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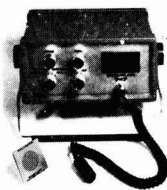


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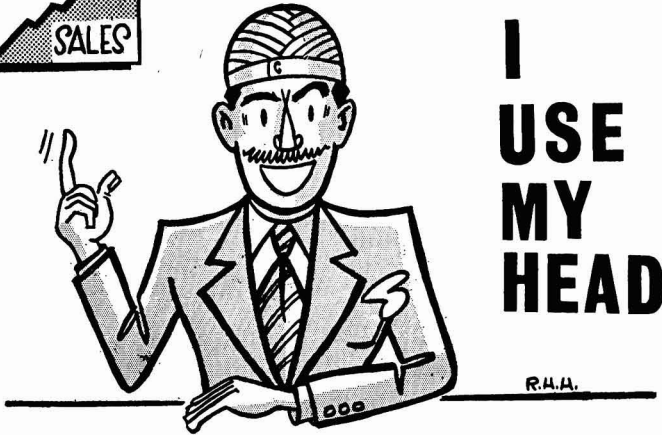


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Priory House, 967 Harrow Road, Wembley, Middlesex, HA0 2SF England

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Contents

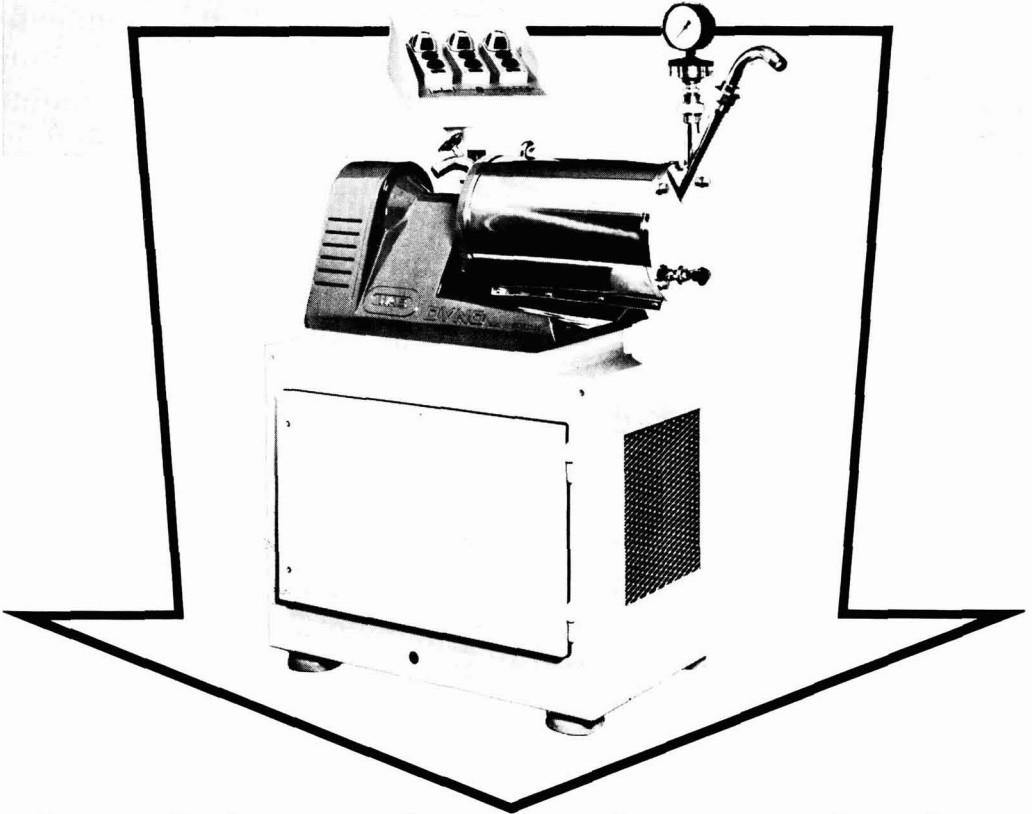
Vol. 62 No. 5

May 1979

Transactions and Communications

The reaction of epoxy side groups in polymers and amines—Influence of solvent and additives	153
<i>S. Paul and B. Rånby</i>	
Lung cancer mortality of workers in chromate pigment manufacture: An epidemiological survey	157
<i>J. M. Davies</i>	
The automatic cleaning of tanks, tankers and plant by high pressure spray	164
<i>W. Hirzel</i>	
Film characteristics of polyepoxide resins based on novolac resins	168
<i>A. K. Vasishtha and V. K. Kaushal</i>	
The efflorescence resistance of certain emulsion coatings	173
<i>J. Boxall and W. Worley</i>	
<i>Reviews</i>	177
<i>Section Proceedings</i>	177
<i>Information Received</i>	180
<i>Notes and News</i>	181
<i>Register of Members</i>	182
<i>Forthcoming Events</i>	182

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Transactions and Communications

The reaction of epoxy side groups in polymers and amines — Influence of solvent and additives

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Summary

The influence of concentration of reactants, hydrogen-bond-donor and hydrogen-bond-acceptor additives and the polarity of the reaction medium on the rate constant of the epoxy-ring opening has been investigated for low molecular weight copolymers of methyl methacrylate (MMA)-glycidyl methacrylate (GMA) with diethanol amine (DEA) at $70 \pm 1^\circ\text{C}$.

In order to account for the observed influence of a hydrogen-bond-donor (HX) and the polar nature of the reaction medium on the reaction rate of the epoxy group, a termolecular reaction mechanism has been proposed, involving a transition state with charge

separation. The kinetic data have been interpreted as a pseudo-second-order reaction between hydrogen bonded epoxy groups (HX with MMA-GMA) and the amine (DEA).

The rate constant data based on the total DEA consumption satisfy the pseudo-second-order reaction, whereas those based on the total epoxy group conversion do not. This deviation is interpreted as being due to a non-specific side reaction, involving coupling between epoxy groups and alcoholic groups, formed from the reaction of the epoxy groups and the amine (DEA) or from the DEA itself.

Keywords

*Raw materials for coatings
binders (resins, etc.)*

methyl methacrylate resin-methacrylate resin copolymers
copolymer resin

*Processes and methods primarily associated with
drying or curing of coatings*

baking
catalytic curing
reaction mechanism

Miscellaneous terms

reaction mechanism

L'influence du solvant et des adjuvants sur la réaction des groupements époxydes latéraux des polymères et des amines

Résumé

On a étudié, dans le cas des copolymères de faible poids moléculaire de méthyle méthacrylate (MMA)—glycidyl méthacrylate (GMA) avec le diéthanolamine (DEA), l'influence qu'exercent la concentration des réactants, les adjuvants soit donneurs de liaisons-hydrogènes soit accepteurs de liaisons-hydrogènes, et la polarité du milieu de réaction sur le constant de vitesse de l'ouverture du noyau époxyde à $70 \pm 1^\circ\text{C}$.

Afin d'expliquer l'influence que l'on a notée et qu'exercent à la fois un donneur de liaison-hydrogène (HX) et la nature polaire du milieu de réaction sur la vitesse de réaction du groupement époxyde, on a proposé un mécanisme de réaction termoléculaire qui entraîne un état de transition avec séparation de charge. Les données

kinétiques ont été interprétées en tant qu'une pseudo-réaction d'ordre du second entre les groupements époxydes rattachés par les liaisons-hydrogènes (HX avec MMA-GMA) et l'amine (DEA).

Les données du constant de vitesse basées sur la consommation totale de DEA accordent avec la pseudo-réaction d'ordre du second, alors que celles basées sur la conversion totale du groupement époxyde n'en font pas. On interprète cette déviation comme étant due à une réaction latérale et non spécifique qui entraîne le couplage des groupements époxydes et groupements alcooliques provenant de la réaction des groupements époxydes avec l'amine (DEA) ou l'amine même.

Die Reaktion von Epoxyseitengruppen in Polymeren und Aminen — Einfluss von Lösungsmitteln und Hilfsstoffen

Zusammenfassung

Die einwirkung der konzentration des reagenz, mit zusatz von wasserstoffbindungsgeber und wasserstoffbindungsnehmer und die polarität des reaktionsmittels auf die geschwindigkeitskonstante der öffnung des epoxy-rings, der sich als seitengruppe in dem niedermolekularen mischpolymer aus methyl methakrylat (MMA)-glycidyl methakrylat (GMA) bei der reaktion mit dietanol amin (DEA) auf $70 \pm 1^\circ\text{C}$ befindet, ist untersucht worden.

Um die beobachteten einwirkungen der wasserstoffbindungsgeber (HX) und die polaritätseigenschaften des reaktionsmittels auf die geschwindigkeitsreaktion der epoxy-gruppe zu interpretieren, wurde einen termolekularen mechanismus, der eine durchgangslage

mit ladnungsseparation beifügt, vorgeschlagen. Die kinetischen werte wurden als eine falschen-zweiten-ranges reaktion zwischen die wasserstoffverbundene epoxy-gruppen (HX mit MMA-GMA) und die amin (DEA) verstanden.

Die werte der geschwindigkeitkonstante, von dem totalen DEA verbrauch bestimmt, stellt die reaktion der falschen-zweiten-ranges zufrieden, da dagegen die veränderung der totale epoxy-gruppe es nicht zufriedenstellt. Diese abweichung, kann man annehmen, beruht auf eine nicht spezifizierter seitenreaktion von epoxy-gruppen mit alkoholischen gruppen an den polymerketten gebildet sind oder in DEA befänglich sind.

The reactions between low molecular weight epoxy compounds and amines have been studied in several previous papers¹⁻⁴. A comprehensive review of the various reaction mechanisms proposed has been published by Smith⁵.

The kinetics of the homogeneous reaction between epoxy groups in polymers and amines have first been reported by Iwakura *et al.*⁶⁻⁷. The authors have studied similar reactions for low molecular weight polymers⁸, and proposed a secondary reaction between the epoxy groups in the polymers and the hydroxyl group formed in the reaction between the secondary amine and the epoxy group. This non-specific reaction results in partial branching of the polymers and a higher consumption of the epoxy groups than would be expected stoichiometrically from the DEA consumption.

Since epoxy groups in the polymer offer possibilities of introducing various functional groups on to the polymer chains, several studies have been reported where epoxy groups in polymer gels have been modified by nucleophilic ring-opening reactions with iminoacetic acid groups⁹, amino groups¹⁰, sulfonate or sulfonic acid groups¹¹ and by acidic or basic hydrolysis¹² in heterogeneous phase reactions. The authors have shown earlier that such functional group-containing polymers can be used as antistatic agents¹³. Several other applications of such polymers, for example as aqueous thickeners, impregnants, adhesives and textile sizes, have been suggested in the literature. Epoxy group containing polymers find extensive application as coating materials due to their excellent adhesion, impact and corrosion-resistance properties. They are usually cured with either carboxylic polymers, amines or hydroxyl group containing compounds¹⁴ to obtain polymer films of high molecular weight.

Since the high viscosity of the reaction medium limits the investigation of the curing reactions between the epoxy groups and the amines in bulk, further investigations of the reactions in solution were undertaken. The reaction conditions were studied, such as the influence of the reactant concentrations, polarity of the reaction medium, the hydrogen-bond-donor and hydrogen-bond-acceptor additive on the rate constants of a homogeneous reaction between the epoxy groups contained in low molecular weight methyl methacrylate (MMA)-glycidyl methacrylate (GMA) copolymer and diethanol amine (DEA).

Experimental

Refs. 8,15

Materials

Copolymers of MMA and GMA ($\bar{M}_n = 3000-4000$) were synthesised by free radical polymerisation of the two monomers with 2,2' azo-bis (isobutyronitrile) (AIBN) as initiator, in the presence of thiophenol (TP) as a chain transfer agent, at 60°C in vacuum sealed ampoules, which has been described elsewhere⁸. The MMA-GMA copolymers have been characterised by the hydrochlorination reaction of the epoxy groups⁸ and by a new IR method¹⁵. The copolymer used for the modification studies, contained 2.01 per cent (by weight) oxirane oxygen.

Kinetic determinations

The reaction was carried out at $70 \pm 1^\circ\text{C}$ by mixing the epoxy-group containing copolymer and the amine (DEA) in the molar ratio of 1:4 with dimethyl formamide (DMF) as solvent.

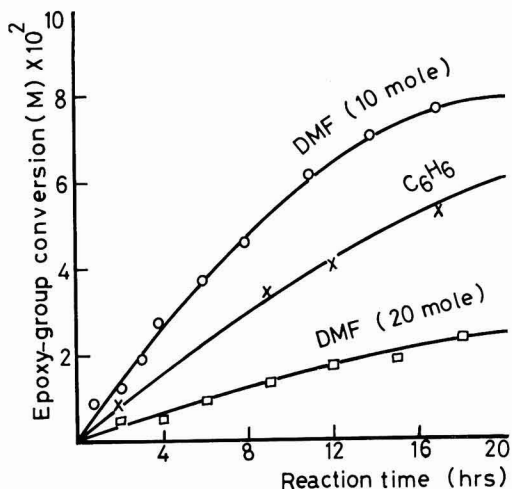


Fig. 1. Rate of the epoxy-group conversion contained in the MMA-GMA copolymers on reaction with DEA. (—○—) in DMF (0.1 mole epoxide/20 mole DMF); (—×—) in benzene (0.1 mole epoxide/10.24 mole C₆H₆); (—□—) in DMF (0.1 mole epoxide/10 mole DMF)

The kinetics of the reaction were determined from analysis of both DEA and epoxy contents in the reaction mixture. Unreacted DEA was determined by potentiometric titration of 5 ml of the reaction mixture with 0.01 N H₂SO₄. The residual epoxy-content was found by determining the chloride ions by Mohr's method after reacting the epoxy groups in the copolymers with an excess of hydrogen chloride⁸.

Results and discussions

Refs. 4,5,7,8,16-18

The rate data for the epoxy-ring opening in the MMA-GMA copolymers in DMF is illustrated in Figure 1. It is evident that the epoxy group conversion is a non-linear function of time and is concentration dependent.

The data in Figure 1 show that a polar solvent, such as DMF, accelerates the epoxy-ring opening, whereas a non-polar solvent such as benzene (C₆H₆), retards it. This suggests that the reaction may involve a transition-state where charge separation occurs.

Since hydrogen bonding of the epoxy groups has been shown to favour the rate of epoxy-ring opening⁸, the following reaction mechanism suggested by Smith⁵ seems more probable than other mechanisms for the reaction of epoxy side groups in the polymer chain with DEA.

It is evident from the reaction scheme 1 that the secondary amine (DEA) and the epoxy group react with each other stoichiometrically in the rate determining step. The rate equation must, therefore, include the concentration terms both for the amine and the epoxide. If the initial concentration of DEA and epoxy groups are a and b respectively and if x is the amount of amine or epoxide that has disappeared per unit volume at the time t , then the rate of disappearance of amine, equal to the rate of disappearance of epoxide, is therefore given by^{16,17}:

$$dx/dt = (a - x)(b - x)(k' + k''x) \dots \dots (1)$$

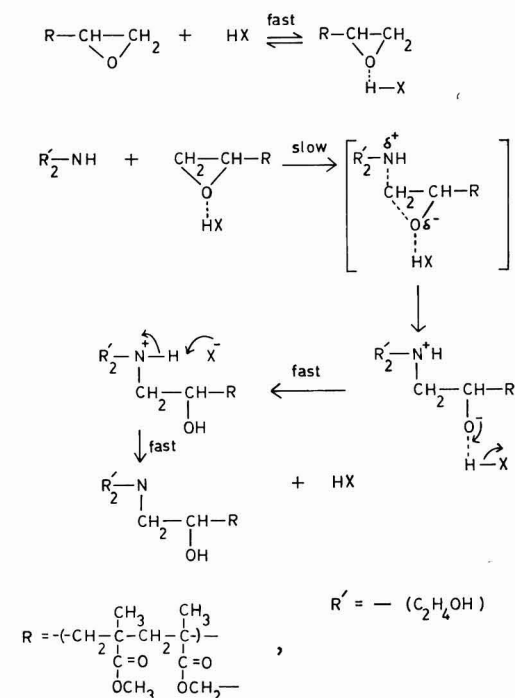
where k' refers to the rate constant of epoxide and DEA and k'' the rate constant of the reaction catalysed by the hydroxyl groups produced. As k'' will be small in the case where DEA is used as the amine as shown previously⁷, eqn. (1) can be approximated as:

$$dx/dt = k'(a-x)(b-x) \dots \dots \dots (2)$$

If a and b are different, the solution of equation (2) will be:

$$k' = \frac{1}{t(a-b)} \ln \frac{b(a-x)}{a(b-x)} \dots \dots \dots (3)$$

Based on equation (3), rate constants of the homogeneous reaction between DEA and epoxy groups in the copolymer have been determined from the simultaneous estimations of DEA and the epoxy content, both for reaction in DMF and in benzene. The kinetic plots are shown in Figures 2 and 3.



Scheme 1. Reaction mechanism scheme between the epoxy-groups contained in the polymer (MMA-GMA copolymer) and amine (DEA).

The straight lines obtained from the DEA consumption in the reaction (Figure 2) suggests that the reaction between DEA and epoxy-groups is a second-order reaction, depending on the concentration of both DEA and epoxide.

