

JOURNAL

OF THE

OIL AND COLOUR CHEMISTS' ASSOCIATION



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April 1967

Radiochemical coating analysis

Vinyl and acrylic modified alkyds: Part VI
The formulation of a glossy water soluble
automotive enamel

Contact leaching antifouling paints

Adhesion as a factor in the performance
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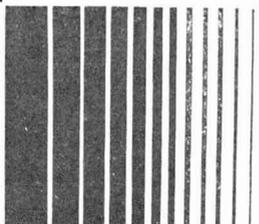
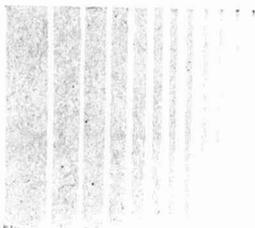
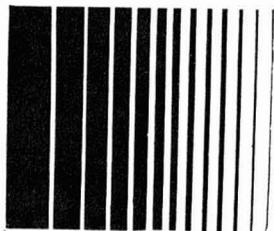
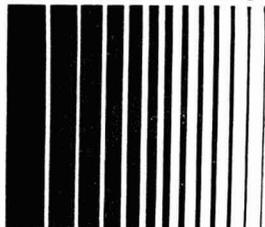
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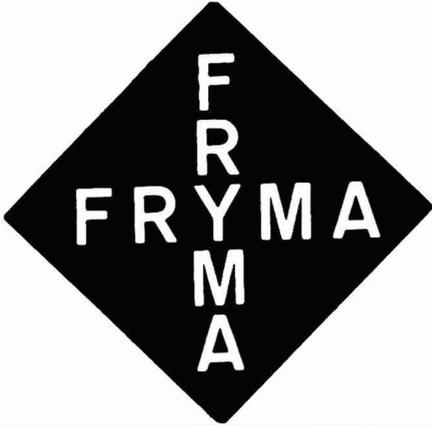
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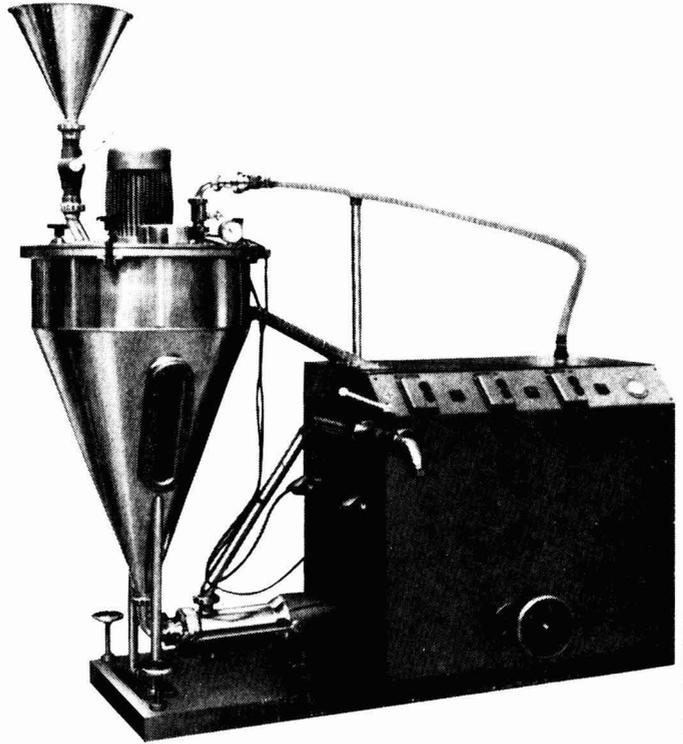
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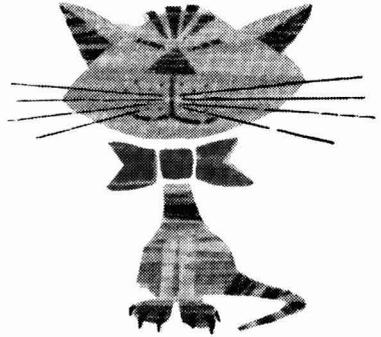
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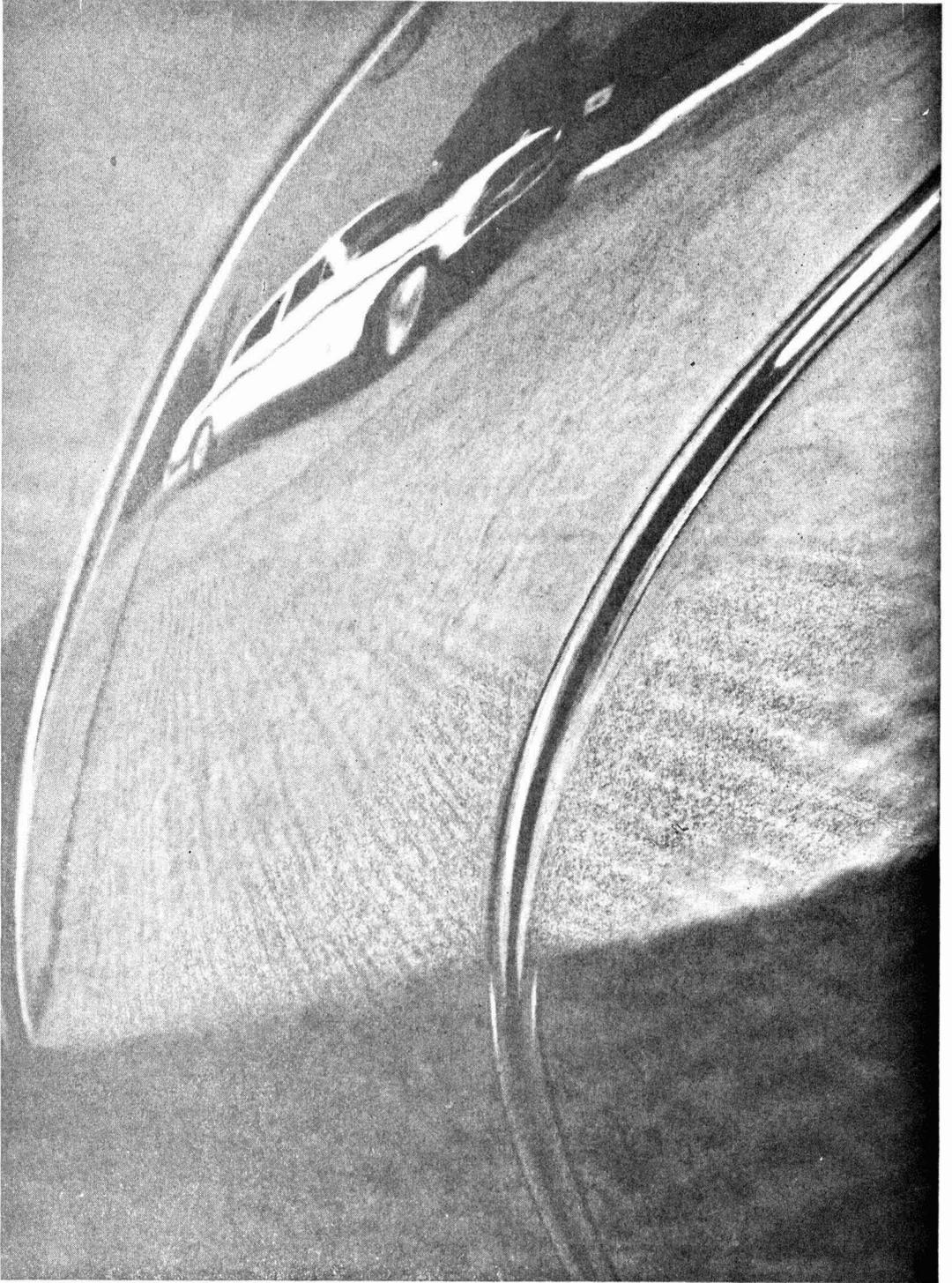
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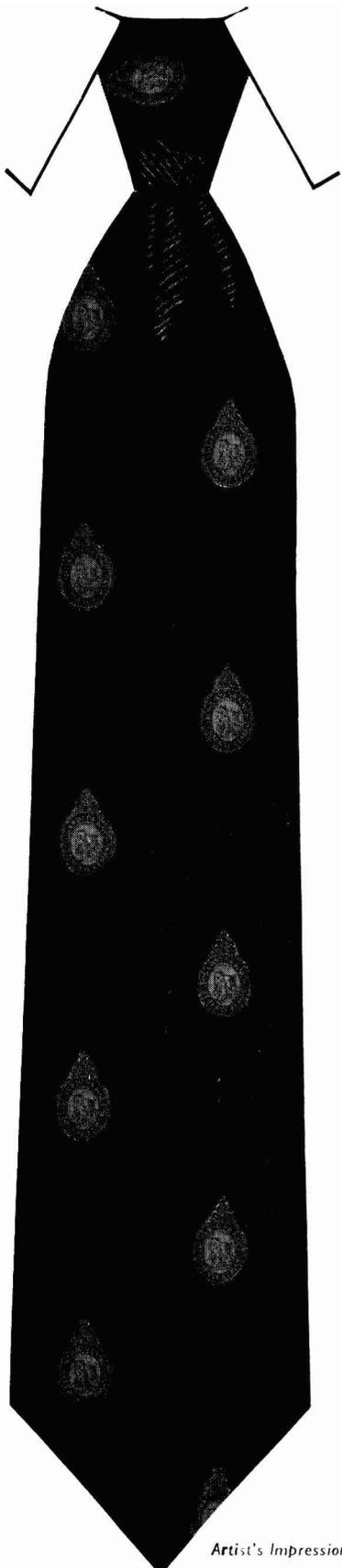
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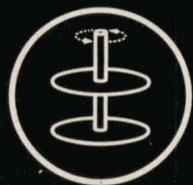
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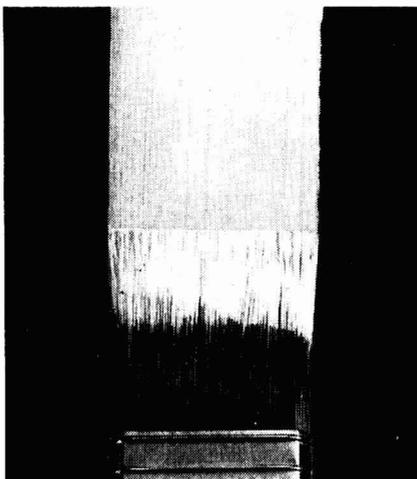
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Transactions and Communications

Radiochemical coating analysis

By G. R. Coe

Department of Chemistry, University of Southern Mississippi, Hattiesburg, Mississippi, 39401

Summary

The literature of radiochemical techniques of coating analysis is reviewed and many of the current applications are discussed. The applications include measurement of the thickness, uniformity and continuity of films; adsorption on metal surfaces; nuclear level gauging, determination of wear resistance and optimum mixing time. Mechanistic investigations of drier action, ester interchange in oils and varnishes, the formation of per-acids, and polymerisation have proved to be amenable to this technique. Other applications that are reviewed include film formation and corrosion.

L'analyse de revêtements par des techniques de radiochimie

Résumé

On passe en revue la littérature à propos de l'analyse de revêtements par des techniques de radiochimie, et l'on discute beaucoup d'usages courants. Ces usages comprennent; la mesure de l'épaisseur, l'uniformité et la continuité de feuil; l'adsorption aux surfaces métalliques; le jaugeage du degré d'aplatissement de feuil au moyen des techniques nucléaires; la détermination de résistance à l'usure et durée optimale de malaxation.

Investigations au point de vue des mécanismes de l'action de siccatifs, de l'échange de groupements esters en huiles et vernis, de la formation de per-acides et de polymérisation ont été effectuées par cette technique. On mentionne des autres usages notamment, la formation de feuil et corrosion.

Radiochemische Analyse von Anstrichmitteln

Zusammenfassung

Die Literatur radiochemischer Techniken für die Analyse von Oberflächenbeschichtungsmitteln wird einer kritischen Prüfung unterzogen, und viele der laufend angewandten Methoden werden besprochen. Die Anwendungsgebiete schliessen das Messen der Filmdicke, Gleichförmigkeit und Kontinuität von Filmen ein; Adsorption durch Metalloberflächen; Kallibrierung des Kernniveaus; Bestimmung der Haltbarkeit und günstigsten Mischdauer. Mechanistische Untersuchungen über das Verhalten von Trockenstoffen, Esteraustausch in Ölen und Lacken, die Bildung von Persäuren, sowie Polymerisation haben sich für diese Technik geeignet erwiesen. Zu den sonstigen besprochenen Anwendungsgebieten gehören Filmbildung und Korrosion.

Анализ радиохимических покрытий

Резюме

Дается обзор литературы относительно радиохимических процессов в анализе покрытий и обсуждается ряд современных применений. Применения включают измерение толщины, однородности и сплошности пленок; адсорбцию на металлических поверхностях; оценку ядерного уровня, определение сопротивления износу и оптимальное время смешивания. Исследования механизма сушительного действия, взаимная смена эфиров в маслах и лаках, образование «пер» – кислот и полимеризация – все подчиняются этой технике. Образование пленок и коррозия также включены в этом обзоре.

Introduction

Radioactivity has been introduced into the field of organic coatings mainly since the early 1950's. Prior to that time, there were only a few isolated reports of this technique, which has developed into one of the most sensitive and useful methods available. Early in this period many research groups began to investigate this technique and consequently a large number of papers were published in this "new" field. The areas of film continuity and uniformity, as well as film thickness, received the greatest amount of attention. While the determination of elements by means of their natural radioactivity has been used extensively, the method is limited to those naturally occurring radioactive elements which have an experimentally detectable level of activity. This limitation may be greatly reduced by the technique of activation analysis, although the method has not been applied to the coatings field. In 1934, Curie and Joliot¹ showed that radioactivity could be induced in light elements upon bombardment with alpha particles while, in the same year, Fermi² used thermal neutrons to show that a large number of elements could be made radioactive and that this induced radioactivity could be used as a method of analysis. This technique of activation analysis consists of the determination of the amount of an element present in a sample by measuring the activity induced in the element upon bombardment with a suitable particle.

Several excellent reviews³⁻⁵ and previews of the uses of radiochemistry appeared in the early 1950's, but the industry has not taken full advantage of this technique. This possibly may be due to the relatively high initial cost as compared to some other techniques. The outstanding advantages of this tool are high sensitivity, non-destruction of the sample, and rapidity.

It is interesting to note that the development of radioisotopic techniques in the technology of protective coatings has closely paralleled many of the paths projected by the investigators of the early 1950's.

One of the oldest and most popular uses of these techniques is the measurement of film thickness, continuity and uniformity. Both beta and gamma ray emission have been used extensively in a number of experimental modifications. Autoradiography has been successfully used. Here, a trace amount of an unstable nuclide, chemically identical with other atoms in the coating, is introduced and the coating placed next to a photographic plate or film coated with a special emulsion. These emulsions are known as nuclear emulsions, and differ from the usual light sensitive films only in grain size and concentration of the silver halide. This technique is particularly valuable in the measurement of the uniformity of a coating. The intensity of the penetrating radiation is modified as it passes through the material being tested. Pinholes and breaks as well as non-uniformity of coating thickness will be detected as either over or under exposed areas on the film. This method offers the advantage of being able to examine the coating without introducing additional variables by the removal of the organic coating, handling, etc.; and provides a permanent record of the location of any internal defects.

An alternative to this procedure is to prepare a radioactive surface, possibly by electrodeposition, and measure the amount and uniformity of radiation after passing through a coating treatment. Utilising this modification, a radioactive surface can be used repeatedly after cleaning. Electrodeposition, vacuum

evaporation and heating are the usual methods of preparing a radioactive surface⁶⁻⁹.

The major disadvantages of autoradiography are that it is relatively slow and that complex shapes are difficult to examine. Autoradiographic methods are not suited for detecting very small flaws in large, complex structures, but they do yield good results for less complicated units¹⁰. Many specific applications of autoradiography have been reported. The detection of hidden defects in plywood, fibreboard and wood-particle boards, and the measurement of the uniformity of the adhesive layers¹¹ has been accomplished by measurement of the absorption of beta-rays from Tl-204 and P-32 as well as S-35, Ca-45 and W-185. Because of their lower energy of radiation, the sulphur, calcium and tungsten isotopes are preferred. The method makes it possible to detect defects in the binder distribution and density variations due to faulty pressing or to the raw material itself.

Rushman⁴ has examined the distribution of phosphorus on a metal surface which had been previously treated with a primer containing free phosphoric acid. The phosphoric acid was labelled with radioactive P-32 and, after stripping the primer from the panel, an autoradiograph was made. The beta emission from the P-32 located the position of the original phosphoric acid present. The presence of the residual activity showed that some of the phosphoric acid had reacted with the panel to give an insoluble layer.

Autoradiography also has been used to investigate monomolecular layers of stearic acid¹², labelled with C-14, formed on the surface of various solid materials including glass, mica, platinum, copper and lead. To emphasise the versatility of the method, successful applications also include the gauging of foils as well as coatings¹³ on metals. Diffusion coefficients of copper and zinc in brass have been measured simultaneously. Autoradiography has been successful in investigations of the porosity of films¹⁴, and in the study of passive films on metals¹⁵.

As an alternative to the autoradiography technique, non-contact methods¹⁶ have received extensive use. Such methods are suitable for soft or gummy substances, where autoradiography is not. The appropriate radioactive source will depend upon the nature of the substance under investigation and may vary from weak beta particle emitters, such as carbon-14, for thin sheets of plastic, to hard gamma-ray emitters, such as cobalt-60, for steel. The principles involved in these non-contact methods are the same as those discussed for autoradiography; the measurement depends only upon the change in radiation intensity from a radioactive source when an object is placed between the source and the counter. The only difference in the technique is the replacement of the photographic plate by a non-contact detector such as a scintillation counter or a Geiger-Mueller counter. Modifications of these non-contact methods are applicable when only one side of the coating is accessible. The radiation source and counter are mounted adjacent to one another and the counter then measures the amount of radiation reflected from the surface of the coating and utilises the relationship between backscattered beta-radiation and the nature and thickness of the scattering¹⁷. A calibration curve is prepared to relate the back-scattered radiation intensity and the coating thickness. Thicknesses between

2 and 200 mg per sq cm have been measured with an accuracy of 1 per cent or better by this method.¹⁸

Specific applications utilising beta particles include the determination of the thicknesses of :

- (1) cellulose acetate, polyvinylchloride, polystyrene, and formvar¹⁹
- (2) ceramic coatings on steel, molybdenum and titanium²⁰
- (3) Cu₂S films formed on pure copper²¹
- (4) various deposits on metal surfaces^{22, 23}
- (5) metallic deposits ²⁴
- (6) bismuth films up to thicknesses of about 300Å ²⁵

Similarly, gamma and x-rays have been used in a variety of coating applications which include :

- (1) coating weights on paper²⁶
- (2) automobile waxes and polishes²⁷
- (3) free-flowing materials ²⁸
- (4) the thickness of fabric coatings²⁹
- (5) titanium films³⁰
- (6) gold films ³¹
- (7) non-ferrous coatings on steel³⁶

A recent modification of thickness gauges, based upon the same principles, is the development of radiation gauges for liquid level determination and control. Nuclear level gauges operate on the radiation blocking principle.

The source of radiation and the detector unit are mounted on opposite sides of the container. When the container is full, the detecting unit receives no signal as the radiation is absorbed by the liquid. As the level of the liquid lowers, more and more of the detector is exposed to the radiation and a corresponding signal is produced. A refinement of this system couples the detector signal to a control switch which maintains a constant liquid level³³. Radioisotopes commonly used in these applications include caesium-137 isotope which has a half-life of 30 years, and is the most commonly used radiation source. Radiation level gauges have found wide application in the many areas of polymerisations, including nylon, melamine condensates, polyesters, polyethylene, and polystyrene. As the reaction proceeds, most polymerisation processes exhibit a specific volume change which can be detected with a nuclear gauge. In systems such as the styrene-butadiene copolymer system, a small density change is exhibited as the reaction proceeds which affects the gross radiation absorption properties of the system. The detector signal correlates with the percent conversion. Although the previous discussion has dealt with liquid systems, the technique is also suitable for slurries or dry solids, which allows the accurate gauging of high solid content resins as well as solvents in bulk blending systems.

Film permeability studies represent another aspect of coating investigations. The porosity of thin films can be measured either by autoradiographic techniques¹⁴ or by diffusion methods³⁴⁻³⁵. These latter methods have been used

successfully in determining the permeability of varnishes to water. The varnish to be tested is sprayed over a gelatin membrane which has been mounted over one end of a glass tube. After the film has thoroughly dried, standardised salt solutions containing a suitable radioactive isotope such as rubidium-86 are introduced into the tube. The tube then is immersed in distilled water which is analysed for radioactivity. In an alternative method, the test varnish is sprayed over a glass panel which has been coated with a gelatin solution containing the radioactive rubidium. After drying, the plate is immersed in distilled water and the permeability measured by the decrease in radioactivity on the plate.

Radioisotopes have proven to be a valuable tool in the study of surface forces and dimensions³⁶, where data has been collected which strongly suggests that the adhesion of mixtures such as commercial resins and oils, metallic soaps, etc., to metals is due to hydrogen bonding. This explanation requires the presence of water molecules, or OH groups, on the metal surfaces and the question arose of whether the solvents used in protective coatings would displace the last layer of water molecules from the metal. Tritiated water was adsorbed on to a number of metal surfaces (Al, Cu, Au, reduced and unreduced steel) that had been heated previously to about 800°C under vacuum. Only a part of the tritiated water could be removed by severe repeated washings with strong solvents or by heating in a vacuum. A number of solvents of varying polarity were investigated, including methanol, benzene and 1,2-dichloroethane.

Another investigation concerning the removal of water from surfaces deals with rust prevention of metals³⁷. The uncoated metal was placed into a water solution containing a small amount of a suitable radioactive isotope such as sodium-24 or sulphur-35. After a short period, the rust preventative was applied and the residual activity due to the water under the coating measured. As the efficiency of a preventative is dependent on its ability to remove water from the metal surface, the residual activity is a measure of the rust-preventing power.

In conjunction with the discussion of adsorption studies, it should be mentioned that a number of investigators have studied oxide coating on metals³⁸⁻³⁹, as well as the adsorption of metals upon metals⁴⁰⁻⁴¹, but these are less directly relevant to the area of organic coatings.

Another important area is film formation and the problems of corrosion⁴² and blistering⁴³. Labelled atoms have been used in the study of the action of anti-corrosive additives in oils⁴⁴.

Many kinds of coatings, including nitrocellulose lacquer, alkyd, epoxy, acrylic, melamine, polyurethane, and silicone, have been tested with radioisotopes and fission products to evaluate their radioactive contamination resistance and ease of decontamination⁴⁵. Wilson⁴⁶ has used Cs-137, Sr-89, Ce-144, and I-131 to investigate the diffusion of water and radioactive material into alkyd paints. The conclusions that arose from the work were that penetration was limited generally to the layers near the surface, and decontamination could be effected by removal of the top five to ten microns of the film.

A new radiochemical tool⁴⁷ has been recently developed which is applicable to investigations of protective coatings. The beta emitting krypton-85 isotope has been incorporated into many solid and semi-solid materials. These

“kryptonates” have proved to be stable at room temperature and relatively stable at any elevated temperature up to the liquefaction point. Any physical or chemical disturbance of the surface results in a proportional loss of krypton-85. Monitoring the radioactivity released affords a means of determining the parameters controlling the reaction process. Breakdown of the solid components in coatings or of the coating itself by abrasion, heat, weathering, etc., can be evaluated, and the corrosion of painted surfaces can be observed continuously. Krypton-85 has been incorporated into many different types of solids either by ion bombardment or by diffusion under high temperature and pressure. Ion bombardment can be accomplished by ionizing the radioactive gas with an electron beam, and making the object to be “kryptonated” a high voltage cathode. Under these conditions the positive krypton ions are accelerated into the solid.

While the measurement of physical properties of coatings has been discussed thus far, the method is equally applicable to the study of reaction mechanisms such as those of drier action⁴⁸, the formation of per-acids⁴⁹, ester interchange in oils and varnishes⁵⁰, and polymerisation⁵¹.

In an associated area, carbon-14 and radioactive cerium have been utilised successfully in the analysis of oils and fatty acids⁵², and cellulose⁵³, respectively. Primary standards of vinyl acetate-acrylonitrile co-polymers have been prepared using labelled vinyl acetate, and analysed by liquid scintillation techniques. Radiochemical determination of acid groups in cellulose has been accomplished by preparing the cerium salt by the addition of excess radioactive cerium acetate. The excess cerium acetate was removed and the radioactivity of the cellulose sample determined. Through comparison with known samples, it was possible to establish a relationship between sample activity and acid groups present. Quantitative elemental analysis of trace metals in pigments has also been accomplished. Another analytical application is the determination of molecular weights of polyesters⁵⁴ and polyolefins.

