a real choice between solvent and solventless coatings would be available. The function of solvents was to facilitate application and a good solvent permitted orientation of polymers and influenced wetting of the substrate. British Rail regarded low toxicity and minimum fire hazard as fundamental requirements. For coaches they had selected and developed a structured vinyl-toluenated alkyd thinned with SPB6. For waggons where dirt retention and cleaning were less important, emulsion paints were used. Experience on the continent and in UK showed them to have good durability on steel as well as on wood. Low viscosity solventless paints for brush application had good chemical resistance and durability but impact resistance was unsatisfactory. Powder coating by fluidised bed techniques was used on some fittings. An example was carriage handles, which at present were non ferrous. Powder coating would permit the use of steel.

Mr. F. Meyer of The Sterling Varnish Co. Ltd. then spoke on Electrical Insulating Varnishes and Compounds. He said that the requirements for insulating varnishes were rather different from those for surface coatings, the varnish having to gel in depth. Its functions were : to cement together, to provide water resistance and protect against mechanical damage and chemical atmospheres. Water soluble systems had not found acceptance because of difficulties with drainage, bubbling and poor gel characteristics. It did not seem rational to use a water-borne system after drying to remove water. After reviewing the history of development of impregnating varnishes of the solvent type with slides of different processing techniques the speaker said that thermal endurance influenced the selection of varnish types. Oil modified phenolics would satisfy Class B, isophthalic polyesters would meet Class F whilst Class H required silicone or imide resins. The use of solventless coatings was being examined. One method was to preheat the component and dip in a tank of resin but this raised problems of tank stability. Other methods of putting the varnish where it was wanted included flooding, rolling and drip feed. The application of 2 pack solventless coatings by drip feed had many advantages. Epoxy powder coatings had been used for cores in America and for small components and total encapulation of small components. The development of new materials depended very much on the development of suitable application plant.

For the afternoon session Mr. C. H. Morris took the chair and introduced Mr. J. Smith of the Central Dockyard Laboratory. Mr. Smith said that as far as painting naval ships was concerned solvents were a necessary evil. Limitations of inflammability, odour, toxicity, solvent retention and speed of drying were increased and magnified by conditions on warships. The most suitable solvent was white spirit and this restricted paints to mainly alkyd and oleoresins. Emulsions had been examined but did not give the required protection to metal. Water thinned alkali zinc silicate had been used in fuel tanks with excellent results. Catalytic epoxy solventless coatings had been used in areas where abrasion was a problem but they lacked flexibility and were unacceptable for fuel tanks. Solvent-free coal tar epoxy resins were potentially useful if the right equipment could be developed.

The final speaker was Mr. V. A. Moore of Pinchin Johnson and Associates Ltd., who spoke on methods of application for finishing domestic appliances and office equipment. The speaker pointed out that a paint with 50% solids by weight could have 65% solvent by volume, and this solvent did not contribute to coverage. For dipping application, solvents were essential to obtain flow and the solvents should be balanced with respect to surface tension. For spraying, there were many methods and it was not practicable to make resins for each method. The use of solvents gave room to manoeuvre and to build systems to suit the method. Electrostatic spraying required solvents and each plant had its idiosyncracies. With office equipment, 40 per cent was dipped and the balance sprayed by various methods.

A lively discussion period followed. The panel of speakers ably dealt with questions about various methods of application. Mr. Dunkley said that solventless paints did not give flow or sufficient control of thickness. The effectiveness of a coating was related to its thinnest point and continuity could not be ensured with one coating. Mr. Smith pointed out that the application of a thick film was not necessarily cheaper than several thin films. Mr. Moore said that solvents could be regarded as expendable tools and their cost was very little. Mr. Sharp pointed out that with vinyls the cost of solvents could be 50 per cent of the paint. In metal coating, where as many as 10 curing cycles were needed, the presence of solvents increased heating and cooling costs enormously. Mr. Wilmin said that this was an application where nuclear irradiation could help.

Dr. S. H. Bell. in proposing a vote of thanks, said that the theme of the symposium was an example of the " Forward Thinking " which he had promoted during his term as President. He congratulated the speakers and the officers and committee of Midlands Section.