It is assumed that the rate-controlling step involves the reaction between a secondary amine (DEA) and a hydrogen-bonded epoxide as shown in Scheme 1 and that the reaction is autocatalytic as indicated by Shechter *et al.*¹⁷. The reaction will then have two rate constants, one is k , accelerated by the hydrogen-bond donor molecule (HX) and the other is k'' referring to the reaction accelerated by the -OH groups

from the product. It will also be assumed that the molecule HX functions as a true catalyst and is not consumed in any side-reaction. If c is the concentration of HX, the rate of consumption of epoxide or amine is given by:

$$dx/dt = (a-x)(b-x)(kc + k''x) \dots \dots \dots (4)$$

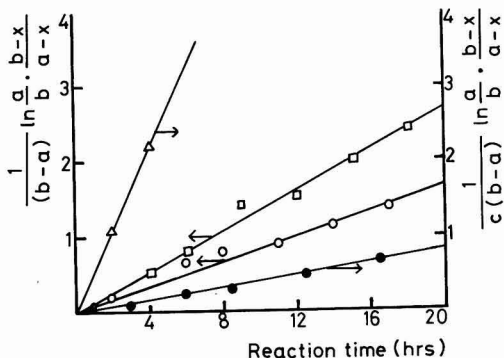


Fig. 2. Rate constant plots as determined from the DEA consumption in the reaction mixture. (●) in DMF (0.1 mole epoxide/10 mole DMF) and nitrobenzene (3.85 mole/0.1 mole epoxide); (○) in DMF (0.1 mole epoxide/10 mole DMF); (□) in DMF (0.1 mole epoxide/20 mole DMF); (△) in DMF (0.1 mole epoxide/10 mole DMF) and phenol (2.5 mole/0.1 mole epoxide).

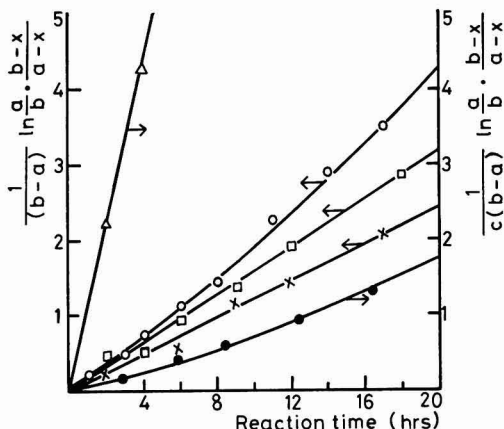


Fig. 3. Rate constant plots as determined from the residual epoxy groups. (●) in DMF (0.1 mole epoxide/10 mole DMF) and $C_6H_5NO_2$ (3.85 mole/0.1 mole epoxide); (×) in benzene (0.1 mole epoxide/10.24 mole C_6H_6); (□) in DMF (0.1 mole epoxide/20 mole DMF); (○) in DMF (0.1 mole epoxide/10 mole DMF); (△) in DMF (0.1 mole epoxide/10 mole DMF) and phenol (2.5 mole/0.1 mole epoxide).

Integration of equation (4) gives:

$$t = \frac{\ln [(b-x)/b]}{(kc + k''b)(b-a)} - \frac{\ln [(a-x)/a]}{(kc + k''a)(b-a)} + \frac{k'' \ln [(kc + k''x)/kc]}{(kc + k''a)(kc + k''b)} \dots \dots \dots (5)$$

Since $k''a$, $k''b$ and $k''x$ may be deleted as much smaller than kc , eqn. 5 becomes:

$$t \approx \frac{1}{kc(b-a)} \ln \frac{a(b-x)}{b(a-x)} \dots \dots \dots (6)$$

Similarly, a rate equation can be derived from eqn. (4) for the presence of hydrogen-bond acceptor additives. If k''' is the rate constant and c' the additive concentration, the rate equation can be expressed as follows:

$$t \approx \frac{1}{k'''c'(b-a)} \ln \frac{a(b-x)}{b(a-x)} \dots \dots \dots (7)$$

The kinetic plots in the presence of a hydrogen-bond-donor, such as a phenol, and a hydrogen-bond-acceptor, such as nitrobenzene, are presented in Figures 2 and 3. The kinetic plots in Figure 3 show that the epoxy group determinations do not give straight lines, but show a slight curvature at higher conversions. This suggests that the reaction between the epoxy groups and DEA either does not strictly follow a pseudo-second-order kinetics or cannot be estimated accurately from the epoxy group consumption. The term "pseudo" is used since the rate constants have also been found to be dependent on the nature of the additives.

In order to confirm one of the two alternatives proposed above, kinetic plots were obtained, based on the amine (DEA) consumed in the reaction (Fig. 2). Straight lines were obtained in this case, indicating that the reaction between the epoxy groups in the MMA-GMA copolymer and DEA is a pseudo-second-order reaction involving three species: the hydrogen-bonded epoxy groups with the hydrogen-bond-donor present (e.g. phenol) and the amine (DEA), as phenols do not react with epoxy groups at this temperature⁸. In addition, epoxy groups are consumed in some side reactions with some species originally present or formed during the main reaction⁸, e.g. with hydroxyl groups.

The dilution effect by the solvent, such as DMF, as determined from the epoxy group estimations has been shown in Figs. 1 and 3. Both the rate constants and the epoxy group conversions were found to decrease with increasing amounts of DMF in the reaction mixture. However, when the rate constants were determined from the amine consumption, it was found to increase with increasing amounts of DMF, cf. Fig. 2. These differences could also be successfully interpreted on the assumption of a non-specific side reaction as proposed above. Retardation of the epoxide-amine reaction at lower dilutions by DMF (cf. Fig. 2) can be assumed to be due to the complex formation between the basic secondary amino groups in DEA and the tertiary amino- and the hydroxyl groups formed during the reaction. This would result in decreased autocatalytic effect by the hydroxyl groups and would also reduce the effective amine concentration in the system. However, when the reactants are diluted by the addition of more DMF to the system, the extent of the

formation of such complexes is considerably diminished due to the high dielectric constant of DMF. Such a phenomenon has been demonstrated earlier by Enikolopiyan¹⁸ where, besides retardation, even a change in the order of reaction was observed when the basicity of the amines used was changed and water was added to the reaction mixture.

Conclusions

The present investigation of an epoxide-amine reaction gives further evidence of a non-specific side reaction between epoxy groups and hydroxyl groups formed in the reaction between the amine (DEA) and the epoxy groups in the polymer. This side reaction gives a higher amount of epoxy group conversion than would be expected stoichiometrically from the primary reaction with the amine (DEA). It is evident that in kinetic studies of the curing reaction of epoxides with amines, the consumption of amines should be estimated and not the consumption of epoxy groups.

Acknowledgements

These investigations are part of a research program on radical polymerisation supported by the Swedish Board for Technical Development (STU) and Swedish Polymer Research Foundation (SSP).

[Received 12 February 1979]

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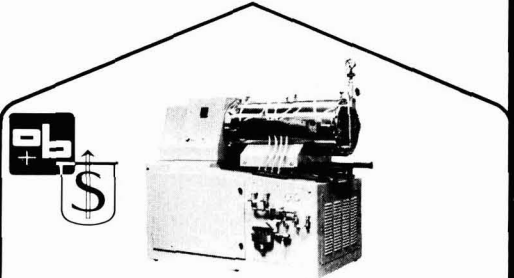
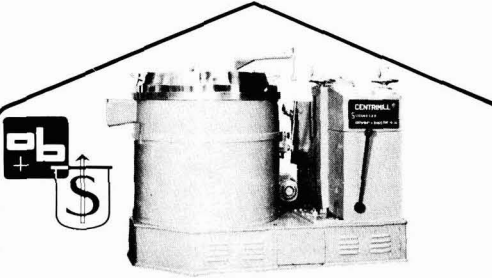
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Lung cancer mortality of workers in chromate pigment manufacture: An epidemiological survey*

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Summary

This paper describes the methods and basic results of a follow-up study of workers at three English chromate pigment factories, especially men employed for at least one year who started work before 1968 and have been followed-up for between ten and forty-five years. Two factories made both lead chromate and zinc chromate, and workers were exposed to both substances; the third factory made only lead chromate. There has been no excess lung cancer mortality amongst workers with chromate exposure rated as "Low", nor among those exposed only to lead chromate. "High" and "Medium" exposure rated workers, who in the past had mixed

exposure to both lead and zinc chromate have experienced a marked excess of lung cancer deaths, even if employed for as little as one year; the excess deaths have occurred within 5-25 years after first exposure. In the author's opinion, the results suggest that the manufacture of zinc chromate may involve a lung cancer hazard, although improved working conditions at one factory appear to have controlled this hazard from about 1955. The results for the third factory provide no evidence that the manufacture of lead chromate involves a similar hazard, even under the conditions prevailing twenty to thirty years ago.

Keywords

*Raw materials for coatings
prime pigments and dyes*

lead chromate
zinc chromate

Miscellaneous terms

carcinogenic material

Properties, characteristics and conditions primarily associated with materials in general

toxicity

Le taux de mortalité à cause de cancer pulmonaire parmi les ouvriers employés à la production des pigments de chrome. Une étude épidémiologique

Résumé

Cet exposé décrit les méthodes et les résultats de base d'une étude des dossiers sur les ouvriers à trois fabriques de pigments de chrome en Angleterre, surtout à propos des hommes employés à cet égard pendant un an au moins et qui ont commencé à travailler avant 1968, et qui ont été contrôlés pendant dix à quarante-cinq ans. Deux fabriques produisaient à la fois les chromates de plomb et de zinc, et les ouvriers étaient exposés à toutes les deux produits; la troisième fabrique ne préparait que le chromate de plomb. Il n'y avait pas d'un excès de mortalité à cause de cancer pulmonaire parmi les ouvriers dont l'exposition au chromate était classé comme "Faible", ni parmi ceux qui étaient exposés seulement au chromate de plomb. Les ouvriers dont l'exposition au chromate était classé comme "Haute" ou "Moyenne" et qui dans le passé

ont subi une exposition mixte au chromate de plomb et au chromate de zinc ont connu un excès bien marqué de mortalité à cause de cancer pulmonaire, même s'ils n'ont pas été employés pour plus qu'un an; l'excès de morts s'est produit entre 5-25 ans après la première exposition. Selon l'avis de l'auteur, les résultats suggèrent que la fabrication du chromate de zinc peut entraîner un risque de cancer pulmonaire, bien qu'une amélioration des conditions de travail à une des fabriques semble à avoir contrôlé ce risque après 1955 à peu près. Les résultats à l'égard de la troisième fabrique ne rendent pas d'évidence que la fabrication du chromate de plomb entraîne un risque pareil, même sous les conditions en vigueur il y a vingt à trente ans.

Sterblichkeit durch Lungenkrebs von Arbeitern in Chromatpigmentfabriken: eine epidemikologische Übersicht

Zusammenfassung

Diese Arbeit beschreibt die Methoden und grundsätzlichen Resultate einer fortlaufenden Untersuchung von Arbeitern in drei englischen Chromatpigmentfabriken, insbesondere von mindestens ein Jahr lang beschäftigten Leuten, welche vor 1968 zu arbeiten begannen und während zehn und fünfundvierzig Jahren überwacht wurden. Zwei Werke stellten sowohl Bleichromat als auch Zinkchromat her, und die Arbeiter wurden beiden Substanzen ausgesetzt; das dritte Werk fabrizierte lediglich Bleichromat. Keine exzessive Sterblichkeit durch Lungenkrebs bestand unter den Chromaten ausgesetzten Arbeitern, wo das Risiko als "niedrig" bewertet worden war, und garnicht unter denen, welche lediglich Bleichromat ausgesetzt waren. Unter Arbeitern, welche "starker" oder "mittelmässig" bewerteter Berührung ausgesetzt waren, und

die früher sowohl mit Blei- als auch Zinkchromat in Berührung gekommen waren, wurde ein merkliches Übermass an Todesfällen von Lungenkrebs festgestellt, selbst wenn die Beschäftigung kürzer als ein Jahr dauerte; die exzessiven Todesfälle fanden zwischen 5-25 Jahren nach der ersten Exponierung statt. Nach Ansicht des Autors legen die Ergebnisse nahe, dass die Fabrikation von Zinkchromat das Lungenkrebs-Risiko mitsichbringt, obwohl in einer der Fabriken diese Gefahr seit etwa 1955 scheinbar unter Kontrolle gehalten wurde. Die Ergebnisse aus der dritten Fabrik beweisen nicht, dass die Herstellung von Bleichromat ein ähnliches Risiko mit sich bringt selbst unter den vor 20 oder 30 Jahren herrschenden Bedingungen.

Introduction

Refs. 1,3

This work has been sponsored by two English manufacturers of chromate pigments, who in 1975 requested that an independent study should be carried out. This request followed a report¹ of animal experiments which suggested that lead

chromate might be carcinogenic, and epidemiological studies in Norway² and the USA³ which cast suspicion on both lead chromate and zinc chromate. A study of chromate pigment factories in continental Western Europe is also being carried out.

*Paper presented to the Manchester Section on 13 March 1978

This survey of English chromate pigment workers belongs to a particular type variously described as a "cohort study", "prospective study" or "follow-up study of mortality"; the author prefers the last description, which is self-explanatory. Such surveys are sometimes compared with laboratory studies on experimental animals, and it may be useful to consider this comparison briefly. One might, for example, set out to test the possible carcinogenic effect of lead chromate and zinc chromate on the lung tissue of mice. One would take a large number of mice of a single strain, and all would be kept in the same conditions except that lead chromate might be applied to one-third of them, zinc chromate to another third, and some "control" substance to the remainder. Those that died would be examined to detect the presence of any tumours, and the remainder would be killed and examined after a predetermined interval judged long enough to achieve reliable results. The incidence of tumours would then be compared in the three groups. The basic idea of a follow-up mortality study is that an unplanned experiment has already been carried out on human beings, quite unwittingly, and that this experiment and its effects should be chronicled in much the same way as if it had been a planned animal experiment. The word "chronicled" is used deliberately, because occupational cancers commonly take many years to develop in man, and if one wants to obtain results at once it is necessary to study a human experiment which took place in the past. In a way carrying out an industrial mortality study can be like reconstructing a piece of history.

But it can readily be seen how unlike an animal experiment such a study will be in practice. Workers at factories enter and leave employment at will, at different dates, stay for differing lengths of time, and nearly all leave long before they die. Their exposures to suspect substances are rarely clear-cut, usually mixed, and probably cannot be measured objectively; there may be no suitable group of unexposed workers for comparison. The basic idea of a follow-up study may be simple, but in practice these surveys may encounter many difficulties. One problem in the present survey is that the total number of workers available for study is small, for the chromate pigments industry is itself small: the present analysis covers less than one thousand men. However, there is a compensating advantage: basically the manufacturing processes and materials have changed little since the time the factories first started production over fifty years ago, so that however far back the study is taken, the effects of exposure to the same suspect substances are observed.

Materials and methods

Three small pigment factories were available for study: Factory *A*, currently employing about one hundred manual workers, and Factories *B* and *C*, each with about fifty; all three had produced chromate pigments since the 1920's or earlier. The main product at Factories *A* and *B* was always lead chromate, but both also used to manufacture zinc chromate: Factory *A* until 1964 and Factory *B* until 1976. Both products were made in the same sheds, and in practice all workers had mixed exposure to both substances. The sole product at Factory *C*, however, has always been lead chromate, and thus a group of workers exposed only to lead chromate can be distinguished although none exposed to zinc chromate alone were available.

The first steps in the survey were as follows:

- Definitions were drawn up of the workers eligible to be included;
- Lists of workers within this defined study population were compiled and checked;

These workers were classified in terms of degree of exposure, length of service, and date of entering employment;

The workers were traced as alive or dead in 1977.

Definition of the study population

It was decided to go back to the earliest date at each factory from which complete personnel records had been kept, and to include from those dates all men who worked in the factories and who completed at least one full year's service, whether in one spell or more than one spell—"broken service" was common at all three factories. A minimum of one year was chosen as a qualification for inclusion, partly for practical reasons, and partly because at the outset it was thought unlikely that less than one year's employment would have presented any hazard; at this stage there were no obvious indications of any lung cancer hazard at the factories and there was no indication of what sort of results would be obtained. To qualify for inclusion, workers had to have completed a year's service by mid-1975, but the present analysis excludes men who entered employment later than 1967, because the period of follow-up observation on such workers is still very short.

Listing the study population

Each factory was visited and there was completely free access to all their records; management had information extracted on each worker to be included in the study, and this information was checked. At Factory *A* it seemed at first that records were complete back to 1947, but no further; from that date the record cards for all new workers had been kept even if the men stayed for a few days only. However, it was thought that there might be some older records stored down in the basement, and indeed a pile of earlier cards was found stacked on the stone floor. Because the floor was damp the bottom few cards were stuck to it or to each other, but otherwise these cards formed a complete sequence going back, with no gap, from 1947 to 1933! To an epidemiologist records going back to 1933 are rare treasure: because there are forty or more years of follow-up observation, nearly the whole story of how the men fared subsequently can be seen, whereas all too often studies have to be carried out with only about twenty years' follow-up. Because of the potential value to the study of these early workers, the qualification for inclusion was extended to cover those of them who had service of less than one year, but not less than three months.

At Factory *C* records had been kept from 1947. At Factory *B* cards for past workers had been kept only from 1952, but old Health Registers kept since 1948 listed virtually the entire workforce, and it was possible to add men who left during 1949-51 after completing at least one year's service. Identifying details on these extra men were scanty, but one of the management staff devoted a great deal of effort to obtaining further information about them. For all three factories the successful completion of the survey owes a great deal to the managements' untiring efforts to supply details on past workers, to the extent that retired staff came up to the factories specially to supply information about past workers whose histories were not known to the present staff.

This presentation covers men actually starting work at the three factories during the defined periods, and excludes those men who were already in employment before 1932 at Factory *A*, 1948 at Factory *B* and 1946 at Factory *C*. One reason for this exclusion is that such men had already been in

service for widely varying lengths of time ranging from one year to more than twenty years, so that their later mortality cannot be related clearly to any specified period of exposure. A more important reason for exclusion is that these men are unlikely to be typical of all earlier starters at the factories: they are a small and highly-selected sample—they are the ones who started work and then stayed on whilst most of their contemporary starters left again and doubtless some died.