Carr and Gordon⁵⁵ have described a method for the determination of tritium and C¹⁴-labelled polyacrolein and have enumerated the advantages of the tracer method for polymer analysis. Since many polymers are not soluble in suitable scintillation solvents, a universal application of the liquid scintillation counting technique requires that the polymer sample be converted to water and carbon dioxide by means of combustion. The modified Schoeniger method⁵⁶⁻⁵⁸ described by Carr and Gordon provides by far the most convenient laboratory combustion procedure. Unfortunately, in the application of this method to polymer samples, errors in the tritium and C-14 radioassay are often introduced due to the formation of soot and the dissolution of oxygen in the liquid scintillation solution. Yang⁵⁹ has modified the procedure of Carr and Gordon by adding benzylamine before the combustion and methanol later. He demonstrated in the analyses of tritiated polystyrene and polystyrene-C-14 that efficient combustion of polymer samples can be obtained by a modified Schoeniger method.

As an indication of the scope of the radiochemical technique, it has been used successfully in studies varying from the analysis of solvent mixtures and optimum mixture times to the stability of organic coating toward radiation effects^{60, 61}.

Up to this point the discussion has been of the uses of unstable isotopes in the analysis of coatings whereby the amount of radiation received by a detector is proportional to the particular property under consideration. It has been seen that this property can vary from coating thickness, permeability, porosity, etc., to the number of carboxylic acid groups present. As was mentioned earlier, the method actually has even broader applications, although it has not received the consideration it deserves.

As long ago as 1934, it was shown that radioactivity could be induced in a large number of elements by bombardment with neutrons or charged particles. This is the technique of activation analysis, and consists of the determination of the amount of an element present in a sample by measuring the activity induced in the sample upon bombardment with a suitable particle. The lack of acceptance of this method of analysis may be due partially to the relatively high initial cost as compared to other techniques. The method has the advantages of being : (1) extremely sensitive ; (2) accurate (3) rapid ; and (4) non-destructive. As an indication of just how sensitive the method is, under normal conditions, the median limit of detection for some 65 elements is about 0.05 micrograms (or five parts per thousand million in a 10 gram sample). Some elements are detectable to levels as low as 10^{-12} grams. Activation analysis service is available commercially with the results being available normally within one to two weeks.

All of the above applications are based on amount of radiation reaching a detector. The nature of the detector will be dependent upon the type of particle or ray emitted by the source. The design of the detector will be function of the intended use, i.e., whether it is used as a levelling gauge, as a coating thickness gauge, etc.

The basic methods of detection available are :

Image-forming Devices

photographic films
cloud chambers
bubble chambers
spark chambers

Light Emission Methods

scintillation counters
Cerenkov counters

Ion Collection Devices

electroscopes
electrometers
semiconductors
proportional counters
Geiger-Mueller counters

Detailed discussions of the particular advantages and disadvantages of each instrument are readily available in the literature as well as in a number of reference and textbooks⁶²⁻⁶⁴.

In summary, although the area of radiochemical analysis has grown tremendously in the last decade, the growth should be even more startling in the near future. Presently, the techniques have become accepted in a number of control applications such as the thickness, uniformity, and permeability of films, the

gauging of liquids and solids ; the determination of optimum mixing times ; the analysis of solvent mixtures ; and the determination of surface area. The future should see increased activity in these areas as well as in the area of reaction mechanisms. The increasing acceptance of activation analysis in all areas of chemistry will add a new and powerful tool for the practicing chemist.

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Vinyl and acrylic modified alkyds : Part VI

The formulation of a glossy water soluble automotive enamel

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Summary

The desirability of using water as a solvent or diluent for surface coatings is discussed with particular reference to the formulation of automotive enamels. The formulation of a water-soluble methacrylated alkyd system is considered, and the available methods for preparing these resins for use in organic solvents are examined as a basis for the production of water-soluble resins.

The method chosen for the preparation of the modified alkyd involved esterification of a methyl methacrylate/methacrylic acid copolymer with the components of an alkyd resin. The influence of the following variables on the water solubility and stability of the resin has been studied : the distribution of the carboxyl groups in the addition polymer, the extent of reaction between the addition polymer and the alkyd components, the degree of polymerisation of the resin, the chemical composition of the polybasic acid mixture, the type of amine and the amount of amine added.

Finally, the preparation of a water-soluble automotive enamel is reported.

Alkydes modifiées avec les groupements vinyliques et acryliques, VI^{ème}. Partie

La formulation d'une peinture-émail brillante, soluble à l'eau, pour automobiles

Résumé

On discute, en rapport particulier à la formulation des peinturesémaux pour automobiles, les avantages de l'emploi d'eau en tant que solvant ou diluant des revêtements. On considère la formulation d'une résine alkyde modifiée au méthacrylate soluble dans l'eau, et on étudie les méthodes valables pour la préparation de ces résines destinées à être utilisées dans des solvants organiques afin d'établir la base de la production des résines solubles dans l'eau.

La méthode sélectionnée pour la préparation de l'alkyde modifiée renferme l'esterification d'un copolymère du méthacrylate de méthyle et de l'acide méthacrylique par les constituants d'une résine alkyde. On a étudié l'influence sur la solubilité et la stabilité aqueuse de la résine que exercent les variables suivantes ; la répartition des groupements carboxyliques dans le polymère d'addition ; l'importance de la réaction entre le polymère d'addition et les constituants de l'alkyde ; le degré de polymérisation de la résine ; la composition chimique du mélange des acides polybasiques ; le type et la quantité d'amine utilisée.

Enfin, on mentionne la mode de préparation d'une peinture-émail, soluble dans l'eau, pour automobiles.

Vinyl—Akrylmodifizierte Alkyde; Teil VI

Die Ausarbeitung einer Rezeptur für eine glänzende, wasserlösliche Autoemaille

Zusammenfassung

Mit besonderer Berücksichtigung eines Rezeptes für Autoemallen wird das Bestreben Wasser als Lösungs- oder Verdünnungsmittel für Lacke zu verwenden, besprochen. Die Ausarbeitung einer Rezeptur für ein wasserlösliches, methakryliertes Alkydsystem wird einer Betrachtung

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unterzogen, und als Grundlage für die Herstellung wasserlöslicher Harze werden die zur Produktion von in organischen Lösungsmitteln löslichen Harzen verwandten Methoden geprüft.

Die zur Herstellung des modifizierten Alkydes gewählte Methode erforderte Veresterung eines Mischpolymers von Methylmethakrylat/Methakrylsäure mit den Komponenten eines Alkydharzes. Der Einfluss folgender Variablen auf die Wasserlöslichkeit und Stabilität des Harzes wurde geprüft: Die Verteilung der Karboxylgruppen in dem Additionspolymer, das Ausmass der Reaktion zwischen dem Additionspolymer und der Alkydkomponente, der Polymerisationsgrad des Harzes, die chemische Zusammensetzung der mehrbasischen Säuremischung, die Sorte von Amin und die Zusatzmenge des letzteren.

Schliesslich wird über die Anfertigung einer wasserlöslichen Autoemalle berichtet.

Виниловые и акриловые модифицированные алкиды. Часть VI. Формуляция блестящей автомобильной эмали растворимой в воде

Резюме

Обсуждается желательность применения воды в качестве растворителя или разбавителя для поверхностных покрытий, особенно при формуляции автомобильных эмалей. Рассматривается формуляция метакрилованной алкидной системы растворимой в воде и доступные методы изготовления этих смол исследовались для применения в органических растворителях с целью производства смол растворимых в воде.

Избранный метод для изготовления видоизмененного алкида включает этерификацию кополимера метил метакрилато/метакриловой кислоты с компонентами алкидной смолы. Изучалось влияние следующих переменных на растворимость в воде и устойчивость смолы: распределение карбоксильных групп в добавочном полимере, степень реакции между добавочным полимером и алкидными компонентами, степень полимеризации в смоле, химический состав многоосновной кислотной смеси, тип амина и количество добавочного амина.

В заключение дается описание изготовления автомобильной эмали растворимой в воде.

Introduction

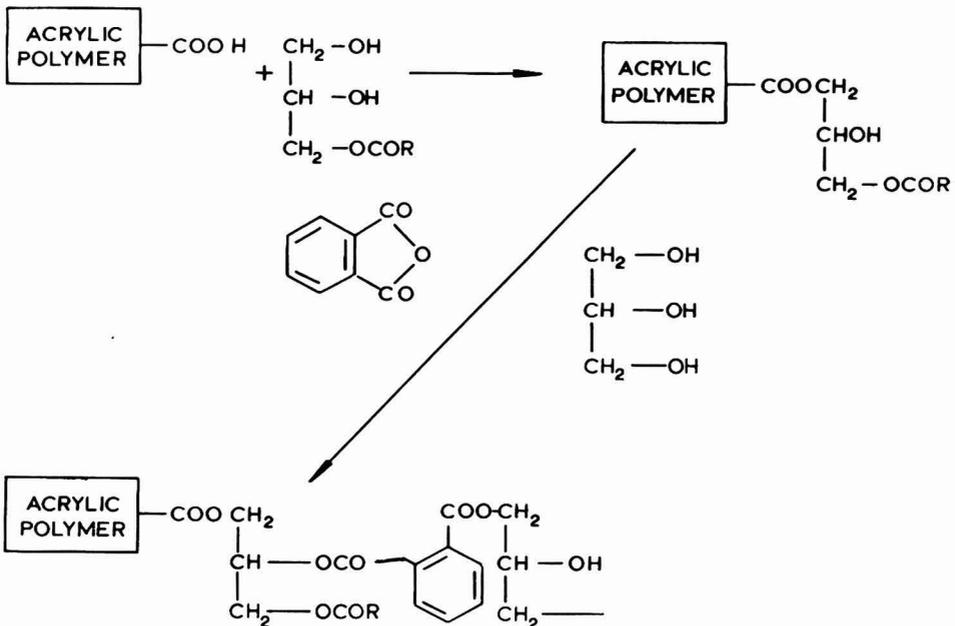
The use of organic solvents or diluents to give polymer solutions or dispersions suitable for use as surface coatings presents certain difficulties. The volatile organic compounds are a fire hazard, they are toxic, they contribute to atmospheric pollution, and they increase the cost of the coating. These problems are reduced when water is used as the solvent or diluent for a coating composition.

The formulation of polymer systems which are thinnable, or dilutable, with water has proceeded along two lines. The polymer structure has been designed so as to be water soluble, or the polymer has been dispersed in water to give a latex. The water-soluble and water-dispersible systems generally offer a different balance of properties when used in surface coatings. For example, pigment dispersion is comparatively simple with the solution polymers and consequently it is easier to prepare coatings with a high gloss. On the other hand, the emulsion system gives coatings with higher solids contents at application viscosity. Water-soluble polymer systems were chosen for investigation, since the work described in this paper had, as one of its aims, the development of a water thinnable or dilutable enamel which was suitable for use on automobiles, where a glossy film is a prime requirement. A further aim of this work was to provide a coating with properties intermediate between those given by alkyd/melamine-formaldehyde blends and thermosetting acrylic formulations. Such a product provides a commercially desirable balance between the technical properties and cost of the coating formulation.

In general, the development of water-soluble polymers for use in surface coatings has started from the existing formulations used to prepare organic-soluble polymer compositions. The usual modifications made are to lower the molecular weight of the polymer, and to introduce polar groups with a strong affinity for water. Typical polar groups used are the hydroxyl, amide, methylol amide and the corresponding alkyl ethers, carboxyl, and ionised carboxyl groups. These polar groups are also involved in the crosslinking reactions which take place during film formation. In considering the formulation of a water-soluble methacrylated alkyd, it is informative to consider the existing organic-soluble polymers and their suitability for modification, in the manner described above, to water-soluble systems.

In organic solution, three distinct approaches have been used to prepare methacrylated alkyds which can be crosslinked with a melamine formaldehyde resin. First, blends of a suitable thermosetting acrylic copolymer and an alkyd resin have been used. Secondly, acrylated alkyds have been prepared by polymerising the acrylic monomer in the presence of the alkyd or alkyd components, and, thirdly, an acrylic copolymer which contains esterifiable functional groups has been condensed with the alkyd components¹.

There are several reaction sequences which can be used in the third method, but the one preferred by the authors is represented by the following equations and will be referred to as the "monoglyceride" process.



Where R = fatty acid

When considered as starting points for water-soluble coating compositions, the first and second methods of preparing methacrylated alkyd have serious limitations. In many cases blended systems give rise to incompatibility even in organic solvents, and this problem is accentuated where water is used as

the solvent². The second type of polymer, the so-called copolymerised methacrylated alkyd, requires the use of unsaturated fatty acids in the alkyd, and these lower the durability of the film and give rise to discoloration on excessive stoving (e.g. in two-tone operations). Also, considerable quantities of acrylic homopolymer are formed, and this will not be solubilised in water unless an acid monomer is also used. This greatly complicates the process, since it becomes necessary to avoid esterification with the hydroxyl groups of the alkyd (to prevent gelation) and to allow for the differences in the reactivity ratios of the monomers. Furthermore, the polymerisation of the acrylic monomer is carried out under far from ideal conditions, since the alkyd components often contain impurities which inhibit chain polymerisation reactions. In contrast to the first and second methods, the monoglyceride process is theoretically capable of yielding water-soluble methacrylated alkyds, since the alkyd and acrylic entities are combined chemically, and the polymer chains contain ionisable carboxyl groups. Therefore, the monoglyceride method was chosen for preparing water-soluble methacrylated alkyds suitable for the preparation of glossy automotive stoving enamels.

Experimental

Methyl methacrylate was washed with 1N sodium hydroxide, then with water, dried, and distilled under reduced pressure and an atmosphere of nitrogen. Glacial methacrylic acid was used without purification and contained 250 ppm of hydroquinone.

The benzoyl peroxide powder used was 99.7 per cent pure when analysed iodometrically. Periodic acid titration showed the glycerol to be more than 99 per cent pure.

The following materials were used without further purification: phthalic anhydride (ICI/ANZ Ltd.), trimellitic anhydride (Amoco Chemicals), butyl Cellosolve (BDH technical grade), toluene (Analar), petroleum ether bp 40-60°C (Analar, aromatic-free), triethanolamine (BDH), and ethanolamine (BDH). Triethylamine was distilled under reduced pressure and the product collected within a 1°C boiling range.

The hydrogenated castor oil had an iodine value of less than 5 and a hydroxyl value of 152 mg KOH/g.

Neutral solvent was prepared by neutralising a mixture of absolute alcohol (50 pts) and toluene (50 pts) to a phenolphthalein end point with alcoholic potassium hydroxide.

Ethylene dichloride was distilled under reduced pressure.

Preparation and characterisation of acid copolymers

Copolymers of methyl methacrylate and methacrylic acid were prepared by adding the monomer mixture (100 g), in which was dissolved benzoyl peroxide (2.0 g), at a uniform rate over three hours, to toluene (100 g) heated under reflux in a round bottom flask fitted with a stirrer and reflux condenser. The mixture was heated under reflux for a further one hour. This method could not be used to prepare a 12 mole per cent methacrylic acid/methyl methacrylate copolymer; large amounts of precipitate formed early in the polymerisation.

Copolymers with a more uniform distribution of the acid groups were prepared by making allowance for the greater reactivity of methacrylic acid compared with methyl methacrylate. The rate of methacrylic acid addition was calculated originally from the copolymer equation using values of $r_1=0.37$ and $r_2=2.2$, where M_1 is methyl methacrylate³. The calculated addition rate was modified, where necessary, after analysis (see below) of the polymer formed in trial runs. To simplify the experimental technique, the monomer was added in five aliquots, each of the same weight but with the monomer ratios shown in Table 1. Each aliquot contained benzoyl peroxide (2 per cent by weight) and was added at a uniform rate over a period of 35 minutes. After the last aliquot was added, the mixture was heated under reflux for one hour.

Table 1
Rate of addition of methacrylic acid used to prepare distributed copolymers

Total mole per cent methacrylic acid in copolymer	Mole per cent methacrylic acid in each aliquot of monomer mixture				
	1	2	3	4	5
4	1.7	2.8	3.9	5.1	6.5
8	3.4	5.6	7.8	10.5	13.1
12	5.8	9.8	12.8	14.4	17.2

The distribution of the acid groups in the polymer molecules was measured on samples taken throughout the polymerisation as follows: the polymer solution (5 g) was added to petroleum ether (2 litres) which was being stirred rapidly, and the precipitated polymer isolated by filtration, and then dried (three hours at 35°C under reduced pressure). The polymer was dissolved in acetone (40 ml), reprecipitated into petroleum ether (2 litres), isolated by filtration, and dried (48 hours at 35°C under reduced pressure). The polymer was dissolved in neutralised ethanol/toluene mixture and titrated to a phenolphthalein end point with 0.1 N alcoholic potassium hydroxide. The acid group distribution in the polymers is shown in Fig. 1.

For molecular weight measurements, the polymer isolated as above was twice reprecipitated from petroleum ether, and dried (three days at 35°C under vacuum). The efflux time of a 0.5 per cent solution in ethylene dichloride was measured in an Ostwald viscometer at 30°C. The solvent efflux time was 120 seconds. The molecular weights were calculated from the following equation:

$$M \text{ Wt} = 1.47 \times 10^6 (N_r - 1 - \log_e N_r)^{0.65}$$

The results are given in Table 2.

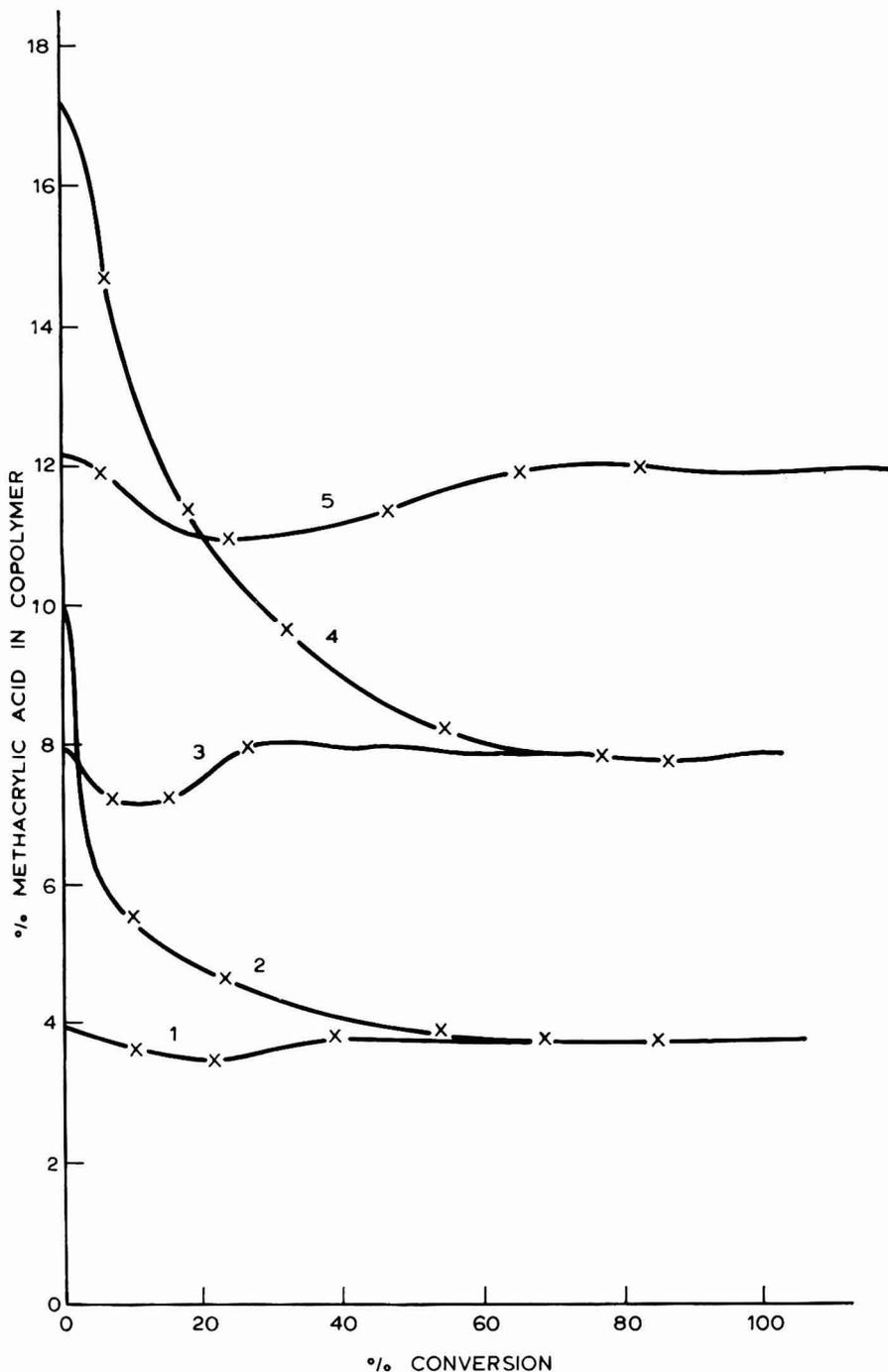


Fig. 1. The distribution of acid groups in methyl methacrylate/methacrylic acid copolymers. (Polymers 1 to 5 in Table 2)

Table 2
 Characterisation of methacrylic acid/methyl methacrylate copolymers

Copolymer number	Mole per cent methacrylic acid in copolymer	Acid group distribution	Molecular weight	Acid value
1	4	Distributed	16,500	21.8
2	4	Non-distributed	16,500	22.3
3	8	Distributed	15,700	44.6
4	8	Non-distributed	15,900	44.4
5	12	Distributed	12,900	66.7

To study the effect, if any, of hydrogen bonding between the carboxyl groups on the viscosity measurements, ethylene dichloride/ethanol=98/2 was used as the solvent. No significant differences were obtained between this solvent mixture and ethylene dichloride.

The yield of polymer was calculated from a solids measurement which was carried out by weighing the polymer solution (0.8-1.0 g) into a dish (8 cm dia), spreading into an even film with acetone (20 ml) and drying (three hours at 105°C). In all cases the solids content was greater than 49.5 per cent (theoretical is 50 per cent).

Preparation of acrylic modified alkyds

The following formula will be referred to as the standard formula. Hydrogenated castor oil (36.0 pts) and glycerine (7.3 pts) were heated to 150°C in a flask equipped with a stirrer, thermometer and Dean and Stark water separator. Lead naphthenate solution (equivalent to 0.1 per cent lead calculated on the weight of oil) was added and the temperature raised to 200°C and maintained for one hour. The solution was cooled (150°C) and the methyl methacrylate/methacrylic acid copolymer (No. 3) solution added (equivalent to 29.4 pts of solid resin). Toluene was removed by distillation until the temperature of the mixture reached 200°C. The mixture was heated at 200°C and the water of reaction removed in the Dean and Stark separator until the required acid value was reached. This acid value will be referred to as AV₁. The mixture was cooled (140°C), phthalic anhydride (20.3 pts), trimellitic anhydride (3.4 pts) and glycerine (3.6 pts) added, and the mixture reacted at 200°C to the required acid value. This second acid value will be referred to as AV₂.

The variations made on the above general formula are listed in Table 3.

Water solubility of methacrylated alkyds

Samples were taken during the second condensation stage of the methacrylated alkyds and solubilised as follows: the polymer (15 g of 97.5 per cent solids in toluene) and butyl Cellosolve (6.6 g) were heated to 90-100°C, and the amine, equivalent to a 20 per cent (by weight) excess over that required to

Table 3
Formulations used in the preparation of methacrylated alkyds

Polymer number	Formulation	AV ₁
6	Standard	10.4
7	8 per cent non-distributed copolymer (No. 4) used in place of 8 per cent distributed polymer (No. 3)	10.4
8	4 per cent distributed copolymer (No. 1) used in place of 8 per cent distributed copolymer (No. 3)†	3.7
9	4 per cent non-distributed copolymer (No. 2) used in place of 8 per cent distributed copolymer (No. 3)†	3.7
10	12 per cent distributed copolymer (No. 5) used in place of 8 per cent distributed copolymer (No. 3)†	18.0
11	Standard*	19.0
12	Standard	3.5
13	Standard but no prior reaction of hydrogenated castor oil and glycerol	Gel
14	Trimellitic anhydride replaced by phthalic anhydride‡	10.8
15	Phthalic anhydride/trimellitic anhydride = 50/50‡	10.6
16	Phthalic anhydride replaced by trimellitic anhydride‡	9.9

*This represents no reaction of the "monoglyceride" with the methacrylate polymer before carrying out the second polyesterification.

†The values of AV₁ correspond to the same percentage esterification of the acid copolymer.

‡These replacements were on an acid equivalent basis.

neutralise the carboxyl groups, was added. This solution was titrated with water either to a permanent cloud point or until the solids content of the solution reached 35 per cent (i.e. 27.1 ml of water had been added). Polymers which could be diluted to 35 per cent solids were then evaluated for storage stability by heating at 25°C for three months. The results of these tests are recorded in Table 4.

If a particular formulation (from Table 3) and AV₂ are not listed in Table 4, then the polymer failed for one or more of the following reasons :

- (a) It was not soluble,
- (b) It would not tolerate reduction to 35 per cent solids with water,
- (c) The solution was unstable, or
- (d) The polymer gelled during manufacture.