Scottish Section

Junior Section

Visit to BTP

In conjunction with the present project in " Paints Through the Ages," some of the members of the Student and Senior Sections paid a visit to British Titan Products' works at Billingham.

The first place visited was the weathering station at Carlton, where members saw some of the more modern methods of correlating weather conditions with form and performance of paint systems. Later, the development laboratories were visited where members were once again impressed by the large number of laboratories and the more advanced laboratory techniques used by BTP in overcoming present day chemical problems.

The visit was voted an outstanding success both academically and socially, and our thanks are due to the members of BTP's staff who kindly gave up their free time to provide the members with a memorable visit.

South Australian Section

The four Past Chairmen who attended (left to right) : A. E. Allen (1962-63), D. R. Turnbull (1951-52-53), H. D. Bruce (1964-65), W. F. Churcher (1958-59)

Past Chairmen entertained

On the night of Friday 14 October, at the Earl of Zetland Hotel, Adelaide, the present South Australian Section Committee entertained their Past Chairmen.

Four Past Chairmen were in attendance, namely Messrs. D. R. Turnbull, W. F. Churcher, A. E. Allen and H. D. Bruce, and during the dinner Past Chairmen's badges were presented by reigning Chairman Mr. M. D. Gilham.

Chairman M. D. Gilham presenting Past Chairman's Badge to Foundation Chairman D. R. Turnbull

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Annual Meeting of the Norwegian Society for Paint and Varnish Technology in Bergen on 28 and 29 October 1966

The function commenced with a meeting in the Chianti Restaurant in Bergen. After the general reports on finance and similar matters had been delivered by the members of the Society, Dr. A. Lowe of ICI gave a lecture entitled " The Development of Urethanes and Urethane-Ureas as Surface Coating Compositions." This consisted of a general background and survey of the polyurethane types available. In the ensuing discussion, contributions were received from members of the Norwegian Society and Mr. A. C. Jolly of Beck Koller. After lunch, Mr. A. Undershaug of Fleischers Kjeniske Fabrikker A/S spoke about " Peeling and Blistering of Paints on Wooden Houses." The discussion which followed aimed at trying to establish on whom the responsibility should fall, whether it be the architect, the paint chemist or the master painter. Several official representatives took part in the proceedings and a good deal of the points made found their way into a sizeable article in one of the national papers.

In the evening of the same day, the annual dinner was held at the old and partially reconstructed, Hakonshallen. This building dated back beyond the 12th century and was designed by the same architect responsible for Westminster Abbey. Permission was given for the function to be held in this building by the Mayor of Bergen in view of the fact that the conference was of an international nature due to the presence of Swedish and Icelandic guests, as well as the two from Britain, mentioned above. The evening was marked by an astonishing spirit of disarming friendliness and genuine cordiality. The reception, the meal and the entertainment afterwards, were extremely well organised.

On the following morning, Saturday 29 October, the majority of those present managed to visit the offices and works of the Bergens Tidende, the third largest newspaper in Norway. This visit was most interesting and showed that the equipment and processes being used were right up to date.

It would be impossible in such a short report to express the charm, good humour and unpretentiousness of the Norwegian hosts. The function will long remain in the memories of the two British guests.

The 5th Congress of the Federation of Scandinavian Paint and Varnish Technicians

The 5th Congress of the Federation of Scandinavian Paint and Varnish Technicians will take place at Gothenburg from 18 to 20 September 1967. Further information may be obtained from the secretary of the Congress, Mr. Leif Augustsson, Box 55, Molndal, Sweden.

News of members

Mr. K. J. Hedgecock, an associate member attached to the London Section, has been appointed Director of Rex Campbell & Co. Ltd. He joined the firm in 1942 and for the last ten years has acted as Technical Sales Manager with particular reference to chemical raw materials used in the paint and plastics industry.

Mr. L. Tasker, an ordinary member of the Bristol Section, has been appointed Technical Service Manager of the new Laporte-Synres Company.

Mr. Tasker, who has been an extremely active member of the Bristol Section, was formerly joint Hon. Publication Secretary and Research Liaison Officer, and became an elected member of Council at this year's Annual General Meeting.