It is important that the list of workers included in a study, the "study population", covers all the men who are eligible according to the definition. Some men may be left out if a series of personnel cards is incomplete, and omissions from personnel cards are unlikely to be random. In the author's experience the commonest reason for a card to be missing is that it relates to an ex-worker who had an accident or industrial disease; in such instances the card may be needed to provide information for insurance or legal purposes, and it may happen that someone forgets to replace it in the file. The omission of such cases is likely to result in bias, and in this study other records were sought by which to check the completeness of the study population. Fortunately, the other series of records listed in Table 1 were available, and whilst not all of these were comprehensive lists of everyone at the factories, their combined use enabled fairly thorough checks to be made. It was found that six men had been omitted; these six were now added to the study population, and it appeared unlikely that any other eligible workers had been omitted.

Table 1
Records used to check the study population

<i>Factory A</i>	Health Registers for 1933-42 and 1959-63 Early medical records covering 1937-51 A list of all new employees starting from 1939-41
<i>Factory B</i>	Health Registers kept from 1948 onwards Factory General Registers kept from 1948 onwards
<i>Factory C</i>	Factory General Registers kept from 1947 onwards Wages Department slips covering workers who started or left during 1955-63 Insurance claim records covering 1948-60 Records of health checks covering 1954-55

Classification of the study population

Each factory was studied separately, and workers were classified as shown in Table 2. For classification by grade of exposure to chromates, work in the "Dry" departments (where pigments were ground, blended and packed) was graded "High"; the "Medium" grade covered work in the less dusty "Wet" departments (where precipitates were washed, pressed and stove-dried) and also jobs such as maintenance or cleaning which required men to spend time in various different departments. The "Low" category was

Table 2
Classification of the study population

By Grade of Exposure to Chromates: High, Medium, Low		
By Length of Service: 1 yr, 2-4 yrs, 5-9 yrs, 10+ yrs		
By Date of Starting Work	Dates	Numbers of Men
Factory A	1932-45	156
	1946-54	96 } 396
	1955-67	144
Also: less than 1 yr's service	1933-45	94
Factory B	1948-67	136
Factory C	1946-67	114

reserved for work involving only slight exposure to chromates, e.g. most laboratory jobs, boiler stoking, painting and bricklaying. Many men changed departments within the factories and did work of different grades; these men were allocated to the most appropriate overall grade. The emphasis was on reserving the High grade for men who experienced severe exposure during most of their service, and the Low grade for men who spent little time in any but Low exposure jobs.

The study populations at Factories B and C were rather small to subdivide by date of starting work, and during the relevant period there were no dates when working conditions changed there significantly. There were important changes at Factory B in 1968, which probably improved conditions markedly, but that date is too recent for the effects to be seen yet. At Factory A, however, with more men and a longer period, two divisions were made. The first division was made at the end of the war, 1945/46, when working conditions might have been expected to improve and when there was a new intake of workers. The second division was made between workers who started employment up to 1954 and those who started from 1955 onwards; around this date various changes were made at the factory which, together, would have considerably reduced the workers' exposure to chromates, including changes in packaging procedures and increased use of respirators for dusty operations.

Tracing

The next step in the survey was to find out whether the men in the study population were alive or dead, and if dead to ascertain the causes of death. It has to be remembered that although some of the men were still working at the factories or were retired pensioners, the majority were ex-workers who had been lost sight of by the factories. Fortunately, in this country there are excellent tracing systems, and for this study the men were traced by the National Health Service Central Register (NHSCR), who will not divulge confidential information such as where persons are living, but will report them to be alive or dead, emigrants or untraced, and will supply copies of death certificates.

The main tracing problem in this study arose at Factory C, where since the late 1950s a gradually increasing proportion of the workforce has been made up of immigrant workers. For various reasons these immigrants may be difficult to trace, and the NHSCR reported that about a third of the 53 immigrants at Factory C could not be traced. The tracing of the other two-thirds may not be completely reliable, and this group has, therefore, been excluded completely from the present analysis; they are already excluded from the figures given in Table 2. However, four immigrants have been traced as dead by the NHSCR, and none of these four died from lung cancer. It is unfortunate that this part of the workforce at Factory C had to be omitted, but the survey still includes all new starters there from 1946 until the late 1950s and all later starters who were not immigrants.

Among the rest of the study population 27 men were initially untraced by the NHSCR, but after considerable effort by all concerned to find out more about these men, all were finally traced except three—one at each factory. Whatever the fate of these three men it could make virtually no difference to the survey results, and they have been omitted from this analysis. There were also a number of men at each factory who emigrated at various intervals after starting work, and they have been removed from follow-up at their date of

emigration. Some of them have kept in touch with the factories and are known to be alive, but most are untraceable. However, it turned out that even if some of them have in fact died from lung cancer, it could scarcely have had any important effect on the results, but might merely have accentuated the trends found.

Calculation of the survey results

Refs. 6,7,8,9

The next step was to classify the causes of death of workers who had died, and pick out those deaths which were attributed to lung cancer. These were the "observed deaths", which had then to be compared to the number of "expected deaths", i.e. the number that one would expect to occur if the lung cancer mortality of these workers was the same as that of other men of the same age at the same dates. This comparison is made using the well-established technique⁶ of computing for each worker the number of "man-years" he had lived since entering observation, defined in detail by age and date, and by adding up the total of man-years experienced by each sub-group of workers at each factory. Lung cancer death rates vary markedly by sex, age and date, and the man-years are totalled in small cells; national lung cancer death rates for all males in England and Wales⁷, similarly defined by age and date, are then applied to the man-years in each cell to obtain the expected numbers of deaths. For each worker in this study mortality observation (and hence the calculation of man-years) commenced five years after the man entered employment at any of the factories, and continued until death, emigration, or until mid-1977 for the present analysis. However, this is an ongoing study; further deaths among the study population will be traced by the NHSCR, and the results will be updated regularly.

This method of calculating the numbers of expected deaths does not take account of two local factors which may render the workers either more or less likely than the "average man in the country" to die from lung cancer, quite independently of any specific work hazard. The first factor is the workers' level of tobacco smoking; there was no reason to suppose that these men smoked on average more than others of the same social class, but it is known that men in the lower social classes—unskilled and semi-skilled manual workers—smoke more than the national average and have higher than average lung cancer death rates. The proportion of unskilled and semi-skilled workers in the study population was higher than in the general population⁸, and therefore the numbers of expected deaths have been slightly increased to allow for this factor. The second factor is that of local geographical variations in lung cancer mortality. Mortality in the area where Factory *A* is situated is close to the national average, but in the area around Factory *B* it is somewhat lower, whilst around Factory *C* it is about 50 per cent higher than the national average⁹. The expected number of deaths has therefore been adjusted downwards for workers at Factory *B* and upwards at Factory *C* by appropriate amounts, to avoid getting "false negative" or "false positive" results.

After these calculations and adjustments it is finally possible to compare the numbers of expected and observed deaths. If the number of observed deaths exceeds the expected number it may indicate a lung cancer hazard, but the "statistical significance" of the difference is measured by the Poisson Test, because small differences will occur simply by chance.

Results

Refs. 4,5

When the survey results were obtained it turned out that those for men in the "High" and "Medium" exposure grades

were similar, and in this presentation the two grades have been combined. Similarly, the results at Factory *A* for men who started before 1946 and those who started from 1964-54 were similar, and the two sub-groups have been combined. Results in more detail will be published elsewhere, and a brief summary has already appeared⁴.

The results for men at Factory *A* who entered employment before 1955 are shown in Table 3. Men in the High and Medium grades combined had more than twice the expected number of lung cancer deaths, and this difference is very unlikely to be due to chance—it is statistically significant at the 1 per cent level. There was no excess of lung cancer deaths among men in the Low exposure grade, which is a reassuring finding. Nor was any excess apparent among the men with less than one year's service: 4.19 deaths were expected, and 5 were observed.

Table 3
Lung cancer mortality at Factory A:
Men starting work during 1932-1954

Exposure Grade	Number of men	Expected Deaths	Observed Deaths
High & Medium	175	8.17	18**
Low	77	2.00	2
Service of less than one year	94	4.19	5

** $p < 0.01$

Table 4 gives the results for the study population at Factory *B*; here the excess of lung cancer deaths among High and Medium grade workers is even less likely to have arisen by chance. These were the two factories where workers had mixed exposure to both lead chromate and zinc chromate, and it seems clear that there was an effective lung cancer hazard operating in both factories at the dates in question. Table 5 shows that at Factory *A* the excess deaths occurred within twenty-five years of the worker's first exposure to chromates (i.e. the start of their employment); the data goes back so early at this factory that 111 workers were still under observation 25 or more years after first exposure, but there have been no extra deaths among them since that point. Few of the men at Factory *B* have yet reached the 25-year point, so that the worst part of their mortality experience has probably been seen; at first sight their mortality appears worse than that of Factory *A* workers, but in the long run it may prove similar.

Table 4
Lung cancer mortality at Factory B:
Men starting work during 1948-1967

Exposure Grade	Number of men	Expected Deaths	Observed Deaths
High & Medium	116	1.43	7***
Low	20	0.10	0

*** $p < 0.001$

This apparent cessation of risk 25 years after first exposure is interesting to an epidemiologist, and rather unusual; it is not characteristic of the lung cancer hazard in the USA dichromates-producing industry⁵. But here the concern is with practical rather than theoretical implications, and it is merely noted that not only did the excess deaths at Factory *A* occur within 25 years, but that of the 22 lung cancer deaths



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at both factories, four occurred within 5-9 years of the men starting work, and another five within 10-14 years. One man died only 5 years and 2 days after starting work, and since he was aged only 32 at death there is a strong presumption that his lung cancer was of occupational origin.

Table 5
Lung cancer mortality of High and Medium grade workers at Factories A and B

Factory and Starting-dates		Interval after starting work		
		5-24 yrs	25+ yrs	Total
Factory A 1932-1954	Number of men	175	111	175
	Expected deaths	3.81	4.36	8.17
	Observed deaths	15	3	18
Factory B 1948-1967	Number of men	116		116
	Expected deaths	1.43		1.43
	Observed deaths	7		7

The practical importance of these relatively short intervals between first exposure and death from lung cancer (unusually short for occupational cancer) is that it should by now be possible to see whether a hazard was still effective at Factory A for men who entered employment after 1954. As shown in Table 6, no excess of deaths has occurred among these workers—indeed, it happens that so far none of them has died from lung cancer. In the normal course of events one or two such deaths might have been expected to occur, and the fact that so far there have been none merely underlines the impression that these men do not appear to have been exposed to an effective hazard. Among the earlier workers, the excess deaths were obvious by 15 years after first exposure, and at Factory B there is already a statistically significant excess of deaths among men who started work from 1961-67 (0.42 expected, 3 observed). This pattern cannot be repeated among the post-1954 starters at Factory A, for whom observation already covers periods ranging from 10-22 years after first exposure according to exactly when they entered employment. A longer period is needed before it becomes certain that there was no effective hazard at Factory A after 1954, but at the time of writing observation has been extended for ten months up to April 1978 and it is still the case that no lung cancer deaths have occurred. It will be recalled that changes which reduced chromates exposure were made in 1955, but that starting materials and final products were largely unchanged. It is to be hoped that the improvements made at Factory B in 1968 will have removed the hazard there; so far there have been no lung cancer deaths among men at either factory who entered employment from 1968-74.

Table 6
Lung cancer mortality at Factory A:
Men starting work during 1955-1960

Exposure Grade	Number of men	Expected Deaths	Observed Deaths
High & Medium	62	1.14	0
Low	14	0.16	0
<i>Men starting work during 1961-1967</i>			
High & Medium	52	0.23	0
Low	16	0.14	0

Table 7 gives the results for Factory C, where only lead chromate was manufactured, and shows that there has been no excess of lung cancer deaths.

Table 7
Lung cancer mortality at Factory C:
Men starting work during 1946-1967

Exposure Grade	Number of men	Expected Deaths	Observed Deaths
High & Medium	95	2.46	1
Low	19	0.37	1
Total	114	2.83	2

Analysis of mortality at Factories A and B by length of service showed that even workers employed for as little as one year experienced excess mortality which was statistically significant (2.65 deaths expected, 9 observed). Indeed, because many of the lung cancer deaths occurred among ex-workers with short service who had been lost sight of by the factories the hazard was inconspicuous until this survey was carried out.

Discussion

The apparent lack of a hazard at Factory C

The importance of this result for Factory C, where only lead chromate was manufactured, can readily be appreciated. But is the result reliable, or can it be questioned? For example, has the omission of the immigrants affected the result? This appears to be unlikely: why should there have been a risk for men starting work from the late 1950's onwards if there was no hazard affecting those who started from 1946? Conditions at Factory C have not been getting worse! Another objection might be that the small number of men makes the result unreliable. Undeniably the number is small—only 114 men were available for study; but on the other hand this was not a *sample* of the workforce but the *whole* workforce, except for the immigrants, and it is a fact that their lung cancer mortality has been normal. A final objection might be that the upward adjustment to the expected number to allow for locally high lung cancer death rates has affected the result; however, even without this adjustment the expected number would be 1.88, to be compared with 2 observed deaths.

In this kind of study a negative result is usually harder to demonstrate than a positive one, but it does appear that at Factory C there was no *effective* lung cancer hazard for men starting work there during 1946-67. However, it is necessary to be quite clear about what inferences may be drawn: it cannot be inferred that lead chromate is, therefore, cleared as a possible human lung carcinogen; perhaps lead chromate can cause lung cancer in man if exposure is very severe; for example, there is a possibility that it caused some lung cancer deaths at Factory C before 1946. What can be stated is that under the conditions prevailing at Factory C since 1946, lead chromate appears not to have caused lung cancer deaths. The author considers that it can reasonably be inferred that under today's stricter conditions of industrial hygiene it should be possible to make and use lead chromate without a lung cancer hazard for those involved.

The hazard at Factories A and B

Three questions raised by the results for these two factories will be considered: How serious was the hazard? Has the hazard ceased, and if so, why? What substance was responsible for the hazard?

Firstly, how serious was the hazard? Unquestionably the past hazard was severe, with men running two to four times

the usual risk of dying from lung cancer. This risk relates to men with High and Medium exposure who had service of at least one year; men with Low exposure do not appear to have been at risk, and nor do men at Factory *A* who had service of less than one year. Among those at risk at the two factories there have been 25 lung cancer deaths where about 10 were expected; some of the 25 men died at unusually early ages—two were only in their thirties, and four in their forties. Numerically, 15 extra deaths may appear a small figure, but these were 15 extra deaths among only 291 workers, for thankfully the factories are small.

Has the hazard ceased? It is too early to know whether the risk at Factory *B* ceased following the improvements made in 1968, although so far there have not been any lung cancer deaths among later starters there. But at Factory *A* there are good reasons to believe that the hazard ceased to be effective in about 1955. There were only minor changes in the starting materials and end products at this time; the main changes were measures which reduced men's exposures to both lead and chromates, and more careful health surveillance of the workers. It should be noted that zinc chromate was still made at Factory *A* until 1964.

Finally, which substance was responsible for the hazard at Factories *A* and *B*? In view of the apparent absence of a hazard at Factory *C* it is the author's opinion that the risk at Factories *A* and *B* probably arose from the manufacture of zinc chromate. It might be argued, however, that the different result for Factory *C* could be explained by working conditions there being better, with less exposure to chromates. Unfortunately, there is no way to make objective comparisons of chromate exposures at the three factories during the relevant period, but the author personally believes this explanation to be unlikely. This opinion is based partly on verbal accounts given of past conditions at all the factories, and partly on the fact that indirect comparisons in the form of data on lead absorption and cases of lead poisoning among workers at Factories *A* and *C* do not support the argument that conditions at Factory *C* since 1946 have been consistently better than those at Factory *A* up to 1954. It could also be argued that if zinc chromate gave rise to a lung cancer hazard and lead chromate did not, it could be because exposures to zinc chromate were more severe than exposures to lead chromate: workers always knew that lead chromate was a toxic substance and would have taken more care to avoid the inhalation of dust from this substance than dust from zinc chromate, which was not considered dangerous. There may be some force in this argument, and the possibility cannot be denied that *severe* exposure to lead chromate might induce lung cancer. However, it could be argued in reply that this exposure would have to be more severe than that at Factory *C* during 1946–60, and would, therefore, have to be such as to induce cases of overt lead poisoning. But here it becomes a matter of opinion rather than fact, and the findings of other studies that have been carried out should also be considered.

The other studies

Refs. 2,3

The Norwegian study² covered three small plants where only zinc chromate was made. Between 1948–72, 133 men worked at these plants, and 24 of them had service of at least three years. By 1972, three out of the 24 men had developed lung cancer, whereas the expected number was only 0.08; none of the men with shorter service had been affected. It is difficult to compare the severity of the hazard in the Norwegian plants with that in the English Factories *A* and *B* because of different study definitions and different background lung

cancer rates; however, it is thought that the Norwegian results for zinc chromate exposure alone are not necessarily dissimilar to the English results for combined zinc chromate and lead chromate exposure, especially those at Factory *B* where the period covered is similar.