Similarly, if an amine listed on page 309 is not shown in Table 4, it did not solubilise the resin or the solution was not stable.

Table 4
Formulations which gave water-soluble, stable methacrylated alkyds

Polymer number	AV ₂	Neutralising* base	Viscosity (Gardner-Holdt)	Viscosity after three months' storage
6/5	50	Triethylamine	Y— $\frac{1}{2}$	Z ₃
6/7	50	Triethanolamine	Y— $\frac{1}{4}$	Z ₃
6/8	50	Dimethylethanolamine	Z ₃	Z ₅
10/1	102	Triethylamine	G	Y
10/2	102	Triethanolamine	F+ $\frac{1}{4}$	U
10/3	80	Triethylamine	O	Z
10/4	80	Triethanolamine	O+ $\frac{1}{4}$	Y+ $\frac{1}{2}$
10/5	62	Triethylamine	X+ $\frac{1}{4}$	Z
10/6	62	Triethanolamine	W	Z ₁
10/7	57	Triethylamine	Z ₃	Z ₃ + $\frac{1}{2}$
10/8	57	Triethanolamine	Z ₃	Z ₃
10/9	57	Dimethylethanolamine	Z ₃ + $\frac{1}{4}$	Z ₃
12/2	95	Triethanolamine	H+ $\frac{1}{2}$	Z ₄
12/5	50	Triethylamine	O	V
12/6	50	Triethanolamine	X+ $\frac{1}{2}$	X+ $\frac{1}{2}$
12/7	50	Dimethylethanolamine	Y+ $\frac{1}{2}$	Z
14/6	58	Triethanolamine	U+ $\frac{1}{2}$	X
15/3	86	Triethylamine	P	Z ₆
15/4	86	Triethanolamine	G	Z
15/6	75	Triethanolamine	L+ $\frac{1}{2}$	M
16/3	102	Triethylamine	O	O+ $\frac{1}{2}$
16/4	102	Triethanolamine	E+ $\frac{1}{2}$	E+ $\frac{1}{2}$

*The polymer solutions were prepared as described on page 312.

Separation and identification of water-insoluble fractions in methacrylated alkyds

The water-insoluble fraction was separated from some of the methacrylated alkyds which did not form satisfactory solutions (see above) as follows: the methacrylated alkyd/amine/butyl Cellosolve/water mixture (30 g) described above was diluted with water (200 g) and butyl Cellosolve (20 g), and the precipitate removed by filtration, washed with water (100 ml) and then N/20 hydrochloric acid (200 ml), and finally with water until the washings were chloride-free. The precipitate was dried (two hours at 35°C under reduced pressure), dissolved in acetone, and precipitated into petroleum ether (2 litres). The precipitate was filtered off and dried (16 hours at 25°C under reduced pressure, followed by four hours at 35°C under reduced pressure).

The molecular weight and acid value of the polymer were measured as described above. The results are reported in Table 5. The infra-red spectra were run as films on rock salt plates on a Unicam SP.200 spectrophotometer. The spectra were similar to those of the methacrylate copolymer used in the preparation of the respective methacrylated alkyds.

Influence of processing conditions and formulation on the water solubility of methacrylated alkyds

The influence of the degree of esterification of the copolymer with the polyol was studied (Table 6) with the standard formulation. The trimellitic anhydride/phthalic anhydride ratio was varied, all substitutions being on a carboxyl

basis. The influence of this ratio on the water solubility and stability of the polymer is recorded in Tables 7 and 8.

Table 5

Characterisation of water-insoluble fractions separated from methacrylated alkyds

Polymer number	AV ₁	AV ₂	Water-insoluble fraction as per cent by weight of total polymer	Molecular weight of water-insoluble fraction	Acid value of water-insoluble polymer
6/1	10.4	84	2.5	—	35.0
6/3	10.4	73	0.6	—	—
7/1	10.4	77	6.3	15,500	40.2
7/3	10.4	66	2.5	18,200	23.8
7/5	10.4	56	Trace	—	—
8/1	3.7	100	13.7	16,300	22.1
8/3	3.7	80	7.5	16,100	18.5
8/5	3.7	64	2.5	16,800	17.6
8/7	3.7	57	Trace	—	—
9/1	3.6	98	18.8	16,700	23.2
9/3	3.6	72	11.3	16,700	12.8
9/5	3.6	59	9.4	17,100	9.5

Table 6

The influence of AV₁ on the water solubility of methacrylated alkyds

Polymer number	AV ₁	AV ₂ at which polymer is water soluble*
12	3.5	95
6	10.4	73
11	19.0	Insoluble at all AV

*Triethanolamine was used as the base.

Table 7

The influence of the phthalic anhydride/trimellitic anhydride ratio on the water solubility of methacrylated alkyds

Polymer series	Phthalic anhydride/ trimellitic anhydride ratio	AV ₁	AV ₂ at which polymer becomes water soluble†
14	100/0	10.8	58
6	80/20*	10.4	73
15	50/50	10.6	86
16	0/100	9.9	Greater than 102

*This is the ratio used in the standard formula.

†These results were obtained using either triethylamine or triethanolamine as the solubilising base.

Table 8

The influence of the phthalic anhydride/trimellitic anhydride ratio on the amount of water insoluble polymer in methacrylated alkyds

Polymer series	Phthalic anhydride/ trimellitic anhydride ratio	AV ₂	Weight per cent of insoluble polymer based on polymer solids
14	100/0	98	17.5
14	100/0	72	7.5
15	50/50	113	9.4
15	50/50	75	—

The influence of the acid content of the methyl methacrylate/methacrylic acid copolymers on the viscosity of the final resin is shown in Table 9.

The degree of neutralisation of the resin with base was also investigated (Table 10).

Table 9

The influence of the acid content of the copolymer on the viscosity of methacrylated alkyd*

Mole per cent acid in copolymer	AV ₂ of methacrylated alkyd	Viscosity (Stokes) of methacrylated alkyd
4	57	5.5
8	50	17.0
12	57	43.3

*The distributed acid copolymers were used in this series and the per cent of esterification of the acid copolymer kept constant. Triethanolamine was used as the base.

Table 10

The effect of the degree of neutralisation of the methacrylated alkyd on the storage stability of the polymer solution*

Per cent of acid groups neutralised	Appearance of polymer solutions				Viscosity stability in Stokes	
	Triethylamine		Triethanolamine		Increase after three months' storage	
	Initially	After three months	Initially	After three months	Triethylamine	Triethanolamine
50	Cloudy	Heavy cloud	Clear	Heavy cloud	†	†
60	Cloudy	—	—	—	†	†
75	Sl. haze	Heavy cloud	Clear	Clear	150	10
90	Clear	Sl. haze	Clear	Clear	0.7	2.1
100	Clear	Sl. haze	Clear	Clear	0.0	0.3
120	Clear	Sl. haze	Clear	Clear	5.5	0.7
150	Clear	Cloudy	Clear	Clear	20.0	0.3

*Polymer No. 12 at an AV_2 of 50 mg KOH/g was used.

†The viscosity was not measured since the mixture had separated into two layers.

Preparation of a water-soluble automotive enamel

A 6 per cent methacrylic acid copolymer with uniform distribution of the acid groups was prepared in a manner similar to that described above. The compositions of the aliquots of monomer which were added are shown in Table 11.

Table 11

Preparation of a 6 per cent distributed methacrylic acid/methyl methacrylate copolymer

Total mole per cent acid	Mole per cent methacrylic acid in each aliquot of monomer mixture				
	1	2	3	4	5
6	2.55	4.2	5.85	7.6	9.8

Methacrylated alkyd preparation

Hydrogenated castor oil (360 pts), glycerine (73 pts) and lead naphthenate solution (1.8 pts) were heated at 200°C for one hour. The mixture was cooled to 150°C and the prepolymer solution added (588 pts at 49.6 per cent solids). Solvent (300 pts) was removed by distillation and the condensation reaction carried out at 190-200°C until $AV_1=1.6$. Phthalic anhydride (203 pts), trimellitic anhydride (34 pts) and glycerine (36 pts) were added and the mixture condensed to $AV_2=53$. The resin was cooled to 120°C, and butyl Cellosolve^(R)

(427 pts) added, followed by dimethylethanolamine (82 pts) and distilled water (1550 g). The resin had a viscosity of X at 25°C.

Discussion

Previous work on organic-soluble methacrylated alkyds had established a formulation which contained a methyl methacrylate/methacrylic acid (96/4) copolymer, hydrogenated castor oil, glycerol and phthalic anhydride⁴. Methyl methacrylate was chosen because of its known durability and polishability in thermoplastic systems; hydrogenated castor oil was selected because it is saturated, and, therefore, not susceptible to discoloration on excessive heating, and the hydroxyl group on the fatty acid chain would contribute to reaction and compatibility with the formaldehyde condensate during film formation.

Attempts to prepare water-soluble methacrylate alkyds by limiting the degree of condensation of the above type resin gave products which were either not water soluble or not stable in aqueous solution. Similar results were obtained in the presence of water which contained a water miscible organic solvent to aid solution of the polymer.

Replacement of some of the phthalic anhydride by trimellitic anhydride, a technique commonly used in rendering polyesters water soluble, did not appreciably improve the water solubility and/or stability of these methacrylated alkyds (Polymer 9).

The insoluble material which was present initially in the aqueous solutions of the methacrylated alkyds, and/or the material which separated from the resin solution on standing, was characterised as methyl methacrylate/methacrylic acid copolymer which had not been esterified by the alkyd components (Table 5). Consequently, methods of reducing further the amount of uncombined methacrylated copolymer were studied. The acid content of the copolymer was increased, and the distribution of the acid groups in the copolymer was improved by allowing for the difference in the reactivity ratios of methacrylic acid and methyl methacrylate³. Both approaches resulted in methacrylated alkyds which were water soluble. However, the distributed acid copolymers showed a number of important technical and commercial advantages over the non-distributed acid copolymers. First, at a given acid content, distribution of the acid groups gives a methacrylated alkyd which becomes soluble earlier in the second stage condensation than the corresponding system in which the acid groups are not distributed. Conversely, if the acid groups are distributed, a methacrylic copolymer with a lower acid content can be used to give a soluble methacrylated alkyd. Since the acid monomer is more expensive than the methyl methacrylate used as the comonomer, distribution of the acid groups is a means of keeping the formulation cost to a minimum. Another reason for aiming at the lowest acceptable acid level in the methacrylate copolymer is that the solution viscosity of the methacrylated alkyd is directly related to the acid content or functionality of the copolymer (Table 9). Consequently, copolymers with low acid contents give methacrylated alkyds with higher solids at a given viscosity and are, therefore, capable of giving a higher film thickness for each coat applied. The results of storage stability tests on the methacrylated alkyds showed up yet a further, and most important, advantage of using distributed acid copolymers: the only

methacrylated alkyds which were stable after three months' storage were those prepared from distributed copolymers.

An additional means of reducing the amount of uncombined methacrylate copolymer in the final methacrylated alkyd was to allow the esterification reaction between the copolymer and the polyhydroxyl compounds (mono-glyceride mixture) to proceed as far as practicable. This resulted in the polymer becoming water soluble at a lower degree of second stage condensation (AV_2) (Table 6). These results demonstrate the basic differences between these methacrylated alkyds and alkyds, when formulated as water-soluble resins. The alkyd composition can be solubilised in water at very low degrees of condensation, and eventually becomes insoluble as the molecular weight increases, and the number of hydrophilic groups (carboxyl, hydroxyl) decreases. On the other hand, the methacrylated alkyd is initially insoluble because of its heterogeneous make up; it then becomes soluble when the methacrylic copolymer and alkyd components are combined sufficiently, and finally it reaches an insoluble stage at higher molecular weights and reduced levels of hydrophilic groups.

The polybasic acid used in the polyesterification of the methacrylate copolymer/polyhydroxy component reaction mixture also has an important influence on the solubility and stability of the methacrylated alkyd in aqueous solutions. A series of polymers prepared with various trimellitic anhydride/phthalic anhydride ratios (replacement was on carboxyl equivalents) showed that, as the trimellitic anhydride content increased, the methacrylated alkyd became soluble at a higher AV_2 (i.e. lower degree of condensation) (Table 8). The most likely explanations of this phenomena are:

- (1) That the trimellitic anhydride, which should give a stronger acid than phthalic anhydride, acts as a more effective catalyst for the esterification of some acid copolymer chains during the second stage condensation reaction, or
- (2) The trimellitic anhydride results in a methacrylated alkyd which, in aqueous solution, has a greater tolerance for uncombined methacrylated copolymer, or
- (3) The trimellitic anhydride gives a more uniform distribution of the residual acid groups which are formed during the polyesterification.

Fractionation studies (Table 8) suggest that the second explanation is unlikely. In support of suggestion (3), Brett⁵ has shown that, with propylene glycol based polyesters, trimellitic anhydride gives a more desirable distribution of carboxyl groups than does phthalic anhydride.

The type and amount of base used to solubilise the methacrylated alkyd influenced the solution properties of the resin. Primary and secondary amines gave solutions which were not stable, probably because of aminolysis of ester linkages. These amines would also be expected to cause instability when melamine-formaldehyde resins were added as the cross linking agent. Therefore, tertiary amines were used because they gave stable solutions. Furthermore, the tertiary amines offered another advantage over primary and secondary amines; they gave solutions with lower viscosities. The amount of base added

influenced the viscosity and stability of the solution. To achieve acceptable solution viscosity, at least 80 per cent of the carboxyl groups had to be neutralised (Fig. 2), and stable solutions were only obtained when the amount

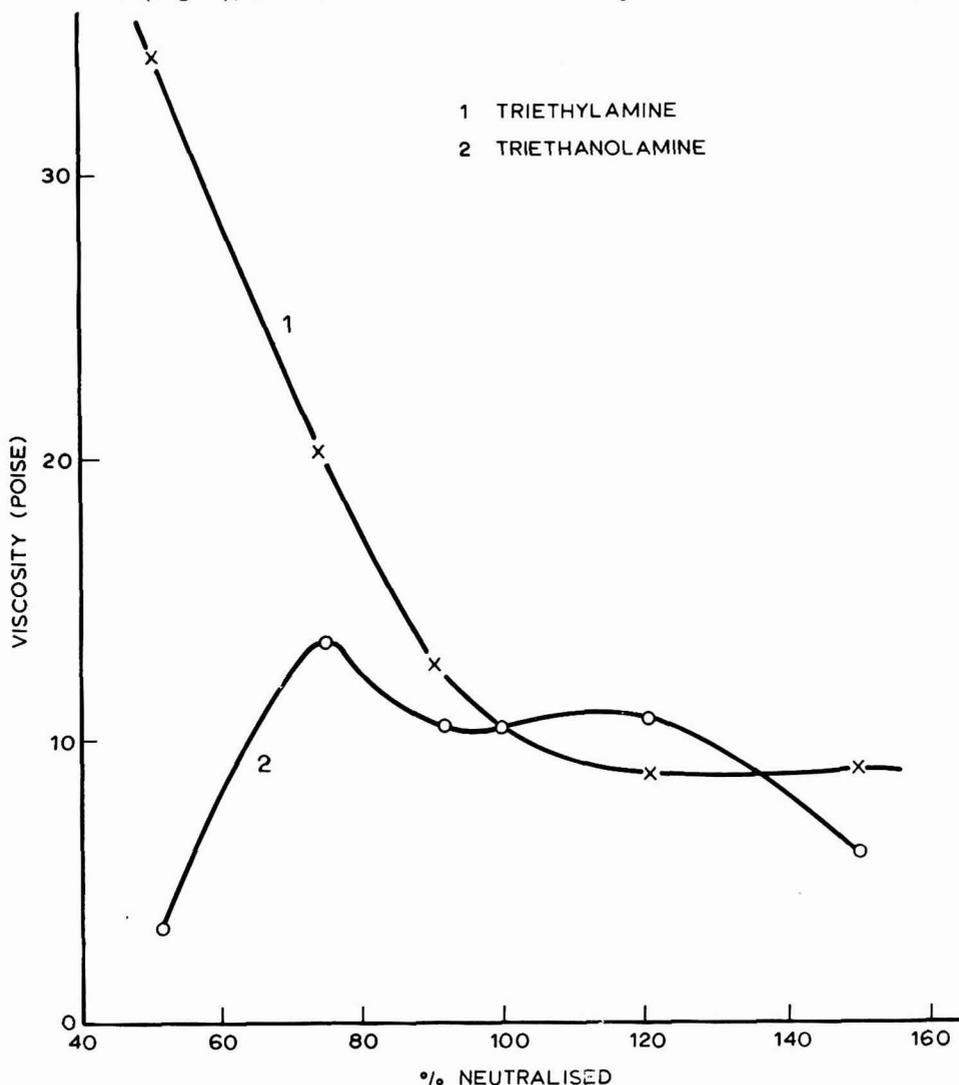


Fig. 2. The variation of viscosity with the degree of neutralisation of a methylated alkyl of base added was equivalent to 80-120 per cent of the carboxyl groups (Table 10). The solution viscosities varied with the structure of the amine. In general, tertiary amines, which also contained hydroxyl groups (triethanolamine and dimethylethanolamine), gave solutions with lower viscosities than those in which triethylamine was used, although in some cases the difference did not become significant until after the solution had aged (three months). The lower viscosity given by the hydroxy amines could be related to the

association of the hydroxyammonium cation with the polymeric anion, by bonding through the hydroxyl group.

From the results discussed above, it is possible to specify a formulation which will give a can-stable water-soluble methacrylated alkyd with the solution properties required for an automotive enamel.

A 94/6 methyl methacrylate/methacrylic acid copolymer, in which the acid groups were "distributed" among the polymer molecules, was selected as an acceptable balance between the formula cost, viscosity of the modified alkyd, and the can stability of the formulation. The first stage esterification was equivalent to the reaction of 95 per cent of the copolymer carboxyl groups. This represents a compromise between the polymer properties which improve with the degree of first stage esterification, and the processing times which become uneconomically long as the percentage reaction increases. The trimellitic anhydride/phthalic anhydride ratio was chosen as 20/80, which is the lowest level of trimellitic anhydride commensurate with good solution properties in the final polymer. The second stage condensation was taken to an acid value of 53, which is a satisfactory compromise between the number of acid groups necessary to solubilise the resin and the presence of a minimum number of hydrophilic groups in the film. A tertiary amine which also contained hydroxyl groups was selected for solubilising the resin. However, since the crosslinking reactions which take place when methacrylated alkyds are heated with a melamine formaldehyde resin require acid as a catalyst⁵, the amine must be readily lost from the film on stoving; dimethylethanolamine satisfied these requirements. The amount of amine used corresponded to the neutralisation of all the carboxyl groups present in the methacrylated alkyd.

An automotive enamel was prepared by pigmenting the above methacrylated alkyd to a pigment : binder ratio of 50/100 with titanium dioxide and, by using a water-soluble melamine formaldehyde condensate, hexamethoxymethyl melamine (Cymel 300^R), as the crosslinking agent. A trace of p-toluene sulphonic acid was used to catalyse the curing reaction. This enamel passed the usual tests applied to conventional solvent borne automotive enamels of this type.

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Quality control of contact leaching antifouling paints*

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Summary

Batches of a vinyl antifouling paint that passed the normal quality control tests had shown different fouling-free lives in practice. Glycine accelerated leaching rate/time curves obtained from samples from two of these batches showed differences consistent with those found in practice. The nature of the curves and the basic factors affecting them are briefly discussed. A simplified technique of measuring the leaching characteristics of antifouling paints is proposed for the quality control of contact leaching antifouling paints.

Le contrôle de qualité des peintures sous marine toxique lixiviant pas contact

Résumé

Des lots d'une peinture anti-fouling vinylique qui ont franchi les essais de contrôle normaux pour faire apprécier leur qualité, ont-ils démontré en pratique de différentes durées d'exemption de salissure. Des courbes de lixiviation, accélérée par glycine, tracées en fonction de temps que rendent des échantillons en provenance de deux tels lots démontraient des différences d'accord avec celles que l'on a trouvées en pratique. On discute brièvement la nature des courbes et également les considérations de base qui les affectent. On propose une technique simplifiée pour mesurer les caractéristiques de lixiviation des peintures anti-fouling afin de contrôler la qualité de telles peintures qui se lixivient par contact.

Qualitätskontrolle von Kontakt-Auslauge-Antifoulingfarben

Zusammenfassung

In der Praxis blieben Partien eines Vinylantifoulings, obwohl sie die normalen Qualitätskontrollprüfungen bestanden hatten, verschieden lange anwuchsfrei. Mit Glykokoll beschleunigte Auslaugegrad/Zeitkurven von Mustern zweier dieser Partien wiesen Unterschiede, die im Einklang mit denen in der Praxis gefundenen standen, auf. Der Charakter der Kurven, sowie die grundsätzlichen sie beeinflussenden Faktoren werden kurz besprochen. Eine vereinfachte Ausführungsart zum Messen der Auslaugecharakteristika von Antifoulings für die Qualitätskontrolle von Kontakt-Auslauge-Antifoulingfarben wird vorgeschlagen.

Качественный контроль контактного вымывания воды в красках против подводных растений

Резюме

Образцы виниловой краски против подводных растений которые выдержали удовлетворительно нормальные качественные контрольные испытания, показали на практике иную картину. Кривые отношения скорости вымывания к времени ускоренные глицином, полученные для двух групп этих образцов, показали те же различия как и на практике. Обсуждались кратко природа этих кривых и основные факторы имеющие влияние на них. Предлагается упрощенная методика для измерения вымывательных характеристик красок против подводных растений с целью качественного контроля контактного вымывания красок против подводных растений.

*Based on papers presented at the Symposium on Marine Paints, Bombay, India, November 1964, and the Inter-Naval Corrosion Conference, Sydney, Australia, November 1965.

Introduction

Most antifouling paints used by the Royal Australian Navy and some Australian shipping companies are initially tested for compliance with the Australian Standard¹. At present, quality control of subsequent batches is limited to the comparison of delivery samples with the original approved sample using simple quantitative tests such as weight per gallon and non-volatile content, which are normally applied to paints for general use².

A theoretical study of the mechanism of action of contact leaching antifouling paints undertaken at Defence Standards Laboratories indicated that substantially different leaching characteristics might be shown by paints indistinguishable by the normal inspection testing procedures³. If this proved to be so in practice it would be possible for tested and accepted batches of antifouling paints to give inferior and, maybe, unsatisfactory antifouling performance on ships.

Batches of a vinyl antifouling paint which was approved under the above-mentioned Standard had shown different fouling-free lives in practice. It was decided to examine the accelerated leaching characteristics and panel immersion performance of old and new batches of this paint, as it was felt that the variation in performance was due either to a change in the paint on storage, to the use of raw materials differing in properties, or to the employment of different manufacturing procedures from batch to batch of the paint⁴. It was hoped that this investigation would establish whether the determination of accelerated leaching rates would be useful in the quality control of antifouling paints.

This paper briefly describes the method used to obtain the accelerated leaching characteristics of old and new batches of a vinyl antifouling paint and the results obtained. The need for an accelerated leaching control test is indicated and a simplified technique for this is described.

Experimental

Samples

The manufacturer supplied Defence Standards Laboratories with three samples of paint. Sample A was four months old and passed the normal acceptance tests. Sample B was 24 months old and had passed the acceptance tests several weeks after manufacture. This sample showed hard settling of the pigment, and, even after prolonged stirring, considerable agglomeration of cuprous oxide particles. It was thought that these agglomerates would affect the leaching characteristics of the paint. Therefore, half the sample was retained for test and the other half was redispersed on a Torrance disperser. The redispersed paint met the acceptance tests. Sample C was a vinyl paint modified to obtain improved storage properties. It was 30 months old and appeared to have changed little on storage apart from pigment settlement.

Panel preparation

Sand blasted glass panels were used with one coat of wash primer applied. The paints to be tested were sprayed on to the panels to give a relatively thick film of 0.002 in to 0.004 in. After drying for 24 hours the edges of the panels were coated with vinyl copolymer to prevent edge effects during leaching.

Leaching rate determination

The method employed to obtain leaching rate-time curves for the four samples has been reported previously⁴. The time between leachate changes was approximately 12 hours.

Panel trials

The paint manufacturer carried out immersion trials of these paints in Sydney Harbour at a site similar in fouling potential to that used in the original approval trials.

Results

Fig. 1 shows the accelerated leaching rate curves for the four samples tested. Sample A had a considerably higher leaching rate than the older Sample B. When redispersed the leaching rate of Sample B appeared to be marginally lower. Sample C had the lowest leaching rate.