Mr. K. O'Hara, an ordinary member of the Bristol Section, has taken up an appointment with the Glidden Company of Cleveland, Ohio. He was formerly employed in the Technical Service Department of British Resin Products, Barry.

Dr. J. A. Wood

Dr. J. A. Wood has been appointed to the OCCA Post Doctoral Research Fellowship at Nottingham University. He succeeds Dr. K. E. Lewis, who recently resigned.

Obituary

C. Rossall Pye

" After a long illness—patiently and bravely born "—how often is this phrase used as an epitaph ?

If such an expression were used about Rossall Pye it would be an understatement. How many members of the Association knew how ill he had been over the past three years ? He was not the type to complain about his health—in fact he was reticent to discuss it at all—he just carried on and did a first-class job however tired and desperately ill he felt ; for this reason even his intimates in the London Section Committee had little idea how gravely ill he was and what a personal sacrifice it was for him to carry on with his duties. It was only his will-power and North Country tenacity which enabled him to behave as if he were a fit man.

C. R. Pye was born in 1913 and was educated at the Lancaster Grammar School, later taking a London external degree, followed by the A.R.I.C. and F.R.I.C. in later years.

All his life he worked in " the industry," his first post being with James Williamson & Son Ltd., then at Mitcham Works Ltd., followed by a long period with Indestructible Paint Co. Ltd. At the time of his death he was chief chemist at Flexitainers Ltd. at Stevenage.

He was a born committee man and had given long and valued service to the London Section Committee, starting as an elective member in the late 'forties. From 1955-59 he was Hon. Secretary of the Section, then taking on the important duty of Hon. Publications Secretary. Perhaps he will best be remembered for his work in that capacity when he was responsible for the write-up of the Technical Exhibition—this has been described in this country and abroad as a magnificent piece of technical journalism—praise was then well deserved as he managed to give an accurate technical account which was at the same time very readable.

In 1965 he became Chairman of the Section and he also served on Council until his death.

Rossall Pye will be missed by all who knew him ; he was one of those people, alas, so rare today, who, when they take on a committee job, put their heart and soul into it—in his case he gave something else—his accuracy, ability and integrity. He leaves a wife and two daughters, to whom our condolences are extended in their great loss.

H. C. W.

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

COONEY, DENIS MICHAEL, Jordan Chemical Works (A'Asia) Pty. Ltd., Sir Thomas Mitchell Road, Chester Hill, New South Wales, Australia. (*New South Wales*)

HEALEY, TERENCE JOHN, 92 White Street, Leichhardt, New South Wales, Australia. (*New South Wales*)

HUDSON, RUPERT OGMAN, Ferro Corp. (Aust.) Pty. Ltd., 16 Bermill Street, Rockdale, New South Wales, Australia. (*New South Wales*)

JACKSON, WILBERT ANDREW, B.SC., PO Box 16, Granville, New South Wales, Australia. (*New South Wales*)

MATTHEWS, JOSEPH, B.SC., 12 Meridian Street, Eastlakes, New South Wales, Australia. (*New South Wales*)

NESBITT, BRUCE ARTHUR, Esso Standard Oil (Aust.) Ltd., ADC House, North Sydney, New South Wales, Australia. (*New South Wales*)

WERNER, RICHARD S., Johns-Manville International Corp., PO Box 388, Crows Nest, New South Wales, Australia. (*New South Wales*)

Junior Members

DICK, JOHN LESTER, 108 Clarendon Street, Ballarat, Victoria, Australia. (*Victorian*)

Forthcoming Events

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

Thursday 1 December

Newcastle Section. " Trends in the Building Industry," by Mr. P. B. L. Keate (Hawthorn Leslie Buildings Ltd.). Joint meeting with the local branch of the Federation of Master Painters and Decorators, to be held at Royal Turks Head Hotel, Grey Street, Newcastle upon Tyne, at 6.30 p.m.

Victorian Section. Annual Dinner, to be held at Melbourne University, Union House, Parkville.