The unpublished USA study³ covered three plants, and at Plants 1 and 2 the workers included were exposed only to lead chromate; the 166 men studied at Plant 2 were engaged only from 1959 onwards. Out of the total of 393 men included at both plants, 23 were untraced, and the cause of death could not be ascertained for three of the 20 workers known to have died by the closing date of 1975. The authors present various tables of results, but only one is based on death rates corrected for date, area and race; this table relates to the 184 men at both plants who were first exposed before 1960 and had at least 10 years' service, and for these men the expected number of lung cancer deaths was 1.7 and the observed number was 2. Thus for Plants 1 and 2 (with exposure only to lead chromate) the result is negative, but the limitations of the basic data prevent the result from being definitive.

Plant 3 made both lead chromate and zinc chromate, and here the study population consisted solely of the 164 men who were on the payroll in 1957 and so had exposure to chromates; all these men had mixed exposures to both lead chromate and zinc chromate, except for two who were only in contact with lead chromate.

A study population defined in this way is unusual and has limitations, because it comprises men who have already been in employment for varying lengths of time; as explained earlier such men form a selected sample of a workforce and their exposures cannot be defined by date. There is again only one table which uses death rates corrected for area and date, and this relates to the 154 men who had at least ten years' service; the expected number of lung cancer deaths was 3.2 and the observed number was 6. Thus the result for men with mixed exposure to lead chromate and zinc chromate appears positive, but it should be noted that one of the six men dying from lung cancer was one of the two in contact with lead chromate alone. Caution should be exercised in drawing inferences from this result based on an unusual type of study population.

The continental study referred to at the beginning of this lecture is being carried out by Dr R. Frenzel-Beyme at the Deutsches Krebsforschungszentrum at Heidelberg, and it covers factories in West Germany and the Netherlands. All these factories manufactured both lead chromate and zinc chromate, and so this study will not be able to distinguish between the effects of exposure to one or the other. Sadly, the author is not aware of any further factories available for study where workers were exposed only to lead chromate, much as it would be desirable to learn more about the effects of such exposure.

Acknowledgements

This study could not have been carried out without the patient and whole-hearted co-operation of staff at each factory. The National Health Service Central Register carried out the necessary tracing, and assistance at various stages of the survey was given by Miss Eve Lister and Miss Jean Miller.

Support was received from the Cancer Research Campaign.

[Received 26 January 1979]

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The automatic cleaning of tanks, tankers and plant by high pressure spray

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Summary

Various types of equipment for automatically cleaning tankers, tanks, mixers and other plant by means of high pressure spraying are described.

Keywords

Processes and methods primarily associated with manufacturing or synthesis

clean up

Equipment primarily associated with manufacturing or synthesis

tank
vessel
mixing equipment

Le nettoyage automatique de bacs, camions-citernes et matériel par les jets de liquide à haute pression

Résumé

On décrit de divers types de matériel mis au point pour le nettoyage automatique de camions-citernes, bacs, mélangeurs et autres éléments au moyen des jets de liquide à haute pression.

On considère les facteurs opératoires tels que la pression, la température, le volume de liquide de lavage, et l'orientation des gicleurs. On fait mention du recyclage du liquide de lavage.

Die automatische Reinigung von Tanks, Tankschiffen und Maschinerie mittels Hochdruckspritzstrahl

Zusammenfassung

Eine Beschreibung von verschiedenen Apparaten für die automatische Reinigung von Tankschiffen, Tanks, Misch- und anderen Maschinen mittels Hochdruckspritzstrahl. Arbeitsbedingungen

wie Druck, Temperatur, Volumen der Waschflüssigkeit und die Positionierung des Spritzstrahls werden in Betracht gezogen. Das Umpumpen der Waschflüssigkeit wird ebenfalls erwähnt.

Cleaning operations in the chemical industry involve the question of what type of possible contamination can best be cleaned with what particular equipment.

independent of the shape and size of the containers, as distinct from appliances using brushes. These are, according to individual requirements, reliable high and low pressure systems. In the various fields discussed in this paper, practically everything seems to indicate the advantages of the high pressure cleaning. This is done by a high pressure jet in which five factors are effective: pressure, quantity of water, temperature, chemicals and time.

It can be said today that the problems of internal cleansing of tanks and silos, vehicles, railway tank wagons as well as transportable containers and stationary storage tanks, have been solved. Any required degree of cleanliness can be achieved in the following stages:

These five factors must be adjusted according to each individual case.

- (1) Visually clean for refilling with other products of a similar type.
- (2) Chemically clean, when tank inspection is to be carried out.
- (3) Biologically clean, if a significant change in the type of product is involved, such as a change from petrochemical material to a basic material of the dyeing and paint industries.

Factors involved

Pressure is of paramount importance for cleaning. The pressure of impact determines the speed at which a layer of dirt is torn away or broken up from its base.

The required degree of cleanliness can be achieved with automatic cleansing by the addition of washing and disinfecting compounds (also with pure solvents), as well as by adjusting the time-factor of the process.

Experiments have shown that approximately 50 bar pressure is ideally suitable for this procedure and also that this does not damage the inside of the container.

Examples of some high pressure cleansing equipment are given below.

The cleaning procedure

There is no doubt that methods using liquids have great advantages in automatic cleaning because their application is

The quantity of the medium (water or solvent) issuing from the high pressure jet per nozzle, must be adjusted according to the pressure and size of the container. The temperature of the medium in the jet depends on the cleaning problem. High temperatures of approximately 100°C for instance, in the case of petrochemical products, are very decisive and have a considerable effect on the amount of solvents used. Account must also be taken of the drop in the temperature of some 2° or more due to the impact on the

object to be cleaned. High temperatures are particularly effective in improving the efficiency of the process. The time cycle must be kept short for reasons of economy (capital investment with respect to water, oil, electric current and chemical usage). Any arbitrary reduction in the time is not possible, as the other four factors cannot readily be increased.

Equipment

The basic elements of equipment may be combined in any way to suit the problem to be solved. These are as follows:

High pressure supply with a dosage device controlling the injection or pump.

High pressure internal cleansing heads of various types.

Automatic programmes (with time adjustment and remote control), the energy supply for instance, by thermo-oil installations with steam generators and temperature control.

On the basis of the considerations mentioned above, the author's company is able to supply ready-made key installations, which are suitable for any individual application. The most frequently used systems are explained briefly below.

Cleaning equipment for tankers and silos

This applies to practically all products in the chemical, food, beverage etc. industries. What types of installation are required to solve the multiple uses in these fields, particularly with regard to the question of economy?

The vehicles are of a variety of constructions, depending on their special uses. Generally speaking, the containers have a diameter of approximately 2500 mm and in the case of those for liquids, they are divided into compartments. Most of these vehicles have three compartments. In the field of silo conveyors, there are large vehicles with a standard capacity of up to 50 m³ without compartments.

On the basis of these measurements, the following working data have proved to be particularly economical:

The quantity of water of 3000 l/h (litres per hour) for each cleansing head, which generally has two nozzles. Thus, the consumption of water is 1500 l/h per nozzle.

Tests have shown that working pressures of 50 bar are the maximum. For cleaning these vehicles, usually three internal cleansing heads are placed in the same cleansing line. This makes it possible to clean the usual type of tanker in one operation. This arrangement may also be applied to silo vehicles having a capacity of up to about 35 m³. For larger capacity silos, up to 50 m³, it is advisable to instal four internal cleansing heads in a line.

The following requirements apply to such an installation: Cleaning with cold or warm water up to approximately 100°C with a high pressure jet, with a choice of adding detergents and/or disinfectants, steaming out with saturated steam, followed by drying with warm air.

The actual cleaning process depends on the type and extent of the pollution, as well as on the product that is to be filled into the container after cleaning. During an average cleaning, the following working programme is practicable:

	Time minutes	Tempera- ture degr. C.	Chemicals %	Pressure Bar	Volume of water
Primary rinsing	4	cold	0	50	3000 l/h
Cleaning	4	90	1	50	3000 l/h
Second rinsing	8	90	0	50	3000 l/h
Steaming	—	160	0	9	1000 kg/h
Disinfecting	1	cold	0.5	50	3000 l/h
Drying	6	100	0	0.3	4000 m ³ /h (air)

This type of installation is shown in Figure 1.

Cleaning of railway tank waggons

Railway tank waggons involve the same principles as road vehicles.

As a rule these tankers have a diameter of approximately 2500mm with the length of the tank approximately 15m. However, these tank waggons usually have a dome constructed in the middle of an opening of approximately 500–600mm. The installation of the cleaning heads is possible only through this opening. This type of construction, as distinct from road tankers, needs longer jet distances. The cleaning installation must, therefore, be adjusted to allow for these changed conditions.

Tests have shown that the following construction is particularly economical: The impact of the cleaning medium on the tank surface is decisive for satisfactory cleaning. As the impact at the same initial parameters depends only on the distance from the jet, the quantity of water and the pressure must be so varied that similar values are produced as for road vehicles. In the case of smaller tank waggons with a length of 6–8m, cleaning is possible with a centrally placed cleaning head. In this case, water quantities of from 6000 to 9000 l/h, using two nozzles, at a spraying pressure of approximately 100 bar, have been found to be economic. In the case of larger tank waggons, owing to the size when using centrally placed heads, the angles of impact are so small that the effective impact pressure is very much reduced. Increasing the quantity of water and pressure does not lead to an economic solution, as only a small part of the increased energy is passed on directly to increase the effective impact pressure. In order to achieve a doubling of the impact pressure, it is necessary either to double the quantity of water or to quadruple the pressure.

Both these increases result in greatly increased working costs, which bear no relation to the improvement in the result. Furthermore, larger quantities of water also have the disadvantage that the expulsion of the water is no longer certain and that a bottleneck of water is produced in the tank waggon, which greatly diminishes the efficiency of cleaning.

For this reason, the cleansing heads must be arranged in such a way as to produce an economic cleaning process. This is done by means of an automatic swivel device, which brings the two cleaning heads to the correct position in the interior of the tank.

This improves the impact angle, and it becomes possible, using a two nozzle construction at approximately 6000 l/h and a pressure of 100 bar, to achieve the same conditions that apply to road vehicles. Figure 2 shows the principle of arrangement in tank waggons.

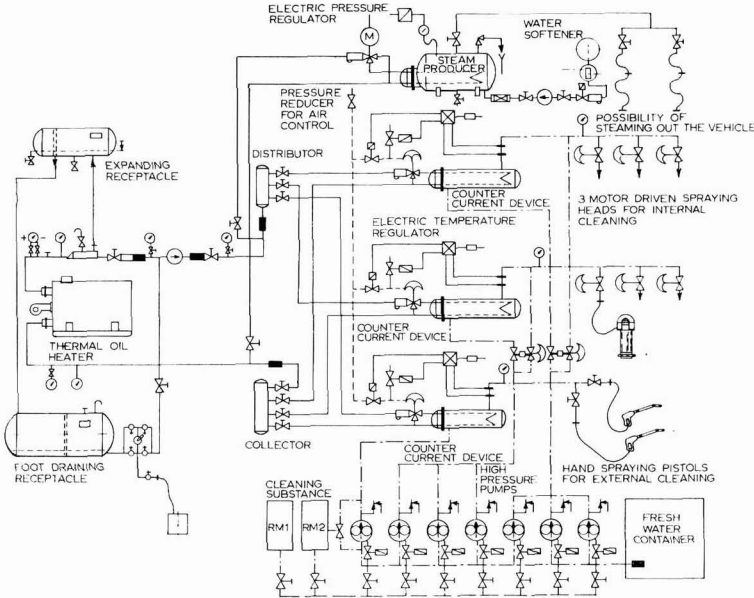


Fig. 1. Diagrammatical representation of the cleaning installation

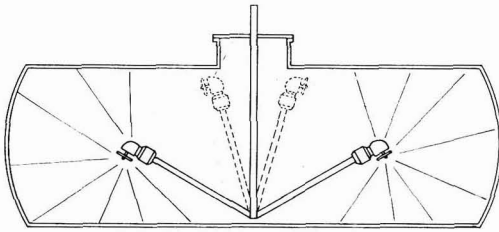


Fig. 2. Operating principle for rail tanker wagon

In the case of older tank waggons with splash-proof walls, or similar devices, the cleansing head must be inserted individually with a skid runner. Almost the same jet composition applies here as in the case of tankers, the compartments being similar in size.

Cleansing installations for treatment containers and storage tanks

The same considerations as described above apply, provided that water with added chemicals can be used as cleaning material.

Transportable containers should be collected at a suitable central cleaning plant. In the case of fixed containers, the number of cleanings required will decide whether the cleansing heads are built into the container or are inserted into the tanks when required.

In the case of containers with internal fixtures (such as stirrer equipment, etc.) it is necessary to provide the cleaning head with two operating positions so that shadow effects can be avoided.

Figure 3 shows a cleaning installation for containers having stirring equipment.

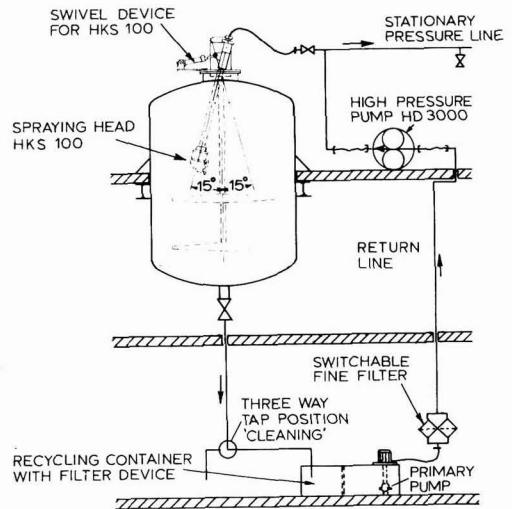


Fig. 3. Cleaning installation for containers with an internal stirring device

Installation for cleaning containers holding materials not dispersible with water (lye, caustic soda, etc)

For the cleaning of mixing and stirring containers, hobbcocks, packing material, etc. or in the entire chemical industry, installations must be provided which use solvents, such as toluol, xylol, acetone, ether or similar substances, or with hot lye (sodium lye of 10 per cent, caustic potash solution of 10 per cent), because the products used in these industries cannot be dissolved in water.

These installations require a special layout and in view of the danger of an explosion, they have to be completely protected. The use of this type of cleansing is economic only if a recycling process is employed.

The general statements already mentioned are valid also for these installations. The impact pressure here is a particularly important point. The containers are usually not cleaned immediately after having been emptied, so that a tendency to polymerisation in the residual varnish on the polluted surface may be expected. This layer must be torn open by the high pressure jet, before there is any possibility of a speedy cleaning with satisfactory results.

Installations with cleansing heads have proved themselves to be particularly useful in those cases where containers of various types had to be dealt with, because an adjustment was unnecessary.

The following types of installation have been found to be particularly useful:

Installation type A. Compact installation for cleaning from below or from above.

Installation type B. Cabin installation. This type of installation has many advantages when mounted in a production department and automatic feeding is desired.

Recycling installation—Installation for treatment of waste water

In view of the environmental protection and working cost, it is essential that cleaning plants are operated without causing pollution and that operational costs are kept to a minimum. The installations described here may, without exception, be either operated with the recycling system or using a system of purification or treatment of the waste water, and this can be done economically and in a manner environmentally acceptable.

Figure 4 shows an installation for treating waste water. Figure 5 shows the flow of the cleaning media.

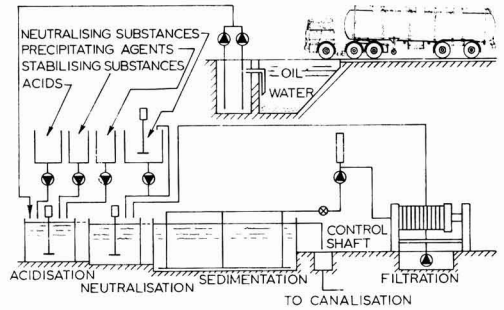


Fig. 4. Installation for treatment of waste water

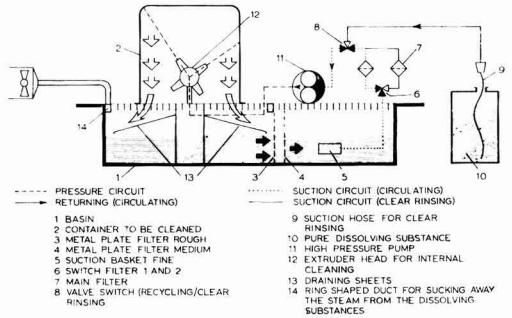


Fig. 5. Flow of the cleaning medium

[Received 22 November 1978

Film characteristics of polyepoxide resins based on novolac resins

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Summary

Epoxy resins were prepared by reaction of phenol-formaldehyde novolac resins with epichlorohydrin. Samples having various epoxide equivalents were prepared and compared with epoxy resins based on bisphenol-A. The effects of two different curing agents, namely butylated melamine formaldehyde resin and castor alkyl resin, on epoxy resin films were studied.

The heat cured films of novolac based epoxy resins were found to be superior to those of bisphenol-A based epoxy resins with regard to scratch hardness. However, no significant difference was ob-

served with regard to flexibility and resistance to alkali, acids and solvents, which varied mainly with the epoxide equivalent and type of curing agent used. Films cured with butylated melamine formaldehyde resin showed good scratch hardness and resistance to alkali and solvents. These films showed poor flexibility and acid resistance. Films cured with castor alkyl resin showed good flexibility and resistance to alkali and acids.

Films of epoxy resins having high epoxide equivalents had an increased tendency towards yellowing, particularly during stoving.