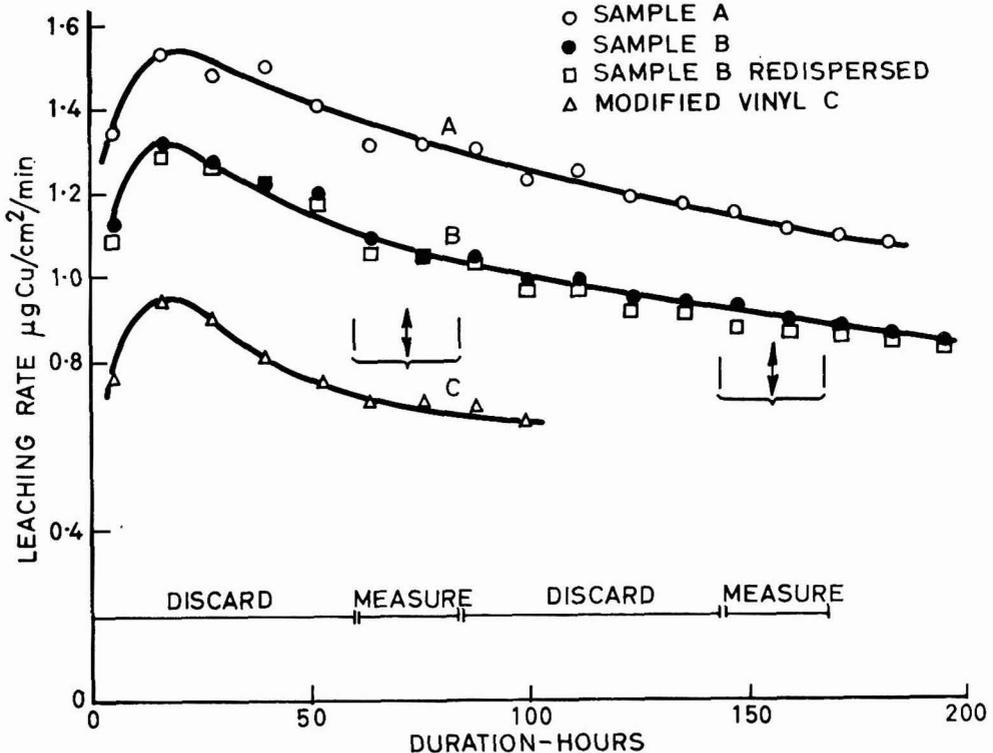


Fig. 1. Accelerated leaching rates of vinyl antifouling paints

Discussion

The new (A) and old (B) samples were both from batches acceptable under the inspection testing procedure, but showed markedly different leaching rates. The aged sample showed a leaching rate only 80 per cent to 84 per cent of that of the newer paint, and redispersion of the pigment did not increase the leaching rate, leading, if anything, to a slightly lower leaching rate. The

differences in leaching characteristics are attributable to changed chemical and/or physical properties caused by variation in raw materials, manufacture or change in storage. Earlier immersion trials indicated that ageing can result in a decrease in effective life.

The leaching curve obtained from Paint C shows a relatively low leaching rate due, in part, to its lower cuprous oxide content.

Panel immersion trials carried out by the manufacturer showed that Paint C had fouled after six months' immersion. Paints A and B were free from fouling after a year but the panels were inadvertently withdrawn before fouling had occurred.

At present, the fouling free life of a paint cannot be accurately calculated from the results of accelerated leaching tests. However, this investigation shows that the accelerated leaching test will differentiate between paints which are supposedly the same, and which meet the normal comparison tests, but have shown different service lives.

The three accelerated leaching rate curves shown in Fig. 1 are typical of vinyl antifouling paints with fairly high cuprous oxide loadings. These and all other contact leaching paints so far examined have given "steady state" leaching curves which are of the form³ :

$$\text{Leaching rate} = \frac{A}{B + Cy}$$

where, for a given paint, applied, dried and leached under uniform conditions, A, B and C are constants and y represents the thickness of the exhausted matrix. Achievement of this "steady state" condition is dependent upon uniform composition of the film. However, the surface layers usually differ in composition from the body of the film. In the paints studied the surface layers contain a lower proportion of cuprous oxide to vehicle than the remainder of the film and this is responsible for the initial rise in leaching rates shown in Fig. 1 prior to the achievement of the "steady state." If the surface layers of such films are mechanically removed the leaching rate shows little or no initial rise and the "steady state" leaching rates are somewhat higher. If the surface layers of the film contained a higher proportion of cuprous oxide to vehicle than the rest of the film an abnormally high initial leaching rate would be obtained.

An accelerated leaching test, in conjunction with normal comparison tests, should greatly reduce the possibility of any serious deviations in service life. A simplified technique is therefore proposed to enable the accelerated leaching rate curve to be characterised. It will be evident from the preceding discussion that the "steady state" portion of the leaching rate curve should be used for the purposes of a quality control test. As the effect of application techniques and conditions during application and drying on the surface layer are imperfectly understood, it seems advisable that the surface be left intact, and that the paint be applied and dried under controlled conditions, similar to those met with in service.

A suggested technique is given below, with explanatory notes.

Control test method

Scope

This method is designed to determine the accelerated steady state leaching characteristics of contact leaching antifouling paints with inorganic copper-containing pigments as the major toxic agent.

(Note : The leaching rates of matrix soluble paints will also be accelerated and these paints can probably be characterised by this technique. However, the presence of organically bound copper may lead to variations in measured leaching rates, depending on the method of copper analysis employed.)

Leaching solution, reagents and water

(a) Leaching solution and reagents. The amino-acetic acid (glycine) used should meet the BP specification and the sodium hydroxide and sodium chloride used should preferably be of analytical reagent grade.

(b) Water. The water used should be distilled or deionised.

(Note : Other grades of reagent may be employed provided their use does not lessen the accuracy of the determination. Poor grades of amino-acetic acid give rise to dark solutions which may interfere with subsequent analysis.)

Preparation of leaching solutions and reagents

(a) Leaching solution. The leaching solution (0.025M sodium glycinate, 0.48M sodium chloride) is prepared as follows : 10.0 g of sodium hydroxide is dissolved in approximately two litres of water, and allowed to cool, 18.75 g of amino-acetic acid and 280.5 g of sodium chloride are then added and the solution made up to ten litres with water.

(b) Colorimetric reagent. 80.0 g of sodium hydroxide is dissolved in approximately 500 ml of water and when cool 150.2 g of amino-acetic acid is added and the solution made up to one litre.

Preparation of test panels

Test panels 8 cm × 6 cm are made from extruded polyvinyl chloride sheet approximately 0.25 cm thick, and lightly roughened to a uniform surface (Note 1). The antifouling paint is applied at a wet film thickness of about 0.005 in, using a doctor blade (Note 2), to one side of the panel. A preliminary coat of primer is sometimes required to obtain satisfactory adhesion to the panel (Note 3). Three of the edges are coated to approx. 0.25 cm with a suitable edging paint or coating and the top edge of the panel to approximately 1.5 cm (Note 4).

(Notes : 1. The size of the panel may be varied as long as the ratio of area to volume of leaching solution is the same. Other materials, such as lightly sand blasted glass may be used for panels.

2. Panels may be spray painted or brush coated, but extreme care is required to obtain a uniform smooth surface.

3. A thin coat of etch primer is suitable for vinyl paints when using glass panels.

4. Microcrystalline wax, solvent vinyls and solventless epoxy coatings have been used successfully.)

Apparatus

(a) Leaching jars. These should be uniform in shape about 8 cm in internal diameter and of approximately 11 cm internal height. They should be provided with suitable lids.

(Note : The size will have to be varied if different panel sizes are employed. The clearance between the bottom and side edges of the test panel and the jar should be approximately 1 cm and the solution should cover all but the top 0.5 cm of the test panel.)

(b) Agitation. The panels should be subjected to uniform mechanical agitation. This can be supplied by rotating the panel at 60 rpm for approximately one minute, stopping the rotation for ten seconds and repeating the cycle.

(Note : Continuous rotation of the panels leads to increased leaching at the outer sides of the panel. By stopping the panel relatively quickly the turbulence caused will tend to even out the leaching over the panel surface. This cycle can be achieved by using a 1 rpm timing motor and micro-switch.)

There should be no slack or possibility of slipping in the drive to the panels. The drive shafts and clamp should be of inert material and the clearance between the holes in the lids and the shafts should be small to minimise losses by splashing or evaporation.

A suitable apparatus is shown in Fig. 2.

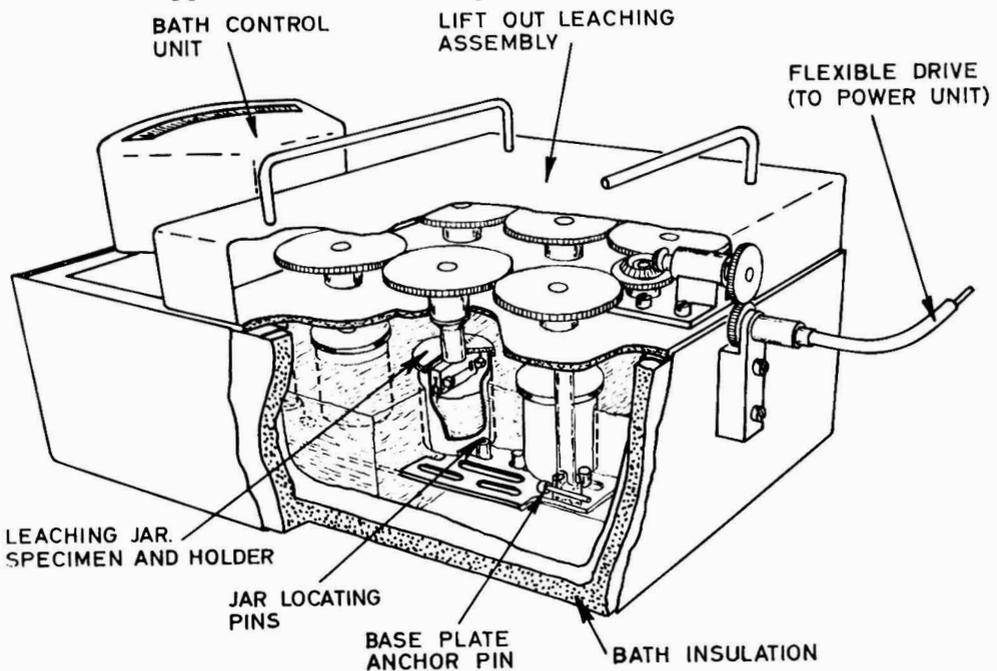


Fig. 2. Suggested design for simplified leaching apparatus

(c) Temperature control. The temperature of the leaching solution should be controlled to $\pm 0.5^\circ\text{C}$.

(Note : This can best be carried out in a thermostat bath. The error at 20°C in the leaching rate of a contact leaching paint is approximately 2 per cent/ $^\circ\text{C}$.)

Procedure

The test panels are carefully positioned in the panel clamps to provide uniform clearances from the leaching jar bottoms and sides. 400 ml aliquots of leaching solution at standard temperature are added to each jar, the panels immersed and covers placed over the jars. (Note 1.)

Agitation is commenced and is continued for 60 hours, the leachate being discarded every eight to 16 hours. (Note 2.) The panels are then withdrawn and allowed to drain while the leaching solution is discarded and fresh jars containing 400 ml of leaching solution are placed in the apparatus. Leaching is continued for 24 hours, the samples withdrawn and kept for analysis. After 60 hours' further leaching, during which the leachate is again discarded every eight to 16 hours, the panels are leached in fresh leaching solution for 24 hours. The final leachate is retained for analysis. (Notes 2 and 3.)

(Notes: 1. If the panel dimensions are different from those stated above, the volume of leaching solution should also be correspondingly varied.

2. As the leaching rate is affected by the amount of copper in solution, the copper concentration should be kept as low as possible and should not exceed 100 ppm if accurate reproducible results are required. If this value is exceeded the leaching rates will be unduly depressed, but will be repeatable provided exactly the same time cycle is employed. With paints having very high leaching rates the analytical samples should be taken over a shorter time period.

3. Fig. 1 shows the procedure graphically. As the curve for the "steady state" leaching is of a given mathematical form only two points are required to characterise it. Thus, by measuring over a fixed time period the average leaching rates at 72 and 144 hours the curve is characterised, and any other paint leached in exactly the same way which shows the same average leaching rates at 72 and 144 hours will have similar leaching rate characteristics. The leaching periods both for discard and analysis are not critical provided the amount of copper in solution does not exceed 100 ppm, but the same time sequence must be followed when comparisons are carried out.)

Determination of copper

The amount of copper in the leachate can be determined by any suitable method of analysis. Both of the methods described below have proved satisfactory, giving an accuracy of approximately ± 2 per cent.

(a) Atomic absorption spectroscopy. The leachate is diluted to give a solution containing between 1 and 5 μg of copper per ml. The absorption at 3247 Å is compared with that obtained using known quantities of copper. The method is rapid and accurate.

(b) Spectrophotometric analysis. The leachate is made up to 500 ml with 75 ml of 2N sodium glycinate and water. The optical density at 650 $\text{m}\mu$ is compared to that obtained using known quantities of copper. The method is accurate, but not as rapid as atomic absorption. An absorptiometer using a 600-650 $\text{m}\mu$ filter has been used and is more rapid, but generally less accurate, although by careful calibration, reasonable accuracy can be obtained.

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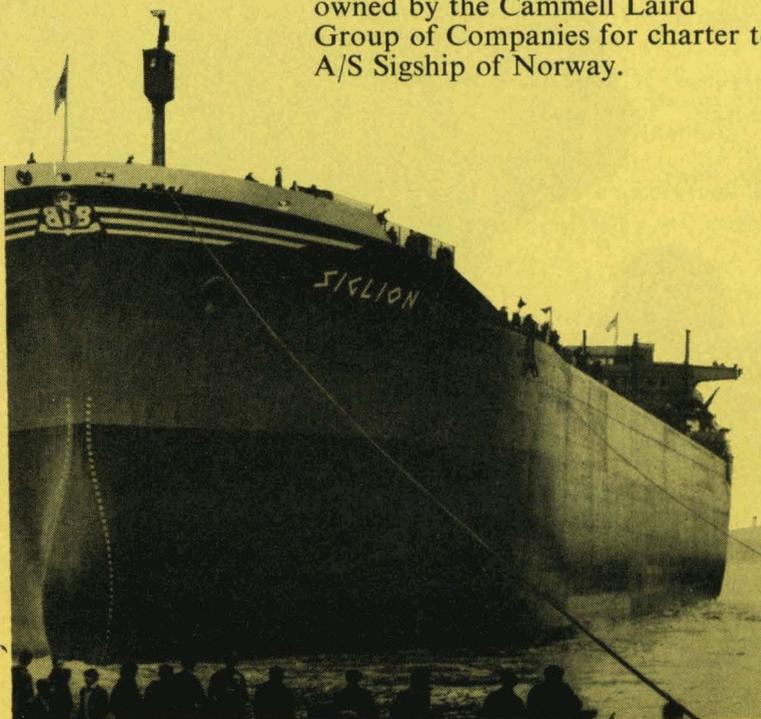
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Whichever method of analysis is employed at least two determinations should be made for each leachate; these should agree within the limits established for the experimental technique using known copper solutions. In each of the above methods considerable care is required to obtain maximum accuracy, and calibration checks should be carried out with each batch of analyses.

Calculation

The average leaching rate, Cu in $\mu\text{g}/\text{cm}^2/\text{min.}$, for each of the leaching periods is given by :

$$\text{LR} = \frac{\text{T}}{\text{A} \times \text{B}}$$

T = total copper in μg in flask

A = area of antifouling paint in cm^2

B = total time in minutes of leaching period

If the leaching period is 24 hours :

$$\text{LR} = \frac{\text{T}}{\text{A} \times 1440}$$

Reproducibility

This method is capable of giving a reproducibility of $\pm 2\frac{1}{2}$ per cent.

Assessment

As little evidence is yet available for the comparison of accelerated results and service life of antifouling paints, it is proposed that for paints having an expected life of up to 15 months, batches be accepted provided their characterisation samples do not differ in leaching rate from the original approved sample by more than 10 per cent. For paints with expected lives of two years or more it is proposed to reduce the allowable variation to 7.5 per cent.

Conclusions

The glycine-accelerated leaching technique will quantitatively distinguish between contact leaching antifouling paints which are supposedly the same, and which meet the normal comparison tests, but which show different fouling-free lives in practice. It is possible that the method could also be applied to matrix soluble paints.

With the simplified leaching procedure and apparatus described, only two measurements are needed to determine the accelerated steady state leaching characteristics of contact leaching antifouling paints, thus providing a test method suitable for quality control purposes.

Acknowledgments

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Adhesion as a factor in the performance of surface coatings*

By P. T. Brown and E. W. Garnish

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Summary

A simple model has been used to consider the likely stresses in a coating in service arising from the effects of attacking reagents. This leads to the hypothesis that adhesive tests involving a peeling element should be of value in assessing the potential performance of a coating. As an example, the properties of a solvent-free epoxy system as both surface coating and adhesive have been examined.

Surface pretreatments, cure regime and resin system composition have been the factors varied. Lap-shear and cleavage tests on thin steel and a new cross-hatch peel test have been compared with corrosion resistance tests. In general, variations that improve adhesive strength also improve corrosion resistance.

Adhésion en tant qu'un facteur du rendement de revêtements

Résumé

Un modèle simple a été utilisé pour considérer les efforts probables dans un revêtement pendant sa durée en service que produisent les réactifs nuisibles. Cette considération suggère que des essais d'adhésion relevant au pelage du revêtement auraient valable pour apprécier son rendement virtuel. On a examiné par exemple les propriétés d'un système époxydique exempt de solvant en tant que revêtement et à la fois adhésif.

On a fait varier les pré-traitements de surface, la mode de durcissement, et la composition du système de résines. Des essais de recouvrement-cisaillé et de clivage sur tôle d'acier, ainsi qu'un essai nouveau de pelage en contre-hachure ont été comparés des essais de résistance à la corrosion. En général, les variations qui augmentent la force d'adhésion améliorent également la résistance à la corrosion.

Haftfestigkeit als ein Faktor für das Verhalten von Beschichtungen

Zusammenfassung

Um die voraussichtlichen Beanspruchungen eines Überzuges, die im Gebrauch durch Einwirkung aggressiver Reagenzien vorkommen können, zu betrachten, wurde ein einfaches Modell benutzt. Dies führte zu der Hypothese, dass mit Abreisskriterien kombinierte Haftfestigkeitsversuche für die Beurteilung der möglichen Leistungsfähigkeit einer Überzugsschicht von Bedeutung sein würde. Als Beispiel wurden die Eigenschaften eines lösungsmittelfreien Epoxysystems sowohl als Anstrichmittel, als auch als Klebstoff geprüft.

Oberflächenvorbehandlungen, Härtungsmethode und Zusammensetzung des Harzsystems wurden variiert. Überlapp—Scher und Spaltungsprüfungen auf dünnem Eisenblech, sowie eine neue Gitterschnitt—Abschälprüfung wurden mit Korrosionsbeständigkeitsversuchen verglichen. Man stellte fest, dass im grossen und ganzen Variationen, welche die Haftfestigkeit verbessern, auch die Korrosionsbeständigkeit vergrössern.

Сцепление как фактор в действии поверхностных покрытий

Резюме

Применялась простая модель для изучения возможных напряжений в рабочем покрытии, возникающих вследствие эффектов атакующих реагентов. Отсюда следует гипотеза что испытания сцепления могут иметь значение при включении в них слоистого элемента

*Read before London Section, 24 March 1966.

с целью оценки потенциального поведения покрытия. Как пример исследовались свойства эпокси-системы без растворителя в качестве поверхностного покрытия и сцепляющего вещества.

Испытывались различные вариации факторов: поверхностные обработки, режимы сушения и составы систем смол. Сравнивались опыты для трансверсального сдвига и раскалывания на тонкой стали и новой слоистой штриховки с испытаниями на противокоррозийность. Вообще говоря, вариации сопровождаемые улучшением силы сцепления также улучшают коррозионное сопротивление.

Introduction and object of work

That paint films should adhere to the substrate to which they are applied is an obvious requirement. Less obvious are the methods by which this adhesion should be measured or the strengths that may be required to ensure adequate protective properties. This paper sets out to examine some of the relations between adhesion and coating performance with one of the newer types of solvent-free coating based on liquid epoxy resins. These coatings have similarities to the epoxy resin systems that are widely used as adhesives. An investigation with this type of material therefore seemed particularly apt.

Before experimental work was begun some hypothesis linking adhesion and coating properties based on accepted theories had to be set up^{1, 2}. The following argument seemed useful.

Adhesion is a manifestation of intermolecular forces. A perfect interface between two materials is one where there is a perfect relationship between the molecules of the two phases. Even if there is no chemical bond between the two, the intermolecular forces are very considerable. However, in practice, it is impossible to achieve a perfect junction. Only a small proportion of the theoretical intermolecular interaction can be utilised because the number of imperfections in and between the phases is high. A junction is usually formed in practice by applying a liquid on a solid and then hardening the liquid. When there is only one solid the liquid is termed a surface coating. When the liquid bridges a gap between two solids it is termed an adhesive. The coating therefore is an adhesive that sticks on one side only.

When a coating is in use some penetration of the film by an attacking agency is possible. Fig. 1 is a simple model that helps in the analysis of this situation. It shows imperfections in the coating and diffusion paths by which attacking media may reach the interface. Where penetration occurs the substrate will usually be impure so that electrolytic corrosion takes place. A pressure is

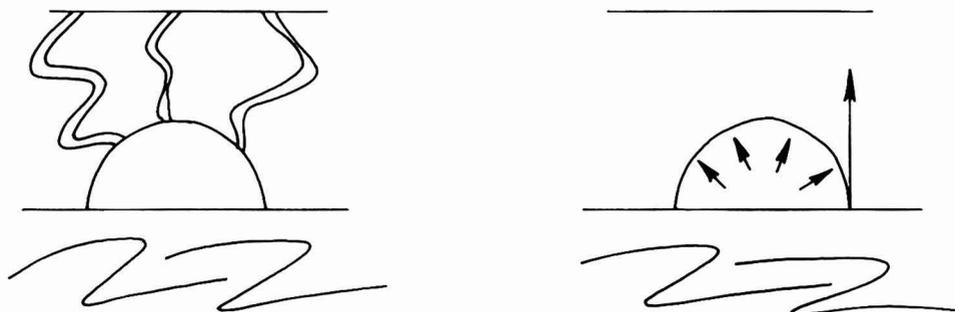


Fig. 1. Penetration of a paint film by an attacking agent

built up in the imperfection so that a strain is placed on the bond between the phases. The corrosion will be localised provided the bond holds. The strain will cause reaction forces in the coating. These will be influenced by the stiffness of the coating, but there will always be some peeling force tending to strip coating from substrate. It may be concluded therefore that adhesive tests having a bearing upon the coating performance should include procedures imposing peeling moments on the bonds.

Having set up the hypothesis, it was necessary to select the methods by which it should be tested. The common types of adhesive joint made are the butt joint, the lap-shear joint, the peel joint and the cleavage joint. The applied forces and geometry are shown in Fig. 2. When the butt joint is stressed there is no peeling moment. When the lap-shear joint is stressed there is a peeling moment if it is made of fairly thin material that can bend. In the other two types the peeling moment is large.

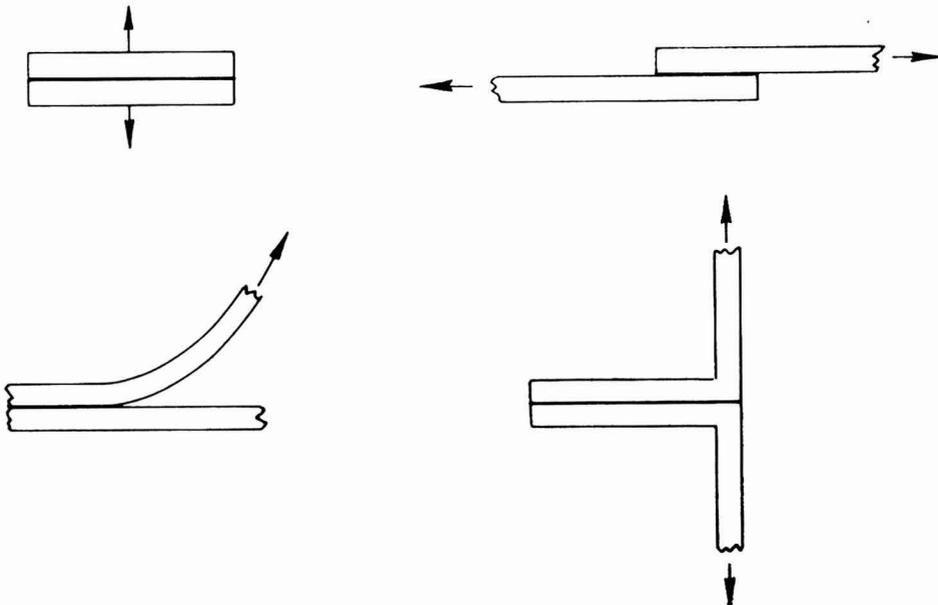


Fig. 2. Adhesive joints. (Top): butt, lap-shear (bottom): peel, cleavage

Failing loads of adhesive specimens where there is a considerable peeling moment are but a small fraction of those where shear forces predominate. In a peel test work is expended in three ways :—

- (a) The work required to create a new interface.
- (b) The work done in deforming the adhesive.
- (c) The work done in bending and stressing the adherends.