Monday 5 December

Hull Section. " Tall Oil," by Dr. M. R. Porter. Joint meeting with SCI Oil and Fats Group, to be held at Royal Station Hotel, Hull, at 7 p.m.

Thursday 8 December

Irish Section. Annual Dinner/Dance, to be held at South County Hotel, Dublin.

London Section. " Metallo-organic Primer Coatings," by Mr. R. N. Faulkner (Paint Research Station), to be held at Physics Department, Imperial College of Science and Technology, South Kensington, London, S.W.7, at 6.30 p.m.

Scottish Section. " Modern Commercial Management," by Mr. M. B. Johnstone, to be held at Lorne Hotel, Sauchiehall Street, Glasgow, at 6 p.m.

Friday 9 December

Manchester Section. " Various Aspects of the Preparation and Testing of Recently Developed Water Soluble Epoxy Esters," by Mr. J. van Westrenen and Mr. L. A. Tysall (Shell International Research Ltd.), to be held at Strand Hotel, Brunswick Street, Liverpool, at 6.30 p.m.

Saturday 10 December

Scottish Section—Student Group. " Works Management," by Mr. J. Louden, to be held at Lorne Hotel, Sauchiehall Street, Glasgow, at 10 a.m.

Monday 12 December

London Section—Southern Branch. " Car Finishes," by Mr. H. A. Shelton, to be held at Royal Hotel, Southampton, at 7.30 p.m.

Tuesday 13 December

West Riding Section. " Protection by Patents and Trademarks," by Dr. Gansser, to be held at Great Northern Hotel, Leeds, at 7.30 p.m.

Wednesday 14 December

Scottish Section—Eastern Branch. " Recent Developments in the Use of Organic Titanium Compounds," by Mr. R. H. Stanley and Dr. G. H. J. Neville (Titanium Intermediates Ltd.), to be held at North British Hotel, Princes Street, Edinburgh, at 7.30 p.m.

Thursday 15 December

London Section—Thames Valley Branch. " Copolymers with Vinyl Esters of Branched Carboxylic Acids in Thermosetting Systems," by Mr. W. H. M. Nieuwenhuis, to be held at Royal White Hart Hotel, Beaconsfield, Bucks, at 7 p.m.

Monday 2 January 1967

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 Mr. F. G. Dunkley, to be held at Royal Turks Head Hotel, Grey Street, Newcastle upon Tyne, at 6.30 p.m.

Friday 6 January

Bristol Section. " Measurement of Colour by Instrumentation," by Mr. 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 Mr. 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 Mr. M. H. M. Arnold, to be held at Manchester Literary and Philosophical Society, at 6.30 p.m.

Scottish Section. Annual Dinner/Dance, to be held at Central Hotel, Glasgow, at 6.30 p.m.

Saturday 14 January

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

Wednesday 18 January

London Section. " Evaluation for Electrodeposition of Recently Developed Water Soluble Epoxy Esters," by Mr. L. A. Tysall and Mr. 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 Mr. 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, at 7 p.m.

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 Mr. 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 Mr. 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 Mr. 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.

Monday 13 February

Victorian Section. " Theoretical Approach to Contact Leaching of Anti-fouling Paints," by Mr. F. Marson, to be held at Union House, Melbourne University, Parkville.

Thursday 16 February

New South Wales Section. Annual General Meeting.

Next month's issue

The following papers have been accepted for publication by the Honorary Editor and these are expected to appear in the January issue :

"Regulation of particle size of vinyl acetate/'VeoVa' 911 copolymer latices," *G. C. Vegter and E. P. Grommers.*

" Water soluble colloids in emulsion paints with special reference to cellulose ethers," *A. Revely and H. Bates.*

" The accuracy of colour measurement," *J. M. Adams.*

" Paint storage stability in relation to pigment surface characteristics," *J. Taylor.*

" Some recent advances in thermosetting acrylic resins," *P. V. Robinson and K. Winter.*

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Key :

(C)—Correspondence
(D)—Discussion
(E)—Editorial and Comment
(N)—Notes and News
(R)—Reviews
(S)—Section Proceedings
(T)—Transactions and Communications

Authors

Subjects

INTRODUCTION TO paint TECHNOLOGY

SECOND EDITION NOW AVAILABLE

Revised by A. A. Drummond, M.SC., A.R.I.C., under the Editorship of I. C. R. Bews, B.SC., A.R.I.C., in consultation with T. E. Johnson, A.M.C.T., F.R.I.C.