Keywords

Types and classes of coatings and allied products

epoxy coating

Raw materials

binders (resins, etc.)

epoxy resin

phenolic epoxy resin

Properties, characteristics and conditions primarily associated with dried or cured films

acid resistance

chemical resistance

alkali resistance

scratch resistance

solvent resistance

hardness

elasticity

yellowing

Les caractéristiques des films rendus par les résines polyépoxydes à base des résines du type novolac

Résumé

On a préparé des résines époxydes par la réaction des résines formophénoliques avec l'épichlorohydrine. Les échantillons ayant de divers équivalents en époxyde ont été préparés et comparés auprès des résines époxydes basées sur le bisphénol-A. On a étudié les effets sur des films de résines époxydes qu'exercent deux différents agents de durcissement, à savoir, une résine du type mélamine-formol butylée, et une résine alkyde à l'huile de ricin.

On a trouvé que les films des résines époxydes à base des novolacs, durcis par la chaleur, sont supérieurs au point de vue de la résistance à la rayure à ceux rendus par les résines époxydes à base de bisphénol-A. Toutefois, on n'a noté aucune différence sensible à l'égard de la flexibilité et à la résistance aux alcalis, acides ou

solvants, ces caractéristiques dépendaient en général de l'équivalent en époxyde et du type de l'agent de durcissement que l'on utilise. Les films durcis par la résine du type mélamine-formol butylée démontraient de bonne résistance à la rayure, aux alcalis, et aux solvants. La flexibilité et la résistance aux alcalis de ces films se démontraient faibles. La flexibilité et la résistance aux alcalis et aux acides des films durcis par la résine alkyde à l'huile de ricin se démontraient bonnes.

Les films des résines époxydes ayant des équivalents en époxyde élevés possédaient une tendance augmentée à jaunir, surtout pendant l'étuvage.

Filmcharakteristika von auf Novolac—Harzen basierenden Polyepoxyharzen

Zusammenfassung

Es wurden Epoxyharze durch Reaktion von Phenolformaldehyd-Novolac-Harzen mit Epichlorhydrin hergestellt. Muster mit verschiedenen Epoxidequivalenten wurden erzeugt und mit auf Bisphenol-A basierenden Epoxyharzen verglichen. Die Wirkung von zwei verschiedenen Härtern, nämlich butyliertem Melaminformaldehydharz und Rizinusölkylidharz, wurde anhand von Epoxyharzfilmen untersucht.

Es wurde gefunden, dass wärmegehärtete Filme von auf Novolac basierenden Epoxyharzen denen auf Bisphenol-A Basis hinsichtlich Kratzhärte überlegen waren. Indessen wurde kein wesentlicher

Unterschied bezüglich Biegsamkeit und Beständigkeit gegen Alkalien, Säuren und Lösungsmittel beobachtet, sie unterschieden sich hauptsächlich je nach Epoxyequivalent und Art des Härters. Mit butyliertem Melaminformaldehyd gehärtetes Harz zeigte gute Kratzhärte sowie guten Widerstand gegen Alkalien und Lösungsmittel. Diese Filme zeigten schlechte Biegsamkeit und Säurebeständigkeit. Mit Rizinusalkylidharz gehärtete Filme zeigten gute Biegsamkeit und Beständigkeit gegen Alkalien und Säuren.

Filme von Epoxyharzen mit hohen Epoxyequivalenten zeigten größere Neigung zum Vergilben, besonders bei Ofentrocknung.

Introduction

Refs. 1-5

Epoxy resins have been widely used in surface coatings on account of their excellent flexibility, adhesion, toughness, and chemical resistance. As a result, these resins can be in-

corporated in coatings where resistance to chemicals, impact, abrasion, and other types of physical abuse are of paramount importance. The commonly available epoxy resins are condensation products of epichlorohydrin and bisphenol-A. A variety of epoxy resins can be obtained if bisphenol is replaced by other phenols having two or more hydroxyl groups.

Epoxy resins based on 2,2' dihydroxy diphenyl propane were prepared and patented by American Cyanamid Company¹. Jaeger *et al.*² used phenol formaldehyde novolacs for the preparation of epoxy resins which were further modified with drying oil fatty acids to yield epoxy esters. Epoxy resins based on condensation products of *o*-cresol and formaldehyde, and bisphenol and *n*-butaldehyde have also been reported^{3,4}. The epoxy resins based on condensation products of various monophenols with formaldehyde have been claimed to possess better hardness and resistance to solvents and alkalis than those based on bisphenol epoxy resins⁵.

The present paper describes a study of the effects of differences in the epoxide equivalents and curing agents on the film properties of epoxy resins based on phenol formaldehyde novolac resins.

Experimental

Ref. 6

Materials

Phenol: BDH, LR grade phenol was used for the preparation of novolac resins.

Formaldehyde: Formaline solution (BDH, 37.4 per cent w/v formaldehyde), LR grade was used for the preparation of novolac resins.

Bisphenol-A: Bisphenol-A obtained from Amrut Industrial Products, India, was used for the preparation of epoxy resins as control samples.

Epichlorohydrin: Danpha Chemicals, LR grade epichlorohydrin was used for the preparation of epoxy resins from both novolacs and bisphenol-A.

Melamine formaldehyde resin: Butylated melamine formaldehyde resin was obtained as a sample from Asian Paints, Bombay and used as curing agent for epoxy resin films.

Castor oil alkyd resin: Castor oil alkyd resin was prepared in the laboratory for use as curing agent for epoxy resin films. 38g castor oil and 14g glycerol were heated to 220°C for 1 hour after which 48g phthalic anhydride was added over a period of 0.5 hour whilst the temperature was maintained at 220°C. After the addition had been completed, the temperature was maintained for an additional 0.5 hour. The resin had an oil length of 40 per cent.

Preparation of novolac resins

Novolac samples of different functionalities were prepared by taking 250g batches of phenol and 250ml water in a three-necked flask. The pH was adjusted to 0.5 with sulfuric acid and the contents were heated to 80°C with constant stirring. Various calculated quantities of formaldehyde were added over a period of 3–4 hours. The temperature was maintained and stirring was continued for 0.5 hour, after which water was removed under vacuum. Five samples of novolacs with different ratios of phenol to formaldehyde were prepared which were used for the preparation of epoxy resins.

Preparation of epoxy resins

Novolac samples prepared as above were reacted with different proportions of epichlorohydrin at 102–105°C. Calculated quantities of 10 per cent sodium hydroxide solution

were added gradually to the reactants over periods ranging between 2–4 hours. Heating was further continued for 0.5 hour after which the contents were washed with hot distilled water to remove completely the salt formed. Water was then removed under vacuum at 80°C. Epoxy resins thus obtained were thinned to 50 per cent solids with a mixture of methyl ethyl ketone, butanol, and toluene in the ratio of 2:1:1.

Control samples of epoxy resins based on bisphenol-A were also prepared in similar manner.

Epoxide equivalents of each resin sample were determined by a pyridinium chloride method⁶.

Preparation of coating compositions

Coating compositions containing the above resins were prepared by addition of stoichiometric quantities of curing agents to 50 per cent resin solutions. The quantity of curing agent required for each epoxy resin sample was calculated on the basis of its epoxide equivalent. The mixtures were thinned to a brushable consistency and applied on previously prepared tin or glass panels with a brush to obtain a uniform coat. After drying in horizontal position for 0.5 hour, the panels were stoved at 135°C for 2 hours where a butylated melamine formaldehyde resin was used as curing agent, and at 145°C for 3 hours where a castor alkyd resin was used.

Testing of epoxy films

Film properties, such as gloss, hardness, flexibility, and resistance to alkali, acids and solvents were, determined by the usual procedures.

Yellowing tendency of epoxy resins was studied by preparing white paints from these resins with rutile titanium dioxide pigment. The paint was cured with butylated melamine formaldehyde resin by stoving the panels at 135°C for 2 hours. The panels were kept in diffused light for one month. The colour measurements were made with a Lovibond tintometer.

Results and discussion

The details of formulations of the epoxy resin coatings prepared for study are given in Table 1. The samples had a wide range of epoxide equivalents and, therefore, these were put in three different groups *A*, *B*, and *C* according to their epoxide equivalents, i.e., group *A* for samples of low epoxide equivalents (427–622), group *B* for samples of medium epoxide equivalents (723–827), and group *C* for samples of high epoxide equivalents (1440–2158). For the purposes of comparison, each group contained one sample prepared from bisphenol-A and other samples prepared from novolac resins. Table 2 gives the scratch hardness and flexibility of the cured films of epoxy resins. The resistance of these films to sodium hydroxide, hydrochloric acid, sulfuric acid, and nitric acid are given in Table 3, whilst their resistance to solvents, namely, acetone, toluene, *n*-hexane, and rectified spirit are shown in Table 4. The results of studies on yellowing during curing and on storage in diffused light of melamine formaldehyde cured films of epoxy resins are given in Table 5.

Scratch hardness

The films of novolac based epoxy resins possessed better scratch hardness in comparison with those of bisphenol-A

Table 1
Epoxy resin coating formulations

Sample No.	Type of phenol used for preparation of epoxy resin	Phenol/Formaldehyde ratio used for novolac preparation	Epoxy equivalent of prepared epoxy resin	Parts of melamine formaldehyde resin used for curing 100 parts of epoxy resin	Parts of castor alkyd resin used for curing 100 parts of epoxy resin
A-I	Bisphenol-A	—	427	82.0	20.6
A-II	Novolac	2:1	459	76.3	19.2
A-III	Novolac	2:1	537	65.2	16.4
A-IV	Novolac	4:3	600	58.3	14.7
A-V	Novolac	5:4	622	56.3	14.2
B-I	Bisphenol-A	—	723	49.8	12.2
B-II	Novolac	3:2	787	44.5	11.2
B-III	Novolac	1:1	827	42.3	10.6
C-I	Bisphenol-A	—	2080	17.3	4.2
C-II	Novolac	3:2	1440	24.3	6.1
C-III	Novolac	5:4	1545	22.7	5.7
C-IV	Novolac	2:1	2158	16.2	4.1

Table 2
Scratch hardness and flexibility of epoxy resin films

Sample No.	Scratch hardness (Load in kg)		Flexibility ($\frac{1}{8}$ in. mandrel)	
	Melamine formaldehyde cured film	Castor alkyd cured film	Melamine formaldehyde cured film	Castor alkyd cured film
A-I	3.5	1.5	pass	pass
A-II	3.4	2.5	pass	pass
A-III	3.6	2.9	fail	pass
A-IV	3.7	3.7	fail	pass
A-V	3.7	3.7	fail	pass
B-I	2.8	1.2	fail	pass
B-II	3.6	3.6	fail	pass
B-III	3.7	3.6	fail	pass
C-I	0.5	0.5	fail	pass
C-II	3.2	2.7	fail	pass
C-III	3.0	2.4	fail	pass
C-IV	1.8	0.7	fail	pass

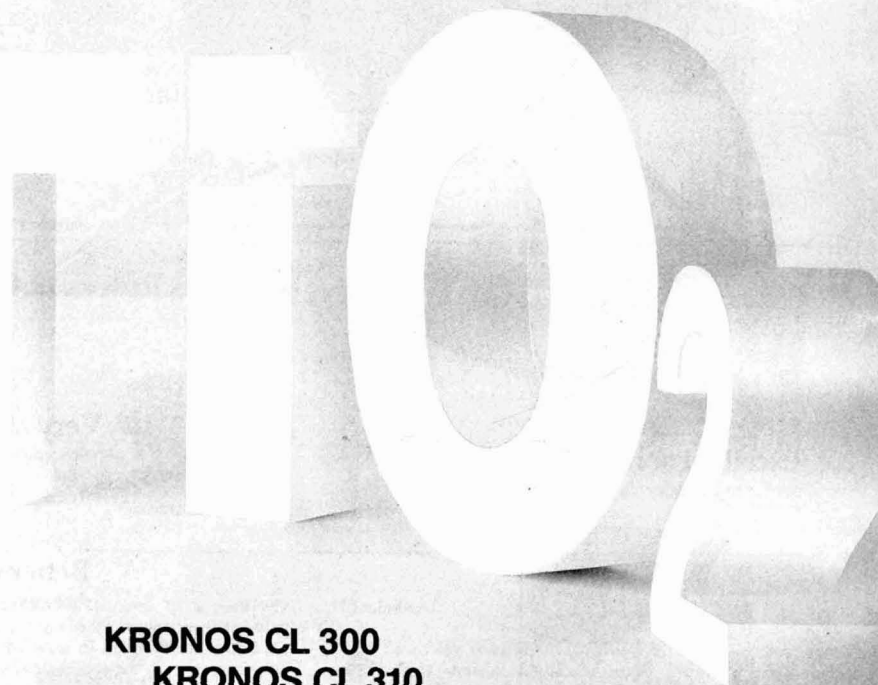
Table 3
Alkali and acid resistance of epoxy resin films* at ambient temperature (30°C)

Sample No.	50% Sodium hydroxide solution (15 days)		37% Hydrochloric acid solution (15 days)		50% Sulfuric acid solution (30 days)		20% Nitric acid solution (7 days)	
	Melamine formaldehyde cured film	Castor alkyd cured film	Melamine formaldehyde cured film	Castor alkyd cured film	Melamine formaldehyde cured film (a)	Castor alkyd cured film	Melamine formaldehyde cured film	Castor alkyd cured film
A-I	5	5	1	4	2	4	2	3
A-II	5	5	0	4	2	4	2	4
A-III	5	5	1	4	2	4	1	4
A-IV	5	5	1	4	3	4	1	4
A-V	5	5	1	4	3	4	1	4
B-I	5	5	2	4	3	5	2	3
B-II	5	5	1	4	2	4	2	4
B-III	5	5	1	4	3	5	2	4
C-I	2	3	4	4	4	4	2	3
C-II	2	2	4	4	5	5	2	4
C-III	2	2	4	4	5	5	1	4
C-IV	2	2	3	4	5	5	1	2

*5 indicates that the film is not at all affected; 4 indicates slight change in colour and loss in gloss; 3 indicates change in the colour of the film or slight wrinkling; 2 indicates wrinkling or blistering of film; 1 indicates flaking or removal of film at some places; and 0 indicates complete removal of film.

(a) panels were kept in solution for 10 days.

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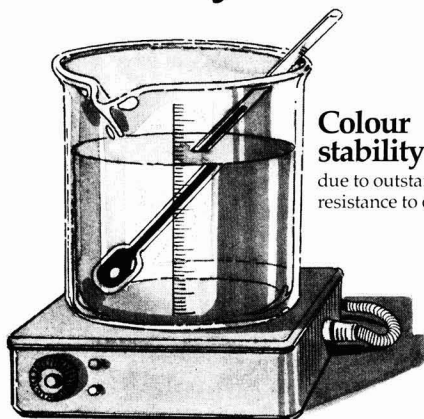


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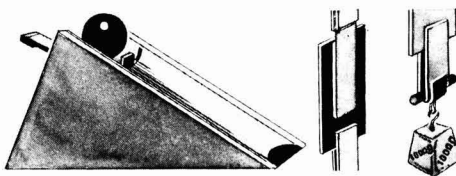
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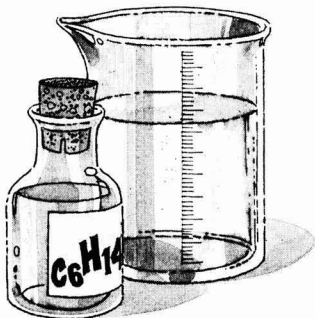
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Table 4
Resistance of epoxy resin films* to solvents at ambient temperature (30°C)

Sample No.	Acetone (15 days)		Toulene (30 days)		n-Hexane (30 days)		Rectified spirit (30 days)	
	Melamine formaldehyde cured film	Castor alkyd cured film	Melamine formaldehyde cured film	Castor alkyd cured film	Melamine formaldehyde cured film	Castor alkyd cured film	Melamine formaldehyde cured film	Castor alkyd cured film
A-I	5	0	5	0	5	2	5	0
A-II	5	2	5	5	5	5	5	5
A-III	5	2	5	5	5	5	5	5
A-IV	5	2	5	5	5	5	5	5
A-V	5	2	5	5	5	5	5	5
B-I	5	0	5	0	5	2	5	0
B-II	5	2	5	2	5	5	5	5
B-III	5	2	5	2	5	5	5	5
C-I	5	0	5	0	5	0	5	0
C-II	5	2	5	2	5	5	5	5
C-III	5	5	5	2	5	5	5	5
C-IV	5	5	5	2	5	5	5	0

*5 indicates that the film is not at all affected; 4 indicates slight haziness and loss of gloss; 3 indicates slight swelling of the film; 2 indicates softness in the film; 1 indicates removal of film at some places; and 0 indicates complete removal of the film from panel

Table 5
Yellowing tendency of melamine formaldehyde cured epoxy resin films (Pigment binder ratio of white paint as 0.4:1)

Sample No.	Colour of panels after application Y+R+B	Colour of panels after curing Y+R+B	Colour of panels after one month in in diffused light Y+R+B
A-I	2.1+0.9+2.2	3.0+1.0+2.1	3.1+1.1+2.0
A-II	2.0+1.0+2.2	3.0+1.1+2.0	3.1+1.2+1.5
A-III	2.0+1.0+2.0	3.0+1.1+2.0	3.1+1.2+1.4
A-IV	2.0+1.0+2.0	3.0+1.1+2.0	3.1+1.2+1.4
B-I	2.2+1.1+2.2	3.4+1.2+2.1	4.2+1.1+2.0
B-II	2.8+1.3+2.6	4.0+1.4+2.5	5.3+1.7+1.5
B-III	3.4+1.4+2.6	5.0+1.6+2.4	7.0+2.1+2.2
C-I	2.3+1.0+2.4	4.8+1.3+2.1	5.2+1.7+2.1
C-II	4.0+1.6+2.7	8.0+2.3+2.4	10.0+3.0+2.4
C-III	5.0+1.7+3.0	11.0+2.5+2.8	14.0+3.3+2.8

based epoxy resins. This can be attributed to a relatively larger proportion of aromatic rings in the molecule of novolac based epoxy resins. A comparison of epoxy films based on novolacs prepared with different P/F ratios further supports this view. Novolacs prepared with higher P/F ratio, which would have a comparatively lower degree of polymerisation (thus having fewer aromatic rings per polymer molecule) gave epoxy films of comparatively lower scratch hardness than the novolacs prepared with lower P/F ratio. Although large differences were not observed in case of melamine formaldehyde cured films, there were quite significant differences in the case of films cured with the castor alkyd resins.