The energy required for (b) and (c) may quite outweigh that for (a), the classical work of adhesion. Two adhesives may give similar results when tested in shear, but the failing loads in peel may differ considerably because of large

differences in (b). In the assessment of any adhesive the tests are chosen to show up these sorts of difference by using more than one type of specimen geometry. By analogy, in the assessment of a coating the use of more than one type of test appeared to be prudent to ensure a fair judgement of the relation between adhesion and coating performance.

An epoxy system based on a resin from bisphenol A and an aromatic amine hardener was chosen for the investigation. All components were liquid. The system had the following experimental advantages :—

- (a) There was no solvent to remove and no air drying reaction so that adhesive joints could be closed immediately without an intermediate cementing layer.
- (b) There was only one mode of reaction so that adhesive joints could be cured at differing temperatures without altering the types of cross-link in the cured resin :—



The system forms a rather rigid coating. This character places a premium upon a good intermolecular bond, for stresses tend to be localised, for example, around imperfections at the interface.

There are several causes for the presence of such imperfections. One is that the liquid may not fully wet the solid. This problem and its relation to adhesion has been extensively studied³. Another is that a weak layer may be present at the interface. Because this is a universal difficulty in practice, it was decided that one aim of the experiments should be to explore ways to minimise its effects.

The experiments to be performed were of two sorts. There were the tests made on the system as an adhesive, where it filled the gap between two surfaces. Lap-shear tests and the cleavage joints were to be made. Then there were the tests made on the system as a coating, where the resin was spread on one surface only. Corrosion resistance was to be determined and a cross-hatch peel test applied. The cured system could be examined at ambient and elevated temperatures. In the corrosion tests some accelerated results could be obtained by use of elevated temperatures.

The first step in using an adhesive or coating is the preparation of the surface. The material chosen for the experiments was rolled mild steel. No practical pretreatment would give a surface of bare metal. The best that could be hoped for was an oxide film with adsorbed atmospheric gases and moisture. Such a surface should be readily wetted by an organic polymer, and adhesive joints should exhibit cohesion failure in the glue line. However, results by Bullett and Prosser⁴, given in Table 1, have shown how difficult it is to produce a good surface. They were working with an adaptation of the Paint Research Station "pull-off" test using an alkyd paint on mild steel. A lengthy treatment was necessary to obtain cohesion failure.

Table 1
Adhesion of an alkyd paint to mild steel

Pretreatment of steel (28 swg)	Bond strength (lbf/in ²)	Per cent adhesion failure
1. Solvent wash in petroleum ether	2250	100
2. Step 1 plus abrasion with emery cloth plus another solvent wash	3150	100
3. Step 2 plus 3h extraction in methyl ethyl ketone	3775	20

The failure of a bond at a weak interfacial layer can be due to contaminants remaining on the substrate after pretreatment, but also to materials migrating to the interface from the interior or to some local chemical reaction between the phases after the bond is formed. The minimum extent of the contamination that will cause some effect is not known, but a few molecular layers may be important.

In this work three rapid methods of pretreatment were used :—

- (a) Vapour degreasing.
- (b) Step (a) plus shot-blasting.
- (c) Step (a) plus phosphoric acid etch.

The second and third are more efficient than the first in removing contaminants present on the original metal, but the third, being a chemical reaction, can introduce further foreign material.

Experimental methods

Resin system

The epoxy resin was a conventional liquid diglycidyl ether based on bisphenol A. The hardener was a liquid, modified, polyfunctional aromatic amine. An acidic accelerator was required. [Respectively : Araldite GY 250, HY 830, DY 830 from CIBA (A.R.L.) Ltd.] The mixing ratio (w/w) of this system was 100 : 60 : 1 : : resin : hardener : accelerator. The components were mixed just before they were required for use. Primers used for special experiments are described in the text.

Substrates

Mild steel was used in all experiments. In the adhesive tests this was used in the following forms: lap-shear tests, strips $4\frac{1}{2}$ in \times 1 in, of 20 swg rolled mild steel; cleavage tests, strips 6 in \times 1 in formed to L-shape with base area 1 in \times 1 in 26 swg rolled mild steel; cross-hatch peel test, panels 5 in \times 2 in \times $\frac{1}{8}$ in smooth steel. The corrosion resistance tests used the same 5 in \times 2 in \times $\frac{1}{8}$ in smooth steel panels.

Pretreatments

All metal was degreased before use, in a trichloroethylene vapour bath (three dips, cooling metal between each). In several experiments the surfaces were shot-blasted by passing the degreased metal for 1-2 seconds beneath a stream

of annular steel grit. Other pretreatments for special experiments are described in the text.

Preparation and testing of adhesive joints

Lap-shear specimens and cleavage specimens were of the form shown in Fig. 3. Jigs were used to maintain overlap and pressure. Glue line thickness was 0.001-0.002 in. From one mixture 12 lap joints and three cleavage joints were

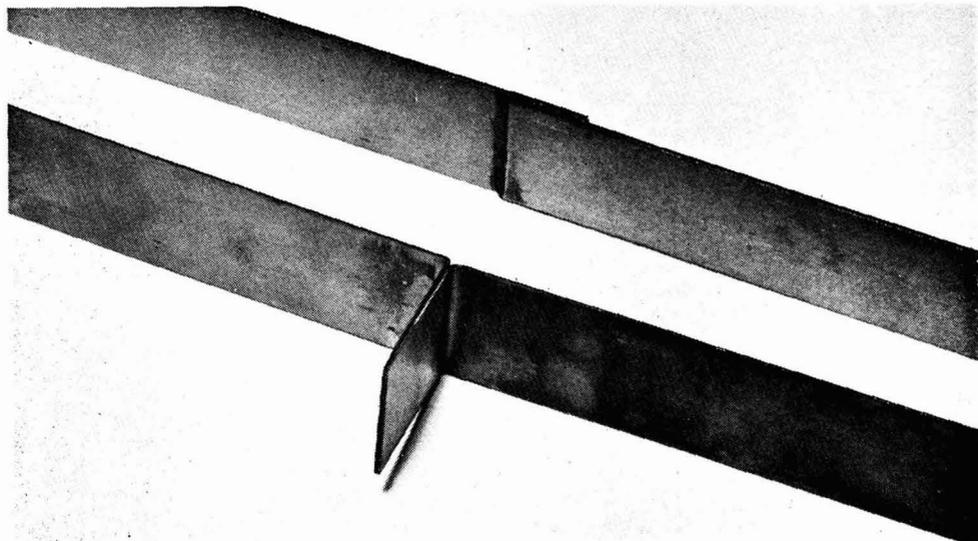


Fig. 3. Examples of adhesive test specimens: lap shear (upper), cleavage (lower)

made. All specimens were given a cure of 24 hours at room temperature (20-24°C) plus 24 hours at 40°C. Lap-joints were tested at room temperature, 40 and 75°C (four at each temperature), and cleavage joints at room temperature on a tensile test machine (Hounsfield Tensometer), crosshead speed $\frac{1}{2}$ in./min. Reliability was checked by making two independent sets of joints for each experiment (except where stated in narrative).

Preparation and testing of specimens in the modified cross-hatch test

The adhesion of the coating was directly assessed by peeling off a pattern of squares cut through to the substrate. The proportions of squares remaining was a measure of adhesion of the coating. A detailed description of the special technique developed for this investigation is given in Appendix A. Unless stated otherwise, the figures quoted in the narrative are the means of six specimens. The cure regime was two weeks at room temperature.

Corrosion test specimens

The coating thickness was 0.009 ± 0.001 in on the panels. Cure was for two weeks at room temperature. The attacking media are described in the narrative. There was usually one panel per test.

Results and discussion

The one method selected to test adhesion when the epoxy system was used as a coating was the cross-hatch peel test. This is a method widely approved by the paint industry. One version is described by DIN/53/151 where a pattern of 100 squares is cut into a paint film with a sharp blade. If the coating withstands this treatment self-adhesive tape is pressed on to the surface of the pattern. The tape is pulled off manually and the number of squares remaining adhering to the substrate is taken as an assessment of adhesion.

There are several difficulties in the test. The size of the squares is important. When the size is reduced there is a tendency for the proportion detached in the test to increase. This is due to the damaging effect of making the cuts and the uncontrolled force used. To assess differences between a number of systems, a suitable balance between the peel strength between coating and substrate and between adhesive tape and coating is necessary. Bias can enter into the results since the strength of the bond of the tape to the coating depends on the pressure used in forming it and on the time of contact under pressure. In addition, there is usually no control of peeling rate or angle; both are important factors.

The difficulties were particularly acute with the epoxy system. The thick coating formed is very hard and very adherent. A modified technique was required. A reproducible method of cutting the cross pattern in coating was sought so that stresses on the adhesive bond were minimised. Adhesives giving better defined and higher bond strengths than self-adhesive tape were wanted. Controlled peel rate and angle of pull-off were needed.

The problem of forming the cross-hatch pattern without damage was solved by utilising a grinding technique rather than the cutting method (see Appendix 1). Fig. 4 shows a machine devised for the purpose. The coated panel is placed

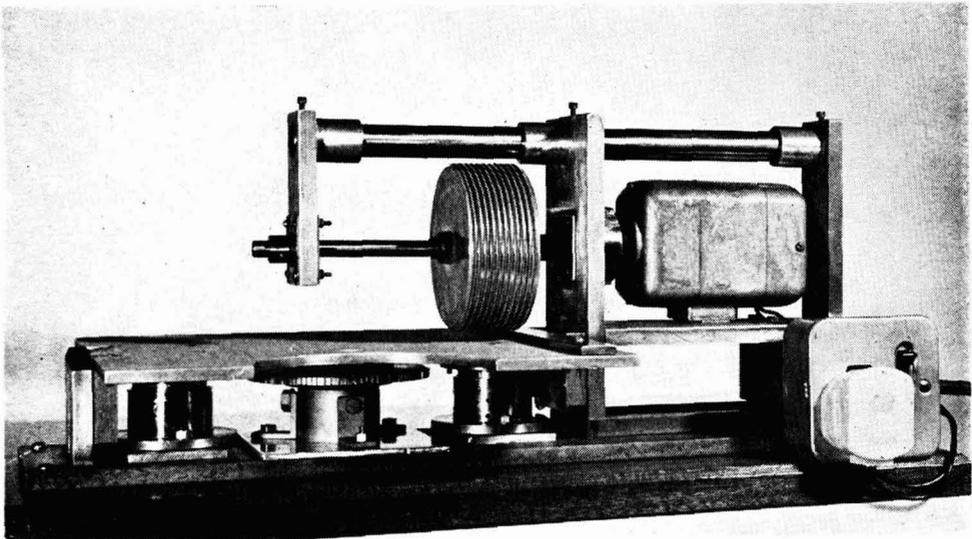


Fig. 4. Machine used to prepare cross-hatch peel specimens

on the table of the machine and pushed gently against a battery of carborundum grinding discs revolving at about 3,500 rpm. The coating is completely penetrated. The process is carried out in two directions to form the cross-hatch pattern. The inadequate pressure sensitive tape is replaced by modified epoxy resin adhesives applied to flexible metal strips. The pull-off procedure is controlled by a jig mounted in a tensile test machine. The jig holds the coated panel normal to the direction of the applied force, as in Fig. 5.

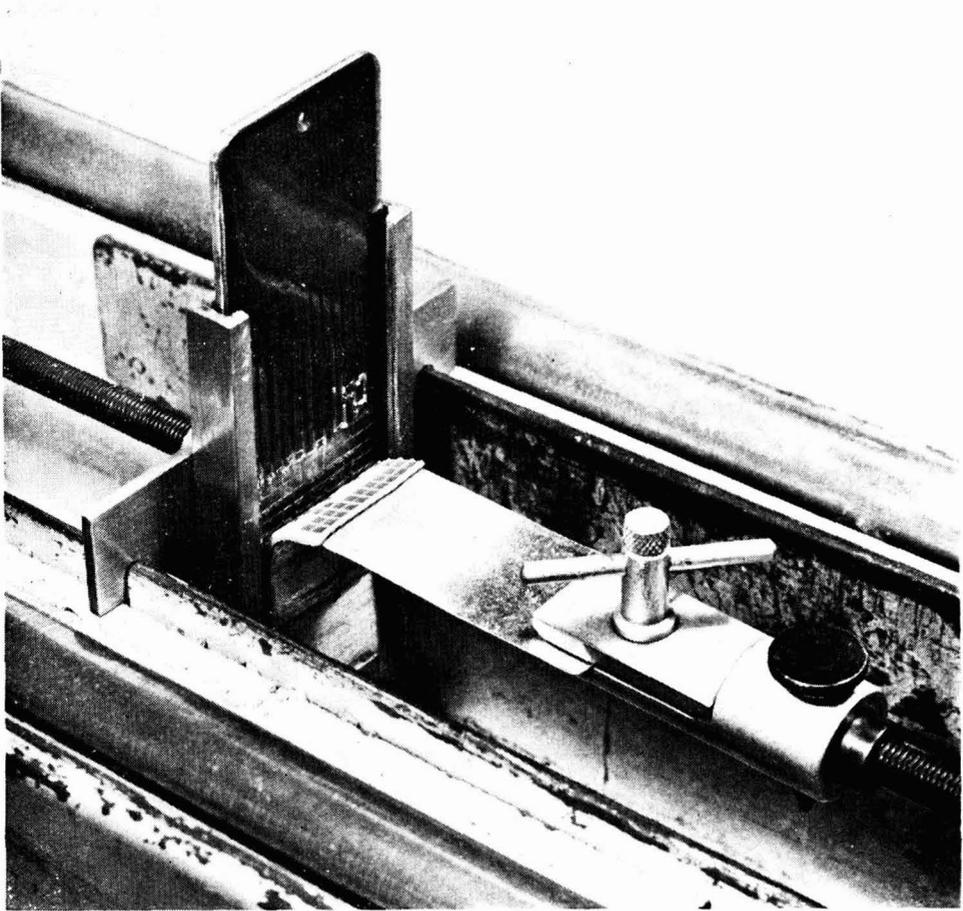


Fig. 5. Cross-hatch peel test in progress

Fig. 6 shows examples of coated panels tested by the method. The left hand panel shows adhesion of high order, 91 per cent of the squares being retained.

The relation between adhesion and surface coating performance was examined by carrying out parallel experiments on the system used as adhesive and coating. The effects of the three pretreatments were tested first. Table 2 shows the results with the adhesive. As well as lap-shear and cleavage specimens

on thin steel, a set of joints using $\frac{1}{8}$ in thick steel strips was made to show the gain in strength when the substrate stiffness was increased.

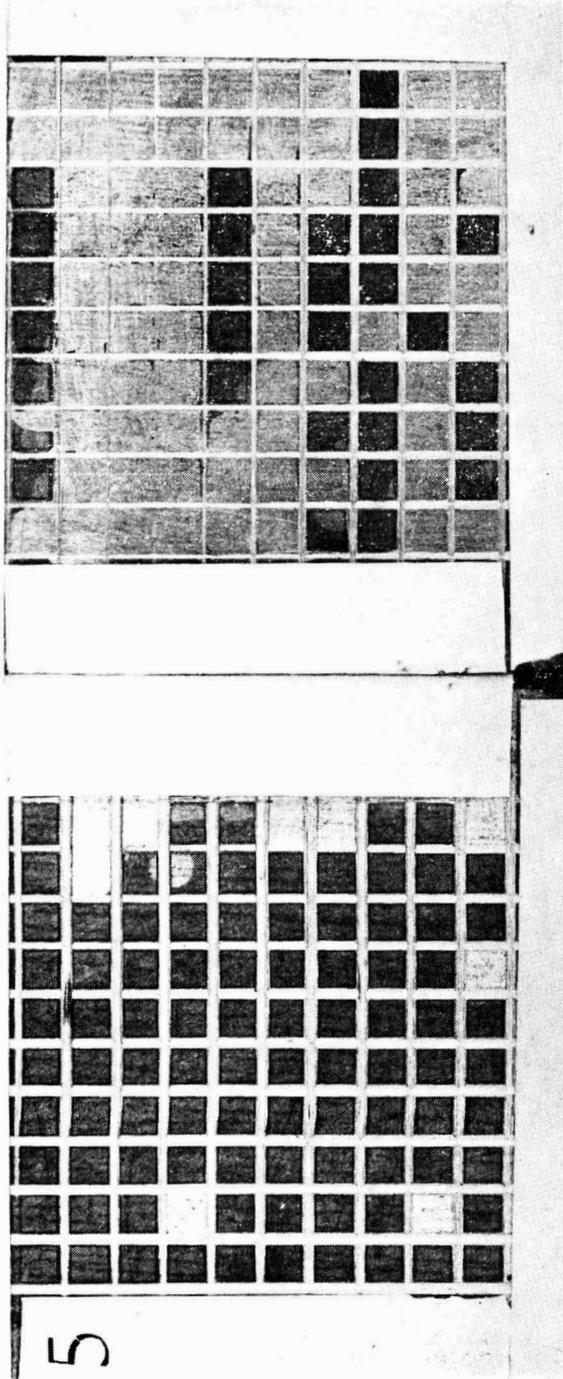


Fig. 6. Cross-hatch peel specimens after test

Table 2
Preliminary assessment of adhesive properties

Adherend	Pretreatment	Cleavage strength (lbf)	Lap-shear strength (lbf/in ²)		
			RT	40°C	75°C
Thin steel	Degreased	27 (6)	660 (12)	632 (12)	612 (12)
do.	Shot-blasted	183 (6)	2132 (12)	2116 (12)	1198 (12)
do.	Acid-pickle	14 (6)	1660 (8)	1692 (8)	734 (8)
Thick steel	Shot-blasted		3744 (4)	3900 (4)	1624 (4)

() no. of joints.

RT = room temperature (20-24°C)

The strength was higher because the peeling moment was small. The cleavage specimens, where the peeling moment was high, gave breaking loads that were but a fraction of the shear values. The results showed the following sequence for the surface preparation methods:—

shot-blast > acid pickle > degrease

The difference was reflected in the appearance of the lap-shear coupons. Shot-blasting and acid pickle caused a mixed cohesive/adhesive failure; degreasing caused complete adhesion failure. When an effective pretreatment was used, it could be seen that the adhesive properties of the system were falling away at 75°C. The cleavage specimens showed apparent adhesion failure in all cases. The effect of imperfections at the interface was obviously very great so that the test might be expected to have a valuable relation to the corrosion resistance of the coating. It was found that degreased metal was not readily wetted. A droplet of water formed a high contact angle upon it. The surface must therefore still have been covered with some low energy organic film.

The film was very strongly adsorbed. This was shown by prolonged treatment with polar solvents of degreased metal strips in a Soxhlet apparatus. Joints were made from these treated strips. Results are shown in Table 3.

All specimens showed adhesion failure. The low energy film still present was the locus of failure.

The thickness of such a film is unknown. The first monolayer would be bound to the metal by strong intermolecular forces. It has been calculated that an orientated monolayer on aluminium is bound by a force equivalent to a shear strength of 1,300 tons per sq in⁵. Subsequent layers would be much less strongly bound, but could still be resistant to pretreatment solvents. An adhesive bond could fail through low cohesive strength in these layers.

The effects of the three surface pretreatments on cross-hatch peel and corrosion resistance of the coating are shown in Table 4.

Table 3
Prolonged solvent treatment

Treatment	Cleavage strength (lbf)	Lap-shear strength (lbf/in ²)		
		RT	40 C	75°C
(1) Degreased in trichloroethylene vapour	12 (3)	682 (16)	602 (16)	584 (16)
(2) Step 1 plus 3. in Soxhlet with trichloroethylene	20 (3)	640 (4)	546 (4)	780 (4)
(3) Step 1 plus 3. in Soxhlet with MEK		874 (4)	1124 (4)	320 (4)

() no. of joints.

Table 4
Effect of pretreatment on coating performance

	Degreased only	Acid pickle	Shot-blasted
Cross-hatch adhesion (3)	69% detached	2% detached	None detached
Boiling 2 per cent acetic acid, 4 days	Poor condition, coating badly damaged	Poor condition, coating badly damaged	Film intact Blisters, No. 4, dense
Boiling water, 10 days	Blisters, No. 4, medium/dense film lifting	Blisters, No. 4, medium/dense	Blisters, No.4, medium/dense
Water at 40 C, 1 month	Blisters, Nos. 4 and 6, medium and medium/dense	No effect	No effect
Continuous salt spray‡ 1 month	Small blisters, No. 8, medium	No effect	No effect

‡DEF 1053 Method No. 24.

*A.S.T.M. Standard D.714 Photographic Blister Classification.

The results of these experiments showed a close agreement between adhesive tests and coating performance. The shot-blast steel gave specimens with the best corrosive resistance and specimens with the best adhesive properties in lap-shear, cleavage and cross-hatch peel.

Given the presence of a contaminating film, it is desirable for coating or adhesive to displace it, diminish it or diffuse into it. A method successful with this epoxy resin was to use a burst of heat before the resin was heavily cross-linked. It is probable that diffusion was achieved in this way.

Table 5
Effect of initial heat treatment

Initial heat treatment (before usual cure)	Cleavage strength (lbf)	Lap shear strength (lbf/in ²)		
		RT	40°C	75°C
None (control)	27	660	632	612
24h 40°C	52	870	732	650
2h 70°C	80	1,570	1,744	1,326
1½h 90°C	95	1,882	2,072	1,658
1h 110°C	146	1,908	1,904	1,956
½h 130°C	166	2,226	2,430	1,784
¼h 150°C	96	1,858	2,100	924

The effect of an initial heat treatment before the standard cure on joints made from degreased metal is shown in Table 5. As the treatment temperature was increased, the adhesive properties were improved. There was a change from adhesion to cohesion failure at the 70°C treatment level. The best treatment (½ hour at 130°C) gave cleavage results six times better than the control, and lap-shear results three to four times better than the control. The heat treatments were chosen arbitrarily so that there was doubt that the cross-linking reaction had proceeded to the same point. To check this the method was also used on shot-blasted strips with the results shown in Table 6.

Table 6
Check of initial heat treatment

Initial heat treatment	Cleavage strength (lbf)	Lap shear strength (lbf/in ²)		
		RT	40°C	75°C
None	183	2,132	2,116	1,198
24h 40°C	69	2,187	2,295	1,082
30 min 130°C	64	2,898	2,774	2,287

The best heat treatment did improve the results, but by a much lower factor than was observed before.

As the cross-linking reaction was allowed to proceed at room temperature, it was progressively more difficult to effect diffusion by giving a heat treatment. A treatment of 15 minutes at 150°C after seven days' cure at room temperature gave an improvement in strength, but such a treatment was ineffective after six weeks at room temperature. By that time the flaws at the interface were frozen in.

This effect was shown in a striking manner by the tests made in the coating. Steel panels were given one coat of the epoxy system. One set of coated panels was stoved immediately at 150°C for ten minutes, after which time gelation had occurred, and was then held at room temperature for six weeks. A second set of panels was held at room temperature for six weeks and was then stoved for ten minutes at 150°C. Thus the two sets of panels had both been given the same stoving cycles, but the order of cycles had been reversed. It was hoped that the degree of cross linking was the same in each. Table 7 summarises tests that we made to compare the two cure regimes in this respect.

Table 7
Comparison of curing regimes

	10 min at 150°C then 6 weeks at RT	6 weeks at RT then 10 min at 150°C
Power factor 10 ³ c/s	0.012	0.011
Water absorption at 40°C .. 1 week exposure*	0.000362 g/cm ²	0.000363 g/cm ²
Ethanol absorption at 21°C .. 2 weeks exposure*	0.0091 g/cm ²	0.0088 g/cm ²

*Free film 0.02 in thick.