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."

The second edition will prove (as did the first edition) of immense value not only to young entrants into the industries but also to technical representatives and others desiring a basic knowledge of the principles and techniques of the Paint and Allied Industries.

LIST OF CONTENTS

Origins and development — Decorative paints — Oils — Industrial finishes and techniques — Natural and synthetic resins — Paint manufacture and hazards — Oleoresinous alkyd and cellulose media — Paint testing — Pigments — Common defects

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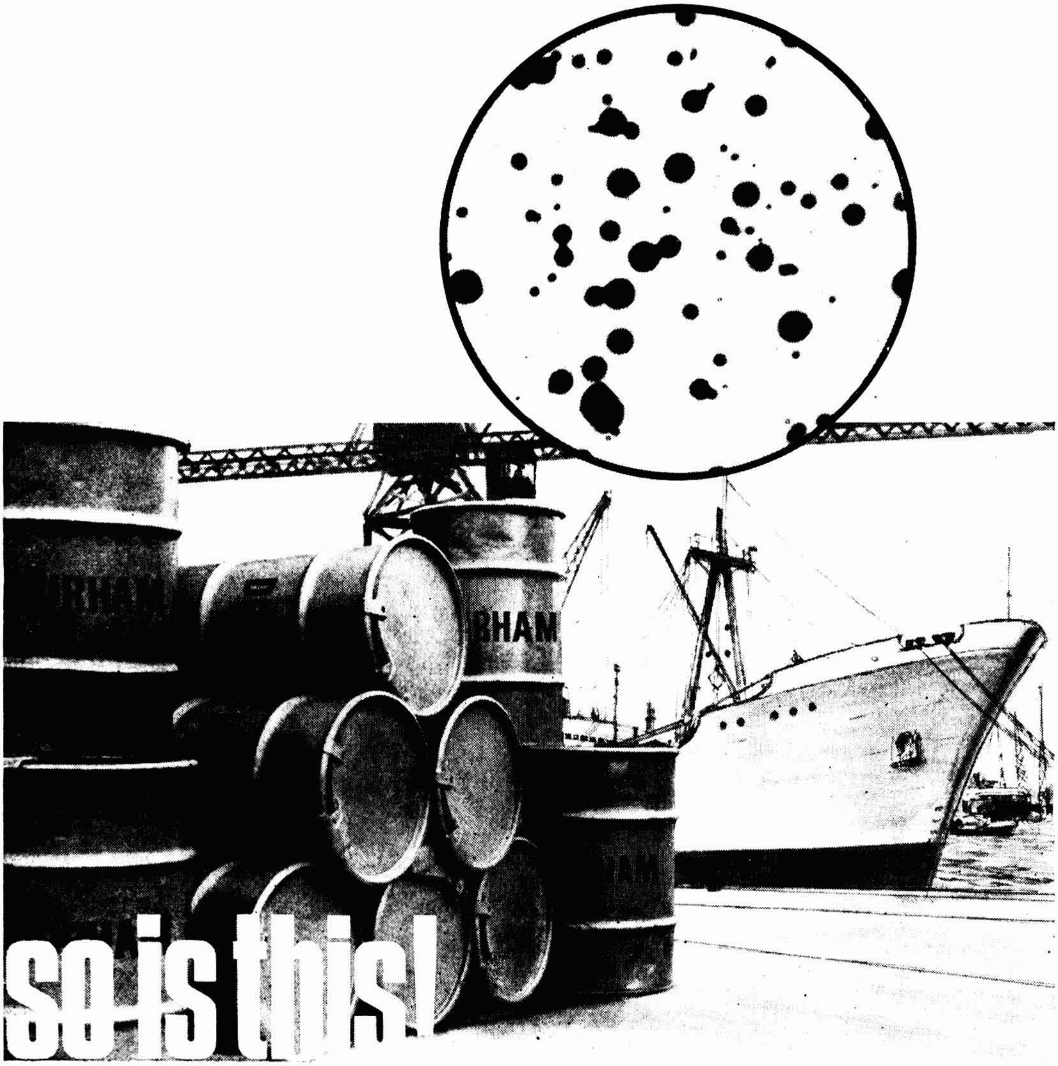
The book contains 186 pages including 10 line diagrams, 8 photographs of common paint defects, and comprehensive index. Copies can be obtained from the Oil and Colour Chemists' Association, Wax Chandlers' Hall, Gresham Street, London E.C.2, price 15s. (post free).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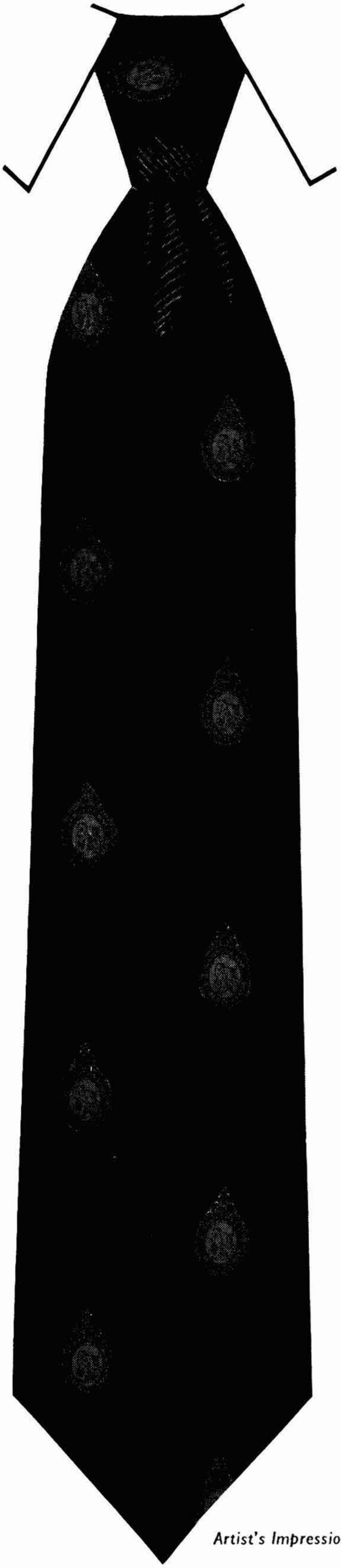