Of the two curing agents employed, the melamine formaldehyde cured films showed better scratch hardness than the castor alkyd cured films in case of bisphenol based epoxies. However, this difference was not observed in case of epoxy films based on novolacs. The scratch hardness of bisphenol based epoxy resin films decreased as the epoxide equivalent of the resins increased. This can be attributed to a higher proportion of curing agents employed for low epoxide equivalent samples (to react with higher proportion of epoxide groups present per unit weight of low epoxide equivalent resins) which would thus contribute towards the hardness of the films.

Flexibility

The flexibility over a 0.125" mandrel of the cured epoxy resin films depended mainly upon the nature of curing agent employed. Except for the films of resins I and II of group A having epoxide equivalents 427 and 459, respectively, all the films cured with melamine formaldehyde resin failed the flexibility test. On the other hand, all films cured with castor alkyd resin passed the flexibility test. The reasons why the melamine cured films of resins I and II of group A passed the flexibility test, whilst the others failed may be attributed to the low molecular weights of the former resins.

Alkali resistance

Films cured with melamine formaldehyde and castor alkyd except those of group C, having high epoxide equivalents, showed excellent resistance to 50 per cent sodium hydroxide solution for 15 days at ambient temperature. What is significant here is that alkali did not affect the alkyd cured films of groups A and B although alkyds are known for their poor alkali resistance. The poor resistance of the epoxy films of group C can be explained by a comparatively larger number of hydroxyl groups present in longer chain epoxy resins of this group.

Acid resistance

Films cured with the castor alkyd showed good resistance to 37 per cent hydrochloric acid at ambient temperature for 15 days. However, all films developed a slight pink colour which was more pronounced in the case of novolac based epoxy films. The melamine formaldehyde cured films were adversely affected by hydrochloric acid, except for resins of group C, having high epoxide equivalents, where there was development of a pink colour with some wrinkling in the case of sample C-IV. Since the acid resistance of melamine formaldehyde cured films was generally poor, there seems to be a possibility of the acid reacting with the residual amino groups of the melamine resin, particularly where larger proportions of this resin were used for curing as in case of resins of group A and B.

More or less similar behaviour had been observed with regard to resistance to 50 per cent sulfuric acid where the alkyd cured films showed good resistance, except for slight loss in gloss for the films of low epoxide equivalent resins. The melamine cured epoxy films showed poor resistance to sulfuric acid except for films of group C resins, having high epoxide equivalents, where only slight loss in gloss was observed in sample C-I, during 10 days exposure.

Castor alkyd cured epoxy films showed fairly good resistance to 20 per cent nitric acid for 7 days at ambient temperature. Alkyd cured bisphenol based epoxy films, however, showed some wrinkling in all cases. Among the novolac based alkyd cured films there was only the one isolated case of sample C-IV where some blisters were observed, whilst the remainder of the samples showed good resistance to nitric acid with some loss in gloss. Films cured with melamine formaldehyde resin showed poor resistance to nitric acid with most of the films forming blisters and flaking after 7 days.

Solvent resistance

Melamine formaldehyde cured films of epoxy resins showed excellent resistance to acetone, toluene, n-hexane, and

rectified spirit. Control samples of bisphenol based epoxy resins cured with castor alkyd showed poor resistance to all the above solvents. Castor alkyd cured films of novolac based epoxy resins showed good resistance to n-hexane and rectified spirit, except for sample C-IV whose resistance to rectified spirit was poor. The toluene resistance of castor alkyd cured films of novolac based epoxy resins of group A was good, whilst those of resins of groups B and C were poor and exhibited softening of films. Castor alkyd cured films showed poor resistance to acetone except in case of novolac based high epoxide equivalent epoxy films (samples C-III and C-IV) which remained unaffected in acetone.

Yellowing characteristics

A study of yellowing characteristics of epoxy films showed that the films of low epoxide equivalent resins showed no significant yellowing after curing, as well as during storage in diffused light for one month. However, the higher epoxide equivalent samples showed an increased tendency to yellowing after curing, as well as during storage in diffused light. The tendency for yellowing during heat curing was more significant. Bisphenol-A based epoxy resin films showed lesser tendency to yellowing than those based on novolacs.

[Received 29 January 1979]

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The efflorescence resistance of certain emulsion coatings

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Summary

A range of proprietary emulsion paints has been assessed for their resistance to efflorescence. The coatings were applied to gypsum plaster panels that had been impregnated with sodium sulfate and then exposed to a source of water.

Of the ten coatings tested, the majority performed poorly, confirming previously reported results. Examples of tolerant emulsion

paints were found however, although the one coating type that was completely resistant to efflorescence was not primarily designed for plaster substrates.

Necessary performance criteria for resistant emulsion paints appear to be a low water vapour permeability and low permeability to efflorescence salts in solution.

Keywords

Types and classes of coatings and allied products

emulsion paint
architectural finish
masonry paint
house paint

Types and classes of structures and surfaces to be coated

gypsum plaster

Properties, characteristics and conditions primarily associated with structures or surfaces to be coated

efflorescence

dried or cured films

permeability
vapour transmission

La résistance à l'efflorescence de certaines peintures-émulsions

Résumé

On a apprécié une gamme de peintures-émulsions de marque à l'égard de leur résistance à l'efflorescence. Les peintures ont été appliquées à des plaques de plâtre de gypse, qui avaient été préalablement imprégnées de sulfate de sodium, et qui ont été exposées à une source d'eau après l'application de la peinture. La plupart des dix peintures qui faisaient l'objet de cette étude se comportaient mal, ce qui confirme les résultats déjà communiqués. Toutefois, on a trouvé certains exemples de peintures-émulsions

plus stables, bien que le seul type de peinture qui fût complètement résistante à l'efflorescence ne fût par conçu en premier lieu pour les supports en plâtre.

Les caractéristiques des peintures-émulsions résistantes, qui sont nécessaires pour assurer un bon rendement, semblent être la faible perméabilité à la vapeur d'eau, et aux solutions des sels efflorescents.

Die Ausblühungsbeständigkeit gewisser Dispersionsfarben

Zusammenfassung

Eine Anzahl von Dispersionsfarben des Handels wurden auf ihre Widerstandsfähigkeit gegen Ausblühen geprüft. Die Farben wurden auf Tafeln aus Gipsputz aufgetragen, die mit Natriumsulfat imprägniert und alsdann einer Wasserquelle ausgesetzt worden waren.

Die Mehrzahl der geprüften zehn Anstriche verhielt sich schlecht in Übereinstimmung mit früher berichteten Ergebnissen. Beispiele

toleranter Dispersionsfarben wurden jedoch gefunden, obwohl der eine völlig gegen Ausblühen beständige Anstrichtyp nicht in erster Linie für Putzsubstrate bestimmt war.

Notwendige Leistungsmaßstäbe für Widerstandsfähigkeit von Dispersionsfarben gegen Ausblühen scheinen niedrige Wasserdampfdurchlässigkeit, sowie niedrige Durchlässigkeit für Salzlösungen zu sein.

Introduction

Refs. 1, 2

Efflorescence damage to applied paint coatings is associated with the presence of water-soluble inorganic salts within the substrate. In gypsum plasters the salt is essentially sodium sulfate and arises either as an impurity from the plaster itself or as a result of migration from concrete or brickwork backings. The movement of these salts during the drying out of the plaster can cause severe disruption of the coatings applied and this problem is a common cause of premature paint failure in new buildings.

A previous paper¹ described an accelerated test for efflorescence resistance of a wide range of coatings on damp plaster panels impregnated with sodium sulfate. Examples of coatings resistant to efflorescence were identified although they were

mostly based on solvent-soluble types of binder. The resistance to efflorescence was found to be dependent upon the use of a coating having a low water vapour permeability and on the formation of a uniform surface film. Failure to meet these requirements, either as a result of over-pigmentation, or excessive thinning which would result in excessive penetration, was found to reduce the coating's efflorescence resistance. The results indicated that paints based on emulsion binders, generally, provided low resistance to efflorescence as was found also in Lindberg's studies on the salt transmission through coatings applied to concrete².

In view of the commercial importance of emulsion paints on plaster substrates, further work has been undertaken on a range of commercial systems to provide a more comprehensive assessment of the resistance of these coating types to efflorescence. This investigation has involved the study of ten commercial emulsion paints, covering a wide range of

formulations. The accelerated efflorescence resistance and water vapour permeability techniques used previously¹ were adopted and the results are reported here, together with studies on the sodium ion transmission characteristics of the films.

Experimental

Paints evaluated

Refs. 1, 3

A number of commercial emulsion paints were selected to cover a range of pigment volume concentrations and polymer types (see Table 1). All paints except systems 1, 2 and 8 were white. Systems 1 and 2 were pale blue and pale green respectively, each on a white pigment and extender base. System 8 was a green colour based on a yellow iron oxide. Organic pigments were used as tinters in these three formulations.

Table 1
Paints evaluated

System No	Paint type	Formulation		
		% PVC*	P:B ratio†	Solids % wt
1	PVAc-copolymer emulsion, flat finish	40	2.4:1.0	55
2	PVAc-copolymer emulsion, flat finish	35	2.0:1.0	50
3	PVAc-copolymer emulsion, flat finish	35	1.8:1.0	55
4	PVAc-copolymer emulsion, semi-gloss finish	20	1.0:1.0	45
5	Acrylic emulsion, semi-gloss finish	20	0.6:1.0	51
6	PVAc-copolymer emulsion, flat finish	40	2.4:1.0	50
7	PVAc-copolymer emulsion, flat finish	45	2.7:1.0	55
8	PVAc-copolymer emulsion, flat finish	35	1.8:1.0	55
9	Acrylic emulsion, eggshell finish	20	1.0:1.0	60
10	Styrene butadiene emulsion, eggshell finish	25	1.2:1.0	65

*Percentage pigment volume concentration (approximate)

†P:B ratio = pigment:binder ratio

Examples of semi-gloss and flat emulsion finishes designed for plaster substrates were included in the systems studied (systems 1–4 and 6–8). Three of the systems were not intended as finishes for plaster but were included in order to extend the range of types under study. System 9 was intended as a primer for plywood and system 10 was a thick-film emulsion coating for a variety of exterior building substrates. The latter system was characterised by having poor flow properties which necessitated "laying-off" of the successive coats at right angles. System 5 was designed as a semi-gloss finish for exterior timber.

Paints of very high pigment volume concentration, through which it is claimed soluble salts are able to pass without causing film disruption, were specifically excluded from this study since previous work has demonstrated that this supposition is not tenable^{1,3}.

Efflorescence testing

Ref. 1

The technique employed has been described previously¹. This involved casting a retarded hemi-hydrate gypsum plaster

panel 200 x 130 x 13 mm and then saturating it in a 2.5 per cent solution of sodium sulfate. After approximately 20 hours' conditioning in an atmosphere of 90 per cent relative humidity (after which time the surface of the panel was damp), two coats were brush-applied, in accordance with the manufacturers' instructions, to one test face of triplicate panels. After painting, the panels were stored at 20°C and 65 per cent relative humidity for 5 days prior to testing.

Testing for efflorescence resistance was performed by immersing the backs of the panels in deionised water for 5 days, then removing the panels and leaving them to dry for 3 days. The test faces were then assessed for salt eruption through the film and for blistering, these being the only types of failure modes observed in this series of tests. A rating system of 0–2, in increments of 0.5, was used to assess performance: with this system 0 represented no failure and 2 severe failure.

Permeability testing

Ref. 1

The water vapour permeability of the emulsion coatings on the plaster substrate was determined using a cup technique as reported previously¹. The permeability testing employed plaster panels, 90 mm in diameter and 8 mm in thickness, prepared and painted by a similar procedure to that described above. The permeability of the paints was measured using the cup technique with the plaster panels mounted, painted face uppermost, in aluminium dishes. A small quantity of water was placed in the cup before sealing the plaster panels in position with a soft wax. After sealing, the cups were placed in a desiccator containing phosphorus pentoxide and weighed periodically. The surface area of the test panels after sealing was 50 cm², and all tests were performed in triplicate.

Sodium ion transmission

Ref. 4

The sodium ion transmission of each system was determined using a specific ion electrode assembly in a partition cell (see Figure 1), similar to that described by Murray⁴. Paint films were brush applied in two coats to polyethylene sheets which were mounted on a rigid base and allowed to dry overnight. Application was controlled to give film weights similar to those deposited on the plaster test panels. Samples of film, 40 x 110 mm, were then peeled from the polyethylene and mounted between the gaskets of the test cell using a soft wax: this gave a test area of 25 x 75 mm.

A sodium ion gradient of 100 mg Na⁺/litre to 1 mg Na⁺/litre was established across the film using sodium sulfate solutions of different concentrations, and the ion transmission was monitored in the dilute compartment using a sodium ion electrode—saturated calomel reference electrode assembly. Osmotic effects were found not to be significant, as it was observed that there was no alteration in the solution levels in either compartment of the cell during the test.

Readings were taken periodically using a high impedance millivoltmeter. The sodium ion transmission, expressed as mg Na⁺/litre of water, was obtained from calibration curves prepared from solutions of known ionic strength.

Prior to each reading the solution was stirred for 5 minutes, and all testing was performed at 20°C.

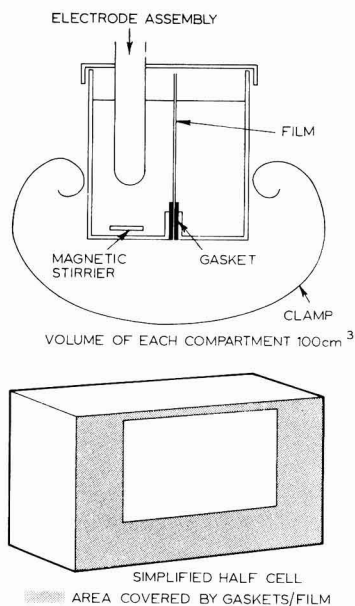


Fig. 1. Partition cell for sodium ion transmission

Results

Efflorescence resistance

The results of the efflorescence testing are shown in Table 2. The majority of the emulsion paints studied exhibited poor resistance to efflorescence. System 10 showed no salt eruption after testing and systems 8 and 9, which both received a 0.5 rating, had only very small isolated areas of failure. Close inspection of these areas indicated that failure occurred from small "point-source" defects in the film.

Table 2
Test results

System No.	Efflorescence resistance		Permeability		
	Salt eruption	Blister resistance	Sodium ion mg Na ⁺ dm ⁻²	Water vapour gm ⁻² (24 h) ⁻¹	C of V* %
1	2	1	38	178	20.0
2	2	0	32	196	15.3
3	1.5	0	22	148	5.5
4	1	2	26	109	13.5
5	1	0.5	3.5	112	5.0
6	0.5	2	20	206	3.5
7	0.5	2	19	140	9.0
8	0.5	1	6.5	146	18.0
9	0.5	0	1.9	91	5.0
10	0	0.5	1.5	12	19.5

* = coefficient of variation

Several systems exhibited a degree of film blistering during testing which, with the exception of system 10, was retained when the panels were dried out after testing. The blisters apparent on system 10 disappeared on drying after testing with no apparent reduction in adhesion.

Water vapour permeability

The water vapour permeabilities of the films are shown in Table 2 together with the coefficient of variation of the results. The water vapour transmission rate is expressed in grammes per square metre of film per 24 hours. As shown in Table 2, most of the systems possessed a permeability in excess of 100 g.m⁻² (24 h)⁻¹ and one, system 9, was 91 g.m⁻² (24 h)⁻¹; system 10 was exceptional in having a very low permeability of 12 g.m⁻² (24 h)⁻¹.

Sodium ion transmission

The sodium ion transmission results are tabulated in Table 2, expressed as mg Na⁺ ion per litre of water transmitted after 24 hours. A sodium ion transmission curve is shown in Figure 2 and this curve is typical for all systems tested, that is with a nearly constant value being obtained in about 24 hours. With systems 9 and 10 however, which had the lowest values, the pattern of performance shown in Figure 2 was not as marked as with the other panels.

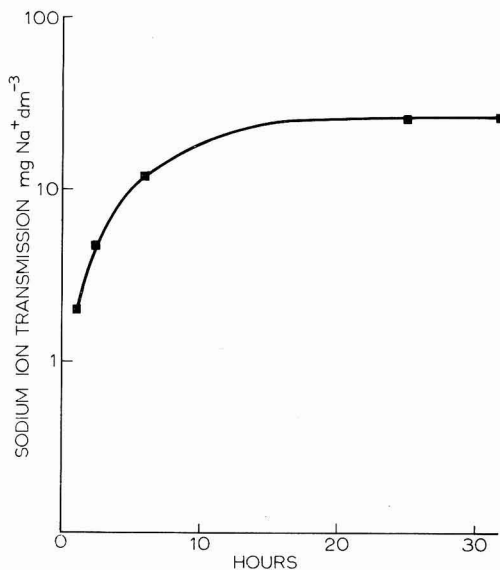


Fig. 2. Sodium ion transmission—System 4

Two trends are apparent: systems 1-4, 6 and 7, all had fairly high sodium ion transmission rates, with systems 1 and 2 attaining the highest values; systems 9 and 10 had similar, very low transmission rates, whilst systems 5 and 8 had values somewhat higher than these.