Table 8
Effect of curing regime on adhesion and corrosion resistance

	10 min at 150°C then 6 weeks at RT	6 weeks at RT then 10 min at 150°C	
Cross hatch adhesion test	5% detached	49% detached	
Corrosion tests	Boiling 2% aq. acetic acid, 2 weeks	Film intact Blisters, No. 2, dense [Fig. 7 C]	Film removed from metal [Fig. 7 D]
	Boiling 1% aq. sulphuric acid, 1 week	Small blisters, No. 8, medium, isolated	Blisters, No. 4, medium, spreading
	Boiling water, 1 week	Micro-blisters [Fig. 7 A]	Blisters, No. 2-4, dense, film lifting [Fig. 7 B]
	Water at 40°C, 2 weeks	Blisters, No. 6	Dense blisters, No. 4
	Continuous salt spray, 1 month	No effect	No effect
	Boiling 1% aq. sodium hydroxide, 1 week	Small blisters, No. 8, isolated	Blisters, No. 2-4, spreading

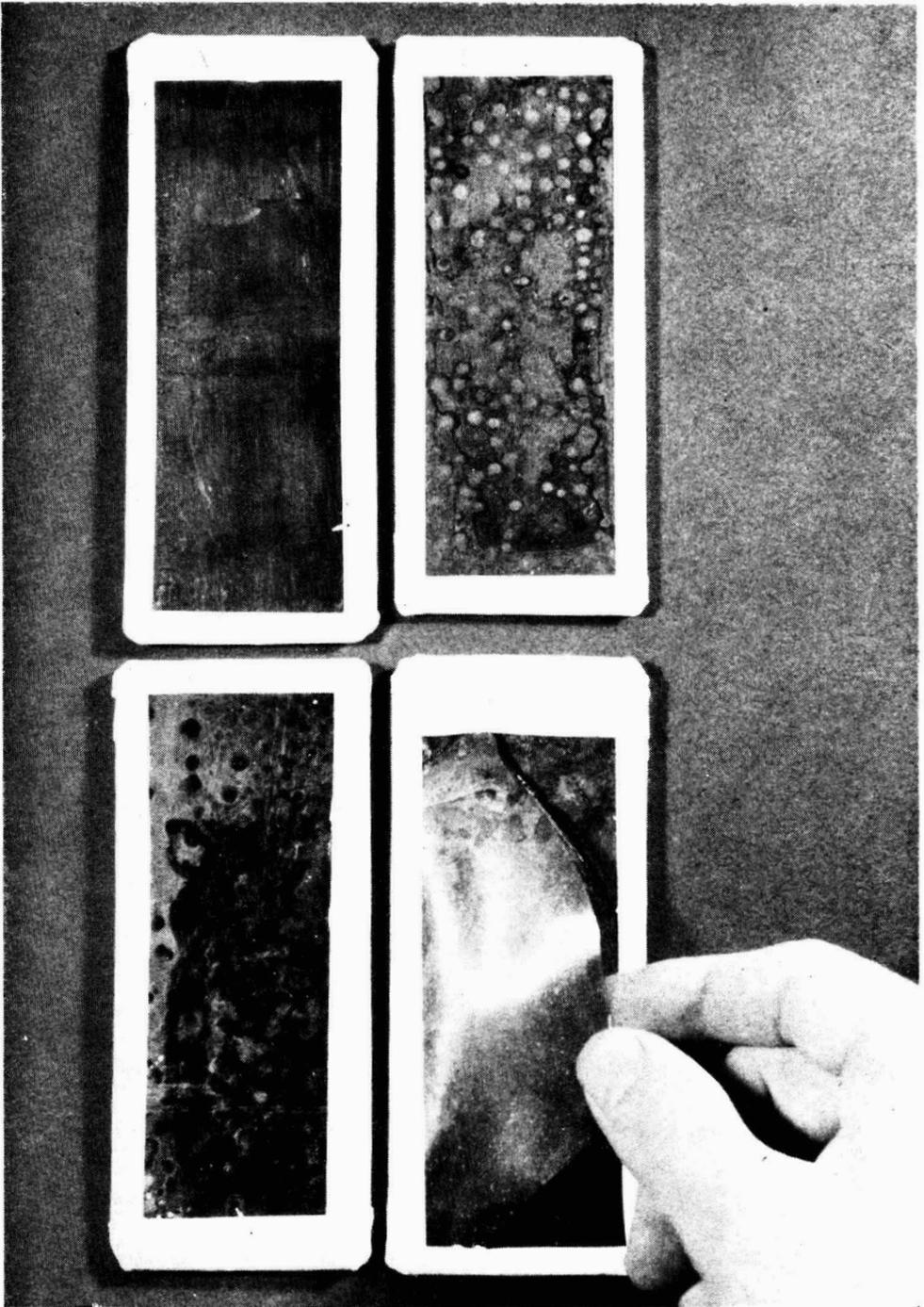


Fig. 7. Effect of curing regime on corrosion resistance

dunlop polymers

polyvinyl acetate, acrylic copolymer, acrylic terpolymer, styrene butadiene and styrene acrylic emulsions and transpolyisoprene polymer.



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Table 8 shows the results of the two treatments upon the coating. The burst of heat before gelation gave almost the same adhesion in the cross-hatch test as that produced by shot blasting. The effect on corrosion resistance was similar. The appearance of some of the test panels is shown in Fig. 7.

Again, in these experiments, there was a broad similarity between effects on adhesive properties and coating performance. However, in practical conditions it would not often be possible to heat a surface. Another way of approaching the problem of the interfacial layer would be to alter the properties of the coating placed on the substrate in such a way that a better relationship between solid and liquid phase is produced, and the number of flaws diminished. There is then the difficulty that the physical properties of the polymer might be changed significantly so as to complicate interpretation of results. However, three experiments of this sort were carried out. There was successively greater modifications of the system.

In the first experiment, degreased steel was brushed over with a suspension in xylene of pyrogenic silica (Aerosil). The formulation contained a small proportion of high molecular weight epoxy resin as a binder. The deposit was left on the metal and joints made up in the usual way. The silica could act as an abrasive and/or absorbant of contaminants. Chemical bridging was also possible. The results of this priming are compared with a control in Table 9. There was a small advantageous effect on cleavage (5 per cent probability level, single sided t-test), but no general advantage in shear. The effects on the coating performance are shown in Table 10. The specimens that had been primed were much more resistant to the corrosion tests.

Table 9
Effect of primer containing pyrogenic silica on adhesive

Recipe : Aerosil	10 pbw
Resin	25 pbw
Xylene	100 pbw

Treatment	Cleavage strength (lbf)	Lap shear strength (lbf/in ²)		
		RT	40°C	75°C
Control	27	660	632	612
Primed	58 (9)	624	595	746

The resin was included in the primer as a binding agent to help the overcoating step. A straightforward solution of the resin was ineffective, but the silica alone as a dispersion, although difficult to use, improved both adhesion and corrosion resistance.

This experiment showed the desirability of using a battery of adhesive tests. The advantageous effect of the primer was exhibited clearly in only one of the two tests with a large peeling moment.

A different approach was to use organofunctional silanes as adhesion promoters. Three organofunctional silanes were tested. They were alkoxy-

Table 10
Effect of primer containing pyrogenic silica on coating

		Degreased only	Primed
Cross hatch adhesion test		69% detached	None detached
Corrosion tests	Boiling water, 10 days	Blisters, No. 6, medium/dense, film lifting	Blisters, No. 6, medium/dense
	Water at 40°C, 8 months	Blisters and extremely severe metal pitting	Almost Unaffected
	Salt spray, 3 months	Blisters, No. 6, medium/dense	No effect
	Weathering†, 4 months	No effect	No effect

†Rural Cambridgeshire.

silanes carrying an amino function, a glycidyl function and a methacrylic function respectively (respectively DP 2712, ESP 2733, ESP 2730 from Midland Silicones Ltd.). With the epoxy system they showed promise.

Tests with solutions applied as priming coats were not successful. The interesting results were found when they were incorporated as an integral part of the coating. The amino-silane slowed down the curing reaction at room temperature. The effect on drying time is shown in Table 11.

Table 11
Effect of silane addition on drying time

Silane addition	None	Amino-	Glycidyl-	Methacrylic-
Beck-Koller drying time (h) ..	8½-13½	23-33	10-16	12-16½

It was found that the slower reaction at room temperature could be countered by increasing the cure time. An improvement in water resistance of the coating

Table 12
Effect of amino-silane addition

Corrosion test	No addition		With amino-silane	
	Standard cure	Long cure	Standard cure	Long cure
Boiling water, 6h	Blisters, No. 6, dense	Blisters, No. 6, medium/dense	Blisters, No. 6, dense	Sound
Boiling water, 30h		Coating lifting from panel Black oxide formation on steel		Blisters, No. 4/6, medium/dense

was obtained in this way as shown in Table 12. The amino silane also gave an improvement in adhesion as shown by the cross-hatch peel test results given in Table 13. Only the amino-silane and glycidyl-silane were tried as

Table 13
Cross-hatch adhesion test with silane addition

Silane additive	None	Amino-	Glycidyl-	Methacrylic-
Per cent detached	69	None	None	50

additives to the epoxy system as an adhesive. In these tests there was no adjustment to the standard cure. Results are shown in Table 14. The amino-silane material gave advantage in both lap-shear and cleavage, but the epoxy-silane material showed a gain only in the cleavage test. The advantages were due to an effect upon the surface layer, as no effect was obtained upon shot-blasted metal.

Table 14
Effect of organo-functional silanes

Metal treatment	Silane additive	Cleavage strength (lbf)	Lap shear strength (lbf/in ²)		
			RT	40°C	75°C
Degrease	None	27	660	632	612
	Amino-functional	57	1,704	1,940	700
	Epoxy-functional	59	660	840	684
Shot-blast	None	183	2,132	2,116	1,198
	Amino-functional	42	2,384	2,580	1,176
	Epoxy-functional	66	1,824	1,870	460

The results with the organo-functional silanes were obtained in too restricted an environment to assess their general applicability, but the evidence does suggest that they can be of use where surface pretreatment is imperfect. It was again interesting to note that it was the cleavage test and cross-hatch peel test that provided the advantageous adhesion data with the two useful additives.

The third method that was tried as an improvement to the corrosive protection properties was to treat the surface with a special tar-epoxy primer. The coating tests summarised in Table 15 showed that this primer was very successful. When the system was tried as an adhesive in its own right, the results were poor on both degreased and shot-blasted steel. However, the metal coupons showed that cohesive failure of the primer occurred under all conditions, so that the adhesive force across the interface had not been measured. The primer is a rather soft material when cured. Its action under the coating would, in part, be due to an ability to dissipate stresses between coating and substrate.

The corrosion tests were carried out on specimens that had had two coats

applied, so that film thickness was constant. The cross-hatch peel test yielded no assessment of the adhesion to metal since the primer failed rather than the bond between it and metal or epoxy system. It gave a mixed adhesion-cohesion failure between the detached epoxy system and the primer.

Table 15
Effect of tar-epoxy primer

		Two coats of unmodified system	One coat of tar-epoxy primer One coat of epoxy system
Cross-hatch adhesion test		50% detached (no intercoat failure)	90% detached (no failure between metal and primer)
Corrosion test	Boiling water, 4 days	Blisters, No. 2-4, medium/dense	Blisters, No. 6, medium
	Water at 40°C, 2 months	Blisters, No. 4-8, slight	No effect
	Salt spray, 3 months	Blisters, No. 8, slight Slight attack of metal	No effect
	Weathering, 3½ months	Very slight attack of metal	No effect

Conclusions

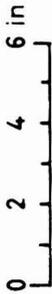
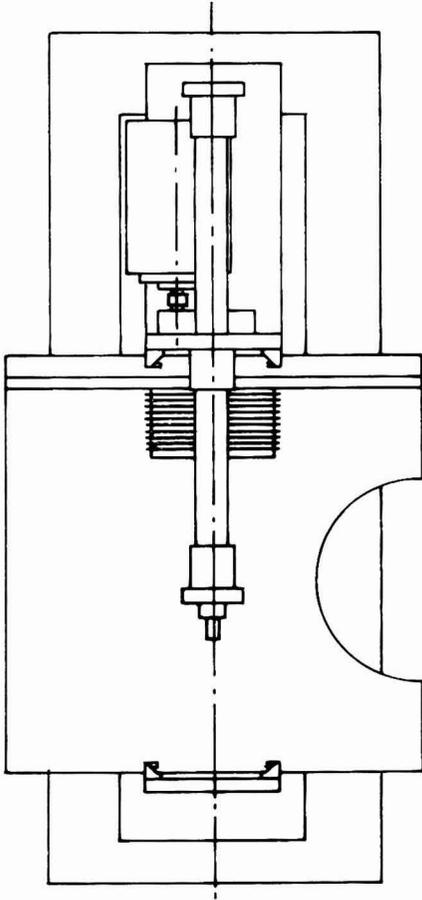
The relations between corrosion resistance and adhesion for a solvent-free epoxy system have been examined with the help of a hypothesis based on a simple model describing surface coating defects. A battery of adhesion tests has been used. The results show that it is unlikely that the protective properties of a coating can be predicted from any single type of test, but that those incorporating a high peeling moment are probably the most indicative. The cross-hatch peel test, as modified for the hard, thick epoxy coating, had a clear association with the coating performance in all the experiments. The method could probably be developed to deal with other coatings of different adhesive properties by suitable choice of adhesive strength and rigidity in the cement, and stiffness and pull-off rate in the flexible element.

Such adaption would be necessary to allow for different levels of adhesion. It was an important aspect of the work with the epoxy system that the adhesive tests usually reflected conditions at, or close to, the interface. In the example where soft tar primer was used, failure occurred in the coating, in cohesion. With this type of failure it was not possible to make any prediction of coating performance. Therefore, with softer coatings, it might be difficult to establish any relation between adhesion and performance unless the experimental methods were also adapted to match cohesive strength.

Appendix 1

Cross-hatch adhesion test

Apparatus : 1, Special grinding machine (see Fig. 8). 2, Tensile test machine, e.g. Hounsfield Tensometer. 3, Jig to hold panel vertically in test machine (see Fig. 9).



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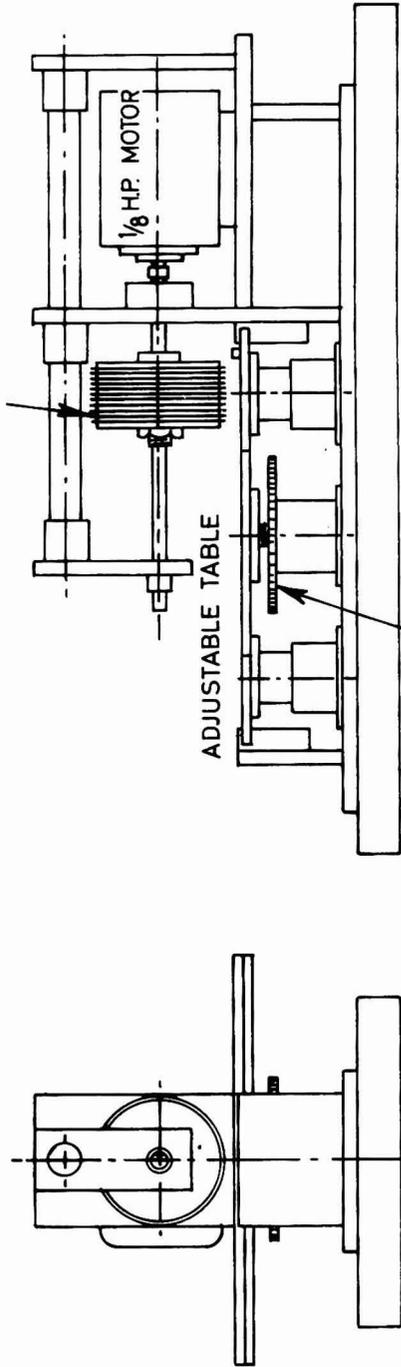


Fig. 8. Grinding Machine

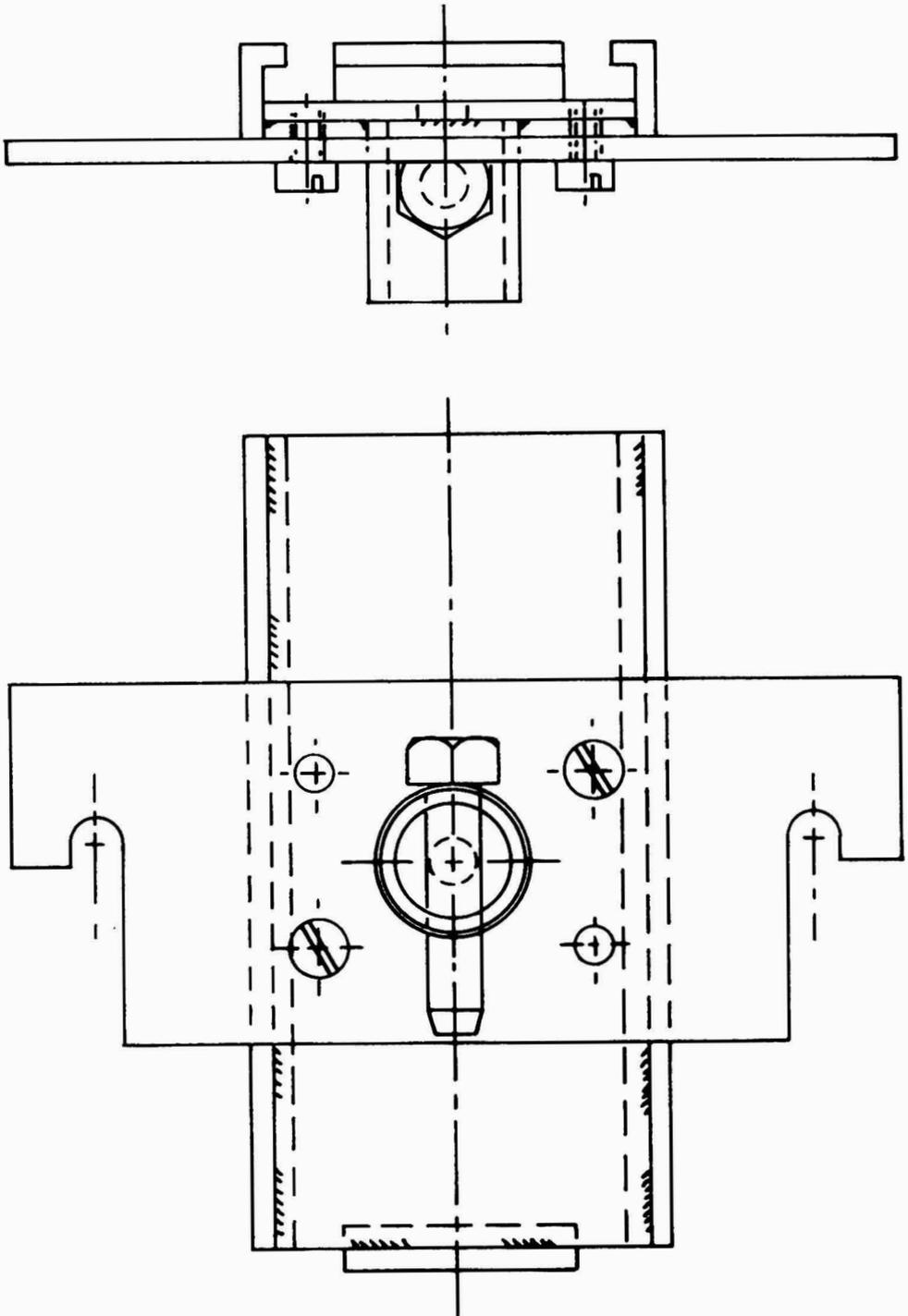


Fig. 9 Test Jig

Specimens : 4 in \times 2 in \times $\frac{1}{8}$ in mild steel panels coated on one side with system to be tested.

Cutting process : Using the micrometer screw on the grinding machine the table is set until the discs just touch an uncoated panel of the type under test. This panel is removed and the table raised a further 0.002 in. The motor is switched on. The test panel is pushed against the revolving discs without causing the motor to labour. The grooves cut should be straight and evenly spaced and the metal substrate clearly visible in the grooves. The process is repeated at right angles to the first cut.

Glueing process : A cold curing epoxy adhesive* is adequate for most coating systems, but where high orders of adhesion are encountered a hot cured flexibilised epoxy adhesive† may be used.

The procedure that follows is used when the cold curing adhesive is chosen. The grooves in the coating are filled with "Plasticine" and the excess washed off with petroleum ether so that the squares stand proud. The surface is abraded with grade 280 wet-and-dry emery paper, held on a flat block so as not to pick up any "Plasticine," until the surface has a uniform, level, matt finish. The surface is doused in a 5 per cent Teepol solution, washed under a mild jet of water, and allowed to dry. One layer of self-adhesive cellulose tape is affixed around the perimeter of the cross-cut pattern. This facilitates application of the adhesive at a constant film thickness.

A strip of tinplate, 0.01 in thick, the width of the cross-hatch pattern, and 4 in long, is shot-blasted and degreased in trichlorethylene vapour. The strip is bent into an L-shape so that one leg is the same size as the cross-hatch pattern. The adhesive is mixed and applied to the cross pattern of the coated panel. The excess is drawn off with a straight edge, leaving a film of adhesive the same thickness as the tape. The part of the metal strip to be glued is just wetted with adhesive. The two pieces are brought together to give a T-shaped specimen. The pieces are clamped together with sufficient pressure to ensure contact, but minimum loss of adhesive by squeeze-out. The adhesive is cured for the prescribed time before the clamp is removed.

If the hot-cure adhesive is used, the "Plasticine" process is eliminated. The pattern is abraded as before and the same type of metal strip is used. The adhesive tape is replaced by two 22 swg (0.028 in) metal shims secured to the edges of the cross-cut.

The adhesive is applied in the same way as before to give a uniform deposit. The surface of the peeling strip is just wetted and the pieces held together with just sufficient pressure to make good contact of the strip with the adhesive. The joint is then stoved.

After cure, the adhesive tape or the metal shims are carefully removed to avoid damage to the joint. The glue line at the bend in the metal strip is examined and if the build-up of resin at this point is excessive it is carefully removed with a knife or a small saw. This ensures that the adhesive peels off with the metal strip and not with the coating.

*Araldite GY 260/HY 830/DY 830 from CIBA (ARL) Ltd.

†X83/236 from CIBA (ARL) Ltd.

In the tests where lap-shear strengths rose from 22° to 40° and then fell at 75°, was there a change from adhesion to cohesion failure?

MR. BROWN said that there was evidence that the effect was confined to underbound systems.

MR. E. W. GARNISH said there was a mixed adhesion/cohesion failure all the way through the lap-shear series even at 75°C. There was a change from adhesion failure to this mixed failure where the resin was subjected to a lot of heat on surfaces that had only been degreased.

MR. G. RAM SUBRAMANIAN asked what methods were used to measure the degree of blistering. Was it visual comparison, or were the size, shape and area of blisters measured?

MR. BROWN said that visual assessment was used, with a rating relating to the number and type of blisters. Slight, medium or severe blistering in the paper described the concentration of blisters. Detailed records were available, these having been simplified for ease of assimilation by the audience.

MR. K. W. GREEN asked how the material was applied when it was examined as a coating. Amino-silane was a toxic material; was the epoxy-silane any safer, taking into consideration that a high solids material might be sprayed?

MR. BROWN said that application was by brush, with a period to allow flow-out. Film thicknesses obtained were in the range 8-10 thou.

Concerning the possible toxic hazard, he had no definite information about the toxicity of the epoxy-silane, but it was believed to be less toxic than the amino-silane. One did not get a lot of fine mist on spraying these solvent-free materials; therefore the toxic risk was minimised.

MR. A. G. ROBINSON asked whether any large scale work had been done with these materials, with particular reference to sagging. What was the pot life of the material, and had any difference been observed between coatings applied straight after mixing and towards the end of the pot life?

MR. G. J. POWELL said that in comparing the effect of heating before and after gelation on the chemical resistance of the solventless coating it was suggested that power factor and water absorption tests had shown that both systems were cured to the same degree. Hence the differences shown in the coatings exposed to different chemicals were said to be due to adhesion differences. For this to be acceptable the tests on the detached film should have been the same as those on the adhering films and should preferably have included mechanical strength (e.g. tensile strength) and several chemical tests. His experience was that heat treatment before or after gelation would be expected to lead to differences in the properties of the cured polymer, making it all the more vital that the comparison should be strictly valid.

MR. BROWN agreed that this was an important point. He suggested that it was more sensitive in the regions of partial cure, but ethanol and water absorption indicated clearly that there were equal degrees of cross-linking. The corrosion tests were in aqueous media; therefore the water absorption was relevant. The material was very good in its curing properties and was not sensitive to variations in temperature and humidity, and it was almost certain that the six weeks at room temperature would result in complete curing.

MR. POWELL said that in using a coal tar-epoxy primer under the solventless coating better chemical resistance was obtained than with a two-coat solventless system, yet the figures for the adhesion tests were much lower for coal tar-epoxy materials than for the solventless mix. Did this suggest that in some cases lower adhesive strengths gave better chemical resistance?

MR. GARNISH said that cohesive failure occurred in the lap-shear tests.

MR. BROWN added that the tar primer was tested in cleavage and never showed an adhesion failure, e.g. in the cross-hatch test, but always failed in cohesion.

MR. A. V. WHITE asked whether the amino functional silane had been considered as a curing agent. He added that the epoxy functional material was normally considered less toxic than the amino-silane.

MR. BROWN said that it reacted into the epoxy system, and also with the metal surface. He had not found it to be very effective as a curing agent in its own right.

MR. D. J. MCCONNELL said that following an earlier question, he would be interested to know whether the fine silica in Primer B adsorbed water from the metal surface, or were fatty acid materials adsorbed?

MR. BROWN considered that both could be adsorbed; oily impurities by physical adsorption and water by hydrogen bonding.

MR. POWELL asked for further details about the cross hatch adhesion test. How was the epoxy adhesive prevented from running into the cross cuts?

MR. BROWN said that the grooves were filled, e.g. with plasticine, and the excess washed off the surface of the squares before applying the adhesive.

MR. F. P. GRIMSHAW inquired whether any work had been done on the effect of varying the time interval between preparing the surface and applying the epoxy adhesive. It is known that in some cases the ease of wetting falls rapidly within a short time of preparation.