Artist's Impression

O.C.C.A. TIE

The Council has authorised the production of an exclusive tie for Members of the Oil & Colour Chemists' Association. The Association's insignia is woven in red and gold silk on a dark blue terylene background.

The tie is sold only to Members of the Association for **20s.** (sterling) post free. If Members resident outside the continent of Europe wish the tie to be sent by airmail **5s.** (sterling) should be added to cover postage and insurance. The tie is available only from :

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As a Member of the Association please accept my order for an O.C.C.A. Tie. Remittance to the value of **20s.** (sterling) (if required to be sent by **airmail** to addresses outside Europe, please add **5s.** (sterling) to cover postage and insurance) is enclosed.

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yes ☐

no ☐

2 *wear hideous ties provided by distant relatives?*

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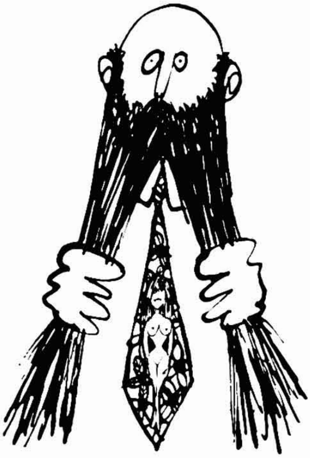
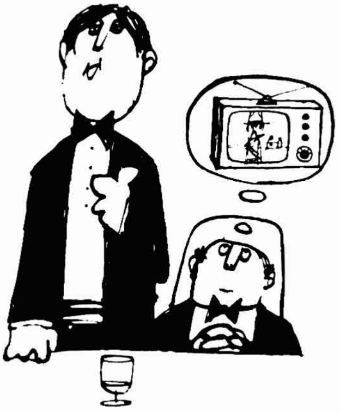
no ☐