Discussion

Refs. 1,5,6

The results of the tests show that the majority of the systems evaluated had poor efflorescence resistance; only one, system 10, was found to be completely resistant and it is noteworthy that this particular coating had exceptionally low water vapour and sodium ion permeability. No other systems had this combination of properties, although systems 8 and 9, which had low salt transmission characteristics

but high water vapour permeabilities, did exhibit only a slight failure during efflorescence testing. This tends to suggest that a combination of properties involving low water and salt permeability is required in resistant emulsion coatings.

All of the emulsion systems studied here would be expected to be formulated somewhere below their critical pigment volume concentration, and they demonstrate a general trend of increased water vapour transmission with increasing pigment volume concentration. The water vapour transmission rate of system 10 is anomalous, and the measured value falls in the range identified in previous work on solvent-soluble systems as being necessary for good efflorescence resistance¹.

It is well established that measurements of a film's salt diffusion characteristics can be related to subsequent coating performance in situations such as metallic corrosion⁵, and the resistance of films to lime bloom from cementitious substrates⁶. In these situations, coatings with low salt transmission characteristics were more resistant than those of higher permeability.

In this work, the influence of sodium ion penetration is less clear. Systems 8, 9 and 10 which were found to have good efflorescence resistance, did have low sodium ion transmissions, and systems 1 and 2 which had high transmission rates, had poor efflorescence resistance. In the middle of the range the relationship is ill-defined and it is possible that this is due to the ancillary requirement for low water permeability, although it is acknowledged that other factors, for example, the permeability of anions, may also be contributory.

In this study it is considered that the tendency of the coatings to blister was related to the adhesion and swelling

characteristics under the wet conditions prevailing during testing and, as found previously¹, there was no well-defined relationship between salt eruption and blistering.

This work has, therefore, served to confirm the difficulties in formulating efflorescence-resistant emulsion paints for plaster, since only one completely resistant product was found. It has not, so far, been possible to establish the reason for the low water and sodium ion transmission of this system, and it is recognised that conclusive proof of the influence of these properties on efflorescence resistance can be achieved only by studying model formulations. It is intended that this will constitute the next phase of the work.

Conclusion

The formulation of emulsion coatings which are resistant to efflorescence damage on gypsum plaster has been shown to be possible; the important characteristics of the films appear to be a low permeability both to water vapour and to sodium ions. The formulation requirements necessary to obtain this combination of properties must, however, be balanced against other considerations, in particular, low blistering tendencies.

[Received 29 January 1979]

References

1. Boxall, J., *J.O.C.C.A.*, 1978, **61**, 345.
2. Lindberg, B., *J.O.C.C.A.*, 1974, **57**, 100.
3. Private communications. Mr G. V. Hill, *Paint Research Association*, Teddington, Middlesex.
4. Murray, J. D., *J.O.C.C.A.*, 1973, **56**, 210.
5. Kittleburger, W. W. and Elm, A. C., *Ind. Eng. Chem.*, 1972, **44**, 326.
6. New York Soc. Paint Tech., Technical Sub-committee No 64, *J. Paint Tech.*, 1969, **41**, 615.

Next month's issue

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

Factors which affect the efficiency of sand grinding by *W. Carr and A. Kelly*

Insulating surface coatings based on castor oil by *B. M. Badran, I. M. El-Anwar, M. S. Ibrahim and W. M. Khalifa*

Some effects of interrupted autoxidation (*Short Communication*) by *S. M. Argandeh and T. W. J. Apperley*

Reviews

UV Curing: Science and Technology

Dr S. Peter Pappas (Ed)

Technology Marketing Corporation, Stamford, Conn., USA, 1978

Pp 263. Price US \$65-00

UV curing of surface coatings and printing inks is a rapidly developing technology which utilises, in part, concepts derived from the closely related area of photoresist printing plate manufacture. Many problems remain to be solved and this book is both timely and useful. Scientific and technological problems are fully discussed and contributors to the book have obvious industrial experience in the appropriate areas.

The following list of Chapter Titles indicates the subject matter covered: Photoinitiation of Free Radical Polymerisation, Photoinitiated Cationic Polymerisation, Effects of Pigmentation in UV Curing, Light Sources, Calorimetric Analysis of UV Curable Systems, Resin Design, UV Curing of Coatings, UV Curing of Printing Inks, Photoresists: Photoformation of Relief Images in Polymeric Films.

A short list of suppliers of raw materials and equipment for UV curing is given as an appendix and the general level of presentation is excellent.

This book will be a highly convenient reference for all those working in the general area of UV curing and an invaluable guide to those entering the field for the first time. Furthermore, because of its timeliness, it is to be recommended to those with interests in photochemistry outside of the general areas of surface coatings.

A. Ledwith

Pigment + Füllstoff Tabellen

By Olaf Lückert

O. Lückert, D-3014 Laatzen, 1978

Pp 288, DIN A5, English translation booklet 8pp

Price DM54 plus postage

This volume tabulates nearly 3,000 pigments and extenders classified in accordance with the German RAL-colour system. There are 6 main chapters. The first one is headed colour pigments and comprises not only white pigments, but also all other inorganic and organic coloured pigments and dyestuffs. Chapter 2, entitled "functional pigments" covers, amongst other things, anticorrosive and flame retardant pigments as well as molecular sieves. Metallic pigments such as zinc dust and stainless steel powders are dealt with in chapter 3, but aluminium and bronzes are classified separately as "effect pigments" in chapter 4. Chapter 5 lists over 500 extenders and fillers. A few special purpose

fillers are described in chapter 6.

Each chapter is divided into a number of sub-sections and a brief general description of every group of pigments precedes the tables. Every entry in the tables is given a running number, and across two pages relevant data are given, such as trade name, manufacturer, composition, lightfastness, oil absorption, chemical resistance, fields of application and a remarks column. In appropriate cases, particle size, solubility in various solvents and the form in which the products is available are given. To convey some idea of the range of products covered it is sufficient to mention that 67 grades of rutile titanium dioxide and 11 grades of anatase are listed.

For the benefit of the English speaking reader, an 8 page booklet is now supplied which gives a translation of the column headings and provides adequate explanations of all symbols and abbreviations. The use of the tables need not, therefore, be confined to the German reader. On the other hand, the reviewer noted gaps in the ranks of products, as some pigments and extenders in use in the UK are not included.

H. R. Hamburg

Section Proceedings

Hull

Training

The fourth Ordinary Meeting of the Hull Section was held on Monday 8 January, at the "George Hotel", Land of Green Ginger, when Mr T. A. Fillingham, a retired member of the Section, gave a talk on "Training".

Alan Fillingham was a founder member of the Hull Section and its first Honorary Secretary when the Section was formed in 1943. He began his talk by recounting the activities of the Section in those early days, remembering the parts played by the first Chairman, G. F. Holcroft, along with Price Jones and Syd Read as Vice-Chairman and Treasurer respectively. Unfortunately, the original records were destroyed in a fire.

Training, at the Marfleet Refining Co Ltd, had been Alan's preoccupation in the years before his retirement. He outlined

in general terms the development of training through the decades up to the Industrial Training Act of 1964. Most training up to that time and since, has been of the form of "sitting alongside Nellie", gaining experience from a well informed operator. The Act enabled the Minister to establish Training Boards and the fixing of levies on companies whose only course was to operate their own training schemes in order to claim the grant. There was no legal obligation on firms. The vast majority responded by training rather than paying the levy.

Training can be a nuisance, taking skilled operators away from their main work tasks. However, there is a need to identify the basic training needs and to supply the necessary supervision, not only for the induction training, but for the further development needs of the company.

Examples of training methods were outlined, leading to a lively exchange of questions and answers from the 16 members and guests who were present. Mr N. Lythgoe proposed the vote of thanks.

Milling and dispersing equipment

At the fifth Ordinary Meeting on Monday 5 February, Mr R. Hildyard of Herbert Smith & Co Ltd, gave a lecture on "Developments in milling and dispersion equipment". At the time of arranging the programme earlier in the year, it was stated that a new development might be available for publication at the lecture. However, the development had not made the progress that was expected.

Mr Hildyard outlined the development of milling equipment from the earliest stone mills to present day high shear mixers. Examples of the earliest mills were conical mills and edge runners, followed by ball mills and pebble mills; the latter charged with round flint stones from the French and English Channel beaches. Developments from ball mills were attritors, sand and bead mills, as well as the Vibro energy mills of the Podmore and Sweco types.

In high shear mixers, the design of the mixing head was the important feature and the lecturer showed diagrams of the various designs used by different manufacturers.

As to the future, Mr Hildyard proposed ultrasonics as being a method of transmitting the energy effectively into the dispersion system.

The Hull Chairman, Mr R. Brooks, gave the vote of thanks, complimenting the lecturer on the many cartoons he had produced to illustrate his talk. Twenty members and guests attended.

F.D.R.

London

Novel ink systems

The fourth technical meeting of the 1978/79 session took place at the Rubens Hotel on 21 February 1979 at 7.00 p.m. Mr P. Richardson of Fishburn Printing Ink Co Ltd presented a paper on "Novel ink systems".

Before discussing what were claimed as being ways of accelerating the drying of printing inks, Mr Richardson reviewed the conventional methods by which inks dried. In describing methods such as absorption (newspaper inks), precipitation (glycol based inks), evaporation (gravure/flexo inks), oxidation and polymerisation, Mr Richardson considered the disadvantages as well as the advantages of these drying systems.

For instance, precipitation dried inks exhibited low gloss, and gravure and flexo inks required heat to obtain dry films at the very fast printing speeds used.

Ways in which inks could be modified for use in existing drying methods were described. Lower temperature drying gravure inks could be achieved by either increasing the solids so that less heat was required to remove less solvent, or by using fast solvent release resins, with a blend of true and latent solvents. The volatility and retention of solvents chosen were such that the latent solvent was the slowest solvent, allowing for rapid release from the film. Press and in-can stability needed to be carefully monitored but the advantages of lower web temperature included, as well as lower energy use, better substrate performance and less atmospheric pollution.

Mr Richardson then went on to describe the alternative techniques available, such as ultraviolet, infrared, electron beam, radio frequency and microwave drying and water borne coatings.

No one alternative looked likely completely to supersede existing systems, although infrared cured inks, using conventional, relatively cheap raw materials compared with those required for electron beam and ultraviolet curing, were considered to be of widest application and acceptability. It was inevitable that all types of alternative to conventional solvent borne inks would be used in the future.

Following an extensive question time, the Chairman for the evening, Mr T. Banfield, called for a vote of thanks from Mr J. A. Hawkey to which the audience of 40 members and guests warmly responded.

A.J.N.

Manchester

Powder versus water based paint

Speaking to an audience of 50 members and visitors present at the Manchester Literary and Philosophical Society on Wednesday 21 February 1979, Mr K. H. Dodd of Carrs Paints Ltd presented his paper to the Student Section, as a final contribution to previous papers presented in the present session on the subject of water borne coating.

Keith Dodd transgressed from conventional "wet" coatings five years ago and is now Product Manager—Powder Coatings. Totally committed to his subject, he initially admitted his complete bias and prejudice in favour of powder coatings and then proceeded to argue their case.

Commencing with a short film depicting a robot operated powder coating application plant at Fiat, Italy, the poor performance of high solids coatings in the USA automobile industry was then allied to the lecturer's claim that so called water borne coatings often contained up to 40 per cent organic solvent.

It was claimed that a product range for powder coating enabled coating thickness to be varied between 0.5 and 25 mils, and types of coatings available included textured, hammer, foam powder, electrical, can and coatings applied to pipes measuring 40" long and 5" diameter in 30 minutes.

The lecturer claimed that the title of his paper showed an equilibrium in relation to dip/low volume applications and he elaborated further with reference to electrophoretic paints. An advantage claimed for powder coating is relatively low energy consumption involved in their application.

The various types and quantities of powder used in Europe were fully discussed; a 7,000 tonne total was divided into 70 per cent epoxy, 20 per cent polyester, the remainder being silicone polyesters, acrylics etc.

The end-use application of powder coatings is increasing and includes domestic/electrical appliances, motor industry, chemical environments etc.

The final topics discussed included sublimation inks, vapour transfer chambers, micro powders and cryogenic grinding, spray drying etc.

A lively question period followed and the vote of thanks was given by Mr G. T. Flood.

F.B.W.



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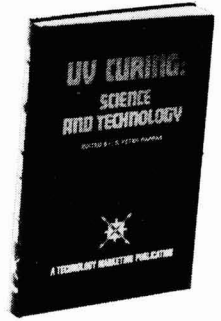
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UV CURING: SCIENCE AND TECHNOLOGY

Just off the press



PUBLICATION CODE

UVCS&T

Editor: DR. S. PETER PAPPAS

Technology Marketing Corporation, the original and leading publishers of radiation curing and processing technology news proudly announces a *NEW SCIENTIFIC BOOK*: "UV Curing: Science and Technology."

This authoritative and highly regarded scientific book has just come off the press and is ready for delivery. Co-authored by leading scientists and professionals from both industry and academic ranks, the book describes the basic principles of the science and technology of uv curing. The integration of scientific and technological aspects of these areas enhances the usefulness of this book to a diverse readership, spanning the gamut from research scientists to sales personnel.

The unique balance between theoretical and practical presentations, makes this book a vital part of any research and development organization currently involved (or desiring to get involved) in the rapidly growing technology of uv curing. Contents of this book are not found in any other publication.

ABOUT THE EDITOR

Dr. S. Peter Pappas, Professor of Chemistry at North Dakota State University, received his B.A. degree from Dartmouth College in 1958 and his Ph.D. degree in Chemistry from the University of Wisconsin in 1962.

Dr. Pappas has authored (or co-authored) over 30 journal articles on synthesis, reaction mechanisms, photochemistry, and coatings technology, including a recent review paper on photochemical aspects of ultraviolet curing. His papers on the photochemistry of pigments as related to chalking and uv curing, received first prize in the Roon Award Competition, sponsored by the Federation of Societies of Coatings Technology in 1974, 1975 and 1976.

ABOUT CO-AUTHORS

In preparation of "Ultraviolet Curing: Science and Technology" Dr. Pappas has been assisted by several internationally recognized authorities from major industrial firms. The editor and each co-author have contributed at least one chapter, in their respective field of specialty, to "UV Curing: Science and Technology." Co-authors and their affiliations are listed below.

**Robert W. Bassemir, Sun Chemical Corporation
Graphic Arts Laboratories**

**Anthony J. Bean, Sun Chemical Corporation
Graphic Arts Laboratories**

**Dr. James V. Crivello, General Electric Company
Research and Development Center**

Dr. Eugene D. Feit, Bell Laboratories

Dr. Gerald W. Gruber, PPG Industries

Research and Development Center

Dr. Vincent D. McGinniss, Battelle Columbus Laboratories

Dr. James E. Moore, General Electric Company

Research and Development Center

Dr. S. Peter Pappas, Polymers and Coatings Department

North Dakota State University

Dr. Zeno W. Wicks, Jr., Polymers and Coatings Department

North Dakota State University

TABLE OF CONTENTS

The following represents the table of contents:

1. PHOTINIATION OF RADICAL POLYMERIZATION
2. PHOTOINITIATED CATIONIC POLYMERIZATION
3. EFFECTS OF PIGMENTATION ON UV CURING
4. LIGHT SOURCES
5. CALORIMETRIC ANALYSIS OF UV CURABLE SYSTEMS
6. RESIN DESIGN
7. UV CURING OF COATINGS
8. UV CURING OF PRINTING INKS
9. PHOTORESISTS: PHOTOFORMATION OF RELIEF IMAGES IN POLYMERIC FILMS
10. SELECTED LIST OF SUPPLIERS OF RAW MATERIALS AND EQUIPMENT FOR UV CURING
11. SOME RELATED PUBLICATIONS

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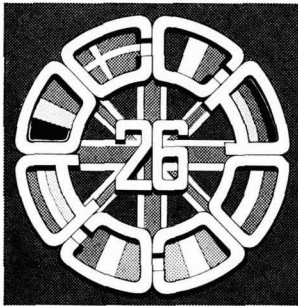
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"The OCCA"

The annual technical exhibition of the Oil and Colour Chemists' Association (known to many simply as "The OCCA") has become the world's most important event for all those connected with the paint, printing ink, polymer, adhesive, colour and allied manufacturing industries. The OCCA exhibition is held every year in London, England. The symbols for the 1974-79 exhibitions were specially designed by Robert Hamblin, Director and Secretary of the Association, to emphasise the very wide coverage which all the Association's activities attract:



The motif for OCCA-26 used the flags of the enlarged EEC converging on the British flag to symbolise the welcome extended to visitors from overseas to the Exhibitions for more than 25 years. (1974)

The INTERNATIONAL Focal Point for the Surface Coating Industries



The motif for OCCA-31 emphasises the unique aspect of the OCCA Exhibitions, which annually provide an international focal point for the surface coatings industries.



The 1975 theme continued at OCCA-27 by showing the world-wide interest aroused by the Association's annual Exhibitions in London which attract visitors from all parts of the globe.

The OCCA Exhibitions provide a unique annual focal point for the surface coatings industries, and bring together technical personnel to meet in an informal atmosphere allowing a free interchange of ideas and the rapid dissemination of knowledge of new products and new developments of existing products.

In recent years, visitors to the OCCA Exhibitions have regularly come from over fifty overseas countries and at the 1978 Exhibition, admissions by season ticket of over 10,000 were recorded at the turnstiles in the hall.