MR. GARNISH said that this occurred if one was dealing with very clean surfaces. With these more practical tests no special precautions had been taken; possibly half an hour elapsed before the adhesive was applied.

MR. BROWN said that in the coatings work application had been made within a few minutes of surface preparation.

MR. N. R. FISK said that the speakers had referred at the beginning to the fact that metals would in the ordinary way not adhere to one another. What was the explanation for the opposite case, where some metals, e.g. titanium, could not be used in contact with itself under conditions of sliding friction, even in the presence of an ordinary lubricant, without immediately welding together?

MR. GARNISH said that this was clearly a function of the metal. With soft metals such as indium adhesion was obtained by applying quite a low pressure. The state of cleanliness of the surface was very important, so that there was sufficient intermolecular attraction for spontaneous adhesion to occur.

MR. BULLETT, in proposing a vote of thanks to the lecturers, said that he had been particularly gratified to hear the stress laid on the necessity for preparing really clean metal surfaces in order to obtain high adhesive strengths.

Next month's issue

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

“The glycerolysis step in the production of oil-modified alkyd resins,” by *Ghanem and El-Mohsen*.

“The analysis of polymeric esters by interesterification and gas liquid chromatography,” by *Rawlinson and Deeley*.

“The behaviour of liquids on rotating rollers,” by *Mill*.

“Grinding,” by *Mathews*.

Editorial

Are you sitting comfortably?

Had it been possible to "Listen with Mother" in mediaeval times, few could have answered in the affirmative. Chairs were known, but they were scarce, and reserved for the Lord of the Manor and his most distinguished guests. In England, at least, chairs were then regarded as symbols of an almost regal dignity and power, descended but a little way from the throne itself. Those not sufficiently qualified had to be content with benches, stools and, later, settles. Sitting "below the salt" implied more than inferiority of altitude; it meant making the best of rough-hewn boards set on trestles whilst My Lord and his privileged friends enjoyed support at their backs if not resilience at their backsides. It was not until the reigns of Elizabeth I and James I that any measure of comfort spread beyond the houses of the nobles; and even then it spread but slowly.

Those were the days of oak, for the few who could afford it. For those who could not, ash, elm and beech were commonplace; imported timbers were yet some way off. Many of the early 16th century chairs were clearly descended from boxes, being boxes themselves with backs and armrests added. Slowly it was realised that the sides of the box did not have to be filled in if all one wanted to do was to sit upon it, but the box frame remained with tie-rails or stretchers at the bottom on all four sides. The simple ornamentation of these box-chairs, comprising rudimentary shaping, moulding and linenfold carving, gave place to more elaborate decorative work and deeply carved and inlaid chairs, some carrying appliquéd or painted coats of arms, were to be found before the end of the Jacobean period.

Probably the most comfortable chairs in those days were the X-framed constructions known in several ancient civilisations, revived in Tudor times, and revived again in the early 17th century. Few examples of the folding Tudor type survive because their backs and seats were composed entirely of fabrics. Examples are in existence, however, of their Early Stuart successors, rigidly constructed and well upholstered.

Without doubt, the least comfortable must have been the elaborately turned constructions which appeared in the early 1600's. One specimen in the Victoria & Albert Museum is built up over 300 separately turned pieces of oak and ash, the only flat surface being an exceedingly hard triangular seat. The Turners guild, though not incorporated till 1604, can be traced back to the early 14th century. Strange are the ways of fashion when, after the acutely uncomfortable Jacobean era, we passed through the supreme elegance of Georgian and Regency turnery, only to re-emerge, with Victoriana, into a period of bulbous monstrosities which lasted until the Second World War!

Austerity probably reached its climax during the Commonwealth; carving was distrusted, though turning, for some reason, remained acceptable. After this, chairs became more comfortable and the years 1660-1688, known as the Early Walnut or Restoration period, saw an increasing taste for luxury developing through the influence which the French court had obviously exercised on the returning Royalists, and the immigration of many skilled Dutch craftsmen resulting from trade with the Netherlands. There were four decorative innovations at this time: gilding, veneering, marquetry and lacquer. The oriental influence was marked, and it is interesting to note that, at first, lacquered panels were imported, or furniture was sent to the Orient for lacquering. English craftsmen learnt how to lacquer during the 17th century and the craft remained popular for 100 years, after which it fell into decline until its revival in the latter part of Victoria's reign. The origins of veneer are particularly noteworthy in view of the disrepute into which it fell in the 1930's. It was originally, and, at its best, is today a means of using highly figured timbers which would not be stable in solid construction.

It is a great pity that the technique also lends itself to disguising poor craftsmanship in inferior materials.

By the end of Grinling Gibbons's life in 1721, few techniques of chair construction in traditional materials remained to be discovered. Further development was largely in design. The names of Chippendale, Hepplewhite and Sheraton figure largely in the popular concept of all that was finest in English furniture during the great Georgian and Regency periods. But were they truly deserving of their fame? More of that some other time.

Reviews

HANDBOOK OF INDUSTRIAL TOXICOLOGY

By E. R. PLUNKETT, M.D. Chemical Publishing Company Inc., New York, 1966. Price \$16.50.

Because of serious unreliability this handbook cannot be recommended. It contains a great deal of information, but no effort to differentiate really dangerous materials has been made. For example, phosgene, a most deadly war gas, is treated similarly to toluene in the section on precautions. Some of the statements are dangerously misleading, e.g. benzidine, a well-known carcinogen, is said to have had no permanent effects reported. Ethylene imine, an exceedingly dangerous material, is treated in the same way as birds' feathers.

Many other relatively innocuous materials are given recommendations disproportionately severe, such as mechanical filter respirators for workers in wood, i.e. carpenters and joiners.

There are omissions of established facts and occasional frank errors, e.g. dichloroacetic acid and trichloroacetic acid are *not* synonyms for acetic acid.

Lastly, a handbook of this type is too expensive at \$16.50 for the market it seeks to fill, particularly as it will inevitably become out-of-date within a year or two.

ROBERT PIPER.

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.)

Gaymel Paints, the decorative paints division of Pinchin Johnston and Associates Ltd., has moved its headquarters to Connaught Road, London, E.16, adjacent to PJA's main London depot.

The **Aro Company** has recently introduced a new pneumatically operated Orbital Sander, Model 8444, intended for woodworking, fibreglass preparation, and vehicle bodywork. The sander weighs less than four lb, has a powerful, stallproof air motor, and, it is claimed, has already been adopted as standard equipment on the finishing lines of two British motor manufacturers.

Société ASTI have recently introduced the PSI pneumatic pump, which, it is claimed, can handle hot, corrosive fluids. The main operating component is a bellows made from "Teflon" PTFE—Fluorocarbon resin, manufactured by **The Du Pont Company Ltd.** The block housing the valve complex is made from a solid block of the resin, and the valve plugs are permanent magnets buried in the same material. The resin is claimed to be completely chemically inert, and capable of working continuously at temperatures up to 260°C.

Hoechst-Cassella Dyestuffs Ltd., announce the opening of a new sales office to cover the South Western area. The office opened on 1 March, at—

Norwich Union House,
High Street,
Bristol 1. Tel : BRISTOL 22739.

At the same time, the main office of Hoechst-Cassella Dyestuffs has moved from Leeds to—

Wordley House,
Little Harton Lane,
Bradford 5.

A novel method of shipping 25 tons of precipitated calcium carbonate across the North Atlantic was recently arranged by **John & E. Sturge Ltd.**

Two Lancashire flats were loaded at Sturge's Birmingham factory, each containing 12½ tons of PCC packed in 112 lb multi-ply paper bags. The flats were sent by road to Avonmouth, and shipped to Port Newark, USA, where they were loaded direct to road vehicles for oncarriage to Clifton, NJ. It is thought that this method is more successful than the use of containers, whilst supplying the large units of cargo necessary.

Berk Ltd. have issued a booklet on the modification of alkyd resins with p-tertiary butyl benzoic acid, claimed to give increased drying speed, hardness, surface brilliance and colour depth, resistance to atmospheric pollution, chemical agents and solvents, and improved compatibility with aromatic solvents.

A new form of aluminium foil container is now offered by **Sealway Products Ltd.**, part of the Star Aluminium group. The pack is claimed to provide a serious challenge to traditional forms of packaging such as plastic portion pots, glass jars and tinplate cans.

Fishburn Printing Ink Company announce the introduction of a new Vivacolor Dense Black DP 1729. The ink is claimed to be a major breakthrough in the field of

offset gloss blacks, and to set a new standard for density and finish. DP 1729 is intended for all classes of lithography on coated paper or board where maximum gloss is the first priority, and has a drying time of 2-4 hours, and a press life of 4-6 hours.

Union Carbide UK Ltd. is to be the new name of **Union Carbide Ltd.** a subsidiary of the Union Carbide Corporation.

Blundell-Permoglaze Ltd. announce the rationalisation of their various paint ranges. The main rationalisation will be the bringing into line of shades and colour names of the Pammastic and Permoglaze ranges. The change is expected to be complete in the next two or three years.

Du Pont de Nemours International SA announce the addition of a new series of stable, inert fluorocarbon fluids to the group of "Freon" fluorocarbon products. These fluids cover a very broad range of operating temperatures, and are claimed to have excellent dielectric and heat transfer properties.

P. W. Allen and Co. have recently introduced the DV2 Viewer, for inspection of the interior of drums, barrels and similar containers. The viewer, it is claimed, enables the whole of the interior surface of a drum to be examined with speed and precision, through a side or end bung of minimum diameter 2".

A new high-speed paint remover is announced by **Takdust Products Ltd.** Styled Takstripper PS/199, the product is non-flammable and, it is claimed, can be used with equal effect on ferrous and non-ferrous metals and most woods, and will remove all types of decorative air-dried and most stoving finishes in a few minutes.

Plastanol Ltd. have recently extended the range of their Plastokyd alkyd resins by the addition of Plastokyd 426X, a short oil alkyd resin based on linseed oil, recommended for industrial stove and air dry applications where colour is not of major importance, and Plastokyd 765W, a long oil alkyd resin based on low rosin content tall oil fatty acids, recommended for brilliant white enamels of good application properties.

Koppers Company Inc. have announced the formation of a new Australian company, which will produce and market a broad range of coal tar products. The company, to be known as Koppers Australian Proprietary Ltd., is jointly owned by Broken Hill Proprietary Company Ltd.

Two new carboxylated butadiene/methyl methacrylate paper coating latices have been introduced by **ICI Ltd.** One of these, "Butakon" Latex XML 262, has been developed for use in conventional coating processes, whilst the second, "Butakon" Latex XML 263, has been developed specially for use in formulations in which high proportions of latex are to be used in the binder system.

Novadel Ltd. have recently published a new data sheet covering their range of Siccator Driers.

Sherwood Parsons Ltd. announce a new primer/undercoat which is claimed to dry in one hour. Named "Hour Dry," the product is alkyd based, and is claimed to be extremely easy to brush and to provide an excellent gloss holdup.

Section Proceedings

Bristol

Measurement of colour by instrumentation

The 152nd Meeting of the Bristol Section took place on Friday, 6 January 1967, at the Royal Hotel, Bristol, under the chairmanship of Mr. R. J. Woodbridge, when a Paper entitled "Measurement of colour by instrumentation" was given by Mr. P. V. Foote of the Paint Research Station.

Mr. Foote commenced his paper by describing the basis and derivation of the CIE system of colour measurement, which did not involve the measurement of the visual sensation produced by a colour, but rather the determination of the amounts of three standard primary radiations (designated X, Y and Z) which would produce a match to the colour.

In the case of surface colours it was the ratio of reflected to incident intensities which was important. The colour was dependent on the spectral distribution of the incident light as well as on the spectral reflectance characteristics of the surface.

Colour measurements could be carried out by two distinct methods :—

(a) By using a spectrophotometer to measure the spectral reflectance of a surface, from which the colour may be calculated for any desired quality of illumination by appropriate weightings at the various wavelengths.

(b) By using a colorimeter which was designed to measure directly the values of X, Y and Z under a specified illuminant.

Each method had its advantages and limitations which affect the precision and the accuracy with which measurements can be made and it was considered that these should be taken into account, together with the nature of the materials and the purpose for which the measurements are required, in approaching any colour measurement problem.

Mr. Foote concluded by discussing examples of colour measurement instruments, describing their optical characteristics and circuitry, and comparing their advantages and disadvantages.

In the discussion opened by Mr. N. T. Butler, Mr. Foote further expanded on several points which arose from the many queries raised.

The proceedings concluded by Mr. J. C. Bearman proposing a vote of thanks to Mr. Foote for his most interesting paper and the clarification of the many points raised during discussion.

F. E. R.

Hull

Electronic data processing

The fifth technical meeting of the session was held at the Royal Station Hotel on 6 February, when the Chairman, Mr. L. W. Wynn, introduced Mr. J. J. Causley, of National Cash Registers Ltd., who gave a lecture entitled "Electronic data processing."

Mr. Causley stated that he did not propose to discuss the electronics of a computer or to describe its technical details. He discussed the kind of operation that it could perform and stressed its advantages in accuracy, reliability and above all its speed of operation. He drew an analogy between a computer lay-out and a clerk working

out a pay roll manually. Information of the hours worked by an employee came to the clerks' "in" tray, which corresponded to the input of the computer; the clerk drew information regarding tax code, and other deductions, from his file, which corresponded to the "store" of the computer; the net wages were calculated by the clerk, which corresponded to the processing in the computer. The method laid down for this calculation was analogous to the "control" in the computer and the final result of the calculation was put in the clerk's "out" tray corresponding to the "output" of the computer.

A film was then shown of how system analysts investigated the whole field of relevant operations within a company, and devised a scheme by which invoices, stock control, raw material control and statistical information could be provided in one cycle of operations by a computer.

Mr. Causley finished his lecture by giving a simple example of how a computer programme could be written in normal language and to illustrate the sequence of operations carried out.

The lecture was followed by a long discussion in which Messrs. Hasnip, Wynn, Lythgoe, Gilmour, Finn, Reed, Willis and Armstrong took part and which had ultimately to be closed by the Chairman on grounds of time. It was generally considered that an excellent introduction to the subject had been given, but it was perhaps a little unfortunate that the lecture covered only the business aspects of computers for an audience having mainly scientific interests.

A vote of thanks was proposed by Mr. E. A. Armstrong and was warmly endorsed.

Nineteen members and four visitors were present.

S. R. F.

Junior Members

Why and how a paint is formulated

A discussion meeting intended for the more junior members and visitors was held at the Queen's Hotel, Hull, on 19 January. The Chairman, Mr. L. W. Wynn, opened the informal meeting and explained that the intention was to discuss "Why and how a paint was formulated" and to take as an example a high gloss white finish.

The more junior members present divided into two groups, each of which discussed and formulated a paint to meet the requirements. One group was under the guidance of Mr. Wenham and the other of Mr. Garbutt. As a number of members had to catch the last ferry to get home, the time available for this stage of the discussion was limited to 20 minutes.

When these formulations were completed they were compared and commented upon by Mr. Robinson, and the meeting was then open to more general discussion. It was of some interest that whilst one group had formulated to meet a cost limit, the other group devised a high quality, high opacity finish regardless of cost. Mr. Robinson finally undertook to prepare the two formulations in his laboratory and to pass comments upon them at the next suitable meeting.

Although only nine members were present, there were eight visitors, and it was considered that the intended purpose of the evening to arouse the interest of potential members of the Association had been well achieved.

S. R. F.

Irish

Open forum

The technical meeting of the Irish Section, held at the Clarence Hotel, Dublin, on Friday 27 January, took the form of an open forum.

Two panels were drawn from the members attending the meeting: Panel A, consisting of Messrs. Adam, Caffrey and Somerville, and Panel B, consisting of Messrs. Jones, McWade and O'Callaghan.

Seven subjects were on the agenda for discussion by the panels, but due to the interest and prolonged discussion that developed, only four of the seven had been raised before the Chairman, J. H. A. Quick, closed the meeting.

The subjects discussed were:

By Panel A—Do specifications meet modern needs?

Causes of discolouration in emulsion paints.

The recruitment of junior staff in the paint and printing ink industry.

By Panel B—The future of the Irish paint and printing ink industries in the advent of Ireland's entry into EEC.

Most of those present took part in the discussions, notably Mrs. Stokes and Messrs. Jenkins, Mullen and Kershaw.

In closing the meeting, the Chairman thanked the members of the panels for their spontaneous opinions, which had led to the success of the evening.

J. H. A. Q.

London

Some aspects of the printing of Bank of England notes

A meeting of the London Section was held on 16 February 1967, at Imperial College, with Mr. R. N. Wheeler in the chair. Dr. A. C. Healey gave a paper on "Some aspects of the printing of Bank of England notes." Dr. Healey described the necessary attributes of banknotes, including certain security aspects, e.g. the use of specially made paper with watermarks, metal threads, etc. On some foreign notes coloured fibres were used. The main design was plate printed, with a background produced by letterpress or lithography. Plate printing was rather unusual, in that it produced a very thick ink film. An engraved plate had the design below the level of the plate; ink was applied and wiped off, and the paper was pressed on very hard; this embossed the paper and applied ink to the top of the embossed areas. By a suitable design, graduations in tone were produced. Plate printing was used for products of high value, e.g. banknotes, travellers cheques, bonds, etc.

Modern plate printing was a development from earlier practices, some of which had gradually been discarded, e.g. damp paper was used to aid the embossing stage, but this was discontinued in 1947. As the ink film is appreciably above the level of the paper, set-off would occur; this was prevented by the use of interleaving paper. Plate inks based on burned linseed oil did not set rapidly, and drying took several days. In 1953 quick setting inks were developed, so that interleaving was no longer necessary. Dr. Healey described the operation of the presses, with the use of wiping pads to remove the last traces of ink. A pressure of two tons per linear inch was used; this led to a large development of heat, and the machine ran with a temperature of about 55°C on the printing cylinders.

Many of the requirements for the heavily pigmented viscous ink were highly conflicting, e.g. it must distribute smoothly and fill even the finest engraving, so that good flow and tack were required, and yet it must be removed easily on the wiping pads. It must not dry in the inking system at 55°C, and yet it must stiffen and dry rapidly on the paper. A number of special faults could occur in plate printing, and these were illustrated with slides. Smearing was due to incomplete removal of ink from clean areas; uniform tinting was frequently associated with fine particle size pigments; starving, poor filling, and wiping out were due to insufficient ink on the

plate after wiping. Dragging out left ink on the last edge during the wiping ; with spewing the paper was forced into the engraving, with ink extruded on both sides ; and with feathering ink passed along the direction of the fibres in the paper. Dr. Healey described the mechanism of ink setting now used, by means of which rapid stacking of the prints was now possible. A mixture of pigments and extenders was used in the inks ; larger sized and acicular pigments wiped easily, and it was necessary to avoid finer sized pigments.

Very close tolerances were required over long periods of time for the finished inks and raw materials, and Dr. Healey described some of the special tests used. The benzyl alcohol number was based on the solubility of the solvent in benzyl alcohol, and showed a linear relation with aniline point. Viscosity, drying time and colour strength were measured conventionally. A special copper disc to fit on the automatic muller was used to measure abrasiveness. A new design of parallel plate plastometer was used for routine control of viscosity and yield value.

Dr. Healey finally described the work which had been undertaken to develop continuous web printing, which had resulted in experimental production starting in 1963. The major change was the requirement for very much faster drying inks, and flame impingement drying for the plate printing was used. Pictures of the unit were shown in which three separate types of printing process were used successively. Mr. N. R. Fisk, Dr. G. L. Fuchs, Mr. K. D. C. Bruce, Mr. P. J. Plant, Mr. R. F. G. Holness, Mr. D. Cooke, Mr. A. Colborn, Mr. J. A. L. Hawkey, Mr. A. H. Soane, Mr. P. Chesterman, Mr. T. Hallas, Mr. J. D. Hunter, Mr. P. Covell and Mr. K. W. Green took part in the extensive discussion. A vote of thanks for an extremely interesting and well presented lecture was proposed by Mr. R. F. G. Holness.

V. T. C.

Southern Branch

Paint test methods

Twenty-six people heard Mr. T. R. Bullett give a lecture, illustrated with slides, on "Paint test methods" at the fifth meeting of the Southern Branch in Portsmouth on 9 January. The Chairman of the Branch, Mr. J. C. Kingcome, before introducing the speaker, welcomed the President, Dr. S. H. Bell, whom members of the Branch were delighted to have at their meeting.

The speaker began by stressing the need for internationally accepted test methods. The post-war growth of international trade, which included UK paint exports worth £10 million a year, plus possibly as much again on manufactured goods, had led increasingly to a need to evaluate products destined for or from other countries. British and international committees were studying this problem. An instance of the need for harmonisation was provided by the Ford cup, of which at least six types were widely used in different countries. Thus, different flow times were given by the different cups, and correlation was needed. However, flow rate did not always give a good indication of paint properties, because viscosities of paints varied with the rate of shearing, and brushing, for example, involved rates of shear very much higher than those involved in a Ford cup measurement. Hence, there were proposals for a better international method, using a high-shear cone and plate viscometer for brushing paints.

Drying time was measured typically at $20 \pm 2^\circ\text{C}$ and 60 ± 5 RH and there was international agreement on the use of ballotini for the first dust/dry measurement. Hardness, a loose term, could mean resistance to scratching, indentation, etc. The pencil method suffered from the variation in hardness of the pencils, which could not be standardised by testing on a paint film! There were several pendulum methods for determining hardness which required correlating for international use. The speaker noted that hardness varied with temperature above the glass transition temperature

or brittle point, so controlled temperature was essential for testing hardness. Flexibility (extensibility) was measured by the mandrel bend test, and the sizes in inches corresponded well with the metric system sizes. The cross-cut test for adhesion was discussed and then flash point determinations were commented on. The speaker informed his audience that the reproducibility of flash point determinations between different laboratories could be up to 18°F, though repeatability was good within the same laboratory. An equilibrium method of maintaining the temperature steady before testing was necessary for reliable results.

Gloss measurement at 45° or 60° reflection were equally used throughout Europe. But the gloss of semi-gloss or matt finishes could not be satisfactorily determined by instruments.

Finally, Mr. Bullett talked about durability measurements. The development of effective test methods for the more durable coatings with expected lives of 10-15 years was proving extremely difficult. Ultraviolet radiation was the cause of breakdown, but again there were problems due to the special absorptions of certain types of paint.

Questions and contributions followed from Mr. P. Targett, Mr. J. C. Kingcome, Mr. J. Smith, Mr. W. Morris, Mr. Gigley, Mr. Day, Mr. Clark and Mr. R. Brown. These included comments on opacity, the possible need for summer and winter paint tests and lower temperature tests, the testing for degree of cure of, e.g. epoxy systems by solvent extractibility or electrical methods, and the suggestion that a test plate should be painted "on the job" to provide a check on possible errors.

The meeting concluded with a vote of thanks to Mr. T. R. Bullett by Mr. W. H. Morris, who expressed the appreciation of all present for a most interesting and useful lecture. It was evident that only lack of time prevented more questions being asked.

J. K. B. B.

Thames Valley Branch

Computers in industry

The fifth technical meeting of the session was held at the Royal White Hart Hotel, Beaconsfield, on 19 January 1967, when Mr. M. Tucker of IBM (UK) Ltd. spoke on the use of computers in industry. Mr. Tucker's talk dealt with the general use of computers in a typical industrial company. The initial slides and content dealt with the definition of computers, what a computer was, and the various types available.

It was pointed out that a computer was not a single entity but a series of machines to take in, process, and put out information. The elements of a typical system were described.

Next, the various functions of an industrial organisation, finance, management, sales, research and development were considered, and how computers were being used in each of these. Sales accounting and invoicing was the most advanced area of computer usage, the computer being used as a high speed clerk and printer, carrying out very simple operations. Great savings are not possible but it is easy to justify the purchase or rent of a computer. Users then find they can progress to more complex units which analyse data and the "clerk" can make simple decisions. Computerised stock control was considered in detail. The third stage was when considerable computation has to be undertaken, this justifying installation of a second type of machine. The use of computers for controlling scientific processes and simulation was described.

While computer usage was at present restricted to limited aspects of companies' activities considered separately, the long term aim was to offer industry facilities for a completely integrated approach, which would enable management to deal with computer operations as a whole. It would be possible for the factory, sales office and warehouse each to be located in the most favourable area and to be linked by a central

computer service. It was expected that traditional computer applications would extend, and the larger companies go to integrated systems. The impact of the computer on people's lives would be greater.

In the discussion which followed, Messrs. Gunn, Skinner, Moore, Chitty, Allen and Pearson took part. Mr. Tucker pointed out that the computer was a machine tool which could only do what it was told. Its use led managers to true management, when they were free to make decisions instead of acting as machines themselves. A vote of thanks was proposed by Mr. Birch.

W. S.

Manchester

What kind of staff does the paint industry need?