3 *attend the Old Boys' Reunion when you could be watching television?*

yes ☐

no ☐



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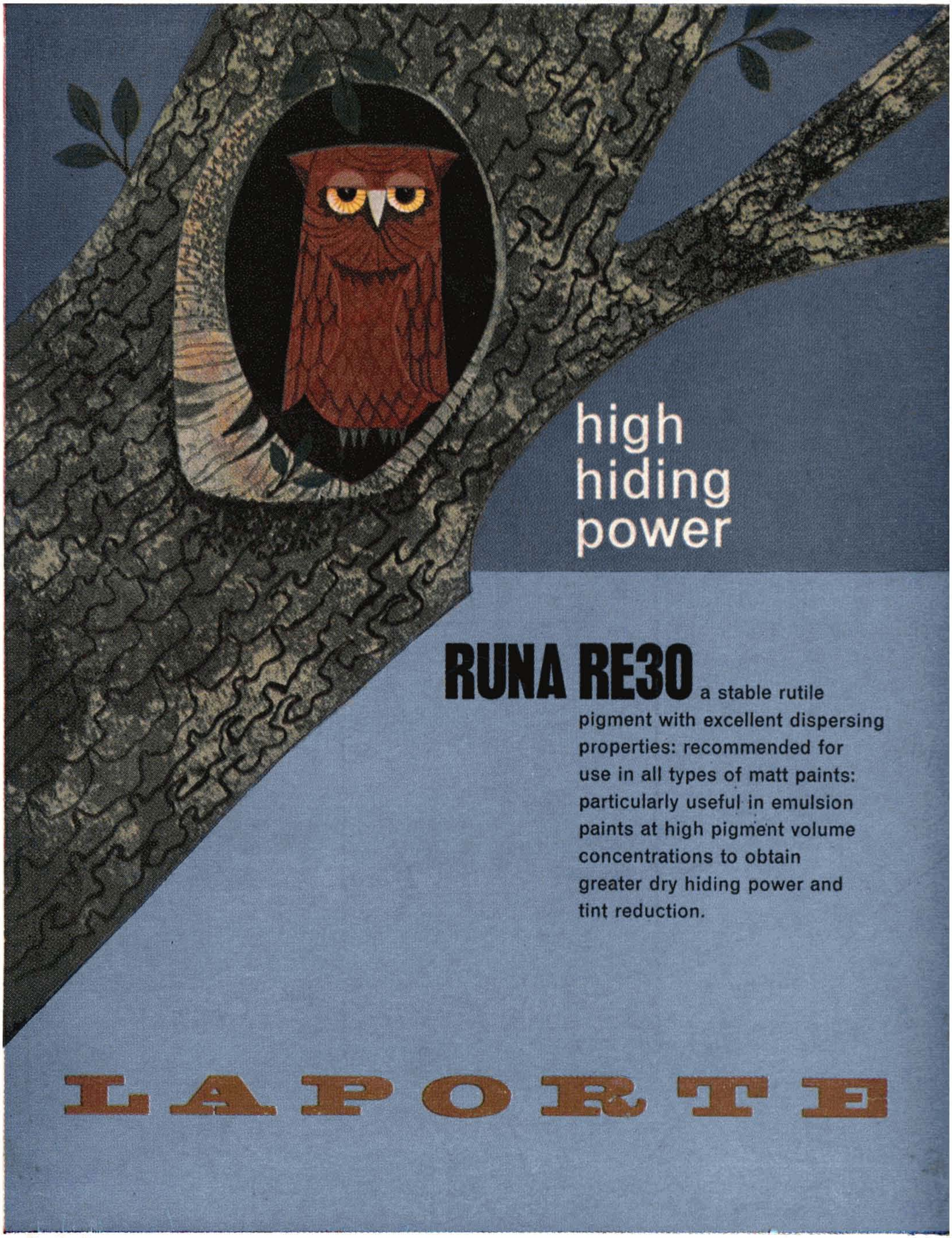

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