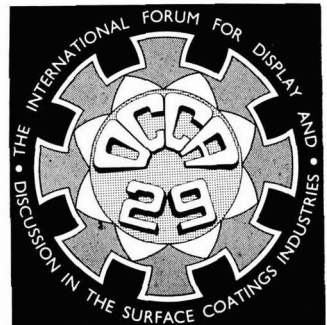
The motif for OCCA-30 used the symbol of a moving indicator on a calendar to emphasise the importance of the continuous dialogue year by year between suppliers and manufacturers.

The Exhibition provides an ideal opportunity for organisations to display and discuss their products and services to a wide spectrum of visitors from all over the world.

Organisations wishing to receive further details should contact the Director & Secretary, Mr R. H. Hamblin, Oil & Colour Chemists' Association, Priory House, 967 Harrow Road, Wembley, Middlesex HA0 2SF, England (Tel: 01-908 1086 Telex: 922670 OCCA G).



The motif for OCCA-28 emphasised that the target for 1976 was London where all the Exhibitions have been held, and continued the theme of its international aspect.



In 1977 the motif for OCCA-29 used inward pointing arrows to show the many places from which people came to the Exhibition, and these arrows formed outward pointing arrows to show the subsequent spreading of knowledge.

Information Received

Enlarged protective coatings division

International Paint has enlarged its Protective Coatings Division, which specialises in the supply of paint for the protection of heavy steel structures in corrosive environments, to include offshore construction contracts and factory maintenance projects, formerly handled by the Marine and Building Paints Divisions respectively. This makes the new Division the largest organisation of its type in the world with an annual turnover in excess of thirty million pounds. The purpose of this new structure is to co-ordinate the Company's world-wide expertise in structural steelwork and chemical plant protection, to rationalise trade names, and to improve the availability of their products from all 37 factories and 24 countries in which they operate.



An offshore structure protected by International Paint

UK Office

Gema AG of Switzerland, who specialise in an extensive range of powder coating equipment, has opened up its own UK Office in Dollis Hill, London, NW2.

New protective coatings service

A specialist section has been set up by Crown Paints to offer a complete sales and service facility to maintenance engineers and other specifiers of protective coatings to provide advice on the correct use of colour from an environmental or safety standpoint.

Re-organisation

The manufacturing, trading and distribution activities of the Chemical Division of Blagden & Noakes (Holdings) Ltd are being re-organised. Victor Blagden & Co

Ltd and Rex Campbell & Co Ltd are being amalgamated under the new name of Blagden Campbell Chemicals Ltd, and will also take over responsibility for some products currently handled by The Chemical Supply Company Ltd.

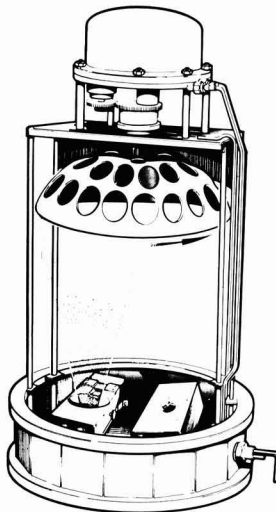
New agency

PAL Services has been appointed sole agents in Europe and certain Middle East countries for the laminating and varnishing machines manufactured by Matsumoto Kikai of Tokyo.

New products

Low pressure ion plating

Ion Tech Ltd has available a new ion source Model B92 Saddle-Field Ion Source which enables a new low pressure ion plating technique to be used for high quality thin films. The ion source is mounted in a high vacuum evaporation work chamber alongside a resistance heated evaporation filament or electron beam gun. Once the chamber is evacuated, the neutral beam cleans contaminants from the substrate surface at low pressure. The cleaning action is continued while the evaporation source is heated and the first layers are deposited. This ensures deposition on a clean surface without the pump down interruption after conventional glow discharge cleaning.



The ion plating chamber from Ion Tech Ltd

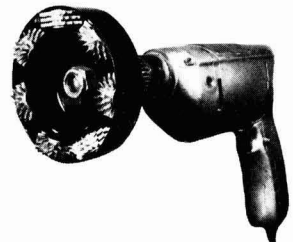
New colour black for lacquers

The Pigments Division of Degussa has extended its range of colour blacks for the pigmentation of lacquers to include a newly-developed, high-quality gas black named "Special Black 6", which can be

used to produce surface coatings with great depth of shade characterised by a blue tinge. The new product's flocculation stability is good compared with other carbon blacks, offering uniform quality and problem-free application of lacquers.

Cleaning wheel

Whirlaway (UK) Ltd has introduced a versatile range of cleaning wheels named the Whirl Away consisting of 3 models designed for attachment to power drills. The cleaning wheels have been developed to give clean, safe, low-cost removal of rust, paint, scale etc. from steel, concrete and other hard materials.



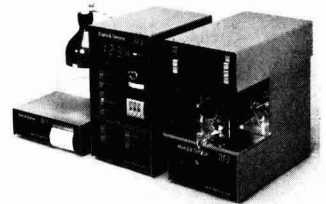
The Whirl Away power drill attachment

New isoindoline pigment

BASF has introduced Paliotol Yellow 1841K, an easily dispersible reddish yellow pigment for colourisation of plastics, which has outstanding light fastness and is resistant to migration.

Direct reading titrator

Baird & Tatlock has announced the addition of the Model AF3 to its range of Karl Fischer titration equipment which employs modern computer technology and a controlled impulse metering pump as the two principal elements of a fully-automated, push-button system.



The new model AF3 titrator from Baird & Tatlock

Conferences, courses, etc.

"Elvanol" information

Du Pont has published a new guide to methods for increasing water resistance of "Elvanol" polyvinyl alcohol, a water-soluble synthetic resin with excellent

film-forming and adhesive properties and outstanding resistance to oil, grease and solvents. The guide contains a section on various chemical agents that will cross-link with polyvinyl alcohol and includes a safe handling and waste disposal section.

Colour co-ordination handbook

The Building Research Establishment has published a new handbook entitled "Colour co-ordination handbook" by H. L. Gloag and M. J. Gold which explains the philosophy and research behind the development of the concept of colour co-ordination for building. The framework for colour co-ordination in the building industry, published in Building Standard 5252: 1976, stems from proposals drawn up by the

BRE for bringing the colours of building materials into a systematic relationship, and on this basis various colour standards have been issued for paints, sheet and tile flooring, vitreous enamel and plastics.

Analytical instruments brochure

Perkin-Elmer Ltd has published a new edition of its Analytical Instruments Catalogue which contains comprehensive information on the Company's major product lines.

Directory of surface active agents

Tergo-Data has published a second edition of Surfactants UK, a directory of surface

active agents available in the UK, first published in 1976.

Safety leaflet

The British Safety Council has issued a six-page leaflet on safety training which gives details of 18 different courses ranging from a basic three-day first aid course to a series of four courses leading to the qualification Diploma in Safety Management.

German address book

Farbe und Lack has published a comprehensive Directory of the paint, adhesive and putty industries and related trade associations and organisations for West Germany, including Berlin.

Notes and News

OCCA Biennial Conference 1979

*Stratford
-on-
Avon*

20-23 JUNE 1979 STRATFORD HILTON HOTEL

The challenge to coatings in a changing world

Registrations

The closing date for registrations for the Conference was given as 1 April 1979, primarily for the benefit of the hotel managements who would be in a position to let any accommodation not taken by that date. Registrations have been received from delegates in the United Kingdom and several overseas Countries.

Applications can still be accepted and delegates are reminded that VAT, 8 per cent at the time of going to press, applies to all registrations.

A list of papers to be presented together with their summaries and biographies of the Lecturers was published in the December 1978 issue of the *Journal* and copies of the Conference brochure and registration form were enclosed in copies sent to Members attached to the General Overseas Section and non-member subscribers to the *Journal*. The brochures have been sent to all Members of the UK and Irish Sections with Section circulars. Any non-member who has not yet received a copy of the brochure and wishes to register for this important Conference should apply for the necessary form to the Association's offices.

Non-members wishing to avail themselves of the preferential Conference fee for Members may do so by sending in a membership application form at the same time as they submit their Conference registration form and the fee enclosed

should cover both the membership entrance fee, 1979 subscription and the Conference registration fee. Membership application forms can be obtained from the Association's offices.

The registration fees for the Stratford Conference will be £60 (plus Value Added Tax at the standard rate) for Members, £80 (plus VAT) for non-members and £20 (plus VAT) for wives. A daily registration fee for Members of the Association of £35 (plus VAT) and of £20 (plus VAT) for Registered Students of the Association has been set.

Preprints

Preprints of the papers are now being prepared and it is expected that these, together with details of accommodation, badges, programmes, etc., will be sent to those who have registered at the beginning of June. It is a feature of the Association's Conference that preprints are sent out well in advance of the function in order that delegates can read them before the Conference, at which Lecturers illustrate their topics, but do not read their papers in their entirety. This allows for a much longer discussion period than at many other conferences and has proved of immense value to those attending previous Association Conferences.



A view of Anne Hathaway's Cottage, situated close to Stratford-upon-Avon, which contains a museum of Shakespearian articles

Social Events

Stratford-upon-Avon is a new venue for the OCCA Conference and it is expected that it will prove popular and interesting to delegates. A full social programme has been arranged for the benefit of delegates and their families, including coach parties to local places of interest such as Shakespeare's Birthplace, Warwick Castle, Coventry Cathedral and Oxford, a golf tournament, a river trip, and a theatre party to the Royal Shakespeare Theatre.

There will be an informal reception for all delegates at lunchtime on Thursday and the Association's Dinner and Dance will take place on the Friday night.

Forthcoming Events

Details are given of Association meetings in the United Kingdom and Ireland up to the end of the month following publication and in other parts of the world up to the end of the second following publication.

June

Irish Section: Annual golf outing, details to be announced.

Wednesday 20 June

London Section: Afternoon visit to Exposure Trials Station, Central Dockyard Laboratory, Ferry Road, Eastney, Portsmouth, commencing at 2.30 p.m.

Wednesday 20—Saturday 23 June

Association Biennial Conference: "The challenge to coatings in a changing world", at the Stratford Hilton Hotel, Stratford-upon-Avon, Warwickshire. See page 181.

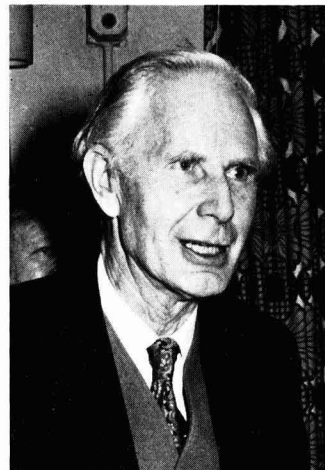
Further information may be obtained from the Director and Secretary at the address shown on the Contents page of this issue.

News of Members

Mr D. J. Morris, an Ordinary Member attached to the General Overseas Section and a Fellow in the Professional Grade, has been appointed as General Manager of HomeCharm Paints (Nigeria) Ltd. He is a past Secretary and past Chairman of the West Riding Section, a Founder Member of the West Riding Chemical Training Group and was a Member of the

Technical Training & Education Committee of the Paintmakers Association.

Mr S. E. Young, an Ordinary Member attached to the London Section, has retired from his position as Technical Liaison Manager of the Donald Macpherson paint group's industrial division, Macpherson Industrial Coatings Ltd, after 40 years with group companies.



Mr S. E. Young

Friday 22 June

Association Annual General Meeting: At the Stratford Hilton Hotel, Stratford-upon-Avon, at 4.00 p.m. or as soon thereafter as the final Technical Session of the Association Conference shall terminate.

July

Monday 2—Tuesday 3 July

South African Division: "The role of protective coatings". Winter school to be held at the Dorothy Susskind Auditorium, University of Witwatersrand.

Professional Grade

At a meeting of the Professional Grade Committee held 21 March 1979, the following Ordinary Members of the Association were admitted to the categories shown. The Section to which each Member is attached is shown in brackets.

Transferred from Licentiate to Associate

Elliott, Peter (*London*)

Associate

Abel, Adrian George (*Manchester*)

Fellow

Pienaar, Dirk Jacobus (*Transvaal*)
Astfalck, Anthony Noel (*Transvaal*)

Register of Members

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

Ordinary Members

BENDALL, GRAHAME DESMOND, Box 61659, Marshalltown 2107, South Africa. (*Transvaal*)

CONNOLLY, ROBERT STEPHEN, BSc, 65 Belmont Terrace, Lower Hutt, New Zealand. (*Wellington*)

HERMAWATI, HAPPY, Jl. Pulogadung No. 37, Jakarta, Indonesia. (*General Overseas*)

MAHILL, VEDAPRAKASH NUNKISSWAR, Box 65, New Germany, Natal, South Africa. (*Natal*)

MEISEL, NICK, Box 7127, Brackenhurst Ext. 2, 1450, South Africa. (*Transvaal*)

MOYNAGH, SHAUN MICHAEL, BSc, Shell Chemicals (NZ) Ltd, PO Box 2091, Wellington, New Zealand. (*Wellington*)

OOSTHUIZEN, CHRISTOPHER, Metal Box (SA) Ltd, PO Box 2226, Cape Town 8000, South Africa. (*Cape*)

OWERS, WILLIAM RONALD, Corner Howard Road and Marine Drive, Eastbourne, New Zealand. (*Wellington*)

PAUL, CHRISTOPHER MICHAEL, PO Box 17-037, Wellington 5, New Zealand. (*Wellington*)

PLOWMAN, DAVID JOHN, 35 Schofield Walk, Blackheath, London SE3. (*London*)

Associate Members

ANDREW, TERENCE SIDNEY, Pennine Chemicals Ltd, Williams & Glyn's Bank Chambers, High Street, Congleton, Cheshire. (*Manchester*)

NAIDOO, VIMOTHAN, Box 65, New Germany, Natal, South Africa. (*Natal*)

Registered Student

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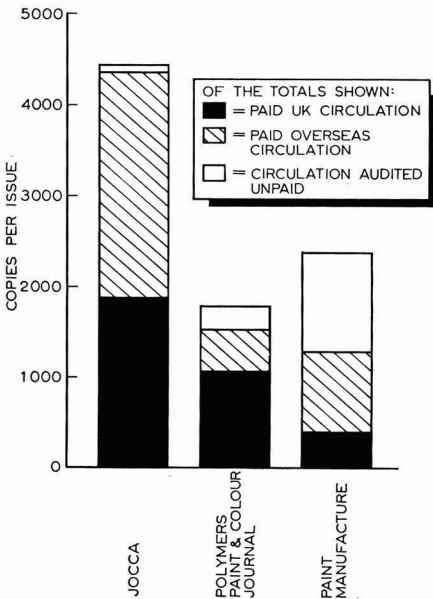
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(Reference Audit Bureau of Circulations Reviews. Jan-Dec 1977)

Comparison of circulations of U.K. publications to the paint, printing ink and allied industries

For full details of advertising in this, and other Association publications, contact D. M. Sanders, Assistant Editor.

Journal of the Oil and Colour Chemists' Association (JOCCA)

Priory House, 967 Harrow Road, Wembley, Middx. HA0 2SF, England

Telephone: 01-908 1086

Telex: 922670 (OCCA Wembley)

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Metal Box

Research and Development Department

Please phone or write for an application form to:
G. P. Smith, Personnel Manager, Metal Box Limited,
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Manchester Section Technical
Discourse

THE WHYS AND WHEREFORES OF CORROSION

The Manchester Section of the Oil and Colour Chemists' Association will be pioneering a novel form of one-day technical meeting in September next which, it is believed, will be an advance on the more traditional formats of conferences and symposia. The overall subject chosen is "The Whys and Wherefores of Corrosion". Within this, the Discourse will cover the key topics of corrosion inhibition (including theoretical background), cathodic protection, microbiological corrosion, and practical aspects of protection against corrosion in the atmosphere, aqueous and specific chemical environments, including protective coatings.

Topics will be introduced and discussions will be led by well known experts from Industry and from the Corrosion and Protection Centre at UMIST. The aim will be to achieve maximum involvement and learning by participants.

The Discourse will be held at UMIST (University of Manchester) on 13 September 1979. Advance information is available from:

Mr G. R. Robson,
AR.TS Dept: Pigments,
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Hexagon House, Blackley,
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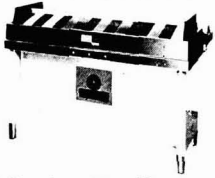
JOCCA

Change of production method

From the June 1979 issue of *JOCCA*, the production method will be changed from letterpress to sheet fed off-set litho.

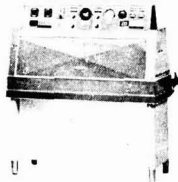
Full details may be obtained from the Assistant Editor, Mr D. M. Sanders, at the address on the Contents page.

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The QCT Condensation Tester tests finishes for resistance to moisture in the form of rain and dew. The QCT's unique condensation system gives faster, more realistic tests than conventional humidity, while maintaining foolproof control of water purity, oxygen saturation, and test temperature. Initial cost is quite low, and maintenance is almost nil. Ordinary tap water may be used, because the QCT distills the water in the process of transporting it to the test surface. Test severity can be varied widely by regulating the temperature.

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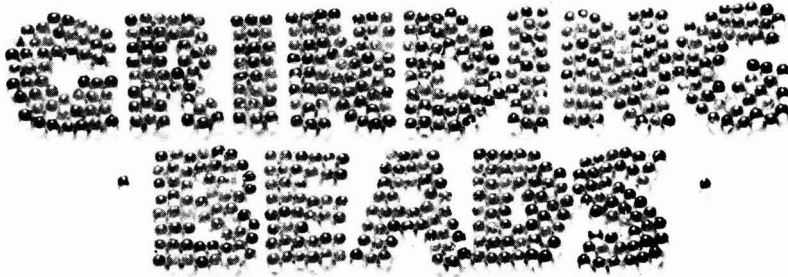
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