At a meeting held at the Manchester Literary and Philosophical Society on 13 January 1967, Mr. M. H. M. Arnold delivered a lecture, "What kind of staff does the paint industry need?" to an audience of 72, under the chairmanship of Mr. I. S. Moll. As the lecture proceeded it became apparent that Mr. Arnold was concentrating mainly on management staff. He pointed out that there was little movement in and out of the industry, and stated that it could be considered backward and inefficient in comparison with the rest of the chemical industry, of which it formed part. He suggested that nepotism played a part in delaying efficiency, as did misuse of technical staff, but he suggested that the main cause was lack of appreciation of the nature of manufacturing and selling functions.

Mr. Arnold developed this theme by stating that the manufacture of decorative paint for shelf goods was a very different operation from making industrial finishes and "specials." He brought out a large number of instances where these processes differed in some detail, with the purpose of suggesting that different types of management were required for each, because the same management philosophy did not apply.

To manage decorative paint production he suggested a man without special paint experience, preferably a production engineer, who could lead an ordered existence. For industrials a paint technologist was essential, but his operations would be a "controlled shambles."

A very lively discussion followed in which many members took direct issue with the lecturer concerning his more provocative statements, with the honours, at the close, fairly even. The vote of thanks was proposed by Mr. N. Seymour.

D. A. P.

Midlands

Polymer characterisation

A meeting of the section was held on 17 February at Birmingham Chamber of Commerce House, to hear Dr. F. W. Peaker speak on Polymer characterisation.

Dr. Peaker said that the molecular weight of a polymer could be expressed as a number average or as a weight average. Only with homogeneous samples were the two values identical and normally the weight average was larger than the number average. The ratio of the two averages, which was a measure of breadth of distribution, could be calculated from theoretical considerations but practical determinations did not usually give good agreement.

There were two groups of experimental techniques for determining distribution. Preparative methods were time consuming and required relatively large samples. Analytical methods were more rapid and needed only small samples but were less precise.

Preparative methods involved fractional precipitation by adding a non-solvent or by lowering the temperature. A method of continuous fractionation employed both techniques simultaneously. The sample and a suitable mixture containing non-solvent were passed through a tube along which there was a temperature gradient. After determination of the molecular weight of the fractions by standard methods, a cumulative distribution curve could be drawn and the weight distribution obtained from the gradient of the curve. This method had been used to examine whether the termination step in the polymerisation of styrene involved combination of chains or disproportionation. The distribution curve obtained by fractionation suggested that both mechanisms were involved.

Turbimetric titration was an example of an analytical method. A non-solvent was added to a solution of polymer and the turbidity produced was measured with a Spekker absorptiometer. The readings could then be used to produce a cumulative distribution curve. The method was not an absolute one but had been made absolute by calibrating with polymers of known molecular weight. This method had been employed to distinguish between a copolymer and a mixture of homopolymers, the copolymer giving a trace over a wide range whilst the homopolymers gave separate narrow peaks. One consideration which had to be kept in mind was that chemical characteristics had a much greater effect than molecular weight differences.

Another analytical method was gel permeation chromatography. A cross-linked polymer was prepared from styrene and divinyl benzene by suspension polymerisation in a non-solvent. By careful regulation of conditions, beads could be produced with a porosity comparable with the molecular size of polymers. When a solution of polymer was passed through a tube packed with such beads, the fractions of high molecular weight "saw" less free volume than the lower molecular weight material, and so passed through more quickly. After leaving the tube the material passed through a sensitive differential refractometer and an automatic volume measurer. The method could be calibrated using control substances. An interesting application of the technique was a study of degradation under shear of solutions of polyisobutylene and natural and synthetic rubbers. With polyisobutylene a low molecular weight peak appeared during shear. With rubber a high molecular weight peak appeared and this had been attributed to degradation of material which was originally insoluble and so was filtered from the earlier samples.

During the ensuing discussion period, Dr. Peaker competently answered a number of questions about the techniques which he had described. Mr. R. Hill proposed a vote of thanks to the speaker.

L. R. S.

Trent Valley Branch

Castor oil chemistry

A technical meeting was held on 12 January at the British Railways School of Transport, Derby. Mr. R. S. Law was in the chair. Twenty-one members and guests were present. Dr. G. Silverstone, of Victor Wolf Limited, gave a lecture entitled "Castor oil chemistry."

Dr. Silverstone briefly surveyed the many uses to which castor oil may be put, with particular reference to the chemistry of ricinoleic acid and the fatty acid mixtures produced from the oil by different techniques of dehydration. He described some work on the simultaneous dehydration and polymerisation of methyl ricinoleate and the clay catalysed polymerisation of a DCO fatty acid of high conjugation, and also recent methods of *cis/trans* isomerisation of unsaturated systems.

A lively discussion period followed the lecture. The vote of thanks was proposed by Mr. Hawley.

J. R. B.

Scottish

Some industrial applications of water based paints

The first meeting of 1967 was held in the Lorne Hotel, Glasgow, on Thursday, 19 January, at 6.00 p.m., when Mr. K. Safe delivered a lecture on "Some industrial applications of water based paints."

Although, to a large degree, the industrial application of water based paints was a new concept, this could not be said to hold absolutely, since, by way of example, the paper coating industry already used some 17-20,000,000 gallons per year, while a figure of 4-5,000,000 gallons was achieved in the carpet industry. Water based metal primers were also increasing in their outlets.

Mr. Safe explained that he intended to confine his talk, in the main, to the application of aqueous paints on production lines in factories as distinct from application to finished buildings. By way of preliminary clarification, he pointed out that two methods of factory based building were practised, these being respectively, systems building, as when one material was used largely in construction (i.e. in large scale manufacture) and methods building, where complete rooms, complete walls, etc. were dealt with in smaller scale production. In point of fact, the question really arose as to whether systems building was actually economical, even for the large operator.

The use of industrialised building would undoubtedly increase, since it was the only really economical approach. The largest users were the local authorities. This type of building offered a challenge to the paint manufacturer; but success could only follow a willingness to adopt an unconventional approach. In other words, conventional emulsion paints, or modifications of them, were not the answer to the problems presented. Application of these new paints would be by air or airless spray, the latter requiring special formulation to prevent destabilisation due to pressure. Curtain coating was another possibility but, again, this involved circulating pumps, with consequent possible destabilisation.

Concrete was likely to be a substrate most frequently encountered, and this could present its own peculiar problems. For example, irregularity of the concrete surface necessitated the filling and bridging of holes. Since the more traditional filling and painting procedure was not practicable because of the labour cost, the surface coating used had to be thick and of the one coat type. Texturing might be necessary in order to hide the fact that a single coat could not produce a completely smooth finish. One-coat stipple finishes could be formulated, which could be curtain coated and passed through a roller to produce the required stipple. Drying could be speeded by the use of infra red heat, and gloss stipple finishes could be produced. Other texturing effects could be obtained by using coarse particle size pigments, and these could be either single-pack or twin-pack systems. The former, producing a multicolour effect, resulted in a finish which was rather rough for interior work and was better used outside. If finer materials were used in their preparation, these finishes could be sprayed; but the multicolour effect was apt to be lost. Nevertheless, one-pack finishes were limited to fairly fine aggregates; the earlier versions were based on vinyl acetate homopolymers and were rather easily damaged when wet on this account. The requirements of the finish were, in fact, better met by a hard vinyl acetate copolymer or a hard acrylic. Twin-pack finishes produced very rough finishes, suitable for exterior decoration. The first coat was a thick, adhesive one, to which a pebble dash was subsequently applied, the whole being finished with a clear coat of vinyl acetate copolymer. This copolymer was of a harder type than was used in conventional paints.

Acrylics could be used, also ; but there was a slight indication that stones might tend to fall out rather more easily. The question of alkali resistance did not arise with these finishes.

As a substrate, wood was not stable, and a polymer was required which was soft enough to cope with the movement involved. Conventional vinyl acetate copolymers or acrylics were satisfactory for site work, but were too soft for factory coating, due to the blocking which ensued on stacking. On the other hand, if a harder polymer were used, adhesion difficulties arose, and no immediate solution to this problem appeared to be on the horizon. Other problems associated with the coating of wood were grain raising and corrosion resistance, the latter being necessary to prevent the rusting of metal fixtures such as nails, hinges and so on.

Board of various types—*asbestos*, *hardboard*, *softboard* and *strawboard*—were encountered widely. For example, it was estimated that 320,000,000 square yards of board were made every year and, if all this were coated, some 10,000,000 gallons of paint would be required. Even at a lower coating rate, a conservative consumption rate of some 2,000,000 gallons could be estimated. A great deal of *asbestos* board was used for sheds, garages, etc., and its appearance could be improved by the use of textured finishes. *Asbestos* shingles were also being used quite widely. One of the main uses of *softboard* was in the production of acoustic tiles.

Mr. Safe then described in detail the development of a heat cured finish specifically for factory coated *softboard*. Board coating was rather less stringent in its general requirements than was decorative painting and, originally, the problem had been approached in a rather conventional way. However, vinyl acetate, vinyl acetate/acrylic, and acrylic emulsions all tended to block. A hard styrene/acrylic emulsion was harder by far ; but the colour left something to be desired and the reflectance was low. Increasing the titanium dioxide content resulted in some improvement ; but not, by any means, a complete solution, some properties of the paint being adversely affected, while the cost was high. The ultimate solution, arrived at after considerable systematic research, was met by a paint which included amongst its features a pvc of 90 per cent at 67 per cent solids. The emulsion used was a hard styrene/acrylic and the only pigment was dolomite, no titanium dioxide being present. The system was so advantageous that board could be coated at the rate of 1s. 3d. per 100 square feet.

A lively discussion ensued, in which a number of members took part. A vote of thanks was proposed by Mr. A. McLean.

A. MCL.

Eastern Branch

Photography in industry and commerce

The second meeting of the session was held in the North British Hotel, Edinburgh, on 23 November 1966. It took the form of a lecture of general interest on the subject "Photography in industry and commerce" and was given by Mr. T. E. Gray. The lecture was accompanied by slides illustrating the various phases employing photographic methods throughout industry.

Following the lecture, a commercially made sound film of good entertainment value, entitled "The home-made motor car," was shown, and was much appreciated.

All the equipment used was by courtesy of Kodak Ltd.

Mr. Gray answered a number of questions from the audience regarding photographic materials and equipment suitable for various commercial and industrial processes.

P. A. G.

Scottish Section



A group at the Scottish Dinner Dance (left to right) Mr. R. J. Woodbridge (Chairman, Bristol), Mrs. Woodbridge, Mr. N. Cochrane (Chairman, West Riding), Mrs. Cochrane, Mr. C. H. Morris (Chairman, Midlands), Mrs. Morris, Mrs. Hutchison, Dr. S. H. Bell (President), Mrs. Holmes, Mr. I. S. Hutchison (Chairman, Scottish) Mr. P. Holmes (Chairman, Scottish, Eastern Franch)

Bal agus Dinnear

Comunn Luchd-ealain Ola is Dath
an Roinn Albannach
Bal agus Dinnear
Seomair chinntire
Taigh Osda a'Mheadhoinn
Di'haoinne an Treas Latha Deug de'n
Fhaoilleach, 1967

For the unhappy few who do not "have the Gaelic," it ought, perhaps, to be repeated that the Annual Dinner-Dance of the Scottish Section was held in the Kintyre Suite, Central Hotel, Glasgow, on Friday 13 January 1967.

A sudden access of national zeal produced a programme and menu printed entirely in Gaelic. This resulted in a measure of mystification which was not, it must be confessed, entirely confined to the visiting Sasunnach. Tables were also set out with serviettes carrying illustrations of some 64 items, each with its Gaelic name and the English equivalent. A quick glance around the room during the earlier part of the evening revealed an encouraging number of guests engaged in the hopeful but

fruitless exercise of endeavouring to translate the menu, using the serviettes as dictionaries. It can be guessed that some bewilderment must have been engendered by the discovery that in Gaelic a "CU" merely barks and delivers no milk at all. At this point confusion was undoubtedly complete. Over the top table hung the Gaelic welcome, "Ceud mile failte air na cairdean a Sasunn." In English, this wishes a hundred thousand welcomes to our friends from England, and does not mean, as one young gentleman endeavoured to persuade his partner, that "patrons are requested not to leave their bicycles outside the hotel."

Bidding "Feasgar mhath" to the company, as being the best way of saying good evening, Mr. I. S. Hutchison, Chairman of the Scottish Section, introduced the official guests of the evening, principal amongst these being Dr. S. H. Bell, President of the Association. Accompanying Dr. Bell were Mr. and Mrs. R. J. Woodbridge (Bristol Section), Mr. and Mrs. C. H. Morris (Midlands

Section), Mr. and Mrs. N. Cochrane (West Riding Section) and Mr. and Mrs. P. Holmes (Scottish Section, Eastern Branch). Mr. Hutchison also welcomed many old friends who, although they were not official guests, were present in such numbers as to make the evening very much a family one. On behalf of the Scottish Section, Mr. Hutchison proposed the toast to "Our Guests."

Replying to this toast, Dr. Bell commented upon the infusion of Gaelic into the proceedings and thanked Mr. Hutchison for the consideration shown to him in kindly providing him with a personal translation of the menu—in French! In the course of an expectedly witty speech, interspersed with a trace of legerdemain, Dr. Bell paid particular tribute to the continuing success of the

Scottish Section in organising and providing for Junior Members.

At this point a number of hibernating haggis were piped in and presented, complete with instructions for the proper care, maintenance, cooking and eventual consumption, to the principal lady guests. Thereafter the evening continued with the customary social rounds and dancing, the latter with such success that, not infrequently, guests were hard put to it to find space in which to operate.

It never seems possible that the progression can continue unchecked; but the fact remains that the evening was accepted as "even better than last year." It concluded appropriately enough, as it had begun when, after the singing of Auld Lang Syne, Mr. Hutchison wished everyone "beannachd leibh."

9th FATIPEC Congress

The ATIPEC have announced that the ninth FATIPEC Congress will take place in Belgium, at the Palais des Congrès, Brussels, from 12 to 18 May 1968.

The theme will be "Fundamental aspects of the test-methods peculiar to the industry of paints, varnishes, printing inks and related products."

Symposium on "Colour measurement in Industry"

The Colour Group (Great Britain) are to hold a symposium on the problems of colour measurement encountered in industry. It will be held on 6 and 7 April 1967, in the Physics Building at Imperial College, London.

North Dakota State University are to hold their 9th Annual Symposium from 5-8 June, on New Coatings and new coatings raw materials.

A course on the Rheology of Suspensions is to be held by the University of

Surrey on five consecutive Tuesday evenings, commencing 2 May. Lecturers will be Mr. R. W. Whorlow, Mr. C. C. Mills and Mr. T. R. Bullett.

Notes for Authors

In response to a number of inquiries regarding the paragraph on Illustrations and Diagrams in the leaflet "Notes for Authors, Lecturers, Reporters and Reviewers," the following clarification is made:—

"All lettering and numerals on and around diagrams should be inserted in pencil, to allow for later setting in type."

The revision of the leaflet with regard to this and other points is in hand.

Errata

In the paper by J. Taylor "Paint Storage Stability in relation to pigment surface characteristics," published in the January edition of the Journal, Figures 2 and 3 were transposed, causing the legends to be incorrect. Also, on page 53, table 2,

line 5, the word 'dispersant', preceding Nuodex 321, is incorrect. Nuodex 321, is not, of course, a dispersant.

In the article on Mr. H. Gosling in the February edition of the Journal, it was stated that Mr. Gosling had retired

as Managing Director of Cornbrook Resin Company Ltd. Mr. Gosling was, in fact, Managing Director of Cornbrook Chemical Company Ltd. We apologise for this error, and for any inconvenience caused to either party.

Scarborough Conference 20-24 June 1967

Interfacial behaviour

Although the closing date for registration for the Conference was given as 1 April to meet the wishes of the hotel managements concerned, the Association's office will make every endeavour to find accommodation for late applicants.

On this occasion there will be **four technical sessions** on the Wednesday morning, Thursday morning and afternoon and Friday morning as well as three workshop sessions, which will be

held simultaneously on the Friday afternoon after the Annual General Meeting. Summaries of the 11 papers were given in the November 1966 issue of this *Journal* and reprints of these summaries together with registration forms may be obtained from the Association's offices at the address shown on the front cover.

The main social occasions will be the Civic Reception on the evening of 21 June and the Association's Dinner-Dance on the evening of 23 June.

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

- BAINBRIDGE, AUSTIN THOMAS, R.M.I.T., 29 Dunblane Road, Noble Park, Victoria, Australia. (*Victorian*)
- BUCKLEY, GRAEME JOHN, B.SC., 41 Bolingbroke Street, Pascoe Vale, Victoria, Australia. (*Victorian*)
- CHOKSI, MAHENDRA CHIMANLAL, B.CHEM., M.SC., 402 Shiv-Tirth, Bhulabhai Desai Road, Bombay-26 (WB), India. (*Overseas*)
- CHROMY, LUDWICK, PH.D., The Paint Research Institute, Gliwice, Chorzowska 50, Poland. (*Overseas*)
- COMISKEY, CHRISTOPHER JOHN, Preston & Hadfield Ltd., Rathfarnham, Dublin, 14. (*Irish*)
- ERICHSEN, PER F., PH.D., Erichsen GMBH & Co., KG, 587 Hemer-Sundwig Westf., West Germany. (*Overseas*)
- GOLDING, STEPHEN ALAN, "Torridon," Green Lane, Chessington, Surrey. (*London*)
- GRAVES, DONALD ARTHUR, B.SC., James Hardie & Co., Pty., Ltd., PO Box 70, Parramatta, New South Wales, Australia. (*New South Wales*)
- GREENE, IVOR VALENTINE, Geigy (Aust.) Pty., Ltd., (Pigment Division), Hale Street, Botany, New South Wales, Australia. (*New South Wales*)

- GRUHN, STEFFEN, Poul Weeke & Co., Gl. Kogevej 73, Kobenhavn-Valby, Denmark.
(Overseas)
- HACKETT, PHILIP PATRICK, 28 Warley Avenue, Dagenham, Essex. (London)
- HASTIE, BOWRAL ALEXANDER HUME, A.S.T.C., British Paints (Aust.) Pty., Ltd., Gow Street, Bankstown, New South Wales, Australia. (New South Wales)
- LUESCHER, Geigy (Aust.) Pty. Ltd., Hale Street, Botany, New South Wales, Australia. (New South Wales)
- PAGE, FREDERICK GRANVILLE, Dawley Brook Papers Ltd., Stallings Lane, Kingswinford, Staffordshire. (Midland)
- ROEBUCK, ALEC, B.SC., A.R.I.C., 6 Ridgewood Drive, Harpenden, Herts. (London)
- SHAH, VINODCHANDRA SHAMALDAS, B.SC., 45 Clarendon Gardens, Ilford, Essex. (London)
- SIMPSON, JOHN, James Hardie & Co. Pty. Ltd., PO Box 70, Parramatta, New South Wales, Australia. (New South Wales)
- SLEVIN, JOHN AUSTIN, L.R.I.C., 9 Campion House, Jocks Lane, Bracknell, Berks. (London)
- WEILER, EDWARD A., B.SC., Advance Division, Carlisle Chemical Works, Inc., 500 Jersey Avenue, New Brunswick, New Jersey 08903, USA. (Overseas)

Associate Members

- RONIGER, PAUL, Taeuber & Corsen (Pty.) Ltd., Box 2953, Cape Town, South Africa. (South African)
- TODD, KARL, 113 Victoria Avenue, Grays, Essex. (London, Southern)
- VAN EGMOND, JAN, Geigy (SA) Pty. Ltd., PO Box 168, Paarden Eiland, South Africa. (South African)

Junior Members

- CHRISTY, ANDREW JOSEPH, 431 Lyons Road, Five Dock, New South Wales, Australia. (New South Wales)
- COOKE, JAMES, 46 Rye Road, Glasgow, N.I. (Scottish)
- HARTE, JOHN JOSEPH, Ault & Wiborg (Scotland) Ltd., 410-414 Hillington Road, Glasgow, S.W.2. (Scottish)
- MCGOWAN, MARK REID, 34 Zena Street, Robroyston, Glasgow. (Scottish)
- ROSS, CHARLES, 15 Burnbrae Street, Balornock, Glasgow, N.I. (Scottish)

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 6 April

Midlands Section—Trent Valley Branch. Annual General Meeting, to be held at British Rail School of Transport, London Road, Derby, at 7.00 p.m.

Newcastle Section. Annual General Meeting, to be held at Royal Turk's Head Hotel, Grey Street, Newcastle-upon-Tyne.

Friday 7 April

Manchester Section. Annual General Meeting. Provisionally in the Pavilion Suite, Lancashire County Cricket Club, Trafford Park, Manchester, 16, at 6.30 p.m.

Scottish Section. Annual General Meeting at Lorne Hotel, Sauchiehall Street, Glasgow, at 6.00 p.m. Followed

by Annual Smoking Concert at the Eglinton Arms Hotel, Eaglesham, at 7.30 p.m.

Monday 10 April

London Section—Southern Branch. Annual General Meeting to be held at Keppels Head Hotel, The Hard, Portsmouth, at 7.30 p.m.

Tuesday 11 April

West Riding Section. Annual General Meeting, to be held at Great Northern Hotel, Leeds, at 7.30 p.m.

Wednesday 19 April

Scottish Section—Eastern Branch. "Epoxy Curing Agents from Conjugated Esters" by Mr. R. V. Crawford, to be held at North British Hotel, Princes Street, Edinburgh, at 7.30 p.m.

Thursday 20 April

London Section. Annual General Meeting, to be held at the Criterion,

Piccadilly, London, W.1, at 6 p.m. Followed by dinner, and a talk by Gluck on "The artist vis-à-vis the Paint Industry."

New South Wales Section. Business prospects for 1967. Mr. W. P. Baker, W. D. Scott & Co., Pty. Ltd.

Friday 28 April

Bristol Section. Annual General Meeting, to be followed by Film Show, to be held at Royal Hotel, College Green, Bristol, 1, at 7.15 p.m.

Thursday 18 May

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

Thursday 15 June

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

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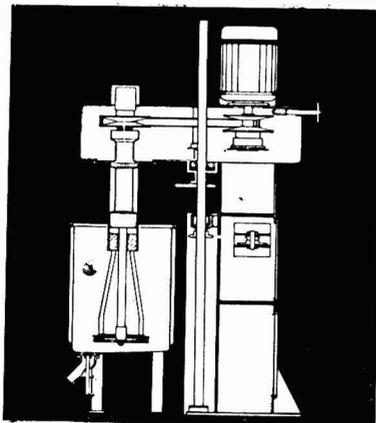
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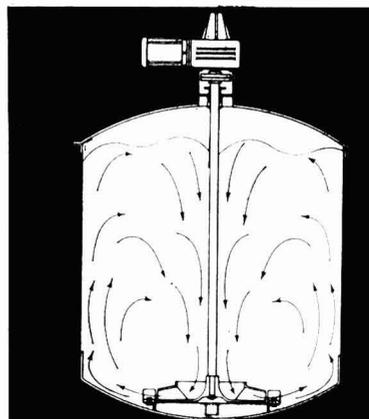
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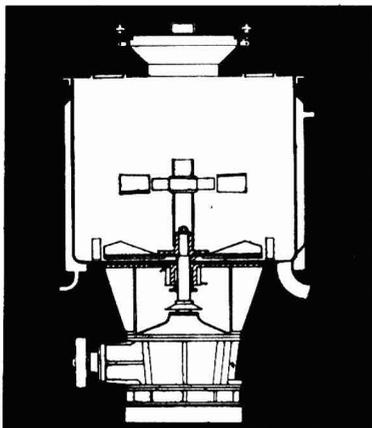
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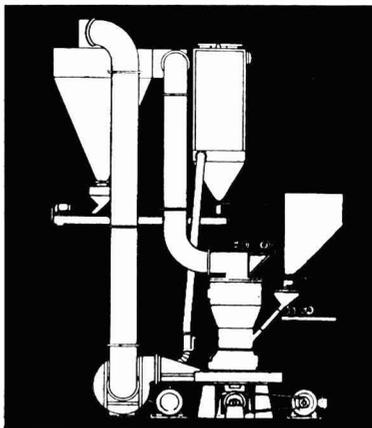
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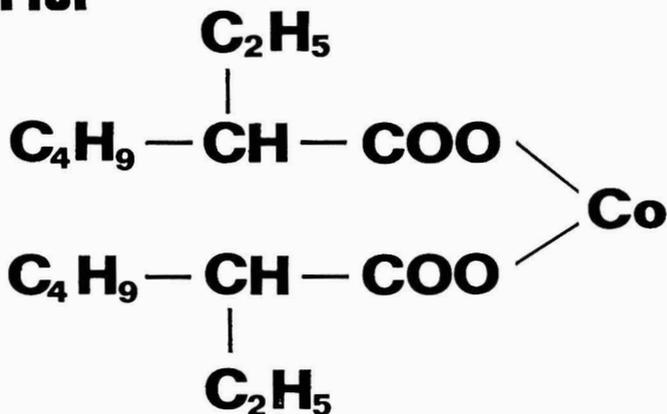


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